La$_{1.85}$Sr$_{1.15}$Cu$_{2-x}$Co$_x$O$_{6+\delta}$ intergrowth oxides as cathodes for intermediate temperature solid oxide fuel cells

Y.N. Kim, A. Manthiram*

Electrochemical Energy Laboratory & Materials Science and Engineering Program, University of Texas at Austin, Austin, TX 78712, USA

ARTICLE INFO

ABSTRACT

The effect of the substitution of Co for Cu in the intergrowth oxide La$_{1.85}$Sr$_{1.15}$Cu$_{2-x}$Co$_x$O$_{6+\delta}$ on the crystal chemistry, thermal and electrical properties, and catalytic activity for oxygen reduction reaction (ORR) has been investigated to determine its viability as a cathode material for intermediate temperature solid oxide fuel cells (SOFCs). The larger size and preference for higher oxygen-coordination number of the La^{3+}/Sr^{2+} ions allow intercalation of excess oxygen between the two CuO$_2$ layers, and vacancies are introduced into the O(1) sites of the CuO$_2$ planes. The La$_{1.85}$Sr$_{1.15}$Cu$_{2-x}$Co$_x$O$_{6+\delta}$ oxides show thermal expansion coefficients (TEC) of $\sim$15 $\times$ 10^{-6} $^\circ$C^{-1} that are compatible with that of the Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (GDC) electrolyte in SOF. Fuel cell data collected with electrolyte-supported and anode-supported single cells reveal that the La$_{1.85}$Sr$_{1.15}$Cu$_{2-x}$Co$_x$O$_{6+\delta}$ + GDC (50:50 vol.%) composite cathodes exhibit lower polarization resistance compared to the pure La$_{1.85}$Sr$_{1.15}$Cu$_{2-x}$Co$_x$O$_{6+\delta}$ cathodes due to the extended triple phase boundary (TPB) where the ORR occurs. Among the various cathode compositions investigated in this study, the La$_{1.85}$Sr$_{1.15}$Cu$_{1.8}$Co$_{0.2}$O$_{6.26}$ + GDC composite was found to be optimal with the lowest polarization loss.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Transition metal oxides with high mixed ionic and electronic conductivity (MIEC) have been widely investigated as cathode materials in solid oxide fuel cells (SOFCs) and as oxygen separation membranes [1–3]. However, the high operating temperatures of SOFCs often lead to interfacial reactions, thermal expansion mismatches, and limitations in the choice of other cell components such as interconnects. To overcome these difficulties, a lowering of the operating temperature to an intermediate range of 500–800 $^\circ$C is being currently pursued, but the conventional La$_{1-x}$Sr$_x$MnO$_3$ (LSM) perovskite cathode shows poor oxide-ion conductivity and inadequate catalytic activity at intermediate temperatures [1,4–7]. In this regard, mixed oxide-ion and electronic conducting oxides with perovskite or perovskite-related structures have been widely investigated as alternative cathode materials.

Among the perovskite-related structures, the Ruddlesden–Popper (R–P) series of intergrowth oxides (AO)(ABO$_3$)$_n$ has drawn attention recently as potential alternative cathode materials [8–18]. These intergrowth oxides have rock-salt AO layers alternating with a single (n = 1), double (n = 2), or triple (n = 3) perovskite (ABO$_3$)$_n$ layers along the c axis [14,19,20]. Various compositions in the R–P series have been studied as oxygen separation membranes and cathode materials in SOFCs due to their good MIEC proper-

ties [9,14–16]. Particularly, cuprates in the R–P series show high electronic conductivity and good oxygen mobility. For instance, La$_{1-x}$Sr$_x$CuO$_{2.5-\delta}$ (n = ∞ member) has a large amount of oxygen defects in the perovskite structure and shows high electronic conductivity [21,22]. Similarly, La$_{2-x}$Sr$_x$CuO$_{4-\delta}$ (n = 1 member) exhibits high electronic conductivity including superconductivity at low temperatures [10,17,23–25].

Another interesting cuprate is the n = 2 member La$_{2-x}$Sr$_{1+x}$Cu$_2$O$_{6+\delta}$ that consists of two CuO$_2$ perovskite layers alternating with two rock-salt AO layers along the c axis [26–28]. Fig. 1 shows the crystal structure of La$_{1.85}$Sr$_{1.15}$Cu$_2$O$_{6+\delta}$; the O(3) site is completely vacant in the case of La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_6$ [27] as the smaller Ca^{2+} ions prefer lower coordination numbers. Structural analysis of La$_{1.85}$Sr$_{1.15}$Cu$_2$O$_{6+\delta}$ has shown that interstitial oxygen are located at the interlayer (0, 0, 1/2) sites between the two AO rock salt layers, with a small degree of vacancies in the O(1) sites of the CuO$_2$ planes [29]. Also, an investigation of the transport properties of La$_{2-x}$Sr$_{1+x}$Cu$_2$O$_{6+\delta}$ (x = 0, 0.1, 0.2) has shown that the activation energy in the low-temperature region at different oxygen partial pressures does not exceed 0.1 eV and the conductivity increases with increasing Sr content [26].

Despite the high electrical conductivity values, these cuprates have not been investigated as cathodes in SOFC. We present here a systematic investigation of the La$_{1.85}$Sr$_{1.15}$Cu$_{2-x}$Co$_x$O$_{6+\delta}$ system with x = 0, 0.1, and 0.2 as cathode materials for SOFC. The substitution of Co is particularly pursued as Co-containing pervoskites are known to exhibit high catalytic activity for ORR. The effect of the substitution of Co for Cu on the crystal structure, electrical

* Corresponding author. Tel.: +1 512 471 1791; fax: +1 512 471 7681.
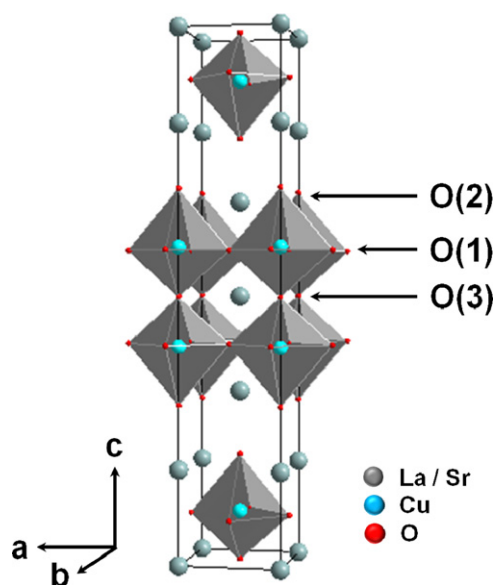*E-mail address:* rmanth@mail.utexas.edu (A. Manthiram).

Fig. 1. Crystal structure of $La_{1.85}Sr_{1.15}Cu_2O_{6+\delta}$.

conductivity, thermal expansion coefficient, and catalytic activity for ORR in SOFC is presented.

2. Experimental

The $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ ($x = 0$, 0.1, and 0.2) samples were synthesized by conventional solid-state reaction methods. Required amounts of La_2O_3, $SrCO_3$, CuO, and Co_3O_4 were thoroughly mixed by ball milling in ethanol for 24 h and calcined at 1000 °C for 20 h in air. The calcined powders were then ground, pressed into pellets, and sintered at 1050 °C for 20 h in air, followed by slow cooling to room temperature at a rate of 0.4 °C min^{-1} in air to maximize the oxygen content. The $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ + GDC (Nextech, Micro grade) composite cathodes (50:50 vol.%) were prepared by ball-milling appropriate amounts of $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ and GDC in ethanol for 3 days.

The products thus obtained were characterized by X-ray diffraction (XRD), and the XRD data were refined with the Rietveld method through the Fullprof program [30]. The average oxidation state of (Co, Cu) and the room-temperature oxygen content values were determined by iodometric titration [31]. Thermogravimetric analysis (TGA) was performed with a Netzsch (STA 449 F3) thermal analysis system. Thermal expansion data were collected with a dilatometer (Linseis L75H) during three consecutive heating/cooling cycles at a rate of 3 °C min^{-1} between 80 and 900 °C with a dwelling at 900 °C for 1 h in air, employing rod-shaped specimens. Electrical conductivities of the $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ pellets were measured with a four-probe dc method using a van der Pauw configuration [32,33] in the temperature range of 40–900 °C. Chemical stability of the $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ samples with the electrolytes (GDC, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (LSGM), and $Y_{0.08}Zr_{0.92}O_{1.96}$ (YSZ)) was evaluated by heating a mixture of $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ and electrolytes powders (1:1 vol. ratio) at 900 °C for 3 h in air.

The polarization resistances (R_p) of the $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ ($x = 0$, 0.1, and 0.2) and $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ + GDC composite cathodes in contact with GDC pellets were measured with symmetrical cells in the temperature range of 550–800 °C by AC impedance spectroscopy (Solartron 1260 FRA). The GDC electrolyte disks were prepared by pelletizing and sintering required amounts of Gd_2O_3 and CeO_2 at 1600 °C for 10 h. All cathode materials were mixed with an organic binder (Heraeus V006) to form slurries and then applied onto both sides of a dense GDC pellets (750 μm) by screen printing. The $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ + GDC cathodes were then heated at 800–1000 °C for 3 h.

Fuel cell performances of the $La_{1.85}Sr_{1.15}Cu_{1.8}Co_{0.2}O_{6.26}$ + GDC cathodes for ORR were evaluated with LSGM electrolyte-supported single cell (500 μm thick) and anode-supported single cell. The LSGM electrolyte disks were prepared by firing required amounts of La_2O_3, $SrCO_3$, Ga_2O_3, and MgO at 1100 °C for 5 h, followed by pelletizing and sintering at 1500 °C for 10 h. The GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$ (10 GDC), and $La_{0.4}Ce_{0.6}O_{1.8}$ (LDC) powders were synthesized by the glycine-nitrate combustion method [34,35]. For the anode, the obtained GDC powder was mixed with NiO (Ni: GDC = 70:30 vol.%) by ball-milling in ethanol for 48 h. All the electrodes and interlayer powders were mixed with an organic binder (Heraeus V006) to form slurries for screen printing. To prevent the formation of $LaNiO_3$ or La_2NiO_4 at the anode|LSGM interface, an LDC buffer layer was applied by screen printing onto the anode side of the LSGM electrolyte [36]. The NiO–GDC cermet was applied onto the LDC layer by screen printing, followed by firing at 1300 °C for 0.5 h. Similarly, the $La_{1.85}Sr_{1.15}Cu_{1.8}Co_{0.2}O_{6.26}$ sample react with LSGM at 900 °C and form undesired reaction products but this reaction problem could be overcome by adopting an interlayer between the cathode and the electrolyte, and there is some knowledge of the CeO_2 based interlayers on the YSZ electrolyte [37–40]. The interlayer or the buffer layer should not react with either the cathode or the electrolyte and should have high oxide ion conductivity to enhance the oxide ion diffusion. To prevent the side reaction between the cathode and LSGM, a GDC buffer layer was applied by screen printing between the cathode and LSGM electrolyte and heating at 1200 °C for 2 h.

The electrochemical performances of the $La_{1.85}Sr_{1.15}Cu_{1.8}Co_{0.2}O_{6.26}$ + GDC cathodes were evaluated with anode-supported single cells consisting of $La_{1.85}Sr_{1.15}Cu_{1.8}Co_{0.2}O_{6.26}$ + GDC composite|GDC|Ni + GDC (functional layer, dense)|Ni + GDC (porous). The anode-supported tri-layer half cell was prepared by a one-step dry pressing/co-firing process [41]. For the cathode, the $La_{1.85}Sr_{1.15}Cu_{1.8}Co_{0.2}O_{6.26}$ + GDC composite cathode slurry was applied onto the GDC layer by screen printing, followed by firing at 900 °C for 3 h. Pt meshes and wires were attached to each electrode with an area of 0.25 cm^2 using Pt paste as a current collector. Pt reference electrode was placed at a distance of 5 mm from the cathode. During the SOFC operation, humidified H_2 (∼3% H_2O at 25 °C) and air were supplied as fuel and oxidant, respectively, at a rate of 100 cm^3 min^{-1}. I–V and cathode over-potentials were measured in situ during cell operation with an Arbin BT2000 test station. After the SOFC electrochemical performance test, the microstructures of the $La_{1.85}Sr_{1.15}Cu_{1.8}Co_{0.2}O_{6.26}$ + GDC composite cathode were observed with a JEOL JSM-5610 scanning electron microscope (SEM).

3. Results and discussion

3.1. Crystal chemistry and oxygen content of $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$

Fig. 2 shows the room-temperature XRD patterns of the $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ samples for $0 \leq x \leq 0.3$. For higher Co contents with $x \geq 0.3$, the XRD patterns show the formation of impurity phases such as $La_{2-x}Sr_xCuO_4$ (JCPDS # 46-0590), indicating a Cu solubility limit of ∼0.2 in $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$. For $0 \leq x \leq 0.2$, the XRD patterns of the $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ samples could be indexed on the basis of a tetragonal structure with the space group $I4/mmm$. Fig. 3 gives the Rietveld refinement data of the $La_{1.85}Sr_{1.15}Cu_{2-x}Co_xO_{6+\delta}$ ($x = 0$, 0.1, and 0.2) samples based on