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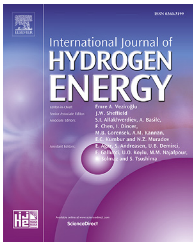

Electrochemical evaluation of double perovskite $PrBaCo_{2-x}Mn_xO_{5+\delta}$ ($x = 0, 0.5, 1$) as promising cathodes for IT-SOFCs

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ABSTRACT

Mn-substituted double perovskites, $PrBaCo_{2-x}Mn_xO_{5+\delta}$ ($x = 0, 0.5, 1$), are evaluated as cathode materials for intermediate-temperature solid oxide fuel cells. The effects of Mn substitution content on their structural and electrochemical properties including crystal structure, thermal expansion coefficient, and cathodic interfacial polarization resistance are investigated. The $PrBaCo_{2-x}Mn_xO_{5+\delta}$ samples exhibit structural changes with increasing Mn contents from tetragonal ($x = 0$) to cubic ($x = 0.5$ and 1.0) symmetry. The thermal expansion coefficient decreases with the increasing Mn content while the cathodic performance increases with the increment of Mn content from $x = 0$ to $x = 0.5$ then decreases with the further increment of Mn content from $x = 0.5$ to $x = 1.0$. When using $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ with 300 μm thickness as electrolyte and $Sr_2Fe_{1.4}Ni_{0.1}Mo_{0.5}O_{6-\delta}$ as anode, the maximum powder density of the $x = 0.5$ composite is 0.638 W cm^{-2}, which is higher than that of the other two samples with $x = 0$ (0.474 W cm^{-2}) and $x = 1.0$ (0.371 W cm^{-2}) at 800 °C.

Introduction

Solid oxide fuel cells (SOFCs) have been considered as an environmentally friendly power generator due to their high energy efficiency and excellent fuel adaptability [1]. Generally, conventional SOFCs operate at high temperatures (around 1000 °C), which would result in strict requirements on the electrode and interconnect materials. Consequently, remarkable efforts have been devoted to the development of intermediate-temperature SOFCs (IT-SOFCs) with the

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purposes to improve the long-term stability, reduce the costs and also provide more cell material choices [2–8]. However, the decrease of operating temperature to intermediate temperatures usually leads to a large over-potential and cathodic polarization loss of conventional $La_{1-x}Sr_xMnO_3$ cathodes because of the high stability of Mn^{4+} ions at intermediate temperatures, resulting in inadequate electrochemical activities [9–11]. With the development of electrolytes (e.g., $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$, $Gd_{0.1}Ce_{0.9}O_{1.95}$) with high conductivities at low and intermediate temperatures, intermediate-temperature solid oxide fuel cells with high energy density become possible [12–14]. Accordingly, it is essential to develop effective cathode materials with high electrochemical activities for the successful IT-SOFCs operating in the intermediate temperature range (600–800 °C) [2,3,15–19].

Recently, perovskite-type oxides with high mixed ionic-electronic conducting (MIEC) properties have been widely investigated as the cathode materials for IT-SOFCs due to their greater concentration of oxygen vacancies for higher ionic conductivities and better performance for oxygen reduction reactions [20–22], among which, cobalt-containing double perovskites $LnBaCo_2O_{5+\delta}$ (Ln = Y and lanthanide) have attracted remarkable interest as cathodes because of their fast oxygen ion diffusion, high electrical conductivity and oxygen surface exchange kinetics [20,23–32]. The structure of $LnBaCo_2O_{5+\delta}$ is composed alternately of Ln-O and Ba–O layers along the c-axis with oxygen vacancies in the LnO layer. Previous reports also have demonstrated that $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Nd, Sm, and Gd) materials represent relatively low polarization resistance and excellent cell performance as cathode materials on $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte operated at intermediate temperatures [28,33–35]. According to Zhang et al. [36], among the $LnBaCo_2O_{5+\delta}$ oxides, $PrBaCo_2O_{5+\delta}$ has a high surface exchange and also bulk diffusion coefficient, suggesting its promising performance as cathodes for IT-SOFC.

Serious inconveniences such as unacceptably high thermal expansion coefficients (TECs) associated with a significant variation of oxygen content with temperature and spin transitions of Co^{3+} in $LnBaCo_2O_{5+\delta}$ limit their practical applications as cathodes of IT-SOFCs [37,38]. The high TEC would cause the delamination of electrode from the electrolyte during the thermal cycle and the readiness of oxygen loss would cause the conductivity or structure variation under the reducing environment of cathodic current. Recently, substitution of Co with other transition metals (e.g., Fe, Ni or Cu) in double perovskite $LnBaCo_2O_{5+\delta}$ has been reported as one of the promising strategies to reduce the TEC for better compatibility with electrolyte, lower the cathode polarization and increase the redox stability of $LnBaCo_2O_{5+\delta}$ as cathodes for IT-SOFCs [33,34,39–45]. In contrast to the substitution of Co by Ni and Cu with a limited substitution range, a larger amount of substitution of Co by Fe or Mn is possible [39,41,42,46]. Mn substitution in $LnBaCo_2O_{5+\delta}$ as cathodes for IT-SOFCs has attracted an increasing interest, such as $NdBaCo_{2-x}Mn_xO_{5+\delta}$ [46]. However, Nd is existed in the perovskite oxide with constant valence of 3+ while Pr can be existed in oxidation states of 3+ and 4+, which would lead to a higher power density [47]. With the aim to lower the TEC and also improve the cathode performance, we present here an investigation into the effect of Mn-substitution for Co on the thermal expansion coefficient, electrochemical properties of $PrBaCo_{2-x}Mn_xO_{5+\delta}$ (x = 0, 0.5, 1.0) as cathodes for IT-SOFCs.

Experimental

Chemicals and materials

$Pr(NO_3)_3\cdot 5H_2O$, $Ba(NO_3)_2$, $Co(NO_3)_2\cdot 6H_2O$, $Mn(CH_3COO)_2\cdot 4H_2O$, $Sr(NO_3)_2$, $Fe(NO_3)_3\cdot 9H_2O$, $Ni(NO_3)_2\cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were purchased from Sigma-Aldrich. Citric acid, glycine, polyvinylpyrrolidone (Mw ≈ 1300000), and terpineol (95%, mixed polymorphs) were obtained from Aladdin Chemicals. Silver wire (0.25 mm, 99.99%) was provided by Advent Research Material Ltd and silver paste (9912-G0) was obtained from ESL EUROPE. All chemical were used without further purification.

Sample synthesis and cell fabrication

Double perovskite $PrBaCo_{2-x}Mn_xO_{5-\delta}$ (x = 0, 0.5 and 1.0) powders were synthesized via a citrate-nitrate combustion process [41]. Stoichiometric amounts of $Pr(NO_3)_3\cdot 5H_2O$, $Ba(NO_3)_2$, $Co(NO_3)_2\cdot 6H_2O$ and $Mn(CH_3COO)_2\cdot 4H_2O$ were dissolved in distilled water to form solutions under continuous stirring. Citric acid with molar ratios of citric acid/metal cation at 1.5 was then added, which was used as complexing agent and combustion promoter. After being stirred for 2 h at room temperature, the solutions were then heated on a hot plate at 100 °C to evaporate the solvent. Then the gels were heated till self-combustion occurred. The as-synthesized powders were ground and then subsequently calcined at 1200 °C for 12 h for $PrBaCo_{2-x}Mn_xO_{5-\delta}$ (x = 0, 0.5 and 1.0) in static air.

Perovskite $Sr_2Fe_{1.4}Ni_{0.1}Mo_{0.5}O_{6-\delta}$ (SFNM) materials were prepared using the combustion method [48,49]. Stoichiometric amounts of $Sr(NO_3)_2$, $Fe(NO_3)_3\cdot 9H_2O$, $Ni(NO_3)_2\cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were dissolved into H_2O under continuous stirring. Then citric acid and glycine were added into the above solution to adjust the pH and promote the combustion, in which the molar ratio of glycine/citric acid/metal cations was 2:1.5:1. The resultant ash was ground and then calcined at 950 °C for 5 h in air to obtain pure SFNM powders.

The LSGMC ($La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$) electrolyte support (15 mm in diameter) was prepared by pressing and sintering the powder at 1450 °C for 8 h in air to form dense bodies as the support for cathode and anode. Then these obtained pellets were polished to a thickness of ca. 300 μm, 5 g polyvinylpyrrolidone were dissolved in 95% terpineol to prepare the vehicle at room temperature. The powder of cathode ($PrBaCo_{2-x}Mn_xO_{5+\delta}$) or anode (SFNM) was mixed with the vehicle under the weight ratio of 1:1 using a mortar and pestle for 30 min and then the slurry were painted on the LSGMC. The coating was dried in an oven at 80 °C for 1 h before the calcination at 1100 °C for 2 h for better bonding. The ramp rate of the calcination process is 3 °C min^{-1}. Silver wires (0.25 mm, 99.99%, Advent Research Material Ltd) and silver paste (9912-G, ESL EUROPE) were employed as a current collector.

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