EVALUATION OF OXYGEN ION CONDUCTION IN DENSE CERAMIC MEMBRANES OF PEROVSKITE TYPE

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abstract: Conductivity measurements have been made on perovskite type ceramic membranes with mixed conduction by oxygen ions and electrons. Conductivity increased with temperature and revealed the change of conduction mechanism at 650 – 700 ^{o}C. E.m.f. measurements on oxygen concentration cells across the studied membranes were made.

Introduction

Ceramic membranes show chemical, thermal and structural stability and high oxygen selectivity. Economical issues brought about by the advantage of conducting pure oxygen directly to the reaction zone in membrane reactors induced new orientations in oxygen selective dense ceramic membrane research [1-3]. A new class of ceramic oxide materials with perovskite structure was developed, which show mixed oxygen ion and electronic conduction at high temperature. By electroreduction of oxygen on the feed side:

$$2O^{2-} = O_2 + 2e^- \qquad (1)$$

followed by ambipolar diffusion - O^{2-} ions down the p_{O_2} gradient and electrons in the opposite direction - through the membrane and reoxidation on the delivering side, these membranes may accurately separate oxygen from mixtures, for organic syntheses or syngas production.

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Theory

Limitations in membrane functionality. The oxygen permeation flux through the mixed conducting membrane depends on material properties like:

➤ the diffusion constant of the oxygen ion through the ceramic material;

➤ the oxygen redox exchange kinetics on the two faces of the membrane;

➤ the electronic conductivity of the membrane.

The influence of these parameters on the overall process rate divides oxygen ion conducting ceramic materials into classes: diffusional control is a sign of weak ionic conduction, control by low electronic conduction characterizes solid electrolytes used in solid oxide fuel cells [4-5], electrochemical oxygen pumps and sensors [6]. Slow electrode kinetics on the membrane faces affects most applications. Kinetics may control the process even for electrocatalitically active ceramic materials, if the membrane is very thin or the temperature has been reduced because of good diffusivity.

Conductivity determination. On open circuit, the diffusion of an oxygen ion is accompanied by the movement of two electrons in the opposite direction. The two fluxes are given by

$$J_{O^{2-}} = -\frac{\sigma_{O^{2-}}}{4F}\nabla\tilde{\mu}_{o^{2-}} \quad (1) \qquad \text{and} \qquad J_e = -\frac{\sigma_e}{F}\nabla\tilde{\mu}_e \qquad (2)$$

While the chemical potential variation for the oxygen ion during the diffusion process is negative, that of the electron will be positive, as it is diffusing from more positive to more negative potential. The variation of the Gibbs free energy in open circuit will correspond to ambipolar diffusion of the oxygen atom (3) governed by the Wagner equation (4) [7]:

$$\partial\mu_O = \partial\mu_{O^{2-}} - 2\partial\mu_e \qquad (3) \qquad J_O = -\frac{1}{4F}\frac{\sigma_{O^{2-}}\sigma_e}{\sigma_{O^{2-}} + \sigma_e}\nabla\mu_O, \qquad (4)$$

which, compared to Fick's first law (5), gives the chemical diffusion constant expression (6):

$$J_O = -\tilde{D}_O\nabla c_O, \qquad (5) \qquad \tilde{D}_O = \frac{1}{4F^2}\frac{\sigma_{O^{2-}}\sigma_e}{\sigma_{O^{2-}} + \sigma_e}\frac{\partial\mu_O}{\partial c_O} \qquad (6)$$

which, for $\sigma_e \gg \sigma_{O^{2-}}$, becomes: $\qquad \tilde{D}_O = \frac{1}{4F^2}\sigma_{O^{2-}}\frac{\partial\mu_O}{\partial c_O} \qquad (7)$

Four point conductivity measurement. For rod samples, current is applied at two points close to the ends and the ohmic voltage drop between two points on the current path is measured, thereby avoiding that current passage through the voltage measurement leads affects accurate voltage reading (figure 1) [8]. Figure 2 shows the Van der Pauw modification of the 4-point conductivity measurement system for plane (membrane) samples.

E.m.f. method for the oxygen ion transference number determination. The electromotoric force (e.m.f.) technique is based on the measurement of the open circuit voltage of an oxygen concentration cell, i.e. a cell made of the sample membrane with two reversible electrodes applied on both faces exposed to a partial pressure (chemical potential) gradient of oxygen [9]. If the electrode polarization of the oxygen concentration cell is negligible, the e.m.f. (E_{obs}) is given by (8):

$$E_{obs} = \frac{RT}{4F} \int_{p_1}^{p_2} \frac{\sigma_O}{\sigma_O + \sigma_e} d\ln p(O_2) \text{ ,} \tag{8}$$

where σ_o and σ_e are the partial conductivity by oxygen ions and by electrons respectively, $p(O_2)$ the partial oxygen pressure and p_1 and p_2 are the $p(O_2)$ values on the two membrane faces. The average transference number of the oxygen ion (t_O) in the given oxygen pressure range can be calculated as the ratio between the measured (E_{obs}) and the theoretical e.m.f. value given by the Nernst equation (E_{theor}), if the conductivity by electrons is much larger than by oxygen ions:

$$t_O = \frac{E_{obs}}{E_{teor}} \qquad \text{with:} \qquad E_{teor} = \frac{RT}{4F} \ln \frac{p_2}{p_1} \tag{9}$$

Results and discussions

From the prepared membranes two compositions were chosen for electrical measurements: $Ba(Bi_{0,1} Co_{0,2} Fe_{0,7}) O_{3-\delta}$ - referred to as **BBC2F7** and $Ba_{0,5} Sr_{0,5} (Co_{0,8} Fe_{0,2}) O_{3-\delta}$ - referred to as **CF2SB**.

Conductivity measurements. Electrical conductivity was measured on ceramic sample
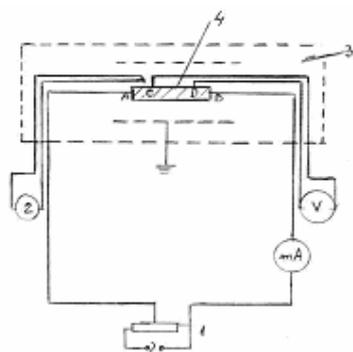
Fig. 1 *Four point conductivity measuring circuit. 1- power source; 2– thermocouple; 3– furnace; 4- sample.*
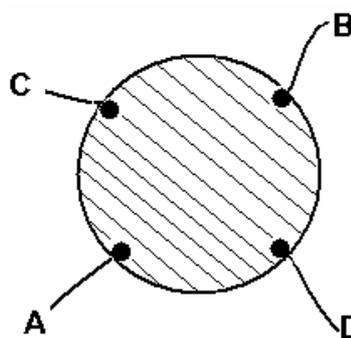
Fig. 2. *Sample preparation for Van der Pauw four point conductivity measurement*

membranes BBC2F7 and CF2SB by the four point Van der Pauw method [10]. Four point electrical conductivity measurements were done on disc membranes Ø = 20 mm, d=1 mm. Four platinum contacts were arbitrarily fixed on the membrane sample circumference, then it was placed between two isolating ceramic supports into an electric oven with the thermocouple positioned in sample proximity.

Measurements were done in the temperature range 400 – 750 ^{o}C every 50 ^{o}C, after temperature stabilization, by passing a current I, for example through the conductors A and B and reading the potential difference between C and D; then the current I was passed between C and D and the potential difference read between A and B. The conductivity was calculated according to the Van der Pauw method [10]. The resistances:

$$R_{AB,CD} = \frac{U_{DC}}{I_{AB}} \text{ and } R_{DC,BA} = \frac{U_{BA}}{I_{DC}} \tag{10}$$

were calculated from the corresponding I and U values registered for the same temperature. From the calculated resistance values $R_{AB,CD}$ and $R_{BC,DA}$, the corresponding resistivity (ρ) and the conductivity ($\sigma = 1/\rho$) were calculated. The conductivity logarithm was plotted against $10^4/T$ in order to identify linear variation domains for activation energy determination from the Arrhenius equation ($\sigma = \sigma_0 \exp(- E/kT)$. Activation energy was obtained from the slope in the identified linear domains.

Table 1 Conductivity data

t/^{0}C	10000/T /K^{-1}	σ/Scm^{-1}	
		BBC2F7	CF2SB
400	14,8	$2,9 \times 10^{-4}$	$3,4 \times 10^{-2}$
450	13,8	$3,6 \times 10^{-4}$	$3,7 \times 10^{-2}$
500	13,0	$1,13 \times 10^{-3}$	$3,8 \times 10^{-2}$
550	12,15	$2,7 \times 10^{-3}$	$4,1 \times 10^{-2}$
600	11.4	$4,0 \times 10^{-3}$	$4,3 \times 10^{-2}$
650	10,8	$4,2 \times 10^{-3}$	$4,6 \times 10^{-2}$
700	10,3	$4,3 \times 10^{-3}$	$5,1 \times 10^{-2}$
750	9,7	$4,48 \times 10^{-3}$	$6,2 \times 10^{-2}$

The obtained results are shown in table 1. The results confirm the mixed ionic and electronic conduction properties of the investigated membranes, as the obtained conductivity values are characteristic for this class of perovskite type materials.

The conductivity values obtained for the CF2SB membrane sample were higher; this may be interpreted as a result of the presence of the perovskite phase. This iron perovskite produces an increase of defect concentration , due to the valence change of the iron ion, a situation not encountered in the BBC2F7 sample, made only of a barium cobaltate perovskite.
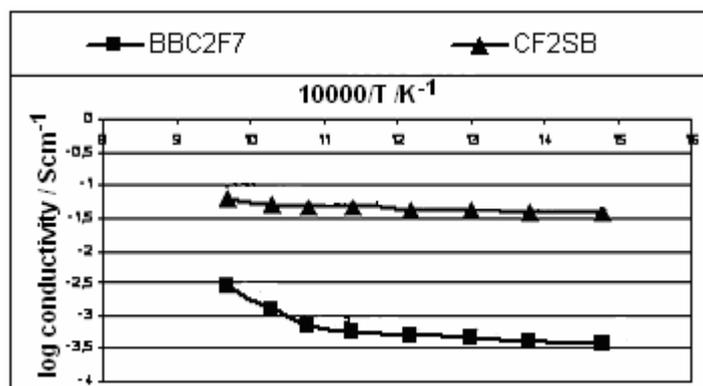
Fig. 3. *Electrical conductivity as a function of temperature.*

The plot of the conductivity logarithm versus $10^4/T$ confirms the results obtained and the differentiation of the two membrane types (figure 3).

One can also identify some differences in representation shape, which are related to the conduction mechanism in the given structure by the slope in the studied temperature range. The CF2SB shows a very small slope, corresponding to an activation energy of max. 0.35 eV, pointing to a mixed conduction mechanism. In contrast, the BBC2F7 sample shows a change of conduction mechanism from predominantly electronic to predominantly ionic in the temperature range 650 – 750 $^{\circ}$C, with the activation energy increasing to cca. 0,9 eV. At temperatures lower than 650 $^{\circ}$C, a mainly electronic conduction mechanism is predominant, as indicated by the low activation energy of 0.3 eV.

E.m.f. measurements. Measurements were made on a laboratory device, in which the sample membrane can be exposed to two different oxygen containing atmospheres having predetermined concentrations, at a working temperature range of 200 – 800 $^{\circ}$C, with two conductors applied on the two tightly separated membrane faces, to measure the electromotoric force. The measuring device is shown in figure 4.
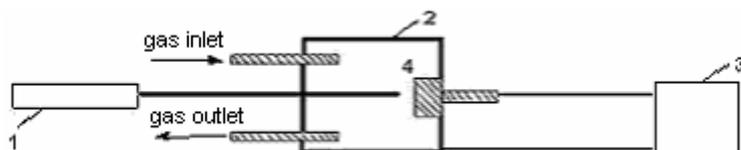
Fig. 4. *Oxygen concentration cell f.e.m. measurements 1 - thermocouple; 2 - furnace; 3 - digital voltmeter; 4- sample fixture.*

The sample membrane was held in a fixture to be placed with one face into the furnace containing the calibrated gas mixture and with the other one exposed to air. The internal resistance of the samples was measured in air, in the temperature range 200 – 800 $^{\circ}$C. The electrochemical data obtained by the f.e.m. measurement are shown in table 2.
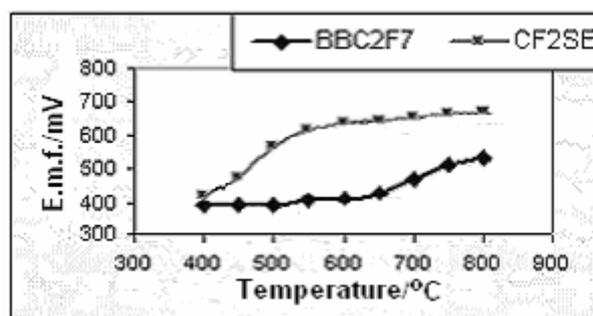
Fig. 5. *F.e.m. variation with temperature.*

Resistance values decrease for both sample membranes with temperature. The ionic conductivity of the BBC2F7 membranes also determined the higher resistance values than for CF2SB, showing prevalent electronic conduction.

Table 2. Electrochemical data

Temperature [^{0}C]	Internal resistance [KΩ]		Electromotoric force [mV]	
	BBC2F7	CF2SB	BBC2F7	CF2SB
400	92	21	387	420
450	83	19,8	390	472
500	78	18,5	395	569
550	75	17	405	615
600	70	16,3	411	637
650	69	15,7	423	642
700	67	14,6	471	655
750	66	13,6	512	663
800	65	13,6	436	672

Conclusions

The conductivity measurements on the two ceramic membranes revealed mixed oxygen ion and electronic conduction in both materials. The change from a prevalent electronic conduction to a conduction predominantly supported by oxygen ions occurs in both materials at high temperature but is much more evident in BBC2F7. Oxygen ion conduction was also confirmed by e.m.f. measurements on oxygen concentration cells employing the membrane as an electrolyte..

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