Electrical properties of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in hydrogen containing atmospheres

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The results of dc and impedance spectroscopy measurements on $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ are presented. The effect of the influence of a hydrogen atmosphere on the conduction mechanism is discussed. A correlation between the electrical conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ and the hydrogen partial pressure has been obtained.

1. Introduction

High-temperature proton conductivity of perovskite-type oxides has been reported by Iwahara some 10 years ago [1,2]. These oxides are based on SrCeO_3 and BaCeO_3 in which cerium has been substituted partially by trivalent cations. These materials are usually electronic or oxygen ionic conductors but in hydrogen-containing atmospheres protonic conductivity is observed. Similar results have been found in KTaO_3 crystals doped with acceptor impurities like Cu^{2+} , Fe^{3+} , Ni^{3+} [3].

Ceramic proton conductors can be used in many solid state electrochemical devices such as fuel cells, steam electrolyzers and gas sensors [4–6]. From a fundamental point of view, the perovskite-type oxides are also interesting because they present a class of materials with mixed ionic and electronic conductivity, in which it is possible to change the ratio of ionic and electronic part of the electrical conductivity. The electrical transport in these conductors is strongly determined by the composition of the gas atmosphere and hence the possibility to generate ionic lattice defects, electrons or holes in these materials.

However, the proton migration mechanism has not yet been determined in detail. Two models have been

proposed to describe the dynamics of the proton transport. The first is the “free migration” mechanism: the proton moves by jumping between stationary host oxygen ions.

The second model is called the “vehicle” mechanism: the proton moves as a passenger on a larger ion, such as OH^- or H_3O^+ [7]. The latter conductivity mechanism can be confirmed by IR-absorption measurements in which it is possible to monitor OH^- stretching vibrations [3,8].

Trivalent impurities in SrCeO_3 or BaCeO_3 probably play an essential role in the proton transport, since pure SrCeO_3 and BaCeO_3 exhibit only low electronic conductivity. Oxygen ion vacancies or electron holes, which are generated by acceptor dopants, like Yb, Y and Sc seem to play an important role in the proton conduction mechanism. However, not all acceptor-doped BaCeO_3 materials exhibit protonic conduction. For example, Gd^{3+} , Eu^{3+} and Yb^{3+} -doped BaCeO_3 are oxygen-ion conductors [9]. This fact indicates that the conduction mechanism has a more complex dependence on dopant ions, and may also be connected with the interaction between dopant ions and oxygen ion vacancies.

In order to understand the relationships between the ionic conductivity, the structure, defect structure, and the composition of $\text{SrCe}_{1-x}\text{Yb}_x\text{O}_3$, Raman spectroscopy and ionic conductivity measurements were conducted [10]. A correlation between the concentration of Yb^{3+} ions and oxygen ion vacan-

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cies, which are formed upon the substitution of Ce^{4+} by Yb^{3+} , has been found. The introduction of Yb^{3+} ions into SrCeO_3 is manifested by a rise in the ionic conductivity, attaining a maximum for $x=0.05$, and a decrease in the conductivity activation energy. The effect of generating oxygen ion vacancies by Yb^{3+} doping is also observed by Raman spectroscopy in the variation of the line shape at a frequency of 348 cm^{-1} , which represents the vibration involving the oxygen octahedron. A linear dependence between the Yb concentration and the half-width of this line has been found [10]. These measurements indicate that Raman spectroscopy can be used to observe the effects of doping the perovskite-type oxides with acceptor impurities.

The introduction of protons into the trivalent-doped perovskite-type oxides can be achieved by annealing the material in water vapor [3,9,11,12], or in hydrogen containing atmospheres [6,13,14]. The first method was proposed by Nowick and coworkers for the study of the protonic conduction in KTaO_3 [3] and SrCeO_3 [11,15]. The samples were treated in an appropriate gas atmosphere at 900°C . The measurements were made in the range from 25 to 200°C in an ambient atmosphere. The results were found to be completely reversible with temperature, and to be unaffected by the atmosphere. The samples retained a fixed proton concentration in a frozen-in condition during all of the measurements.

This method of studying proton conductivity in cerates contrasts with that reported by others, who made measurements at high temperatures allowing the samples to equilibrate dynamically with the ambient atmosphere at each temperature. In this case the electrical properties of the cerates will be determined by the partial hydrogen or water pressure in the ambient atmosphere. This later method seems to be more realistic for operating conditions of the solid state electrochemical hydrogen devices. Our recent electrical conductivity measurements of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ show that the concentration of hydrogen in the surrounding atmosphere has no effect on the bulk electrical conductivity [16]. For this reason we have conducted a more detailed study of the electrical properties of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in different hydrogen atmospheres.

In this paper the results of Raman scattering and electrical conductivity measurements for

$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ are presented. Previous work demonstrated that this composition exhibits the most optimal conductivity [11,12,17].

The aim of this work is to study the influence of the hydrogen atmosphere on the electrical conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$, and to find a correlation between the hydrogen partial pressure and the electrical properties of this material. Impedance spectroscopy and potentiostatic methods were used for the determination of the bulk and low frequency conductivity in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$. Raman spectroscopy was used for the observation of the OH^- group which is formed in the cerate in hydrogen containing atmospheres.

2. Charge carrier generation and mixed conductivity in oxides

Generally, the electrical properties of oxygen ion conductors are determined by the partial oxygen pressure or a reducing gas atmosphere. Solid-gas interactions will generate or annihilate ionic defects, and electrons or holes in ceramic electrolytes. At high oxygen partial pressures the dissolution of oxygen into the lattice produces holes at the expense of oxygen ion vacancies [13,18,19]:

At low oxygen partial pressures oxygen ions may leave the lattice, thereby generating electrons and oxygen ion vacancies [19,20]:

From these reactions it can be concluded that the concentration of holes or electrons is a function of the oxygen partial pressure. Reactions (1) and (2) describe the deviation from stoichiometry that leads to mixed conductivity. The expression for the total conductivity is given by [20] provided that the concentration of oxygen ion vacancies is fixed by the acceptor dopant:

$$\begin{aligned} \sigma_{\text{tot}} &= \sigma_i + \sigma_e + \sigma_h \\ &= \sigma_i + B(P_{\text{O}_2})^{-1/4} + C(P_{\text{O}_2})^{+1/4}, \end{aligned} \quad (3)$$

where P_{O_2} is the oxygen partial pressure in the ambient atmosphere. Fitting the experimental data to

eq. (3) allows one to determine the partial conductivities.

Mixed conductivity is observed in stabilized zirconia [21,22] and in many other oxides [20]. Also in the case of $\text{BaCeO}_3\text{:Gd}$ a strong dependence of the electronic conductivity with oxygen ambient atmosphere was observed [18]. The generation of electron holes in BaCeO_3 may be described by reaction (1). Recently, it has been reported that $\text{CaTiO}_3\text{:Fe}$ and BaCeO_3 ceramics are mixed oxide ion and electron hole conductors, stable under reducing atmospheres up to high temperatures [23].

The electrical conductivity of some oxides can be modified by dissolution of water into the lattice [9,12]:

This reaction leads to the introduction of protons into the electrolyte, which will be bonded to oxygen ions forming OH^- groups. In this case the ionic conductivity is a function of the water partial pressure, as has been reported in [9,12]. Protons can also be introduced as a result of the reaction of hydrogen with oxygen lattice ions:

In this case we can expect an increase of the electronic conductivity, and its value will be determined by the hydrogen partial pressure. This reaction leads to mixed conductivity. For this reason we conducted electrical conductivity measurements of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as a function of temperature and hydrogen partial pressure. We used reaction (5) to interpret the obtained results.

3. Experimental aspects

Ceramic $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ samples were obtained from the SCK/VITO in Mol (Belgium) in the framework of a joint research program under Joule Contract number JOUF 0029-C. The procedure reported by Iwahara [24] was used. A well-determined mixture of SrCO_3 (99.4%, Johnson Matthey), CeO_2 (99.999%, Jansen Chimica) and Yb_2O_3 (99.9%, Fluka Chemie) was calcined at 1673 K for 10 h in air. The calcined oxides were subsequently milled, shaped into pellets via cold isostatic pressing,

and finally sintered at 1823 K for 10 h in air.

The structure of the samples was checked with X-ray diffraction. The samples exhibit the orthorhombic perovskite-type structure after this synthesis procedure. The $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ samples obtained in this way were then investigated using impedance spectroscopy, potentiostatic and Raman scattering measurements.

The electrical conductivity was determined from impedance measurements, performed using a Solartron 1260 Frequency Response Analyzer. The spectra were recorded for frequencies in the range of 0.1 Hz to 10 MHz in a temperature region of 450 K to 1225 K in pure argon as well as in hydrogen containing gas mixtures. The concentration of hydrogen in $\text{Ar} + \text{H}_2$ atmosphere was varied between 0 and 100%. The impedance spectra were analyzed to yield the bulk and low-frequency conductivity using the curve-fit computer program EQUIVCRT, by Boukamp [25]. The low-frequency conductivity was also determined from current-voltage characteristics, which were obtained from potentiostatic measurements. In all electrical measurements sputtered platinum electrodes have been used.

The Raman spectra were recorded at room temperature for samples annealed in hydrogen atmospheres in the frequency range 1200–4000 cm^{-1} using a Jobin-Yvon "U1000" double monochromator equipped with two holographic gratings. The excitation source was the 5145 Å line of an Ar^+ ion laser at a power level of 100 mW.

4. Experimental results

Fig. 1 shows the impedance spectra of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ measured with platinum sputtered electrodes in atmospheres with different hydrogen concentration at fixed temperatures of 573, 758 and 1013 K. The spectra could be fitted with the equivalent circuit shown in the insert of fig. 1. The Q -element in fig. 1 represents the constant-phase element, and has an impedance $Z_Q = B(i\omega)^{-\alpha}$ and is connected with the polarization effects at the electrode-electrolyte interface. C_g and R_b represent the bulk response, R_F represents Faradaic processes at the electrode interface. Elements R_{gb} and C_{gb} are connected with the grain boundary resistance and capacity, re-

Fig. 1. Impedance spectra of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ with platinum sputtered electrodes in different H_2 +Ar atmospheres and temperatures.

spectively. The equivalent circuit which was used (fig. 1) gives the possibility to separate the bulk and electrode phenomena and also to determine the elec-

tronic resistance, R_e which is connected with the electron transport through the sample and electrode-electrolyte interface as the result of reaction (5).

The high-frequency semicircle is connected with the bulk resistance, while electrode polarization phenomena predominate at low frequencies. At intermediate frequencies, grain boundary polarization effects are manifest at low temperature. It should be noted that this interpretation needs to be confirmed by other experimental techniques. At high temperatures the grain boundary effects are reduced, and the spectra can be fitted with a simplified circuit. As can be seen, the major differences between the spectra occur in the electrode effects. In hydrogen free atmospheres the impedance spectra revealed substantial electrode blocking effects. In hydrogen containing atmospheres a curvature to the real axis is observed with increasing hydrogen concentration and temperature (fig. 1). This difference can be attributed to hydrogen diffusion through the platinum layer, thereby reducing the electrode blocking effects. A similar dependence of the impedance spectra for $\text{BaCeO}_3\text{:Gd}$ with silver electrodes was reported by Bonanos [14].

The fitting procedure of impedance spectra provides the possibility to separate the high- (σ_1) and low- (σ_2) frequency part of the conductivity. Figs. 2 and 3 present the results of these calculations conducted for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ at two temperatures as a function of hydrogen concentration. The value of σ_1 was calculated from the high-frequency part of the impedance spectra and is connected with the bulk resistance (R_b). The conductivity σ_2 was derived from R_F , resulting from the fitting procedure. In the impedance spectrum the low-frequency intercept with the real axis equals $R_b + R_F$ (fig. 1).

When the high- and low-frequency effects are separated, as has been presented in figs. 2 and 3, it is seen, that at high temperatures the bulk conductivity is nearly independent of the hydrogen concentration. This confirms our previous results [16].

The bulk conductivity at 758 K changes from $9 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ to $1.1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ when the hydrogen concentration is changed from 0 to 5% (fig. 2). For higher concentrations of hydrogen the bulk conductivity remains practically constant (figs. 2 and 3). Similar effects of minor changes in the bulk

Fig. 2. Bulk (σ_1) and low-frequency (σ_2) conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as a function of the hydrogen concentration in H_2 -Ar gas mixtures at 758 K. Values of σ_1 and σ_2 were determined from a fit of the impedance spectra to the equivalent circuit.

Fig. 3. Bulk (σ_1) and low-frequency (σ_2) conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as a function of the hydrogen concentration at 1013 K. Values of σ_1 and σ_2 were determined from fit parameters.

conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ were reported in [13]. At a temperature of 673 K the bulk conductivity in air equals a value of $1.4 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. In 5% H_2 atmosphere this value increases to $2.2 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$.

The electronic conductivity (σ_e) which has been obtained from the fitting procedure is about two orders of magnitude smaller than the bulk conductivity (σ_b), and its value increases in hydrogen atmosphere. The electron conductivity at 758 K changes from $1.15 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ to $4.5 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ when the hydrogen concentration is varied from 0 to 5%. For all hydrogen atmospheres the electronic conductivity is smaller than the bulk conductivity. The ratio σ_b/σ_e attains a value of 70 at 758 K in argon, while in hydrogen its value changes to 7–9, which may suggest that the electrical transport in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ is dominated by ionic conductivity in both argon and hydrogen atmospheres.

The low-frequency part of the conductivity σ_2 , which is connected with the Faraday processes, is a function of the concentration of hydrogen and changes for all concentrations of hydrogen (figs. 2 and 3). The value of σ_2 increases about two orders of magnitude.

For stabilized zirconia in oxygen ambient a similar effect has been observed, where the low-frequency part of the conductivity changes with the oxygen concentration [21]. This effect indicates chemical reactions occurring between electrodes and solid electrolyte. With regard to the role of the oxygen exchange between the gas and the solid electrolyte (reaction (1)), it is generally assumed that the electrons are stripped off from the metallic electrode and the reaction happens only at the triple contact line where the gas, the electrolyte and the electrode come together [22]. The result of reaction (1) will be the generation of holes in the solid electrolyte which can take part in the conductivity.

A similar effect has been observed here for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in the different ambient atmospheres. Fig. 4 shows the impedance spectra of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in argon, hydrogen and air at 758 K. The bulk resistance is not changed in argon or hydrogen (figs. 1 and 4) but in air a very large change of impedance spectra is observed (fig. 4). This variation can be explained also by reaction (1) as the result of the electron hole generation. The presented

Fig. 4. Impedance spectra of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ with platinum sputtered electrodes in different ambient atmospheres at 758 K.

results confirm the hypothesis that the bulk conductivity in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ is determined by oxygen ions and that hydrogen atmosphere does not influence its value.

Parallel with impedance spectroscopy, we have conducted dc measurements on $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as a function of the hydrogen concentration. Current-voltage characteristics were recorded only when the current was independent of time. On application of a constant voltage currents decayed with time, and became stabilized after 40 min. In principle, this gives the possibility to separate electronic and ionic parts of the current provided that the electrodes are ionically blocking. The dc resistance was derived from the slope of the straight line in the I - V characteristics.

In pure argon the I - V characteristics are non-linear, as is shown in fig. 5, indicating that the current is limited partly by mass and electron transfer phenomena. In this case the current will be defined by charge carrier transfer between electrodes and electrolyte. An increase in the current with a factor of 100 is observed in hydrogen containing atmospheres (figs. 6 and 7). Furthermore, the I - V characteristics show a linear ohmic behavior over a relatively large range of voltages suggesting that the time-independent dc current is connected with electronic conduction. The presence of the electronic conductivity can be the result of chemical reactions between the electrodes, electrolyte and hydrogen.

Fig. 5. I - V characteristics of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ with Pt electrodes in argon atmosphere at 758 and 1013 K.

It should be stressed that a correlation exists between the electrical conductivity which was determined from I - V measurements and the electronic conductivity obtained from impedance spectroscopy. The dc conductivity at 758 K changes from $10^{-5} \Omega^{-1} \text{cm}^{-1}$ to $4 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ when the hydrogen concentration is changed from 0 to 5%. In this case the conductivity increases by a factor of about 40 which is concordant with the electronic

Fig. 6. I - V characteristics of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ with Pt electrodes for different hydrogen concentration in H_2 -Ar gas mixtures at 758 K.

Fig. 7. I - V characteristics of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ with Pt electrodes for different hydrogen concentration in H_2 -Ar gas mixtures at 1013 K.

conductivity values determined from impedance spectroscopy. This relation confirms the increase of the electronic conductivity to be the result of a chemical reaction between hydrogen and lattice oxygen ions (5).

Electronic conductivity in perovskites in a hydrogen atmosphere has been observed also for $\text{BaCeO}_3:\text{Gd}$ [14,18]. The impedance spectra at 200°C indicate ionic conduction, but the distortion of the electrode part of the spectrum at 600°C has been interpreted as associated with electronic conductivity. In [18] it is demonstrated that $\text{BaCeO}_3:\text{Gd}$ shows n -type conductivity at low oxygen partial pressure. This suggests that in a hydrogen atmospheres also n -type conductivity can occur.

In a study of the transport properties of $\text{BaCeO}_3:\text{Nd}$ [9] in water vapor it has been demonstrated that although protonic conduction dominates at lower temperatures, the ionic transport number for hydrogen strongly decreases at temperatures higher than 550°C . This observation can also be explained by increasing the electronic conduction.

From the I - V characteristics the conductivity of the sample can be determined. From the impedance

Fig. 8. Total conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as a function of hydrogen concentration at 758 and 1013 K.

spectra an overall conductivity can be derived from the sum of diameters of the semicircles in the impedance diagrams $-(R_b + R_F)^{-1}$. Fig. 8 presents these conductivities as a function of the hydrogen concentration. A good agreement between the results from dc measurements and impedance spectroscopy is observed. From fig. 8 it is seen that the total conductivity is a function of the hydrogen concentration. This correlation confirms the hypothesis that the electronic conductivity is determined by chemical reactions between the electrode, solid electrolyte and gas. On the other hand the low-frequency part of the conductivity can also be due the motion of OH^- groups resulting from reaction (5).

5. Conductivity behavior

As is shown in fig. 8, the electrical conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ is a monotonically increasing function of the hydrogen partial pressure. The predominance of electronic conductivity in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in hydrogen atmosphere can be demonstrated by the following three points:

(i) The platinum electrodes loose their blocking character in hydrogen containing atmospheres. Taking into account the fact that hydrogen in "free" form is not observed in this material (hydrogen is bonded in the OH^- group) we can expect that platinum electrodes will be blocking in case of ionic conduction, unless that transfer of protons from the electrodes to the lattice and vice versa is very fast.

(ii) The current-voltage characteristics in hydrogen atmospheres are linear and the electrical conductivity is a function of hydrogen partial pressure.

(iii) The values of the electrical conductivity determined from dc measurements and the low-frequency parts of impedance spectra are similar. The increase of the electrical conductivity in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ with the hydrogen concentration can be explained as a result of a chemical reaction (5) between hydrogen from the atmosphere and the solid electrolyte.

The hydrogen is incorporated into the lattice and is bonded to oxygen ions. The results of this reaction will be the formation of OH^- groups and electrons, which can take part in electrical transport. The presence of OH^- can be demonstrated by Raman spec-

troscopy and will be discussed later. If we apply the mass action principle to eq. (5) we obtain:

$$P_{\text{H}_2} * K(T) = [\text{OH}^-]^2 * [\text{e}']^2, \quad (6)$$

where $K(T)$ is the equilibrium constant of the reaction, P_{H_2} the hydrogen partial pressure, $[\text{OH}^-]$ and $[\text{e}']$ the concentrations of OH^- groups and electrons, respectively. The charge neutrality equation will then be:

$$[\text{Yb}_{\text{Ce}}'] + [\text{e}'] = 2[\text{V}_{\text{O}}^{\bullet\bullet}] + [\text{OH}^-]. \quad (7)$$

The hydrogen dependence of the electronic conductivity can be explained if we assume that the electron concentration in the solid electrolyte is generated by reaction (5). This assumption is supported by the increase of the dc conductivity with about two orders of magnitude in hydrogen containing atmospheres compared with the conductivity which was determined in argon (figs. 5–7), indicating that the time-independent dc conductivity has an electronic nature. It has been demonstrated that Yb_{Ce}' is mainly compensated by $\text{V}_{\text{O}}^{\bullet\bullet}$ [15]. An experimentally determined pre-exponential factor of the temperature dependence of the conductivity for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ is two orders of magnitude smaller than theoretically calculated under the assumption that the proton concentration is equal to the Yb concentration. From this it was concluded that only a small fraction of the dopant ions is compensated by protons [15]. Therefore,

$$[\text{Yb}_{\text{Ce}}'] = 2[\text{V}_{\text{O}}^{\bullet\bullet}]. \quad (8)$$

Based on eqs. (7) and (8) we obtain:

$$[\text{OH}^-] = [\text{e}']. \quad (9)$$

This implies that the incorporation of hydrogen into the lattice does not substantially affect the defect chemistry of the system, besides generating an equal number of electrons. However, in all cases $2[\text{V}_{\text{O}}^{\bullet\bullet}] = [\text{Yb}_{\text{Ce}}'] \gg [\text{OH}^-] = [\text{e}']$.

From eqs. (6) and (9), and assuming that the mobility of the electrons generated in reaction (5) is independent of the partial hydrogen pressure, and much larger than that of the OH^- groups, we can expect that the electronic conductivity is a function of hydrogen pressure:

$$\sigma_e \sim P_{\text{H}_2}^{1/4}. \quad (10)$$

Eq. (10) was used to fit the experimentally determined values of the conductivity as a function of the hydrogen partial pressure. The results of the calculations are the following: for $T=758\text{ K}$ $\sigma = 1.3 \times 10^{-4} + 7.3 \times 10^{-4} (P_{\text{H}_2})^{1/4}$ and for $T=1013\text{ K}$ $\sigma = 1.54 \times 10^{-4} + 9.7 \times 10^{-4} (P_{\text{H}_2})^{1/4}$. A good agreement between the calculations and the experimental results is observed (fig. 8). It should be noted that the conductivity in the absence of hydrogen resulting from these fits is larger than has actually been measured in argon, supporting the idea that the conduction mechanism changes in the presence of hydrogen in the lattice.

The presence of hydrogen in perovskite-type oxides is confirmed by infrared absorption measurements. This technique was used to monitor the concentration of OH^- in Fe-doped KTaO_3 [3] and Y-doped SrCeO_3 [8]. After annealing these materials in water vapor two absorption bands have been found at frequencies around 2400 and 3200 cm^{-1} , which are in the frequency region characteristic for OH stretching vibrations in crystals [8]. These results show that the interstitial protons are strongly associated with a neighboring oxygen ion.

Raman spectroscopy can be used also for observations of the OH^- vibrations. Fig. 9 presents the Raman spectra of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ before and after annealing in hydrogen at 500°C during four hours. In the annealed sample two additional Raman lines at the frequencies 1646 and 2289 cm^{-1} have been observed, which can be interpreted as OH^- group vibrations. This result supports the mechanism of hydrogen incorporation into $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as is presented in the chemical reaction (5).

The conductivity mechanism of protons in perovskite-type oxides is an open question. As confirmed by the infrared absorption and Raman scattering measurements, protons cannot be in "free" H^+ states, and are bound to OH^- groups. In ref. [11] it is pointed out, that the protons can migrate by a hopping mechanism from one oxygen ion to the next nearest neighboring one. In this case the protonic conductivity seems to be independent of the concentration of dopants, which influence $[\text{V}_{\text{O}}^{\bullet\bullet}]$. This conclusion is contrary to the experimental results. The ionic conductivity of acceptor doped cerates and the oxygen ion vacancies, which are formed during doping play an essential role in protonic transport

Fig. 9. Raman spectrum of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ annealed in hydrogen atmosphere.

[3,5,9,10,17]. Another possibility to explain the motion of protons is the "vehicle" mechanism, where the proton moves as a passenger on a larger oxygen ion. The fact that the bulk conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ is independent of the hydrogen concentration in the surrounding gas atmosphere supports the vehicle model. The protonic conductivity will then be determined by the oxygen ion conductivity and therefore by the concentration of oxygen ion vacancies. Therefore, the oxygen and proton conductivity are interrelated [13,14].

Taking into account the results presented above on the electrical conductivity we arrive at the conclusion that the electrical properties of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in hydrogen containing atmospheres at high temperatures are determined by chemical reactions between electrodes, ambient atmosphere and solid electrolyte. The electrons are generated by the chemical reaction between hydrogen and lattice oxygen ions. The ionic conductivity is practically independent of the hydrogen concentration. The protons are present in the lattice in OH^- groups which can be observed in infrared absorption and Raman scattering.

In order to improve the understanding of the role

played by the acceptor impurities in protonic conductivity, it is necessary to conduct more detailed studies on the electrical properties of $\text{SrCe}_{1-x}\text{Yb}_x\text{O}_3$ in different hydrogen and for ytterbium concentrations. Also it is necessary to conduct a more detailed study of the chemical reactions at the interface electrode–electrolyte using other electrode materials and different gas atmospheres.

5. Conclusions

On the basis of the presented result of electrical conductivity measurements in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$, it is concluded that the electrical properties of this material are strongly dependent on the gas atmosphere. The hydrogen atmosphere has not effect on the bulk conductivity in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$, which is dominated by ionic transport.

Linear current–voltage characteristics and a good correspondence between the values of conductivity obtained from dc measurements and the impedance spectroscopy, suggest that the electrical conductivity of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ in the presence of hydrogen is dominated by electrons which are generated as a result of interface reactions. The increase of electronic conductivity with the hydrogen concentration can be explained as resulting from a chemical reaction between hydrogen and lattice oxygen ions. The products of this reaction are an equal number of OH^- groups, which can be monitored by Raman scattering, and electrons which can take part in the electrical transport. The mobility of the electrons will be much larger than that of the OH^- groups resulting in predominantly electronic transport.

The proton conductivity is probably connected with the motion of OH^- groups in the “vehicle”-type of mechanism. The oxygen and proton conductivity are interrelated.

The relation between the electronic conductivity and the hydrogen partial pressure has been determined. The electrical conductivity can be fitted to a function of $(P_{\text{H}_2})^{1/4}$, both at 758 and 1013 K (fig. 8).

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