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Tradeoff optimization of electrochemical performance and thermal expansion for Co-based cathode material for intermediate-temperature solid oxide fuel cells

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ABSTRACT

Solid oxide fuel cell (SOFC) is a new electric power generation system with the advantages of high efficiency, no emissions of pollutant, and a wide range of fuels. Layered perovskite oxides have received extensive attention as promising cathode materials for SOFCs because of their faster diffusion coefficient and transport kinetics of oxygen compared to those of ABO_3-type perovskite oxides. With the goals of lowering the thermal expansion coefficient (TEC) and maximizing electrochemical properties, this study focuses on the copper (Cu) effect in $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ ($x = 0, 0.5, \text{and } 1.0$) layered perovskite oxides by investigating their structural characteristics, electrical properties, and electrochemical performance. The electrical conductivity decreases with increasing Cu content, mainly due to the decreasing amount of $Co^{3+/4+}$. The average TEC values are also identified and the substitution of Cu for Co is beneficial to lower the TEC by suppression of the spin state transitions of Co^{3+} and reduction of Co^{4+}. To better understand the thermodynamic behavior of the materials while checking redox stability, coulometric titration experiment is performed. We also investigate the electrochemical performance of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ cathode materials using a Ni-GDC anode-supported cell. All samples show sufficiently high power density around over 1.0 W cm^{-2} at 600 °C.

1. Introduction

The development of hydrogen technology as an alternative energy source to fossil fuels has been accelerated with the key benefit of no greenhouse gases or other pollutants. Solid oxide fuel cells (SOFCs) are one of the hydrogen-based electrochemical devices that convert chemical energy to electrical energy directly. Features that make them attractive include their high efficiency, fuel flexibility, and low emission of pollutants stemming from high operating temperature (800 ~ 1000 °C) [1–4]. Despite these excellent advantages, conventional high operating temperature demands material compatibility challenges and high costs. These problems have inspired efforts to lower the operating temperature to 500 ~ 800 °C, and intermediate temperature solid oxide fuel cells (IT-SOFCs) have been accordingly introduced. The major obstacles of IT-SOFCs, however, are poor oxide-ion conductivity and inadequate catalytic activity of the conventional cathode [5–7]. Therefore, the development of a new cathode material with high electro-catalytic activity could be a key step toward the commercialization of IT-SOFCs.

In this regard, mixed oxide-ion and electronic conducting (MIEC) oxides, containing Mn, Fe, Co, and/or Ni with perovskite structures, have been widely investigated as alternative cathode materials. For example, cobalt containing oxides, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Pr_{1-x}Sr_xCoO_3$, $Sm_{0.5}Sr_{0.5}CoO_3$, and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ have attracted intense interest due to their high electro-catalytic activity for the oxygen reduction reaction (ORR) [8–11]. Recently, many groups have studied layered perovskite oxides, because they offer much higher chemical diffusion and a high surface exchange coefficient relative to those of ABO_3-type perovskite oxides. The layered perovskite oxides can be described with the general formula $AA'B_2O_{5+\delta}$, consisting of sequential layers $[BO_2]$-$[AO]$-$[BO_2]$-$[A'O]$ stacked along the *c*-axis [12]. This layered structure reduces the oxygen bonding strength in the [AO] layer and provides a disorder-free channel for ion motion, which enhances oxygen diffusivity [13]. On the basis of these advantages, a large volume of work has suggested that the layered perovskite oxide $LnBaCo_2O_{5+\delta}$ (Ln = La, Pr, Nd, Sm, and Gd) could be a potential cathode material for IT-SOFCs [14–23]. Meanwhile, Kim et al. found that a $PrBaCo_2O_{5+\delta}$ layered perovskite exhibits

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unusually higher activity for oxygen activation and mobility even at low temperature (300 ~ 500 °C), which result in relatively low area specific resistance of electrodes [23].

In spite of their excellent properties, cobalt-containing cathodes exhibit high thermal expansion coefficients (TECs) and easy evaporation of cobalt [24,25]. In perovskites, cobalt is predominantly present in the form of Co^{3+}cations in low-spin (LS, $t^6{}_{2g}e^0{}_g$), intermediate-spin (IS, $t^5{}_{2g}e^1{}_g$), and high-spin (HS, $t^4{}_{2g}e^2{}_g$) states. At low temperatures, the LS and IS states are more energetically favorable. Raising the temperature, however, may cause LS → IS and IS → HS transitions of Co^{3+} ions, which brings about high TEC values due to the larger ionic radius of HS compared to LS or IS [26–30]. Moreover, the formation of oxide ion vacancies accompanied by reduction of the transition metal ions accounts for high TEC values [31].

This mismatch in TEC during the operation of SOFC cells at such a high temperature generates a stress between the cathode and electrolyte which may reduce the long term stability of SOFC-single cells. Hence, to optimize cobalt-based cathode systems, partial substitution of the cobalt element with other elements could potentially mitigate these disadvantages while retaining adequate electrochemical activity of the cobalt-containing cathode materials. As a method to lower TECs, Cu-doped $LnBaCo_2O_{5+\delta}$ (Ln = La, Pr, Nd, Sm, and Gd) has been introduced and researchers have reported considerable findings on the effect of Cu doping on the Co site including their thermal expansion behaviors [32–37]. Furthermore, the studies on partial substitution for Ba in $LnBaCo_2O_{5+\delta}$ (Ln = La, Pr, Nd, Sm, and Gd) have been conducted with the aim to enhance the electrochemical properties [38,39]. For instance, Park et al. recently reported that partial substitution of Ba site by Sr in $PrBaCo_2O_{5+\delta}$ layered perovskite oxides can potentially improve the electrical conductivity [38].

Based on these findings, we present here Cu doped $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ with the aims of stabilizing thermal properties and maximizing electrochemical properties. This study focuses on the effects of Cu doping on the structural characteristics, electrical properties, thermodynamic behavior with the redox stability, and electrochemical performances in terms of its application as an IT-SOFC cathode material. The fixed strontium composition of $x = 0.5$ in $PrBa_{1-x}Sr_xCo_2O_{5+\delta}$ has been verified to give optimum performance in our previous work [38].

2. Experimental

The $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ ($x = 0$, 0.5, and 1.0) powders were synthesized by the Pechini process using $Pr(NO_3)_3{\cdot}6H_2O$ (Aldrich, 99.9%, metal basis), $Ba(NO_3)_2$ (Aldrich, 99 + %), $Sr(NO_3)_2$ (Aldrich, 99 + %), $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich, 98 + %), and $Cu(NO_3)_2{\cdot}2.5H_2O$ (Aldrich, 98%) with the addition of ethylene glycol and citric acid as heterogeneous agents in distilled water. The solution was heated at 270 °C until submicron particles were formed via a self-combustion process. These powders were calcined at 600 °C for 4 h and then ball-milled in acetone for 24 h. The calcined powders were then dry-pressed into pellets at 5 MPa and sintered at 1100 °C and 1050 °C for 12 h in air for Cu-free and Cu-doped samples, respectively, due to the melting of Cu-doped samples. For measurement of the cell performances of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ cathodes, slurries consisting of powders, GDC, and an organic binder (Heraeus V006) at a weight ratio of 6:4:12 were used.

The phase identification of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ was confirmed by X-ray powder diffraction (XRD) (Rigaku-diffractometer, Cu Ka radiation) with a scanning rate of 0.5 ° min^{-1} in the 2θ range of 20 ° to 100 °. The microstructures of the interface between the GDC electrolyte and $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ cathodes were examined using a field emission scanning electron microscope (SEM) (Nova SEM). A thermogravimetric analysis (TGA) was carried out by a SDT-Q600 (TA Instruments, USA) at a temperature range of 100 ~ 800 °C with a heating/cooling rate of 2 °C min^{-1} in air. The initial oxygen content values at room temperature were determined by iodometric titration. The electrical conductivities of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ were evaluated by a four-terminal DC arrangement and a potentiostat (BioLogic) was used to measure the current and voltage at intervals of 50 °C at temperature ranging from 100 °C to 750 °C. The TECs of sintered samples were measured from 100 to 800 °C with a heating/cooling rate of 5 °C min^{-1}.

Electrochemical impedance spectroscopy of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ was measured using a symmetrical cell. The GDC electrolyte powders were pressed into pellets, and then sintered at 1350 °C for 4 h in air to obtain a dense electrolyte substrate. Slurries composed of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$-GDC powders were screen-printed onto both sides of the GDC electrolytes to form symmetrical half-cells, followed by calcination at 1000 °C for 4 h. A silver paste was used as a current collector for the electrodes. Impedance spectra were recorded under OCV in a frequency range of 1 mHz to 500 kHz with AC perturbation of 14 mV from 500 to 650 °C.

Ni-GDC anode-supported cells were fabricated by co-pressing method to measure the electrochemical performances of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$-GDC. The Ni-GDC cermet anode was prepared by a mixed nickel oxide, GDC, and starch at a weight ratio of 6:4:1.5 via ball-milling in ethanol for 24 h. The GDC electrolyte powder was pressed over a pelletized disk of a Ni-GDC cermet anode. The Ni-GDC/GDC anode-electrolyte layer was sintered at 1350 °C for 5 h and the $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$-GDC composite slurries were screen-printed on the GDC electrolyte layer. Cells consisting of 3 layers (Ni-GDC as an anode, GDC as an electrolyte, and a cathode) were finally sintered at 1000 °C for 4 h under an air atmosphere with an active electrode area of 0.36 cm^2. Both the electrolyte and cathode thickness of a single cell were about 20 μm. Ag wires were attached at both electrodes of single cells using an Ag paste as a current collector. An alumina tube and a ceramic adhesive (Aremco, Ceramabond 552) were employed to fix the single cell. Humidified hydrogen (3% H_2O) was applied as fuel through a water bubbler with a flow rate of 20 mL min^{-1} and static air was fed as an oxidant during single cell tests. *I-V* curves were examined using a BioLogic Potentiostat at operating temperature from 500 to 650 °C.

The oxygen nonstoichiometry of $PrBa_{0.5}Sr_{0.5}Co_{2-x}Cu_xO_{5+\delta}$ under the oxygen partial pressures (pO_2) was measured by coulometric titration using yttria-stabilized zirconia (YSZ) tube (McDanel Advanced Ceramic Technologies, Z15410630) that functions as to pump oxygen out of the system and to detect the equilibrium pO_2 inside the tube. The detailed procedures are described elsewhere [40]. The samples were placed inside an oxygen ion conducting membrane of a YSZ tube. Ag paste (SPI Supplies, 05063-AB) was painted on the both outside and inside of the tube as electrodes. Platinum wire was employed as a lead wire to provide electrical connections to the instruments. After purging 5% O_2–Ar gas over the sample in the tube for 12 h, pO_2 was determined from the open-circuit voltage (OCV). Oxygen could be added or removed from the tube by passing current through the same electrodes as used for the OCV sensor. The sample was allowed to equilibrate until the potential varied in a range of less than 1 mV h^{-1}. Oxygen nonstoichiometry was determined through this procedure at 700 °C over a wide range of oxygen partial pressure. Electrical conductivity was simultaneously measured by a four-terminal DC arrangement with a BioLogic Potentiostat.