Synthesis and Properties of Fuel Cell Anodes Based on \((La_{0.5+x}Sr_{0.5-x})_1-yMn_{0.5}Ti_{0.5}O_3-\delta \) \((x = 0-0.25, y = 0-0.03)^{1}\)

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Abstract—Results are presented of studying electrochemical properties of perovskite-like solid solutions \((La_{0.5+x}Sr_{0.5-x})_1-yMn_{0.5}Ti_{0.5}O_3-\delta \) \((x = 0-0.25, y = 0-0.03)\) synthesized using the citrate technique and studied as oxide anodic materials for solid oxide fuel cells (SOFC). X-ray diffraction (XRD) analysis is used to establish that the materials are stable in a wide range of oxygen chemical potential, stable in the presence of 5 ppm H2S in the range of intermediate temperatures, and also chemically compatible with the solid electrolyte of \(La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3-\delta\) (LSGMC). It is shown that transition to a reducing atmosphere results in a decrease in electron conductivity that produced a significant effect on the electrochemical activity of porous electrodes. Model cells of planar SOFC on a supporting solid–electrolyte membrane (LSGMC) with anodes based on \((La_{0.6}Sr_{0.4})_0.97Mn_{0.5}Ti_{0.5}O_3-\delta\) and \((La_{0.75}Sr_{0.25})_0.97Mn_{0.5}Ti_{0.5}O_3-\delta\) and a cathode of \(Sm_{0.5}Sr_{0.5}CoO_3-\delta\) are manufactured and tested using the voltammetry technique.

Keywords: solid oxide fuel cells, anode, perovskite, citrate synthesis, redox stability

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INTRODUCTION

Perovskite-like oxygen–ion conductors based on lanthanum gallate are one of the most promising groups of solid electrolytes for solid–oxide fuel cells (SOFC) functioning at intermediate temperatures [1, 2]. Application of gallates in SOFC is, however, limited by the relatively high reactivity towards many electrode materials, including Ni–cermet anodes [3]. This regularity and degradation of nickel cermets in atmospheres containing hydrocarbon fuels and sulfur compounds [4, 5] at enhanced temperatures and at significant variation of chemical potential of oxygen in the gas phase cause a necessity of developing new anodic materials based on oxide compounds with mixed ion–electron conductivity. Such materials must have high electron and anion conductivity, high catalytic activity in the reactions of fuel oxidation, thermal expansion coefficients close to those of the other fuel cell materials, and thermodynamic stability both in the oxidative atmosphere in the course of SOFC manufacturing and in reducing atmospheres under the conditions of practical application. The above standard requirements are in part satisfied by the solid solutions of \((La_{0.5+x}Sr_{0.5-x})Cr_{1-y}Mn_{0.5}Ti_{0.5}O_3-\delta\) with a perovskite \(ABO_3\) structure, where \(A\) and \(B\) stand for metal cations [6]. However, the presence of chromium in the \(B\)-sublattice of the perovskite structure may cause negative effects related to evaporation of chromium oxides at high temperatures and formation of \(Cr^{6+}\) during storage in air. Therefore, chromium–free compounds are of practical interest. For example, perovskite with the composition of \(La_{0.6}Sr_{0.4}Ti_{0.8}Mn_{0.2}O_3-\delta\) was studied as an anodic material for SOFC with solid electrolyte membranes based on zirconia [7]. Some works [8–10] also showed the possible prospects for using lanthanum–strontium manganites–titanates as SOFC anodes.

This work was centered on synthesis of submicron powders of perovskite-like oxides of the system \((La_{0.5+x}Sr_{0.5-x})Cr_{1-y}Mn_{0.5}Ti_{0.5}O_3-\delta\) (LSTM) using the citrate technique. Stability of the obtained materials in reducing media containing small amounts of H2S, reactivity towards the material of electrolyte, and specific conductivity in oxidative and reducing atmospheres were investigated. To estimate practical applicability, model SOFCs with anodes based on \((La_{0.5+x}Sr_{0.5-x})Cr_{1-y}Mn_{0.5}Ti_{0.5}O_3-\delta\), where \(La_{0.6}Sr_{0.4}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3-\delta\) (LSGMC) was used as electrolyte, were manufactured and characterized. This electrolyte was chosen for the case studies, as introduction of 5% of cobalt into the \(B\)-sublattice of gallate might cause a significant increase in ionic conductivity [11]. Perovskite \(Sm_{0.5}Sr_{0.5}CoO_3-\delta\) (SSC),

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also well known in the literature [12], was used for cathodes.

**EXPERIMENTAL**

**Synthesis of** \((\text{La}_{0.5+x} \cdot \text{Sr}_{0.5-x})_1 - y \text{Mn}_{0.5} \text{TiO}_3 – \delta (x = 0–0.25, y = 0–0.03)\)** was carried out using the citrate technique according to the Pechini modification [13]. The initial compounds used were: \(\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \text{ (reagent grade)}, \text{Sr(NO}_3\text{)}_2 \text{ (analytical grade), Mn(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O} \text{ (pure grade), TiO}_2 \text{ (ultra high grade)}, \text{ and citric acid (pure). Metal salts were dissolved in distilled water with addition of citric acid under vigorous mixing on a magnetic stirrer until the medium was completely homogenized. Evaporation at 400 K was carried out until a viscous mass was formed, to which highly dispersed TiO\(_2\) was added under vigorous mixing. After weakly bound water was fully removed, the sample was heated to \(\sim 570\) K to initiate the combustion reaction. The obtained precursors were thoroughly ground in an agate mortar and sintered in air at \(1073\) K for 5 h. Then, the powders were ground in ethanol (a Fritsch planetary ball mill, containing, and balls of partially stabilized zirconia) and ultimately sintered at \(1473\) K with isothermal conditioning for 10 h in air. Submicron powders of LSGMC and SSC were synthesized using a similar technique. X-ray diffraction (XRD) patterns were registered at the room temperature using a Siemens D-500-Braun X02-1878 diffractometer (CuK\(_\alpha\)-radiation, the step was 0.02°, the angle range was 20° ≤ 2θ ≤ 90°). X-ray patterns were processed and unit cell parameters were determined using the PowderCell software package (version 2.4).

Ceramic samples for measurement of specific conductance were made using the obtained LSTM powders by the hydraulic compaction technique (~100 MPa) with the further sintering at \(1723\) K for 30 h in air. Conductivity was measured by a standard dc four-probe technique using ceramic plates with the size of \(22 \times 3 \times 1.5\) mm\(^3\). Current electrodes made of platinum-based electrode paste were supported onto sample faces after purification in a sonication bath in ethanol. Platinum wires were used for manufacturing potential pressure electrodes. In the course of measurements, the sample was placed into oxidative and reducing atmospheres consisting of 80% nitrogen and 20% oxygen or 80% nitrogen and 20% hydrogen, accordingly. The sample temperature was maintained to the accuracy of ±1 K. Conductivity measurements were carried out in the temperature range of 673–1073 K. The conductivity value was determined from the slope of the voltammetric characteristic measured at a constant temperature.

Chemical stability of LSTM towards the LSGMC solid electrolyte was estimated using the technique of powder mixture contact sintering at the mass ratio of 1 : 1 at 1623 K in air.

Studies of powder morphology and structure of electrodes, ceramic samples, and model fuel cells was carried out using a scanning electron microscope with a LEO SUPRA 50VP field emitting cathode at the accelerating voltages of 5–10 kV.

A planar SOFC design with a supporting solid electrolyte membrane was used for electrochemical studies. Laboratory SOFC samples represented high-density disks of anion LSGMC conductor (diameter, 20 mm, thickness, 0.5 mm) with porous anode and cathode layers. Anode and cathode powders were mixed with the Heraeus V-006 binder at the mass ratio of 1 : 1 and were consistently applied onto LSGMC disks using the screen-printing technique with the further sintering at \(1573\) K (for anodes) and at \(1473\) K (for cathodes). Measurements were carried out in a two-chamber test bench at \(1173\) K. The gas supplied to the anode was a mixture of \(\text{H}_2\) (50 mL/min) and \(\text{N}_2\) (50 mL/min). On the cathode side, the mixture of \(\text{O}_2\) (50 mL/min) and \(\text{N}_2\) (50 mL/min) was supplied. The gas flow rate was regulated using Bronkhorst controllers. The techniques and equipment for tests for model SOFC were described in detail earlier in [14].

**RESULTS AND DISCUSSION**

According to the data of XRD analysis, LSTM powders obtained in air at \(1473\) K were single-phase and had a structure of rhombohedrally distorted perovskite with space groups \(R\bar{3}c\) (table). Unit cell parameters grew consistently at an increase in the content of lanthanum (table) which resulted in a decrease in the average degree of oxidation of manganese cations and therefore an increase in their radius.

One of the key requirements imposed on anodic SOFC materials is thermodynamic stability under oxidative conditions (in the course of synthesis and supporting on solid electrolyte membranes) and in reducing gas mixtures supplied to the anode in the course of operation of SOFC. In the latter case, application of partially converted hydrocarbon fuels was generally related to the presence of sulfur-containing admixtures that should not result in the poisoning of porous anodes at least due to kinetic causes. In stability tests, LSTM powders manufactured in air were subjected to heat treatment in a mixture of \(80\%\ \text{N}_2, 20\%\ \text{H}_2\) at \(973–1073\) K. In one case, gas flows were a pure mixture of \(\text{N}_2\) and \(\text{H}_2\), in another, 5 ppm \(\text{H}_2\text{S}\) were additionally introduced into the atmosphere. Figures 1 and 2 show examples of XRD patterns for \(\text{La}_{0.5} \cdot \text{Sr}_{0.5} \cdot \text{Mn}_{0.5} \cdot \text{TiO}_3 – \delta\) stoichiometric by \(A\)-sublattice and cation-deficient \((\text{La}_{0.6} \cdot \text{Sr}_{0.4})_{0.97} \cdot \text{Mn}_{0.5} \cdot \text{TiO}_3 – \delta\) after sintering under different conditions. In all cases, no formation of new phases as a result of reduction and reaction with \(\text{H}_2\text{S}\) was observed; the perovskite structure is preserved. However, the radius of cations of \(B\)-sublattice grows under reducing conditions (apart from partial reduction of Ti\(^{4+}\) to Ti\(^{3+}\), the predominant part of Mn\(^{4+}\) ions is