Developments in Solid Oxide Fuel Cells and Lithium Ion Batteries

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Preface

The growing environmental concerns and the increasing depletion of fossil fuels have created enormous global interest in alternative energy technologies. Fuel cells and high energy density batteries are appealing in this regard as they offer clean energy. They are attractive for a variety of power needs ranging from portable electronic devices to electric vehicles to stationary power.

Batteries are the major power sources for portable electronic devices. The exponential growth of popular portable electronic devices such as cellular phones and laptop computers has created an increasing demand for compact, lightweight power sources. Lithium-ion batteries have become appealing in this regard as they offer higher energy density compared to other rechargeable systems. The higher energy density also makes them attractive for hybrid and electric vehicles. Commercial lithium-ion cells currently use the layered lithium cobalt oxide as the cathode and carbon as the anode. However, the practical capacity of lithium cobalt oxide is limited, and cobalt is relatively expensive and toxic. On the other hand, the currently used graphite anode exhibits irreversible capacity loss. These difficulties have created enormous worldwide interest to develop alternative cathode and anode materials.

Unlike the battery technology, the fuel cell technology has not quite matured, and it is confronted with materials issues and high cost. For example, the high operating temperature of the conventional zirconia-based electrolyte limits the choice of electrode and interconnect materials for solid oxide fuel cells (SOFC). There is immense interest to lower the operating temperature of SOFC and use hydrocarbon fuels directly without requiring external reformers. The research activities focus on the development of compatible cathode, anode, and electrolyte combinations that can operate at an intermediate temperature of around 700°C. Additionally, cost-effective manufacturing and development of stable seals are critical for the success of the SOFC technology. In this regard, development of new materials as well as processing and characterization of ceramic materials play a key role.

To bring the ceramics community up to date on the fuel cell and battery technologies, the American Ceramic Society has been hosting symposia on related topics since 1995. This volume consists of 14 papers that were presented at the 106th Annual Meeting of the American Ceramic Society, Indianapolis, IN, April 18-21, 2004. A number of leading experts in materials science and engineering, solid state chemistry and physics, electrochemical science and technology from academia, industry and national laboratories presented their research and developments at this symposium. The presentations covered development of new materials and a fundamental understanding of the structure-property-performance relationships and the associated electrochemical
and solid state phenomena. The symposium was sponsored by the Electronics, Basic Science, and Nuclear and Environmental divisions of the American Ceramic Society. Of the papers presented at this symposium, including several invited talks, 14 peer-reviewed papers are included in this volume under two subtopics: solid oxide fuel cells and lithium-ion batteries.

The editors acknowledge the support of several members of the Electronics, Basic Science, and Nuclear and Environmental divisions of the American Ceramic Society. The editors also thank all the authors, session chairs, manuscript reviewers, and the society staff who made the symposium and the proceeding volume a success. It is the sincere hope of the editors that the readers will appreciate and benefit from this collection of articles in the area of solid oxide fuel cells and lithium ion batteries.

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S. K. Sundaram
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Solid Oxide Fuel Cells
CHARACTERIZATION OF Sr-DOPED NEODYMIUM COBALT OXIDE CATHODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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ABSTRACT

With an aim to explore as cathode materials for intermediate temperature solid oxide fuel cells, the structure and properties of Nd$_{1-x}$Sr$_x$CoO$_{3.5}$ oxides have been investigated for 0 ≤ x ≤ 0.5. The Nd$_{1-x}$Sr$_x$CoO$_{3.5}$ system crystallizing in the orthorhombic perovskite structure exhibits a semiconductor to metal transition at x ≈ 0.3, and the electrical conductivity increases with x. The thermal expansion coefficient decreases initially with increasing x, reaches a minimum at x = 0.3, and then increases. While the increasing electrical conductivity leads to an increase in electrocatalytic activity and power density initially with x, the enhanced interfacial reactions between the cathode and the La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ (LSGM) electrolyte result in a decline in the activity at higher values of x > 0.4. Thus the x = 0.4 sample exhibits the highest catalytic activity with a maximum power density value of 0.24 W/cm$^2$ at 800 °C in single cells fabricated with the Ni-Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (GDC) cermet anodes.

INTRODUCTION

Solid oxide fuel cells (SOFCs) based on yttria-stabilized zirconia (YSZ) electrolytes generally need an operating temperature of around 1000 °C, which leads to difficulties arising from thermal expansion mismatch, interfacial reaction between the electrolyte and electrode, and limitations in the choice of interconnect materials. These difficulties have generated interest in the development of SOFCs that can operate at an intermediate temperature of 500-800 °C, but the lower temperatures lead to large over-potential at the oxygen reduction electrode. Although the Sr-doped LaMnO$_3$ (LSM) perovskite oxides exhibit acceptable electrochemical activity at 1000 °C with YSZ, the low oxide ion conductivity prevent their use for intermediate temperature SOFCs. With this respective, the Sr-doped LaCoO$_3$ (LSC) perovskite oxides have drawn attention due to their high electronic and ionic conductivities, but they experience high thermal expansion and low chemical stability. The replacement of La by other lanthanides Ln = Sm and Gd can lower the thermal expansion due to the decrease in the ionicity of the Ln-O bond. However, replacement of the larger La by smaller Ln = Pr, Sm, and Gd will lower the electronic conductivity due to a bending of the O-Co-O bonds from 180° and a consequent decrease in the bandwidth. To realize a compromise between these two parameters, we focus on the Nd$_{1-x}$Sr$_x$CoO$_{3.5}$ compositions since the ionic size of Nd$^{3+}$ is intermediate between those of La$^{3+}$ and Sm$^{3+}$ or Gd$^{3+}$ and the ionicity of the Nd-O bond is intermediate between those of La-O and Sm-O or Gd-O bonds. We present here the crystal chemistry, electrical conductivity, thermal expansion, and electrochemical performance of Nd$_{1-x}$Sr$_x$CoO$_{3.5}$ for 0 ≤ x ≤ 0.5.

EXPERIMENTAL

The Nd$_{1-x}$Sr$_x$CoO$_{3.5}$ samples were synthesized by firing required amounts of Nd$_2$O$_3$, SrCO$_3$, and Co$_3$O$_4$ in air first at 900 °C for 12 h, followed by regrinding, pressing into pellets, and...
sintering at 1200 °C for 24 h. In order to study the effect of material synthesis procedure, the \( \text{Nd}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3.6} \) composition was also synthesized by a coprecipitation method. For the coprecipitation method, required amounts of \( \text{Nd}_2\text{O}_3 \), \( \text{SrCO}_3 \), and \( \text{Co(CH}_3\text{COO})_2\cdot4\text{H}_2\text{O} \) were dissolved in dilute nitric acid and the metal ions were then coprecipitated as carbonates and hydroxides by adding a mixture of KOH and \( \text{K}_2\text{CO}_3 \).\(^{12}\) The coprecipitate was washed with deionized water, dried, fired at 500 °C for 5 h, ground, pressed into pellets, and sintered at 1200 °C for 24 h. The \( \text{NiO-Ge}_{0.5}\text{Gd}_{0.5}\text{O}_{1.55} \) (GDC) cermet (\( \text{Ni-GDC} = 70:30 \) vol %) anode was synthesized by the glycine-nitrate combustion method.\(^{13}\) Glycine was added to a nitric acid solution containing stoichiometric amounts of \( \text{Gd}_2\text{O}_3 \), \( \text{Ge}_2\text{O}_3 \), and \( \text{Ni(CH}_3\text{COO})_2\cdot4\text{H}_2\text{O} \). The metal nitrate/glycine solution was heated on a hot plate to evaporate excess water and the anode cermet powder was obtained by self-sustaining combustion of the solid mass. The residual carbon was then removed by calcination at 600 °C for 3 h in air. The \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Gd}_{0.8}\text{Ge}_{0.2}\text{O}_{2.8} \) (LSGM) electrolyte was prepared by firing required amounts of \( \text{La}_2\text{O}_3 \), \( \text{SrCO}_3 \), \( \text{Ga}_2\text{O}_3 \), and \( \text{MgO} \) at 1100 °C for 5 h, followed by palletizing and sintering at 1500 °C for 10 h.

Crystal chemistry characterizations were carried out with X-ray diffraction (XRD) employing Rietveld method. Thermogravimetric analysis (TGA) and thermal expansion measurement were carried out with a heating/cooling rate of, respectively, 2 and 10 °C/min in air. The electrical conductivity data were collected with a four-probe dc method in the temperature range of 200-900 °C in air. Electrochemical performances were carried out with single cells at 800 °C. The \( \text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3 \) cathodes and \( \text{NiO-GDC} \) cermet anode were prepared by screen printing on a 1 mm thick LSGM electrolyte pellet, followed by firing for 3 h at 1000 °C for the cathode and 1200 °C for the anode. The geometrical area of the electrode was 0.25 cm\(^2\) and Pt paste was used as the reference electrode. Humidified \( \text{H}_2 \) (3% \( \text{H}_2\text{O} \) at 30 °C) and air were supplied as fuel and oxidant, respectively, at a rate of 100 cm\(^3\)/min.

**RESULT AND DISCUSSION**

All the \( \text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3 \) (0 ≤ x ≤ 0.5) samples synthesized were found to be single phase and were indexed with the orthorhombic \( \text{GdFe}_2\text{O}_5 \) type perovskite structure (space group Pbnm, No. 62). The variations in the lattice parameters and lattice volume with Sr content x are shown in Figure 1. The lattice parameters and lattice volume increase with increasing x. The substitution of \( \text{Sr}^{2+} \) (ionic radius = 1.44 Å) for \( \text{Nd}^{3+} \) (1.27 Å) causes an oxidation of the larger \( \text{Co}^{3+} \) (0.61 Å) to a smaller \( \text{Co}^{4+} \) (0.53 Å) and/or the formation of oxygen vacancies. Nevertheless, a significantly larger size of \( \text{Sr}^{2+} \) compared to that of \( \text{Nd}^{3+} \) results in an overall increase in the lattice parameters and volume with x.

When \( \text{Sr}^{2+} \) ions are substituted for \( \text{Nd}^{3+} \) ions, the charge imbalance could be compensated by either or both of the following two mechanisms: electronic compensation by an oxidation of \( \text{Co}^{2+} \) to \( \text{Co}^{4+} \) in \( \text{Nd}_{1-x}\text{Sr}_x\text{Co}^{2+}\text{O}_3 \) and/or ionic compensation by the formation of oxygen vacancies in \( \text{Nd}_{1-x}\text{Sr}_x\text{Co}^{3+}\text{O}_{3-x} \). Petrov et al.\(^{6}\) reported that the concentration of \( \text{Co}^{4+} \) in the \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) system increases with x, reaches a maximum at x ~ 0.4, and then decreases at higher values of x. This result suggests that at higher doping levels (x > 0.4), the charge imbalance is primarily compensated by the formation of oxygen vacancies. In order to verify the defect structure of \( \text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3 \), we investigated the samples with thermogravimetric analysis (TGA) in air, and the TGA data of \( \text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3 \) on heating in air are shown in Figure 2.
Figure 1. Variations of the lattice parameters and lattice volume of Nd$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (0 $\leq x \leq 0.5$) with Sr content, $x$.

Figure 2. TGA plots of Nd$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (0 $\leq x \leq 0.5$) recorded in air with a heating rate of 2 °C/min.