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Abstract

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STUDY OF TRANSPORT NUMBERS IN SOLID OXIDES

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We have shown (1) that in the systems CeO_2—La_2O_3, CeO_2—Nd_2O_3, and CeO_2 —Y_2O_3, for a number of compositions practically ionic electrical conductivity is observed over a wide temperature range. It is of interest to clarify which ions carry the current in these cases.

The starting materials for preparing tablets of the solid electrolyte were purified cerium dioxide (impurity content of the order of 0.010%), lanthanum oxide (“chemically pure”), neodymium oxide (grade I), and yttrium oxide (grade I). To obtain electrolytes of a specified composition, the preliminarily calcined oxides were mixed in the required ratio and thoroughly ground in an agate mortar. Tablets 2-3 mm thick and 20 mm in diameter were pressed from the resulting powder at a pressure of about 1700 kg/cm^2. The tablets were fired at 1600° (holding time 2 hours). To overcome difficulties associated mainly with the deposition of metal at the cathode (2), it was necessary to modify the gravimetric method for measuring transport numbers.

In order to exclude metal deposition at the cathode, we made use of the ability of oxygen to dissolve on an oxygen gas electrode. If electrolysis is carried out with reversible oxygen electrodes at a voltage below the decomposition voltage of the electrolyte, then oxygen ionization will occur at the cathode ($O_2 \rightarrow 2\ O \rightarrow 2O^{2-} - 2e$), and at the anode, as usual, discharge of oxygen ions ($2O^{2-} - 2e \rightarrow 2O \rightarrow O_2$). In this case, changes in the weight of the cathodic and anodic electrolyte plates should be observed only if cations participate in current transport. Having determined these changes, one can immediately calculate the cation transport number. If, however, there are no weight changes after electrolysis, and it is known that electronic conductivity is absent, this means that the current through the electrolyte under study is carried only by anions. Thus, in the present case the fraction of electronic conductivity must first be determined by some other method. As noted above, for the electrolytes considered in the present work the fraction of electronic conductivity was determined by the emf method (1). It was, however, of interest to try a new method for studying it (determination of the current yield of oxygen during electrolysis) and to compare the results obtained.

In the case of passage through the electrolyte of an amount of electricity equal to 1 faraday, the amount of oxygen equivalents evolved will be equal to:

$$q = t_{\mathrm{A}} + t_{\mathrm{K}} = 1 - t_e, \tag{1}$$

where t_{A}, t_{K}, and t_e are the transport numbers of anions (oxygen ions), cations, and electrons or electron holes, respectively. It follows from this that, having determined the cation transport number from the change in the weight of the catholyte and anolyte and knowing the amount of oxygen evolved at the anode, one can determine the transport number of oxygen ions. By equation (1) the transport number of electrons (electron holes) can also be determined.

Methodologically it proved more expedient to carry out the measurement of transport numbers in two steps, in accordance with the assumptions set forth above—

references. Initially, experiments were set up to determine the cationic conductivity in an oxygen atmosphere by carrying out electrolysis of three tablets of solid electrolyte pressed against one another. In this case, as usual, weighing was performed before and after electrolysis.

It should be noted, however, that measurement of transport numbers need not be divided into two stages, especially if the specimens have high conductivity.

The experiments on measuring transport numbers were carried out at 1000-1100° in the same apparatus as the investigation of the nature of conductivity (1). Three tablets of solid electrolyte were taken.

Table 1

No. of composition	Composition, mol. %	Temp., °C	Voltage on cell, V	Amount of electricity passed, A • h	Catholyte	Middle	Anolyte	Cation transport number
1	100 CeO_2	1100	2.0	0.705	−0.0002		0.0010	<0.004
2	26.1 $LaO_{1 \cdot 5}$ + 73.9 CeO_2	1000	1.5	1.090	−0.0010	−0.0001	−0.0001	<0.004

No. of composition	Composition, mol. %	Temp., °C	Voltage on cell, V	Amount of electricity passed, A · h	Catholyte	Middle	Anolyte	Cation transport number
3	62.1 $LaO_{1\cdot5}$ + 37.9 CeO_2	1000	2.0	0.271	−0.0011	+0.0011	−0.0003	<0.004
4	26.1 $NdO_{1\cdot5}$ + 73.9 CeO_2	1000	1.5	1.220	−0.0006	−0.0006	−0.0006	<0.004
5	51.9 $NdO_{1\cdot5}$ + 48.1 CeO_2	1000	1.5	0.746	−0.0005	−0.0009	−0.0006	<0.004
6	75.0 $NdO_{1\cdot5}$ + 25.0 CeO_2	1100	1.5	0.733	−0.0016	−0.0012	−0.0007	<0.004
7	3.9 $YO_{1\cdot5}$ + 96.1 CeO_2	1000	1.5	0.771	−0.0002	+0.0001	−0.0003	<0.004
8	26.1 $YO_{1\cdot5}$ + 73.9 CeO_2	1000	2.0	0.815	−0.0007	−0.0005	−0.0004	<0.004
9	75.0 $YO_{1\cdot5}$ + 25.0 CeO_2	1100	2.0	0.210	−0.0005	−0.0003	−0.0006	

Platinum electrodes exactly like those used in measuring the emf were applied to the end faces of the two outer tablets. To exclude discharge of cations at the

Fig. 1. Schematic of the apparatus for determining the amount of oxygen evolved during electrolysis of solid oxides with oxygen electrodes

Figure 1: Fig. 1. Schematic of the apparatus for determining the amount of oxygen evolved during electrolysis of solid oxides with oxygen electrodes

cathode, a direct-current voltage not exceeding 2.0 V was applied to the cell, i.e., below the decomposition voltage of the solid electrolytes under study (since the voltage drop occurred mainly across the ohmic resistance). The current passing through the cell in different experiments (depending on the resistance of the specimen under study) was from 3 to 100 mA. The amount of electricity passed in most cases was 0.7-1.2 A • h, and only in some cases (high electrolyte resistance) about 0.2-0.3 A • h. Thus, in the worst case, with a weighing accuracy of ±1.0 mg, we could detect cation transport numbers of 0.004 (assuming current transport by Ce^{4+} ions). True, in some experiments the changes in tablet weight somewhat exceeded 1.0 mg. In this case, however, as a rule, only a loss in tablet weight is observed, which obviously is not due to transport of substance.

The experiments showed (Table 1) that, for the compositions studied, the cation transport number is smaller than the value indicated above, i.e., the cations are practically immobile.

The apparatus for determining the amount of oxygen evolved during electrolysis is shown schematically in Fig. 1. In this very simple apparatus, particular attention was paid to avoiding, as far as possible, leakage of the evolved oxygen through imperfect seals (primarily in the ground joint), and also through diffusion through pores and by the Wagner mechanism (^{3}) through the thickness of the electrolyte. For this purpose we very carefully ground the tablets to the end of the tube and practically eliminated the pressure drop and the difference in concentrations on the two sides of the tablet. Elimination of the difference in pressure drop (drop less than 1.0 cm water column) was achieved by using, as the collecting vessel, a bag made of very thin and elastic rubber; moreover, oxygen was collected only until the rubber began to stretch. To minimize the difference in oxygen concentrations on the cathode and anode sides of the tablet, the latter was continuously flushed on the cathode side with cylinder oxygen.

In carrying out the experiment, the system was first thoroughly flushed with cylinder oxygen, and gas was removed from the collecting vessel up to a certain slight vacuum. Upon completion of the experiment, the amount of oxygen evolved was measured with a measuring burette; when the oxygen was drawn off with the burette, the same vacuum was created in the collecting vessel as before the start of the experiment.

Fig. 1. Schematic of the apparatus for determining the amount of oxygen evolved during electrolysis of solid oxides with oxygen electrodes:
1 –porcelain tube (in a tubular electric furnace); 2 –specimen; 3 –porcelain tube with a ground end; 4 –porcelain tube; 5 –rods of heat-resistant alloy; 6 –

asbestos shield; 7 —steel springs; 8 —rubber stopper; 9 —glass tip; 10 —current leads made of platinum wire; 11 —collecting vessel (rubber bag); 12 —two-way stopcocks; 13 —measuring burette; 14 —vessel for water; 15 —three-way stopcock; 16 —Pt—PtRh thermocouple; 17 —alundum tube.

The amount of electricity passed was determined with a copper coulometer.

Table 2

Composition Nos.	Temp., °C	Voltage across cell, V	Current, mA	Amount of electricity passed, A • h	Volume of oxygen evolved during electrolysis at the anode, cm^3 (at 0°C, $P =$ 760 mm Hg)	Transport number (taking into account the data of Table 1): anions	Transport number (taking into account the data of Table 1): electrons (electron holes)
1	1100	1.75	145	1.221	19.7	0.078	0.922
2	1000	0.45	215	0.657	138.7	1.005	~0
3	1000	0.78	200	0.693	141.7	0.981	0
4	1000	0.42	239	0.701	142.6	1.003	0
5	1000	0.79	210	0.750	136.6	0.875	0.125
6	1100	1.78	138	0.611	52.7	0.413	0.587
7	1000	0.66	210	0.735	150.5	0.982	~0
8	1000	1.85	90	0.815	168.8	0.994	0
9	1100	2.55	24	0.489	97.10	0.853	0

Note. The composition numbers correspond to the numbers in Table 1.

Table 2 gives the experimental data on determining the amount of oxygen evolved at the anode during electrolysis of the same solid solutions and in the same sequence as in Table 1. It also gives the transport numbers of oxygen ions and electrons (electron holes), calculated taking into account that the cation transport numbers in all the compositions studied

are close to zero. We estimate the accuracy of the measurements as ±(2.0—3.0%). It can be seen that in all three systems the solid solutions of the fluorite type (4) that are formed have a practically oxygen-ion character of conductivity. This indicates the presence of defects specifically in the oxygen part of the crystal lattice (5). It is also interesting that, in the range of compositions possessing mixed conductivity (ionic + electronic), the cations take practically no part in charge transport.

A comparison of the values obtained for the ion transport numbers with the results of measuring the mean ion transport number by the emf method (1) shows that they are in good agreement. This fact indicates that both methods can be successfully used to investigate the nature of the conductivity of oxides and their mixtures. For investigating the nature of the conductivity of solid substitution-subtraction solutions of the type considered in the present work (when ions of one kind participate in charge transport), it is most expedient to use the emf method. Measurements by this method require considerably less time, especially when it is necessary to elucidate the nature of the conductivity of solids with low electrical conductivity. Conversely, in a number of cases, by directly determining transport numbers one can obtain more interesting data, making it possible to judge, in particular, the type of defects in the crystal structure.

In some cases, determination of transport numbers gives more accurate results than the emf method. In particular, the porosity of specimens (1), difficulties in the course of processes at the electrodes (electrode polarization) due to diffusion by the Wagner mechanism, and a number of other causes associated with the absence of equilibrium in the system will affect the measured value of the emf, being superimposed on the decrease, caused by the presence of electronic conductivity, relative to its thermodynamic value. The good agreement of the results obtained by the two indicated methods shows that oxygen diffusion by the Wagner mechanism does not substantially affect the results of investigating the nature of conductivity by the emf method with the measurement procedure adopted, even in specimens possessing comparable values of ionic and electronic conductivity. It should be borne in mind, however, that the measurements were carried out at sufficiently high temperatures, when electrode polarization is small.

In conclusion, we note that the results obtained are valid only within a certain range of partial oxygen pressures. In particular, if the partial pressure of oxygen is very low, in specimens containing a considerable fraction of CeO_2, the share of electronic conductivity will increase owing to the reduction of cerium (5).

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Note: Figure translations are in progress. See original paper for figures.