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**Solid oxide fuel cells operating on uniform mixtures
of fuel and air****I. Riess^{*}, P.J. van der Put, J. Schoonman***Laboratory for Applied Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

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Abstract

Fuel cells operating on uniform mixtures of fuel and air have been demonstrated by a few researchers. No clear explanations for these results were given. We present here an analysis of the cell operation principles. It is shown how the selectivity of the electrodes to certain reactions leads to the experimental observation. A quantitative relation between the open circuit voltage and cell parameters is derived.

Keywords: Solid oxide fuel cell (SOFC); Cell operation

1. Introduction

A unique design of fuel cells was suggested many years ago [1]. In this design the same uniform mixture of air with fuel is supplied to both the cathode and the anode. Therefore, there is no need to direct the fuel and air into two separate and sealed compartments as is done in conventional fuel cells. Furthermore, the solid electrolyte (SE) may be porous as leaks are of no concern. This then allows the construction of fuel cells made of a thin layer of a porous electrode on porous or gas permeable solid electrolyte, which in turn is on a dense counter electrode applied on a support. The mixture of air with fuel can be supplied from one side only, as it reaches both electrodes through the permeable SE

[2]. (Care must be taken in this design that the cathode and anode have no direct contact through pores in the SE).

Despite the enormous simplification of this design and its potential technological importance, very little work was done to investigate this idea further. We are aware of only four more works in the field [3-6]. Experimental evidence for the operation of the cell was presented by Eyraud et al. [1], and recently also by Dyer [2], and Hibino and Iwahara [6].

The aim of this note is to summarize the key experimental findings and to provide an explanation for them. In particular, it is intended to show how the reaction of oxygen with fuel can drive the ionic current through the fuel cell, while maintaining a uniform oxygen partial pressure in the gas phase. We state from the outset that the a-symmetry needed to drive the current in a particular direction originates from the difference in the catalytic properties of the two electrodes.

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2. Model and analysis

Hibino and Iwahara [6] used an yttria stabilized zirconia (YSZ) disk as the solid electrolyte. A Ni (80 wt%) YSZ (20 wt%)-cermet served as one electrode and Au as the other. The disk was placed in a stream of a mixture of air and methane (CH_4). The Au electrode turned out to be the cathode (positive). The open circuit voltage measured was 600 mV at 600°C and 350 mV at 950°C. A power output of 2.36 mW/cm² was demonstrated. By isolating the gas flow at each electrode and analyzing the exhaust gases Hibino and Iwahara found the following: At the cathode almost no oxidation of methane took place. Near the Ni-YSZ cermet anode, almost all oxygen disappeared, half the methane was consumed, and the products of the reaction methane with oxygen were obtained.

The operation of such a fuel cell under ideal conditions can be understood as follows. Let one electrode, denoted by C (later shown to be the cathode), be reversible with respect to oxygen adsorption

while totally inert with respect to the fuel, which we take, for simplicity, to be H_2 . Let the other electrode, denoted by A (later shown to be the anode), be reversible with respect to hydrogen adsorption

while totally inert with respect to oxygen. Let the SE conduct oxygen ions, but not protons. The oxygen ions formed at C can migrate into the SE. At the A electrode oxygen ions recombine with protons to form water:

where the place SE/A is on or near the A electrode. We assume that the motion of H_2O from the gas to the SE/A and vice versa and of $\text{H}^+(\text{A})$ to the SE/A and vice versa is not impeded.

The driving force for the motion of O^{2-} ions through the SE is determined by $\Delta\tilde{\mu}_{\text{O}^{2-}}$, the difference in $\mu_{\text{O}^{2-}}$ between the C electrode, where oxygen ions are formed, and the place SE/A where they are consumed by reaction with H^+ . To calculate $\Delta\tilde{\mu}_{\text{O}^{2-}}$

we first write for the reversible reaction (1) (for which local equilibrium is assumed)

$$\frac{1}{2}\mu_{\text{O}_2}(\text{gas}) = \tilde{\mu}_{\text{O}^{2-}}(\text{C}) - 2\tilde{\mu}_{\text{e}}(\text{C}). \quad (4)$$

For the reversible reaction (2):

$$\frac{1}{2}\mu_{\text{H}_2}(\text{gas}) = \tilde{\mu}_{\text{H}^+}(\text{A}) + \tilde{\mu}_{\text{e}}(\text{A}), \quad (5)$$

and for reaction (3) also assumed to be in local equilibrium,

$$\tilde{\mu}_{\text{O}^{2-}}(\text{SE/A}) + 2\tilde{\mu}_{\text{H}^+}(\text{A}) = \mu_{\text{H}_2\text{O}}(\text{gas}). \quad (6)$$

Eq. (6) then defined $\tilde{\mu}_{\text{O}^{2-}}$ at SE/A.

Combining Eqs. (4)–(6) yields

$$\begin{aligned} \Delta\tilde{\mu}_{\text{O}^{2-}} &= \tilde{\mu}_{\text{O}^{2-}}(\text{C}) - \tilde{\mu}_{\text{O}^{2-}}(\text{SE/A}) \\ &= \frac{1}{2}\mu_{\text{O}_2}(\text{gas}) + \mu_{\text{H}_2}(\text{gas}) \\ &\quad - \mu_{\text{H}_2\text{O}}(\text{gas}) + 2(\tilde{\mu}_{\text{e}}(\text{C}) - \tilde{\mu}_{\text{e}}(\text{A})). \end{aligned} \quad (7)$$

Two terms in the RHS of Eq. (7) are related to the voltage of the cells:

$$-qV = \tilde{\mu}_{\text{e}}(\text{C}) - \tilde{\mu}_{\text{e}}(\text{A}), \quad (8)$$

where q is the elementary charge. The other terms on the RHS of Eq. (7) are the change ΔG in the free energy of the gases O_2 , H_2 and H_2O when one mole of H_2O is produced. ΔG refers to the actual conditions of the experiment, and not to the standard conditions

$$-\Delta G = \frac{1}{2}\mu_{\text{O}_2}(\text{gas}) + \mu_{\text{H}_2}(\text{gas}) - \mu_{\text{H}_2\text{O}}(\text{gas}). \quad (9)$$

ΔG is the cause for the driving force for the motion of the oxygen ions in the fuel cell while μ_{O_2} stays uniform in the gas phase. Combining Eqs. (7), (8), and (9) yields

$$\Delta\tilde{\mu}_{\text{O}^{2-}} = -\Delta G - 2qV. \quad (10)$$

Expressing ΔG in terms of a theoretical voltage V_{th}

$$-2qV_{\text{th}} = \Delta G \quad (11)$$

Eq. (10) becomes

$$\Delta\tilde{\mu}_{\text{O}^{2-}} = 2q(V_{\text{th}} - V). \quad (12)$$

Under open circuit condition the total current through the SE vanishes. For an ideal SE no electronic current flows through it. Hence, under open circuit conditions I_i , the ionic current in the SE, vanishes. Then the driving force for the ions $\nabla\tilde{\mu}_{\text{O}^{2-}}$

vanishes, and, therefore, also $\Delta\tilde{\mu}_{\text{O}^{2-}}$. Eq. (12) yields then the open circuit voltage,

$$V_{\text{oc}} = V_{\text{th}} = \frac{1}{2q} \left(\frac{1}{2} \mu_{\text{O}_2}(\text{gas}) + \mu_{\text{H}_2}(\text{gas}) - \mu_{\text{H}_2\text{O}}(\text{gas}) \right). \quad (13)$$

Thus despite the fact that the concentration of oxygen stays uniform in the gas phase a driving force is generated which yields an open circuit voltage given by the free energy change per mole H_2O for the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$. In view of the polarity of the open circuit voltage (C positive, A negative), and the reactions taking place at the electrodes we notice that C is the cathode and A the anode of the fuel cell.

While μ_{O_2} in the gas phase is uniform μ_{O_2} in the SE is not. μ_{O_2} in the SE near the cathode equals μ_{O_2} in the gas phase in view of the reversibility of cathode with respect to oxygen. On the other hand μ_{O_2} in the SE near the anode is not fixed by μ_{O_2} in the gas, because the anode can be considered as a blocking electrode for oxygen. The value of μ_{O_2} there is determined by the local values of $\tilde{\mu}_{\text{O}^{2-}}$ and $\tilde{\mu}_e$.

$$\frac{1}{2} \mu_{\text{O}_2}(\text{SE/A}) = \tilde{\mu}_{\text{O}^{2-}}(\text{SE/A}) - 2\tilde{\mu}_e(\text{A}). \quad (14)$$

Combining Eqs. (4), (7) and (14) yields

$$\begin{aligned} \mu_{\text{O}_2}(\text{gas}) - \mu_{\text{O}_2}(\text{SE/A}) \\ = \mu_{\text{O}_2}(\text{gas}) + 2\mu_{\text{H}_2}(\text{gas}) - 2\mu_{\text{H}_2\text{O}}(\text{gas}), \end{aligned} \quad (15)$$

which can be written also as

$$\mu_{\text{O}_2}(\text{SE/A}) = 2\mu_{\text{H}_2\text{O}}(\text{gas}) - 2\mu_{\text{H}_2}(\text{gas}). \quad (16)$$

The low value of $\mu_{\text{O}_2}(\text{SE/A})$ is determined by the reaction $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$. The theoretical voltage V_{th} can now be interpreted as the Nernst voltage generated by the oxygen chemical gradient in the SE.

3. Comparison with conventional fuel cells

A conventional fuel cell is driven by the chemical potential difference $\Delta\mu_{\text{O}_2} = \mu_{\text{O}_2}(\text{C}) - \mu_{\text{O}_2}(\text{A})$ as determined by the gas in the air (cathode) and fuel (anode) compartments [7,8]. For a reversible anode

$$\mu_{\text{O}_2}(\text{A}) = 2\mu_{\text{H}_2\text{O}}(\text{A}) - 2\mu_{\text{H}_2}(\text{A}). \quad (17)$$

Therefore $\frac{1}{2}\Delta\mu_{\text{O}_2}$ in a conventional fuel cell equals ΔG of Eq. (9). This shows that the Nernst voltage is the same for both types of fuel cells.

Having an expression for V_{th} one can calculate the I - V relations of the cell [7,8]

$$I_i = \frac{V_{\text{th}} - V}{R_i}, \quad (18)$$

where R_i is the resistance of the SE to ion current. Eq. (18) holds for both types of fuel cells.

4. Experimental considerations

Experimentally, the open circuit voltage measured depends on the electrode material [2] and temperature [6], and obtains values lower than the theoretical value V_{th} . We argue that this is because the electrodes are not ideally selective as assumed before. We still assume the SE to be ideal in the sense that the permeation current under open circuit conditions can be neglected. The side reaction that lowers V is the direct reaction $\frac{1}{2}\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$ on the electrodes. This occurs because the cathode is not totally inert to H_2 , and the anode not totally inert to O_2 and both types of ions, O^{2-} and H^+ , are produced (at different rates) on the electrodes and combine to form H_2O . As a result $\mu_{\text{O}_2}(\text{SE/A})$ does not obtain the value given in Eq. (16), but rather an intermediate value between that one and $\mu_{\text{O}_2}(\text{gas})$. As a result $\Delta\mu_{\text{O}_2}$ on the SE is lowered, and, therefore, the driving force for the motion of oxygen through the SE is lowered as well. The side reaction causes also fuel waste.

Dyer [2] has shown that an open circuit voltage as well as power output can be measured in a uniform oxygen and fuel mixture on a cell comprising a SE (γ - AlOOH or Nafion) with two metal electrodes. The cell construction is: quartz substrate, Pt, Ni or Pd electrode, SE, and a second porous Pt, Ni or Pd electrode on top of the SE. Two special properties of the cell are to be noticed: (a) the gas mixture can be supplied only from the side of the outer porous electrode; (b) both electrodes can be made of the same material Pt. Then the anode is the outer electrode and the cathode the inner electrode.

The fact that the gas mixture can be applied only on one side can be understood if the SE is permeable for O_2 , H_2 and H_2O .

The fact that Pt can be used on both sides requires an explanation which shows where the symmetry does break. It is obvious that a symmetric cell cannot deliver power. Gottesfeld [5] suggests that the difference in Pt catalytic behaviour of the two Pt electrodes is due to a thin oxide layer which is more likely to form on the inner Pt electrode than on the outer one, because of the more impeded hydrogen supply.

One interesting conclusion is that the SE need not be prepared impervious. Furthermore it may be advantageous not to prepare it impervious to O_2 , H_2 and H_2O , and to supply the gas mixture only from one side. This can simplify considerably the cell construction. The substrate can then be a conductive foil or plate on which submicron thick solid electrolyte layers are applied. In comparison, in the conventional construction of fuel cells with thin SEs one has to worry about the impedance of gas permeation through a porous but thick support. On the other hand the cell performance depends on the catalytic properties and research has to be done to improve the selectivity of the electrodes. This will reduce voltage loss and fuel waste, which originate from a direct fuel–oxygen reaction. It should be noticed that three reactions should be catalyzed, i.e.

O^{2-} formation, H^+ formation and H_2O formation and desorption (Eqs. (1)–(3) respectively). The SE may participate in the reactions. However, even if the reaction occurs only on the electrodes, the SE determines at which electrode water is produced. If the SE conducts protons, then it is the cathode, and when it conducts oxygen ion, it is the anode where water is formed. In either case one of the electrodes has to catalyze two processes: formation of one kind of ion, and water formation and desorption.

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