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Characteristics of cathode materials for solid oxide fuel cells with mixed conductivity

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Abstract. In this article, we define promising materials for creating the structure of a non-porous cathode-electrolyte. The synthesis of initial powders by the method of self-propagating high-temperature synthesis is studied and described. The specific surface area, morphology and phase composition of powders were investigated.

1. Introduction
When developing solid oxide fuel cells (SOFCs), an important task is to increase their power, which depends on the internal resistance consisting of ohmic resistances of the electrolyte and electrodes, as well as the polarization losses caused by the processes on the electrodes. The generally accepted structure of a SOFC consists of a dense layer of an electrolyte separating the porous layers of electrodes. In this structure, electrode reactions occur on the three-phase (electrolyte-electrode-gas) boundary, and the values of polarization resistances depend on the structure of electrodes (composition, porosity of the electrolyte-electrode boundaries, etc.).

One can avoid many difficulties related to the formation of gas-diffusion electrodes and increase the specific power of SOFCs by forming a new nonporous cathode-electrolyte structure, in which the electrode reaction zone would be located on the electrode-gas interface. The main condition for the realization of the proposed structure is a high mixed electron-ion conductivity of the cathode material. In addition, the cathode material must have stable chemical, phase, dimensional properties in an oxidizing environment, chemical compatibility with the electrolyte material and the value of thermal expansion coefficient (TEC) similar to the one of the electrolyte. Also, to enable manufacturing the cathode-electrolyte structure by means of simultaneous sintering, the shrinkage on sintering of the cathode material and the electrolyte should be similar.

Finding a material that meets all the above requirements is not an easy task. Especially, considering that all characteristics of materials are determined by their chemical composition and structure and, therefore, are interrelated, it is not possible to change one parameter without affecting the others. A possible way to solve this contradiction is to create a composite cathode material. Thus, it is possible to increase the ionic conductivity and make the TEC of the cathode close to the one of the electrolyte.

2. Selection of cathode materials for research
Basing on the literature review, we have determined the following promising materials for developing the structure of a nonporous cathode-electrolyte: $SmSrCo_2O_{5+\delta}$ and $NbBa_{0.5}Sr_{0.5}Mn_{0.5}O_{5+\delta}$. However,

additional studies have shown that these materials interact with ZrO_2 electrolyte stabilized with Y_2O_3 (YSZ). Therefore, basing on the whole set of parameters, such as electronic and ionic conductivity, TEC, surface exchange coefficient (k), and interaction with electrolyte YSZ, the following compositions were chosen for further investigation: materials with the perovskite structure $Pr_{1-x}Sr_xFe_{1-y}Co_yO_3$, (x = 0, 0.2, 0.3, y = 0.2, 0.5) and materials with the Ruddlesden-Popper structure $La_2Ni_{1-x}Co_xO_4$ (x = 0, 0.1, 0.2, 0.3) and Pr_2NiO_4. Characteristics of some of the selected compositions are presented in table 1. It should be noted that the determination of the ionic conductivity is a rather difficult task, therefore literature data on this parameter are rare. In this regard, the table shows the oxygen diffusion coefficient $D*$, which is related to the ionic conductivity σ_i through the Nernst-Einstein equation.

Table 1. Characteristics of cathode materials (at 800 °C) [1-3].

Material	σ_e, S/cm	σ_i, S/cm	$D*$, cm^2/s	k, cm/s	TEC ($\times 10^{-6}$), K^{-1}
$Pr_{0,8}Sr_{0,2}Fe_{0,8}Co_{0,2}O_3$	76	0.0015			12.8
$Pr_{0,7}Sr_{0,3}Fe_{0,8}Co_{0,2}O_3$	171				12.4
La_2NiO_4	47		1.2×10^{-7}	1.7×10^{-6}	13.0
Pr_2NiO_4	94		1.2×10^{-7}	3.1×10^{-6}	13.6
$La_2Ni_{0,8}Co_{0,2}O_4$			9.8×10^{-8}	2.2×10^{-6}	11.3

In addition, a nonporous cathode-electrolyte structure from a perovskite-based composite $La_{0.7}Sr_{0.3}MnO_3$ (LSM) also was fabricated. This material does not have mixed ion-electron conductivity, is a well-studied and widely used cathode for high-temperature SOFCs. Thus, the characteristics of this structure will be the reference point for all studies.

3. Experimental

The ZrO_2 electrolyte powder, stabilized with 8.5mole%Y_2O_3 (8.5YSZ), was obtained by the laser evaporation method at the Institute of Electrophysics, Urals Branch of the Russian Academy of Sciences [4]. Powders of cathode materials were obtained by self-propagating high-temperature synthesis. The starting reagents were hydrogen carbonates and nitrates of the corresponding elements.

The specific surface area of the powders was determined by the Brunauer-Emmett-Teller (BET) method on a TriStar 3000 automatic analyzer. The morphology of the powders was examined using a LEO 982 electron microscope, and the phase composition was studied on a D8 DISCOVER diffractometer.

The sintering kinetics of the electrolyte and cathode materials was studied in an air atmosphere in the temperature range of 20-1500 °C using a Dil 402C dilatometer at a heating rate of   5 °C/min. Using the same instrument, the TEC of the compositions under study was determined in the temperature range of 20-1000 °C. To measure the electrical conductivity, the powders were pressed to bars of a rectangular cross section, sintered to a density close to the theoretical one (the sintering regime was determined from the dilatometric data), and platinum wire probes were deposited on the samples. The electrical conductivity measurements were carried out by a 4-probe method at a direct current in the temperature range of 20-800 °C in the air atmosphere using a Solartron Sl-1260/1267 impedancemeter.

4. Results and discussion

The initial nano-sized powder of electrolyte 8.5YSZ was characterized by a specific surface $S_{BET} = 40.1$ m^2/g, which corresponds to an average particle size $<d> = 21$ nm. In the following, we will denote this powder YSZ$_{20}$. To change the sintering kinetics, YSZ$_{20}$ was heated at 1000 °C for 4 hours. The resulting powder YSZ$_{20}$ was characterized by $S_{BET} = 22.8$ m^2/g ($<d> = 45$ nm). The results of dilatometric studies of samples made of YSZ$_{20}$ powders and their mixtures are shown in figure 1.
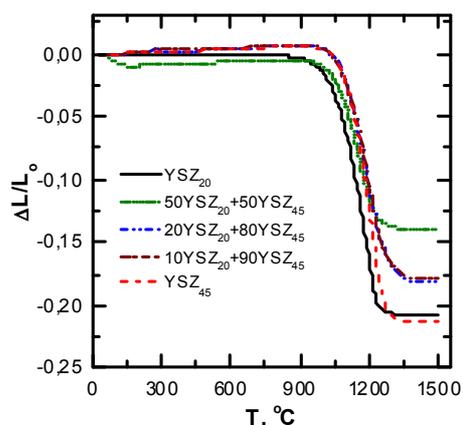
Figure 1. Curves of linear shrinkage of samples made of YSZ$_{20}$ powders and their mixtures (figures in the notations of the mixtures correspond to weight percents.)
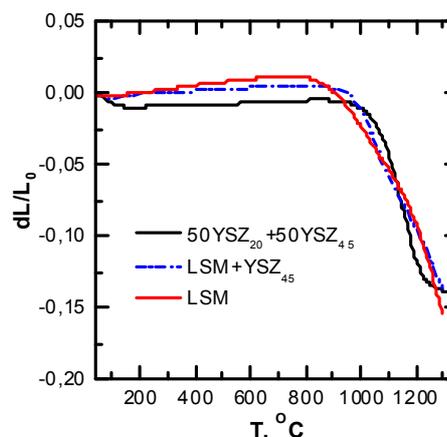
Figure 2. Curves of linear shrinkage of electrolyte material, composite LSM + YSZ45 and cathode material LSM/

From a comparison of the shrinkage curves for the cathode material based on LSM and electrolyte materials with different dispersions, it was determined that the composition 50YSZ$_{20}$ + 50YSZ$_{45}$ is the most suitable for realizing simultaneous sintering (figure 2).

5. Conclusions

On the basis of the literature review, promising cathode materials were determined for the development of a nonporous cathode-electrolyte structure: perovskites based on praseodymium ferrite and lanthanum and praseodymium with the Ruddlesden-Popper structure. The initial powders were synthesized by the method of self-propagating high-temperature synthesis. From a comparison of the shrinkage curves for the cathode material based on LSM and electrolyte materials with different dispersions, it was determined that the composition 50YSZ$_{20}$ + 50YSZ$_{45}$ is most suitable for realization of simultaneous sintering.

Acknowledgments

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