Electrical Conductivity of LaCo_{1-x}Fe_{1-x}O_3-δ and LaLi_{0.1}Co_{x}Fe_{0.9-x}O_3-δ (0 ≤ x ≤ 0.4) Oxides

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Received July 8, 2010

Abstract—We have studied the effect of Co and Li concentrations on the phase composition and electrical conductivity of LaCo_{1-x}Fe_{1-x}O_3-δ and LaLi_{0.1}Co_{x}Fe_{0.9-x}O_3-δ perovskite-like oxides synthesized in air at 1470 K. Single-phase materials with an orthorhombic crystal structure were obtained in the range 0 ≤ x ≤ 0.3. The composition dependences of conductivity have a minimum at x_c = 0.1 and 0.2, respectively. In the range x > 0.1, the conductivity of LaCo_{1-x}Fe_{1-x}O_3-δ increases with increasing Co concentration for T > 700 K and decreases for T < 600 K. The conductivity of La(Li_{0.1}Co_{0.9-x})O_3-δ increases with Co concentration throughout the temperature range studied.

INTRODUCTION

Perovskite-like La_{1-y}B_{Fe_{1-y}}M_{M_{O_{3-δ}} (B = alkaline-earth metal; M = Mn, Co, Ni, Ga, Li; 0 ≤ x ≤ 1; 0 ≤ y ≤ 1; δ ≥ 0) oxides have attracted researchers’ considerable attention because their structure; the spin state and oxidation state of the transition metals and the oxygen vacancy concentration in these materials; and, as a consequence, their transport, magnetic, and catalytic properties depend significantly on the nature and concentration of the substituents (B and M) and external influences (temperature, pressure, atmosphere) [1–7]. There is currently increased interest in oxides with high mixed electronic–ionic (oxygen ion) conductivity, because they can be used, e.g., as materials for oxygen permeable membranes in reactors for conversion of methane to syngas [1, 4] and as materials for the oxygen electrode of solid oxide fuel cells [7]. On the other hand, of no less interest are oxides that offer high electronic conductivity and are stable under typical working conditions of molten carbonate fuel cells (MCFCs) [8].

The most important requirements for MCFC cathode materials are as follows [9]:

1. corrosion resistance of the cathode material to cathode gases (a mixture of CO_2 and O_2 or air) and molten lithium–containing alkaline metal carbonates,
2. high catalytic activity for oxygen reduction, and
3. high electron–hole conductivity (above 100 S/m) at the working temperature of MCFCs (920 K).

Currently, MCFC cathodes are typically fabricated from in situ lithiated LiNi_{1-x}O with x ≈ 0.02 [8]. Unfortunately, this material has a significant drawback: the products of its dissolution in melts can be reduced at the anode to metallic Ni, short-circuiting the MCFC [8]. A radical approach to this problem is to replace LiNi_{1-x}O with Ni-free materials.

Possible candidates include La_{1-x}Sr_{x}CoO_3-δ with 0 ≤ x ≤ 0.3 [8, 10]. These materials were reported to basically meet the above requirements [8]. At the same time, equilibrium solubility data for the constituent components of La_{0.7}Sr_{0.3}CoO_3-δ indicate that Sr has an abnormally high solubility in molten (Li_{0.6}K_{0.38})_2CO_3, which is often used as an electrolyte (0.21 kg/m^3 against 8.5 × 10^{-3} kg/m^3 for Co and 4.0 × 10^{-2} kg/m^3 for La at T = 920 K [10]). This reduces the electrical conductivity and catalytic activity of the material [10]. Moreover, the high cost of Co compounds limits the use of these oxides as MCFC cathode materials.

To reduce the Co concentration and improve the corrosion resistance of the oxides in lithium-containing electrolytes, Vecherskii et al. [11, 12] substituted Fe and Li ions on some Co sites in LaCoO_3 and examined La(Li_{0.1}Co_{0.9-x}O_3-δ, having an orthorhombic crystal structure. A porous gas diffusion cathode based on this material stably operated in a laboratory-produced fuel cell for 2000 h, and its polarization characteristics measured in molten (Li_{0.62}K_{0.38})_2CO_3 turned out to surpass those of LiNi_{1-x}O cathodes [12]. After the experiments, no changes in the phase composition of the material were detected.

Data on the physicochemical properties of phase-pure La(Li_{0.1}Co_{0.9-x}O_3-δ are not available in the literature. As the first step in this direction, we studied the phase composition and temperature-dependent (300–1030 K) conductivity of air-synthesized La(Li_{0.1}Co_{0.9-x}O_3-δ samples with x varied from 0 to...
0.4 in steps of 0.1. For comparison, we studied the phase composition and temperature-dependent conductivity of LaCoFe1–xO3–δ samples synthesized under similar conditions.

The purpose of this work was to determine the highest Co concentration at which the materials in question retain their orthorhombic structure and to examine the influence of Li and Co concentrations on their conductivity.

**EXPERIMENTAL**

The starting chemicals used were La2O3 prepared through thermal decomposition of La2(CO3)3 ⋅ 6H2O (reagent grade) in air at T = 1270 K for 24 h in air, Li2CO3 (exrapure grade), and carbonyl Fe and Co. They were dissolved in aqueous HNO3 (1 : 1 volume ratio), evaporated, and then slowly heated in air to 1020 K and held there for 2 h to decompose the nitrates formed. The resultant oxide mixture was homogenized by mixing in a ball mill and pressed at 107 Pa into pellets. Synthesis was carried out in air at T = 1470 K. The lithium-containing samples were packed with a mixture of La, Fe, Co, and Li oxides in roughly the same ratio as in the samples. In the process of synthesis, the samples were cooled twice, ground, mixed, and pressed. The total synthesis time was 36 h.

The phase composition of the samples was determined by X-ray diffraction (XRD) on a D/Max-2200V/PC diffractometer with CuKα radiation. Lattice parameters were determined using a Si standard.

Electrical conductivity was measured by a four-probe dc method in air with an accuracy below 6%. Correction factors for converting the measured conductivity of porous samples (σdc) to the conductivity of dense material (σ) were found using the relation

$$\sigma = \sigma_{dc} q.$$  

Here, \(q = \xi / \left[ r(1 + \xi) \right] - 1 \), where \(r = 1 - P / 100 \) is the volume fraction of the conducting phase \((P \) is the percent porosity), and \(\xi = (\varepsilon / 2) - 1 \) (\(\varepsilon \) is the number of particles of the conducting phase in contact with a given particle of the same phase). Relation (1) was derived from the Landauer–Bruggeman formula for a two-phase mixture of particles with conductivities \(\sigma_1\) and \(\sigma_2\) [13] under the assumption that air-filled pores are nonconductive \((\sigma_2 = 0)\). For definiteness, \(\sigma\) was calculated for \(\varepsilon = 6\). The porosity of the samples was determined by the Archimedes method.

**RESULTS AND DISCUSSION**

XRD examination showed that the synthesized LaCoFe1–xO3–δ and La(Li0.1Co0.4Fe0.5)O3–δ samples with \(x \leq 0.3\) had an orthorhombic crystal structure similar to that of LaFeO3. Their unit-cell parameters \((a, b,\) and \(c)\) and volume \((V)\) were found to decrease with increasing Co concentration (Table 1). Formally, the crystal structure of LaCo0.4Fe0.6O3–δ was also orthorhombic, but its XRD pattern showed rather broad peaks, suggesting that it contained domains of a different phase similar in crystallographic parameters. By contrast, there was clear evidence that La(Li0.1Co0.4Fe0.5)O3–δ consisted of two phases: LaO3 and a hexagonal perovskite-like phase similar in structure to LaCoO3.

Figure 1 presents the composition dependences of conductivity for LaCoFe1–xO3–δ (here and in what follows, the data are corrected for porosity; see Table 2). The curves have a minimum at \(x = 0.1\). In the range \(x > 0.1\), the conductivity increases with increasing Co concentration for \(T > 700\) K and decreases for \(T < 600\) K.

Figure 2 shows Arrhenius plots of conductivity for LaCoFe1–xO3–δ. As the temperature is raised from 300 to 1030 K, the conductivity of all the samples increases. It is known [14] that the electron–hole conductivity of LaFeO3 is due to small-polaron hopping. In different temperature ranges, \(\sigma(T)\) follows the relation

$$\sigma = A \exp \left( \frac{-E}{kT} \right).$$  

### Table 1. Unit-cell parameters \((a, b, c)\) and volume \((V)\) of the perovskite-like phase in LaCoFe1–xO3–δ and La(Li0.1Co0.4Fe0.5)O3–δ samples

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a \times 10, \text{nm})</th>
<th>(b \times 10, \text{nm})</th>
<th>(c \times 10, \text{nm})</th>
<th>(V \times 10^4, \text{nm}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.558 ± 0.001</td>
<td>5.571 ± 0.002</td>
<td>7.859 ± 0.003</td>
<td>243.3 ± 0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>5.541 ± 0.002</td>
<td>5.543 ± 0.001</td>
<td>7.842 ± 0.002</td>
<td>240.9 ± 0.2</td>
</tr>
<tr>
<td>0.2</td>
<td>5.520 ± 0.002</td>
<td>5.527 ± 0.002</td>
<td>7.810 ± 0.003</td>
<td>238.3 ± 0.2</td>
</tr>
<tr>
<td>0.3</td>
<td>5.510 ± 0.003</td>
<td>5.533 ± 0.003</td>
<td>7.795 ± 0.003</td>
<td>237.6 ± 0.4</td>
</tr>
<tr>
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<td>5.554 ± 0.001</td>
<td>5.568 ± 0.001</td>
<td>7.865 ± 0.001</td>
<td>243.2 ± 0.1</td>
</tr>
<tr>
<td>0.1</td>
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<td>7.845 ± 0.002</td>
<td>241.0 ± 0.2</td>
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<tr>
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<td>5.517 ± 0.001</td>
<td>7.790 ± 0.003</td>
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<td>5.515 ± 0.002</td>
<td>7.757 ± 0.003</td>
<td>234.1 ± 0.3</td>
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