Short communication

Charge transfer properties of BaCe$_{0.88}$Nd$_{0.12}$O$_{3-\delta}$ co-ionic electrolyte

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Abstract

Charge and mass transfer in an electrochemical cell, based on an electrolyte possessing both oxygen ion and proton conductivity (co-ionic electrolyte), under the gradient of steam partial pressure was considered from theoretical point of view. It is shown that, due to simultaneous carry of oxygen ions and protons in the same directions, steam permeation through the co-ionic electrolyte occurs. Experiments performed with the BaCe$_{0.88}$Nd$_{0.12}$O$_{3-\delta}$ have confirmed the existence of steam permeation through the co-ionic electrolyte.
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1. General

Solid oxide fuel cells (SOFCs) are considered as the most attractive means for environmentally friendly production of electrical energy in the future. The base of the SOFCs is solid oxides with ionic conductivity. At the first stage, oxides with oxygen ion conductivity were used in the SOFCs. Forrat [1] supposed that some complex solid oxides, namely A$_l$La$_{1-x}$M$_x$O$_3$ (M = Ca, Sr, Ba) had proton conductivity at high temperatures (600–1000 °C). Later, Takahashi [2] demonstrated the presence of proton conductivity in solid oxides like SrZrO$_3$. Since then, many complex solid oxides with proton conductivity had been discovered and studied [3]. It was considered that these types of conductors could also be a basis for SOFCs. Furthermore, it was stated that all "proton conductors" presented also oxygen conductivity. It was offered to call them "co-ionic electrolytes". Each charge carrier "q" can be characterized by a conductivity provided by transfer of this charge carrier, σ_q, namely ions transfer number. The ratio of a partial conductivity to the total conductivity, σ, is called "transfer number", t_q.

One of interesting peculiarity of the oxide conductors having both oxygen ion and proton conductivities, namely, simultaneous transport of both ion carriers in the case of a steam partial

pressure gradient, was theoretically predicted [4]. In the result of this phenomenon, steam "penetrates" (in the form of fluxes of oxygen ions and protons) through the conductor from one side with higher steam concentration to the other side with lower steam concentration. The analysis showed that the steam permeation influenced the SOFC characteristics. It is important from theoretical and practical point of view to experimentally investigate this theoretically predicted phenomenon.

2. Theory

A model cell based on a co-ionic electrolyte is shown in Fig. 1a. It represents a ceramic sample having both oxygen ion and proton conductivity, opposite sides of which are in contact with gas phases. The electrolyte is characterized by total conductivity, σ, and partial conductivities, σ_O and σ_H; ratios σ_O/σ and σ_H/σ are called ionic transfer numbers, t_O and t_H. The gas phase is characterized by dimensionless (relative) partial pressures of oxygen, hydrogen and steam: p_{O_2}, p_{H_2} and p_{H_2O}. In the case when oxygen or hydrogen are the components of gas mixture their partial pressures are equal to their molar fractions; in the case when oxygen or hydrogen is chemically bonded their partial pressures are calculated by equations

$$p_{O_2} = \left(\frac{p_{H_2O}}{K p_{H_2}} \right)^2 \tag{1}$$

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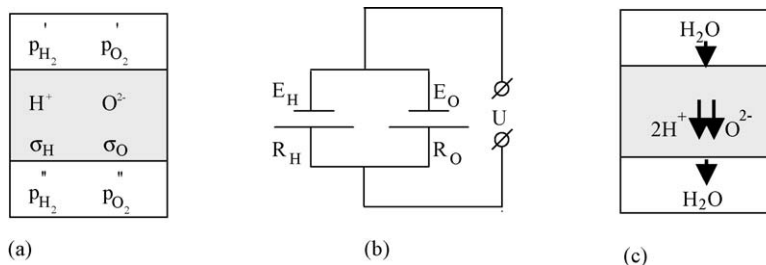
Fig. 1. A schematic view of the cell based on the co-ionic electrolyte (a), an equivalent scheme of this cell (b) and a schematic diagram of a process of steam permeation (c).

$$p_{H_2} = \frac{p_{H_2O}}{K p_{O_2}^{1/2}} \tag{2}$$

where K is equilibrium constant of the hydrogen oxidation reaction. International System of Units (SI) was used for all equations and all calculations in this work.

An equivalent circuit of the cell is shown in Fig. 1b. It consists of two current sources connected in parallel. Each current source is characterized by corresponding electromotive force (emf), E_{O_2} or E_{H_2} due to oxygen partial pressure or hydrogen partial pressure drop, and internal resistance, R_O or R_H, for transfer of oxygen ions and protons, respectively. In principle, the scheme must include resistances of reactions at gas–electrolyte interface; however, experiments testify that these resistances are negligible compared to the volume resistances R_O and R_H. According to the results obtained in the Institute of High Temperature Electrochemistry, a specific resistance of an electrode reaction in reduced atmosphere at about $900\,°C$ was about $0.1\,\Omega\,cm^2$, whereas the Ohmic specific resistance of the sample of about 1 mm thick was more than $3\,\Omega\,cm^2$ [5].

The electromotive forces are calculated according to the following equations

$$E_{O_2} = -\frac{RT}{4F} \ln \frac{p''_{O_2}}{p'_{O_2}}, \tag{3}$$

$$E_{H_2} = \frac{RT}{2F} \ln \frac{p''_{H_2}}{p'_{H_2}}. \tag{4}$$

It can be demonstrated that these electromotive forces are connected by the equation

$$E_{H_2} = E_{O_2} + E_{H_2O}, \tag{5}$$

where the electromotive force due to steam partial pressure drop is defined as follows

$$E_{H_2O} = \frac{RT}{2F} \ln \frac{p''_{H_2O}}{p'_{H_2O}}. \tag{6}$$

Resistances R_O and R_H for transport of oxygen ions and protons, respectively, can be calculated by the following equations

$$R_O = \frac{h}{t_O \sigma S} \tag{7}$$

$$R_H = \frac{h}{t_H \sigma S} \tag{8}$$

where h is the sample thickness and S the electrode working area.

Analyzing the scheme 1b and taking into account Eqs. (4)–(8), one can derive the following equations for the partial ionic currents densities in the electrolyte

$$i_O = -\frac{t_O t_H \sigma E_{H_2O}}{h}, \tag{9}$$

$$i_H = \frac{t_O t_H \sigma E_{H_2O}}{h} \tag{10}$$

Hence, oxygen ion and proton fluxes move in the same direction. At the gas–electrolyte interface, where the steam partial pressure is higher, the water molecule of the gas phase is decomposed to an oxygen ion and two protons of the electrolyte according to the following reaction

$$H_2O_g = 2H_e{}^+ + O_e{}^{2-} \tag{11}$$

At the opposite side, an oxygen ion and protons of the electrolyte combine forming the water molecule of the gas phase according to the inverse reaction (11). On the whole, steam permeates through the co-ionic electrolyte, as shown in Fig. 1c and its flux is as follows:

$$j_{H_2O} = \frac{t_O t_H \sigma E_{H_2O}}{2Fh} \tag{12}$$

This kind of permeation is quite different from oxygen permeation through the mixed oxygen ion–electron conductor and from hydrogen permeation through the mixed proton–electron conductor. The aim of this work is to confirm experimentally the phenomenon of steam permeation in the co-ionic electrolyte.

3. Experimental

The cell for the study of steam permeation is shown in Fig. 2. It consists of two YSZ tubes (2) sealed co-axially by their ends to YSZ disc (5). Each tube has two pair of Pt-electrodes: big ones (3) serve for oxygen pumping and small ones (4) serve for emf measuring. The long tube was fixed in the teflon plug (9) and its open end was exposed to the ambient air. Porcelain tubes (8) were used for the inlet and outlet of gases. Pt wires (7) are inserted hermetically into the plug. The investigated sample (1) was pressed to the open end of the short tube by special springs (not shown). Before the operation, the sample was separated from the end of the tube by a washer made of powder of a seal and an organic binder. The cell was placed into
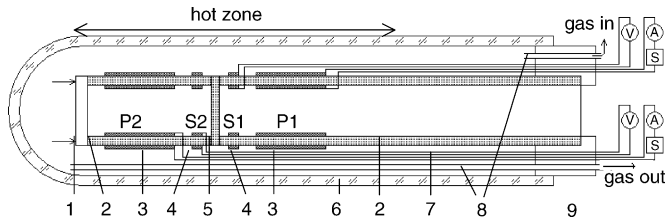
Fig. 2. A scheme of a cell for measuring electrochemical permeability of ceramic samples: 1, disc sample; 2, YSZ tube; 3, pump electrode; 4, sensor electrode; 5, YSZ disc; 6, quarts tube; 7, Pt wires; 8, porcelain tube; and 9, teflon plug.

the quarts test-tube (6); the plug was joined to the quarts tube hermetically.

The cell was heated to 600 °C in the oxygen atmosphere to burn the organic binder. After this, oxygen was replaced by helium and then helium was replaced by humidified hydrogen. The melted point for the seal is 900 °C, so at lower temperature, gas can penetrate through a gap between the sample and the short tube end. The temperature of 600 °C was kept until the sensor S2 showed zero voltage value, which indicated that the gas mixture composition inside and outside of the short tube was the same. Then the cell was heated to 900 °C at which the sample was sealed to the short tube end, and after this, the cell was cooled to 805 °C. Gas mixture composition outside the tubes can be changed by the pump P1 and measured by the sensor S1. Gas mixture inside the short tube can be changed by the pump P2 and calculated from the values obtained from both S1 and S2 sensors.

At each temperature and each gas mixture composition, the cell was kept until zero indication of S2 was reached. Then a little portion of oxygen was pumped into the short tube so the steam partial pressure inside became higher than outside, which induced the electrochemical steam flux through the sample out of the short tube. The amount of steam formed in the short tube due to oxygen pumped into the tube can be found by using the equation

$$\Delta N_{H_2O} = \frac{I \Delta \tau}{2F} \tag{13}$$

where I is the pumping current and $\Delta \tau$ the time of the pumping. Using this value one can calculate the expected change in the steam partial pressure inside the cell:

$$\Delta p_{H_2O} = \frac{\Delta N_{H_2O} V_A T}{273 V_c} \tag{14}$$

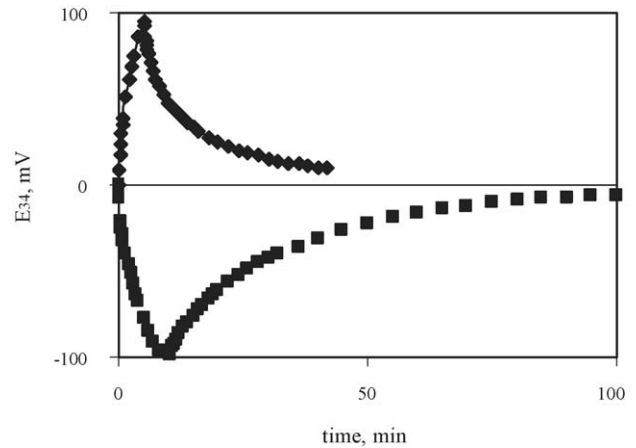where $V_A = 0.0224 \, m^3 \, mol^{-1}$ and V_c is the short tube inner volume.

Fig. 3. Time dependence of S2 sensor reading. Pumping oxygen in (upper curve up to the top) and pumping oxygen out (lower curve down to the bottom). Right parts of the curves correspond to steam permeation regime. Case of significant amount of pumped oxygen.

The change of the S2 indication with time after cutting off the pumping was used for determination of the dependence $p_{H_2O} - \tau$. The latter allowed to calculate and to plot the dependence $N_{H_2O} - \tau$. By performing graphical differencing of the plot one can obtain the steam flux value out of the tube in any moment:

$$J_{H_2O}\big|_\tau = \frac{dN_{H_2O}}{d\tau}\bigg|_\tau . \tag{15}$$

On the other hand, the dependence $p_{H_2O} - \tau$ allowed to obtain the dependence $E_{H_2O} - \tau$, which in turn gave the dependence $J_{H_2O} - \tau$ calculated using Eq. (12).

4. Results and discussion

The co-ionic electrolyte of composition $BaCe_{0.88}Nd_{0.12}O_{3-\delta}$ was used for the experiment. At 800 °C its total conductivity is about $0.03 \, S \, cm^{-1}$ and proton transfer number is about 0.1. A disc sample of the electrolyte had a thickness of 1 mm and a diameter of 11 mm.

Typical time dependence of the S2 readings are plotted in Fig. 3 for cases both oxygen pumping into the short tube and out of it. Comparison of real change of the steam partial pressure after oxygen pumping into the short tube and the expected steam partial pressure value testified that real amount of steam was considerably less than the expected one for a wide range of applied currents and times of pumping (see Table 1). The only

Table 1
Comparison of the expected and real changes of steam partial pressures in the short tube

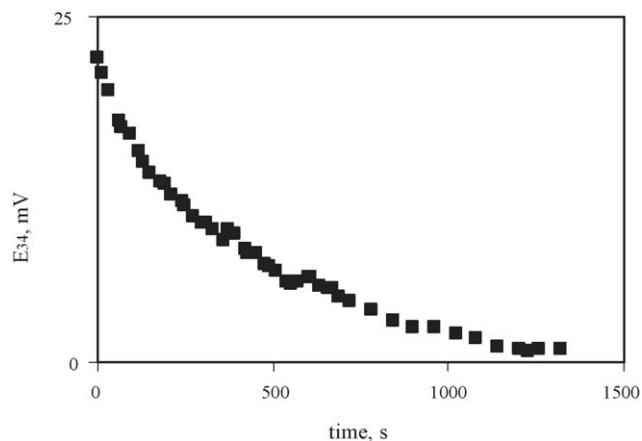| I (mA)	t (min)	P_{H_2O} change (expected)	E (expected) (mV)	E (real) (mV)	P_{H_2O} change (real)
5	10	0.977	−0.751	−1.014	0.108
4	1.333	0.128	−1.021	−1.094	0.011
1	25	0.502	−0.929	−1.077	0.050
1	15	0.311	−0.967	−1.081	0.029
1	8	0.178	−1.002	−1.086	0.015

Fig. 4. Time dependence of S2 sensor reading during steam permeation regime. Case of moderate amount of pumped in oxygen.

reasonable explanation of this can be absorption of oxygen by the sample due to change its stoichiometry. A deviation from the stoichiometry is considerable for cerates under reducing conditions; even slight change in the oxygen partial pressure leads to significant exchange of oxygen between gas phase and the sample according the reaction:

$$H_2O = H_2 + O^{2-} \tag{16}$$

Typical change of the S2 sensor reading after interrupting the pumping current is shown in Fig. 4. Comparison of the steam flux calculated from absolute values of E_{H_2O} by using Eq. (12) and the steam flux calculated from data of graphical differencing by using Eq. (15) testifies that these two values differed insignificantly (less than 30%).

5. Conclusions

At least two important conclusions can be made from the results of the experiments: (1) taking into account very big difference between the expected and real steam partial pressures, which testifies on rapid disappearance of steam in the short tube due to transfer of oxygen into non-stoichiometric oxide, we can conclude that the rate of the reactions at the co-ionic electrolyte–gas interface is very high and (2) the experimental results undoubtedly show existence of steam electrochemical permeation through the co-ionic electrolyte.

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