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Layered $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ ($\text{Ln} = \text{Nd}$ and Gd) perovskite cathodes for intermediate temperature solid oxide fuel cells

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ABSTRACT

The effects of Sr substitution on the crystal chemistry, phase stability, and electrochemical performance as cathodes in intermediate-temperature solid oxide fuel cells (IT-SOFCs) of the layered $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ ($\text{Ln} = \text{Nd}$ and Gd) perovskites have been investigated. The $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ oxides crystallize in tetragonal $P4/mmm$ symmetry for $0 \leq x \leq 0.75$. The $x = 0.75$ samples show a significant improvement in electrochemical performance compared to the $x = 0$ samples for both $\text{Ln} = \text{Nd}$ and Gd . In an electrolyte ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$)-supported single cell configuration (thickness = 0.50 mm), the $\text{Ln} = \text{Gd}$ series shows an improved maximum power density from 468 mW cm^{-2} for the Sr-free ($x = 0$) sample to 530 mW cm^{-2} for the $x = 0.75$ sample. In the $\text{Ln} = \text{Nd}$ system, the $x = 0.75$ sample shows a maximum power density of 562 mW cm^{-2} . The Sr substitution was found to have negligible effect on the thermal expansion coefficients (TEC) between the $x = 0$ and $x = 0.75$ samples in both series.

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1. Introduction

Solid oxide fuel cells (SOFCs) are a promising technology, particularly for stationary power plants [1]. SOFCs offer a range of benefits compared to other fuel cells; they are more efficient, require less expensive catalysts, and are able to use a wider range of fuel sources without the need for external reforming [1,2]. Current research efforts are focused on lowering the operating temperatures from the conventional 800–1000 °C range to the intermediate-temperature (IT) range of 500–800 °C to allow for the use of less expensive interconnects and to reduce thermal expansion mismatches between components [1,2]. However, the currently used industry standard cathode material $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) does not possess adequate catalytic activity at these lower

temperature ranges, and consequently new cathode materials need to be developed [3,4].

Studies have shown that the oxygen reduction reaction (ORR) rate in traditional SOFC cathodes is highly dependent on surface chemistry, specifically the triple phase boundary (TPB), or the interfacial area shared by the electrolyte, cathode, and oxidant [5]. In order to overcome this dependency, attention has been focused on cathode materials that are mixed ionic and electronic conductors (MIECs), i.e. cathodes that can conduct both O^{2-} ions and electrons, allowing the ORR to occur at all cathodic surface area in contact with the oxidant [6]. A number of perovskite-based structures display MIEC properties, and one of the most promising of these is the recently investigated layered $\text{AA}'\text{B}_2\text{O}_{5+\delta}$ ($\text{A} = \text{Ba}$, $\text{A}' = \text{lanthanide}$, and $\text{B} = \text{transition metal}$) perovskite. Due to the large difference between their ionic radii,

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the Ba^{2+} and Ln^{3+} cations tend to order along the *c* axis with the oxygen vacancies located predominantly in the Ln planes as the Ln^{3+} ions prefer lower coordination numbers [7].

The $\text{LnBaCo}_2\text{O}_{5+\delta}$ (Ln = lanthanide) series of oxides is one of the best-studied layered perovskite systems. Previous studies on this system have shown that it is highly amenable to cationic substitutions [4,8]. For example, the substitution of Sr for Ba in $\text{LnBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$ (Ln = Nd and Gd) resulted in improved electrical conductivity, but it also increased the thermal expansion coefficient (TEC) at high temperatures, which can cause delamination of the cathode during cycling [8]. In contrast, the substitution of Cu for Co in $\text{LnBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ (Ln = Nd and Gd) decreased the TEC, but it also decreased the electrical conductivity and melting temperature, making it difficult to synthesize without impurities [4].

To utilize the advantageous, positive effects of both the Sr and Cu substitutions, this study focuses here on the $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ (Ln = Nd and Gd, and $0 \leq x \leq 1$) system. The Co:Cu ratio of 1:1 was chosen based on a previous study that showed the optimal performance for the $\text{LnBaCo}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ (Ln = Nd and Gd) system around $x = 1.0$ [4]. Accordingly, the effects of Sr content on the crystal chemistry, oxygen content, electrical conductivity, and electrochemical performance in SOFC of $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ (Ln = Nd and Gd, and $0 \leq x \leq 1$) are presented.

2. Experimental

The $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ (Ln = Nd and Gd) samples were synthesized by conventional solid state reactions. Required quantities of Gd_2O_3 (or Nd_2O_3), BaCO_3 , SrCO_3 , Co_3O_4 , and CuO were mixed with ethanol in an agate mortar and pestle, pressed into pellets, and decarbonated at 850°C in air for 6 h. The resultant powders were ground, pressed into pellets, and sintered at 960°C for 12 h. Two to three additional steps of grinding and sintering were carried out at varying temperatures in the range of 970 – 1000°C to achieve single-phase samples while avoiding melting of the samples [4]. The resulting powders were annealed in air at 900°C and slowly cooled to room temperature at a rate of 1°C min^{-1} to maximize the oxygen content.

The resultant products were characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation, and the Rietveld method was employed to refine the data with the aid of the FullProf program [9]. Thermal expansion data were obtained with a dilatometer (Linseis L75H) during three heating and cooling cycles between 80 and 900°C at a rate of 3°C min^{-1} . Electrical conductivity data were gathered using a four probe dc method in the van der Pauw configuration during a cooling cycle from 900 to 40°C at 20°C intervals [10,11]. The oxidation state of (Co, Cu) and oxygen content at room temperature were determined by iodometric titration [12]. Thermogravimetric analysis (TGA) data were collected from room temperature to 900°C at a heating/cooling rate of 2°C min^{-1} in air with a Netzsch STA 449 F3 thermal analysis system. The samples used in the titration and TGA analysis were first annealed at 900°C and cooled to room temperature at a rate of $0.5^\circ\text{C min}^{-1}$ to maximize the oxygen content values in the samples.

The $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM) electrolyte was synthesized by mixing required amounts of La_2O_3 , SrCO_3 , Ga_2O_3 and MgO in ethanol with an agate mortar and pestle, followed by grinding the dry powder, pressing into pellets, and firing at 1100°C for 5 h. The resultant powder was then ground and ball-milled in ethanol for 48 h, mixed with a binder (Butvar B76) in ethanol, dried, pressed, and sintered at 1500°C for 10 h. $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) and $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8}$ (LDC) were synthesized by the glycine nitrate combustion process (GNP) [13,14]. Required amounts of Gd_2O_3 , $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, and La_2O_3 were dissolved in dilute HNO_3 with glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and heated on a stir plate to form a viscous gel until it combusted. The resultant powder was then fired at 600°C for 2 h.

The polarization resistances (R_p) of the $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ (Ln = Nd and Gd) cathodes on LSGM electrolyte-supported symmetric cells in the range of 550 – 800°C were determined by ac impedance spectroscopy (Solartron 1260 FRA). To ensure good contact, an intermediate layer of $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ and LSGM (50%:50% weight ratio) was prepared by mixing with an organic binder (Heraeus V006) to form a slurry, screen-printing onto the dense LSGM electrolyte (0.5 ± 0.05 mm thick) on both sides, and sintering at 950°C for 1 h. The cathode layer was prepared by mixing $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ with the organic binder to form a slurry, screen-printing the slurry on both sides of the intermediate layer three times, and sintering at 950°C for 3 h. Platinum current collectors were applied by screen-printing platinum paste on both sides and attaching a platinum mesh, followed by sintering at 800°C for 20 min.

Electrochemical performances of the $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ cathodes were evaluated on LSGM-electrolyte-supported single cells with GDC/NiO cermet anodes (30:70 vol%). The cathode intermediate layer and cathode were prepared as previously described for the symmetric cell. To prevent side-reactions between the LSGM electrolyte and the anode, an intermediate LDC layer was applied in the same manner as for the symmetric cell intermediate layer [15]. The GDC/NiO anode was prepared by ball-milling the required amounts of NiO and GDC powders in ethanol for 24 h. The resultant powder was dried and mixed with an organic binder (Heraeus V006) and then screen-printed onto the intermediate layer three times. The single cell performance was evaluated at 700 – 800°C after a 3 h dwell at 800°C with air as the oxidant and hydrogen as the fuel, respectively, at 120 and $100\text{ cm}^3\text{ min}^{-1}$. After measurement, the microstructures of the single cells were examined by a JEOL JSM-5610 scanning electron microscope (SEM).

3. Results and discussion

3.1. Crystal chemistry of $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ (Ln = Nd and Gd)

Fig. 1 shows the room-temperature XRD patterns of the $\text{LnBa}_{1-x}\text{Sr}_x\text{CoCuO}_{5+\delta}$ (Ln = Nd and Gd) samples for $0 \leq x \leq 1.0$. As mentioned in the experimental section, each sample was prepared at different sintering temperatures to obtain single-phase samples [4]. Previous work has shown that the layered perovskites tend to adopt different space groups depending on their compositions; for example, $\text{GdBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$ was shown to transition from orthorhombic (*Pmmm*) at $x = 0$ to

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