Theses accompanying the dissertation "Hydrogen Mixed Conductors properties and applications"

1. Today's commercially available batteries are a waste of energy. Chapter 6.

2. Values of diffusion coefficients are meaningless without the information on sample history. Chapter 3.

3. "COLD FUSION" may not be cold fusion.

4. Many successful companies have demonstrated that their achievements were mainly based on interdisciplinary teamwork. For this reason, the curriculum should credit teamwork equally to individual achievements.

5. Reduction of nitric oxides in gas systems of fossil fuel combustion engines requires more than a good working catalyst.

6. Lithium manganese oxides are very interesting cathode materials for rechargeable lithium batteries. However, they may not be suitable for high-power, long-life applications.

7. No individual lithium electrolyte material can stand a potential difference of 4 V as required in many lithium batteries.


10. The I/V characteristic of ZnO varistor ceramics cannot be exactly described by a power law.

Delft, October 13, 1997               Martha Schreiber
Stellingen behorende bij de dissertatie "Hydrogen Mixed Conductors properties and applications"


2. Zonder informatie over de geschiedenis van een monster hebben waarden voor diffusiecoëfficiënten geen betekenis. Hoofdstuk 3.

3. "KOUDE FUSIE" hoeft geen koude fusie te zijn.

4. Vele succesvolle bedrijven hebben laten zien, dat hun successen gebaseerd zijn op interdisciplinaire groepsarbeid. Om deze reden zouden in het curriculum successen van groepsarbeid en individuele successen gelijkwaardig gehonoreerd moeten worden.

5. Reductie van stikstofoxide in uitlaatsystemen van verbrandingsmotoren voor fossiele brandstoffen vereist meer dan een goed werkende katalysator.

6. Lithiummangaanoxide zijn zeer interessante kathodematerialen voor herlaadbare lithiumbatterijen. Het is echter de vraag of zij geschikt zijn voor toepassingen, die een hoog vermogen en een lange levensduur vereisen.

7. Geen enkel lithium electrolytmateriaal is bestand tegen het in vele lithiumbatterijen heersende potentiaalverschil van 4 V.


10. De I/V karakteristiek van ZnO varistor keramieken kan niet exact beschreven worden met een exponentieel verband.

Delft, 13 Oktober 1997 Martha Schreiber
HYDROGEN MIXED CONDUCTORS

PROPERTIES AND APPLICATIONS

Martha Schreiber
HYDROGEN MIXED CONDUCTORS

PROPERTIES AND APPLICATIONS

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof.dr.ir. J. Blaauwendraad,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op maandag 13 oktober 1997 te 13.30 uur

door

Martha Charlotte SCHREIBER

Diplom-Ingenieur Technische Chemie, TU-Wien
geboren te Linz, Oostenrijk
Dit proefschrift is goedgekeurd door de promotoren:
Prof.dr. J. Schoonman
Prof.dr. R.A. Huggins

Samenstelling promotiecommissie:

Rector Magnificus, voorzitter
Prof.dr. J. Schoonman, Technische Universiteit Delft, promotor
Prof.dr. R.A. Huggins, Christian-Albrechts Universität zu Kiel, promotor
Prof.ir. C.M. van den Bleek, Technische Universiteit Delft
Prof.dr. G. Frens, Technische Universiteit Delft
Prof.dr.ir. S. van der Zwaag, Technische Universiteit Delft
Prof. J.M. Tarascon, Université de Picardie Jules Verne
Dr. A.P.L.M. Goossens, Technische Universiteit Delft

Published and distributed by:
Delft University Press
Mekelweg 4
2628 CD Delft
The Netherlands
Telephone: +31 15 2783254
fax: +31 15 2781661
E-mail: DUP@DUP.TUDelft.NL


Copyright c 1997 by M. Schreiber

All rights reserved. No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission from the publisher: Delft University Press.

Printed in the Netherlands
Mixed Conductors that's the trick
Ions and Electrons make it klick.

Josh Thomas
SSI 8, Lake Luise, 1991
PREFACE

This thesis is written to fulfil the requirements for the PhD degree at the Delft University of Technology. It covers the results of my work performed at Stanford University, at SRI International, at the Daimler Benz Research Institute, and at the Austrian Research Centre Seibersdorf.

I like to acknowledge my gratitude to my promotor Prof. Dr. R.A. Huggins, who has guided my work at Stanford University.

My special acknowledgment I wish to express to my promotor, Prof. Dr. J. Schoonman for he has given me the opportunity to finish this PhD study at Delft University of Technology. His dedicated interest in the work as well as his fruitful comments and suggestions were of great importance to my professional and personal forthcoming.

I am most thankful to all my colleagues at the Stanford Solid State Ionics Laboratory, the Electrochemistry Group at SRI International, my colleagues at the Daimler Benz Research Institute in Ulm, and the materials group of the Austrian Research Centre in Seibersdorf.
CONTENTS

CHAPTER 1: GENERAL INTRODUCTION 1

1.1 What is a mixed conductor? 1
1.2 Hydrogen-mixed conductors 2
  1.2.1 Thermodynamic properties 4
  1.2.2 Structural changes 15
  1.2.3 Electronic properties 18
  1.2.4 Kinetic properties 19
1.3 Materials families of hydrogen-mixed conductors 21
  1.3.1 Hydrogen storage and purification 21
  1.3.2 Heat pumps 22
  1.3.3 Rechargeable nickel metal-hydride batteries 23
  1.3.4 Composite S/L/S hydrogen "Solid Electrolyte" 26
  1.3.5 Hydrogen cycle thermoelectric device 29
  1.3.6 Hydrogen insertion compounds of metal oxides 29
1.4 Advances in the hydrogen economy & hydrogen ecology 32
  1.4.1 Hydrogen production by water splitting 37
  1.4.2 The energetic use of hydrogen 45
1.5 Introduction to concepts and tools 57
1.6 Scope of the thesis 58
1.7 References 59

CHAPTER 2: THEORETICAL CONCEPTS AND EXPERIMENTAL TOOLS 71

2.1 Galvanic and electrolytic cells 71
2.2 Thermodynamic properties 78
  2.2.1 Potential-phase diagram relationships 78
  2.2.2 The coulometric titration technique 79
  2.2.3 Application of the coulometric titration technique 82
2.3 Chemical diffusion of active species 84
  2.3.1 Chemical diffusion in mixed conductors 89
  2.3.2 Measurement of the chemical diffusion coefficient 90
2.4 Electrolyte conductivity 95
  2.4.1 Conductivity measurements 98
2.5 Thermodynamic stability windows, electrode potentials 105
2.6 The reference electrode 112
2.7 Summary 115
2.8 References 115
CHAPTER 3: TITANIUM-NICKEL BASED SYSTEM

3.1 Introduction ................................. 119
3.2 Experimental aspects ......................... 121
3.3 Results .................................. 127
3.4 Summary .................................. 135
3.5 References ................................ 137

CHAPTER 4: PALLADIUM-HYDROGEN BASED SYSTEM

4.1 Thermodynamic and kinetic properties of hydrogen insertion in Pd and Pd-Li alloy
   4.1.1 Introduction .............................. 139
   4.1.2 Experimental aspects ..................... 141
   4.1.3 Results ................................ 145
   4.1.4 Discussion ................................ 157
4.2 Aspects of the electrochemical loading of hydrogen and its isotopes into palladium
   4.2.1 Introduction .............................. 161
   4.2.2 Preparation and characterization of the β-phase ..................... 161
   4.2.3 Experimental aspects ..................... 168
   4.2.4 Results and discussion ..................... 171
   4.2.5 Conclusions ................................ 174
4.3 References ................................ 175

CHAPTER 5: CONCEPTS FOR APPLICATIONS FOR HYDROGEN MIXED CONDUCTORS

5.1 Use of solid state ionic technique to modify in situ the behaviour of catalytic surfaces
   5.1.1 Introduction .............................. 183
   5.1.2 Experimental approach ..................... 186
   5.1.3 Discussion ................................ 191
5.2 Intermediate temperature water vapour electrolysis ...................... 192
   5.2.1 Introduction .............................. 192
   5.2.2 General concept ........................... 195
   5.2.3 Experimental aspects ..................... 198
   5.2.4 Discussion ................................ 222
5.3 Novel concept to reduce nitric oxides ................................ 225
5.4 References ................................ 228
CHAPTER 6: SUMMARY AND LOOK TO THE FUTURE

6.1 Summary 237
  6.1.1 Titanium-nickel-hydrogen system 239
  6.1.2 Palladium-hydrogen based systems 240
  6.1.3 Concepts for applications of hydrogen mixed conductors 242

6.2 General conclusion 247
  6.2.1 Materials properties 247
  6.2.2 System performance 248

6.3 Look to the future 249

6.4 References 255

SUMMARY 257

SAMENVATTING 260

ZUSAMMENFASSUNG 264

CURRICULUM VITAE 269

LIST OF RELEVANT PUBLICATIONS 271
Chapter 1

General Introduction

1.1 What is a mixed conductor?

Michael Faraday reported in 1839 (1) that, contrary to the behaviour of normal metals, several materials have a negative temperature coefficient of resistance. One of the materials that he found to have this abnormal behaviour was silver sulfide, Ag$_2$S, whose electrical conductivity jumps to higher values at temperatures over 175°C. This material was also the center of controversy for several years around 1930, for it was shown to carry current primarily by the flow of electrons, yet the application of an electric potential difference also caused the transport of silver. This apparent quandary was resolved by a series of clever experiments by Wagner, who was able to separate the electronic and ionic contributions to the total charge flux (2), (3).

Silver sulfide has become the typical example of a mixed conductor, in which electrical charge is carried by two species, one electronic, and one ionic. In actual fact, it is an extreme example, for the ionic component of the elevated temperature alpha phase has been found (4) to have the largest value of chemical diffusion coefficient of any known solid material.

While in the case of silver sulfide the mobile ionic species are silver cations, similar mixed-conducting behaviour has been found in other materials in which the ionic component is hydrogen.
1.2 Hydrogen mixed conductors - what are their characteristics?

In 1866, Thomas Graham, one of the founders of modern chemistry in Great Britain, discovered the ability of the metal palladium to absorb large amounts of hydrogen. He also observed that hydrogen can permeate through Pd membranes at an appreciable rate, and thus Pd membranes can be used to either extract $\text{H}_2$ from a gas stream or to purify hydrogen (5). Further basic experiments on the change of the physical properties of Pd due to absorption of hydrogen, such as lattice expansion, electrical resistivity, or magnetic susceptibility date back to Graham (6), who also introduced the concept of metal-hydrogen alloys without definite stoichiometry, in contrast to stoichiometric non-metallic hydrides (7).

An extensive description of the basic properties and application-oriented properties of HYDROGEN IN METALS is given in the two volumes on Hydrogen in Metals by Völkl and Alefeld (8), (9) and on HYDROGEN IN PALLADIUM by Lewis (10). A recent book on this topic is THE METAL-HYDROGEN SYSTEM (11). Since then, the work on binary hydrides, mainly of transition and rare earth metals, has been widely pursued. The more recent results on ternary hydrides are described in (12).

Hydrogen reacts with many elements to form so-called binary hydrides. They were described by Remy (13) in four classes: (i) gaseous or volatile hydrides, (ii) polymeric hydrides (solid hydrides which are neither ionic nor metallic in character), (iii) metallic hydrides, (iv) ionic hydrides. In Figure 1 the various classes of binary hydrides are represented.

Metallic hydrides meet the requirements for mixed conductors as they conduct protons (hydrogen atoms in the metal lattice behave like protons) and electrons. Also a number of oxides are known that exhibit electronic conduction and can insert mobile hydrogen at specific lattice sites.
### Figure 1: Classes of binary hydrides

A simplified model of the dissociation of molecular hydrogen at a metallic interface and the subsequent dissolution of hydrogen into the metal bulk is represented in Figure 2.

The potential energy indicates from left to right a shallow minimum for the physisorption process of $H_2$, then a deep minimum for the dissociated $H$ to be chemisorbed, a rather deep minimum for near surface $H$, and periodic minima for $H$ in interstitial lattice sites of the host metals separated only by diffusion barriers.

If the local hydrogen concentration exceeds a certain limit, a hydride phase precipitates. The thermodynamic aspects of hydride formation can be described by pressure-composition isotherms. In general, the host metal dissolves some hydrogen in solid solution ($\alpha$-phase) and as the hydrogen pressure, and herewith the hydrogen activity increases, the $H-H$ interaction becomes locally more important, and nucleation and growth of a hydride phase ($\beta$-phase) occur. In some of
these cases, the hydrogen species can have a very high mobility. Thus these materials can be considered mixed electronic-ionic conductors.

Figure 2: Schematic of metal-hydride formation (12)

The properties of hydrogen mixed conductors are due to the modification of the metal lattice, and the contributions due to the influence of the hydrogen, and due to the changes as the metal itself is varied.

1.2.1 Thermodynamic properties

In general, metals combine with hydrogen in two principally different ways, forming either ionic or metallic bonds. This is due to
the position of hydrogen in the periodic table according to which it may tend to complete its 1s-shell, resembling the halogens, or loose its 1s-electron, resembling the alkali metals. In the first case, the 1s state lies below the Fermi energy of the solvent metal, acquiring an electron from the electron gas of the metal. This leaves the dissolved H atom in what may be called an anionic state. The alkali and alkaline earth metals as well as the rare earths form hydrides of this type. In the second case, the 1s-state lies above the Fermi energy of the host metal, donating its electron to the electron gas of the metal. This leaves the hydrogen in what may be called the protonic or metallic state. The latter was predicted by theoretical studies on hydrogen in some transition metal alloys (14), (15).

Hydrogen is soluble in many metals and often has a high diffusion rate which is seen as both a positive and a negative property, depending upon whether one is investigating metals for their hydrogen storage properties or from the viewpoint of hydrogen embrittlement. The absorbed hydrogen atoms occupy interstitial sites in the crystalline host lattice, and their concentration depends strongly on the hydrogen pressure.

The reaction of hydrogen with a metal M in which a stable hydride $MH_y$ is formed can be described in the following way

$$MH_x + \frac{1}{2}(y-x) \ H_2 = MH_y$$  

\[ / \ 1 / \]

with $y > x$

where the transition to $MH_y$ is the absorption process and the reverse reaction is the desorption process. Since the absorption reaction is generally exothermic, the heat of reaction for the desorption process is negative and causes cooling. If this is not desired, it must be balanced by the supply of heat from the surroundings.

The equilibrium lattice position of an interstitial hydrogen atom is determined by the requirement that the local electron density be as low as possible. This means that in fcc metals it will typically be an
octahedral position while in bcc metals tetrahedral sites are preferred, which is in agreement with experimental results (16). This rule might slightly change when taking the lattice relaxations and zero point motion of the hydrogen atoms into account, as found experimentally in a few cases (17).

When an interstitial hydrogen atom moves in the lattice, the variations in the potential energy along the diffusion path will be a reflection of the variations in the electron density. In open structures, where the atom does not have to pass regions of high electron density, the diffusion coefficient will be higher than in more close-packed structures. This explains why the diffusivity of hydrogen is significant larger for bcc than for fcc metals (18). However, it must be noted that the role of lattice relaxation in the diffusion process is very important, and this can modify these general rules. A theory of hydrogen interaction with metals is given in (19).

The absorption and desorption of metal-hydrogen systems is conventionally studied by pressure-composition experiments at constant temperatures. The resulting pressure-composition isotherms have generally the following features as shown in Figure 3 (20).

At low hydrogen concentrations there is a strong composition dependence of the hydrogen pressure. This region, the α-phase refers to the original metal phase which is able to dissolve generally a small fraction of hydrogen gas in solid solution without the occurrence of a second phase.

In many cases, the activity of hydrogen in solid solution at any temperature is proportional to the square root of the external hydrogen pressure. This is known as Sievert's Law.

\[ 2 \text{M} + \text{H}_2 = 2 \text{H/M} \]
\[ k = \frac{a_{H/M}^2}{P_{H_2}} \quad \text{if } c_H = a_H \]

\[ P_{H_2} = k^{-1}a_{H/M}^2 \]

where \( k \) is a constant.

![Graph showing equilibrium pressure-composition isotherms](image)

**Figure 3:** Equilibrium pressure-composition isotherms

In a number of metals and alloys, the limit of solubility can be exceeded and new phases can form in the presence of appreciable hydrogen activities. Some of these metallic "hydride" phases can contain very large hydrogen concentrations.
This stage is indicated in Figure 3 as the region where the hydrogen pressure is concentration independent and where the saturated solid solution in the $\alpha$-phase is in equilibrium with a hydrogen-rich hydride phase, the $\beta$-phase. In some cases a second hydride $\beta'$ with an even higher hydrogen concentration than the $\beta$-phase exists. In these cases one observes a second region where the pressure is concentration independent due to the equilibrium $\beta + H_2 = \beta'$. The $\beta$-phases are to be regarded as binary compounds, for example LaH$_2$, or ternary intermetallic compounds, for example LaNi$_5$H$_6$, in which one of the components is hydrogen.

One often sees these hydride phases referred to in the literature as though they had fixed stoichiometries. This is often far from the case, though. Instead, metal-hydrogen systems should be considered in the same way as phases in many other alloy systems. The general principle is that phases have ranges of composition - in some cases rather narrow, in others quite broad.

As an illustration, the phase diagram for the titanium-hydrogen system is shown in Figure 4. It is seen that the concept of titanium having two hydrides, with compositions "TiH" and "TiH$_2$", that one often finds in the literature, is grossly misleading. This phase diagram contains an eutectoid reaction at about 300°C. If we neglect the epsilon region, which is still in dispute, we can come to the following conclusions. Below about 300°C, only one hydride phase is stable, and its composition range is rather wide, starting at about 51 atomic percent hydrogen at the eutectoid temperature. At lower temperatures, it starts at about 60 atomic percent hydrogen, and extends well above 66%. Despite the fact that its lower boundary is near "TiH", this phase is generally called "TiH$_2$". At temperatures above the eutectoid, a second phase appears at lower hydrogen concentrations. At the eutectoid temperature its hydrogen composition is about 38 atomic percent hydrogen, and it extends over a wider compositional range as the temperature is increased. At about 600°C, this phase has indeed a hydrogen content as high as 50 atomic percent, although it also extends down to only 20 atomic percent hydrogen at that temperature. This phase is sometimes
referred to as "TiH" in the literature. This designation becomes even more meaningless when one realizes that it is stable all the way down to zero hydrogen above 885°C, where it is identical to the well-known beta phase of pure titanium.

![Graph showing the titanium-hydrogen system](image)

**Figure 4:** The titanium-hydrogen system

The concentration region determined by the horizontal parts of the isotherms can be regarded as a miscibility gap between two well defined phases. It originates from the fact that the partial heat of solution of hydrogen, starting from the hydrogen free compound becomes more negative with increasing hydrogen concentration. The process of dissolution becomes more exothermic so that it is energetically more favorable for the hydrogen atoms to be
concentrated locally rather than be distributed evenly throughout the metal (21). At higher temperatures the influence of the entropy counteracts this tendency to form two separate phases so that the miscibility gap may disappear. This is represented schematically in Figure 5 where a critical pressure and temperature are indicated above which the homogeneous hydrogen alloy will be stable at any composition up to that of the saturated hydride. The isotherms then have no region where the pressure is independent of the concentration.

\[ \begin{align*}
\text{Hydrogen Concentration} & \rightarrow \\
\text{P}_{\text{H}_2} & \rightarrow T_c \\
\text{P}_{\text{eq}}(T_2) & \rightarrow \alpha \cdot \beta \rightarrow \beta \\
\end{align*} \]

**Figure 5:** Schematic diagram of pressure-composition isotherms of a metal-hydrogen system (12) that forms a single hydride phase. The hydrogen concentrations in the $\alpha$-phase and $\beta$-phase are temperature dependent. Above the critical temperature $T_c$, a random distribution of hydrogen occurs over the entire concentration regime.

An example of such a phase diagram is shown for the Pd-H system later in the text.

The equilibrium pressure in the two-phase $\alpha/\beta$ region is usually known as the plateau pressure, but is also sometimes called the transition pressure. It can be considered as a measure of the stability of the hydride with respect to the solid solution $\text{MH}_x$. This plateau pressure, which varies strongly with temperature, can be described
approximately in a limited temperature range by the Van 't Hoff equation

$$\ln p_{H_2} = -\frac{\Delta S_r}{R} + \frac{\Delta H_r}{RT}$$

which is derived using the Gibbs free energy change and the equilibrium constant

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

$$\Delta G_r = RT \ln p_{H_2}$$

where $\Delta S_r$ and $\Delta H_r$ are the changes in entropy and enthalpy per mol $H_2$ involved in the reaction. When $\Delta S_r$ and $\Delta H_r$ are taken to be temperature-independent in the limited temperature range considered, a plot of $\ln p$ versus $1/T$, the Van 't Hoff plot, yields the values for $\Delta S_r$ and $\Delta H_r$. The entropy effect is predominantly determined by the difference between the entropy of hydrogen in the gaseous state and in the hydride (solid state). Since the latter energy contribution is relatively small, $-\Delta S_r$ will not be much different from the entropy contained in the gas, which is about 120 J/deg mol $H_2$ at 1 atm and at room temperature. From experimental data on the temperature dependence of the equilibrium pressure for metal-hydrogen phases one finds values for $\Delta S_r$ close to $\Delta S = -120 \pm 25$ J/deg mol $H_2$ (22), (23). Hence, for a hydride having a plateau pressure near 1 atm at room temperature (300 K) and for which $\Delta G_{r300,p=1} = RT \ln p_{H_2} = 0$, one obtains for the enthalpy effect (heat of formation) the value $\Delta H_r = T\Delta S_r = -36 \pm 8$ kJ/mol $H_2$. Each factor of ten in the equilibrium pressure at room temperature corresponds to a change in $\Delta H_r$ of 5.86 kJ/mol $H_2$. The enthalpy effect is, therefore, a direct measure of the relative stability of hydride phases. Very stable hydrides have a large negative reaction enthalpy and dissociate (at atmospheric pressure) only at very high temperatures. Only those hydrides having an enthalpy of formation more negative than -37.6 kJ/mol $H_2$ are stable at room temperature and 1 atm hydrogen pressure. In Table I the enthalpies of formation of elemental hydrides are represented and it can be seen that only
those metallic hydrides are stable at room temperature which contain the elements Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, La, and other lanthanides, Ti, Zr, Hf, V, Nb, Ta, Th, U, or Pu.

**TABLE I**: Binary hydrides and their enthalpy of formation in kJ/mol H₂. The numbers below indicate the experimental values for the enthalpy of formation. The values in brackets are estimated by Miedema et al. (24).

<table>
<thead>
<tr>
<th>LiH</th>
<th>MgH₂</th>
<th>NaH</th>
<th>MgH₂</th>
<th>CaH₂</th>
<th>ScH₂</th>
<th>TiH₂</th>
<th>VH</th>
<th>CrH</th>
<th>MnH</th>
<th>FeH</th>
<th>CoH</th>
<th>NiH</th>
</tr>
</thead>
<tbody>
<tr>
<td>-158</td>
<td>-75</td>
<td>-117</td>
<td>-158</td>
<td>-158</td>
<td>-201</td>
<td>-126</td>
<td>(-59)</td>
<td>(-17)</td>
<td>(-17)</td>
<td>(+33)</td>
<td>(+33)</td>
<td>(+17)</td>
</tr>
<tr>
<td>KH</td>
<td>CaH₂</td>
<td>ScH₂</td>
<td>TiH₂</td>
<td>VH</td>
<td>CrH</td>
<td>MnH</td>
<td>FeH</td>
<td>CoH</td>
<td>NiH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-117</td>
<td></td>
<td></td>
<td></td>
<td>(-59)</td>
<td>(-17)</td>
<td>(-17)</td>
<td>(+33)</td>
<td>(+33)</td>
<td>(+17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbH</td>
<td>SrH₂</td>
<td>YH₂</td>
<td>ZrH₂</td>
<td>NbH</td>
<td>MoH</td>
<td>TcH</td>
<td>RuH</td>
<td>RhH</td>
<td>PdH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-109</td>
<td>-158</td>
<td>-226</td>
<td>-163</td>
<td>(-75)</td>
<td>(+17)</td>
<td>(+50)</td>
<td>(+67)</td>
<td>(+38)</td>
<td>(-33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsH</td>
<td>BaH₂</td>
<td>LaH₂</td>
<td>HfH₂</td>
<td>TaH₂</td>
<td>WH</td>
<td>ReH</td>
<td>OsH</td>
<td>IrH</td>
<td>PtH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>-158</td>
<td>-209</td>
<td>-134</td>
<td>(-59)</td>
<td>(+42)</td>
<td>(+92)</td>
<td>(+84)</td>
<td>(+67)</td>
<td>(+17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CéH₂</td>
<td>PrH₂</td>
<td>NdH₂</td>
<td>SmH₂</td>
<td>GdH₂</td>
<td>TbH₂</td>
<td>DyH₂</td>
<td>HoH₂</td>
<td>ErH₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-205</td>
<td>-209</td>
<td>-209</td>
<td>-222</td>
<td>-201</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-226</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EuH₂</td>
<td>YbH₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Under the assumption that $\Delta S_r$ is a constant and the same for different hydrides, and also assuming that in the small temperature range considered $\Delta H_r$ may be taken as a constant for each hydride, the temperature dependence of the plateau pressures of various hydrides is shown in Figure 6. The lines are described by equation /5/, each with a different value of $\Delta H_r$. Under the above conditions all hydrides are represented by a bundle of lines converging in the point

$$\ln p_{H_2} = -\frac{\Delta S_r}{R} \quad \text{at } T \to 0$$

$\rho_{H_2}$ (atm)

$1/T \rightarrow 0 \quad p = 3.4 \times 10^6$

$\Delta H_r = -6$

$\Delta S_r/R = 15.1$

Figure 6: Van 't Hoff plot of various model metal-hydrogen systems
Although this presentation of metal-hydrogen systems is very much simplified it can be a useful tool in finding hydrides suitable for practical applications.

For many practical applications it is desirable that the hydride be stable at room temperature and moderate hydrogen pressure, but also decomposes under conditions which are technically still easy to achieve (e.g. several hundred degrees and about 10-20 atm). As can be seen from Table 1 and Figure 6 that the number of binary hydrides that meets these requirements is very limited.

As a consequence investigations were undertaken to react hydrogen with alloys (intermetallic phases) which contained at least one of the elements that absorbs hydrogen.

The heat of formation of a hydride which is a measure of its stability is generally taken with respect to the pure metal phase under the assumption that the region of solid solution is very small. If, however, the region of solid solution is more extensive, the plateau pressure in the two-phase region is no longer an exact measure of the stability of the hydride with respect to the pure metal but rather with respect to the coexisting solid solution. In such a case the heat of formation is not constant, because the compositions of the coexisting phases are changing with temperature. The plot of ln p versus 1/T is then not expected to result in a straight line.

When hydrogen reacts with an ordered intermetallic compound such as LaNi₅ to form LaNi₅H₆, the hydride has no relation to the binary hydrides of the constituents La and Ni. Since this hydride is formed under ambient conditions, where diffusion of La and Ni is negligible, the crystal structure of the hydride can be derived from that of the intermetallic compound with small corrections in the La and Ni positions. In fact, the crystal lattice has to expand in order to accommodate the hydrogen atoms.

For compounds that absorb hydrogen at temperatures above 300°C the diffusion of the metal atoms can no longer be neglected (25, 26).
The first extended reports on the reaction of hydrogen with intermetallic compounds were published by Beck (27), Pebler, and Gulbranson (25), who were interested in very stable hydrides and the deleterious effect of hydrogen on Zr alloys in connection with nuclear reactors.

The discovery and description of hydride formation of Mg$_2$Ni and FeTi by Reilly and Wiswall (28), (29), and particularly of the hydride formation of LaNi$_5$ by Van Vucht et al. (30) initiated a worldwide series of studies on hydrogen storage of intermetallic compounds. Neumann (31) studied the behaviour of hydrogen and deuterium in LaNi$_5$ a few years earlier but did not realize the consequences of his observations. Several years later hydrides of the AB$_2$ type were discovered independently by Shaltiel et al. (32) and Ishido et al. (33), (34).

The most intensively investigated intermetallic phases are of the AB$_5$, AB, AB$_2$, and A$_2$B, types, where A denotes an element that absorbs hydrogen. Examples are LaNi$_5$, TiFe, ZrCr$_2$, and Ti$_2$Ni. An overview of the structure and phase relationships of these intermetallic hydrides is given by Andresen (35).

Today, intermetallic hydrides have proven successful in a number of applications, some of which will be described later in the text.

1.2.2 Structural changes

Upon hydrogenation most binary metal compounds undergo a lattice expansion which is between 2 and 3 Å$^3$ per H atom. For some hydride structures the space group symmetries at room temperature are identical to those of the binary metal compounds. In other cases, hydrogenation leads to a lowering of the lattice symmetry but does not induce a major reconstruction of the metal atom substructure. Only a few hydrides with reconstructed metal atom arrangements have been reported to date. In general, the hydride structure lattice symmetries depend upon hydrogen activity and temperature. Thus
the symmetry decreases as a function of hydrogen content and increases as a function of temperature.

Elemental metal hydride structures are characterized by a few, relatively simple and usually highly symmetrical crystal structures, mostly face- or body-centered cubic in which the hydrogen atoms occupy interstitial sites. Most of the structures are similar to those of the corresponding binary metal compounds.

For example, in fcc structures such as rare earth metals and those of the titanium group hydrogen occupies preferentially tetrahedral interstitial lattice sites resulting in the fluorite (CaF$_2$) structure with an H/M ratio up to 2, while in Pd and Ni hydrogen will occupy preferentially octahedral sites resulting in the NaCl structure type with an H/M ratio approaching 1.

In contrast to elemental hydride structures, which are often ordered, ternary metal hydride structures are usually disordered at room temperature. As a consequence, the local hydrogen atom configurations around the metal atoms are unknown. However, one of the most characteristic and intriguing structural features of ternary metal hydrides is their preferential hydrogen site occupancies. As can be seen in Figure 7, the deuterium atoms exclusively occupy those interstices of the metal atom network which allow them to be in contact with at least one hydride-forming element (Mg, Ti, Zr, rare earths). In structures with several types of interstices, those surrounded by a larger fraction of hydride forming elements, or those surrounded by an element which can form a more stable binary hydride, appear to be preferentially occupied. A thorough and detailed description of crystal structures of ternary metal hydrides is given in (36).
Figure 7: Transition metal environments in Mg$_2$FeD$_6$, Mg$_2$CoD$_5$, and Mg$_2$NiD$_4$ (36)
1.2.3 Electronic properties

The dissolution of hydrogen into a metal lattice and the formation of a metal hydride perturbs considerably the electrons and phonons of the host metal. Accordingly, the study of the electronic properties of a hydrogen-metal system is not only of fundamental interest to understand the hydrogen-metal interactions in the bulk and at the surface, but also sheds light on technologically important parameters, such as the heat of formation and heat conductivity, and, to some very practical extent, also the phenomena of hydrogen storage, hydrogen embrittlement (decohesion), and catalysis.

Until the late sixties, research on the electronic properties of metal hydrides involved mainly experimental work (22). The first theoretical investigations started in the early fifties with the pioneering work of Friedel in which he studied the screening of a hydrogen impurity and the heats of dissolution of H₂ in noble metals (37), (38) However, up to the early seventies, oversimplified models were often used to describe the bonding mechanisms of H in transition metals. The first ab initio band structure calculations on binary hydrides, performed by Switendick (8), gave a new impetus and stimulated a number of experimental and theoretical efforts. From the theoretical results on concentrated binary hydrides several important features have emerged and hydride phases are no longer considered, as they were earlier, as interstitial solid solution alloys but rather, as separate phases. The role of chemical bonding has been emphasized and the crude rigid-band model in its protonic or anionic form is no longer being applied to the electronic structure of the host metal to interpret the experimental data on hydrides. Earlier both theoretical and experimental work was limited to hydrides of elemental metals, e.g. Pd, Ti, rare earth metals and Th (8). In the last decade the first results on the electronic structure of ternary hydrides of intermetallic compounds elaborated by band structure calculations (FeTi) (39-43), and experimentally by photoelectron spectroscopy (ZrMn₂) (44), while X-ray emission spectroscopy (crystalline and amorphous alloys of Zr and V) (45-48) became
available. Recent reviews on theoretical and experimental work on crystalline and amorphous materials have been presented. (49-60).

One of the goals of the analysis of electronic properties of intermetallic compounds and their hydrides is to understand why some compounds of non-hydride forming components form a stable ternary hydride e.g. Fe-Ni alloys (61), or vice versa why a compound of hydride forming components does not form a ternary hydride e.g. ZrPd₂ (62).

A detailed discussion of the electronic properties of metal hydrides is given in (63).

1.2.4 Kinetic properties

The hydrogen atoms in metal-hydrogen systems often exhibit a high mobility. The application of a difference in hydrogen activity (or pressure) across such materials can cause hydrogen transport. Because such metals cannot maintain an appreciable internal electric field, this particle flux is the result of a chemical potential gradient in hydrogen, and obeys Fick's laws of diffusion. In some cases, very large particle flux densities can be present, and it was pointed out (64) that hydrogen transport in some metals has characteristics similar to those found in some of the well known so-called fast ionic conductors (sometimes also called superionic conductors), such as silver iodide.

Changes in hydrogen pressure in the environment can cause the formation, or disappearance, of hydride phases at appreciable rates, even at quite low temperatures. Since they typically form by diffusion of hydrogen down concentration profiles in individual phases, and the resulting motion of interphase boundaries, this implies very high chemical diffusion rates in these materials as well. This was first verified on an atomistic scale by nuclear magnetic resonance measurements (65).
Electrochemical methods can also be advantageously employed to measure the chemical diffusion of atomic species in solids (66), and such techniques have been used for the measurement of hydrogen diffusion in a number of metals. Some of these data are included in Table II.

**TABLE II: Hydrogen diffusion in some metals (64):**

\[ D = D_0 \exp \left( -\frac{\Delta H}{RT} \right) \]

<table>
<thead>
<tr>
<th></th>
<th>( D_0 ) (cm(^2)/s)</th>
<th>( \Delta H ) (kJ/mole)</th>
<th>( \dot{D}_{at} ) 25°C (cm(^2)/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>2.9 x 10(^{-4})</td>
<td>4.15</td>
<td>5 x 10(^{-5})</td>
</tr>
<tr>
<td>Nb</td>
<td>5.0 x 10(^{-4})</td>
<td>10.2</td>
<td>8 x 10(^{-6})</td>
</tr>
<tr>
<td>Ta</td>
<td>4.4 x 10(^{-4})</td>
<td>13.5</td>
<td>2 x 10(^{-6})</td>
</tr>
<tr>
<td>Fe</td>
<td>4.0 x 10(^{-4})</td>
<td>4.5</td>
<td>8 x 10(^{-5})</td>
</tr>
<tr>
<td>Fe</td>
<td>7.5 x 10(^{-4})</td>
<td>8.5</td>
<td>1 x 10(^{-5})</td>
</tr>
<tr>
<td>FCC metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>6.0 x 10(^{-3})</td>
<td>25.1</td>
<td>3 x 10(^{-7})</td>
</tr>
<tr>
<td>Pd</td>
<td>2.9 x 10(^{-3})</td>
<td>22.2</td>
<td>3 x 10(^{-7})</td>
</tr>
<tr>
<td>Ni</td>
<td>4.8 x 10(^{-3})</td>
<td>39.6</td>
<td>5 x 10(^{-10})</td>
</tr>
</tbody>
</table>

One of the problems, that has been encountered in the determination of diffusion parameters in many metals, is the sensitivity of some of such metals to the formation of hydrogen-blocking surface oxide.
films in the presence of even very small activities of either oxygen or water vapour. One method that has been used by a few investigators to circumvent this problem involves the use of careful annealing at elevated temperatures in high vacuum (67), followed by the application of a thin external layer of palladium (68), (69).

An alternative method (70) involves the use of a special molten salt electrolyte environment that has a very low value of oxygen or water activity, so that superficial oxide layers are not stable, and thus do not form.

1.3 Materials families of hydrogen-mixed conductors and some of their applications

Hydrogen-transporting mixed conductors can be divided into three classes of materials, i) those in which hydrogen is in solid solution in a metal whose crystal structure is that of the parent metal, ii) those which form new so-called hydride phases in the presence of hydrogen, generally at relatively high hydrogen concentrations - the metal hydrides, and iii) metal-conducting oxides containing appreciable concentrations of hydrogen.

In the following the most important applications of hydrogen-mixed conductors will be described briefly.

1.3.1 Hydrogen storage and purification

One of the well-known applications of metal-hydrogen systems in which intermediate phases are found in the phase diagram involves the reversible formation and decomposition of such phases by changing conditions that control their thermodynamic stability, such as temperature or external hydrogen pressure. In this manner, large concentrations of hydrogen are either absorbed or given off. This procedure can, therefore, be used for the reversible storage of hydrogen. In a number of cases, the volumetric concentration of
hydrogen atoms in such hydride phases is very high, even greater than that of liquid hydrogen.

Reviews of the use of the hydride formation reaction for reversible hydrogen storage are available in a number of places (71-77).

One of the older uses of hydrogen - transporting mixed conductors has been for the purpose of providing high purity hydrogen. This can readily be accomplished if a mixed conductor with highly selective ionic transport is used as a filter.

While the permeability of hydrogen in palladium is very high, and it does not form an oxide hydrogen-blocking external film, even in air at normal temperatures and pressures, the material typically used for this purpose is an alloy of palladium and silver. This alloy does not have the miscibility gap, and, therefore, does not have the problem with volume change-induced stresses and fracture, that is characteristic of pure palladium.

A second approach to the production of pure hydrogen involves the formation of a metal hydride by the absorption of hydrogen, and the subsequent decomposition of this phase. If the diffusion coefficient of other elements is significantly lower than that of hydrogen, only pure hydrogen will form the hydride phase. After changing the conditions such that the hydride is no longer stable, the hydrogen comes back out of the material in quite pure form. Thus a scheme involving periodic cycling of a metal - hydride system can be used to provide high purity hydrogen. The use of metal hydride slurries is a practical approach (78), (79).

1.3.2 Heat pumps

Because of the large entropy changes accompanying the reaction of hydrogen (gas) with a solid metal to form a solid hydride, another solid, the heat of reaction is quite large. This effect can be used for heat pumps, refrigerators, thermal storage systems, etc. Some large
scale applications are being given serious consideration. Reviews of this area are available in several places (75-77), (80-83).

1.3.3 Rechargeable nickel metal-hydride batteries

The rechargeable nickel metal-hydride battery is a relatively new technology based on the nickel-cadmium battery technology. The difference is that the nickel metal-hydride battery uses a metal-hydride negative electrode in place of the cadmium.

The discovery of the hydriding properties of intermetallic compounds such as LaNi₅ (30), (84) and TiFe (29), which absorb and desorb hydrogen at pressures around 1 atm and near room temperature, has provided a new family of rechargeable battery electrodes, the metal hydride electrodes.

This is especially attractive in the case of cells with alkaline hydroxide electrolytes at ambient temperature. During charging of such an electrode hydrogen is formed at activities lower than unity by the electrochemical reduction of water, and its subsequent absorption by the intermetallic compound. During discharge the hydrogen is released and oxidizes. The metal hydride system can be chosen such that the potential plateau hydrogen activity can be rather close to unity. Thus such electrodes will have potentials close to that of elemental hydrogen. This is almost the same as the potential of the Cd/Cd(OH)₂ electrode. Thus when such hydride electrodes are used in conjunction with Ni(OH)₂/NiOOH positive electrodes, the cell voltage will be about 1.3 Volts, approximately the same as that of the well known Cd/Ni batteries.

The overall cell reaction on discharge is

\[ \text{MH} + \text{NiOOH} = \text{M} + \text{Ni(OH)}_2 \]

There is a considerable amount of concern about the environmental pollution and health problems related to the use of cadmium, and
this, as well as the increasing price of this element, is causing a number of battery manufacturers to give serious consideration to the development of a Hydride/Ni alternative to the Cd/Ni cells. In Japan such batteries are commercially available now. Matsushita and Toyota are developing this type of battery for EV applications.

In today's nickel metal-hydride batteries two types of intermetallic alloys are used. These are the rare-earth alloys of the AB5 class, based on the lanthanum-nickel system, and alloys of the AB2 class, consisting mainly of titanium and zirconium. In both cases, some of the base metals are replaced with other metals to achieve the desired characteristics (85).

Primary attention has been given to the use of hydride electrodes based upon the LaNi5Hx system. The addition of certain other elements has led to significant increases in kinetics and lifetime in ambient temperature rechargeable cells (86-89). For example, the volume expansion is reduced by a partial substitution of Ni with Co, and the interfacial properties improved with small amounts of Al and Si. The cycle life improves upon the substitution of Ni in the order Mn < Ni < Cu < Cr < Al < Co. A substitution of the rare earth metal site with Ti, Zr, or other lanthanides such as Nd and Ce result in the formation of a protective surface film and enhance the cycle life. This eventually led to the use of relatively inexpensive misch metal, Mm, a naturally occurring mixture of rare-earth metals (mainly La, Ce, Pr, and Nd) in place of La. The use of misch metal also improved the durability of the alloy, as evident from the long cycle life as well as the quantitative estimates of the surface layers La(OH)3 and Mm(OH)3 on the cycled electrodes (90).

The AB2 alloys have been improved by using vanadium-titanium-zirconium-nickel based alloys. The functions of the various elements are:
V: good hydrogen storage (VH2), soluble oxide increases surface porosity, high ΔH.
Zr, Ti: good hydrogen storage (ZrH2), (TiH2), passive oxides, high ΔH.
Ni: no hydrogen storage, resistant to oxidation, destabilizes $\Delta H$, catalyst for hydrogen oxidation.
Cr: vanadium corrosion inhibitor

In addition, small amounts of other elements are added to alter one or more properties such as high-temperature/low-temperature performance, self-discharge, and rate capability. The uniqueness of these alloys rests in their disordered microstructures and the presence of multiple phases (91).

The $\text{AB}_2$ alloys typically have a higher capacity than the $\text{AB}_5$ alloys, approximately 400 mAh/g compared to 250-300 mAh/g. As the hydrogen storage alloys are denser than the cadmium electrode, the volumetric energy density of the metal hydride electrode is about 50% higher than the cadmium negative electrode of the nickel cadmium cell.

An alternative is to use materials based upon the titanium-nickel hydrides, and considerable development effort has gone into this direction as well (89), (92). In this case, as well as with the $\text{LaNi}_5\text{H}_x$ materials, reduced capacity upon recycling is due, to a large extent, to the formation of a blocking oxide layer upon the electrode structure. This effect is reduced by increased nickel activity, for nickel does not form a surface oxide in ambient temperature aqueous hydroxide solutions at the potentials imposed by the hydride formation reactions.

The nickel metal-hydride battery is becoming competitive with the nickel-cadmium cell for use in consumer electronics such as lap tops, cellular phones, and camcorders, which is a fast growing market (it will reach $10^{13}$ USD/year by the year 2000 for cordless consumer electronics, including the battery; the fraction for the battery being about 1% on the average)

An extensive description of the nickel metal-hydride batteries in terms of constituents, construction, performance, and charging
characteristics is given in the Handbook of Batteries (93) and in (75-77).

1.3.4 Composite S/L/S Hydrogen "Solid Electrolyte"

If a liquid hydrogen-transporting electrolyte can be sandwiched between two mixed-conducting membrane electrodes that are highly permeable to hydrogen, such a solid/liquid/solid (S/L/S) configuration will act as though it were a solid electrolyte (94). This concept can be especially useful in hydrogen systems, where all of the presently known hydrogen transporting solid electrolytes have significant practical limitations, such as low conductivities and limited stability at low to intermediate temperatures.

The S/L/S configuration can have a high conductivity at intermediate temperatures. An example is shown schematically in Figure 8, in which a liquid molten salt electrolyte is employed that conducts hydrogen in the form of hydride ions, rather than protons, between two hydrogen-transparent mixed conductors. Examples of possible hydride-conducting molten salt electrolytes are LiCl-KCl-LiH and KOH-KH solutions. The characterization of the LiCl-KCl-LiH molten salt in terms of stability and conductivity will be presented in chapter 5.

![Diagram](attachment://figure8.png)

**Figure 8:** S/L/S (Solid/Liquid/Solid) hydrogen conducting "Solid Electrolyte" configuration
Properties required of the mixed conductors include a high permeability at the temperature of operation, and at the hydrogen activities imposed across the cell. In addition, they must be stable in contact with the chemical and electrochemical environment imposed at the respective electrodes and the external surroundings.

Such S/L/S hydrogen-conducting "solid electrolyte" configurations can serve in various applications:

- Batteries
- Fuel Cells
- Water Electrolysis
- Hydrogen Cycle Thermoelectric Converters
- Hydrogen Sensors
- Hydrogenation and Dehydrogenation Catalysis

Hydrogen sensors are of increasing interest for a wide variety of purposes. Aside from reproducibility and reliability, the two most important properties are sensitivity and selectivity. The latter is often a much more difficult problem. Mixed conductors should be useful in this regard, because their properties are generally highly selective to specific atomic species.

Two general types of application can be considered. In one case, a mixed conductor can be used as a selective membrane. If used as an electrode in an electrochemical cell in which the electrolyte also transports the desired species, measurements of the current through the cell will provide information about the species present in the adjacent phase on the other side of the mixed-conducting membrane.

One could also employ a potentiometric, rather than galvanometric arrangement. In this case, the mixed conductor acts as a selective solid solution, whose potential is measured at the electrolyte/electrode interface by an electrochemical cell. If one can assume selective equilibrium between the mixed conductor and the adjacent phase, so that the chemical potentials of the desired species
correspond, and that the chemical diffusion coefficient is sufficiently high in the mixed conductor, this scheme may also be employed. The S/L/S hydrogen-conducting solid electrolyte is a very welcome configuration for water electrolysis since it can be used at intermediate temperatures where the decomposition voltage for water is decreased. A novel concept for decomposition of water vapour at intermediate temperatures and separation of the hydrogen through a permeable membrane is shown schematically in Figure 9.

![Diagram of water vapour electrolysis](image)

**MEMBRANE**

**Figure 9:** Water vapour electrolysis at intermediate temperatures

The electrochemical cell consists of two chambers, which are separated by a hydrogen-permeable metallic membrane (hydrogen mixed-conductor). The electrolyte in the right chamber is a KOH/NaOH eutectic mixture. The electrolyte in the left chamber is a
molten salt, containing LiH. Water vapour is provided into the KOH/NaOH electrolyte. The total voltage \( E = (E_1 + E_2) \) across the cell is determined by the decomposition voltage of water vapour at the working temperature. When applying a voltage \( E_1 \) between the oxygen electrode and the membrane, which is smaller than the decomposition voltage, that voltage fixes the hydrogen activity at the interface between the electrolyte and the membrane according to the Nernst equation. Due to the concentration gradient the hydrogen passes through the membrane and can be evolved at unit activity in the left chamber by applying a voltage \( E_2 \) between the membrane and the hydrogen electrode. The arrangement can be considered as two separate circuits which are electronically connected through the membrane. If \( E_1 \) and \( E_2 \) are held constant, a steady state current is attained in each of the chambers with \( I_1 = I_2 \).

1.3.5 Hydrogen Cycle Thermoelectric Device

A novel thermoelectric device has been proposed by Roy (95) and uses the S/L/S configuration as a composite electrolyte to extract electrical energy from a difference in temperature. This concept involves a continuous hydrogen cycle that produces a pressure difference across the S/L/S electrochemical cell. Hydrogen reacts with an alkali metal at a low temperature and low pressure to form a soluble hydride. This is then mechanically pumped to a location with a higher temperature, where the hydride decomposes, and the hydrogen is released at a higher pressure. This high-pressure hydrogen is brought into contact with one side of the S/L/S cell, whereas the other side is in contact with the lower pressure hydrogen that is in equilibrium with the alkali metal at the lower temperature. The pressure difference gives rise to a voltage according to the Nernst equation, and the passage of current produces electrical work.
1.3.6 Hydrogen insertion compounds of metal oxides

Most transition-metal oxides are unreactive towards molecular hydrogen below elevated temperatures. However, dissociated hydrogen reacts topotactically with a wide range of binary and ternary transition-metal and uranium oxides at ambient temperature to produce hydrogen insertion compounds with the general formula $\text{H}_x\text{MO}_n$ or $\text{H}_x\text{MM'}\text{O}_n$ which are often referred to as hydrogen bronzes. $\text{M}$ is a transition metal, and the value of $n$ specifies the stoichiometry of the relatively stable host metal-oxygen structure. The value of $x$ indicates the amount of hydrogen inserted into the structure and can often vary over an appreciable range. Powder X-ray diffraction confirms that the lattice parameters of the parent oxide are little changed on hydrogen insertion, with the implication that the metal-oxygen framework is largely retained. At high $x$ values, however, amorphous products are sometimes found implying that a structural collapse has occurred. The maximum hydrogen contents achieved under standard conditions are controlled by both structural factors and the redox characteristics of the metal oxygen states involved (96).

The hydrogen insertion compounds $\text{H}_x\text{MO}_n$ are formally mixed valence and, in marked contrast to the parent oxides, often have deep colours and behave as good electronic conductors, either metallic or semiconducting. The controllable variation in electronic properties has been exploited in electrochromic displays, which utilize the colour changes induced by insertion of hydrogen into e.g. WO$_3$ or IrO$_2$ films (97) and in other sensors, which respond to conductivity or optical changes in oxides on hydrogen incorporation (98). The recovery of hydrogen on heating, $\text{H}_x\text{MO}_n = \text{H}_{x-y}\text{MO}_n + y/2 \text{ H}_2$ (for favourable systems at high $x$ values), suggests a possible application as hydrogen storage materials (99). The reactivity of inserted hydrogen towards neutral Lewis bases such as NH$_3$ and organic amines, and the function of $\text{H}_x\text{MO}_n$ as a hydrogen source in hydrogenation reactions have both been investigated (100), (101).
Originally, analogies were assumed due to the apparent similarities between the electronic and structural properties of the hydrogen-containing phases and those of the well known alkali-oxide bronzes in which alkali ions reside in cavities in the parent-oxide matrix. They were misleading. The alkali metal in an oxide bronze has a definite ionic radius which requires a minimum cavity size for its central accommodation, usually of >0.2 nm radius. This is not so for hydrogen which invariably attaches itself in oxide materials to oxygen as -OH or -OH₂, with a characteristic bond length of about 0.1 nm. This is found to be so for the many oxy-hydroxides and oxide hydrates which occur naturally. The same mode of attachment is found in those hydrogen insertion compounds HₓMOₓn for which complete structure determination have been carried out. For this reason, hydrogen bronzes, HₓMOₓn, should be formulated as oxy-hydroxides, MOₓ₋ₓ(OH)ₓ, rather than Hₓ⁺MOₓn(xe⁻), which might seem to imply the existence of isolated protons.

In regard to their electronic properties, hydrogen insertion compounds of transition metal oxides are analogous to the corresponding alkali-metal bronzes. They are, however, structurally distinct with hydrogen directly bonded to oxygen within the oxide framework. Several reviews (102-105) cover different aspects of the hydrogen insertion into metal oxide compounds.

The most common application of hydrogen bronzes is in electrochromic devices, in which hydrogen is transported across an electrochemical cell with an aqueous proton-conducting electrolyte to and from a hydrogen bronze electrode, e.g. HₓWO₃. As the value of x varies, so does the free electron concentration, and thus the optical absorption. The optical density is proportional to the inserted solute concentration up to a charge transfer of about 50 millicoulombs per cm². Over that range, such materials can be changed from quite transparent to a very dark blue-black, and thus can give very good optical contrast.

Whereas earlier efforts to develop such configurations for practical applications were aimed at their use in watch and small instrument
displays, attention has more recently turned to the possibilities of their employment as electrically-controlled mirrors, and as "smart windows" for thermal control in buildings. To date, electrically controlled mirrors are on the market. The firm Gentex, USA, manufactures electrochromic mirrors for use as rear-view mirrors in both cars and trucks. They have sold a number of million already, mostly in the United States.

All these and some more applications of hydrogen mixed conductors play a very important role within a global energy concept that is based upon the use of renewable hydrogen as the only energy carrier on earth. Hydrogen is a renewable source of energy when it is being extracted from water using solar energy (or wind or hydropower), and converted back into water by the reaction with oxygen giving off the energy of reaction. This hydrogen energy cycle is known as the hydrogen economy concept.

Although the concept of the hydrogen economy was initiated some thirty years ago, when its significance to the global energy and environmental situation had been recognized, its commercial utilization is advancing very slowly. In the following section a brief insight into the concept and the current stage of development of some of the important factors will be given.

1.4 Advances in The Hydrogen Economy and Hydrogen Ecology

Hydrogen is undoubtedly the ideal energy carrier on earth. It reacts with oxygen to form water which carries an energy of 273 kJ per mole. Because of the high reactivity its occurrence in our environment is limited to trace amounts in the air but it is very abundant in a large number of compounds of which water is by far the most important. However, hydrocarbons, better known as combustible fossil fuels, are to date still the cheapest energy sources. Such a view is suggested and encouraged by low oil prices.
Current prospects as to a steady supply of sufficient energy in the future are diffuse. Some time ago it was thought that nuclear power will gradually supply an increasing fraction of electricity and, when the liquid fossil fuel supply rate will begin to decline, the losses will be replaced by synthetic products derived from coal. As we know better today, this classical type of energy thinking is no more acceptable, since it neglects the environmental consequences of its implementation.

During the combustion of fossil fuels, a number of undesired products are emitted into the atmosphere of which some have been identified as being responsible for disadvantageous global changes. Combustion of fossil fuels (hydrocarbons and coals) causes the introduction of \( \text{SO}_2, \text{CO}_2 \), and oxides of nitrogen into the atmosphere. \( \text{SO}_2 \) has been identified as a cause of acid rain (106). Oxides of nitrogen lead to photochemical smog reactions. These reactions require hydrocarbon vapours, oxides of nitrogen, and sunlight. Adverse health and environmental effects include eye and respiratory irritation, production of ozone in the atmosphere, interference with visibility and characteristic forms of vegetation damage. The injection of \( \text{CO}_2 \) into the atmosphere by combustion of non-renewable fossil fuels will increase the greenhouse effect (107), (108), (109). Increased \( \text{CO}_2 \) emissions into the atmosphere are most probably the cause of the rise in the global temperature (110), (111), and it has been predicted that the continued injection of \( \text{CO}_2 \) may lead to a rise of the sea level. Another identified damage arising from the burning of fossil fuels is that due to the secondary formation of ozone by the decomposition of \( \text{NO}_2 \).

\[
\text{NO}_2 + \text{hv} = \text{NO} + \text{O}^* \quad /11/
\]

\[
\text{O}^* + \text{O}_2 = \text{O}_3 \quad /12/
\]

Ozone near the ground attacks humans and plants.

Although theories and forecasts concerning changes in the global atmosphere in the near and far future are controversial, there is no
question that emissions have to be reduced and eventually avoided due to the expectation of a continously increasing demand for energy as a result of an increasing life standard in the industrialized countries, and a strongly increasing population in the third world countries.

So far not much has been undertaken to broadly apply technologies which avoid undesired emissions in the first place because they are not profitable. Earlier predictions concerning the exhaustion of fossil fuels, and resulting in a breakdown of the world energy sources are now being seen in a different context, which is related to the deleterious effects of burning fossil fuels upon mankind and its environment.

On the long run, there seems to be only one other possibility which is safe and non-polluting, and that is to collect solar energy upon a massive scale, at first from desert areas and the sea, and possibly from space-based collectors. The solar based energy could then be converted into a medium which would have to be environmentally acceptable, and could be distributed economically on a large scale over long distances. There are three media which may be considered: ELECTRICITY, HYDROGEN, and METHANOL because all other media are environmentally damaging. In the absence of room temperature superconducting cable, passing very high currents, the media for large distance distribution are reduced to two. The Methanol medium is only environmentally acceptable when it is produced by reducing local CO₂ emissions with hydrogen from solar or bio mass.

Thus, from an environmental point of view hydrogen ecology could be the scientific answer, if hydrogen economy were to be the political response.

Solar light as a "FUEL"
Light as an energy source has usually been rejected because of the apparent difficulty of its storage and transmission. These difficulties are largely removed, if light can be used to split water and the hydrogen used as the energy medium or fuel.
The most suitable non-polluting and environmentally acceptable medium for the storage of solar energy is hydrogen.

Proponents who have discussed such a scenario in the past have usually concluded that it was environmentally desirable and technologically feasible, but economically then not acceptable. However, this consideration was before the idea of "REAL ECONOMICS" was proposed by Bockris (112). In real economics, accounting is made not only from the cost of producing, transporting, and refining fuel, but also of the concommitant costs related to the pollution of the atmosphere. In addition, accounting is made for the efficiency of conversion of the fuel concerned in the scenario to mechanical and electrical energy, which varies with various fuels. Further, the recent emergence of fuel cells (because of the ease of modular construction together with enhanced efficiency of energy conversion) also greatly favours the hydrogen scenario because an important fuel cell fuel is hydrogen. Their use at this time with natural gas is deceptive since the natural gas is only used as a source of the hydrogen which is fed to the fuel cell. Furthermore, the dominant component in the cost of the fuel cell is then the reformer. Internal reforming has, therefore, attracted much attention.

The concept of a hydrogen economy requires the production of hydrogen from non-fossil fuels which have been known for some time and so have the technologies for the energetic utilization. Figure 10 represents the various energy conversion steps and processes for non-fossil primary energy.

In the following a number of these processes will be described briefly in terms of hydrogen producing reactions.
Figure 10: Energy conversion steps and processes for non-fossil primary energy
1.4.1 Hydrogen production by water splitting

Water, undoubtedly the most important hydride, was first recognised as the product of the combination of hydrogen and oxygen by Cavendish in 1781, who had also discovered hydrogen in 1766.

In TABLE III a comparison of the hydrogen contents in various hydrogen compounds is shown.

TABLE III: Hydrogen contents in various hydrogen compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight kg/kmole</th>
<th>Density kg/m³</th>
<th>Number of H atoms per Unit Volume $10^{28}$ /m³</th>
<th>Weight Percent of Hydrogen wt %</th>
<th>Partial Hydrogen Density kg H/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>18</td>
<td>1000</td>
<td>6.7</td>
<td>11</td>
<td>111</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>98.1</td>
<td>1841</td>
<td>2.2</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>liq. CH₄</td>
<td>16</td>
<td>425</td>
<td>6.3</td>
<td>25</td>
<td>105</td>
</tr>
<tr>
<td>liq. H₂</td>
<td>2</td>
<td>71</td>
<td>4.2</td>
<td>100</td>
<td>71</td>
</tr>
<tr>
<td>TiH₂</td>
<td>49.9</td>
<td>3800 a)</td>
<td>9.2</td>
<td>4</td>
<td>153</td>
</tr>
<tr>
<td>LaNi₅H₆</td>
<td>438.5</td>
<td>6225 b)</td>
<td>5.3</td>
<td>1.4</td>
<td>88</td>
</tr>
<tr>
<td>TiFeH₁.₉₅</td>
<td>105.7</td>
<td>5470 c)</td>
<td>6.2</td>
<td>1.85</td>
<td>101</td>
</tr>
</tbody>
</table>

a) from Kleinert (113)

b) from references (30), (114)

c) from Reilly and Wiswall (29)
Chemical water splitting methods
Probably by far the oldest technique used to split water is by running steam over iron (115) followed by the reduction of iron oxide to metallic iron with carbon monoxide.

\[
3 \text{H}_2\text{O} + 2 \text{Fe} = \text{Fe}_2\text{O}_3 + 3 \text{H}_2 \quad \Delta G_{r(700K)} = -8.9 \text{ kJ/mol} \quad /13/
\]

\[
2 \text{Fe}_2\text{O}_3 + 6 \text{CO} = 4 \text{Fe} + 6 \text{CO}_2 \quad \Delta G_{r(700K)} = -69.6 \text{ kJ/mol} \quad /14/
\]

This process is only of historical importance and has been replaced by the "shift reaction" in which steam is reduced in a gas phase reaction with carbon monoxide using a heterogeneous catalyst (116), or by the reaction of steam with hydrocarbons. The carbon monoxide produced during the "steam reforming" of hydrocarbons is subsequently used to reduce H\textsubscript{2}O into hydrogen and CO\textsubscript{2}(116) by the "shift reaction" (117).

\[
\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad \Delta G_{r(700K)} = -12.93 \text{ kJ/mole} \quad /15/
\]

\[
\text{C}_m\text{H}_{2n} + m \text{H}_2\text{O} = m \text{CO} + (n+m) \text{H}_2 \quad /16/
\]

Electrochemical water splitting - Water Electrolysis
Water can be separated into its fundamental components, hydrogen and oxygen, by the utilization of electrical energy. The total amount of energy for the reaction

\[
\text{H}_2\text{O (gaseous or liquid)} = \text{H}_2 (\text{g}) + 1/2 \text{O}_2 (\text{g}) \quad /17/
\]

can be provided in part as electrical energy and part as thermal energy, the ratio between electrical and thermal energy being dependent upon the fundamental thermodynamic relationships of the process given by equation /6/.

It must be kept in mind that the reactant water in equation /17/ can either be gaseous or liquid. The difference in energy in the respective reactions is equal to the heat of vaporization of water.
In TABLE IV values for the heat and free energy of formation of water in units of Joules per mole (118) are given for several temperatures. Also shown are the equivalent values for electrolysis given in volts based on

\[ \Delta G_r = -zFE \]

where \( z \) is the number of electrons involved in the reaction, \( F \) is the Faraday constant, and \( E \) the voltage.

**TABLE IV: Enthalpies and free energies of formation of water in the liquid and gaseous state from reaction /17/.

<table>
<thead>
<tr>
<th></th>
<th>( T ) in K</th>
<th>( \Delta H_r ) kJ/mole</th>
<th>( \Delta G_r ) kJ/mole</th>
<th>( \Delta H_r - \Delta G_r ) kJ/mole</th>
<th>( \Delta H_r ) V</th>
<th>( \Delta G_r ) V</th>
<th>( \Delta H_r - \Delta G_r ) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} ) liquid</td>
<td>298</td>
<td>-285.830</td>
<td>-237.141</td>
<td>-48.689</td>
<td>1.481</td>
<td>1.229</td>
<td>0.252</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>-283.456</td>
<td>-225.169</td>
<td>-58.287</td>
<td>1.468</td>
<td>1.167</td>
<td>0.090</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) vapour</td>
<td>298</td>
<td>-241.826</td>
<td>-228.620</td>
<td>-13.206</td>
<td>1.253</td>
<td>1.184</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-242.847</td>
<td>-223.951</td>
<td>-18.896</td>
<td>1.258</td>
<td>1.160</td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>-249.475</td>
<td>-175.934</td>
<td>-73.541</td>
<td>1.293</td>
<td>0.912</td>
<td>0.381</td>
</tr>
</tbody>
</table>

If liquid water is decomposed in an electrolysis cell the values in the first group at the top of Table IV apply. Thus, at \( 25^\circ \text{C} \) (298 K) one must apply at least 1.229 volts to drive the reaction to form hydrogen and oxygen gas. In addition, one must add an amount of heat equivalent to 0.252 volts, or the cell would cool down. In order to hold the cell at constant temperature (isothermal conditions) without supplying heat one must apply a minimum of 1.481 volts, the thermoneutral voltage. In practice, practical current densities require that conventional water electrolyzers operate at voltages
exceeding 1.481 volts. Internal resistances and polarization impedances due to the reactions cause voltage losses.

The relationship between the voltage and the heat necessary for reaction (16) is shown in Figure 11.

![Graph showing variation of enthalpy and free energy](image)

**Figure 11**: The variation of enthalpy and free energy for the decomposition of water, as well as the level of endothermic heat required, as a function of temperature.

It can be seen, that at 1000°C (1273 K), for a partial pressure ratio of water vapour to hydrogen equal to 1 (p_{H2O}/p_{H2} = 1), the minimum voltage required is 0.92 volts and heat equal to 0.37 volts must be added to the system, along with the heat of vaporization of water.
(0.21 volts), coming to 0.58 volts. Thus the total energy added is 1.50 volts, of which one third of the energy enters the process as lower-cost heat.

In general, two basic modes of operation are possible:
- Operation at or above the thermoneutral voltage with no requirement for heat addition from any high-temperature source
- Operation with the maximum allowed heat input and minimization of electrical energy input

Up to date, three different types of processes have been developed:

- Water electrolysis utilizing alkaline aqueous electrolytes and a porous diaphragm to separate the cathode and anode compartments

- Water electrolysis utilizing a proton-conducting solid polymer electrolyte (SPE) membrane

- High-temperature steam electrolysis utilizing oxygen-conducting ceramic electrolytes operated between 700 and 1000°C.

All three techniques are represented schematically in Figure 12 (119).

When a proton conducting ceramic electrolyte (120) with porous electrodes on both sides is exposed to air with different humidities, a stable e.m.f. is observed. In this case, the electrode in the higher humidity environment is the negative pole. Thus, such a system are proposed for steam electrolysis. It is the analog to the high temperature steam electrolysis utilizing an oxygen-conducting ceramic electrolyte, but has the advantage of the lower operation temperature of around 700°C (121), (122).

At present, alkaline water electrolysis and membrane electrolyzers are commercially available, while steam electrolysis is still far from being technologically mature.
Water electrolysis in alkaline electrolytes has many similarities with Ni/metal hydride batteries. Although the electrodes of the electrolyser have very little storage capacity, they act in the same way as in the battery when operated at hydrogen activities below the hydrogen evolution potential. Thus, much can be learned from the Ni/metal hydride batteries to improve the performance of alkaline electrolysers. This will mainly relate to conditions under which these systems will be used in an intermittent operation mode, i.e. for electric power load levelling, or coupled to electric power generated by an array of solar cells (solar field).

It is often stated that electrolytic production of hydrogen from water is more expensive than production of hydrogen by chemical reaction of fossil fuel (e.g. coal) with water. The main reason for the apparent expense of electrolytic hydrogen is the cost of the electricity. The efficiency of conversion to hydrogen by means of electrolysis is certainly greater than by any other means. Thus, in regions of the world where very cheap electricity is available, hydrogen can be obtained very cheaply by means of water electrolysis. Thus, for 0.05 $/kWh electricity, the cost of a Gigajoule of hydrogen could be around $4 (equivalent to 15 cents per liter gas). But it is not valid to compare hydrogen obtained by electrolysis using expensive (say 5 cents/kWh) electricity with hydrogen obtained, e.g., from coal, for here, the pollutional costs are neglected. The cost of the electricity in making a Gigajoule of H₂ in $ is 2.29 Ec, where E is the electrode potential in Volts and c the cost of fuel to produce electricity in cents/kWh. Costs vary from $ 1-3/GJ.

Electrochemical water splitting is, from an environmental viewpoint, by far the most attractive method to produce hydrogen. However, economic factors are delaying major progress in this field. These are the high costs for electricity for the room-temperature systems and the high costs of heat in case of the high-temperature electrolysis. An intermediate solution, for which the thermodynamics of the system are more favourable could be intermediate temperature steam electrolysis, which would be especially attractive, when waste heat at about 400°C is available.
30% KOH, 80 °C
Alkaline water electrolysis

OH⁻, K⁺-ions as charge carriers

H₂O + H₂O → H₂O + H₂ + O₂

ZrO₂
Steam 800-900 °C
Steam electrolysis

O₂²⁻-conductive solid electrolyte

Highest purity H₂O, 100 °C
Solid Polymer Electrolyte
SPE - Electrolysis
H⁺-conductive ion exchange membrane

Figure 1.2: Schematics of the three electrochemical water splitting processes (119)
In Chapter 5 a novel intermediate temperature steam electrolysis concept will be introduced, that utilises a Solid/Liquid/Solid (S/L/S) composite membrane to electrochemically decompose H₂O.

**Thermal steam splitting**
Thermal steam splitting occurs at temperatures above 2000 K without any auxiliary system. However, the temperatures required are so high that the process is economically unattractive.

**Thermochemical processes**
Thermochemical processes utilise a series of chemical steps in which hydrogen and oxygen are released in separate reactions at different temperatures.

\[
\text{Me}_2\text{O} \quad \text{high temperature} = 2 \text{Me} + 1/2 \text{O}_2
\]

\[
2 \text{Me} + \text{H}_2\text{O} \quad \text{low temperature} = \text{Me}_2\text{O} + \text{H}_2
\]

The requirement of several process steps leads to complicated process engineering for the total system, which in turn places this technique among those with poor economic viability.

**Photoelectrochemical water splitting**
Solar energy conversion using a photoelectrochemical cell (PEC) is a widely studied research topic. This process is based on the absorption of photons and the generation of electron-hole pairs in a semiconducting photoanode and a metallic counter electrode which are separated by a proton-conducting electrolyte. Photoelectrolysis of water is achieved upon irradiation of the photoanode, where oxygen evolves. Hydrogen is formed at the metallic counter electrode. The economic storage of this hydrogen is very important in the harvesting of solar energy.

The most promising approach for the storage of the energy from a solar cell (either photovoltaic or photoelectrochemical) is by integration of the solar cell and the storage device into a single unit. Examples have been demonstrated by Sammels and Ang (123) for an
all solid state battery system, which can be recharged directly from solar radiation, and by Schoonman (124), who incorporated a hydride forming metal as the negative electrode to in situ store the hydrogen produced.

Photochemical methods
This technique requires just like the photoelectrochemical water splitting a suitable absorber within which radiation is transformed into potential energy of an excited electronic state which can in turn trigger chemical reactions by electron transfer from the excited absorber system to the chemical redox system.

Photobiological hydrogen production
Some biological systems, such as blue algae prokaryotes and green algae eukaryotes, which themselves contain enzymes, have the capability to decompose water under the influence of light to release hydrogen and oxygen. The potential advantage of such systems is that they are self-reproducing, building themselves up on the basis of the presence of CO₂ and other natural materials.

The most expensive part of the photoconversion methods mentioned above consists of the materials costs themselves, and their deployment supports over large areas. However, in the algae approach, the principal costs would appear in the collection of hydrogen. Because of the low hydrogen production rates and the problem of separating hydrogen and oxygen from the reaction zone this technique has not been technologically successful thus far.

In principle, any system which lives by means of photosynthesis, and contains hydrogenase, is a candidate for possible work on the production of hydrogen from water by biocatalytic means.

1.4.2 The energetic use of hydrogen

Hydrogen combustion
Hydrogen (a side product in a number of chemical reactions) is burned in large amounts in the chemical industry to provide process heat. Industrial combusters operate with partially premixed air (the Bunsen principle), with total air pre-mixture, or without air pre-mixture (jet burners).

Hydrogen and oxygen in the molar ratio 2:1 do not react readily to form water, when they are present in the molecular state. The diatomic oxygen or hydrogen molecules must be split, and prior to their recombination to form the combustion product, H₂O. This can be achieved on the surface of a catalyst or at high temperatures, for example, in a glow discharge. Once an atomic species is formed a chain reaction sets in in which H₂O is produced. In addition, recombination reactions that produce H₂, O₂, and H₂O₂, may take place, the ratio to water production being dependent upon process parameters such as temperature, pressure, and catalyst.

When air is used as an oxygen source under certain process conditions the nitrogen in the air participates in the overall reaction process, becoming oxidised to nitric oxides. When this occurs (generally at high temperatures and pressures), these undesired products have to be removed in a separate step by catalytic decomposition.

In hydrogen combustion heat is the major product. This can, in turn, be transformed into electrical energy via thermomechanical conversion devices. Its conversion ratio is then limited by the Carnot factor.

The preferred way to convert hydrogen into electrical energy is by reacting hydrogen and oxygen electrochemically using either a proton or an oxide-ion conducting electrolyte in a fuel cell system. When this direct conversion of chemical into electrical energy is being performed in a fuel cell device it is not limited by the Carnot factor.
Fuel cells
Fuel cells, a form of primary batteries, are electrochemical devices, which are able to convert chemical energy - fuel - into electrical energy, the product being water or steam. The fuels are supplied on one side of an either proton or oxide-ion conducting wall and depending on the type of ionic conductor the reaction occurs at the oxygen electrode/electrolyte interface, or at the hydrogen electrode/electrolyte interface, respectively.
The general design of a fuel cell is schematically shown in Figure 13.

![Fuel cell diagram]

- **B** - Bipolar plate with process air & fuel channels
- **CA** - Anode DIGAS cooling plate
- **CC** - Cathode DIGAS cooling plate

**Figure 13:** Schematic representation of a fuel cell

Today's most important energy source to the individual user is electrical energy. In the concept of hydrogen economy fuel cells
represent the most efficient way to convert hydrogen energy into electrical energy. Together with the hydrogen generation processes from water, fuel cells represent the foundation of the hydrogen economy concept.

Compared with other electricity-generating systems, which are currently in use, fuel cells offer the following potential advantages: substantially higher conversion efficiency of fuel energy to electricity, modular construction, high efficiency at partial load, minimal siting restrictions, potential for co-generation of electricity and heat, and, depending on the kind of fuel used, much lower production of pollutants (including acid-rain precursors). The anticipated results of effective fuel-cell commercialisation will be reduced fuel and capital cost, cleaner environments, and hence lower costs to users of electricity.

To date five general types of fuel cells, listed according to their temperature of operation, are commonly considered (see TABLE V):

- near ambient temperature systems utilizing aqueous and polymeric electrolytes (AFC, SPEFC)

- phosphoric acid fuel cells (PAFC), which operate at temperatures around 150 - 200 °C

- intermediate-temperature (600 - 700 °C) systems utilizing a molten carbonate electrolyte (MCFC)

- high-temperature systems utilizing a solid oxide-ion conducting ceramic electrolyte (SOFC)

An extensive description of fuel cell developments was published by the Department of Energy Advanced Fuel Cell Working Group (AFCWG) in 1985 (125) and the recent state-of-the-art has been described by Kartha and Grimes (126).
It is not intended to describe each system in detail. However, given the importance of these hydrogen energy conversion devices, it is considered worthwhile to review the important aspects of the different types of fuel cells.

Thus a condensed description of the various fuel cell systems concerning the state of development as well as recommendations for further research needs has been extracted from the recent literature.

**TABLE V: Types of fuel cells**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temperature in °C</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>70 - 200</td>
<td>high current and power densities, high efficiency</td>
<td>CO₂ intolerance</td>
<td>extensive field testing</td>
</tr>
<tr>
<td>Alkaline Fuel Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPEFC</td>
<td>80 - 110</td>
<td>high current and power densities, long operating life</td>
<td>CO intolerance, water management</td>
<td>field testing (kW scale) including prototype vehicles (EV)</td>
</tr>
<tr>
<td>Solid Polymer Electrolyte Fuel Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAFC</td>
<td>150 - 210</td>
<td>technologically well advanced</td>
<td>relatively low efficiency, limited lifetime, noble metal catalyst</td>
<td>commercially available</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCFC</td>
<td>550 - 650</td>
<td>high efficiency, internal fuel processing, high grade waste heat</td>
<td>electrolyte instability, short operating life</td>
<td>field testing (2 MW-scale)</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOFC</td>
<td>1000 - 1100</td>
<td>internal fuel processing, high grade waste heat, long operating life, potentially inexpensive</td>
<td>high operating temperature, limited thermodynamic efficiency, relatively low ionic conductivity</td>
<td>field testing, and laboratory testing (kW-scale)</td>
</tr>
<tr>
<td>Solid Oxide Fuel Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Alkaline fuel cell (AFC)

The alkaline fuel cell technology was developed in the early 1960's for the NASA space programme and AFC's powered all of the life-support systems in the Apollo space craft. Its development for terrestrial uses is less advanced than that of the PAFC's and the high temperature FC's, because of electrolyte sensitivity to CO₂. Operation of AFC's requires the use of pure hydrogen, and, therefore, often requires cost effective removal of CO₂ from hydrocarbons. However, AFC's offer the best prospects among the low-temperature FC systems of finding substitutes for noble metal electrocatalysts. Any major penetration of FC's into the transportation market requires elimination of Pt-group metals as electrocatalysts. Other advantages the AFC's are having over the PAFC's are higher power capability and potentially higher energy efficiency because of higher rates of oxygen reduction, lower operating temperatures, and hence better materials tolerances, better performance which offer the possibility of electric vehicle operation without hybridization with a battery, and a faster start-up time.

Further research is needed and should include
- alternative electrocatalysts (single phase and mixed metal oxides)
- basic electrode structures with improved wetting properties and optimized electrolyte distribution
- materials research related to stability and lifetime of cell components
- the cell design should be aimed at development of bipolar systems, minimization of ohmic losses, heat and water management, and evaluation of circulatory electrolyte systems
- new, low-cost stable supports (carbons, carbides, nitrides, and oxides) for the more expensive catalysts are needed

The successful development and commercialization of AFC's is closely linked to the availability and price of pure hydrogen. This fuel may become available in off-peak periods from hydroelectric power, as at
present in Canada, or, according to Japanese programmes on hydrogen storage and alternative inexpensive methods for the production of high purity hydrogen from solar cells. In view of this, continued work on hydrogen storage is recommended.

Phosphoric acid fuel cell (PAFC)

The phosphoric acid fuel cell (PAFC) is the most mature FC in terms of technological advancement and readiness for commercialisation in near- and medium term applications. PAFC's have been under development for about 20 years. The PACF was selected for development as the most viable acid FC type because of its superior and unique stability characteristics, despite its inherently poor ionic properties. The major driving force for its dominant position has been the widespread view, that it alone among the lower temperature FC's shows relative tolerance for reformed hydrocarbon fuels, since the steam raised in the FC is used for the reforming, CO is removed by a shift reaction, and rejection of CO₂ occurs naturally by acid.

Significant improvements in the performance, cost and durability have involved all aspects of PAFC development, from basic electrochemistry to overall system optimization. Crucial accomplishments to make PAFC's into a commercially acceptable power system have involved the qualification and exploitation of carbon materials as the backbone of the fuel-cell stack, reduction of electrocatalyst platinum loadings by more than an order of magnitude with the substitution of highly-dispersed, carbon-supported catalysts for the Pt-black types used previously, and elevation of the temperature by 60-80°C to about 200°C, which has resulted in significant augmentation of cell and overall system efficiencies. For larger PAFC's of the type directed towards electric utility applications, the development of pressurised systems has further improved efficiency and, hence, economic attractiveness. PAFC's are now projected to establish a significant niche in the electric- and gas-utility markets, and other application areas while providing benefits in terms of fuel savings, environmental impacts, and packaging and siting logistics. However, the total market
penetration for PAFC's will be directed by hard economic decisions, and further technological advances are likely to have a major effect on the economic attractiveness of the PAFC relative to available competing systems. There are substantial incentives to identify research areas with significant potential impact upon operation at higher efficiencies. The following research areas are recommended for preferred consideration:

- improvements in electrocatalyst activity
- improvement of the electrolyte-interface properties by retaining the other requisite electrolyte properties such as stability, volatility, compatibility, and capillary properties
- optimized electrode structures which consistently provide the three-phase-interface reactive surface area for the electrochemical charge transfer reaction
- credible new material approaches to directly oxidise hydrocarbons

Solid polymer electrolyte fuel cell (SPEFC)

The SPEFC was the first fuel cell system to find practical application, when it was used as the non-propulsive power plant for the manned Gemini terrestrial-orbit missions in 1963-65. Since then, the SPEFC has been substantially improved, particularly with respect to membrane reliability and power density. The present design was developed by the General Electric Company for terrestrial applications and has the following advantageous features: relative simplicity, CO₂ rejection, and moderately high cell voltages at applicable power densities. Nevertheless, this system presently exhibits the following shortcomings, which render terrestrial non-military applications impractical: i) high cost of the polymer membrane electrolyte, ii) high Pt-loadings for the cathode and anode, iii) satisfactory operation only on hydrogen with very low CO content, iv) relatively low operation temperatures (<100°C), which severely restrict the use of cell heat for fuel processing to produce hydrogen. The low tolerance of the Pt anode catalyst to CO with hydrogen fuel would be relaxed, if the operating temperatures could be increased
to about 150°C, or if an effective, CO-tolerant, alternative to Pt can be found. The vapour pressure of water with the presently used proton-conducting NAFION membranes is too high for operation at temperatures much above 100°C, without dehydrating the membranes, and the subsequent loss of conductivity. Pressurization of cells permits operation at somewhat higher temperatures, but to achieve temperatures of about 150°C requires pressures that are impractically high for most applications. A more promising approach is the identification of modified or new membrane materials.

If the indicated shortcomings can be overcome, the SPEFC system may be competitive with the PAFC for electric utility dispersed-power-plant applications and, provided catalysts other than noble metals can be found, superior for vehicular applications, including the personal transportation vehicle. The SPEFC system as a whole is probably about a decade behind the PAFC in the development and commercial use.

Polymer membrane electrolyte research should be conducted towards new and modified proton conducting membranes offering the promise of low cost, and operation at temperatures around 150°C. For stability reasons, the most promising new polymeric materials are likely to involve fluorinated organic structures, but inorganic proton conductors should also be considered. Potential candidate materials for electrolytes include i) fluorinated organic proton-conducting polymers with alternative acid groups to the presently used sulfonic acids (e.g. phosphoric, phosphonic, phosphinic, silicic acids); ii) NAFION-type membranes impregnated with very concentrated phosphoric acid or other highly conducting acids to suppress the vapour pressure of water in the inverse micellar structure, while still maintaining sufficient conductivity and stability at temperatures above 140°C; iii) gelled ion-exchange type proton-conducting polymeric materials; iv) gelled concentrated-acid electrolytes with adequate conductivities and stabilities at elevated temperatures (e.g. borophosphates, borofluorosulfonic acids); v) multilayer polymeric proton-conducting membranes with different anolyte, bulk and catholyte layers, optimized for low electrode
polarization, while retaining high conductivity and low leakage of hydrogen and oxygen between the electrodes; vi) proton-conducting inorganic solid membrane materials such as heteropolyacids (e.g. polymolybdates and -tungstates) including dispersions of these in TEFлон and other fluorinated polymeric matrices.

The inorganic materials have to be operated at much higher temperatures because of their low conductivities under ambient conditions and, hence, they offer the possibility of direct oxidation of methanol and other fuels. They can be considered as an extension of the SOFC high-temperature concept, but involve proton conductors rather than solid oxide-ion conductors.

Further research needs for SPEFC include

- improved Pt-based and new electrocatalysts for anode and cathode and this relates to more effective utilization of the Pt-catalysts. Also lower cost alternative catalysts to Pt (e.g. oxides, transition metal complexes, and non-precious metals) and supportive substrates are required.

- electrocatalysts for direct oxidation of methanol and other fuels to accomplish oxidation at reasonable potentials and current densities

- improved electrode structures and surface morphologies; the present structures and surface morphologies do not show a clear picture between the amount of catalyst and the accessible area for the electrochemical reaction; specific recommendations include i) characterization of the structures of existing SPEFC electrodes; ii) studies of O₂ and H₂ transport and electrolyte access to the catalysts, including modelling; iii) innovative development of more effective electrode structures.
Molten carbonate fuel cell (MCFC)

The MCFC, following a very intensive development effort during the last 30 years, may now be only few years away from commercialisation, depending on the particular application involved. An important attraction of the MCFC is the overall plant design, because of its ability to accept CO, CO$_2$, and H$_2$. The other inherent advantage of the MCFC is its favourable ratio of high-quality heat to total energy. This feature opens up a significant market for stand-alone applications, with the possibility of internal reforming of natural gas, and at a wide range of sites. However, there remain several difficulties which must be resolved before successful commercialisation can occur. These relate to improved endurance and performance. MCFC endurance has its limits below 40,000 hours, because of electrolyte loss from cells and stacks by corrosion and vapourization, long-term creep and corrosion under compressive stress of non-electrode parts. MCFC performance can be further improved by optimization of the electrolyte composition, improvement of the cell tolerance to contaminants such that direct hydrocarbon oxidation could be achieved.

The research needs are related to

- conductive ceramics which may be used as a MCFC electrode substrate or electrode.
- transport mechanisms in the molten salt electrolyte as a function of the electrolyte composition and resulting interface properties with the electrodes
- corrosion mechanisms and corrosion rates at the three-phase interface molten salt - solid - gas
- development of a direct hydrocarbon electrode that is also tolerant to sulphur and chlorine
- development of in-situ diagnostic techniques for applications to cells and stacks
Solid Oxide Fuel Cells (SOFC)

Currently, the major industrial development effort is located at Westinghouse and is at the demonstration stage. The programme aims for laboratory demonstration test-units with a tubular cell-design for selected technically sophisticated customers. Other R&D efforts focus on a monolithic cell design to achieve higher specific power, and on flat planar cells.

SOFC's have several characteristics which are distinct from those of other fuel cells. The electrolyte is an oxide-ion conductor that requires an operation temperature around 1000°C. This allows the electrochemical oxidation process without specific catalysts, and has the advantage of fuel versatility. The components of the SOFC are primarily ceramics - ionic and mixed ionic/electronic conductors -, and the most important need for research falls in the area of ceramic science, and is centralized around the chemical processes occurring at the atomic level at the three-phase reaction sites (gas, mixed ionically/electronically conducting solid, ionically conducting solid).

Research needs are related to

- cheaper ceramic processing technologies to develop macrostructures such as novel cell geometries and microstructures, which are advantageous for the efficient three-phase interface reaction, and also provide microstructural stability. In addition, alternatives for expensive electrochemical vapour deposition of gas impervious solid electrolyte layers on foam electrode structures, as developed by Westinghouse, should be developed.

- better understanding of the electrochemical reaction at the atomic level to optimize electrode microstructures, also from the point of heat transfer and kinetics

- structural modelling and verification by critical measurements
- non-destructive techniques as a research tool and for quality control to measure stresses due to thermal expansion

The extended list of further research needs in the very important field of fuel cells does indicate, where we want to be tomorrow.

Although major achievements have been made in the generation and conversion of hydrogen the concept of the hydrogen economy is still far from being accepted, and this is not only because of the high prices which consumers would have to pay. There is after all intensive research necessary that must lead to higher efficiencies in almost all systems involved.

The key players responsible for the performance of devices to split, store, adsorb/absorb, recombine, and transmit hydrogen are functional materials - often electrodes and electrolytes - which allow an electrochemical reaction to occur at their interface. In order to improve the overall device performance we have to gain a better understanding of the various processes involved, and translate this know-how into desired materials properties.

This thesis will describe a number of these materials which are being involved in various intermediate steps of the overall concept of hydrogen economy.

1.5. Introduction to Concepts and Tools

The concepts and tools which are being applied to several materials described in this thesis will be briefly described using experimental results on hydrogen absorption in the intermetallic compounds in the Ti-Ni system.

While most of the investigations of the formation of metal hydrides have employed gas phase absorption methods, with pressure and temperature as the controlling parameters, one can also use electrochemical methods.
According to the Nernst equation, if proper electrolyte and cell configurations are used, the hydrogen activity or pressure at the interface between the electrolyte and a solid electronically conducting electrode can be controlled by the electrical potential. Thus control of the cell voltage can be used under isothermal conditions to cause a metal (hydride) to either absorb or desorb hydrogen. Such an electrochemical technique has several advantages over the traditional methods: (i) as there is no temperature change necessary for adsorption or desorption, the hydrogen activity at the surface of the electrode material can be changed very rapidly; (ii) large variations in the hydrogen activity can be obtained by relatively small differences in the cell voltage, so that the effective pressure can be changed easily, and with high accuracy over several orders of magnitude; (iii) the amount of hydrogen added or deleted can be readily determined by electrical current measurements. However, in spite of these potential advantages, there have been only a few electrochemical investigations of hydride systems to date (127-130). Experimental investigations can be carried out at room temperature by using a galvanic cell of the type

\((-\text{Metal Alloy} / 25\% \text{KOH, H}_2\text{O} / (\text{Ni(OH)}_2/\text{NiOOH}) \, (+)\)

A convention followed throughout this work is to treat quantities such as the chemical potential, electrochemical potential, and the activity as properties of single particles. Voltages and currents in a galvanic cell are assumed to be positive if the right-hand side has a positive charge relative to the left, and positive species tend to move to the right, and negative ones to the left, respectively.

The experimental details of the reaction of intermetallic phases in the Ti-Ni system with hydrogen are described in Chapter 3.

Coulometric titration experiments were performed using pellet-shaped samples as electrodes, and by applying constant currents through the cell, typically 10-500 mA/g of active species, for fixed periods of time. Subsequently the electrode potential was observed as equilibrium took place. The results were a series of equilibrium
potential versus hydrogen content points, which define the thermodynamic properties of the electrode material.

The coulometric titration curve of hydrogen in an intermetallic phase in the Ti-Ni binary system, together with the relationship of hydrogen of the other phases of the system, can be used to contract the isothermal phase diagram relationship between Ti, Ni, and H.

In addition, the chemical diffusion coefficient of hydrogen can be determined in the single phase regimes.

1.6. Scope of the thesis

This thesis comprises

a) The use of solid state ionics concepts to study the thermodynamic and kinetic properties of hydrogen mixed conductors of two Pd-based systems and the Ti-Ni-H system by electrochemical techniques.

b) The application of hydrogen-mixed conductors in an intermediate temperature water vapour electrolysis system. The system was designed and constructed as a simple laboratory version to verify the underlying ideas.

Chapter 1 presents an introduction into hydrogen-mixed conductors and their major applications in electrochemical energy conversion systems and devices. In addition, an introduction into the concept of the hydrogen economy is given.

In chapter 2, the theoretical principles and experimental tools which were used during the course of the experimental work reported here, will be described in detail. These refer to the potential-phase relationships in binary systems, the thermodynamic stability regimes of electrodes and electrolytes, the chemical diffusion coefficient of the active species in electrochemical devices, and the electrolyte conductivity.
Chapters 3 describes the ternary phase relationship and some results on the chemical diffusion coefficient of hydrogen-mixed conductors of the Ti-Ni based system.

Chapter 4 deals with the absorption of hydrogen by two Pd-based systems. The coulometric titration curves of the Pd-H and Pd-Li-H systems and relevant chemical diffusion data will be presented.

Chapter 5 of this thesis will concentrate on applications of hydrogen mixed conductors in three novel concepts of electrochemical energy conversion systems.

In chapter 6 a summary of the work is presented and an outlook on future prospects will be given.

1.7. References


113. J. Kleinert, Atomkernenergie (ATKE) 18, 261 (1971).


Chapter 2

Theoretical Concepts and Experimental Tools

The theoretical concepts used in this work are based on electrochemical principles and thus the major experimental tool involved in most of the investigations is a galvanic cell of the type that is shown schematically in Figure 1.

![Galvanic Cell Diagram]

**Figure 1:** Schematic representation of a galvanic cell.

2.1. Galvanic and electrolytic cells

The experimental work of this thesis is concerned with the processes and factors affecting the transport of charge across interfaces between chemical phases and the properties of the phases obtained by these charge transport processes. Almost
always, one of the phases contributing to an interface of interest will be an electrolyte, which is merely a phase through which charge is carried by the movement of ions. Electrolytes may be liquid solutions or fused salts, or they may be ionically conducting solids, such as sodium \( \beta \)-alumina, which has mobile sodium ions. The other phase at the boundary might be another electrolyte, or it might be an electrode. Electrodes can be metals, semiconductors, mixed conductors or composite materials, consisting of insulating materials and electrically conducting materials in an intimate mixture on a microscopic scale (i.e. the positive electrode of the Na/NiCl\(_2\)-battery is a mixture of NaCl, NiCl\(_2\) and Ni particles).

It is natural to think about events at a single interface, but we will find that one cannot deal experimentally with such an isolated boundary. Instead, one must study the properties of collections of interfaces called electrochemical cells. These systems are defined most generally as two electrodes separated by at least one electrolyte phase.

In general, there is a measurable difference in potential between the two electrodes, whether the cell is passing a current or not. The magnitude of the potential difference at the interface affects the relative energies of the carriers in the two phases; hence it controls the direction of charge transfer. Thus the measurement and control of cell voltages (the difference of potential between the electrodes of a cell) is one of the most important aspects of experimental electrochemistry.

The relationship between the cell voltage \( E \) of an electrochemical cell and the spontaneity of the chemical reaction of the electrodes when no current is allowed to flow is given by

\[
\Delta G_r = -zFE
\]

where \( \Delta G_r \) is the Gibbs free energy change of reaction of the electroactive phases, \( z \), the number of moles of electrons in the balanced reaction, and \( F \) Faraday's constant. For a negative value of \( \Delta G_r \) (a positive value of \( E \)), the reaction is spontaneous, and the cell
is called a galvanic (or voltaic) cell. If $\Delta G_i$ and $E$ are zero, a state of equilibrium exists. If $\Delta G_i$ is positive ($E$ is negative) the reaction does not occur unless energy is provided via the external circuit. This is then called an electrolytic cell. In this sense, a rechargeable battery is by definition a galvanic cell during discharge and an electrolytic cell during charge.

The processes that produce electricity in a galvanic cell are chemical reactions which either release or consume electrons as the electrode reaction proceeds to completion. This can be illustrated with the specific example of the reactions of the nickel-metal hydride battery, represented as the following galvanic cell:

(-) Ti-Ni hydride / 25% KOH, H₂O / (Ni(OH)₂/NiOOH) (+)

At the negative electrode (Ti-Ni hydride), the discharge reaction is the oxidation of the metal hydride with the release of one electron. This occurs by transfer of hydrogen species across the electrode / electrolyte interface. Atoms from the metal hydride are oxidized as they move into the electrolyte where they join with $OH^-$ ions to form neutral H₂O.

\[( - ) \quad (Ti-Ni)\_xH + OH^- = x(Ti-Ni) + H_2O + e^- \quad /2/\]

At the positive electrode (NiOOH), the discharge reaction is due to the reduction of NiOOH to Ni(OH)₂ by adding positively charged hydrogen to the electrode from the electrolyte and the consumption of one electron.

\[( + ) \quad H_2O + e^- + NiOOH = Ni(OH)_2 + OH^- \quad /3/\]

When these two ‘‘half-cell’’ reactions occur by connection of the two electrodes to an external load, the overall cell reaction involves the transport of hydrogen across the cell. This converts metal-hydride to metal and NiOOH to Ni(OH)₂ according to the following overall chemical reaction:

\[(Ti-Ni)\_xH + NiOOH = x(Ti-Ni) + Ni(OH)_2. \quad /4/\]
This reaction can be reversed when a voltage greater than the open circuit voltage is placed across the cell.

The potential of the cell is related to the energy of the overall cell reaction by equation /1/. It can be measured experimentally and used to calculate the Gibbs free energy of the reaction. As will be shown later, voltage measurements of properly configured galvanic cells are successfully used to infer thermodynamic data.

The electrical current that passes through a galvanic cell is directly related to the dynamic processes involved in the transport of mobile ionic and electronic species in all components of the experimental cell arrangement. However, the voltage, the difference in the electrochemical potentials across the cell, is primarily determined by thermodynamic considerations. Despite this clear separation between kinetic and thermodynamic information, well-defined observations of materials properties always involve the determination or the control of both types of electrical quantities.

In mixed conductors electrical conduction is effected by concurrent migration of ions and electronic charge carriers (e\(^-\) or h\(^+\)). Substances in which electrical conduction is substantially due to an ionic species are categorized as being solid electrolytes. In materials called electronic conductors, such as metals, the situation is reversed. However, materials having appreciable ionic conductivity are still classified as mixed conductors if their partial ionic conductivity is significantly smaller than the total conductivity.

Theories unifying the two types of electric conduction in the solid state have been developed by Wagner (1), Hebb (2), and Yokota (3). The results of these studies can be expressed by the following differential equations for the ionic current \( J_i \) and electronic current \( J_e \):

\[
J_i = -\sigma_i \text{grad} \ (\eta_i/e) \\
J_e = -\sigma_e \text{grad} \ (\eta_e/e)
\]
\( \sigma_i \) ionic conductivity
\( \sigma_e \) electronic conductivity
\( \eta_i \) electrochemical potential of the mobile ionic species
\( \eta_e \) electrochemical potential of the electron
\( z \) number of ionic charges per particle
\( e \) elementary charge of the electron

As described above, the reaction of electrochemical interest occurs at the interfaces between the electrolyte and the electrodes, and is thus determined by the properties of the phases involved. The participating phases can be deduced from the half-reactions of the galvanic cell as shown in equations /2/ and /3/. In the case of the metal-hydride negative electrode reaction, these are:

the metal-hydride phase, \((\text{Ti-Ni})_x\text{H}\)
the electrolyte phase \((\text{OH}, \text{H}_2\text{O})\)
the electronically conducting phase \((\text{Ti-Ni}, e^-)\)

The electrochemical reaction at the negative electrode as presented in equation /2/ occurs only in locations where these phases meet - the active interface area.

In practical electrodes, the various components involved have particle sizes which are distributed over a wide range, and their shapes are often irregular. This results in a rather undefined situation with respect to the active interface area, as can be seen from Figure 2, in which the case of a hydride electrode is schematically illustrated. Furthermore, during mixing with binders, the electrode powders often tend to agglomerate and large volumes of the electrode become unaccessible for the energy conversion process. Such situations are very undesirable but in practice often the case. Electrode fabrication for large scale production today is still a very empirical process. As can be seen from Figure 2, the number of locations for the electrochemical charge transfer reaction to occur, indicated as black dots, is small compared to the geometrical surface area of the constituent electrode and electrolyte phases.
Figure 2: Schematic two-dimensional representation of the 3-phase interface of an electrochemical system.
It depends upon the local arrangement of the phases present. Hence, the number of locations per unit volume is strongly dependent upon the relative volumes of the phases involved as well as their particle sizes and particle morphologies. Thus for every application, an ideal constellation between the phases must exist, which is determined by the transport properties of the phases involved, which in turn determine the ideal particle sizes of the contributing components.

The techniques used to prepare samples for investigations of the thermodynamic and kinetic properties reported in this thesis were of the traditional type and thus encompass the problems described above, which means that, especially for the calculation of the chemical diffusion coefficient from kinetic measurements, the true geometric parameters are not accessible. However, in order to compare the results with those obtained from other authors, it was decided that the classical sample preparation techniques were suitable. As will be shown later, the discrepancies among the results reported in the literature may well have their cause in the rather undefined situation at the electrode/electrolyte interface. Possible ways to improve this situation are described in chapter 6 of this thesis.

A convention followed throughout this thesis is to treat quantities such as the chemical potential, electrochemical potential, and the activity as properties of single particles. In the galvanic cell notation, a slash represents a phase boundary, and a comma separates two components in the same phase. Voltages and currents in a galvanic cell are assumed to be positive if the right-hand side has a positive charge relative to the left, and positive species tend to move to the right, and negative ones to the left, respectively (i.e. Zn/Zn\(^+\), Cl\(^-\)/AgCl/Ag).

As discussed above, the overall chemical reaction taking place in a cell is made up of two independent electrochemical half-reactions which describe the chemical changes at the two electrodes. Each half-reaction occurs at the potential at the interface of the corresponding electrode with the adjacent electrolyte. One is often particularly interested in studying only one of these reactions. To do this,
configurations can be used in which the electrode at which the reaction of interest occurs is called the working electrode, and its potential is compared to that of a well defined reference electrode.

2.2. Thermodynamic properties

2.2.1 Potential-phase diagram relationships

The reversible work $\Delta G_r$ of a galvanic cell is directly related to its equilibrium potential-composition (E-x) curve

$$\Delta G_r = -z_r F \int_0^1 E \, dx$$

The total free energy change in the electrochemical reaction, therefore, represents the integral of the equilibrium potential-composition curve (4). Thus, the computed $\Delta G_r$ of a given reaction represents the area under this curve, but in itself, says nothing about the shape of the curve.

The total free energy change of the electrochemical reaction can be rewritten as

$$\Delta G_r = \Delta G_r^\circ \text{(Products)} - \Delta G_r^\circ \text{(Reactants)}$$

That is, the available energy stored in a cell is limited by the difference between the free energy of formation $\Delta G_r^\circ$ of reactants and products. Therefore, a high energy cell is the result of formation of very stable products from very unstable reactants.

The information about the shape of the curve, that is, the relationship between the potential and the composition of an electroactive species can be obtained experimentally by applying the coulometric titration technique.
2.2.2 The coulometric titration technique

Let us consider a binary system with components A and B and the possibility to form intermediate phases, i.e., an alloy that can act as a reversible electrode in an electrochemical cell by a change in its composition. The activity versus composition data of a binary system denoted by the general formula $A_yB$, where $y$ is the atomic ratio of component A to component B, can be obtained by using the coulometric titration technique. This technique was first introduced by Wagner (5) for studying the stoichiometry of $Ag_2S$, and is a very elegant method by which precisely controlled changes in the composition of a substance can be brought about. For the purpose of illustration consider the following galvanic cell

$$A^0 / \text{Electrolyte for } A^{z+} / A_yB$$

where $A_yB$ is the one-phase or two-phase sample electrode under investigation and $A^0$ serves as a source or sink of the electroactive species $A^{z+}$ and also provides a reference activity for component A. For simplicity $A^0$ is assumed to be pure A at its standard state with an activity of unity. It is also assumed that both $A^0$ and $A_yB$ are mixed conductors with predominant electronic conductivity and that the electrolyte used is a single ion conductor. Under isothermal and isobaric conditions, the equilibrium open-circuit voltage, $E$, of the above cell provides a direct measure of the activity of A, $a_A$, in the electrode $A_yB$, since

$$zFE = -RT \ln a_A$$

where $R$, $T$, $z$ and $F$ are the gas constant, the absolute temperature, the charge of the electroactive species A in the electrolyte phase, and the Faraday constant, respectively.

Upon passing current $I$ across the cell for a period of time $\tau$, a defined amount of component A will be transported across the cell via ions passing through the electrolyte and electronic conduction in the external circuit. Depending upon the direction of the applied current,
the species A can thus be electrochemically added to or removed from the binary system A_yB. Assuming that the transference number for the electroactive species A in the electrolyte is unity, the change in composition, Δy, obeys Faraday's law,

\[ \Delta y = \frac{\int_0^t \text{Idt}}{z_F \eta_B} = \frac{Q}{z_F \eta_B} \]

where \( \eta_B \) is the number of gram-atoms of component B in A_yB and Q represents the total charge transferred during current flow. The activity of component A in A_yB corresponding to the new composition can be evaluated from the open-circuit voltage after waiting a time sufficiently long to allow the composition to become homogeneous throughout the sample electrode A_yB as evidenced by the achievement of a new steady-state open-circuit voltage, E. If chemical diffusion within the binary system A_yB is relatively fast, it is possible, within certain limitations, to obtain a large number of activity measurements of species A over an appreciable range of composition within a reasonable time. Under isothermal conditions, this set of potential differences versus composition is known as the coulometric titration curve.

In the electrochemical cell shown above for simplicity A^0 was assumed to be pure A. However, an electrode containing A at fixed activity other than unity may also be used as the reference electrode as well as the counter electrode. However, in order to avoid composition-dependent changes, it is generally best to use a third electrode through which no significant current passes as a reference electrode. A reference electrode made of a two-phase binary mixture of A and B is preferable in order to maintain a constant activity of component A according to the Gibbs phase rule. Then the directly measured cell EMF, E_{meas}, represents the voltage with respect to A^0. Under these circumstances an additional term, RT ln a_A^0, must be added to the right hand side of equation /9/.

\[ z_F E_{meas} = -RT \ln \frac{a_A}{a_A^0} \]

/11/
Then, if the conventional thermodynamic standard states are desired, the cell voltage relative to pure A will be given as

\[ E = E_{\text{meas}} - \frac{RT}{z_F} \ln a_{A^0} = -\frac{RT}{z_F} \ln a_A \]  

Here the constant activity of component A in A⁰, a_{A⁰}, is assumed to be known as a function of temperature from separate experiments.

The success of using the coulometric titration technique relies upon several assumptions. Firstly, it is assumed that there is no steady state loss of either component A or B from the sample electrode AₓB by evaporation, dissolution in the electrolyte or diffusion into the electrical lead materials. The second assumption is that the electrolyte is an essentially ionic conductor with no electronic leakage current to reduce the coulombic efficiency so that the open circuit voltage of the cell is related to the activity of species A in AₓB by the Nernst equation. Finally, the rate of equilibration via chemical diffusion within the sample electrode must be reasonably rapid. Since most solids have relatively low chemical diffusion coefficients, a thin film of the sample under investigation has to be used in some cases in order to reduce the time required for obtaining steady-state conditions.

In general, the exact composition of AₓB must be known for at least one point within the concentration range under study in order to convert the precisely measured composition change, Δy, to the exact compositions using equation /8/. A sample made of known quantities of components A and B may be employed in experiments and its starting composition can be determined by conventional chemical analysis techniques.

In principle, one can achieve unusually high resolution in composition, with increments as small as 10⁻¹⁰ mole, for example by passing a constant current of 1.0 μA for 10 seconds. The accuracy of the absolute values of the exact compositions is then limited by the techniques used to determine the initial composition of the sample. This problem may become very critical if one wants to study a single phase in a binary system with a rather narrow range of
stoichiometry. In this case, the coulometric titration curve yields the EMF or the logarithm of the activity of component A as a function of the change in composition, but not the absolute value of the composition. However, the latter information may be obtained from experiments starting the coulometric titration from pure B.

2.2.3 Application of the coulometric titration technique

At constant temperature and pressure, the Gibbs-phase rule requires that the activity of each component of a single-phase binary system be a function of composition only. As a result, the measurement of the hydrogen activity or the EMF as a function of composition can be used to determine the compositional range of, for example, a single phase binary metal-hydrogen alloy. The voltage thus provides an electrical measure of the hydrogen concentration in a single-phase binary solid hydrogen alloy.

The coulometric titration technique can be best illustrated by the schematic representation in Figure 3.

On top of the diagram a typical three-electrode galvanic cell as used in this work is shown.

Consider a binary hydrogen-metal system with the hypothetical phase diagram as shown in Figure 3. If the experiments were carried out at temperature $T_0$ by electrochemically adding H into the pure metal, the overall electrode potential will traverse three single phase regions and two two-phase regions, designated as $\alpha$, $\alpha+\beta$, $\beta$, $\beta+\gamma$, and $\gamma$. Then the corresponding EMF versus composition curve for H/metal at $T_0$ looks like that shown at the bottom in Figure 3. In the single phase regions, the EMF is a unique function of the composition. The voltage plateaus represent the two-phase regions within which the EMF is independent of composition.
Figure 3: Schematic representation of the information gained from coulometric titration measurements.
Thus Figure 3 gives information about the phase boundaries and concentration regimes of the various phases involved. These potential/concentration regimes can also be expressed in terms of thermodynamic stability windows of electrodes or electrolytes, since their boundaries indicate the limiting values of activity at which a particular phase becomes unstable.

This technique, combined with results of the transient behaviour between equilibrium measurements has been successfully applied to investigate a large number of electrode materials in secondary batteries and has contributed a great deal to the development of a better understanding of electrode reactions, the chemical diffusion of the electroactive species in the electrodes and the ionic conduction in the electrolytes.

2.3 Chemical diffusion of active species

If an electrical current is either forced or permitted to pass through any part of the experimental arrangement as shown in Figure 1, the partial current density \( i_n \) of any species \( n \) is, in general, proportional to the overall transport force acting upon that species. This force can be expressed as the gradient of the electrochemical potential \( \eta_n \) of the species in question. If the transport involves no volume change, one can neglect all but chemical and electrostatic forces; correlation with the fluxes of other particles may be neglected too (6). The proportionality constant between the current and the electrochemical potential gradient, \( \text{grad} \ \eta_n \), is given by the partial specific electrical conductivity \( \sigma_n \) of species \( n \).

\[ i_n = -\frac{\sigma_n \partial \eta_n}{z_n q \partial x} \]

where \( z_n \) is the charge number (or effective valence) and \( q \) the elementary charge.

The conductivity may be written in terms of the product of the concentration of the mobile species \( c_n \) and the diffusivity \( D_n \):
\[ \sigma_n = \frac{c_n D_n z_n^2 q^2}{kT} \]

This diffusivity, which is identical to quantities that are also called the "component diffusion coefficient" (6), "elementary diffusion coefficient" (7), "self diffusion constant" (8), or "self diffusion coefficient" (9), is defined as the quantity that obeys the Einstein relation (10, 11) between the electrical mobility \( v_n \) (drift velocity per unit electric field) or the general mobility \( b_n \) (drift velocity per unit general force) (8), and the diffusion coefficient.

\[ D_n = v_n \frac{kT}{|z_n|q} = b_n kT \]

The diffusivity \( D_n \) is a measure of the random motion of the particles of species \( n \) in the absence of concentration gradients. It is related to the diffusion coefficient [also sometimes called the "self diffusion coefficient"], that is determined by the use of radioactive isotopic tracers, \( D_n^T \), with \( D_n^T = f_n D_n \) (12), where \( f_n \) is the correlation factor, or generally, the Haven ratio (13).

From equation (14), it can be seen that \( D_n \) is also the quantity that contains the kinetic contribution to the conductivity of species \( n \).

From equations (12-14), equation (11) can be cast into the form

\[ i_n = -\sigma_n \frac{\partial \phi}{\partial x} - z_n q D_n \frac{\partial \ln a_n}{\partial \ln c_n} \frac{\partial c_n}{\partial x} \]

The first term on the right-hand side is identical to Ohm's law for the migration of species \( n \) under the influence of an internal electrostatic field. The second term is related to Fick's first law for diffusion under a concentration gradient. Equation (15) is general for isothermal conditions and is valid at any point in the galvanic cell, assuming that there is no mass motion or volume change and that no other forces are involved in the transport of species \( n \), such as correlation effects due to the simultaneous transport of other components.
Equation /16/ holds both in an electrolyte phase, in which the transport of charge is primarily due to the motion of ionic species, and in mixed ionic-electronically conducting phases.

**Ionic current in the electrolyte**

It is desirable that an electrolyte to be applied in a galvanic cell is characterized by a large concentration of mobile ions or ionic defects. Then the chemical potential of the mobile ionic species, which is proportional to the logarithm of its activity, may be regarded as essentially independent of position within the material. Thus any ionic transference in such phases must be predominantly due to the influence of an internal electrostatic field:

\[ i_{\text{ion(electrolyte)}} = - \sigma_{\text{ion}} \frac{\partial \phi}{\partial x} \] /17/

For the electronic defects, itinerant (or "excess") electrons and holes, which can be considered relatively dilute in an electrolyte, the situation is different, and either an internal electrostatic field, a concentration gradient, or both may be important. This will depend upon the differences of the chemical potentials of the electronic species at the two sides of the electrolyte. When the concentration of the electronic species is high, the influence of an internal electric field is more important than when the concentrations of such species are low.

If the ionic current is blocked by the use of ionically polarizing electrodes so that only electrons and holes may pass through the electrolyte, the internal electrostatic field must become negligible under steady state conditions, in accordance with equation /17/. In that case, the transport of electronic species may occur only as the result of their concentration gradients.

**Ionic current in the electrode**

In electrodes where we can assume that the transport of charge occurs predominantly by the motion of electronic species, a different situation holds. In that case the chemical potentials of the itinerant
electrons or holes may be regarded as practically independant of location within the solid, due to their high concentrations. Thus their transport is primarily due to the effect of an internal electric field in such materials. Because of the large concentrations of these electronic species, as well as their high mobilities, this field will, of course, be very small.

Therefore, if ionic transport occurs across an electrode/electrolyte interface in connection with current flow by the motion of ionic species in the electrolyte, the ionic flux within the electrode material must be predominantly determined by the presence of a local ionic concentration gradient in that phase. That is,

$$ i_{\text{ion(electrode)}} = -z_{\text{ion}} q D_{\text{ion}} \frac{\partial \ln a_{\text{ion}}}{\partial \ln c_{\text{ion}}} \frac{\partial c_{\text{ion}}}{\partial x} $$

/18/

It should be noted that the factor $$ \frac{\partial \ln a_{\text{ion}}}{\partial \ln c_{\text{ion}}} $$, which is often called the "thermodynamic factor" and which can sometimes be very large, acts to enhance the ionic flux density above that which would be expected from the concentration gradient alone (14-16). In a predominantly electronic conductor in which the concentration of excess electrons or holes is very large, so that the chemical potentials of the electronic species are essentially uniform throughout the body, the gradients of the chemical potentials of neutral atoms and their respective ions are identical. Thus the transport of ions may be considered to be the same as the net transport of neutral species.

** Ionic current in a mixed conductor **

If an electrode material is not overwhelmingly an electron or hole conductor so that the sum of the transference numbers of the electronic species differs appreciably from unity, the internal electrostatic field may not be completely neglected with regard to the movements of ions. In such a case the transport of ionic species occurs under the combined influence of electrostatic and chemical potential gradients. This situation can be expressed by an equation similar to equation /18/ by replacing $$ \frac{\partial \ln a_{\text{ion}}}{\partial \ln c_{\text{ion}}} $$ by a more general "thermodynamic enhancement factor", W (17).
\[ i_{\text{ion (mixed conductor)}} = -z_{\text{ion}} q D_{\text{ion}} W \frac{\partial c_{\text{ion}}}{\partial x} \]

Values of these enhancement factors under various conditions are given in (18).

In addition to being expressible in terms of thermodynamic quantities, this enhancement factor can be interpreted kinetically as the generation of an internal electric field by a displacement of the concentration profiles of two differently charged mobile species within the solid. If one of them, e.g. electrons, have a significantly greater mobility than the other, e.g. ions, in a concentration gradient, the more mobile species will tend to move ahead of the other. The requirement for overall charge flux neutrality causes the more mobile species to be slowed down and provides an additional driving force for the less mobile one (18).

**Total charge transport current**

The total charge transport current within a solid (e.g. an electrode material) may be composed of several partial currents whose magnitudes vary with position. Such a situation would, of course, not be measured by instruments in an external circuit, since these observe only the total current passing through the overall cell. However, an electrolyte serves as an ion-pass filter if the electron and hole conductivities within it are very small. As a result, only ionic species can cross phase boundaries between electrodes and such an electrolyte. Since, under steady state conditions the ionic current must be continuous across an electrolyte-electrode interface, the total externally measureable current must be equal to the partial ionic current, as expressed in equation /19/, within the electrode material just inside the interface. However, it is possible that the most mobile ions within the electrolyte are not those that are predominantly transferred in the electrode. In such a case, the overall cell current is given by equation /19/ when it is written in terms of the species that are most mobile in the electrode phase.
2.3.1 Chemical diffusion in mixed conductors

In addition to the question of the range of chemical potential and composition over which specific phases exist, practical utilization of mixed conductors as electrodes also requires reasonable kinetics. The primary question is the rate at which the electroactive species can be added to or deleted from the static lattice. In many cases the critical step is transport within the mixed conductor itself under the influence of a composition gradient, rather than kinetic phenomena related to the charge transfer reaction at the electrode/electrolyte interface. The governing parameter under the conditions of a composition gradient is the chemical diffusion coefficient, \( \tilde{D} \).

Studies of diffusion within solids are often carried out by the use of radioactive tracers and result in a tracer diffusion coefficient, \( D_T \), that is related to the self diffusion by the correlation factor as follows:

\[
D_T^n = D_n f_n
\]

with \( f \) being the correlation factor. The value of \( f \) is related to the crystal structure and is typically between 0.5 and 1. However, in some solid electrolyte materials which have crystal structures that contain one-dimensional tunnels or two-dimensional layers, \( f \) has more extreme values, e.g. in a linear tunnel, \( f \) will have the value \( 1/N \), where \( N \) is the number of atoms in the linear chain. Thus, if \( f \) is not known from independent experiments, radiotracer measurements may give misleading information about self diffusion kinetics.

The chemical diffusion coefficient, \( \tilde{D} \), which relates to transport in a concentration gradient, can have values quite different from those of the self diffusion coefficient, \( D_n \), which describes the random motion of species in a chemically homogeneous environment. They are related by the expression:

\[
\tilde{D} = D_n W
\]
in which \( W \) is the chemical enhancement factor. Experimental data have shown that the enhancement factor can be very large, e.g. about 70,000 in the intermetallic compound Li\(_3\)Sb at 360\(^\circ\)C (17). Therefore, without firm information about the magnitude of the enhancement factor, it would be unwise to depend upon the use of self diffusion data to determine the chemical diffusion coefficient.

### 2.3.2 Measurement of the chemical diffusion coefficient

For better illustration of electrochemical methods for obtaining information about chemical diffusion, consider the galvanic cell

\[ A^o / \text{Electrolyte for } A^{\pm z} / A_{y+\delta}B \]

in which \( A^o \) represents a source for the electroactive species \( A \), and \( A_{y+\delta}B \) is a single phase alloy electrode under investigation. In the formula \( A_{y+\delta}B \), \( \delta \) denotes the deviation from the nominally stoichiometric composition \( A_yB \). In order to avoid polarization effects at the reference electrode, a three electrode arrangement to separate the potential measurement from the current measurement is typically used.

Under the assumption that neither the charge transfer process at the electrode/electrolyte interface nor the ionic transport through the electrolyte are rate limiting steps, the measured voltage of the cell provides a direct measure of the activity of component \( A \) in the sample electrode at the electrode/electrolyte interface and, thus, the concentration of \( A \) at this interface. By perturbing this concentration in an experimentally controllable manner and solving Fick's second law for one-dimensional diffusion, i.e.

\[
\frac{\partial c}{\partial t} = - \frac{\partial}{\partial x} \left[ D \frac{\partial c}{\partial x} \right]
\]

where \( c, t, D \), and \( x \) are the molar concentration of species \( A \), the diffusion time, the chemical diffusion coefficient, and the distance,
respectively. With the appropriate initial and boundary conditions, the chemical diffusion coefficient can be determined.

Experimentally, either the current or the potential can be used as the controlled variable. The other is then the dependent variable. Thus, the electrochemical techniques can be divided into:

- potentiostatic
- galvanostatic
- potentiometric and
- steady-state AC methods.

They are schematically shown in Figure 4.

Figure 4: Schematic representation of 4 different electrochemical techniques to measure the chemical diffusion coefficient of solids
In general, the chemical diffusion coefficient is a single-valued function of composition. When sufficiently small increments of composition are used in experiments, the chemical diffusion coefficient, as well as the volume of the sample, may be considered approximately constant over this narrow range of concentration. With this assumption, equation /22/ reduces to the form

$$\frac{\partial c}{\partial t} = \tilde{D} \frac{\partial^2 c}{\partial x^2}$$ /23/

In this work, the potentiostatic method was applied and will therefore be discussed in more detail.

**Potentiostatic method**

In this method, it is assumed that a planar electrode has an initial uniform concentration $c_0$ of species A, corresponding to an equilibrium potential $E_0$, with respect to a suitable reference electrode. At $t = 0$, a new activity of A is imposed upon the electrode surface by applying a voltage step, $\Delta E$, measured between the sample electrode and the reference electrode. Hence, a new concentration of component A, $c_s$, is established and maintained at the electrode/electrolyte interface at $x=0$. Under the above assumptions, re-equilibration through chemical diffusion will take place until the composition of the solid electrode reaches the imposed constant value $c_s$ throughout the sample. The rate of re-equilibration can be easily measured by monitoring the electric current passing through the cell, $I(t)$, as a function of time. This time-dependent current is then related to the concentration gradient of species A at the electrode/electrolyte interface ($x = 0$) by Fick's 1st law of diffusion as follows

$$I(t) = -zFSD \left\{ \frac{\partial c}{\partial x} \right\}_{x=0}$$ /24/

where $z$, $F$, and $S$ are the charge number of the electroactive species A in the electrolyte phase, the Faraday constant, and the cross-
sectional area common to both the electrode and the electrolyte, respectively.

The concentration gradient at the electrode/electrolyte interface is evaluated from solution of equation /23/ under the following initial and boundary conditions.

\[
\begin{align*}
    c &= c_o & 0 \leq x \leq L & t = 0 & /25/ \\
    c &= c_s & x = 0 & t > 0 & /26/ \\
    \frac{\partial c}{\partial x} &= 0 & x = L & t \geq 0 & /27/ 
\end{align*}
\]

Equation /27/ expresses the condition that species A enters or leaves the sample electrode only at \( x = 0 \), and that the phase boundary at \( x = L \) is impermeable. This condition also holds if two electrolyte bodies are in contact with each side of a planar electrode of thickness \( 2L \) and there is no diffusion across the mid-plane symmetry.

For numerical evaluation, equation /24/ can be expressed in terms of the current as a function of time by

\[
I(t) = zFS(c_s - c_o)\left(\frac{\bar{D}}{\pi t}\right)^{1/2} \quad \text{if} \quad t << \frac{L^2}{\bar{D}} /28/ 
\]

for short times and

\[
I(t) = \frac{2zFS\bar{D}(c_s - c_o)}{L} \exp\left(-\frac{\pi^2 \bar{D} t}{4L^2}\right) \quad \text{if} \quad t >> \frac{L^2}{\bar{D}} /29/ 
\]

for longer times.

Using these expressions, values of chemical diffusion coefficients in solids as low as \( 10^{-14} \text{ cm}^2/\text{sec} \) have been successfully determined, while conventional metallurgical techniques cannot be extended below about \( 10^{-12} \text{ cm}^2/\text{sec} \) (19-21).
After equilibration following each voltage step, the concentration difference \((c_e - c_o)\) is given by

\[
c_e - c_o = \frac{\int_0^1 dt}{zFv} = \frac{Q}{zFv}
\]

where \(V\) and \(Q\) are the volume of the sample electrode and the total charge transferred during each applied voltage step, respectively. Using the relation \(V = L \cdot S\), the expression for the time-dependent current may be rewritten as

\[
I(t) = \frac{Q}{L} \left( \frac{D}{\pi \tau} \right)^{1/2}
\]

if \(t \ll \frac{L^2}{D}\) / 31/

and

\[
I(t) = \frac{2QD}{L^2} \exp \left( \frac{\pi^2 D t}{4L^2} \right)
\]

if \(t \gg \frac{L^2}{D}\) / 32/

In the initial stage of diffusion (at short times) when \(t \ll \frac{L^2}{D}\), the chemical diffusion coefficient can be determined from the slope of a linear plot of \(I\) versus \(\frac{1}{\sqrt{t}}\). At longer times, when \(t \gg \frac{L^2}{D}\), the chemical diffusion coefficient can be evaluated from either the slope of a linear plot of \(\ln I\) versus \(t\) or the intercept on the logarithmic \(I\) axis at \(t = 0\).

Because the electrode potential is controlled, this technique offers the advantage that unwanted side reactions such as the nucleation of new phases can be avoided so long as the voltages are kept within the stability range of a single-phase alloy. A disadvantage is that the ohmic voltage drop, being due primarily to the resistance in the electrolyte between the working electrode and the reference electrode, varies with time, and this resistance polarization cannot be entirely eliminated by placing the reference electrode very close to the sample electrode.
2.4 Electrolyte conductivity

Partial ionic - electronic currents

As has been shown above, the total current in a mixed-conducting solid is the sum of the partial ionic and electronic current contributions, caused by the ionic and electronic parts of the conductivity. For true electrolytes the electronic contribution to the overall conductivity is negligible. However, when such electrolytes are utilized in galvanic cells under reducing conditions at one interface and oxidizing conditions at the other, situations can occur in which the electronic contribution to the conductivity can become significant, leading to high leakage currents. It is therefore desirable to investigate electrolyte materials under the conditions that are actually applied in the galvanic cell and to determine the various contributions to the overall conductivity in that case.

Total and ionic conductivity

The total conductivity of an electrolyte can be obtained by measuring the relationship between the steady state charge flux and a steady applied electric potential difference between a pair of properly chosen electrodes that are fully reversible to both ionic and electronic species. Under the assumptions that one can neglect the electrolyte/electrode interfacial impedance and the impedance of the electrode itself relative to the impedance of the electrolyte, the total conductivity of the sample of constant cross section is given by

\[ \sigma = \frac{I \cdot d}{V \cdot S} \]

where I and V are the current and the voltage, and d and S are the length and cross sectional area of the electrolyte. This technique also assumes the absence of concentration polarization and other electrochemical effects at the sample-electrode interface.

This ideal condition is seldom fulfilled, and there are usually large voltage drops across the interface between the electrolyte and the
electrodes. This problem may be overcome by using separate voltage probes in the form of identical electronic leads connected to the electrolyte at positions separated by a distance $d$, as shown in Figure 5.

![Diagram showing a four-point technique for measuring ionic conductivities](image)

**Figure 5:** Four point technique to measure ionic conductivities (21)

There should be no net exchange of particles between these two voltage probes and the electrolyte. As a result, potential measurements are not perturbed by polarization effects if the steady state interface resistances and the electrolyte resistance are small compared to the internal resistance of the voltmeter. The stiochiometry of the sample can be defined by equilibrium with the electrodes, or it may be fixed according to the Nernst equation (9) by applying a fixed voltage between one of the electrodes and a wire attached to the electrolyte, e.g. one used for potential measurements. The current is measured in the lower circuit of Figure 5.

Under these conditions, the total conductivity is given by

$$\sigma_{\text{ion}} = \frac{I}{V} d$$

with $d$ being the distance between the voltage leads.
This technique is known as the 4-point dc technique for determining conductivities. Except for the matter of fixing the stoichiometry of the sample, it is similar to the 4-point method commonly used to measure the conductivity of electronic conductors.

The ionic conductivity can be measured by using the same technique but blocking off all other moving species such that only the ions under investigation can move. This can be done experimentally by using a second electrolyte, which is known to transport the ionic species only, in series.

The identity of the mobile ionic species may be determined in simple cases from changes in the mass of the ionic sink and source electrodes after a known charge has passed through the cell. Electrodes must be used that are able to exchange all potential ionic species involved in ionic transport within the electrolyte. If one species dominates the total charge transport, Faraday’s law can be used to relate the mass change $|\Delta m|$ of either one of the electrodes per unit time and unit current as

$$\frac{|\Delta m|}{I\Delta t} = \frac{A}{|z|F}$$

where $A$ is the atomic weight of the particles transferred as ions of charge $z$ through the electrolyte (22).

If two different ionic species with transference numbers $t_1$ and $t_2$ contribute to the total conductivity within the solid electrolyte, the transference numbers of both ionic species may be calculated from the total change of the electrode masses according to

$$t_1 = 1 - t_2 = \frac{\left\{ \frac{|\Delta m|}{I\Delta t} F |z_1 z_2| - |z_1| A_2 I \right\}}{I(|z_2 A_1| - |z_1| A_2)}$$

The contribution of electrons and holes to the total conductivity will be discussed in a later paragraph of this chapter.
An alternative that may be used to overcome polarization problems in such systems is the use of alternating current techniques. In order to separate electrode and interface-related effects from those due to transport processes within the electrolyte, the response of the electrode/electrolyte system is usually experimentally evaluated over a wide range of frequencies, e.g. $10^{-4}$ to $10^{2}$ Hz.

### 2.4.1 Conductivity measurements using AC Impedance Spectroscopy

Simple dc techniques can yield information about electrolyte conductivity if reversible electrodes can be applied under the assumption that parasitic reactions at the electrodes and polarization effects within the electrolyte can be excluded. Because these side effects can almost never be excluded and can lead to erroneous values of the conductivity, a technique has been developed that can separate these effects by their frequency behaviour. This technique is called "impedance spectroscopy" and is used to describe a technique in which a small amplitude sinusoidal voltage is applied to an electrode/electrolyte system. The real and imaginary parts of the response, a complex electrical quantity, are evaluated as a function of frequency. These can be plotted on the complex plane, often called Nyquist plot, or simply as a function of the frequency. The latter representation is called a Bode plot.

**Impedance and admittance of a system**

The complex impedance $Z$ of a galvanic cell is defined as the complex potential $V = V_0 e^{j\omega t}$ of the cell divided by the complex current $I = I_0 e^{j(\omega t + \phi)}$.

\[
Z = \frac{V_0 e^{-j\phi}}{I_0}
\]

or

\[
Z = |Z| \cos \phi - j |Z| \sin \phi
\]

The complex admittance, $Y$, is the reciprocal of the impedance.
Theoretical Concepts and Tools

\[ Y = \frac{I_0 e^{i\phi}}{V_e} \]

or \[ Y = |Y| \cos \phi + j|Y| \sin \phi \]

The general notation for the impedance is

\[ Z = Z' - jZ'' = R - jX \]

with the real part of the impedance, \( R \), called the resistance, and the imaginary part, \( X \), called the reactance.

Correspondingly, the complex notation for the admittance is

\[ Y = Y' + jY'' = G + jB \]

with the real part, \( G \), called the conductance, and the imaginary part, \( B \), called the susceptance.

The admittance (impedance) of a cell generally is a function of frequency and thus results in a time-dependent current

\[ I(t) = Y V(t) \]

A set of complex impedance data as a function of frequency contains a complete description of the small-signal dynamic behaviour of a system. It can be used to calculate a system's transient response to any input signal, provided small-signal (linear) conditions pertain and the system remains causal (i.e. does not respond to some extraneous input such as noise). In general, one can obtain information about mass and charge transport, as well as electrolyte and electrode polarization by means of impedance/admittance measurements. This is typically done as a function of frequency, temperature, and other parameters such as dimensions of the electrolyte, thermal history of the sample and chemical composition. This ac technique then makes possible the separation of the various components due to their different characteristic times under the
conditions mentioned above. This then allows the representation of the behaviour of the galvanic cell in terms of an equivalent circuit in which the various elements or combination of elements represent the physical phenomena within the sample as well as the interaction with the electrodes. In Figure 6 an example is given for a solid ionically conducting electrolyte using ionically blocking electrodes.

\[ \text{Figure 6: Impedance plot and equivalent circuit representation of an ionically-conducting ceramic solid electrolyte with inert electrodes.} \]

The process of assigning physical phenomena in the galvanic cell to equivalent circuit elements and vice versa is by far the most critical step in impedance spectroscopy, since there are several mathematically possible equivalent circuit interpretations for one spectrum but only one represents the physical phenomena of the
experiment. By varying the above mentioned parameters and with
the exclusion of experimental side effects it is possible to determine
an equivalent circuit in which the values of its elementary
components relate to specific physical phenomena.
The complex electrical quantity may be the impedance, conductance,
permittivity, electric modulus, etc. Although the most widely used
data acquisition technique is single-point detection in the frequency
domain, measurement methods based on injection of multiple
frequencies, Fourier transformation from the time domain, and
analysis of noise spectra are also possible. The results, however, are
generally presented and discussed in the frequency domain. In
recent years, acquisition of impedance data has been dramatically
simplified, first by automatic phase-sensitive detectors, and secondly
by direct digital sampling of signals. For the determination of bulk
properties, such as ionic conductivity, two point measurements are
adequate; but for studies of interfacial phenomena three electrode
measurements are usually made, often by use of a potentiostat,
which allows the dc bias at the working electrode/electrolyte
interface to be independently varied. Depending on the relative
values of the sample and the lead impedances compared with the
input impedance of the measuring system, varying amounts of care
may have to be taken to avoid spurious effects.

Data analysis is best carried out by a nonlinear least-squares
regression procedure, for which several software programs are now
available. Both the real and imaginary parts of the impedance are
simultaneously fitted to give the best values of equivalent circuit
parameters.

The use of this technique to separate the various components of the
total conductivity of ionically/electronically conducting materials has
become very popular. It has been successfully applied to single
components using blocking electrodes as well as to whole battery
systems to monitor the changes of their components upon cycling
under varying boundary conditions. The information deduced from
these experiments has contributed a great deal to the understanding
of electrolyte, electrode and interfacial phenomena in a number of
battery systems.
A number of integrated systems are now available to measure the ac response of galvanic cells that are very comfortable to use. However, the success of the technique depends critically upon the success of the user in establishing the equivalent circuit element combination that is a realistic representation of the physical phenomena that actually take place in the experiment.

**Electronic conductivity in electrolytes**

By definition, the electronic conductivity must be small compared to the ionic conductivity within a useful electrolyte. Nevertheless, itinerant electrons and holes, which are the minority electronic charge carriers in solid materials, determine many kinetic and other properties. For example, electronic conductivity acts as an internal short circuit within a galvanic cell. Batteries with electrolytes with appreciable values of electronic conductivity can self-discharge at appreciable rates, thus reducing the stored energy available to do useful work in an external circuit. In addition, electronic conductivity reduces the cell voltage. Furthermore, the transport of electrons and holes controls the rate of equilibration of the composition within electrolytes that can exist over a range of compositions by influencing the process of chemical diffusion, since the conditions of local charge and charge flux neutrality require that equivalent amounts of different charged species be simultaneously transported within the solid in order to modify its composition. The kinetics of electronic transport can also act as an important factor in the growth of reaction product layers as well as in various other types of transport-controlled solid-state reactions involving solid ionic conductors.

Since the minority electronic properties of solid electrolytes may vary considerably with changes in composition, it is often necessary to study this question by investigation of the dependence of transport kinetics upon the activity of the components.

Transference measurements were used in early experiments to determine the partial electronic conductivity or to confirm the
virtually pure ionic conductivity of a number of materials. Due to the transport of ions through the electrolyte the masses of the electrodes will be changed by plus and minus $\frac{tA m}{\Delta t}$, respectively. The electronic transference number can then be calculated using equation /35/

$$t_e = 1 - t_{ion} = 1 - \left[ \frac{[\Delta m]}{\Delta t} \right] \left[ \frac{|z|F}{IA} \right]$$

Another method that has been employed to determine the transference number is the so-called emf technique. This approach depends upon the effect of a partial internal short circuit within the electrolyte due to the movement of electrons or holes which results in a decrease of the externally measurable voltage of the galvanic cell. For quantitative evaluation of this kind of measurement, the electrolyte has to be sandwiched between two electrodes that have different, but precisely known chemical potentials for the electroactive species. When the transference number depends strongly upon the the composition, only a rather small difference in chemical potentials should be applied across the system in order to evaluate the composition-dependence of this parameter.

The evaluation of the transference number is especially easy if only one type of ionic species is predominantly conducted. In this case the transference number is determined by

$$t_{ion} = 1 - t_e = \frac{E_{observed}}{E}$$

where $E$ is the theoretical cell voltage, given by equation 1, that would be obtained due to the thermodynamic driving force relating to the difference in the chemical potential of the electroactive species in the two electrodes if there were no electronic conduction within the electrolyte.

It is also possible to determine the partial electronic conductivity by using blocking electrodes to suppress the ionic transport so that only electrons and holes can pass through the system. This technique is
known as the asymmetric polarization or the Hebb-Wagner technique (1), (2), (23) and is illustrated in Figure 7.

Figure 7: DC polarization technique for determining the partial electronic conductivity of electrolytes with predominant ionic conductivity (21).

By using a chemically inert material that allows only electronic species to pass as the electrode at the left-hand side of the sample, no atoms will be discharged from this electrode and delivered to the electrolyte when a voltage is applied. Thus the mobile ions tend to be depleted from the left-hand interface. This means that ionic transport is blocked and no ionic current can flow under steady-state conditions. If an electrode that is reversible to the electroactive species is used on the right-hand side, it fixes the chemical potentials of the components at that interface. Under these conditions, steady state transport of electrons and holes can be due only to diffusion under the influence of gradients in their concentrations. The steady state current is then due solely to minority electronic species:

\[ I_t = I_n + I_p = \frac{RTS}{LF} \left[ \sigma_n^0 [1 - \exp(-u)] + \sigma_p^0 [\exp(u) - 1] \right] \]
where \( u = \frac{EF}{RT} \) and \( \sigma_n^o \), \( \sigma_p^o \) are the specific conductivities due to electrons and holes in the material equilibrated with the metal. \( L \) is the inter-electrode spacing, and \( \frac{L}{S} = g \), the geometric factor. Usually, either \( n \) or \( p \) conduction will dominate, and the dominant species can be determined from the shape of the current voltage curve. A useful rearrangement of the above equation allows electron and hole partial conductivities to be determined from a single experiment by plotting \( I_i[\exp(u) - 1]^{-1} \) versus \( \exp(-u) \).

\[
\frac{I_i}{\exp(u) - 1} = \frac{RTS}{LF} \left[ \sigma_n^o \exp(-u) + \sigma_p^o \right]
\]

\( \sigma_n^o \) is then calculated from the slope of the curve and \( \sigma_p^o \) from the intercept (24). The limitations of the method for solid electrolytes and mixed conductors have been discussed by Ries (25).

2.5 Thermodynamic stability windows, electrode potentials, and electrolyte stability

In addition to the question of the magnitude and selectivity of the ionic conductivity and the suppression of the electronic conductivity, another critical question related to the application of electrolytes is the matter of their chemical and electrochemical stability with respect to the materials with which they will be in contact in an electrochemical cell. Although kinetic considerations are important in some cases, this is primarily a matter of thermodynamics.

If we look at the negative electrode of a galvanic cell, the critical question is the stability of the electrolyte to the reducing conditions imposed at the high activity of the neutral species related to the cation. For example, lithium metal is a very strong reducing agent.

Binary case

With binary phases, this is a relatively simple question if the phase diagram is known. Let us consider a simple case, lithium nitride,
which is known to be a lithium ion conductor with a high conductivity, even at ambient temperatures.

An electrolyte, that is the most cation-rich intermediate phase in a binary phase diagram will always be thermodynamically stable in contact with the metal itself (or its saturated solution) as can be seen for the case of Li$_3$N from Figure 8 of the Li-N phase diagram. However, most metal-rich phases also have an appreciable electronic conductivity, which in turn leads to some electronic conduction at high metal activities and practical problems such as battery self-discharge.

Figure 8: Li-N Binary phase diagram
The stability of a binary phase electrolyte on the positive side (oxidizing conditions) can be a problem too. The thermodynamic limit can be calculated directly from its free energy of formation. Thus, Li$_3$N is thermodynamically stable to only 0.44 volts positive of lithium at unit activity.

**Ternary case**

Stability questions related to electrolytes that are ternary phases are somewhat more complicated. For discussion, let us consider a ternary Li-M-O phase, where M is some metallic species. On the negative side, the requirement of stability with elemental lithium is quite stringent. If there are no intermediate lithium metal phases, it can be stated in terms of the free energy change accompanying the reaction

\[
\text{Li} + \alpha \text{EL} = \beta \text{Li}_2\text{O} + \gamma \text{M}
\]

where EL represents the Li-M-O electrolyte phase, and $\alpha$, $\beta$, and $\gamma$ the appropriate stoichiometric numbers. If $\Delta G$ for this reaction is negative, the electrolyte will not be stable in contact with elemental Li, but will react to form Li$_2$O and M. This is indicated by the solid line that connects Li$_2$O and M in the ternary phase triangle Li-M-O shown in Figure 9. Since Li$_2$O has a large negative free energy of formation, $-\Delta G_f(\text{EL})$ must be very large to avoid this reaction. From data on Li$_2$O one can show that this is equivalent to the requirement that the electrolyte EL be stable at an oxygen partial pressure of $10^{-80}$ atm at 400°C and $10^{-200}$ atm at 25°C.

The question of electrolyte stability at positive potentials relative to lithium (oxidizing conditions) can be more difficult to understand, as the identity of possible reaction products depends upon relevant phase equilibria. For discussion, we shall consider the ternary Li-M-O system as already shown in Figure 9 from above, and also assume that the positive electrode constituents might be binary M-O phases of the same system. For simplicity, we shall assume that the only stable binary oxides in this system are MO and MO$_2$, and that their composition ranges are very narrow. Furthermore, we shall assume, that the electrolyte phase has the nominal composition Li$_2$M$_2$O$_3$, and that this is the only stable ternary phase in the Li-M-O system. If the
electrolyte were stable against Li, the tie line between Li$_2$O and M would not exist, but there would be one between Li and Li$_2$M$_2$O$_2$ would.

In such a ternary phase diagram, tie lines represent 2-phase equilibria, and triangles are composition regions within which three phases are in equilibrium. Translated to the problem of stability in a lithium-transporting electrochemical cell, this means that the voltage versus Li is constant within each triangle, its value being determined by the equilibrium of the phases at the corners.

Figure 9: Example of a Li - M - O ternary phase diagram.

If we consider a Li-transporting cell with Li$_2$M$_2$O$_3$ as the electrolyte, we can examine the stability of that phase by following the dotted
line in Figure 9. As that hypothetical phase diagram is drawn, the Li-rich boundary of the electrolyte phase occupies one corner of triangle B, in equilibrium with Li₂O and M. This three-phase equilibrium will occur at a certain lithium activity, and thus a fixed voltage relative to pure lithium.

The value of the lithium activity in triangle B can be determined by consideration of the reaction

\[ 4 \text{Li} + \text{Li}_2\text{M}_2\text{O}_3 = 3 \text{Li}_2\text{O} + 2 \text{M} \]

The requirement for equilibrium is that the free energy change for this reaction is zero. For such a reaction we can write

\[ \Delta G^0 = -RT \ln K \]

where K is the equilibrium constant. If the electrolyte, Li₂O, and M can all be considered to be in their standard states, so that their activities are unity, K becomes merely equal to \(a_{\text{Li}}^{-4}\). Thus if we know the standard free energies of formation of Li₂M₂O₃ and Li₂O, the lithium activity characteristic of triangle B can be calculated for any temperature. This can then be simply converted to a voltage with respect to pure elemental lithium at the same temperature by relation /9/.

For the case of this hypothetical ternary system and electrolyte Li₂M₂O₃ this establishes the maximum lithium activity, or minimum voltage relative to pure lithium, at which it will be stable against reduction.

One can go through a similar analysis to find the limit of stability against oxidation of the electrolyte. In that case, we consider triangle D, where the pertinent reaction is

\[ \text{Li}_2\text{M}_2\text{O}_3 = \text{MO} + \text{MO}_2 + 2\text{Li} \]

/51/
Again, if the relevant thermodynamic data are at hand, one can calculate the critical values of minimum $a_{Li}$ and maximum $E$ versus Li beyond which the electrolyte will be oxidized.

If we have such data, we can thus calculate the "stability window" for the electrolyte from these simple theoretical considerations. The electrolyte will be stable in any cell in which the lithium activities and potentials of both electrodes lie within this range. In some cases this stability window is quite broad, even though it does not extend to the pure alkali metal, and useful cells could be constructed if electrodes can be found which both lie within that range.

In actual cases, however, all the relevant thermodynamic data may not be available, and experimental work must be undertaken. One approach is to employ an electrochemical cell to directly measure the equilibrium potentials which define the limits of stability of the electrolyte. For example, the potential of triangle B in the hypothetical phase diagram in Figure 19 can be directly obtained by measuring the voltage across a cell of the type

$$(-) \text{Li/Li}^+ \text{electrolyte/ Li}_2\text{O, Li}_2\text{M}_2\text{O}_3, \text{M (+)}$$

in which the three phases defining that triangle are in equilibrium with each other in the right hand electrode. The electrolyte employed for this purpose must, of course, be stable over the potential span of this cell.

The potential of triangle D could similarly be determined by use of a cell in which the right hand electrode contains Li$_2$M$_2$O$_2$, MO, and MO$_2$. If none of them is an electronic conductor, it may be necessary to also add a chemically inert electronically-conducting material for that purpose.

The magnitude, but not the absolute values, of the stability window, could, of course, be determined by a cell containing the phases defining triangle B as one electrode, and those defining triangle D as the other.
Another approach is to devise a cell to determine the free energy of formation of the electrolyte phase, and to use that information in conjunction with other known data to determine both the span and the absolute values of the stability window. In the hypothetical case under discussion, that might involve a cell of the type

\[ \text{M, Li}_2\text{O, Li}_2\text{M}_2\text{O}_3 /\text{Li}^+ \text{ electrolyte/ Li}_2\text{M}_2\text{O}_3, \text{ MO, M} \]

which would give a voltage defined by the difference in the potentials of triangles B and C. Since the potential electrolyte phase appears in both electrodes, it is possible to also use it as the electrolyte. In this case, that would result in the simplified cell

\[ \text{M, Li}_2\text{O }/ \text{Li}_2\text{M}_2\text{O}_3 / \text{ MO, M} \]

**Quaternary case**

As a thinking tool, let us consider a tetrahedron in which the four components of a quaternary system occupy its corners. The binary intermediate phases are located along the tie lines connecting the four corners. Ternary phases are located on the triangular faces of the tetrahedron. Any intermediate quaternary phases would be located within the tetrahedron. As in the ternary case, the stable tie lines between the various phases are calculated from relevant thermodynamic data. This can be first done for each triangular face. The Gibbs phase rule constrains a 4 component system in equilibrium at fixed pressure and temperature to share the corners of a tetrahedron. This means that the total tetrahedron is composed of many sub-tetrahedra which by themselves constitute groups of four phases being in equilibrium with each other. If no intermediate quaternary phases are existent, the tie lines crossing the inner space of the tetrahedron can be calculated from thermodynamic data of the boundary phases. This is not often the case, as intermediate quaternary phases are relatively common. However, if thermodynamic data are available, the boundaries between the various tetrahedra can be established from the values of the free energies of reaction between the phases involved. If intermediate
quaternary phases exist and their free energies of formation are not known, the case becomes more complicated.

In this work, an example of a quaternary phase diagram has been worked out from thermodynamic data. The results are described in chapter 5.

2.6 The reference electrode

The purpose of the reference electrode is, as its name already indicates, to act as a voltage reference under the conditions of the electrochemical experiment. For binary systems this can be achieved in two-phase mixtures, where the chemical potential is independent of the concentration (in a two phase portion of a binary system, the phase rule constrains the system to only two degrees of freedom - i.e. temperature and pressure).

The internationally accepted primary reference for aqueous systems is the standard hydrogen electrode (SHE) which has all components at unit activity:

\[
\text{Pt} / \text{H}_2 \text{ (a=1)} / \text{H}^+ \text{ (a=1, aqueous)}
\]

In practical experiments, however, reference electrodes containing solid materials are typically used (i.e. Ag/AgCl, Hg/Hg_2Cl_2, Hg/HgO, Hg/HgSO_4).

A very common reference electrode which has been used frequently in the electrochemical experiments of this thesis is the Hg/HgO couple in a KOH aqueous electrolyte. The voltage versus oxygen can be calculated from thermodynamic data using the following equations

\[
2\text{Hg} + \text{O}_2 = 2\text{HgO}
\]

\[
\Delta G_r = 2\Delta G_{\text{HgO}}^0
\]
The voltage of the Hg/HgO electrode versus O\textsubscript{2} at unit activity is -0.305 V at 22°C. This potential is also +0.925 V relative to H\textsubscript{2} at unit activity.

The Hg/HgO reference electrode can be easily made in the laboratory. Two general designs have been used. They are shown schematically in Figure 10.

Such electrodes can be made very simply. HgO (yellow) is mixed with KOH electrolyte of the same concentration as used in the experiment (usually 6 molar) to form a paste. A drop of Hg metal is placed at the bottom of a small diameter glass tube and the paste is placed on top of the metal. Subsequently, more electrolyte is added to the tube until it flows via the connecting tube into the compartment of the electrochemical cell.

If reference electrodes are used, a so-called three-electrode system is arranged in the electrochemical cell. This means that the potential of the working electrode is measured with respect to the reference electrode, while the current flows between the working and the counter electrode.

In principle, every two-phase system that is stable under the experimental conditions within the electrochemical cell, can be utilized as a reference electrode. Examples are PdH\textsubscript{x}(α-phase)/PdH\textsubscript{y}(β-phase), TiH/TiH\textsubscript{2}, Li/LiAl, etc.). They can also be made in situ by using the coulometric titration technique.
Figure 10: Two possible designs of the Hg/HgO reference electrode.
2.7. Summary

In this chapter, the principles which can be applied to investigate the thermodynamic and kinetic properties of solids by using electrochemical techniques have been described.

The coulometric titration technique has been used to determine the amount of hydrogen that can be stored in the various phases of the Ti-Ni system under the conditions of an aqueous electrochemical cell at ambient temperature. The results have been used to construct the ternary Ti-Ni-H phase relationship at room temperature. The experimental details and corresponding results are described in chapter 3.

The suitability of the coulometric titration technique to study hydrogen in metals is also shown in the case of the Pd-H system in chapter 4. Hydrogen absorption data have been obtained and the phase boundaries in the Pd-H system have been constructed and compared with literature data. In addition, diffusion data have been obtained in the single phase compositions.

In many of the experiments of this thesis, electrochemical techniques have been used to study the properties of electrodes and electrolytes. None of these materials are stand-alone components but are always incorporated into electrochemical systems. In chapter 5, a novel electrolysis cell is introduced and the materials proposed for utilization in the system were characterized by using several of the electrochemical techniques described in this chapter.

2.8. References


Chapter 3

3. Titanium-Nickel based System

3.1. Introduction

Ti-Ni alloys have been investigated by a number of authors because of their potential use for hydrogen storage as well as in negative electrodes in several types of secondary battery systems.

Based upon the results of earlier work on the systems Ti-H and Zr-H (1), Ti-Zr-H (2), and Ti-Ni-H (3), a considerable amount of pioneering work has been done by Buchner and his co-workers (4-6) on the influence of hydrogen on Ti-Ni intermetallic phases.

According to Hansen and Anderko (7), three intermetallic phases exist in the binary system Ti-Ni above 640 °C, Ti$_2$Ni, TiNi, and TiNi$_3$, but only Ti$_2$Ni and TiNi$_3$ are stable at lower temperatures. On the other hand, numerous authors have demonstrated that the phase TiNi, which undergoes a martensitic transition, and is thus of interest as a mechanical memory material, is also present at ambient temperatures.

Ti$_2$Ni and TiNi can store appreciable amounts of hydrogen, and based upon pressure-concentration isotherms at about 150°C, it has been reported (4) that the Ti$_2$Ni intermetallic phase forms four isotypic hydrogen phases, with the stoichiometric formulas Ti$_2$NiH$_{0.5}$, Ti$_2$NiH, Ti$_2$NiH$_2$, and Ti$_2$NiH$_{2.5}$.

On the other hand, TiNi forms only one hydride phase, with the nominal composition TiNiH (4). These conclusions were supported by X-ray diffraction analysis after cooling these materials to ambient temperatures.

The Buchner (8) group also investigated the hydrogenation of Ti$_2$Ni by using a cycling programme which consisted of four steps:
evacuation at 400°C, heating under hydrogen (20 bar) at 400°C, cooling under hydrogen (30 bar) to 150°C, and cooling to ambient temperature under one bar of hydrogen. From X-ray data on the resulting materials, these investigators have proposed tentative isothermal phase diagrams for the system Ti-Ni-H at 80 and 150°C.

Mintz et al. (9), (10) have also investigated the hydrogenation characteristics of Ti$_2$Ni, as well as of related oxygen-containing Ti$_2$NiO$_x$ phases by using a combination of thermogravimetric analysis, differential thermal analysis, pressure-volume-temperature measurements, and X-ray diffraction analysis.

They found that the pure intermetallic phase Ti$_2$Ni reacts with hydrogen in an irreproducible manner; different samples reaching various H/Ti$_2$Ni composition ratios upon heating in hydrogen pressures up to 700 Torr. They also reported (10) that heating the hydrogenated Ti$_2$NiH$_x$ (2.5 < x < 2.7) samples in a hydrogen atmosphere results in an increase in weight, related to a disproportionation reaction which converts part of the Ti$_2$NiH$_x$ into TiH$_2$ and TiNiH$_y$, with y approximately 1. The oxygen-containing compounds Ti$_2$NiO$_2$ showed more consistent hydrogenation, and did not display such disproportionation reactions. However, they had a reduced hydrogen capacity, as the oxygen atoms occupy the same interstitial lattice position in the E9$_3$ (Fd3m, η carbide) structure (11) as those available for the hydrogen atoms.

Yamanaka et al. (12) reported that results of isobaric absorption and desorption measurements indicated that at 270°C and 130 atm hydrogen pressure TiNi reacts with hydrogen to form TiNiH$_{1.4}$, and Ti$_2$Ni reacts with hydrogen to form TiH$_2$ plus TiNiH$_{1.4}$. They also found that when treating TiNi and Ti$_2$Ni at 500°C and 130 atm hydrogen pressure, both hydride phases decompose into TiH$_2$ and TiNi$_3$. Both reactions can be reversed by degassing at 550°C and 850°C, respectively.

In contrast to these high temperature and high pressure observations, Wakao et al. (13) formed hydrides of both Ti$_2$Ni and TiNi, as well as two-phase mixtures, electrochemically in an aqueous
KOH solution at ambient temperatures. They observed that during cycling the initial capacity (first charge) for hydrogen for the Ti$_2$Ni phase corresponds to Ti$_2$NiH$_{2.5}$, and for the TiNi phase to TiNiH under ambient pressure and temperature conditions. They also found that the hydrogen capacity was significantly reduced upon cycling. This was especially true for the Ti$_2$Ni materials, as the capacity loss was significantly lower with decreasing Ti/Ni ratio in mixtures of Ti$_2$Ni and TiNi. However, the variations of low temperature charge and discharge potentials with composition (6), (13) are not consistent with the elevated temperature information about phases present in these systems.

The purpose of the investigations reported here was to understand this disparity, and to establish the Ti-Ni-H phase relationships at ambient temperature in the aqueous hydroxide environment, where these Ti-Ni intermetallic phases appear to have attractive properties as negative electrode materials in hydrogen-based rechargeable battery systems (6) of which this and other materials of interest have been described in chapter 1. For such an application, the properties of interest are the voltage versus hydrogen concentration (or hydrogen capacity), which determines the energy that can be stored in the system, and the kinetic behaviour, especially the chemical diffusion of hydrogen, which determines, together with microstructural parameters, to which current levels the system can be operated.

In this work, the voltage versus hydrogen concentration has been determined for the Ti$_2$Ni and for the TiNi intermetallic phases. In addition, the chemical diffusion coefficient of hydrogen has been measured in the Ti$_2$Ni and TiNi$_3$ single phase alloys. In both cases, electrochemical techniques have been employed.

3.2. Experimental Aspects

While most of the investigations of the formation of Ti-Ni hydrides have employed gas phase absorption methods, with pressure and temperature as the controlling parameters, one can also use
electrochemical methods such as the coulometric titration technique to determine the thermodynamic properties and the galvanostatic intermittent titration technique (GITT) to determine the chemical diffusion coefficient. Both techniques are described in Chapter 2.

Experimental investigations were carried out at room temperature using a galvanic cell of the type

(-) Ti-Ni alloy / 25% KOH, H₂O / (Ni(OH)₂/NiOOH) (+)

The reactions at the electrodes during discharge are:

(-) \((\text{Ti-Ni})_x\text{H} + \text{OH}^- = x(\text{Ti-Ni}) + \text{H}_2\text{O} + e^-\) \quad / 1 /

(+) \(\text{H}_2\text{O} + e^- + \text{NiOOH} = \text{Ni(OH)}_2 + \text{OH}^-\) \quad / 2 /

The overall cell reaction can then be written as:

\((\text{Ti-Ni})_x\text{H} + \text{NiOOH} = x(\text{Ti-Ni}) + \text{Ni(OH)}_2.\) \quad / 3 /

Samples of TiNiₐ with \(a=0.5\) to 3 were prepared by two different methods:

- arc melting mixtures of the elements, Ti and Ni, supplied by Alpha Chemicals, in an argon atmosphere; an arc-melter, designed and constructed in the machine shop of the Electrical Engineering Department of the Stanford University was used.

- reaction sintering of mixtures of TiH₂ and Ni powders, both from Alpha Chemicals, at 850 to 900°C under a hydrogen atmosphere, followed by degassing at 600°C in vacuum for 15 hours.

Ti₂NiOₓ alloys with \(x=0.012\) to 0.33 were prepared by arc melting of the elements, Ti and Ni, with additions of TiO₂ in an argon atmosphere. The pellets were then ground into fine powders of undetermined particle size. It was found to be very difficult to make useful powders from the pure TiNi phase, and so experiments
undertaken to evaluate this material, were actually made on polyphase samples of the nominal composition TiNi$_{2.33}$, containing both TiNi and TiNi$_3$. Under the conditions of the experiment, the TiNi$_3$ phase showed very low hydrogen absorption and thus the properties of such samples were essentially those of the pure TiNi phase.

The powders were then coated with a thin layer of copper by using an electroless plating process (14). The copper layer, which amounted about 10-25 wt%, served primarily as a protection against corrosion during cycling in the aqueous electrolyte, but also has other functions: (i) the freshly coated powders have sufficient ductility that they can be formed into compacts easily; (ii) the compact obtained after pressing does not disintegrate during repeated hydrogen sorption cycles; (iii) the copper coating seems to influence the hydrogen diffusion in a positive manner, which indicates that $\bar{D}$ in Cu is higher than $\bar{D}$ in the alloy, as will be shown later.

The coated powders were pressed into compact samples at a pressure of 2 MPa.

The electrochemical cell arrangement used in all experiments is schematically shown in Figure 1.

It consisted of a U-shaped tube that allowed the separation of the anode and cathode compartments. A ribbon-shaped piece of a nickel electrode, extracted from a Ni/Cd battery, was wound into a coil and served as the positive electrode (anode). The sample under investigation was used as the negative electrode (cathode). A Hg/HgO electrode was used as a reference. A thermocouple in a glass tube was placed next to the sample electrode, and the temperature was measured periodically.

If oxygen is present in the electrolyte (from the anode reaction or from the air) it will react with the hydrogen in the cathode under open circuit conditions. The separation of the two electrodes was necessary in order to avoid oxygen poisoning of the electrolyte. In addition, the cathode environment was continuously purged with
high purity nitrogen to carry out any possibly dissolved oxygen, and also to provide proper stirring of the electrolyte.

Figure 1: Schematic representation of the electrochemical cell arrangement.
This procedure was necessary in order to obtain reproducible equilibrium measurements. Disregarding this procedure resulted in a gradual drift of the equilibrium potential due to self-discharge of the metal hydride electrode due to the reaction

\[
2(Ti-Ni)_x H + 1/2 O_2 = 2x(Ti-Ni) + H_2O. \quad /4/
\]

After the sample electrode was inserted into the cell and all electrical connections were made, the sample was fully charged with hydrogen by applying potentials up to -1 V vs the Hg/HgO reference electrode.

A potentiostat/galvanostat form Princeton Applied Research, PAR, Model 173, was used to perform coulometric titration experiments. When the sample was fully loaded with hydrogen, the discharge half-cycle was started by applying constant currents through the cell, typically 10-500 mA/g of active species, for fixed periods of time. Subsequently, the electrode potential was observed as equilibrium took place. The result was a series of equilibrium potential versus hydrogen content points, which define the thermodynamic properties of the electrode material as a function of composition.

All potentials were measured versus the Hg/HgO (in 25wt% KOH) reference electrode, and a change of potential of less than 1 mV over the period of one hour was used as the criterion of equilibrium.

In addition to providing information about the equilibrium coulometric titration curve, this procedure can also be used to determine the chemical diffusion coefficient of the moving species as a function of activity (15).

When the equilibrium condition was satisfied at a particular hydrogen concentration \(c_p\), the potential was stepped to a slightly more positive value, corresponding to a lower hydrogen activity. The resulting current was recorded as a function of time until the sample reached its new hydrogen equilibrium concentration \(c_f\) at \(I=0\). The current as a function of time, \(I = f(t)\), provides information of the chemical diffusion of hydrogen, \(\tilde{D}\), in the metal. With a planar
electrode of thickness $x$, this time-dependent current is related to the instantaneous concentration gradient of hydrogen by Fick’s first law:

$$I(t) = -zFS\left(\frac{dc}{dx}\right)_{x=0}$$

where $S$ is the surface area of the electrode, $z$ is the charge number of the hydrogen transporting species in the electrolyte, and $F$ is the Faraday constant.

By setting proper initial and boundary conditions

$$c = c_i \quad 0 \leq x \leq L \quad t = 0 \quad /6/$$

$$c = c_f \quad x = 0 \quad t > 0 \quad /7/$$

$$\frac{\partial c}{\partial x} = 0 \quad x = L \quad t \geq 0 \quad /8/$$

and solving Fick’s second law, we can obtain the following approximations for short and long times

$$I(t) = zFS*(c_f - c_i)*\left[\frac{D}{\pi^2t}\right]^{1/2} \quad \text{for} \quad t \ll \frac{L^2}{4D} \quad /9/$$

$$I(t) = \frac{4zFS\bar{D}}{L}*(c_f - c_i)\exp\left[-\frac{\pi^2D t}{L^2}\right] \quad \text{for} \quad t \gg \frac{L^2}{4D} \quad /10/$$

The difference in the equilibrium concentrations, $(c_f - c_i)$, can be related to the total charge, $Q$, passed through the sample:

$$c_f - c_i = \frac{2Q}{zFSL} \quad /11/$$

The time-dependent current may then be written as:

$$I(t) = \frac{2Q}{L}\left[\frac{D}{\pi^2t}\right]^{1/2} \quad \text{for} \quad t \ll \frac{L^2}{4D} \quad /12/$$
\[
I(t) = \frac{8Q \tilde{D}}{L^2} \exp \left[ -\frac{\pi^2 \tilde{D} t}{L^2} \right] \quad \text{for } t \gg \frac{L^2}{4\tilde{D}}
\]

For short time measurements, or thick samples \( t \ll \frac{L^2}{4\tilde{D}} \) the chemical diffusion coefficient may be obtained from a plot of \( \ln I \) vs \( \ln t \).

For longer times \( t \gg \frac{L^2}{4\tilde{D}} \), \( \tilde{D} \) may be obtained from either the intercept or the slope of a plot of \( \ln I \) vs \( t \).

The diffusion of hydrogen was determined in solid slabs of Ti2Ni and TiNi3 of defined surface area and thickness (1 cm\(^2\) area, 0.03-0.1 cm thick) at very low hydrogen activities in order to avoid disintegration of the sample due to the volume expansion upon hydrogen uptake. The slabs were cut from the arc melted materials. Ti2Ni was also investigated in form of the Cu-coated powders pressed into a pellet at a pressure of 2 MPa.

X-ray diffraction measurements, using a Siemens diffractometer with CuK\(_\alpha\) radiation, were made of various samples, including initial alloys and pressed powder electrodes in various states of charge and discharge.

### 3.3. Results

Figure 2 shows the coulometric titration curves of two samples. In Figure 2a, the hydrogen absorption behaviour of the TiNi phase after the first discharge cycle is shown. The nominal composition of the sample was TiNi\(_{2.33}\) and was a combination of the TiNi phase and the TiNi3 phase. Since the TiNi3 phase absorbs very little hydrogen, but shows very good diffusion for hydrogen in comparison to the other Ti-Ni intermetallic phases, the behaviour of the first of these samples was considered essentially the same as the pure TiNi phase. The TiNi phase can store about 1.1 H atom per TiNi formula unit at a potential of -0.925 vs the Hg/HgO reference, but not all hydrogen could be removed during discharge to a potential of -0.67 V vs the
Hg/HgO reference electrode in the electrochemical cell. Polarising the electrode to even more positive potentials than -0.46 V vs Hg/HgO would lead to oxidation of the copper protective layer.

In Figure 2b, the hydrogen absorption behaviour of the Ti$_2$Ni phase after the first discharge cycle is shown.

The Ti$_2$Ni phase can store 2.5 H atoms per Ti$_2$Ni formula unit at a potential of -0.910 V vs the Hg/HgO reference. However, only 1.4 H atoms per Ti$_2$Ni formula unit could be extracted during the first discharge cycle, which was terminated at a potential of -0.67 V vs Hg/HgO.

It is seen that the TiNi phase had more negative potentials, and reacted to form a product, presumably TiNiH$_y$, with $y$ somewhat above 1.0. On the other hand, Ti$_2$Ni reacted with hydrogen to give a product Ti$_2$NiH$_x$, with $x$ of 2.5, of which only 1.4 could be used during the first discharge. It is important to note that both these curves have shapes characteristic of topotactic insertion reactions. This indicates broad ranges of solid solution in both cases, with no evidence for the formation of phases with intermediate compositions, as reported by other authors from experiments at higher temperatures. Such a disparity between ambient temperature and elevated temperature reaction mechanisms is often found in cases in which a relatively mobile interstitial species is inserted into a more stable host crystalline lattice at low temperatures (16). The possibility of an insertion reaction in the case of the Ti$_2$NiH$_x$ phase at ambient temperature is reinforced by observation of the almost linear dependence of the interatomic spacings upon the value of $x$. This is shown in Figure 2c for three of the major X-ray peaks. This is exactly what one would expect for a solid solution.

Quite different results were obtained upon the second discharge cycle of the TiNi and Ti$_2$Ni phases. The reaction of TiNi to form TiNiH$_y$, was found to be quite reversible during the first two cycles, as shown by the titration curves in Figures 3a. On the other hand, a distinct loss of capacity was experienced upon cycling the Ti$_2$Ni phase. This is shown for two successive titration curves in Figure 3b. Although the sample
Figure 2: a) top: Coulometric titration curve for TiNiH$_x$; b) middle: Coulometric titration curve for Ti$_2$NiH$_x$; c) bottom: lattice parameters versus composition relationship in Ti$_2$NiH$_x$, (□) hkl=422, (●) hkl=333, (■) hkl=440, all from reference (8); (⊙) present values.
Figure 3: a) top: Coulometric titration curve of TiNiH_y: (□) first cycle, (♦) second cycle; b) bottom: Coulometric titration curve of Ti_2NiH_x: (□) first cycle, (♦) second cycle.
Although the sample could be charged up to a potential of -0.910 V, like in the first charging procedure, only 0.8 H per Ti₂Ni formula unit could be extracted during the second discharge.

The reasons for this difference are ascribed to the volume change during hydriding Ti₂Ni, which is considerably greater, approximately 20%, than for TiNi, which is about 10% (6). This could well lead to the disruption of the protective copper layer, and subsequent attack of the Ti₂Ni particles by the electrolyte. The titanium activity is quite high in this phase, and there is, therefore, a great tendency for leaching titanium from the surface, and the formation of titanium oxides, at the potentials at which these electrodes reside in the KOH electrolyte. From the Ti-H-O phase diagram and relevant thermodynamic data (17) one can calculate that titanium at unit activity would only be immune at potentials more than -2.26 V of the Hg/HgO reference. For the case that the oxides dissolve in the electrolyte, a continuous loss in capacity would be expected. If the oxides do not dissolve, they will protect the interior of the electrode from further hydrogen penetration and thus reduce the hydrogen capacity dramatically as soon as a continuous layer has been formed, presumably already after the first cycle. The severe capacity loss of the Ti₂Ni phase was certainly enough reason not to employ this alloy in a Ni/metal hydride battery.

We can now compare these ambient temperature results with the high-temperature results (4-6), (8) in terms of the respective isothermal ternary phase diagrams. According to Buchner (8), the Gibbs triangle at 80°C is as shown in Figure 4a. On the other hand, the data reported here can be rationalized in terms of a Gibbs triangle at ambient temperature as shown in Figure 4b. It should be noted that the composition of the titanium hydride phase in Figure 4b has been drawn to be consistent with reported data (18).

According to our coulometric titration data, the value of y in TiNiHₙ decreases by about 1.07 from the fully hydrided composition. If we assume that the latter is approximately 1.1, we see that the solid solution region extends all the way down to essentially pure TiNi.
Figure 4:  a) top: Proposed Ti-Ni-H phase diagram at 80°C from (8)  
b) bottom: Proposed phase relations in the Ti-Ni-H system at ambient temperature from this work.
In the case of Ti$_2$NiH$_x$, if we assume that the fully hydried material can be represented as Ti$_2$NiH$_{2.5}$, dehydration at ambient temperature in the KOH electrolyte leads to a composition of approximately Ti$_2$NiH$_1$. Further reduction of the hydrogen content upon dehydration could not be accomplished in the KOH electrolyte without going to potentials more positive than -0.450 V vs the Hg/HgO reference electrode, at which the copper protective layer begins to oxidize.

X-ray diffraction measurements of the lattice parameters, which corresponded very well with those presented elsewhere (4), confirmed this span of hydrogen content in the Ti$_2$Ni case.

The tentative construction of the region of the ambient temperature Ti-Ni-H phase diagram between the two insertion reaction solid solution phases was based upon the observation that the potential range in the Ti$_2$NiH$_x$ phase is generally more positive, and thus has lower hydrogen activities, than in the TiNiH$_y$ phase. Thus the tie line bundle between Ti$_2$NiH$_{2.5}$ and TiNi is farther from the H corner of the diagram than the tie line bundle between Ti$_2$NiH$_{2.5}$ and TiNiH$_y$.

Investigations of the reaction of oxygen stabilized Ti$_2$Ni alloys with hydrogen in terms of their thermodynamic properties have not been successful. The samples tend to loose the electrical contact during the first cycle in an irreversible manner.

The measurement of the chemical diffusion coefficient in the single phase alloys turned out to be quite difficult from an experimental point of view.

In order to use equations /5/ to /10/ to calculate the numerical value of the chemical diffusion coefficient, $D$, from transient measurements, sample geometries with high ratios of area to thickness have to be used. For samples of the Ti$_2$Ni and the TiNi$_3$ phases, thin slabs, 0.03 cm thick, 1 cm$^2$ in area, were cut from arc melted pellets. Each slab was mounted within a loop of platinum strip for electrical contact and inserted into the electrochemical cell. They were charged with hydrogen only at low hydrogen activities, as indicated in Table I, in order to avoid large volume changes that
could cause disruption of the sample and, as a consequence, could lead to undefined changes in the sample geometry during the course of the measurement. This was observed in several cases and for this reason, experimental data were only gathered at low hydrogen activities.

In the case of the TiNi phase, the situation was much worse. The TiNi intermetallic phase, which shows the shape memory effect, is, depending on its history during preparation, very sensitive to temperature changes and mechanical deformation. This was experienced when attempts were made to cut slabs from arc melted pellets. During cutting, the slabs, half way cut through, suddenly bent in a 90° angle away from the cutting wheel. Nevertheless, the pieces were measured in their dimensions and mounted in the electrochemical cell. However, several attempts to charge them with hydrogen under the conditions in the aqueous electrochemical system failed. The reason for this behaviour was not further investigated, but is probably due to a phase transformation during the cutting procedure. The newly formed phase has a different pressure composition isotherm for hydrogen probably at higher pressures than can be achieved under the conditions in the electrochemical cell.

The hydrogen transport characteristics of the Ti$_2$Ni phase have been investigated in a fully loaded sample by using the copper coated powders of the same sample batch used for the coulometric titration measurements. A pellet of 0.01 cm thickness and 1 cm$^2$ area was made by pressing the powder at a pressure of 2 MPa. The sample was mounted in the cell and charged with hydrogen to activities, corresponding to -0.919 V versus the Hg/HgO reference electrode. Transient behaviour was observed starting from different hydrogen activities during discharge. The values are shown in Table I. They reveal that the copper coating has a very positive influence upon the hydrogen transport in the electrode. With a chemical diffusion coefficient of 10$^{-7}$ cm$^2$/sec, the time for hydrogen to penetrate a distance of 10 μm diameter, is about 100 seconds, using the relationship
\[ \frac{x^2}{t} = \bar{D} \]

where \( x \) is the distance in cm, \( t \) the time in sec, and \( \bar{D} \) the chemical diffusion coefficient in cm\(^2\)/s.

The results of the kinetic measurements are shown in Table 1.

### TABLE I: Chemical Diffusion Coefficient, \( \bar{D} \), in cm\(^2\)/s, of hydrogen in Ti\(_2\)Ni and TiNi\(_3\) alloys.

<table>
<thead>
<tr>
<th>Potential (V) versus Hg/HgO</th>
<th>Current Density (mA/cm(^2))</th>
<th>( \bar{D} ) of Ti(_2)Ni Cu-coated Powder</th>
<th>( \bar{D} ) of Ti(_2)Ni Solid Slab</th>
<th>( \bar{D} ) of TiNi(_3) Solid Slab</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.745 to -0.746</td>
<td>1</td>
<td>1 \times 10^{-8}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.919 to -0.916</td>
<td>2</td>
<td>4.5 \times 10^{-7}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.916 to -0.910</td>
<td>5</td>
<td>4.1 \times 10^{-7}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.910 to -0.904</td>
<td>8</td>
<td>4.1 \times 10^{-7}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.904 to -0.889</td>
<td>10</td>
<td>1.7 \times 10^{-7}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.735 to -0.740</td>
<td>1</td>
<td></td>
<td></td>
<td>2.3 \times 10^{-7}</td>
</tr>
</tbody>
</table>

### 3.4. Summary

The reaction of hydrogen with the binary phases Ti\(_2\)Ni and TiNi at ambient temperature has been studied using electrochemical techniques. The results indicate that these are both topotactic
insertion reactions which produce solid solutions with wide compositional ranges under these conditions, contrary to the observations by others of reconstitution reactions at elevated temperatures.

Samples have been prepared from powders which were coated with a copper protective layer by an electroless plating process.

The potential versus hydrogen concentration characteristics were investigated using the coulometric titration technique. From transient behaviour, the chemical diffusion coefficient of hydrogen was deduced.

TiNi absorbs 1.1 H atoms per formula unit, of which 1 H atom per formula unit was discharged in the electrochemical environment. This was also observed in a second cycle.

Ti$_2$Ni can absorb 2.5 H atoms per formula unit, but only 1.4 H atoms could be discharged in the first cycle under the conditions of the electrochemical cell. In the second cycle the sample had lost already about two thirds of its initial hydrogen capacity and was left with 0.9 H atoms per formula unit.

From this information, the ternary phase diagram has been constructed at room temperature and compared with intermediate temperature results from other authors.

Kinetic measurements have shown that hydrogen diffuses reasonably fast through Ti$_2$Ni and TiNi$_3$ at ambient temperature. Chemical diffusion coefficients of $1 \times 10^{-8}$ cm$^2$/s for Ti$_2$Ni and $2.3 \times 10^{-7}$ cm$^2$/s for TiNi$_3$ were measured at room temperature.

Several attempts to measure the diffusion of hydrogen in the pure TiNi phase failed because of experimental difficulties.

The better reversibility of the TiNiH$_x$ reaction, along with its more negative potential range, make these materials more interesting candidates than those based upon the Ti$_2$NiH$_x$ formation reaction for use in hydrogen-based electrochemical cells. As reported elsewhere,
a cell voltage of 1.35 V is obtained when these materials are used in combination with Ni(OH)$_2$/NiOOH positive electrodes.

3.5. References


2. AEC, Clearinghouse Distribution, Research and Development Report, Number NAA-SR-7132,


Chapter 4

4. Palladium-Hydrogen based System

In this chapter the insertion of hydrogen into palladium-based systems over a wide range of hydrogen activity is described. In the first part, the hydrogen absorption into palladium and a palladium-lithium alloy at potentials corresponding to pressures up to 1 atm hydrogen has been studied at ambient conditions using electrochemical techniques. Thermodynamic and kinetic properties were evaluated simultaneously as a function of the hydrogen activity.

In the second part, the electrochemical loading of hydrogen and its isotopes into palladium at room temperature has been studied by measuring the change in palladium resistance as a function of H(D) content. The effects of several electrochemical variables on the loading process have been examined. In particular, it has been demonstrated that loadings up to and in excess of H(D)/Pd = 0.9 may be achieved under suitable conditions.

4.1. Thermodynamic and kinetic properties of hydrogen insertion in Pd and Pd-Li alloy

4.1.1 Introduction

Investigations of the thermodynamic and kinetic properties of hydrogen and its isotopes in palladium have been the subject of many research efforts for many years. An extended compilation of the work performed up to 1967 was published by Lewis (1).

More recently, renewed attention was given to earlier research on the H/Pd system and in particular the D/Pd system, following the announcement by Fleischmann and Pons (2) of anomalous effects
when deuterium is inserted into palladium electrochemically. The electrolyte used in those experiments was 0.1 molar LiOD dissolved in heavy water. It has been observed that lithium was deposited onto the palladium cathode and found in the near surface layer of the palladium electrodes (3-5).

It was, therefore, of paramount interest to determine if, and in which way, the addition of lithium to palladium would influence the hydrogen absorption process.

Hydrogen absorption in pure palladium as a function of the hydrogen pressure has been extensively investigated by the use of various methods, such as the conventional gas absorption method (6-9), direct absorption from hydrogen-stirred acidic solutions (10), (11), electrochemical techniques (10), (12), (13), and magnetic susceptibility measurements (14). The binary alloy H-Pd is produced by the diffusion of hydrogen into the metal. When the terminal α-solid solution is saturated (H/Pd atomic ratio values between 0.008 and 0.03 have been reported at room temperature), a new phase, the so-called β hydride, is formed. The two phases coexist up to the ratio of about 0.6. Above this ratio, only the β phase is stable.

Hydrogen diffuses very fast in palladium at low hydrogen concentrations. The chemical diffusion coefficient in the α phase has been studied extensively in the temperature range from -50 to 600°C, and the results obtained by different authors and methods are in good agreement (15).

At higher hydrogen activities (in the β-phase), inconsistent results have been reported for the chemical diffusion coefficient. The frequency factor and the activation energy yield diffusion coefficients between $8.5 \times 10^{-9}$ (16) and $3.5 \times 10^{-6}$ cm$^2$/s (17) at 23°C. This discrepancy may be due to the fact that experiments were compared for different compositions, and samples were prepared in different ways. The chemical diffusion coefficient is strongly dependent upon the thermodynamic enhancement factor.
If the composition is not known, or the sample under investigation is in the two-phase regime, the results will not be consistent.

The behaviour of palladium alloys in contact with hydrogen has also been the subject of several investigations which were oriented toward improving the mechanical properties of permeation membranes or to study the solid state storage of hydrogen. The relative importance of the elastic and electronic interactions has been studied using fcc alloys with different lattice parameters or electronic structures: Pd-Ag (18), Pd-Pt (19), (20), Pd-Rh (21-23), Pd-Ni (24), Pd-Cu (9), Pd-V (25), and Pd-Ti (26), (27).

Only sparse data have been reported on the Pd-Li alloys. However, several reports have shown a potential interest in those materials for hydrogen storage applications (28-30). The intermetallic hydride Li$_2$PdH$_2$ which was described in these reports was obtained by reacting a mixture of lithium hydride and palladium powder at 407°C in hydrogen.

The purpose of the investigations reported here was to use an electrochemical method applicable to samples of varying thickness to compare phase equilibria and the chemical diffusion coefficient of hydrogen in a Pd-Li alloy with that in both annealed and deformed samples in the binary Pd-H system.

### 4.1.2 Experimental Aspects

While most of the investigations of the formation of palladium and palladium alloy hydride phases have employed gas phase absorption methods, with pressure and temperature as the controlling parameters, one can use electrochemical methods to simultaneously determine thermodynamic and kinetic properties as described in Chapter 2.

Experimental investigations were carried out at room temperature using a galvanic cell of the type:
(-) Pd alloy / 1 M LiOH, H₂O / Pd (+)

Palladium wire from the Engelhard Company (0.31 cm diameter, 99.9% purity) was arc melted in an argon atmosphere several times to ensure homogeneity, and then cut into 1 mm thick slabs and annealed at 900°C in vacuum for 1 hour. Four samples (Pd0, Pd1, Pd2, and Pd3) were cleaned and polished with sand paper, weighed and attached to a 0.5 mm palladium wire by spot welding. The wire, which served as a current lead, was protected by a tight TEFLO® sleeve to avoid contact with the electrolyte. These electrodes were rinsed with deionized water and electrolyte prior to insertion into the electrochemical cells.

A palladium-lithium alloy of composition PdLi₀.₁₄ was prepared electrochemically at 400°C from pure palladium by electrochemical decomposition of LiD in a LiCl-KCl molten salt. At the start of the experiment, both electrodes consisted of pure palladium. The LiD salt was decomposed at voltages ranging from 0.8 to 1.2 V in order to maintain current densities of between 10 and 50 μA/cm². At the negative electrode, lithium was inserted into the palladium to form a Pd-Li alloy. At the positive electrode, deuterium was absorbed into the palladium to form a solid solution of composition PdD₀.₁₄. The initial sample thickness of the palladium wire was 0.45 mm, which was achieved by rolling the 0.31 cm diameter wire (about 70% deformation). Thinner samples were preferred because of the slow diffusion of lithium into palladium, even at 400°C.

The crystal structure and lattice parameter of the pure palladium as well as the alloy were determined by X-ray diffraction using Cu-Kα radiation. The alloy was found to have a face-centered cubic (fcc) structure with a unit cell of 7.78 Å (instead of 3.889 Å for pure palladium). These results are concordant with data reported for the compound LiPd₇ (31).

The palladium-lithium samples were polished, weighed, and rinsed in de-ionized water and electrolyte (the same as was also
used in the experiment) before inserted into the electrochemical cell.

The electrochemical cell used in all experiments is schematically shown in Figure 1. It consists of a U-shaped tube which allows the physical separation of the anode and cathode compartments. A palladium ribbon, made by rolling a 0.31 cm diameter palladium wire, was wound into a coil and served as the anode. The sample under investigation was the cathode. A Hg/HgO electrode was used as a reference. A thermocouple in a glass tube was placed next to the cathode, and the temperature was measured periodically.

The 1 M LiOH electrolyte was cleaned of impurities by pre-electrolysis using a sacrificial palladium cathode. This procedure was conducted at currents of several mA over night. A hard brown layer, covered with a fine black deposit appeared on the cathode after this operation.

Oxygen from the air and dissolved into the electrolyte acts to poison the surface of the palladium. The oxygen-evolving electrode was, therefore, moved far away from the cathode. In addition, the cathode environment was continuously purged with oxygen-free nitrogen to carry out any dissolved oxygen from the electrolyte, and to provide proper stirring. This procedure was necessary to obtain reproducible equilibrium measurements. When this was not done, hydrogen from inside the solid was oxidized at the surface, resulting in a gradual potential drift.

After the cathode was inserted into the cell and all electrical connections were made, the sample was charged with hydrogen potentiostatically. During this first absorption half-cycle, only a few equilibrium measurements were made. When the sample was fully loaded with hydrogen at 1 atm pressure, the discharge half-cycle was started. Small voltage steps (typically 20 mV) were imposed, and the amount of charge transported as a result of each step was recorded. Typical discharge currents decreased from 2
mA to 1 µA. Subsequently, the circuit was opened, and the electrode potential was observed as equilibrium took place.

Figure 1: Electrochemical cell arrangement
The result was a series of equilibrium potential versus hydrogen content points, the coulometric titration curve, which defined the equilibrium thermodynamic properties of the electrode material as a function of composition.

All potentials were measured versus the Hg/HgO (1 M LiOH) reference electrode, and a change in potential of less than 1 mV over a period of one hour was used as the criterion of equilibrium.

In addition to providing information about the equilibrium coulometric titration curve, this procedure can be used also to determine the chemical diffusion coefficient as a function of activity (32).

When the equilibrium condition was satisfied at a particular hydrogen concentration $c_i$, the potential was stepped to a slightly more positive value, corresponding to a lower hydrogen activity, as described earlier. The resulting current was recorded as a function of time until the sample reached its new hydrogen equilibrium concentration at $c_f$ at $t=0$. The current as a function of time, $I=f(t)$, provides information about the chemical diffusion coefficient $D$ of hydrogen in the metal (see Chapter 2).

### 4.1.3. Results

**Coulometric Titration Data**

Figure 2 shows the equilibrium potential of an annealed palladium electrode as a function of its hydrogen concentration during several desorption runs at 23°C. From this curve, the stability range for the $\alpha$-phase region for these samples, expressed as the H/Pd ratio, was determined to be 0.01. Two phases, $\alpha+\beta$, are stable up to a H/Pd ratio of 0.6. After that, the $\beta$-phase is stable and reaches a H/Pd ratio of 0.74 at a hydrogen pressure of 1 atm.
Figure 2: Coulometric titration curve for hydrogen desorption from palladium at 23°C.

Thus we see that the electrochemical technique used in this work gives results in excellent agreement with data in the literature (14), (33). It provides very good compositional resolution, for the incremented charge between two equilibrium measurements can be very small and still measured with high precision. For example:
the charge of 1 Coulomb corresponds to \( \frac{1}{96500} \) gram equivalents of hydrogen. Steps as small as 0.01 to 0.1 C for samples weighing 200 to 500 mg were typical for these titration experiments. Extremely small steps were taken on both sides of the phase boundaries.

The plateau potential in the two-phase region was \(-0.065 \pm 0.002\) V versus 1 atm hydrogen for the desorption experiments. It was somewhat more positive but less reproducible during absorption. This plateau potential can be compared with measurements at different temperatures. Figure 3 shows the Van't Hoff isobar for the H-Pd system over a wide range of temperatures. It can be seen that the results obtained in this work are in good agreement with the desorption data reported in the literature.

As expected from the literature, a pronounced hysteresis effect was observed during the first absorption/desorption cycle. The desorption plateau was always flatter and more reproducible than the absorption plateau. However, the extent of the hysteresis diminishes as the number of cycles increases and thus allows a comparison of this work with absorption data from the literature. This is shown in the Van't Hoff plot in Figure 4.

The palladium-lithium alloy was charged and discharged with hydrogen in the same manner as discussed above for the experiments on the pure palladium. Figure 5 shows the coulometric titration curve at room temperature of the PdLi\(_{0.14}\) alloy. For each sample (PdLi\(_{0.14}/1\) and PdLi\(_{0.14}/2\)), at least two absorption/desorption cycles were measured. There were no signs of physical disintegration during these few cycles.

The hydrogen content in the alloy was expressed as \( H/(Pd+Li) \), the ratio of the number of hydrogen atoms to the total number of metal atoms. The general shape of the curve is similar to the pure palladium case. However, the total solubility up to a hydrogen pressure of 1 atm is significantly smaller (0.52 instead of 0.74 for Pd).
Figure 3: Van 't Hoff plot for hydrogen desorption from palladium at 23°C. Frieske (14), Gillespie (6), Burch (9), Wicke (33).
Figure 4: Van 't Hoff plot for hydrogen absorption in palladium at 23°C. Ratchford (11), Gillespie (6), Federova (13), Nace (7), Hoare (10).
Figure 5: Coulometric titration curve for desorption of hydrogen from two PdLi$_{0.14}$ samples.

In addition, the two-phase region occurs at a lower hydrogen pressure, 0.083 V/hydrogen, instead of 0.065 V/hydrogen, which
indicates that the hydrogen activity is reduced in the presence of lithium. The solubility of hydrogen in the α-phase increased due to the addition of lithium to the palladium. It occurred at a \( \text{H}/(\text{Pd+Li}) \) ration of 0.03 (instead of 0.01 for pure palladium).

**Diffusion Measurements**

The chemical diffusion coefficients were calculated from the current transients as discussed above, using the equations 22-32 of chapter 2.

Results for the short-time and long-time behaviour for a typical experiment are shown in Figure 6. In all cases, quite good agreement was found between the values obtained from both the short-time and long-time data. The data listed in Tables I, II, and III, and discussed below are averages of the short-time and long-time values.

For the measurements in the α-phase in the unalloyed palladium, three metallurgical states were investigated:

- fully annealed (sample Pd0)
- annealed and then charged and discharged with hydrogen several times (sample Pd1)
- cold-worked, approximately 70% (sample Pd4)
Figure 6: Typical transient current for short time and long time behaviour.
TABLE I: Chemical diffusion coefficient for hydrogen in α-palladium at room temperature

<table>
<thead>
<tr>
<th>Metallurgical State</th>
<th>Temperature in °C</th>
<th>$\tilde{D} \times 10^{-7}$ in cm²/s</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>as received</td>
<td>25</td>
<td>1.3</td>
<td>electro-chemical</td>
<td>(34)</td>
</tr>
<tr>
<td>unknown</td>
<td>25</td>
<td>1.6</td>
<td>permeation</td>
<td>(35)</td>
</tr>
<tr>
<td>flaming</td>
<td>23</td>
<td>0.87-1.3</td>
<td>permeation</td>
<td>(36)</td>
</tr>
<tr>
<td>unknown</td>
<td>25</td>
<td>3.1</td>
<td>permeation</td>
<td>(37)</td>
</tr>
<tr>
<td>annealed</td>
<td>26</td>
<td>1.9</td>
<td>electro-chemical</td>
<td>(38)</td>
</tr>
<tr>
<td>annealed</td>
<td>25</td>
<td>3.8</td>
<td>electro-chemical</td>
<td>(39)</td>
</tr>
<tr>
<td>unknown</td>
<td>25</td>
<td>3.4</td>
<td>electro-chemical</td>
<td>(39)</td>
</tr>
<tr>
<td>annealed</td>
<td>23</td>
<td>3.4</td>
<td>electro-chemical</td>
<td>(40)</td>
</tr>
<tr>
<td>annealed</td>
<td>22</td>
<td>3.2</td>
<td>electro-chemical</td>
<td>(41)</td>
</tr>
<tr>
<td>annealed</td>
<td>23</td>
<td>3.0-3.8</td>
<td>electro-chemical</td>
<td>this work</td>
</tr>
<tr>
<td>cycled/H₂</td>
<td>23</td>
<td>1.6-2.2</td>
<td>electro-chemical</td>
<td>this work</td>
</tr>
<tr>
<td>cold worked</td>
<td>23</td>
<td>1.5-2.2</td>
<td>electro-chemical</td>
<td>this work</td>
</tr>
</tbody>
</table>
TABLE II: Chemical diffusion coefficient for hydrogen in β-palladium and β-palladium-lithium at room temperature

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>(\text{H/Pd+Li)})\text{init}</th>
<th>(\text{H/Pd+Li)})\text{final}</th>
<th>(\tilde{D} \times 10^{-9}) cm(^2)/s</th>
<th>Thermodynamic Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd4 cold-worked</td>
<td>0.74</td>
<td>0.732</td>
<td>2.2</td>
<td>30-40</td>
</tr>
<tr>
<td>Pd4 cold-worked</td>
<td>0.74</td>
<td>0.736</td>
<td>2.5</td>
<td>30-40</td>
</tr>
<tr>
<td>Pd1 cycled/H(_2)</td>
<td>0.74</td>
<td>0.734</td>
<td>5</td>
<td>30-40</td>
</tr>
<tr>
<td>PdLi(_{0.14})(_2)</td>
<td>0.53</td>
<td>0.43</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>PdLi(_{0.14})(_2)</td>
<td>0.55</td>
<td>0.46</td>
<td>3</td>
<td>19</td>
</tr>
</tbody>
</table>

Results for the fully annealed sample are shown in Table I and Figure 7 together with data compiled by Völkl and Alefeld (42), which are in good agreement. The solid line drawn in Figure 7 as the best fit yields a value for the chemical diffusion coefficient of \(3.4 \times 10^{-7}\) cm\(^2\)/s at 23°C. All the data obey the Arrhenius equation.

\[
\tilde{D} = \tilde{D}_o \exp \left[ \frac{-\Delta H}{kT} \right]
\]

The cyclically hydried and cold-worked samples were found to have a lower effective hydrogen diffusivity. As will be discussed later, this is consistent with reported experiments which indicated internal trapping of hydrogen by defects. In our experiments, this trapping reduced the chemical diffusion coefficient by a factor of 2.

The chemical diffusion coefficient of hydrogen was also measured in the \(\alpha\)-phase of the two PdLi\(_{0.14}\) samples at room temperature. It was found to be about two orders of magnitude smaller than for pure palladium, \((4.1 \pm/ 0.6) \times 10^{-9}\) cm\(^2\)/s.
Figure 7: Diffusion coefficient of hydrogen in α-palladium (42). The references in the figure relate to the numbers of reference (42).
TABLE III: Temperature dependence of the chemical diffusion coefficient, $\tilde{D}$, for hydrogen in $\beta$-palladium from literature references. $D_n$ denotes component diffusion coefficient.

<table>
<thead>
<tr>
<th>$\Delta H$ (kJ/mole)</th>
<th>$\tilde{D}_o$ (cm$^2$/s)</th>
<th>$\tilde{D}_{23rC}$ (cm$^2$/s)</th>
<th>H/Pd</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.9</td>
<td>$1.9 \times 10^{-2}$</td>
<td>$1.15 \times 10^{-6}$</td>
<td>0.6-0.7</td>
<td>(43) $\tilde{D}$</td>
</tr>
<tr>
<td>24.12</td>
<td>$5.7 \times 10^{-3}$</td>
<td>$3.8 \times 10^{-7}$</td>
<td>0.74</td>
<td>(44) $D_n$</td>
</tr>
<tr>
<td>25.57</td>
<td>$1.1 \times 10^{-2}$</td>
<td>$3.42 \times 10^{-7}$</td>
<td>0.69</td>
<td>(45) $D_n$</td>
</tr>
<tr>
<td>14.19</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$3.47 \times 10^{-6}$</td>
<td></td>
<td>(17) $D_n$</td>
</tr>
<tr>
<td>15.54</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$1.82 \times 10^{-8}$</td>
<td>0.53</td>
<td>(46) $D_n$</td>
</tr>
<tr>
<td>10.04</td>
<td>$5.0 \times 10^{-7}$</td>
<td>$8.51 \times 10^{-9}$</td>
<td>0.63</td>
<td>(16) $D_n$</td>
</tr>
<tr>
<td>28.47</td>
<td>$2.6 \times 10^{-2}$</td>
<td>$2.49 \times 10^{-7}$</td>
<td></td>
<td>(47) $\tilde{D}$</td>
</tr>
<tr>
<td>12.26</td>
<td>$3.8 \times 10^{-4}$</td>
<td>$2.63 \times 10^{-6}$</td>
<td></td>
<td>(48) $\tilde{D}$</td>
</tr>
</tbody>
</table>

Some experiments have also been undertaken to evaluate the chemical diffusivity of hydrogen in the $\beta$-phase region of both the pure palladium and the palladium-lithium alloy. For these experiments, the samples were fully loaded with hydrogen at 1 atm pressure. The discharges were performed using small potential steps. As shown in Table II, the amount of hydrogen desorbed during the experiments was smaller for the palladium than for the alloy. The results show that at a high hydrogen content (H/Pd form 0.73-0.74), the chemical diffusion coefficient is very small in the $\beta$-phase of palladium compared with the $\alpha$-phase (some two orders of magnitude). For the alloy, which had a lower hydrogen concentration, the apparent values in the $\beta$-phase are comparable to those in the $\alpha$-phase.
4.1.4. Discussion

Electrochemical techniques using both steady-state and transient measurements at room temperature can be employed to study thermodynamic and kinetic properties of solids containing dissolved hydrogen. They can readily provide accurate data for samples with high hydrogen surface activity.

In order to obtain steady-state data one must avoid dissolved molecular oxygen in the electrolyte. This can be achieved by a proper experimental set-up (separation of the two electrode compartments of the cell, and nitrogen gas bubbling near the sample under investigation). Pre-electrolysis with a sacrificial palladium electrode to remove the ionic impurities from the electrolyte on the sample cathode surface has also been found to be important. Samples can be mechanically polished under water to obtain reproducible surfaces.

Equilibrium Coulometric Titration

The isotherm measured at 23°C on several samples of pure palladium shows the expected two-phase plateau, which is in agreement with earlier measurements. In the two homogeneous solution phases (α and β), isotherms for absorption and desorption coincide. In the two-phase (α + β) region, however, hysteresis is always observed. As the isotherms obtained during the desorption are flatter and more reproducible, we assume that the desorption curves more closely represent the equilibrium isotherm, and have used them to determine the influence of lithium alloying.

As shown in Figure 3, the pressure deduced from the plateau potential value agrees with the reported data for desorption of hydrogen from pure palladium over the temperature range from 20 to 295°C.

Measurements on sample Pd1 showed a smaller hysteresis loop after three absorption/desorption cycles. This behaviour can be
attributed to the increasing dislocation density generated during cycling. As a consequence, nucleation of the second phase is easier in a highly distorted lattice. Smaller hysteresis effects have also been reported with palladium black and have been attributed to the large surface area of the samples as well as their deformed structure (7), (14).

The lower limit $\alpha_{\text{max}}$ of the two-phase region has been given as between 0.008 and 0.03 for H/Pd in various investigations (10), (14), (19), (49), (50). As the lower values were obtained from precise measurements of the magnetic susceptibility as a function of the hydrogen content, and are generally accepted as being the most precise (8), our experimental value of 0.01 confirms the sensitivity of the coulometric titration method at low hydrogen concentrations.

The solubility of hydrogen in the $\beta$-phase measured at a potential equivalent to a hydrogen pressure of 1 atm is also close to the reported data.

It has been shown that alloying with small amounts of lithium affects the thermodynamic properties of the Pd-H system markedly:

- increased solubility in the $\alpha$-phase (from 0.01 to 0.03)
- increase of the equilibrium plateau voltage (from 0.065 to 0.083 V versus H$_2$)
- decreased solubility at 1 atm hydrogen pressure in the $\beta$-phase (from 0.74 to 0.52)

These differences can be attributed to the change in both the elastic and electronic properties of the palladium due to the addition of lithium. As the lattice parameter increases with the lithium content, the hydrogen solubility in the $\alpha$-phase increases and the equilibrium plateau pressure decreases. The decreased solubility limit in the $\beta$-phase can be attributed to the competition between hydrogen and lithium to fill the 4d band holes in the palladium electronic band structure.
Diffusion measurements

In the present study of annealed samples in the α-phase D-values in the range of 3.0 to $3.8\times10^{-7}$ cm$^2$/s were obtained, which is in agreement with reported data ($1.9$ to $3.8\times10^{-7}$ cm$^2$/s in Table I).

For deformed samples, a decrease of the hydrogen diffusivity as a function of the degree of deformation due to internal trapping of hydrogen by defects has been reported (8), (51-53). Buchold (51), for instance, has found a decay for tritium diffusivity from $5.2\times10^{-7}$ cm$^2$/s for annealed samples to $2\times10^{-7}$ cm$^2$/s for 60% deformed samples. Several samples investigated in this work were either cycled or 70% cold-worked. The results on the hydrogen diffusivity were reduced up to a factor of two in comparison with virgin samples reported in the literature.

Contrary to the high consistency of the reported diffusion results in the α-phase, those in the β-phase show a considerable inconsistency as can be seen in TABLE III. This discrepancy may be due to variations in the sample preparation as well as the measurement procedure. It is very important that the sample remains in the β-phase during the measurement. This implies that only minor changes in the composition can be made during desorption, since the slope of the titration curve in the β-phase is rather steep. The present results of the chemical diffusion coefficient in the β-phase at hydrogen pressures close to 1 atm is smaller than most data reported in the literature. The reason for this discrepancy is not clear, however, one could speculate, that the different sample preparation methods are responsible for the inconsistent diffusion data. Even small amounts of a second phase, not detectable by X-ray diffraction measurements, can lead to erroneous results since the boundary conditions in the equations used are only applicable for single phase samples. Except for the coulometric titration for loading a sample to a specific H/metal value, this is very difficult to obtain by other techniques, and it is very likely that measurements were performed on samples which consisted of two phase mixtures. Values of the chemical diffusion coefficient obtained from such samples would then be similar to
the values obtained from the phase with the better diffusion properties.

The chemical diffusion coefficient, $\tilde{D}$, is concentration dependent. It is related to the component diffusion coefficient $D^*$ by the thermodynamic enhancement factor. This factor has been determined at high hydrogen concentrations and has been found to be 30 to 40 for the H/Pd system, and 15 to 20 for the H/Pd-Li system (TABLE III).

The substitution of palladium by a small amount of lithium makes the alloy less transparent to hydrogen, even at low hydrogen activities. The influence of minor amounts of solute on hydrogen diffusivity is usually small (8). Buchold (54) has discussed the activation energy in terms of elastic strain energy of the lattice and the electronic band structure.

The large decrease of the diffusivity of hydrogen in Pd-Li alloys may be due to the reduced number of sites for hydrogen and because of blocking of pathways by lithium, like in the mixed ion effect of ionic conductivity, as it has been observed in the Na-\(\beta\) alumina isomorphs, when Na was partially replaced by other mono-, and di-valent ions (55-57).
4.2. Aspects of the electrochemical loading of hydrogen and its isotopes into palladium

4.2.1. Introduction

At room temperature, palladium reacts with each of the isotopes of hydrogen to form two binary phases, designated $\alpha$- and $\beta$-, both of which are considered to contain the light element in the octahedral interstices of the f.c.c. palladium lattice (1), (8). After Wicke, at 303 K, the phase limits in the cases of hydrogen and deuterium are (33): $\alpha_H 0 \leq x \leq 0.009$; $\beta_H x \geq 0.608$; $\alpha_D 0 \leq x \leq 0.01$; $\beta_D x \geq 0.60$, where $x$ denotes the loading, i.e. the H (or D) / Pd molar ratio. However, H/Pd atomic ratio values between 0.008 and 0.03 have been reported at room temperature for the $\alpha$-phase, as has been described earlier in this chapter. Although the properties of the $\alpha$-phase have been extensively documented (1), (8), somewhat less characterization has been reported for the $\beta$-phase, especially at loadings significantly larger than those corresponding to 1 atm of gas pressure (i.e., at 303 K, for loadings larger than 0.70 in the case of hydrogen (58), and 0.67 for deuterium (33), (59). Some aspects of the preparation and characterization of the highly loaded $\beta$-phases of the H-Pd and D-Pd systems are briefly reviewed below. Included in this review is a brief discussion of some of the methods employed for the measurement of high hydrogen loadings.

Although electrochemical methods have been employed to load hydrogen into palladium, vide infra, it is not widely recognized that, in addition, such methods may be used in order to prepare highly loaded $\beta$-phase-compositions in the H-Pd and D-Pd systems. In this work, some experimental demonstrations of the attainment and in situ measurement of high loadings in these systems, using electrochemical means, are presented.

4.2.2. Preparation and characterization of the $\beta$-phase

Measurement of high hydrogen loadings
Although a variety of techniques have been employed to measure loadings in the H-Pd and D-Pd systems, not all of these are suitable for the measurement of high loadings in the β-phase. It is of interest to describe briefly some that have been employed.

i) Mass spectrometry
A direct, but *ex situ*, method entails vacuum desorption of the absorbed hydrogen at elevated temperature, followed by quantitative mass spectrometric analysis (60-62). Owing to the tendency of highly loaded palladium to loose some hydrogen relatively quickly once the confining gas pressure is removed, any *ex situ* method will necessarily give a conservative estimate of the loading. However, this method, among others, is useful in that it serves to calibrate indirect, but *in situ*, loading measurement methods.

ii) Resistance ratio
Since the work of Fischer (63), it is recognized that the electrical resistance of a sample of palladium exposed to hydrogen (or deuterium) varies systematically with hydrogen content (1), (64). At room temperature, the resistance ratio, defined as \( R/R_0 \), where \( R \) is the resistance at a particular loading and \( R_0 \) is the resistance of pure palladium, increases from unity as the loading increases from zero, reaching a maximum at a loading of approximately 0.7, irrespective of the hydrogen isotope employed. Thereafter, the resistance ratio decreases relatively quickly with increasing loading. The resistance ratio / loading variations for hydrogen and deuterium are shown in Figure 8.

These composite curves are designed to best represent the results obtained from a variety of loading studies (50), (61), (62), (65-70). Although the detailed form of the variations shown in Figure 8 has been the subject of discussion (71), (72), they are treated here as a convenient empirical tool by which the loading may be estimated. The measurement of the electrical resistance of a β-phase sample is particularly useful for electrochemical loading, since it enables relatively subtle loading effects associated with
changes in, for example, current density and overvoltage, to be monitored.

![Graph showing R/R₀ vs H or D/Pd](image)

**Figure 8**: Resistance / loading variations in the H-Pd and D-Pd systems at 298 K.

iii) Volumetric methods

A volumetric method has been employed in order to measure directly the composition during the electrochemical loading of palladium cathodes (73). In this technique, an otherwise sealed electrochemical cell is connected to the manometer. Initially, the empty space above the cell is filled with hydrogen (or deuterium), and contains a hydrogen-oxygen recombination catalyst. During electrolysis, the oxygen evolved at the anode is converted into water; hence, at constant pressure, a decrease in volume is observed due to hydrogen uptake by the cathode. Using this technique, the loading may be measured to an accuracy of a few per cent.
Preparation of the β-phase

Two methods are commonly employed for the preparation of highly loaded β-phase, i.e. gas phase loading and electrochemical loading. The former has been more extensively studied, most notably by Baranowski and co-workers (74-76).

Using high pressure apparatus, the properties of the β-phase have been characterized up to approximately 20,000 atm of gas pressure, corresponding to loadings in excess of unity, as described further below. In gas-loading experiments the pressure, P, is conveniently employed as the independent variable. When the chemical properties of the β-phase are of interest, it is more useful to express results in terms of the gas fugacity, f, as the independent variable. The gas fugacity and the pressure are related for a pure gas (77), by

$$\ln \frac{f}{P} = \int_0^p \left[ \frac{V_m - 1}{RT \cdot p} \right] dp$$

where \( f \to 1 \) as \( p \to 0 \) and \( V_m \) is the pressure-dependent molar volume. Up to the pressure of approximately 20,000 atm, \( V_m \) has been determined for both hydrogen and deuterium (see, for example (78), (79). The resulting fugacity /pressure relationship at 298 K for either gas is shown in Figure 9 (the results for hydrogen and deuterium are closely similar using the scales in Figure 9).

Further, for convenience in calculations, it is of interest to note that the fugacity / pressure variation in Figure 9 is closely approximated by

$$f = p \exp \left[ \frac{\alpha P}{RT} \right]$$

with, for \( p \) in atm, \( R = 8.314 \ \text{K}^{-1} \ \text{mol}^{-1} \), \( T = 298 \ \text{K} \), and \( \alpha = 1.3 \) (in appropriate units).
Figure 9: Fugacity / pressure variation for hydrogen at 298 K.

It is not readily apparent from the early literature that electrochemical loadings of palladium cathodes can produce a highly loaded β-phase. For example, loadings of 0.7 in the case of hydrogen (67) and 0.67 for deuterium (69) have been reported. However, later studies showed that still higher loadings could be achieved at modest current densities. Thus, for deuterium, a loading of approximately 0.9 was obtained at 273 K with an acidic electrolyte (61). Further, in the hydrogen case, a loading of approximately 0.95 has been achieved under similar conditions (62). It is also interesting that one can observe deloading in situ, apparently related to the formation of cracks or voids. Furthermore, the gradual accumulation of certain impurities such as platinum on the surface reduces the observed loading.

Physical properties of the β-phase

As a result of primarily gas-loading measurements, the following physical properties, amongst others, of the β-phase may be described:
i) Loading / pressure variation
Experimental data for the variation of loading with pressure for the β-phase of the H-Pd system at 298 K are shown in Figure 10 (68), (70), (80).

![Graph showing loading variation with pressure](image)

**Figure 10:** Loading / pressure variation in the H-Pd system at 298 K (68), (70), (80).

These data indicate that a hydrogen pressure in excess of 10,000 atm, is necessary to achieve an approximate loading of unity at this temperature. It may be noted that, at a pressure of 10,000 atm, the corresponding hydrogen fugacity is approximately 2.5×10^6 atm. For loadings in excess of 0.9, the corresponding data for deuterium do not appear to have been measured directly. However, an approximation of the loading / pressure variation for deuterium may be obtained by using the results of Wicke and Nernst (8), as described by Baranovski et al. (70). It is apparent that, for the same gas pressure, the deuterium loading is approximately 0.025 less than the corresponding hydrogen loading in the range 0.9 ≤ x ≤ 1.0.
ii) Resistance ratio / fugacity variation
The variations of the resistance ratio of the highly loaded \(\beta\)-phase (with both hydrogen and deuterium) with fugacity at 298 K has been determined experimentally and are shown in Figure 11 (68), (70), (71), (81).

![Graph showing resistance ratio (R/R₀) vs. logarithm of fugacity (log(f/f₀)) for H and D phases.]

**Figure 11**: Resistance / fugacity variations in the H-Pd and D-Pd systems at 298 K (68), (70), (71), (81).

At very high fugacities, corresponding to loadings approximately equal to and in excess of unity, a distinct change in the slopes of the resistance / fugacity curves is apparent. This change of slope has been interpreted in terms of the occupation of tetrahedral sites at very high loadings (70), (71). Firm crystallographic evidence, at the moment absent, is required in order to substantiate this interpretation. In this context, the preparation and preliminary characterization of a tetragonal hydride phase of nominal composition \(\text{PdH}_{1.33}\) has been reported (82), (83). This phase, formed either by bombarding palladium films with hydrogen ions or by heating palladium films in hydrogen and cooling rapidly, is stated to contain the hydrogen within the
approximately tetrahedral interstices of a body-centered tetragonal palladium lattice.

iii) Chemical diffusion coefficient
The time-dependent relaxation behaviour of the resistance ratio of the β-phase sample exposed to an incremental change in loading may be employed to evaluate the composition dependence of the chemical diffusion coefficient of hydrogen (or deuterium) (84), (85). At 298 K, the chemical diffusion coefficients of both hydrogen and deuterium in the β-phase are roughly equal; both decrease smoothly from approximately $10^{-6}$ cm$^2$ s$^{-1}$ at $x = 0.8$ to less than $10^{-7}$ cm$^2$ s$^{-1}$ as the loading approaches unity.

iv) Hydrogen overvoltage
In the case of the electrochemical loading of palladium, it is of interest to determine how the loading is related to the thermodynamic part of the cathode overvoltage. In the case of hydrogen evolution reaction, various relationships between the overvoltage, equivalent pressure, and the details of the hydrogen evolution kinetics have been discussed (86). Referred to the standard hydrogen electrode, the purely thermodynamic part of the hydrogen overvoltage, $\eta_{\text{th}}$, is related to the gas fugacity on the cathode surface (and, hence, the loading) via

$$\eta_{\text{th}} = -\frac{RT}{2F} \ln f$$

Thus, at 298 K, a fugacity of $10^7$ atm is equivalent to a thermodynamic overvoltage of approximately -0.2 V.

4.2.3. Experimental Aspects

In order to study the electrochemical loading of palladium, two (similar) designs of electrochemical cells were employed, one of which is shown in Figure 12.
Figure 12: Electrochemical cell used for loading experiments

In this design, a quartz tube, approximately 2.5 cm in diameter and 10 cm long, was employed as the cell container. The top of the tube, of somewhat larger diameter, was used to contain the recombination catalyst. A cylindrical cage was constructed of quartz rods, held together with PTFE discs, and located within the cell container. A platinum wire (0.5 mm diameter, 1 m long) was wound on the outside of this cage, and served as the anode. The cylindrical palladium cathode was mounted vertically in the centre of the cage. In order to monitor the pressure changes inside the cell, and thus determine the reliability of the recombination catalyst over long time periods, the cell, otherwise sealed, was connected via a gas vent, to a bubbler. In a second cell configuration, designed for use at moderately elevated pressures,
if necessary, a sealable cell container was constructed of nickel. The dimensions of the nickel cell body, as well as the internal cell configuration, were similar to those of the quartz cell body described above. A thin PTFE liner was inserted within the cell body in order to prevent corrosion of the cell by the alkaline electrolyte. During loading measurements, the cells were mounted within a water bath held at 30°C.

Cylindrical palladium cathodes, 0.3 cm diameter and 3 to 5 cm long, were made from wire supplied by Engelhard. (The as-supplied wire diameter was slightly larger than 0.3 cm; the excess material was removed mechanically). Typically, the cathodes were annealed in vacuum at 800°C for three hours and cooled in 1 atm of argon. The cathodes were then etched in aqua regia (deuterated if necessary) and rinsed with (light or heavy) water, in order to remove any oxide surface films.

Loading measurements were made via determination of the axial resistance of the palladium cathode with a TECRAD DMO-350 (3 1/2 digit) digital micro-ohmmeter. This instrument is capable to measure resistance values in the range 10⁻⁸ to 0.2 Ω. Each cathode was furnished with four notches (each 0.1 cm wide and 0.1 cm deep), two at each end of the rod (0.1 cm apart). Platinum leads were wound and spot-welded within each notch. One pair of leads, located effectively at the end of the cathode, served to deliver a 10 A square-wave pulse of approximately 20 ms duration; the resulting voltage was detected using the second pair of leads (located within the first pair, with respect to the rod axis). Resistance measurements were made at five minute intervals during loading. For the cathode geometry employed here, the unloaded palladium resistance was approximately 410 μΩ for a "3 cm" rod.
4.2.4. Results and Discussion

The variations of cathode resistance with time for three loading experiments are shown in Figures 13-15. The conditions for each experiment are described in the relevant figure caption.

![Graph showing the variation of resistance](image)

**Figure 13:** Resistance / time variation for a palladium cathode under the following conditions: 1 M LiOH, 100 mA/cm².

These three examples are only a small fraction of the loading experimentation that have been carried out; however, they are representative of the results that may be obtained if proper attention is paid to certain aspects of the loading process. In all three experiments, the formation of highly-loaded β-phase occurs in a few tens of hours at the current densities employed here. The results in Figures 13-15 indicate that, for both hydrogen and deuterium, the maximum value of the resistance ratio is lowered under dynamic conditions, relative to the value expected under equilibrium conditions, as shown in Figure 9. This is due to the presence of H (or D) concentration gradients within the cathodes.
during the loading process; this effect is effectively absent once a steady-state loading has been achieved. By reference to Figure 9, it is apparent that steady-state loadings of at least 0.9 have been achieved in the three experiments reported here.

![Graph](image)

*Figure 14: Resistance / time variation for a palladium cathode under the following conditions: 1 M LiOD + (NH₂)₂CS; 100 mA/cm².*

From the data shown in Figures 13-15, it is apparent that a current density of approximately 100 mA cm² is required in order to achieve loadings of 0.9 or more in the cell configuration employed here. Previous studies have reported similarly high loadings for deuterium in fine palladium wires using a current density of approximately 12 mA/cm² (61). In this previous study, a porous membrane was used in order to minimize the possibly deleterious effects of diffusion of oxygen from the anode to the palladium cathode. The observation that similar loadings may be achieved at different current densities is not surprising. As discussed above, the steady-state loading is determined essentially by the thermodynamic part of the cathode overvoltage and is not, in the first instance, determined directly by the current
density. Thus, for cells with different geometries and, more importantly, differing states of the cathode surface, at the same current density, the cathode overvoltages (and, hence, loadings) may differ. For a given electrode, however, the cathode overvoltage and the current density are, of course, related. Hence, in order to achieve uniform loading, it is important that the current density be uniform over the entire electrode.

![Graph](image)

**Figure 15:** The bold line shows the resistance / time variation for a palladium cathode under the following conditions: 1 M LiOD, current density 33 mA/cm², ramped to 333 mA/cm². The current ramp profile is also shown.

In order to attain and sustain high loadings, it is essential to guarantee that the cathode surface is maintained in a suitable condition, and thus minimize those effects, both mechanically and electrochemically, which tend to promote de-loading. Two effects are particularly important in this regard:

1) It is unlikely that the current density will be uniform within a surface crack or fissure, and such features will act as
sites for de-loading. Cracks may form during the loading process as the \( \alpha/\beta \) miscibility gap is traversed. The tendency for crack formation may be minimized by loading relatively slowly in the initial stages; it is observed that cathodes which load quickly up to the resistance maximum rarely load further. An alternative procedure is to pre-load the palladium from the gas-phase (to a loading of approximately 0.7) at an elevated temperature such that the miscibility gap is not encountered, and then cool slowly to room temperature.

ii) Certain chemical species, when deposited on the cathode surface, will tend to lower the cathode overvoltage by catalysing the recombination of adsorbed hydrogen atoms. Platinum may be particularly deleterious in this regard. Clearly, the presence of such species should be minimized. Another group of additives, the so-called "recombination poisons" may be advantageous in the early stages of loading. However, they are typically complex chemical species which are susceptible to decomposition within the electrochemical cell. Thus, their effects are typically short-lived.

This list is not intended to be exhaustive. The reproducible attainment and maintenance of high loadings may be realized only when a suitable cathode surface state has been achieved. Undoubtedly, several factors are important in determining the optimum surface condition, not all of which are presently understood.

4.2.5. Conclusions

Highly-loaded compositions within the \( \beta \)-phase of the H-Pd and D-Pd systems may be prepared by both gas-phase and electrochemical means. Several physical properties of the \( \beta \)-phase have been studied up to loadings of unity and possibly beyond.
On-line resistance measurements provide a particularly convenient method for monitoring the loading in the palladium cathode.

Loadings of 0.9 or more may be achieved electrochemically.

4.3. References


73. A. M. Riley, J. D. Seader, D. W. Pershing, *J. Electrochem. Soc*


Chapter 5

5. Concepts for Applications of Hydrogen Mixed-Conductors

In this chapter three concepts for possible applications for hydrogen mixed-conductors will be described. One is in the general area of catalysis and will describe the use of solid state ionic techniques to modify the behaviour of catalytic surfaces. The other is in the area of hydrogen production by electrolysis and describes a novel electrochemical double-cell concept for water vapour electrolysis at intermediate temperatures (600-700 K) near the thermoneutral voltage, and separation of the hydrogen through a permeable metallic membrane. It involves the use of a combination of liquid electrolytes and inexpensive hydrogen-transparent metal membrane materials. In this study the overall concept has been verified and the results are very encouraging and reveal the potential for further exploration. The third concept is a combination of the first two and describes a novel device to reduce nitric oxides with the aid of atomic hydrogen to nitrogen and water. The hydrogen is produced on the back-side of a metallic membrane using aqueous electrolysis and transported through the membrane to the front side, at which it meets the nitric oxides at the surface. This concept has been published recently by the Daimler-Benz company with the expectation that such devices be inserted into the exhaust system of combustion engines to reduce nitric oxide emissions.

5.1. Use of solid state ionic technique to modify in situ the behaviour of catalytic surfaces

5.1.1. Introduction

Catalysis is conventionally described as a process whereby a material that is itself not consumed increases the kinetics of a reaction that is thermodynamically favoured, but otherwise slow. In some cases,
catalysts also serve a selective role, giving preference to the
production of certain products over others which are also
thermodynamically stable. Thus catalysis is not generally considered
to be applicable to reactions which are thermodynamically
unfavourable, and useful catalysts have either one or both of the two
major characteristics, rate enhancement, and selectivity.

The traditional approach has been to use the parameters of
composition, temperature, and pressure to define the thermodynamic
equilibrium conditions of a reacting system, and to search for a
catalyst that enhances the kinetics of the desired reaction. Product
selectivity can be difficult to control, especially for highly exothermic
processes, and often represents the most difficult problem in
selecting or designing a catalyst and optimum process conditions.

The approach discussed here is a rather radical departure from the
conventional wisdom and the common present approaches to such
problems. It has two major features, the measurement and control of
the thermodynamic parameters upon the catalyst surface during a
catalytic reaction, and the rapid introduction or removal of one of the
species involved, e.g. oxygen or hydrogen, by transport through the
underlying solid.

It will be seen that, by this technique, it is possible to not only
quantitatively study the local chemical reaction kinetics by the use of
electrical measurements, but also to separate and individually
measure and influence the reaction steps involving surface
intermediates.

By the use of methods to be described later, involving the controlled
addition or removal of one of the reactants or products locally, the
thermodynamic conditions actually present on the reacting surface
can be significantly displaced from those imposed upon the overall
system by the external macro-variables, such as the composition of
the reactant stream, temperature, and overall pressure.

The approach that is followed involves the use of solid state ionic
techniques employing an unusual type of electrochemical system. It
is analogous to methods and configurations which have been under exploration for quite different purposes. In addition to the ionic conductor, a solid mixed ionic-electronic conductor with a very high chemical diffusion coefficient and permeability for specific species can be used to control the chemical potentials upon a catalytically active surface during operation. This scheme can be used to pump ions to and from the surface, thus shifting the local thermodynamic equilibrium, and driving the reaction in the desired direction.

This general approach has already been sucessfully demonstrated in the case of several simple reduction reactions involving oxygen at elevated temperatures, including the decomposition of NO to N₂ and O₂ (1-3), and the reaction of either CO or CO₂ with H₂ to form CH₄ and O₂ (4-7). In those cases, oxygen was transported from the catalytic interface by oxygen ionic motion through an underlying solid electrolyte of yttrium-doped zirconium oxide.

A new phenomenon, now known as the non-faradaic electrochemical modification of catalytic activity (NEMCA effect) has been described by Vayenas (8). It was found that the catalytic activity and selectivity of metals interfaced with solid electrolytes can be altered dramatically and reversibly by application of an electrical potential. The increase in catalytic rate can be several orders of magnitude higher than that anticipated from Faraday's law, typically 10-10⁵ times larger. This implies that each ion supplied to the catalyst can cause up to 10⁵ product molecules. Today, more than 50 catalytic reactions exhibiting this novel effect have been studied and the effect has been demonstrated for several catalysts (Pt, Pd, Rh, Ag, Ni, Au, IrO₂, RuO₂) deposited on O²⁻, F⁻, Na⁺, and H⁺ conducting solid electrolytes (9).

Background and principles related to controlled-interface catalysis

Quite a number of years ago Carl Wagner and his co-workers pointed out that if a catalyst surface is exposed to a reacting mixture for a sufficiently long time under steady state conditions at elevated temperatures, thermodynamic equilibrium becomes established
between the species in the surface region, i.e. adsorbed reactants and intermediates, and atomic and electronic species in the bulk underlying solid. As a result, if species transport in the bulk solid to and from the surface is sufficiently fast, one can obtain information about the thermodynamic state of the surface species during the catalysis reaction by observation of some suitable physical property relating to the corresponding species in the bulk solid.

Furthermore, this information, in conjunction with the macroscopic system and rate parameters, can be used to evaluate the activities of surface species, and to identify the rate-determining step in a typical sequential catalytic reaction.

This approach was used as a diagnostic tool in a number of simple cases at elevated temperatures, where surface-bulk equilibrium could be readily established. Early examples by the Wagner group included studies of:

(i) oxygen transfer reactions, such as

\[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}, \text{ and} \]

\[ \text{2N}_2\text{O} = \text{2N}_2 + \text{O}_2 \]

on the surface of oxide catalysts (10), and

(ii) gaseous hydrogenation and dehydrogenation reactions, such as hydrogenation of ethylene (11), and decomposition of formic acid (12) on metals.

5.1.2. Experimental Approach

Alternative use of back-side solid state electrochemical cell

In addition, Wagner showed that, under appropriate conditions, a properly designed solid state electrochemical cell on the back side of the catalyst material could also be used for this purpose.
Demonstrations included the use of an indirect silver-conducting solid electrolyte cell for the evaluation of the sulfur activity on the surface of Ag$_2$S when used as a catalyst for reactions such as

$$\text{H}_2 + \frac{1}{2} \text{S}_2 = \text{H}_2\text{S} \quad (13, 14)$$

and

$$\text{H}_2 + \text{CO} = \text{CO} + \text{H}_2\text{S} \quad (15)$$

Again, an important criterion is rapid transport of ionic and electronic species in the solid catalyst material, so that equilibrium can be attained between the bulk solid and the catalyst surface on one side, i.e., the front side, upon which the heterogeneous reaction takes place, and also on the back side between the catalyst material and the adjacent electrolyte.

Active, rather than passive, use of such cells to control interface properties and influence heterogeneous reactions

Instead of using such cells in a passive diagnostic mode, one can also employ them in an active mode to pump ionic and electronic species to and from the electrolyte/catalyst surface, and thus to impose control of the activity of selected species at a catalytic interface. Such configurations, employing doped zirconia as a solid electrolyte, have been used to adjust the oxygen content in gas streams (16), as well as to decompose oxygen-bearing gaseous species such as CO, CO$_2$, SO$_2$, H$_2$O, and NO (1), (2), (17).

Furthermore, it has been demonstrated (18), (19) that oxygen-transporting solid electrolyte cells can be used for the oxidation of SO$_2$ and NH$_3$. And more recent work (4-7), (18), (19) has shown that this approach can be used to enhance Fischer-Tropsch type reactions of H$_2$ with either CO or CO$_2$ to produce CH$_4$ and O$_2$.

In connection with the work on NO decomposition (2) it was shown that in addition to displacing the equilibrium, the use of such solid state ionic methods can produce large changes in the catalytic behaviour of a gas/solid surface. For example, sufficient reduction of
the oxygen activity upon the surface of doped zirconia changed the solid state defect equilibria, increasing the electron and oxygen vacancy concentrations, and caused the specific reaction rate to be increased by a factor of $10^6$, reaching values about $10^3$ times greater than those for the supported Pt catalysts which are normally used for such purposes.

**Use of these techniques with hydrogen-based systems**

Essentially most of the work done in this area to date has involved the control of the oxygen activity on the catalyst surface and pumping oxygen to or from it by the use of oxygen-conducting solid electrolytes. The low ionic conductivity of all presently known oxygen-transporting solid electrolytes at lower temperatures has necessarily limited this work to temperatures above 600°C.

It is very attractive to apply this approach to hydrogen-based systems, especially if considerably lower operating temperatures could be achieved. Iwahara (20) discovered that certain perovskite-type oxide solid solutions, based upon SrCeO$_3$ exhibit protonic conduction from $10^{-4}$ to $10^{-2}$ S/cm in an atmosphere containing hydrogen or steam at temperatures between 400 and 1000°C. An overview of the preparation and properties of high temperature proton conductors based on perovskite-type oxides and a comparison with other protonic conductors is given in (21).

An example of the straightforward analogy to the applications of oxide-ion conductors to use solid state electrochemical cells employing proton-conducting solid electrolytes is described in a recent TOYOTA patent (22) for reducing nitrogen oxides with the reducing power of hydrogen.

**Novel electrochemical cell configuration that can be used with hydrogen-based systems and reactions**

Recent work on new materials and concepts related to hydrogen-based advanced batteries, fuel cells, and thermoelectric devices, as
well as the storage of hydrogen in metal hydrides, has led to the recognition that an entirely new approach is feasible.

Work at Stanford University on the use of electrochemical techniques to control the hydrogen content in metal hydrides (23), (24) has shown that low oxygen activity molten salts containing hydride anions are very attractive liquid hydrogen carriers.

This alternative uses a three-layer solid/liquid/solid (S/L/S) electrochemical cell configuration instead of the solid electrolyte/porous electrode configuration typical of oxygen-related systems. In this case, a thin film liquid electrolyte is sandwiched between two solid electrode layers. The outer side of one of the electrodes is the catalyst surface in contact with the reacting species, while the outer side of the other electrode is in contact with a hydrogen reference, source or sink. This general configuration is shown in Figure 1.

![Diagram](image)

1. Mixed ionic-electronic conductor
2. Liquid electrolyte
3. Potentiostat
4. Thin layer of catalyst

**Figure 1:** Schematic illustration of a simple S/L/S electrochemical cell configuration
In order for this approach to be useful, both electrodes must have very rapid diffusion of the electroactive species, i.e. hydrogen. Otherwise, the total impedance of the three-layer system will be too great.

Experiments using new low-temperature molten salts with extremely low oxygen and water activities have identified a group of metal alloys, which have the requisite high hydrogen diffusion coefficients. Indeed, if surface conditions are carefully maintained such that no adsorbed oxide or hydroxide layers or thin oxide films are present, these materials become quite transparent to the passage of hydrogen.

Significantly, some liquid electrolytes have also been found which are good hydrogen conductors, and whose thermodynamic properties are such that these alloys are essentially inert, so that such deleterious surface reaction products do not form.

Thus it is now possible to construct a mechanically stable solid/liquid/solid sandwich structure, using metallic alloys on both sides of a thin layer of liquid electrolyte that acts like a high conductivity hydrogen-transporting solid electrolyte electrochemical cell, and has a very low impedance for hydrogen transport, even at low temperatures.

Furthermore, if the electrode material itself is not an attractive catalyst, a thin catalyst surface layer can be placed upon it. Then, if an appropriate reference and reservoir system is incorporated with the opposite electrode, such a configuration can be used to provide back-side measurement and control of the hydrogen activity on the catalyst surface during a heterogeneous reaction on the front side. The permeability of these alloys is so large that hydrogen can be pumped into or out of the reaction interface at relatively high rates. Large area configurations are easily to imagine, so that very high current, large capacity systems should be feasible.
5.1.3. Discussion

Difference between this approach and conventional electrocatalysis

The approach discussed here is quite different from conventional electrocatalysis in several important respects. An important distinction is that the heterogeneous reaction takes place on the front side of the catalyst electrode, whereas the electrolyte is on the back side. Thus the reactants and products of the catalytic reaction are not part of an electrochemical cell, and are, therefore, not in an electrolyte environment.

Importantly, separation of the heterogeneous reaction and the electrochemical cell allows independent control of the electric potential of the catalytic interface and the rates at which species, i.e. oxygen or hydrogen, move to and from it. It is not necessary that the reaction itself be electrochemically driven. In addition, one of the reactants (or products) e.g. oxygen or hydrogen, can arrive at (or leave from) the heterogeneous interface through the underlying bulk solid, rather than through the reactant-product mix.

A modification of these concepts is the intermediate temperature electrolysis of steam by the extraction of hydrogen.
5.2. Intermediate Temperature Water Vapour Electrolysis

5.2.1 Introduction

Although water electrolysis is the most sophisticated and, from an environmental viewpoint, the ideal process to produce hydrogen, its technical application is strongly impeded by economical factors such as the availability and price of electrical energy. The development efforts in electrolysis technology have focussed upon various aspects of the overall process optimization. However, the main goal is the reduction of the cell voltage to bring it as close as possible to the theoretical value. The theoretical energy required for electrolyzing water at ambient conditions is 237.141 kJ mol\(^{-1}\), or, expressed as a voltage, 1.23 V. Part of this energy can be provided thermally. As a result, the voltage required decreases if the electrolysis takes place at higher temperatures.

Another alternative is to use chemical energy to lower the electrical energy required. An example is the use of a sacrificial iron anode which is converted into iron oxide, with the result that the applied voltage is reduced by an amount equivalent to the chemical free energy change related to the oxidation of the iron (25).

One can divide the different technologies which do not involve extra chemical reactions that are currently being pursued for water electrolysis into two major groups according to their operating temperatures:

i) ambient or near-ambient temperature systems, and
ii) very high temperature systems employing solid electrolyte membranes.

There are three general types of low-to-moderate temperature systems, and they all generally suffer from electrode kinetic problems, primarily at the oxygen evolution electrode. For thermodynamic reasons, they all require larger voltages than higher temperature approaches as was mentioned above.
One of these employs NAFION, or a similar polymeric electrolyte, such as MEMBREL, which primarily passes protons. They generally operate at about 350 - 360 K. Several R&D groups pursued this approach (26), (27), and in some cases, catalysts are deployed directly onto the membrane. These membranes are quite expensive and cannot be used at higher temperatures. The transference number for proton conduction is also somewhat low, leading to a loss of efficiency.

Efforts aimed at the use of crystalline solid electrolytes which conduct by the transport of protons or H$_3$O$^+$ ions, although having higher transference numbers and reasonable conductivities, have not been as attractive to date. Attempts to operate these electrolytes at higher temperatures to reduce the voltage and increase kinetics have not been successful, because of loss of structural water from the solid electrolyte, which causes a severe reduction of the conductivity.

The third low-temperature method employs alkaline electrolytes with inert physical separators. Asbestos is the separator that has been used the most, but there have been some investigations of alternatives, such as nickel oxide-based ceramics, which apparently reduce the cell impedance and voltage, and allow operation at somewhat higher temperatures, 370 - 390 K (28), (29). Other experiments on a different alternative, KTiO$_3$-porous TEFLOM composites, based upon earlier work in Japan (30) have also not been very impressive.

There has also been some work on improved catalysts and electrode materials to reduce the voltage losses in alkaline environments. Examples are the studies of Raney nickel and titanium-nickel alloys for cathodes (31), and ternary cobalt oxides and related perovskites for anodes (32). Evidently, the best results show a current density of about 1 A cm$^{-2}$ of electrode area at a cell voltage of 1.75-1.8 V.

The high temperature approaches generally involve operation at 1100-1300 K, and are based on the concept of the Solid Oxide Fuel Cell (SOFC) in reversed mode of operation. Doped zirconia is used as an oxide-ion transporting solid electrolyte. The electrode materials of
choice are nickel-zirconia cermets on the anode fuel side, and mixed-conducting oxides, such as strontium-doped lanthanum manganite on the cathode air side. The interconnect material is generally a doped lanthanum chromite.

There are three types of designs which have been attracting attention for quite some time (33-35). They are the tubular design, introduced by Westinghouse (36-39), the flat planar design, which is studied extensively in Europe and Japan (40-48), and the monolithic design, developed at Argonne National Laboratory and followed up and improved by others (49-51). The key technology for the manufacture of thin gas-impermeable layers of stabilized zirconia on top of the porous air electrode as well as the ceramic interconnect is electrochemical vapour deposition (EVD) at SOFC operating temperatures and beyond. This deposition technique contributes substantially to the costs of the tubular cell configuration. In addition, the long conduction pathways lead to large ohmic losses in the cermet and ceramic electrodes. These problems are circumvented in the planar design. Here, the solid electrolyte should be as thin as possible in order to reduce ohmic losses. Both the tubular and planar designs are close to being mature which is not true for the monolithic design. The manufacture of this design requires the control over a variety of product parameters, as a complex series of stacks is produced in a single thermal treatment process.

Several generic types of problems have been encountered with these very high temperature approaches, and they all relate to reproducible fabrication of ceramic components and interfaces, reaching and matching of thermal expansion coefficients. For both, the tubular and planar designs, great progress has been achieved. There is also an inherent high energy cost connected with operation at such high temperatures, and thermal management requires continuous attention. The state-of-the-art has been reported recently (35).

As has been pointed out some time ago, e.g. (52), (53), operation at intermediate temperatures, high enough to reduce electrode polarization problems, yet not so high as to have to confront the
practical problems inherent in the very high temperature zirconia systems, would be optimal. In fact, recent improvements in the manufacture of thin films of solid oxide electrolytes, has enabled the operation of flat planar SOFC's at temperatures around 700°C with efficiencies and power specifications normal for the molten carbonate fuel cell, which operates at these temperatures (41).

The concept reported here is a novel approach to the electrolysis of water vapour at intermediate temperatures (e.g. 700 K) by the use of a double cell configuration. The hydrogen that is produced is of very high purity and is free of water, for it passes through a metallic membrane between the two cells. The method utilized cheap metals, which are easy to fabricate and join, as electrodes, intermediate membrane, and construction material.

5.2.2 General Concept

The double electrochemical cell, which is shown schematically in Figure 2, consists of two compartments.

![Diagram of double cell concept](image)

**Figure 2**: Schematic illustration of the double cell concept.
Cell I is the basic electrolysis cell. Water vapour is introduced into a hydroxide molten salt, consisting of an eutectic mixture of NaOH and KOH, with a melting point of 173°C, and decomposed at a voltage $E_1$ applied between the oxygen electrode and the membrane. Voltage $E_1$ is lower than the decomposition voltage of water to produce hydrogen and oxygen gas at 1 atm pressure at the temperature of operation, because the hydrogen enters the membrane at an activity lower than unity. Cell II acts as a hydrogen concentration cell, and contains a hydrogen-conducting molten salt electrolyte, consisting of the KCl-LiCl eutectic mixture, saturated with LiH to provide the $\text{H}^-$ ions for conduction. The voltage $E_2$, which is applied between the membrane and the hydrogen electrode, fixes the hydrogen activity at the left side of the membrane at a very low value. This causes hydrogen to move through the membrane by chemical diffusion down its concentration gradient. This voltage also drives the hydrogen across electrolyte II, so that it evolves at the hydrogen electrode. In the absence of losses, $E_1 + E_2 = E_{\text{decomp}}$, and oxygen is evolved at the oxygen electrode on one side of the membrane, and dry, clean hydrogen on its other side.

The membrane thus acts not only as a separator between the two electrolytes but also serves as an intermediate hydrogen storage medium at hydrogen pressures below 1 atm.

The key role in this approach is played by electrolyte II, a hydrogen-conducting molten salt containing hydride ions, which serves two important purposes. It conducts hydrogen at elevated temperatures and also provides an environment with very low oxygen activity, so that a number of oxygen-sensitive transition metals can be used as the hydrogen-permeable membrane material.

This double cell arrangement can be described as two separate electrochemical cells, in which the membrane is considered as the negative electrode in cell I as well as in cell II. This can be more easily understood by writing down the simplified electrode reactions for each electrode in each of the cells:

In compartment I, a variety of processes seems possible:
Let us take NaOH$_{(\text{liquid})}$ as example.

At the membrane side:

\[ (-) \quad \text{Na}^+ + e^- = \text{Na} \quad \quad \quad \quad \quad / \ 5 / \]

the sodium that is formed is dissolved in the molten salt electrolyte. The solubility decreases with increasing temperature. However, diffusion coefficients increase with increasing temperature.

At the anode of cell I the reaction as given can proceed:

\[ (+) \quad 4\text{OH}^- = 2\text{H}_2\text{O} \ (\text{g}) + \text{O}_2 + 4e^- \quad \quad \quad \quad \quad / \ 6 / \]

The water formed at the anode may lead to the following reaction at the membrane:

\[ (-) \quad \text{H}_2\text{O} + e^- = \text{OH}^- + \text{H}^{(\text{in \ metal})} \quad \quad \quad \quad \quad / \ 7 / \]

However, in this experiment H$_2$O is bubbled through the molten salt electrolyte, which means that H$_2$O is quite abundant and may lead continuously to the occurrence of reaction /7/ instead of reaction /5/.

Excess of water in the molten salt electrolyte may lead to the additional reactions (54):

\[ 2\text{Na}_{(\text{dissolved})} + 2\text{H}_2\text{O} = 2\text{NaOH} + 2\text{H}^{(\text{in \ metal})} \quad \quad \quad \quad \quad / \ 8 / \]

\[ 2\text{Na}_{(\text{dissolved})} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2 \quad \quad \quad \quad \quad / \ 9 / \]

\[ 2\text{Na} + \text{O}_2 = \text{Na}_2\text{O}_2 \quad \quad \quad \quad \quad / \ 10 / \]

\[ 2\text{Na} + \text{Na}_2\text{O}_2 = 2\text{Na}_2\text{O} \quad \quad \quad \quad \quad / \ 11 / \]

\[ 2\text{Na}_2\text{O} + \text{H}_2\text{O} = 4\text{NaOH} \quad \quad \quad \quad \quad / \ 12 / \]
It would be advantageous if reaction /8/ were to occur predominantly, as reactions /9/ and /6/ lead to \( \text{H}_2 + \text{O}_2 \) mixtures. Also reaction /10/ is quite exothermic. Hence, continuous observation of the cell processes is required. However, \( E(\text{NaOH}) = 2.2 \text{V} \) and \( E(\text{H}_2\text{O}) = 1.4 \text{V} \). Hence, reaction /5/ will not occur under the present experimental conditions, and the process in cell I will mainly comprise reactions /6/ and /7/, consuming the water vapour added to this cell compartment.

### 5.2.3 Experimental Aspects

#### Materials Requirements

The important property requirements for the membrane electrode material, both in the bulk and at its two interfaces are:
In the bulk,
- it must have high hydrogen permeability, and
- it must undergo no phase transformation upon heating or cooling.

The membrane interface that is exposed to the water vapour side, indicated as interface A in Figure 2, has to exhibit three major materials properties:
- it must have high interfacial hydrogen permeability,
- it must be stable under the chemical and electrochemical conditions in electrolyte I, and
- it must not be sensitive to interfacial oxygen poisoning as a result of the diffusion of molecular oxygen from the oxygen evolution electrode.

The requirements for the membrane at interface B are:
- high interfacial hydrogen permeability and
- stability in the chemical environment imposed by electrolyte II

All the above have one thing in common, the requirement for high hydrogen permeability. The transport of a species in a bulk metallic
material under these conditions is driven by the internal chemical activity gradient, and the resulting permeability is the product of the chemical diffusion coefficient and the imposed activity gradient of the moving species. Thus, several materials that might be considered because of their high chemical diffusion coefficients, but which have low solubilities, such as iron, will not give satisfying results in terms of efficiencies when employed for this purpose in practical cells.

As has been described in chapter 3, many metals react with hydrogen to form solid solutions, and at higher hydrogen concentrations form metal hydride phases. Such second phase formation generally is accompanied by changes in specific volume, which can cause large local stresses, and dislocation generation and motion. This often results in changes in shape, the formation of microcracks, or even the mechanical disintegration of the metal (this is being used to form fine metal powders). The presence of dissolved hydrogen can also cause deleterious changes in the ductility. These effects are often included under the general term "hydrogen embrittlement". We can prevent this potentially serious problem if we use metals which do not form hydride phases at the imposed hydrogen activities, or restrict the experimental parameters, such as temperature, so that metal hydride phases will not be formed. This can be accomplished with some otherwise attractive metals that form hydride phases at low temperatures if we maintain the electrochemical cell temperature in a range such that it is always within the solid solution region of the metal hydride system.

Some of the transition metals are known to possess very high permeabilities for hydrogen if their surfaces can be kept free of blocking oxide films. Their bcc and fcc host structures are very attractive host lattices for interstitials such as oxygen, nitrogen, carbon, and hydrogen, sometimes in restricted ranges of temperature. Since their affinity for oxygen at room temperature is generally extremely high, most of them are typically covered with oxide layers. These oxide layers act as barriers for the entry of hydrogen into the lattice, and thus cause a high impedance for hydrogen permeation.
Several of these metal-hydrogen systems have been shown to exhibit fast transport kinetics if their surfaces are sufficiently clean. Examples are V, Ta, Nb, and Ti. However, Pd and Pd-Ag alloys are the most commonly employed hydrogen mixed-conductors to date, especially when gases containing oxygen or water species are involved. This is because they remain noble in these environments. However, they are also quite expensive, and do not have as high values of the hydrogen permeability as several of the transition metals.

Several reviews are available concerning experimental measurements of hydrogen transport in metals (55-64), evaluated by the use of a variety of different techniques. A thorough and detailed discussion of the data collected from a number of studies can be found in references (56), (58). Birnbaum and Wert (58) showed, that the published results of fcc metals (e.g. Ni, Cu, and Pd) were generally consistent. However, for bcc metals (e.g. Fe, Nb, Ta, Mo, W, and V), widely scattered results have been reported, probably due primarily to the influence of the presence of other interstitial species within the bulk, or to blocking species on the surface.

Thus it is clear that a very important factor that has contributed to the inconsistent results reported in the literature is the extreme sensitivity of transition metals to surface effects, or to the inadequacy of surface treatments. Because of their thermodynamic properties, bcc metals usually suffer more from surface oxide problems, which retard hydrogen reactions, than fcc metals. In addition, the greater solubility and diffusivity of other interstitials, such as oxygen, nitrogen and carbon, in bcc metals can interfere with the determination of their hydrogen diffusivity.

Therefore, extremely careful materials preparation is necessary for consistent measurements. One of the successful surface cleaning techniques involves annealing under ultra-high vacuum conditions at a relatively high temperature, followed by coating the surface with a protective thin Pd film that allows the passage of hydrogen. This was already described in the literature (57), (60), (61).
The other way to avoid oxide formation at the metal surface is to provide such a low oxygen activity environment that the metal cannot form its oxide. The oxygen activity above which a particular metal will tend to form its oxide can be calculated from thermodynamic data. Table I shows such data for several potential membrane metals at four different temperatures.

As can be seen from this table, the oxygen activities, expressed in atmospheres oxygen partial pressures which must not be exceeded, are often so low that they never can be achieved by the use of any commercially available vacuum system. For example, a good working ultra-high vacuum system can provide pressures in the range of $10^{-11}$ to $10^{-13}$ torr. This is equivalent to an oxygen activity of $10^{-14}$ to $10^{-16}$ atm relative to pure oxygen, or $10^{-20}$ to $10^{-22}$ atm for an inert gas system in which oxygen is 1 ppm of the total gas present. Table I shows that in the case of Ti, oxygen activities, equivalent to partial pressures lower than about $10^{-69}$ atm have to be achieved in order to clean the surface and prevent local oxide formation at 700 K.

Earlier work showed that a method that can be used to provide such low oxygen activities is to employ a chloride molten salt containing a hydride, e.g. LiH as the reducing species (65, 66, 67). To calculate the oxygen activities that can be produced by the use of this system, let us consider the schematic simplified isothermal ternary phase stability diagram for the lithium, hydrogen, and oxygen system at 700 K as shown in Figure 3.

The oxygen activities in triangles A and B can be calculated from the following equations:

for all compositions in triangle A:

$$4 \text{LiH} + \text{O}_2 = 2 \text{Li}_2\text{O} + 2 \text{H}_2$$

$$p_{\text{O}_2} = 9 \times 10^{-66} \text{ atm, or } -2.26 \text{ V versus } \text{O}_2 \text{ at 1 atm}$$

for all compositions in triangle B:

$$4 \text{Li} + \text{O}_2 = \text{Li}_2\text{O}$$
\[ p_{O_2} = 1 \times 10^{-76} \text{ atm}, \text{ or } -2.64 \text{ V versus } O_2 \text{ at } 1 \text{ atm} \]

For the metals considered in Table I this means that in case of Nb, Ta, and V we can provide low enough oxygen activity to prevent the formation of surface-oxide films by producing conditions equivalent to operation in triangle A. However, Ti and Zr require even lower oxygen activities in order to prevent oxide formation. This can be achieved by operating under conditions equivalent to triangle B.

Similar calculations can be done for determining the critical H\textsubscript{2}O pressure above which surface reactions will take place. The values given below were calculated for 700 K.

**TABLE I:** Oxygen activities (atm) and electrochemical potentials E(V) vs O\textsubscript{2} (at 1 atm), required for oxide formation of some metals at different temperatures.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>300 K</th>
<th>500 K</th>
<th>700 K</th>
<th>900 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( p_{O_2} ) (atm)</td>
<td>( E(V) ) vs O\textsubscript{2}</td>
<td>( p_{O_2} ) (atm)</td>
<td>( E(V) ) vs O\textsubscript{2}</td>
</tr>
<tr>
<td>NbO</td>
<td>( 8 \times 10^{-134} )</td>
<td>-1.98</td>
<td>( 6 \times 10^{-77} )</td>
<td>-1.89</td>
</tr>
<tr>
<td></td>
<td>( 9 \times 10^{-134} )</td>
<td>-1.98</td>
<td>( 8 \times 10^{-77} )</td>
<td>-1.89</td>
</tr>
<tr>
<td>TiO</td>
<td>( 4 \times 10^{-173} )</td>
<td>-2.57</td>
<td>( 9 \times 10^{-101} )</td>
<td>-2.48</td>
</tr>
<tr>
<td>V</td>
<td>( 4 \times 10^{-141} )</td>
<td>-2.09</td>
<td>( 3 \times 10^{-81} )</td>
<td>-2.00</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>( 1 \times 10^{-181} )</td>
<td>-2.69</td>
<td>( 3 \times 10^{-105} )</td>
<td>-2.59</td>
</tr>
</tbody>
</table>
Figure 3: Phase stability diagram of the ternary system Li-H-O at 700K.

Triangle A:

\[ 2 \text{LiH} + \text{H}_2\text{O} = \text{Li}_2\text{O} + 2\text{H}_2 \]
\[ p_{\text{H}_2\text{O}} = 2\times10^{-17} \text{ atm} \]

Triangle B:

\[ 4 \text{Li} + \text{H}_2\text{O} = \text{Li}_2\text{O} + 2\text{LiH} \]
\[ p_{\text{H}_2\text{O}} = 2\times10^{-28} \text{ atm} \]

These simple calculations show that while surface oxide formation on such materials can not be avoided in modern ultra-high vacuum systems (ca. 10^{-13} torr), this can indeed be done by the use of appropriate molten salt environments.
Because of this, the thermodynamic and kinetic properties of a number of oxygen-sensitive materials can be studied using electrochemical methods with molten salts containing hydride ions, which provide these very low oxygen activities (65-67). A number of other practical applications of such salts have also been proposed, including their use in a solid/liquid/solid (S/L/S) system as a hydrogen -transporting composite "solid" electrolyte that can easily be produced in a variety of shapes (67-69) for hydrogen-transporting fuel cells, enhanced catalysis, hydrogen-cycle thermoelectric devices (67), and sensors (70), (71).

**Experimental verification of the double cell concept**

In order to verify the overall concept as shown schematically in Figure 2, a number of choices had to be made for the components to be utilized in the system. This refers to the two electrolytes, the membrane material, and the materials for the containments. Thus, prior to the double cell experiment, a number of experiments were undertaken to characterize the various components.

**Electrolyte I:**

An eutectic melt, KOH/NaOH, with a melting point of 173°C, was selected for use as electrolyte I. In order to verify the validity of this choice, and that no large impedances, leading to overvoltages (particularly on the oxygen evolution side) are present in this case, preliminary experiments were undertaken at a relatively low temperature, 175°C, compared to the operating temperature of 400°C for the final device.

Under these conditions, any noble metals or few polymers can be used as containers. In this experiment, TEFLON, which has a softening point at about 200°C, was used as the container material.

The following cell arrangement has been used:

(-) $\text{H}_2(\text{Pd-Ag}) / \text{KOH-NaOH eutectic, H}_2\text{O(gas)} / \text{O}_2(\text{Au})$ (+)
A Pd-Ag alloy with 25 at% Ag was chosen as the gas-evolving electrode (negative electrode or working electrode, WE), because hydrogen can be evolved on its surface without the need for special surface treatments. Thin surface layers of this material, which is also hydrogen transparent, may be later also used in the double cell experiment, protecting the less noble metal membrane on the water-vapour-side from oxidation. The Pd-Ag alloy was in the form of a sheet with an area of 0.20 cm², and a thickness of 0.0127 cm.

An Au-rod with a 0.07 cm diameter and an area of 0.25 cm² was used as the oxygen electrode (positive electrode, counter electrode, CE).

A schematic set-up of the electrochemical cell is shown in Figure 4.

The steam, H₂O(gas), was supplied to the electrolyte by allowing nitrogen gas to bubble through a flask that contained boiling water. The resulting N₂(gas) + H₂O(gas) mixture was then passed into a TEFLOntube with small holes at the end, which was immersed into the electrolyte.

A PAR potentiostat/galvanostat was used to control the voltage in respect to the reference electrode and measure the current of the cell during the experiment, which was performed at 175°C.

A plot of the cell current versus cell voltage is shown in Figure 5.

From this figure, the decomposition voltage under the imposed conditions was inferred as 1.28 V.

The comparison of the decomposition voltage of this work with the theoretical value, obtained from thermodynamic data (72) for the reaction

\[ \text{H}_2\text{O}_{(\text{gas})} = \text{H}_2(\text{gas}) + \frac{1}{2} \text{O}_2(\text{gas}) \]

is represented in Figure 6.
The experimental data point of 1.28V at 175°C deviates only by 10% from the theoretical value of 1.16V. The current densities which were achieved at a voltage of 1.4 V are 50 mA/cm² at the hydrogen electrode, and 40 mA/cm² at the oxygen electrode, respectively. They have to be compared at this voltage with current densities of 100 mA/cm² for the electrolysis in aqueous KOH at 100°C, and 200-300 mA/cm² for steam electrolysis in molten NaOH at 350°C (73).

The present choice for the electrolyte has already been investigated for use in the intermediate temperature range by others (74). However, the solubility of water vapour in this electrolyte is
somewhat low at 700 K (75), which can also limit the useful current density. The differences in the current densities in this work compared to (73) can be attributed to the poor experimental set-up for introducing the water vapour into the electrolyte. However, at this point this was considered as an engineering aspect which should be taken care of in the final design of the system.

![Graph](image)

**Figure 5:** Current versus voltage characteristic of the decomposition of steam in a KOH/NaOH molten salt at 175°C.

**Electrolyte II**

The use of a novel hydrogen-conducting molten salt electrolyte in combination with hydrogen transparent membranes for hydrogen sensor applications has been reported by Deublein, Liaw, and Huggins (71). To make practical use of such a device, detailed
information about the electrolyte including its stability regime and the total conductivity as well as the fraction of the charge flux transported by ionic and electronic species, is required.

![Graph](image)

**Figure 6:** Theoretical and experimental data of the voltage versus temperature relationship for the decomposition of steam.

Calculations and measurements of the stability regime and decomposition potentials of a hydrogen-conducting molten salt electrolyte containing hydride ions and based upon the LiCl-KCl-LiH system near 400°C were performed. In addition, the total conductivity, as well as the separate ionic and electronic contributions were determined by dc and ac methods, respectively.
Thermodynamic considerations

The phase diagram of the K-Li-Cl-H quaternary system has been calculated from relevant thermodynamic data (72) for 600 and 700 K. It is shown in Figures 7a and 7b.

Figure 7a: Schematic representation of the K-Li-Cl-H quaternary phase diagram at 600 K.
Figure 7b: Schematic representation of the K-Li-Cl-H quaternary phase diagram at 700 K.

At 600 K, LiH at unit activity is in equilibrium with KH, K and KCl, forming a tetrahedron with the corresponding voltage of 0.089 V vs H₂ (top of Figure 7a) and with K, Li and KCl, forming another tetrahedron with a voltage of 0.457 V vs H₂ (bottom of Figure 7a) at 1 atm. At 700 K (Figure 7b), KH is thermodynamically no longer stable, and LiH at unit activity is in equilibrium with Li, K and KCl, sharing only one tetrahedron, with the corresponding voltage of 0.369 V vs H₂.

These thermodynamic considerations reveal that the stability range of the molten salt mixture LiCl - KCl - LiH is dominated by the stability of KH at 600 K and LiH at 700 K, respectively, which are both dissolved in the chloride eutectic mixture.

The information from the quaternary phase diagram leads to a very significant conclusion in respect to consideration of the relative
feasibility of the double cell design of the water vapour electrolysis. The comparatively narrow stability window of the LiCl-KCl-LiH molten salt electrolyte restricts its utilization to voltages not greater than 0.089 V at 600 K, and 0.369 V at 700 K.

**Electrolyte preparation**

The KCl-LiCl-LiH molten salt electrolyte was prepared by melting the eutectic mixture of KCl and LiCl, obtained from LITCO, with a melting point of 360°C, in an aluminium crucible inside an inert gas-filled glove-box at 400°C for about 1 hour. This is necessary to remove residual water from the salt. Then the LiH, supplied by Alpha Chemicals, was added. The amount depended on the condition of the melt, which was determined by the oxygen and water vapour content inside the glove-box., but up to 20 wt% of LiH were typically needed to saturate the chloride molten salt with LiH. The preparation was successful when, at 400°C, a crystal clear low viscosity melt (water-like) was obtained.

**Voltage / current characteristic**

A molybdenum sheet and a Ti/TiH two-phase mixture, both of 1 cm² cross section, positioned at a distance of 1 cm, were used in two subsequent dc transport experiments in the molten salt electrolyte. A TiH/TiH₂ two phase mixture served as a reference electrode at a potential of -0.175 V vs H₂ at the operating temperature of 410°C.

Starting at the point of H₂ evolution, the positive Mo electrode was first polarized up to +0.1 V vs H₂, acting as a hydrogen evolution electrode. In the next step, it was polarized as far negative as -0.440 V vs H₂. The resulting current/voltage relation from that experiment is shown in Figure 8.

The I/V relationship shows three sections with different slopes, of which the voltages of the intersections mark the stability regime of the electrolyte under the imposed conditions. From this, a value of 0.3 V can be deduced for the decomposition voltage. This must be compared with the value of 0.369 V, obtained from thermodynamic
calculations. It can be seen from Figure 8 that the current densities in those ranges are extremely small, which indicates that the electrode reactions are greatly impeded.

![Graph](image)

**Figure 8**: I/V characteristic of the LiCl-KCl-LiH molten salt electrolyte at 410°C.

Also, apparent deposition of H$_2$ at the more positive potentials, and deposition of Li metal at the more negative potentials occurs at values somewhat different than expected. This may be due to the behaviour of molybdenum under the imposed conditions, under which the metal may dissolve some lithium and hydrogen in solid solution causing the current to rise at potentials, at which unit activity of the elements, lithium and hydrogen, has not yet been reached (the Mo electrode does not show blocking behaviour over
the entire stability regime of the LiH). The slopes of the graph are related to the different charge transfer reactions occurring at the electrode/electrolyte interface. At potentials more negative than -0.35 V vs H₂, lithium ions are discharged to elemental lithium, thus the slope of 0.507 is related to the lithium ion conductivity. In the section between -0.35 to -0.05 V vs H₂, neither lithium- nor hydride ions can be discharged at the interface, and the current is thus related to some electronic conductivity of the molten salt electrolyte. At potentials from -0.05 to +0.10 V vs H₂, hydride ions are discharged at the electrode/electrolyte interface to give off hydrogen gas. In this section, the slope of 0.997 is related to the hydride-ion conductivity of the molten salt.

Electronic Conductivity

Electronic leakage under open circuit conditions is a result of the electronic or hole conductivity of the system, as mentioned earlier in chapter 2. It occurs especially at elevated temperatures where phases often change their composition or become unstable.

The partial electronic conductivity of the LiCl-KCl-LiH molten salt mixture was investigated by using the Hebb-Wagner asymmetric DC-polarization technique (76).

The experiments were performed in an electrochemical cell as described above where Ti/TiH served as the reversible electrode, and Mo was used as an ionically blocking electrode. The measurements were made within the potential range from -0.35 to -0.08 V vs H₂, where no ionic discharge reaction can occur at the interface of the blocking electrode. This situation is identical to the middle section in Figure 8 and is shown in Figure 9 on a different scale.

Figure 9 can be analysed to determine whether the electronic conductivity is due to the transport of electrons or holes using equations /46/ and /47/ from chapter 2. The relevant plots are shown in Figures 10 and 11.
Figure 9: I/V characteristic within the stability range of the LiCl-KCl-LiH molten salt electrolyte at 410°C.

From Figures 10 and 11 it can be seen that the electronic leakage current in the molten salt electrolyte is mainly due to hole conduction, rather than electron conduction. The corresponding value for the electronic conductivity is $1.66 \times 10^{-3}$ S/cm at 410°C.

Total conductivity and ionic conductivity

The total conductivity of the LiCl-KCl-LiH molten salt was determined at various temperatures using ac-impedance spectroscopy.
Molybdenum sheets of 1 cm² cross section, mounted 1 cm apart in an Al₂O₃ holder, were used as electrodes. Using a Solartron Frequency Analyzer, model 1250, in combination with an Solartron Electrochemical Interface, model 1286, measurements were taken over the frequency range of 0.01 Hz to 63 kHz and at temperatures from 364 to 416°C. The results are shown in the Arrhenius plot in Figure 12, from which the activation energy was found to be 6.21 kJ/mole. The total conductivity of the electrolyte, measured by this method, was inferred as 0.879 S/cm at 410°C. This number is reduced by the electronic conductivity to obtain the ionic conductivity of the system. Since the electronic conductivity amounts only about 0.001 % of the total conductivity, the total conductivity is essentially due to ionic transport properties only.

Figure 10: Hole conductivity of the LiCl-KCl-LiH molten salt electrolyte at 410°C, analyzed after (77).
Figure 11: Electron conductivity of the LiCl-KCl-LiH molten salt electrolyte at 410°C, analyzed after (77).

Membrane materials

It has been reported from electrochemical diffusion measurements (78) that some bcc-metals possess fairly high chemical diffusion coefficients for hydrogen. Among these are V, Nb, Ta, and Fe, all of which could possibly meet the requirements to serve as the membrane in the double cell as has been described above.

Fe was chosen as the membrane material because of its thermodynamic stability in the KOH/NaOH molten hydroxide electrolyte. It is also cheap and can be more easily brought into shapes than the refractory metals V, Nb, and Ta.
Figure 12: Arrhenius plot of the total conductivity of the LiCl-KCl-LiH molten salt electrolyte measured by ac-impedance spectroscopy.

A Fe-membrane of the shape of a crucible, covered by a lid of insulating material which was equipped with an inlet for the water vapour, an electrical feed-through for the positive electrode, and an outlet for the oxygen and excess water vapour, served in the double-cell experiment as will be described later.
Double-cell experiments

A Pd-Ag membrane and a KOH/NaOH molten salt electrolyte was used on both sides.

The purpose of this experiment was to proof the double cell concept with decomposition of water in one compartment and hydrogen evolution in the second compartment, as schematically shown in Figure 13. The reason for using the hydroxide molten salt was simply to learn how to handle the experiment in terms of connections to the instruments, supply of water vapour, currents and voltages, and other unexpected parameters. The hydroxide molten salt has the advantage that it can be used under ambient conditions, i.e. in the laboratory under a hood, and the experiment can be run at temperatures below 200°C, where TEFLOX can be used as containment material.

Pd-Ag (25at% Ag) was used as the membrane to demonstrate the principles involved, but other, more practical materials will, of course, be used later. The membrane surface area was 0.28 cm² and the thickness 0.0127 cm. Pd-Ag has good permeation for hydrogen, and is stable in the hydroxide electrolyte.

The Pd-Ag foil divided the total cell into two separate electrolyte chambers, which were via foil contact isolated from each other. The electrolyte in each chamber was a eutectic mixture of KOH/NaOH with a melting point of 173°C. The container material was TEFLOX, whose practical upper working temperature is about 200°C. H₂O was fed into cell I through a TEFLOX tube.

The minimum value of the total voltage $E$, composed of $E_1+E_2$, across the cell is determined by the decomposition voltage of water vapour at the working temperature of 173°C.

Two PAR potentiostats, model 173 A, were used to set the potentials and measure the corresponding currents. They were connected to the membrane via ground (low voltage electrode). At potentiostat I, the oxygen electrode was chosen as the working electrode, having the
higher potential. At potentiostat II, the hydrogen electrode was chosen as the working electrode, but driven to more negative potentials with respect to the membrane, which acted as the counter electrode.

Figure 1.3: Schematic representation of the experimental set-up to proof the double cell concept using a molten hydroxide electrolyte on both sides.

By applying a voltage $E_i$ between the positive electrode and the membrane, that is smaller than the decomposition voltage of water vapour, the hydrogen activity at the interface membrane/electrolyte
is fixed. In order to evolve hydrogen in cell II, the hydrogen activity at unity has to be fixed in cell II by applying a voltage $E_2$, where $E_1 + E_2$ give the decomposition voltage of water vapour. This creates a concentration gradient across the membrane, which forces the hydrogen through the membrane to the negative electrode in cell II, where it can evolve at unit activity. One can consider this arrangement as two separate circuits which are electronically connected via the membrane. If $E_1$ and $E_2$ are held constant, a steady state current is attained in each of the chambers with $I_1 = I_2$.

Figure 14 shows the results of a series of four experiments on the current versus voltage characteristics of this double-cell experiment for a number of voltages $E_1$ and $E_2$. The sign of the current in cell II is reversed as a consequence of the experimental set-up. As can be seen from Figure 14, the overall behaviour is what was expected. The currents in the cells are equal. Current densities up to 350 mA/cm$^2$ were achieved at $E_1$-potentials of 1.3 V, and $E_2$-potentials of 0.7 V.

Design and construction of a prototype double-cell system

A concentric tubular design of the double cell is shown in Figure 15.

The membrane had the shape of a crucible, with an active surface area of 11 cm$^2$. Fe was chosen as the membrane material because of its thermodynamic stability in the KOH/NaOH electrolyte under the experimental conditions. The open end of the crucible was closed with a lid of insulating material. The lid was equipped with an inlet for water vapour, which was carried into the electrolyte through a tube, an electrical feed-through for the oxygen electrode, and an outlet for oxygen and excess water vapour. A nickel electrode was inserted into cell I to act as the positive electrode.

The outer crucible material was aluminum and contained the LiCl-KCl-LiH molten salt electrolyte. Molybdenum wire was used as the hydrogen electrode in cell II. The whole set-up was operated inside a glove-box with controlled atmosphere (since cell II was not closed to the outside environment). The water vapour supply and the gas-outlet were carried to the outside of the glove-box.
Figure 14: Results of four experiments of the voltage-current characteristics of the double cell experiment.

Two PAR potentiostats, model 173 A, were used to set the potentials and measure the corresponding currents. They were connected to the membrane via ground (low voltage electrode). At potentiostat I, the oxygen electrode was chosen as the working electrode, having the higher potential. At potentiostat II, the hydrogen electrode was chosen as the working electrode, and driven to more positive potentials (because H ions discharge at more positive potentials to H atoms) in respect to the membrane, which acted as the counter electrode.
Figure 1.5: Schematic illustration of the concentric tubular double cell design.

The voltages $E_1$ and $E_2$ ranged from 1.0 to 1.3 V and 0.1 to 0.3 V, respectively. The corresponding currents are shown in Figure 16. Note that the currents for cell I are given in A, and for cell II in mA, respectively.

5.2.4. Discussion

In comparison to the results of the experiment described above, the current densities achieved in the last double cell experiment are by a
factor of 7 lower (50 mA/cm² compared to 350 mA/cm²). This can be mainly attributed to the low solubility of hydrogen in Fe, which reduces the hydrogen flux through the membrane, compared to a very high solubility of hydrogen in Pd-Ag, under the imposed conditions. Pd metal absorbs by a factor of 1000 more hydrogen than Fe (79). This cannot be compensated by the higher diffusion coefficient of hydrogen in Fe (10⁻⁴ cm²/s at 400°C, (80) compared to that in Pd-Ag (7×10⁻⁶ cm²/s at 25°C, and an activation energy of 5700 cal/mol (79).

Figure 16: Results of the voltage-current characteristics of the double cell experiment.
It is also interesting to see that the currents in the two cells are not equal. The low current in cell II can have several reasons of which some are probably related to the overall experimental set-up, which did not allow proper introduction of the LiCl-KCL-LiH electrolyte. It could well be, that the electrolyte was not wetting the entire membrane area. Another reason could be that the Fe membrane was in such poor initial condition in terms of surface oxides, that most of the LiH was used up by cleaning off the oxide. This would then reduce the amount of LiH in the molten salt electrolyte and thus reduce the hydride conductivity.

In general, the experiments were very difficult to perform, and it was concluded that a point was reached where serious reengineering of the device became necessary in order to make further achievements.

However, the overall concept has been verified and hydrogen was observed on the Mo electrode at potentials that are sufficient to extract hydrogen from the membrane, but not sufficient to decompose the LiH in the molten salt electrolyte in cell II.

The key element of the concept is the hydride-ion conducting molten salt electrolyte, and much effort was taken for its characterization.

An investigation of alternative electrolytes to use in cell I, instead of the hydroxide electrolyte in order to provide enough water vapour at temperatures around 400°C, is necessary.

The use of metallic construction materials and the idea of a concentric design provide an opportunity for the use of novel configurations with high surface/volume ratios, such as clusters of fine tubes.

For further improvements, engineering aspects will have to be considered seriously and leak-proof set-ups have to be constructed and tested with the components that were characterized in this work.
5.3. Novel concept to reduce nitric oxides

A novel device to reduce nitric oxides to nitrogen and water with the aid of atomic hydrogen, as shown schematically in Figure 17, is described.

![Diagram of electrochemical reactor]

**Figure 17**: Electrochemical reactor to decompose nitric oxides.
The hydrogen is produced on the back side of a metallic membrane using aqueous electrolysis and is transported through the membrane to the front side, at which it meets the nitric oxides at the surface. This concept has been announced in a patent recently by the Daimler-Benz company (81) with the expectation that such devices be inserted into the exhaust system of combustion engines to reduce nitric oxide emissions. The patent application describes a composite membrane, consisting of metal alloys that possess a wide range of solid solution for hydrogen, i.e. Pd-, Ti-, V-, and Zr-alloys, covered with a porous layer of zeolite on one side.

Since hydrogen is provided through a membrane, the following questions are relevant for the application under consideration:

i) how much hydrogen is needed and can this be transported through the membrane within the timeframe of the reaction

ii) how much energy is needed to produce the necessary amount of hydrogen, and

iii) how much surface area is needed to make the hydrogen available for the reduction reaction in the time frame of the exhaust system.

Under the assumption of no parasitic side reactions of hydrogen with other gas constituents, the amount of hydrogen necessary for the reduction process can be calculated from the gas throughput and the average NO\textsubscript{x} content. With a gas throughput of 50-300 m\textsuperscript{3}/h and a maximum of 500 ppm NO\textsubscript{x}, 150 l NO\textsubscript{x}/h have to be reduced. Since most of the NO\textsubscript{x} is present as NO, the equivalent amount of hydrogen needed can be calculated from the following reaction

\[
2\text{NO} + 2\text{H}_2 = \text{N}_2 + 2\text{H}_2\text{O}
\]

This results in 150 l H\textsubscript{2}/h or 120 ml H\textsubscript{2}O/h, respectively.

The time which is needed for the hydrogen to pass through the membrane can be estimated from the following relationship:

\[
\bar{D} = \frac{d^2}{t}
\]
where $D$ is the chemical diffusion coefficient of hydrogen in the membrane material, $d$ the thickness of the membrane, and $t$ the time. With a $D$ value of $10^{-4}$ cm$^2$/s, which is very typical for Pd-membranes at temperatures around 300°C, and a membrane thickness of 0.01 cm, the time for hydrogen to pass the membrane will be 1 second. This may be too slow to provide a continuous stream of hydrogen to the reaction site, but can be further improved by making the membrane thinner or raising the temperature.

The energy to produce this amount of hydrogen can be calculated from Faraday's law. At an average voltage of 1.5 V for the electrolysis, 180 Ah/h are necessary to produce 150 l H$_2$/h. The energy needed is then 270 Wh/h.

The third parameter relates to the surface area available for the reduction. This is mainly dependent upon the maximum current densities that can be achieved. From a realistic standpoint of view, current densities between 10 and 100 mA/cm$^2$ are feasible. With a total current of 180 000 mA, this leads to surface areas of 18 000 cm$^2$ at 10 mA/cm$^2$, and 1 800 cm$^2$ at 100 mA/cm$^2$.

These numbers had to be taken into account for designing a preliminary device. Up to now, no experimental details are available to the public.

As already mentioned earlier in this chapter, another electrochemical approach to reduce nitric oxides was announced in a patent application by the TOYOTA company (22). In their approach, a proton conducting solid electrolyte is utilized between two porous electrodes, of which one is exposed to the exhaust gas and the other is in contact with hydrogen gas.

It will be very exciting to watch how much these concepts are worth in making a contribution to the reduction of nitric oxides in emissions from combustion engines.
5.4. References


Chapter 6

6. Summary and Look to the Future

6.1. Summary

Hydrogen mixed conductors are the products of the reactions of many elements and compounds with hydrogen. They can be divided into three classes of materials families:

i) those, in which hydrogen is in solid solution in a metal whose crystal structure is that of the parent metal

ii) those which form new so-called hydride phases in the presence of hydrogen, generally at relatively high hydrogen activities - the metal hydrides

iii) oxides containing appreciable concentrations of hydrogen bronzes

Hydrogen mixed conductors are materials (solids or liquids) that transport hydrogen as ionic or atomic species and in addition some show an appreciable electronic conductivity due to the metallic character of the host metal lattice. Thus, they can be utilized in a number of applications such as

- hydrogen storage and purification devices
- heat pumps

in which gaseous hydrogen, H$_2$, is the reactant, and the reaction occurs at the gas/metal interface.

In other applications such as

- rechargeable nickel metal-hydride batteries
- water electrolysis cells and fuel cells
- hydrogen thermoelectric devices, and
- electrochromic devices

the reaction with hydrogen takes place in an electrochemical cell at the electrode/electrolyte interface. In such systems hydrogen mixed conductors can serve either as electrodes or as electrolytes, depending on their individual thermodynamic and kinetic properties.

This thesis discusses the use of solid-state-ionic concepts to study the thermodynamic and kinetic properties of hydrogen mixed conductors by applying electrochemical techniques. These refer to the potential phase relationships in binary, ternary, and quaternary systems, the thermodynamic stability regimes of electrodes and electrolytes, the chemical diffusion coefficient of the active species in electrochemical devices, and the electrolyte conductivity.

The central experimental set-up used in several investigations was a galvanic cell of the general type as described in Chapters 1 and 2. The techniques that were used throughout the work were the coulometric titration technique to look at materials under equilibrium conditions, and the galvanostatic or potentiostatic intermittent titration techniques, transient techniques, to observe moving species. It has been shown that these techniques are very well suited to analyse the behaviour of electrochemical systems in terms of the materials and their interfaces involved under both equilibrium and non-equilibrium conditions. The potential equilibrium measurements give information on the thermodynamic properties. The results of the kinetic measurements provide information about the diffusivity of a moving species under the influence of a concentration gradient.

Two systems, one based on titanium-nickel and the other on palladium and palladium-lithium have been investigated in terms of their potential/hydrogen concentration relationships, and diffusion measurements have been performed in the single phase regimes using electrochemical techniques at room temperature.
In addition, two new concepts involving the application of hydrogen mixed-conductors in water vapour electrolysis at intermediate temperatures and the use of electrochemical means to influence the behaviour of catalytic surfaces were presented. In both cases, metallic hydrogen-conducting membranes were utilized.

In the following, the results of the experimental work are summarized.

6.1.1. Titanium-nickel-hydrogen system - see chapter 3

The reaction of hydrogen with the binary phases Ti$_2$Ni, TiNi and TiNi$_3$ at ambient temperature has been studied using electrochemical techniques. The results indicate that these are both topotactic insertion reactions which produce solid solutions with wide compositional ranges under these conditions, contrary to the observations by others of reconstitution reactions at elevated temperatures.

Samples were prepared from powders which were coated with a copper protective layer by an electroless plating process.

The potential versus hydrogen concentration characteristics were investigated using the coulometric titration technique. From transient behaviour, the chemical diffusion coefficient of hydrogen was deduced.

TiNi absorbs 1.1 H atoms per formula unit, of which 1 H atom per formula unit was discharged in the electrochemical environment. This was also observed in a second cycle.

Ti$_2$Ni can absorb 2.5 H atoms per formula unit, but only 1.4 H atoms could be discharged in the first cycle under the conditions of the electrochemical cell. In the second cycle the sample had already lost about two thirds of its initial hydrogen capacity and was left with 0.9 H atoms per formula unit.
From this information, the ternary phase diagram has been constructed at room temperature and the relation to intermediate temperature results from other authors was discussed. At room temperature, the hydrogen absorption occurs via a topotactic insertion reaction, while at more elevated temperatures, reconstitution reactions were observed.

Kinetic measurements have shown that hydrogen diffuses reasonably fast through both Ti$_2$Ni and TiNi$_3$ at ambient temperature. Chemical diffusion coefficients of $1 \times 10^{-8}$ cm$^2$/s for Ti$_2$Ni and $2.3 \times 10^{-7}$ cm$^2$/s for TiNi$_3$ were measured for low hydrogen activities at room temperature.

Several attempts to measure the diffusion of hydrogen in the pure TiNi phase on solid slab samples failed because of experimental difficulties. However, the phase reacted reversibly with hydrogen when it was in the form of a powder coated with copper and pressed into pellets.

The better reversibility of the TiNiH$_x$ reaction, along with its more negative potential range, make these materials more interesting candidates than those based upon the Ti$_2$NiH$_x$ formation reaction for use in hydrogen-based electrochemical cells. As reported elsewhere, a cell voltage of 1.35 V is obtained when these materials are used in combination with Ni(OH)$_2$/NiOOH positive electrodes.

6.1.2. Palladium-hydrogen based systems (see chapter 4)

Pd-H and Pd-Li-H

Hydrogen absorption into palladium and a palladium-lithium alloy at hydrogen activities corresponding to hydrogen pressures up to 1 atm hydrogen have been studied at ambient conditions using electrochemical techniques. Thermodynamic and kinetic properties were evaluated simultaneously as a function of the hydrogen activity.
The equilibrium potential of an annealed palladium electrode as a function of its hydrogen concentration during several adsorption/desorption cycles was determined at 23°C. From these data, the upper stability limit for the α-phase region, expressed as H/Pd, was determined to be 0.01. From there, two phases, α + β, are stable up to a H/Pd ratio of 0.6. After that, the β-phase is stable and reaches a H/Pd ratio of 0.74 at a hydrogen pressure of 1 atm. The plateau potential in the two-phase region was -0.065 V versus 1 atm hydrogen during desorption. These data are in excellent agreement with data obtained by the gas absorption method reported in the literature.

A palladium-lithium alloy, PdLi$_{0.14}$, which was made by diffusing Li into Pd electrochemically in a molten salt electrolyte at 400°C, was charged and discharged with hydrogen in the same manner as the pure palladium. The shape of the coulometric titration curve obtained is similar to the palladium case. However, the total uptake of hydrogen up to a hydrogen pressure of 1 atm is significantly smaller. The upper limit of the solid solution α-phase was determined at a H/(Pd+Li) ratio of 0.03, and the upper limit of the α+β two-phase regime at a H/(Pd+Li) ratio of 0.52. The two-phase plateau occurs at a potential of -0.083 V versus 1 atm hydrogen.

The chemical diffusion coefficient of hydrogen in palladium was determined in the single phase regimes. The values are strongly dependent on the sample history and different results were obtained for virgin samples and others which had gone already through several absorption/desorption cycles. This disparity is also observed in the literature and is probably due to changes in the microstructure of the sample due to changes in the dislocation density.

The Pd-Li alloy is less transparent to hydrogen than pure palladium at low hydrogen activities. The chemical diffusion coefficient in the α-phase regime was found to be two orders of magnitude smaller than in pure palladium. This may be due to the reduced number of interstitial crystallographic sites for hydrogen
and because of blocking of the interstitial pathways by lithium. In the β-phase, the chemical diffusion coefficients of hydrogen in Pd and PdLi<sub>0.14</sub> are comparable.

**Electrochemical loading of hydrogen and deuterium into palladium**

The electrochemical loading of hydrogen and deuterium into palladium has been studied by measuring the change in the electrical resistance of palladium as a function of H(D) content.

Cylindrical palladium cathodes, 0.3 cm in diameter and 3 to 5 cm long, were made from wire. The samples were preconditioned in a three-step process which included annealing at 800°C in vacuum, cooling to room temperature, and etching in aqua regia. Loading measurements were made in an electrochemical cell utilizing a platinum counter electrode in a LiOD-electrolyte. The degree of loading was recorded via determination of the axial resistance of the palladium cathode. The effects of several electrochemical variables on the loading process have been examined. In particular, it has been demonstrated that loadings up to and in excess of H(D)/Pd = 0.9 may be achieved under suitable conditions in an electrochemical cell.

**6.1.3. Concepts for applications of hydrogen mixed-conductors** (see chapter 5)

**Use of solid state ionic techniques to modify catalytic surfaces**

An unusual type of electrochemcial system, a three-layer solid/liquid/solid (S/L/S) electrochemical cell configuration is suggested to modify catalytic surfaces in situ. It consists of a thin film liquid electrolyte which is sandwiched between two solid electrode layers. The outer side of one of the electrodes is the catalyst surface in contact with the reacting species, while the outer side of the other electrode is in contact with a respective reference, source or sink.
This general approach has been successfully demonstrated by others in the case of several simple reactions involving oxygen at elevated temperatures, including the decomposition of NO to N₂ and O₂. In those cases, oxygen was transported to or from the catalytic interface by oxygen ionic motion through an underlying solid electrolyte of yttrium-doped zirconium oxide.

It was suggested that one can also use this concept to transport hydrogen to and from a catalytic surface. Two approaches were considered.

Intermediate temperature water vapour electrolysis

A concept for the electrolysis of water vapour at intermediate temperatures by the use of a double cell configuration was proposed and verified. The hydrogen that is produced is of very high purity and is free of water, for it passes through a metallic membrane between the two cells (Figure 2 in chapter 5). Cell I is the basic electrolysis cell. Water vapour is introduced into a hydroxide molten salt, consisting of an eutectic mixture of NaOH and KOH with a melting point of 173°C, and decomposed at a voltage E₁ applied between the oxygen electrode and the membrane. Voltage E₁ is lower than the decomposition voltage of water to produce hydrogen and oxygen gas at 1 atm pressure at the temperature of operation, because the hydrogen enters the front side of the membrane at an activity lower than unity. Cell II acts as a hydrogen concentration cell, and contains a hydrogen conducting molten salt electrolyte, consisting of the KCl-LiCl eutectic mixture, saturated with LiH to provide H⁻-ions for conduction. The voltage E₂, which is applied between the membrane and the hydrogen electrode, fixes the hydrogen activity at the back side of the membrane at a very low value. This causes hydrogen to move through the membrane by chemical diffusion down its concentration gradient. The voltage E₂ also drives the hydrogen across electrolyte II, so that it evolves at the hydrogen electrode. In the absence of losses, E₁ + E₂ = E_{decomp}, and oxygen is evolved at the oxygen electrode on one side of the membrane, and dry, clean hydrogen on its other side.
The membrane thus acts not only as a separator between the two electrolytes but also serves as an intermediate hydrogen storage medium at hydrogen pressures below 1 atm.

The key role in this approach is played by electrolyte II, a hydrogen-conducting molten salt containing hydride ions, which serves two important purposes. It conducts hydrogen at elevated temperatures and also provides an environment with very low oxygen activity, so that a number of oxygen sensitive-transition metals can be used as the hydrogen-permeable membrane material.

In order to verify the overall concept a number of choices had to be made for the components of the system. This refers to the two electrolytes, the membrane material, and the materials for the containments. Thus, prior to the double cell experiment, a number of experiments were undertaken to characterize the various components. The results of these led to the following components to be used for the verification experiment:

**Electrolyte I**

It consisted of a KOH/NaOH eutectic mixture with a melting point of 173°C and was saturated with water vapour at a temperature of 175°C. The decomposition voltage of water in this electrolyte was determined to be 1.28 V at 175°C, which deviates by only 10% from the theoretical voltage of 1.16, indicating a relatively small interfacial impedance and overvoltage. The current densities which were achieved at a voltage of 1.4 V were 50 mA/cm² at the hydrogen electrode, and 40 mA/cm² at the oxygen electrode. These values are somewhat low compared with the relevant literature (200-300 mA/cm² at 350°C (1)).

**Electrolyte II**

It consisted of a LiCl-KCl eutectic mixture with a melting point of 360°C which was saturated with LiH at 400°C. Calculations based on relevant thermodynamic data and measurements of the stability regime of the LiCl-KCl-LiH quaternary molten salt electrolyte near 400°C were performed. The information from the
quaternary phase diagram led to a very significant conclusion in respect of the relative feasibility of the double-cell design. The comparatively narrow stability window of the LiCl-KCl-LiH molten salt electrolyte restricts its utilization to voltages not greater than 0.089 V at 327°C, and 0.369 V at 427°C. The results of the experimental determination of the electrochemical stability reveal a value of 0.3 V at 410°C. This reduced value is probably due to the nonblocking behaviour of the Mo-electrode at high lithium and high hydrogen activities.

The total conductivity of the LiCl-KCl-LiH molten salt electrolyte was determined at temperatures from 364 to 416°C using impedance spectroscopy. The activation energy was found to be 6.21 kJ/mole. The conductivity at 410°C was found to be 0.879 S/cm. In addition, the electronic conductivity was determined from the leakage current using the Hebb-Wagner asymmetric depolarization technique. It was found to be $1.66 \times 10^{-3}$ S/cm at 410°C and was attributed mainly to hole conduction rather than electron conduction.

Membrane material
Based on data of the diffusion behaviour of hydrogen, potential candidate materials for the membrane were Pd-Ag, Fe, V, Nb, and Ta.
Pd-Ag and Fe were the preliminary choices for the membrane material because of their thermodynamic stability in the KOH/NaOH molten hydride electrolyte, and their excellent hydrogen diffusion in the α-phase solid solution.

Double cell experiments
Two kinds of double cell experiments were undertaken. One was performed at 175°C, using the KOH/NaOH electrolyte on both sides of a Pd-Ag membrane in a TEFLON compartment. The expected behaviour was observed and equal currents were obtained in both cells with current densities of 350 mA/cm² at an overall voltage of 2.0 V. The second double cell experiment was performed in a concentric tubular design. The membrane consisted of Fe and had the shape of a crucible with the open end closed with a lid of
insulating material. The lid was equipped with an inlet for water vapour, which was carried through an attached tube into the molten KOH/NaOH electrolyte to the inside of the crucible. The lid also had an electrical feed-through for the oxygen electrode and an outlet for oxygen gas. The outer crucible material was aluminium and contained the LiCl-KCl-LiH molten salt electrolyte and a Mo wire for the hydrogen electrode. The whole set-up was operated inside a glove-box with a He atmosphere. The water vapour supply and the oxygen gas outlet were carried to the outside of the glove-box. Experiments were performed at voltages from 1.0 to 1.3 V in cell I, and 0.1 to 0.3 V in cell II. The results obtained from electrical measurements and the observation of hydrogen gas bubbling off the Mo electrode verified the overall concept. However, the currents were not equal in the two cells, and the largest values achieved were much lower than in the previous experiment using the Pd-Ag membrane. The lower current in cell II must be due to a parasitic reaction on one side of the membrane, probably at the interface in cell I, where oxides were being reduced at the interface, consuming the hydrogen at low activities before it can enter the membrane. The low overall current can have several reasons, such as poor wetting of the electrolyte in cell II due to design constraints, or loss of LiH in cell II because of reduction of some residual oxide on the Fe membrane.

In general, the experiments were very difficult to perform, and it was concluded that serious reengineering of the device was inevitable in order to make further advances.

Novel concept to reduce nitric oxides

This concept involves the use of an electrochemical reactor to decompose nitric oxides at a catalytically active surface of a hydrogen-transporting metallic membrane. The hydrogen is produced at the back of a metallic membrane, using aqueous solution electrolysis, and is transported through the membrane to the front side at which it is exposed to nitric oxide gas, arriving at the surface.
This concept was made public recently through a patent application by the DAIMLER-BENZ company (2) with the assumption that such devices could be inserted into the exhaust system of combustion engines to reduce nitric oxide emissions. Unfortunately, no experimental data are currently available, for proprietary reasons.

A similar approach utilizing a hydrogen-conducting solid electrolyte has been patented by the TOYOTA company (3).

6.2 General conclusion

6.2.1 Materials properties

The coulometric titration technique and the galvanostatic intermittent titration technique are suitable for characterizing the thermodynamic and kinetic properties of hydrogen mixed-conductors when proper electrolytes (in terms of stability window and ionic and electronic conductivity) are used, and when sample preparation methods are employed that allow well-defined interface conditions for the electrochemical charge transfer reaction.

Throughout the work it was observed that the properties under investigation strongly depend upon the history of the sample. This is especially pronounced in the results on the diffusion measurements. The sample history, in this case the kind of processing, cooling and annealing, or other treatments such as etching, is responsible for the microstructural features of the sample and thus causes different behaviour of the moving species due to various types of crystal defects (zero-, one-, two-, and three-dimensional). For example, zero dimensional defects are very likely responsible for the hysteresis effect in the absorption and desorption process. The influence of crystal defects on the hydrogen diffusion can be very significant. It is known that hydrogen often diffuses along grain boundaries and dislocations by a different mechanism from that in the bulk material. In this
work, differences up to an order of magnitude have been observed on two samples of palladium of which one was annealed and the other had already gone through several absorption/desorption cycles that greatly increased the dislocation density. In addition, hydrogen can be easily trapped in dislocations which can lead to erroneous results in the hydrogen storage capacity.

Hydrogen diffusion data in hydrogen mixed-conductors reported in the literature, as well as the data from this work, would be better understood if the microstructural features of the samples were taken into account.

6.2.2. System performance

As has been described in chapter 1, hydrogen mixed-conductors are utilized in electrochemical systems such as water electrolyser, fuel cells, rechargeable batteries, electrochromic devices, sensors and electrocatalysts and thus their properties determine to a significant extent the overall system performance.

Some of the applications of hydrogen mixed-conductors have already become commercial products. Examples are the

Ni/metal hydride rechargeable batteries for consumer applications (portable telephones, camcorders, laptop computers)

phosphoric acid fuel cells for load levelling in natural gas-burning block power stations

alkaline electrolyser systems for the production of very clean hydrogen

electrochromic rear view mirrors for luxury cars and trucks.
Other applications such as the SOFC, MCFC, and SPFC, are still in the pilot production and testing phase. A vast amount of data are available on the basic properties of the materials used in these systems. However, predictions for system performance based on the materials properties typically differ greatly from the experimental results obtained under real conditions. This has been also experienced in the double cell experiment involving water vapour electrolysis as described in chapter 5.

Electrochemical devices, as they are designed and their components manufactured today, suffer from a common problem, which is related to the local arrangement of the various species involved in the electrochemical reaction at the electrode/electrolyte interface.

Since the major and environmentally most important applications of hydrogen mixed-conductors is their utilization in electrochemical devices, some thoughts and suggestions for further improvements, based upon recent scientific achievements in other disciplines, are given below.

6.3. Look to the future

In order to follow the users continuously increasing demands for better and cheaper products, industrial production development must find ways to better utilize the materials our todays products are made of.

For electrochemical devices the demands are related to

- higher quality standards in terms of power, energy and lifetime
- miniaturization of the devices
- better utilization of resources.
With this information in mind let us now look at the situation inside an electrochemical system at the microscopic level.

For better understanding, the microstructure at the electrode/electrolyte interface of an electrochemical system is shown schematically in Figure 1. It can be seen that a three-phase interface is required for the electrochemical charge transfer reaction to occur. These electrochemically active zones at which the boundary conditions for the reaction to occur are given, are indicated by black dots. The local current at these active sites is related to the electrical charge of the moving ion, the mobilities of the species involved, the number of charge carriers that are available at the site, and the electrochemical driving force. The current is limited by the diffusion behaviour of the charge carriers to and from the reaction site.

From Figure 1 we can see immediately that two important parameters come into play, namely grain size and grain morphology of the species involved. Both determine the pattern in which the phases can meet and thus the number of active sites and the local arrangement for the diffusion path of the moving species.

Since the total current of the system is directly proportional to the number of active sites, one can easily understand the discrepancy between materials properties under ideal conditions and the results of system properties in which only part of the materials involved can meet under ideal conditions.

This situation is very typical for today's electrochemical systems.

The strategy to leap-frog forward in system performance should therefore relate to microstructural design.
Figure 1: Schematic representation of the microstructure at the electrode/electrolyte interface of an electrochemical system.
In Figure 2, the microstructure from Figure 1 was redesigned in terms of maximization of the number of active sites. This can be achieved by creating patterns in which two particles of different kind and size meet in an electrolyte environment. One possibility is shown in Figure 2b, where large grains of electrode material are surrounded by many small grains of current collector material. The active sites per grain of electrode material are indicated by black dots in Figure 2.

The grain sizes of the various components have to be adjusted to the particular application. For example, the microstructural design of Figure 2 could be applied to the metal hydride/electrolyte interface in Ni/metal hydride batteries. The electrode material refers then to the metal hydride alloy under the assumption that the hydrogen absorption occurs via a topotactic insertion reaction. The electrolyte is an aqueous solution of KOH, and the electronic conductor is typically a metal, Cu or Ni. The metal hydride alloy powders are often partially coated with a thin metal layer prior to electrode manufacture. The reaction that occurs at the electrochemically active sites indicated in Figure 2c as black dots is the following:

\[ M_xH + OH^- = xM + H_2O + e^- \]

and represents the electrode reaction at the negative electrode during discharge from left to right, and during charge from right to left. M stands for the metal alloy.

This concept is not only applicable to electrochemical systems but in general to composite materials, in which two or more phases with distinct properties meet in specific patterns in order to combine their intrinsic or extrinsic properties to produce unique and novel system behaviour.
Figure 2: Microstructural design of the electrode/electrolyte interface of an electrochemical system in a schematic representation.
The value of composite materials has been recognized long time ago. Examples are structural materials such as precipitation hardened steel, fiber reinforced ceramics, ceramic reinforced polymers, etc. However, in electrochemical systems the fabrication techniques are based on the statistical distribution of the materials involved and thus the quality standard is based on a statistical number of electrochemically active sites at the electrode/electrolyte interface.

As we have seen from Figure 2, microstructural design requires the use of a number of novel tools and fabrication techniques have to be developed to precisely control

- particle size
- particle morphology, and
- particle arrangement

Today, there are already many techniques known to obtain monodispersed particles from nano- to micrometer diameters over wide ranges of sizes and in many different shapes from gaseous and liquid precursors, Some examples are given in (4-9).

Control over particle arrangement on the molecular scale and creation of patterns on the nanoscopic scale is currently a hot topic in materials science, chemistry, physics, biochemistry and biology, and much can be learned from the current literature (10-18).

The advancement of materials on the microscopic scale has been successfully demonstrated in semiconductor fabrication. Progress in the development and characterization on the mesoscopic scale has been spectacular and the preparation of nanostructured materials, by physical or chemical methods, has become an important branch of advanced materials science and technology. Increasingly, chemists are contributing to the synthesis of advanced materials with enhanced or novel properties. Colloid chemistry is particularly well suited to this end, since nanoparticles, by definition, are colloidal and since processing of
advanced materials involves reactions at solid-solid, solid-liquid, or solid-gaseous interfaces (19).

At this point I would like to leave the reader with an even more advanced look into the future of materials and technologies that was described by G.M. Whitesides (20) as the following:

_In the 21st century, scientists will introduce a manufacturing strategy based on machines and materials that virtually make themselves. Called self-assembly, it is easiest to define by what it is not. A self-assembling process is one in which humans are not actively involved, in which atoms, molecules, aggregates of molecules, and components arrange themselves into ordered, functioning entities without human intervention. In contrast, most current methods of manufacturing involve a considerable degree of human direction. We, or machines that we pilot, control many important elements of fabrication and assembly. Self-assembly omits the human hand from the building. People may design the process and they may launch it, but once under way it proceeds according to its own internal plan, either toward an energetically stable form or toward some system whose form and function are encoded in its part. In the next few decades, materials scientist will begin deliberately to design machines and manufacturing systems explicitly incorporating the principles of self-assembly. The approach could have many advantages. It would allow the fabrication of materials with novel properties. It would eliminate the error and expense introduced by human labor. And the minute machines of the future envisioned by enthusiasts of so-called nanotechnology would almost certainly need to be constructed by self-assembly methods._

6.4. References


Summary

Hydrogen mixed conductors are the products of the reactions of many elements and compounds with hydrogen. They can be divided into three classes of materials families: i) those, in which hydrogen is in solid solution in a metal whose crystal structure is that of the parent metal; ii) those which form new so-called hydride phases in the presence of hydrogen, generally at relatively high hydrogen activities - the metal hydrides, and iii) oxides containing appreciable concentrations of hydrogen, called hydrogen bronzes.

As described in Chapter 1, hydrogen mixed conductors are materials (solids or liquids) that transport hydrogen as ionic or atomic species and in addition some show an appreciable electronic conductivity due to the metallic character of the host metal lattice. Thus, they can be utilized in a number of applications such as hydrogen storage and purification devices and heat pumps, in which gaseous hydrogen, H2, is the reactant, and the reaction occurs at the gas/metal interface. In other applications such as rechargeable nickel metal-hydride batteries, water electrolysis cells and fuel cells, hydrogen thermoelectric devices, and electrochromic devices the reaction with hydrogen takes place in an electrochemical cell at the electrode/electrolyte interface. In such systems hydrogen mixed conductors can serve either as electrodes or as electrolytes, depending on their individual thermodynamic and kinetic properties.

This thesis discusses the use of solid-state-ionic concepts to study the thermodynamic and kinetic properties of hydrogen mixed conductors by applying electrochemical techniques (see Chapter 2). These refer to the potential phase relationships in binary, ternary, and quaternary systems, the thermodynamic stability regimes of electrodes and electrolytes, the chemical diffusion coefficient of the active species in electrochemical devices, and the electrolyte conductivity.
The central experimental set-up used in several investigations was a galvanic cell of the general type as described in Chapters 1 and 2. The techniques that were used throughout the work were the coulometric titration technique to look at materials under equilibrium conditions, and the galvanostatic or potentiostatic intermittent titration techniques, transient techniques, to observe moving species.

Two systems, one based on titanium-nickel (see Chapter 3) and the other on palladium and palladium-lithium (see Chapter 4) have been investigated in terms of their potential/hydrogen concentration relationships, and diffusion measurements have been performed in the single phase regimes using electrochemical techniques at room temperature.

In addition, two new concepts involving the application of hydrogen mixed-conductors in water vapour electrolysis at intermediate temperatures and the use of electrochemical means to influence the behaviour of catalytic surfaces were presented in Chapter 5. In both cases, metallic hydrogen-conducting membranes were utilized.

From the results obtained in Chapters 3 through 5 the following general conclusions can be drawn:

The coulometric titration technique and the galvanostatic intermittent titration technique are suitable for characterizing the thermodynamic and kinetic properties of hydrogen mixed-conductors when proper electrolytes (in terms of stability window and ionic and electronic conductivity) are used, and when sample preparation methods are employed that allow well-defined interface conditions for the electrochemical charge transfer reaction.

Throughout the work it was observed that the properties under investigation strongly depend upon the history of the sample. This is especially pronounced in the results on the diffusion measurements. The sample history, in this case the kind of processing, cooling and annealing, or other treatments such as etching, is responsible for the microstructural features of the sample and thus causes different
behaviour of the moving species. In this work, differences up to an order of magnitude have been observed.

Hydrogen diffusion data in hydrogen mixed-conductors reported in the literature, as well as the data from this work, would be better understood if the microstructural features of the samples were taken into account.

However, some of the applications of hydrogen mixed-conductors have already become commercial products. Examples are the i) Ni/metal hydride rechargeable batteries for consumer applications (portable telephones, camcorders, laptop computers); ii) the phosphoric acid fuel cells for load levelling in natural gas- burning block power stations; iii) the alkaline electrolyser systems for the production of very clean hydrogen; iv) electrochromic rear view mirrors for luxury cars and trucks.

Other applications such as the solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), and the solid polymer fuel cell (SPFC), are still in the pilot production and testing phase. A vast amount of data are available on the basic properties of the materials used in these systems. However, predictions for system performance based on the materials properties typically differ greatly from the experimental results obtained under real conditions.

Electrochemical devices, as they are designed and their components manufactured today, suffer from a common problem, which is related to the local arrangement of the various species involved in the electrochemical reaction at the electrode/electrolyte interface.

Since the major and environmentally most important applications of hydrogen mixed-conductors is their utilization in electrochemical devices, some thoughts and suggestions for further improvements, based upon recent scientific achievements in other disciplines, are given in Chapter 6.
Samenvatting

Waterstof gemengde geleiders zijn het resultaat van reacties van vele elementen en verbindingen met waterstof. Waterstof gemengde geleiders kunnen onderverdeeld worden in drie klassen van materialen: i) die, waarin waterstof is opgelost in een metaal en waarvan de kristalstructuur overeenkomt met die van het metaal, ii) die, welke nieuwe, zogenaamde hydridefasen vormen in aanwezigheid van in het algemeen relatief grote waterstofactiviteiten, de metaalhydriden en iii) oxiden welke aanzienlijke hoeveelheden waterstof bevatten, de waterstof-bronnen.

Zoals beschreven in Hoofdstuk 1, zijn waterstof gemengde geleiders materialen (vaste stoffen of vloeistoffen) welke waterstof als ion of atoom geleiden. Enkele van deze materialen vertonen eveneens een substantiële elektronische geleiding als gevolg van het metallische karakter van het gastrooster. Deze materialen kunnen derhalve aangewend worden voor een aantal toepassingen, zoals in waterstofopslag- en zuiverings-systemen en warmtepompen, waarin gasvormige waterstof de reactant is en de reactie aan het gas/metaalgrensvlak plaatsvindt.

Herlaadbare nikkel-metaalhydride batterijen, waterelektrolysecellen, brandstofcellen, waterstof thermoelektrische en elektrochrome systemen zijn toepassingen, waarin de reactie met waterstof plaatsvindt aan het elektrode/elektrolyt grensvlak in een elektrochemische cel. In zulke cellen kunnen waterstof gemengde geleiders of als elektrode, of als elektrolyt gebruikt worden, afhankelijk van hun individuele thermodynamische en kinetische eigenschappen.

In dit proefschrift worden met behulp van elektrochemische technieken en gebruikmakend van concepten uit de vaste-stof ionica thermodynamische en kinetische eigenschappen van waterstof gemengde geleiders bestudeerd (Hoofdstuk 2). Met name worden de
potentiaal-fasenrelaties in binaire, ternaire en quaternaire systemen en de thermodynamische stabilitéts-domeinen van elektroden en elektrolyten bestudeerd, alsmede de chemische difusiecoefficient van de ladingdragers en de elektrische geleiding van de elektrolyt.

De belangrijkste experimentele opstelling die gebruikt werd in de verschillende onderzoeken was een bepaald type galvanische cel, welke beschreven wordt in Hoofdstukken 1 en 2. Voor de bestudering van de materialen onder evenwichtscondities werd gebruik gemaakt van de coulometrische titratietechniek, terwijl het dynamische gedrag van de ladingdragers bestudeerd werd met galvanostatische of potenioostatische pulstechnieken (GITT, PITT).

De relaties tussen de potentiaal en de waterstofconcentratie werden bestudeerd voor de systemen gebaseerd op titanium-nikkel (Hoofdstuk 3) en op palladium en palladium-lithium (Hoofdstuk 4). Met de electrochemische technieken werden bij kamertemperatuur diffusiemetingen verricht in de eenfasige regimes.

In Hoofdstuk 5 worden twee nieuwe concepten gepresenteerd. Het eerste concept betreft de toepassing van waterstof gemengde geleiders in de elektrolyse van waterdamp bij intermediaire temperaturen, terwijl het tweede concept gebaseerd is op de electrochemische beinvloeding van het gedrag van katalytische oppervlakken. In beide gevallen wordt gebruik gemaakt van metallische waterstof-geleidende membranen.

De resultaten van Hoofdstukken 3, 4 en 5 leden tot de volgende conclusies. De coulometrische titratietechniek en GITT zijn geschikt voor de karakterisering van de thermodynamische en kinetische eigenschappen van waterstof gemengde geleiders, indien elektrolyten met een geschikt stabiliteitsdomein en goede ionen- en elektronische geleiding gebruikt worden. Bovendien dienen de methoden voor de bereiding van de te onderzoeken monsters tot goed gedefinieerde grensvlakcondities te leiden voor de electrochemische ladingsoverdrachtreactie.
Gedurende het onderzoek werd geconstateerd, dat de te bestuderen eigenschappen sterk afhankelijk waren van de voorgeschiedenis van de monsters. In het bijzonder gold dit voor de resultaten van de diffusiemetingen. Voor wat betreft de voorgeschiedenis zijn consolidatie, warmtebehandeling en afkoelprocedures van de monsters, alsmede bijvoorbeeld etsen verantwoordelijk voor de microstructuur en daarmee voor een verschillend gedrag van de migrerende deeltjes. In dit onderzoek werden verschillen van een orde van grootte waargenomen.

Gegevens over the diffusie van waterstof in waterstof gemengde geleiders, zoals gerapporteerd in de literatuur en de in dit onderzoek verkregen gegevens zouden beter begrepen kunnen worden, indien de microstructurele aspecten van de monsters mede in beschouwing zouden zijn genomen.

Niettemin zijn thans verschillende toepassingen van waterstof gemengde geleiders gecommunaliseerd. Voorbeelden zijn i) de nikkel-metaalhydride batterij voor consumentengebruik (mobiele telefoons, camcorders en laptop computers), ii) de fosforzure brandstofcel voor load-levelling in aardgasgestookte energie centrales, iii) de alkalische elektrolyeurs voor de productie van ultrazuivers waterstof en iv) de elektrochrome achteruitkijkspiegels voor luxe auto's en vrachtwagens.

Andere toepassingen, zoals de vaste-oxide brandstofcel (SOFC), de gesmolten-carbonaat brandstofcel (MCFC) en de vaste-polymeer brandstofcel (SPFC) verkeren nog in een test- of pilot productiefase. Een grote hoeveelheid gegevens van de fundamentele eigenschappen van de materialen welke gebruikt worden in deze brandstofcellen, is thans beschikbaar. Echter, voorspellingen van systeemgedrag zoals gebaseerd op de materiaaleigenschappen wijken veelal sterk af van de experimentele resultaten onder realistische operationele condities.

De huidige ontwerpen en vervaardiging van elektrochemische cellen, respectievelijk, hun componenten vertonen een gemeenschappelijk probleem, dat gerelateerd is aan de lokale inbedding van de
verschillende deeltjes, die betrokken zijn bij de elektrochemische reactie aan het grensvlak elektrode/elektrolyt.

Aangezien de voornaamste en vanuit milieu-oogpunt meest belangrijke toepassingen van waterstof gemengde geleiders hun gebruik in elektrochemische cellen is, worden in Hoofdstuk 6 mede gebaseerd op recent verkregen wetenschappelijke resultaten van andere disciplines, enkele gedachten over en suggesties voor verdere verbeteringen gepresenteerd.
Zusammenfassung

"Hydrogen Mixed Conductors" sind die Produkte der Reaktion von Wasserstoff mit vielen Elementen und Komponenten. Sie werden in drei Materialfamilien unterteilt: i) solche, in denen Wasserstoff in fester Lösung vorliegt und die Struktur des metallischen Wirtsgitters erhalten bleibt; ii) solche, in welchen neue Phasen entstehen, die sogenannten Metallhydride; iii) und Oxide, welche hohe Konzentrationen an Wasserstoff speichern können, bekannt auch als Wasserstoffbronzen.


In Kapitel 2 dieser Arbeit wurden Konzepte und Methoden vorgestellt, an Hand welcher die thermodynamischen und kinetischen Eigenschaften von "Hydrogen Mixed Conductors" mit elektrochemischen Methoden untersucht werden können. Diese beziehen sich auf die Zusammenhänge zwischen chemischen Potentialen und Phasen in binären, ternären und quaternären Systemen, den thermodynamischen Stabilitätsbereichen von
Elektroden und Elektrolyten, den chemischen Diffusionskoeffizienten aktiver Spezies und Leitfähigkeiten von Elektrolyten.

Die experimentellen Untersuchungen wurden in einer galvanischen Zelle, so wie sie in den Kapiteln 1 und 2 beschrieben ist, durchgeführt. Die Techniken, welche zur Untersuchung der thermodynamischen und kinetischen Eigenschaften von "Hydrogen Mixed Conductors" eingesetzt wurden waren die Coulometrische Titrationsmethode für Untersuchungen unter Gleichgewichtsbedingungen, sowie galvanostatische und potentiostatische Transientenmethoden zur Untersuchung der kinetischen Eigenschaften.


In Kapitel 5 wurde der mögliche Einsatz von wasserstofftransparenten metallischen Membranen demonstriert. Einmal in einer Wasserelektrolyse bei mittleren Temperaturen und zum anderen in einem elektrochemischen Rektor für katalytische Reaktionen.

Aus den Ergebnissen der Untersuchungen in den Kapiteln 3 bis 5 können folgende Schlußfolgerungen gezogen werden:

Die Coulometrische Titrationsmethode sowie die Galvanostatische und Potentiostatische Transientenmethode sind geeignete Techniken, um "Hydrogen Mixed Conductors" bezüglich ihrer thermodynamischen und kinetischen Eigenschaften zu untersuchen. Das ist vor allem dann der Fall, wenn geeignete Elektrolyte mit entsprechenden Stabilitätsbereichen und ionischen Leitfähigkeiten vorhanden sind, und die Präparationsmethoden klar definierte Bedingungen an der Grenzfläche Elektrode/Elektrolyt erlauben.


Andere Anwendungen, wie z.B. die oxidische Brennstoffzelle (SOFC), die Karbonatbrennstoffzelle (MCFC) und die Polymerbrennstoffzelle (SPFC) befinden sich noch im Test- und Pilotstadium. Obwohl die dafür eingesetzten Materialien intensiv untersucht wurden und viele Ergebnisse über ihre Eigenschaften vorliegen, sind die Betriebseigenschaften unter Realbedingungen noch nicht zufriedenstellend.

Im allgemeinen kann man sagen, daß elektrochemische Systeme, wie sie heute technisch hergestellt werden, hauptsächlich an einer Problematik leiden. Diese ist in der Mikrostruktur verankert und bezieht sich auf das lokale Gefüge der am elektrochemischen Ladungsaustausch beteiligten Phasen.

Da die meisten und aus umweltrelevanten Gründen wahrscheinlich auch wichtigsten Anwendungen von "Hydrogen Mixed Conductors" in
den elektrochemischen Systemen zu sehen sind, wurden in Kapitel 6, ausgehend von neuen wissenschaftlichen Erkenntnissen in anderen Disziplinen, einige Gedanken und Vorschläge zur Verbesserung beschrieben.
# CURRICULUM VITAE

**Personal Data**

<table>
<thead>
<tr>
<th>Academic Title/Name:</th>
<th>Dipl.-Ing. Dr. Martha Maly-Schreiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address:</td>
<td>Ungargasse 9, A-2340 Mödling,</td>
</tr>
<tr>
<td></td>
<td>Austria</td>
</tr>
<tr>
<td>Date/Place of Birth:</td>
<td>January 18, 1954, Linz, Austria</td>
</tr>
<tr>
<td>Marital Status:</td>
<td>Married</td>
</tr>
<tr>
<td>Citizenship:</td>
<td>Austria</td>
</tr>
<tr>
<td>Languages:</td>
<td>German, English</td>
</tr>
</tbody>
</table>

**Education**

<table>
<thead>
<tr>
<th>Year Range</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960 - 1964</td>
<td>Elementary School, Schwertberg, Austria</td>
</tr>
<tr>
<td>1964 - 1968</td>
<td>Secondary School, Gleiß, Austria</td>
</tr>
<tr>
<td>1973 - 1980</td>
<td>Technical University, Wien, Austria</td>
</tr>
<tr>
<td></td>
<td>Technical Chemistry, Dipl. Thesis: 'Anodic dissolution of aluminum in</td>
</tr>
<tr>
<td></td>
<td>aqueous electrolytes containing chloride ions'.</td>
</tr>
<tr>
<td>1980 - 1983</td>
<td>Technical University, Wien, Austria</td>
</tr>
<tr>
<td></td>
<td>PhD Thesis: 'Contribution to the development of ceramic cutting tools</td>
</tr>
<tr>
<td></td>
<td>consisting of alumina, titanium nitride, titanium carbonitride,</td>
</tr>
<tr>
<td></td>
<td>titanium carboxinitride, and zirconium nitride'.</td>
</tr>
</tbody>
</table>

**Professional Experience**

<table>
<thead>
<tr>
<th>Year Range</th>
<th>Position/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1976 - 1978</td>
<td>Technician at the Technical University Wien, Institut of Analytical Chemistry</td>
</tr>
<tr>
<td>1980 - 1981</td>
<td>Technical Staff at the Punzierungsmant Wien</td>
</tr>
<tr>
<td>1984 - 1987</td>
<td>University Assistent at the Technical University Wien, Institut of Electrochemistry</td>
</tr>
<tr>
<td>Year Range</td>
<td>Position</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1987 - 1988</td>
<td>Erwin Schrödinger Fellowship&lt;br&gt;Stanford University, Department of Materials Science and Engineering&lt;br&gt;Stanford, California</td>
</tr>
<tr>
<td>1988 - 1990</td>
<td>Research Associate&lt;br&gt;Stanford University, Department of Materials Science and Engineering&lt;br&gt;Stanford, California</td>
</tr>
<tr>
<td>1989 - 1990</td>
<td>Consultant for the Electric Power Research Institute (EPRI), Palo Alto, California</td>
</tr>
<tr>
<td>1991 - 1996</td>
<td>Scientific Staff at the Corporate Research Centre of the Daimler-Benz Company, Division of Functional Materials, Ulm, Germany&lt;br&gt;Project manager: Lithium Battery for EV application</td>
</tr>
<tr>
<td>since April 1996</td>
<td>Scientific Staff at the Austrian Research Centre Seibersdorf, Engineering Division&lt;br&gt;Project manager: Establishment of smart technologies for advanced materials and products</td>
</tr>
</tbody>
</table>
RELEVANT PUBLICATIONS

1) Thermodynamic properties of titanium-nickel hydrides
   M. Maly-Schreiber, K. Maly, R.A. Huggins
   see Chapter 3

2) Recent experimental work on titanium-nickel hydrides and
   related materials
   M. Maly-Schreiber, R.A. Huggins
   Hydrogen Absorbing Materials / Catalytic Materials, ed. by D.
   see Chapter 3

3) Use of solid state ionic technique to modify the behaviour of
   catalytic surfaces in situ
   T.M. Gür, G. Deublein, M. Schreiber, J. Wolfenstine, R.A. Huggins
   Hydrogen Absorbing Materials / Catalytic Materials, ed. by D.
   see Chapter 5

4) Hydrogen - transporting mixed conductors
   M. Schreiber, R.A. Huggins
   Solid State Ionics, ed. by G.A. Nazri, R.A. Huggins, D.F. Shriver,
   see Chapter 1

5) Novel method for the production of hydrogen by the dissociation
   of water at intermediate temperatures using an electrochemical
   hydrogen pump
   M. Schreiber, R.A. Huggins
   Workshop, Port Jefferson, New York, August 1989
   see Chapter 5

6) Intermediate temperature water vapour electrolysis
   M. Schreiber, G. Lucier, J.A. Ferrante, R.A. Huggins
   Int. J. Hydrogen Energy 16 (6), 373 (1991)
   see Chapter 5
7) Thermodynamic and kinetic properties of hydrogen insertion in Pd and Pd-Li
A. Falanga, M. Schreiber, R.A. Huggins
submitted to Internat. J. of Hydrogen Energy
see Chapter 4

8) Aspects of the electrochemical loading of hydrogen and its isotopes into palladium
see Chapter 4

9) Thermodynamic and kinetic properties of a hydrogen conducting molten salt electrolyte
M. Schreiber, J. Schoonman, R.A. Huggins
to be submitted to Solid State Ionics
see Chapter 5

10) Vorrichtung zur Verminderung von NOx in Abgasen von Kraftfahrzeugen
M. Maly-Schreiber
see Chapter 5