Stability and Functional Properties of Sr$_{0.7}$Ce$_{0.3}$MnO$_3–\delta$ as Cathode Material for Solid Oxide Fuel Cells

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Abstract—Studies of oxygen diffusion, interphase exchange, specific electric conductivity, and thermal expansion showed that perovskite-like Sr$_{0.7}$Ce$_{0.3}$MnO$_3–\delta$ (SCMO) as a potential cathode material for solid oxide fuel cells (SOFCs) has considerable advantages over the conventional materials based on lanthanum–strontium manganites. To prevent the interactions of SCMO with solid electrolyte membranes of stabilized zirconia and lanthanum gallate, it is necessary to deposit protective layers of solid solutions based on cerium oxide, which do not form new phases in contact with SCMO and electrolytes. The trials of model SOFCs with porous SCMO-based cathodes demonstrated satisfactory electrochemical and endurance characteristics of these electrodes.

Keywords: solid oxide fuel cells, cathode materials, stability tests, diffusion, electric conductivity

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INTRODUCTION

Zirconia stabilized with 8–10 mol % Y$_2$O$_3$ (YSZ) currently is the main material for anion-conducting membranes of solid oxide fuel cells (SOFCs) [1, 2]. However, a significant disadvantage of SOFCs based on YSZ is the high temperature (above 900°C) of cell operation, which entails specific requirements to the properties, compatibility, and chemical stability of cathode, anode, and interconnect materials and makes the construction of the SOFC module expensive [1–3]. The decrease of the working temperature requires the development of new materials of electrolytes and electrodes. One of the promising solid electrolytes is La$_{0.8}$Sr$_{0.2}$Ga$_{0.85}$Mg$_{0.15}$O$_3$–\delta (LSGM) [3]. At the same time, new cathode and anode compositions are required for LSGM membranes to provide high electronic conductivity in the intermediate temperature range (600–800°C), high electrochemical and catalytic activity and chemical stability, and thermal expansion coefficients (TECs) comparable to those of the solid electrolyte under these conditions. It was shown [4, 5] that Sr$_{0.7}$Ce$_{0.3}$MnO$_3–\delta$ demonstrated a good combination of transport and catalytic characteristics in the range 600–800°C and was a promising cathode material for SOFCs. However, there were no direct studies of this material in fuel cells.

In this work, we studied the isotopic diffusion of oxygen, surface exchange, specific electrical conductivity of Sr$_{0.7}$Ce$_{0.3}$MnO$_3–\delta$ (SCMO) and the chemical stability of this material in contact with other components of SOFCs in the range of working temperatures. The electrochemical characteristics of the SCMO cathode were investigated on the laboratory SOFC samples with the supporting electrolytes ZrO$_2$ + 1 mol % Y$_2$O$_3$ + 10 mol % Sc$_2$O$_3$ (10Sc1YSZ) and La$_{0.8}$Sr$_{0.2}$Ga$_{0.85}$Mg$_{0.15}$O$_3$.

EXPERIMENTAL

SCMO powders were prepared by the citrate method. The starting materials were strontium nitrate Sr(NO$_3$)$_2$, cerium nitrate Ce(NO$_3$)$_3$·6H$_2$O, and manganese acetate Mn(CH$_3$COO)$_3$·4H$_2$O taken in a stoichiometric ratio. The salts and citric acid were dissolved in distilled water. After the solution was evaporated and partially decomposed at 300°C, the resulting precursor was ground in an agate mortar and then annealed at 800°C for 5 h in air. The powder was finally annealed at 1300°C for 10 h in air.

The X-ray diffraction analysis of polycrystalline samples was performed at room temperature on a SIEMENS D-500 BRAUN, X02-1787 diffractometer with a position-sensitive detector and a primary monochromator for CuK$_\alpha$ radiation (Siemens AG, Germany). The X-ray diffraction patterns were calculated and the unit cell parameters were refined with the Powder Cell 2.4 program package.
The gas-tight ceramic samples formed from single-phase powder by uniaxial pressing were sintered in air at 1420°C for 20 h. These samples were used for measuring the conductivity and isotopic diffusion coefficient of oxygen anions. The specific conductivity was studied at different temperatures and oxygen partial pressures by the DC four-probe method with platinum contacts; the equipment and measurement procedure were described in [6]. The oxygen diffusion in the structure of the cathode material was studied by the isotope exchange method [7–9]. The thick polished samples were at first annealed at 700°C in order to achieve the thermodynamic equilibrium between the oxygen sublattice of oxide and atmospheric oxygen. Then the annealing chamber was evacuated for a short time and filled with oxygen containing 95% \(^{18}\)O and 5% \(^{16}\)O isotopes at a pressure of 0.2 atm. In this atmosphere, the samples were annealed for 2 h at 700°C. The concentration ratio of the \(^{18}\)O and \(^{16}\)O isotopes in the depth of the sample (diffusion profiles) were studied with a time-of-flight secondary ions mass spectrometer (TOF-SIMS.5-100P, Germany). The depth of the crater after TOF-SIMS analysis was determined with a Taylor–Hobson Talystep profilometer.

The electrochemical studies of CSMO porous cathodes were performed on planar SOFCs with supporting electrolytes. The model elements consisted of gas-tight electrolytic membranes 20 mm in diameter and with deposited porous anode and cathode layers and platinum current collectors. All layers were deposited on the electrolyte membranes by screen printing followed by heat treatment. The solid electrolyte membranes were obtained by uniaxial compression of LSGM (Fuel Cell Materials, United States) and 10Sc1YSZ (Daiichi Kigenso Kagaku Kogyo) powders, which were then sintered in air at 1480°C (10 h) and 1520°C (7 h), respectively. The resulting gas-tight membranes with a diameter of 20 mm were polished on both sides to a thickness of 0.5 mm. The pastes for screen printing were prepared based on the Heraeus V-006 solvent, which was mixed with the corresponding finely divided powder. The anode consisted of two layers: the current collector with a high nickel content (the NiO to 10Sc1CeSZ weight ratio in the original batch was 73 : 27) and the functional layer with the content of the anion conductive material near the percolation threshold (NiO : 10Sc1CeSZ = 44 : 56) to provide an extended zone of electrochemical reaction and low polarization resistance. At first, the functional anode layer was deposited on the surface of the 10Sc1YSZ discs and sintered at 1400°C for 4 h and then the current collector layer was deposited and sintered by the same procedure. To prevent the chemical interaction between the cathode and solid electrolyte materials, a Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{2-\delta}\) (GDC) layer was deposited, which was burnt in at 1300°C for 3 h. The cathode layer of the material under study was sintered at 1200°C for 4 h. For the cell with LSGM, protective La\(_{0.6}\)Ce\(_{0.4}\)O\(_{2-\delta}\) (LCO) layers were deposited on the electrolyte on both sides. The layers were co-sintered at 1250°C for 3 h; the composition of the anode and cathode and the deposition procedure were the same as in the case of the 10Sc1YSZ electrolyte. The LCO powder was also prepared by the citrate method from Ce(NO\(_3\))\(_3\)· 6H\(_2\)O and La(NO\(_3\))\(_3\)· 6H\(_2\)O with final annealing at 1450°C for 20 h. The synthesized LCO was single-phase; the structure was identified as cubic fluorite \((a = 0.542 \text{ nm, } V=170.03 \text{ Å}^3, \text{ and } \rho = 6.705 \text{ g/cm}^3)\).

The microstructure of the multilayer electrodes of model SOFCs was studied using a SUPRA 50VP high-resolution scanning electron microscope with an INCA Energy+ microanalysis system (Oxford).

To test the chemical interaction between the SOFC layers, the corresponding powders for each layer and electrolyte were mixed in a weight ratio of 1 : 1 and annealed at the temperatures of layer deposition on