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Effects of strontium doping on the structure, oxygen nonstoichiometry and electrochemical performance of $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ $(0.1 \le x \le 0.5)$ cathode materials

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HIGHLIGHTS

- $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ (PSNCO) materials are first utilized as SOFC cathode.
- The lowest area specific resistance is 0.063 Ω cm^2 at 800 °C.
- PSNCO cathode is promising for SOFC at intermediate temperature.

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ABSTRACT

$Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ (PSNCO, $x = 0.1, 0.3, 0.5$) oxides with K_2NiF_4-type structure are synthesized by a glycine–nitrate process as potential cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs). The influence of strontium substitution on the structure, oxygen nonstoichiometry, electrical property and electrochemical performance is investigated. Iodometric titration method is employed to study the oxygen nonstoichiometry and the formal valence of nickel. The maximum electrical conductivity reaches 109 S cm^{-1} at 450 °C in air for $Pr_{1.7}Sr_{0.3}Ni_{0.6}Cu_{0.4}O_{4+\delta}$ material. Area specific resistance (ASR) values of all compositions are below 0.11 Ω cm^2 at 800 °C, and the $Pr_{1.7}Sr_{0.3}Ni_{0.6}Cu_{0.4}O_{4+\delta}$ composition has the lowest ASR value of 0.063 Ω cm^2 at 800 °C. Open circuit voltage (OCV) and maximum power density of the single cell (NiO–SDC/SDC/PSNCO) are 0.767 V and 353 mW cm^{-2} at 800 °C, respectively. The preliminary results indicate that $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ materials could be good candidates for IT-SOFCs cathode materials.

1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) have drawn more and more attention in the past decades and great efforts have been devoted to reduce the operating temperature from traditional high temperature range (800–1000 °C) to intermediate temperature range (500–800 °C) [1–4]. The development of IT-SOFC is expected to allow using low-cost metallic interconnects and diminishing problems associated with ageing process kinetics [5,6]. However, lower operation temperatures also lead to the decrease in the ionic conductivity of the electrolyte and the increase of the polarization resistance of the electrode, especially the cathodic polarization resistance. As a consequence, the electrochemical properties and power density are drastically impaired [7–10]. In order to overcome these problems and to reach reasonable cell performance, it is desirable to develop new electrode materials, especially cathode materials with high performance at relatively low temperatures. The mixed ionic–electronic conducting (MIEC) materials have been widely investigated as cathode materials for IT-SOFC due to the enhancement of active area for oxygen reduction, which is of great importance for the decrease of the operating temperature. Up to now, most studies of cathode materials based on MIEC oxides have been focused on perovskite-type oxides.

Perovskite oxides with structures which mainly consist of simple perovskite, K_2NiF_4 structure and double ordered perovskites have been extensively studied as potential cathode materials for IT-SOFCs. The original perovskite-type oxide can be formulated as $ABO_{3-\delta}$, where A is either rare earth or earth alkaline cation, B is transition metal element. Both A and B sites can be partially or fully substituted, which can remarkably change the defect structure, oxygen stoichiometry and transport properties of this kind of

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materials [11,12]. By altering the proportion of the substitution element, their oxygen substoichiometry can be modified, thereby providing a possibility to alter the oxygen vacancy concentration and oxygen diffusivity, such as the LaSrFeCoO and BaSrCoFeO systems [13–18].

In recent years, K_2NiF_4 type oxides with mixed transport properties have attracted more and more attention as promising alternatives to the original perovskite structure oxides. These compounds with the general formula $A_2BO_{4+\delta}$ (A = La, Nd, Pr, B = Ni, Cu) belong to the Ruddlesden–Popper type materials [19]. An important feature of these compounds is their oxygen overstoichiometry correlated with the mixed valence of B-site transition metal cation leading to a mixed ionic–electronic conduction [20–22]. Their structure comprises ABO_3 perovskite layers alternating with AO rocksalt layers. The oxygen excess is caused by the incorporation of additional oxygen ions into the rocksalt layers [23,24]. At ambient temperature, the maximum value of the incorporated oxygen ions (δ) may reach as high as 0.18 in $La_2NiO_{4+\delta}$ and 0.22 in $Pr_2NiO_{4+\delta}$ [20,25]. Mauvy et al. investigated the electrochemical performance of Ln_2NiO_4 (Ln = La, Nd, Pr) and found that the praseodymium nickelate exhibited the lowest cathode ASR value [26]. Furthermore, the oxygen transport and the electrode properties of this system can be easily modulated through A and/or B site substitution. Many studies have indicated that $Ln_{2-x}Sr_xMO_{4+\delta}$ (Ln = La, Nd, Pr, M = Ni, Fe, Cu, Co) oxides are mixed ionic–electronic conducting (MIEC) materials, which possess both good electronic conductivity (due to the transition metal mixed valency) and ionic conductivity (due to the oxygen excess) [20–22]. It has been reported that the ionic conductivity of this kind of material is only approximately the same order of magnitude as the one of 8YSZ, while the values of electronic conductivity are in the magnitude of 10^1–10^2 S cm^{-1} [11]. The electronic conductivity of these oxides almost reaches the requirement for the application as cathode materials and the enhancement of electronic conductivity can be achieved by doping strontium on the A site [22,27]. As for substitution on Ni site in $Pr_2NiO_{4+\delta}$, our previous work has shown that $Pr_2Ni_{0.6}Cu_{0.4}O_4$ is observed with the best cell performance in the Cu substituted $Pr_2NiO_{4+\delta}$ systems [28]. In addition, the result reported by Allancon et al. demonstrated that doping large cation Sr on the Pr site in $Pr_2NiO_{4+\delta}$ could improve the structural stabilization [29].

In the present work, a series of $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ oxides were synthesized via a glycine–nitrate process (GNP). Phase structure, oxygen overstoichiometry, thermal expansion coefficient and microstructure studies were performed on these materials. Electrical conductivity and electrochemical properties were also studied to evaluate the performance of $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ series as potential SOFC cathode materials. The aim of this work was to discuss the correlation between the dopant concentration of strontium and oxygen overstoichiometry, as well as the influence of strontium concentration on the properties of the target materials.

2. Experimental

2.1. Powder synthesis

$Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ ($x = 0.1$, 0.3 and 0.5) powders were synthesized via a glycine–nitrate process with stoichiometric amounts of analytical grade reagents of Pr_6O_{11}, $SrCO_3$, $Ni(NO_3)_2 \cdot 6H_2O$, CuO as starting materials and glycine as fuel [30]. These raw materials were dissolved in an aqueous solution of nitric acid and subsequently glycine was added as fuel at a molar ratio of metallic ions: glycine of 1:1.5 to form a transparent and homogeneous solution. Under stirring and heating, the viscosity of the solution increased gradually and a viscous gel was obtained. Keep heating until a self-sustaining combustion occurs. The resultant precursors were then calcined in air at 1000 °C for 2 h to obtain the pure-phase powders. The final products were denoted as PSNCO1901 for $Pr_{1.9}Sr_{0.1}Ni_{0.6}Cu_{0.4}O_{4+\delta}$, PSNCO1703 for $Pr_{1.7}Sr_{0.3}Ni_{0.6}Cu_{0.4}O_{4+\delta}$ and PSNCO1505 for $Pr_{1.5}Sr_{0.5}Ni_{0.6}Cu_{0.4}O_{4+\delta}$. Composite powders of NiO–SDC were prepared by mechanically blending commercial NiO powders (2.5 μm) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ powders (SDC, prepared by the gel-casting process, about 30 nm) with zirconia grinding media in alcohol at a ratio of NiO:SDC = 60:40 wt%.

2.2. Sample preparation

The as-synthesized $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ ($x = 0.1$, 0.3 and 0.5) powders were uniaxially pressed into rectangular bars under a pressure of 100 MPa and then sintered in air at 1150 °C for 5 h. The obtained dense ceramic samples were used for microstructure observation and thermal expansion coefficient (TEC) measurements and electrical conductivity tests. Pressed green SDC pellets were sintered in air at 1450 °C for 5 h as electrolyte disks. The PSNCO slurry was obtained by thoroughly mixing the PSNCO powders with terpineol and ethylcellulose and was subsequently painted on both sides of SDC to form symmetrical cells. Green compacts of NiO–SDC anode substrates were prepared by pressing the as-prepared powders in a steel die under a pressure of 100 MPa, and were subsequently sintered in air at 1000 °C for 2 h to form the anode substrates samples. The SDC slurry was coated onto the sintered NiO/SDC substrates by a dip-coating method and then co-sintered at 1450 °C for 5 h to obtain the anode/electrolyte bilayer structure. Finally, NiO–SDC/SDC/PSNCO single cells were prepared by screen-printing the PSNCO slurry onto the electrolyte side of the NiO–SDC/SDC bilayer and subsequently fired at 1100 °C for 2 h.

2.3. Sample characterization

The structure and phase stability of the $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ ($x = 0.1$, 0.3 and 0.5) powders were confirmed by X-ray diffraction (XRD) analysis (Cu Kα radiation, D/Max-3B, Rigaku, Japan) from 20° to 90° with a step of 0.2°. The lattice spacing of PSNCO powders was observed by high-resolution transmission electron microscopy (HR-TEM) analysis combined with selected area electron diffraction (SAED) on a JEM-2100F field emission transmission electron microscope. The surface analysis of PSNCO powders by X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB

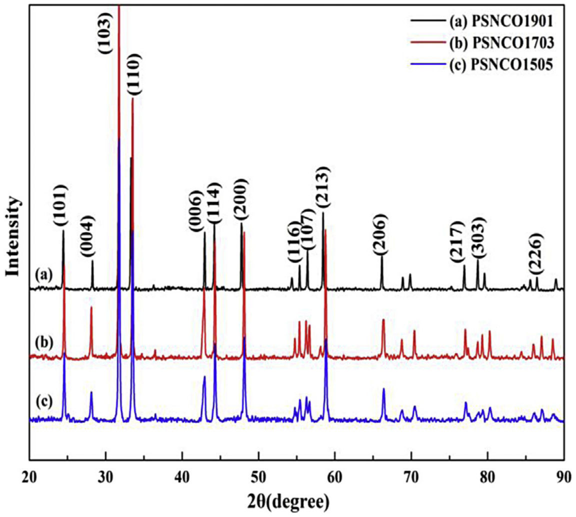

Fig. 1. XRD patterns of $Pr_{2-x}Sr_xNi_{0.6}Cu_{0.4}O_{4+\delta}$ ($x = 0.1$, 0.3 and 0.5) powders calcined at 1000 °C for 2 h.