Electrochimica Acta 212 (2016) 522–534

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effects of Pr-deficiency on thermal expansion and electrochemical properties in $Pr_{1-x}BaCo_2O_{5+\delta}$ cathodes for IT-SOFCs

Leilei Zhang[a,*], Guibin Yao[a], Zhaoyuan Song[a], Bingbing Niu[a,b], Wen Long[a], Lei Zhang[a], Yu shen[c], Tianmin He[b]

[a] College of Sciences, Liaoning Shihua University, Fushun, 113001, PR China
[b] Key Laboratory of Physics and Technology for Advanced Batteries, Ministry of Education, College of Physics, Jilin University, Changchun, 130012, PR China
[c] Materials Science and Engineering, Changchun University of Science and Technology, Changchun, 130022, PR China

ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 7 June 2016
Accepted 4 July 2016
Available online 5 July 2016

Keywords:
Solid oxide fuel cell
Layered perovskite cathode
Thermal expansion
Oxygen reduction
Electrochemical performance

ABSTRACT

Pr-deficient $Pr_{1-x}BaCo_2O_{5+\delta}$ (P_{1-x}BCO) oxides are evaluated as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs). Effects of Pr-deficiency on electrical conductivity, thermal expansion and electrochemical properties are investigated. Both the conductivity and thermal expansion coefficient (TEC) decrease with increasing Pr-deficiency. All of the conductivity, thermal expansion and TGA measurements demonstrate the existence of high temperature order-disorder transition. The oxygen reduction mechanism for P_{1-x}BCO cathodes are characterized by electrochemical impedance spectroscopy. Over the temperature range of 600–800 °C, the cathode polarization resistance is mainly contributed from electronic charge transfer over the cathode surface. Proper Pr-deficiency reduces cathode polarization resistance (R_p), and the lowest R_p (0.081 Ω cm^2 at 700 °C) is obtained for the $P_{0.92}$BCO cathode. In addition, the effects of order-disorder transition on the properties of P_{1-x}BCO cathodes have also been discussed. Maximum power densities of a single-cell with $P_{0.92}$BCO cathode on 300-μm thick $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte achieve 446–987 mW cm^{-2} at 650–800 °C. These results suggest that, among various P_{1-x}BCO oxides, $P_{0.92}$BCO is the most promising candidate cathode material for IT-SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical power generation devices characterized by high-energy conversion efficiency and low pollution emission. Among the components of SOFCs, there is particular attention paid to the cathode since it is the primary limitation of resistance in SOFCs and consequently induces large activation and concentration polarization [1–3]. Traditional SOFC cathodes are composed of $LaMnO_3$-based perovskites, which are pure electronic conductors and typically operated at ~1000 °C [4]. However, such high-temperature operation introduces a series of problems such as the sintering of electrodes, high reactivity between cell components, and strict requirements on interconnect materials. Consequently, lowering the operating temperature to intermediate temperature (IT, 600–800 °C) has been one of the main goals in current SOFC research. However, the rapid deterioration of cathode polarization resistance with the drop of operating temperature is a major obstacle to the development of IT-SOFCs. Hence, the development of new cathode materials with low polarization resistance is of great importance to achieving high power densities at reduced temperatures.

Recently, cobalt-containing layered perovskite oxides $LnBaCo_2O_{5+\delta}$ (Ln = rare earth) have been investigated as potential cathode materials for IT-SOFCs [5–15]. These compounds have an oxygen-deficient perovskite-related structure with alternating stacking layers of $|BaO|CoO_2|LnO_x|CoO_2|$ along the c-axis. Moreover, oxygen vacancies are preferably located in the LnO_x layer due to different radius of Ln^{3+} and Ba^{2+} ions and different Ba—O and Ln—O bond strength [11,16,17]. Among various $LnBaCo_2O_{5+\delta}$ oxides, $PrBaCo_2O_{5+\delta}$ (PBCO) has been demonstrated to possess the highest electro-catalytic activity for oxygen reduction [9], which can be attributed to its high oxygen-ion diffusion and surface exchange kinetics [9,18,19]. Zhang et al. [9] reported that PBCO exhibits the best electrochemical performance in $LnBaCo_2O_{5+\delta}$ (Ln = La, Pr, Nd, Sm, Gd and Y) cathodes and the polarization resistance of this cathode on SDC electrolyte is 0.213 Ω cm^2 at 600 °C; Xia' group [10] also reported that PBCO is one of the best

---

[*] Corresponding author.
E-mail address: leizhang1983@163.com (L. Zhang).

http://dx.doi.org/10.1016/j.electacta.2016.07.014

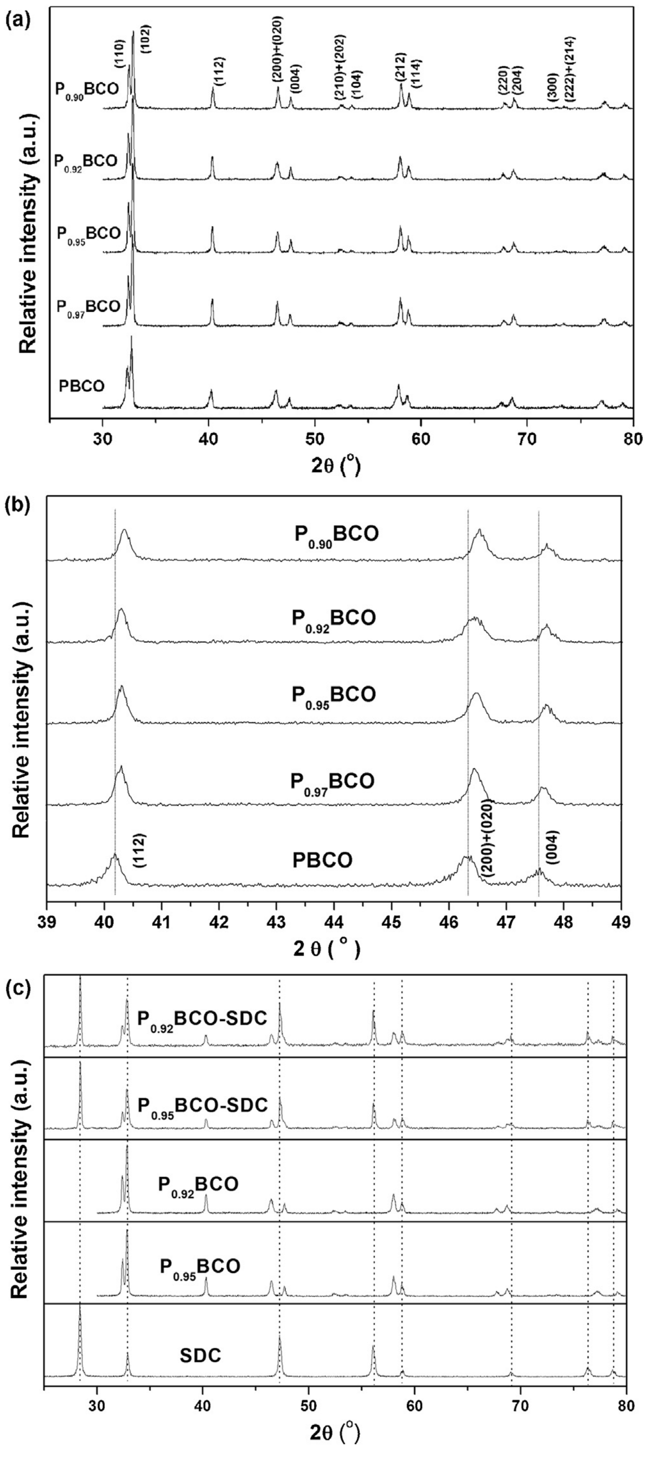

Fig. 1. (a) XRD patterns of P_{1-x}BCO samples; (b) magnified XRD patterns from 39°–49°; (c) XRD patterns of SDC, $P_{0.95}$BCO, $P_{0.92}$BCO, $P_{0.95}$BCO-SDC and $P_{0.92}$BCO-SDC. SDC and P_{1-x}BCO samples were sintered at 1400 °C and 1100 °C for 10 h, respectively. $P_{0.95}$BCO-SDC and $P_{0.92}$BCO-SDC mixtures were calcined at 1000 °C for 10 h.

layered perovskite cathode and its polarization resistance on $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) electrolyte attains 0.078 Ω cm^2 at 700 °C; Kim et al. [19] demonstrated that the diffusion coefficient and the surface exchange coefficient for PBCO could be 2–3 orders of magnitude higher than that of $GdBaCo_2O_{5+\delta}$. However, the electrochemical performance for PBCO cathode is still worse than those of both $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode (0.055–0.071 Ω cm^2 at 600 °C [20]) and $Ba_{0.6}Sr_{0.4}Co_{0.9}Nb_{0.1}O_{3-\delta}$ cathode (0.056 Ω cm^2 at 700 °C [21]).

Some studies have demonstrated that, introducing A-site cation deficiency into the lattice structure of perovskite oxides could significantly improve the electrochemical performances. Hansen et al. [22] observed that introducing A-site deficiency into $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ facilitates electro-catalytic activity for oxygen reduction, which can be attributed to the additional oxygen vacancies induced by A-site cation deficiency [23]; Pang et al. [12] and Donazzi et al. [24] have also demonstrated that polarization resistance could be reduced by introducing Ba-deficiency into the parent $PrBaCo_2O_{5+\delta}$ and $NdBaCo_2O_{5+\delta}$. Very recently, Pr-deficient $Pr_{1-x}BaCo_2O_{5+\delta}$ (P_{1-x}BCO) oxides were reported to show excellent electrochemical performance as SOFC cathodes [25,26]. For example, a polarization resistance as low as ~0.028 Ω cm^2 has been reported at 700 °C by Jiang et al. [26] for $P_{0.95}$BCO cathode on GDC electrolyte.

To optimize the performances of SOFC cathodes, it is crucial to know their thermal expansion behavior and mechanism of oxygen reduction. However, such information is still lack in the literature with respect to Pr-deficient P_{1-x}BCO cathodes. In the present work, single-phase layered perovskite oxides P_{1-x}BCO ($x = 0.00$–0.10) were synthesized and evaluated as cathode materials for IT-SOFCs. The effects of Pr-deficiency on thermal expansion and electrochemical properties were systematically investigated. The rate-limiting step for oxygen reduction process in P_{1-x}BCO cathodes has also been elucidated and discussed. Taking all these factors into account, an optimal level of Pr-deficiency was proposed. In addition, the conductivity, the chemical compatibility between the P_{1-x}BCO cathode and SDC electrolyte, and the performance of a complete single-cell have also been studied.

2. Experimental

2.1. Sample synthesis and cell fabrication

Layered perovskite oxides $Pr_{1-x}BaCo_2O_{5+\delta}$ (P_{1-x}BCO, $0.00 \leq x \leq 0.10$) were synthesized by a combined EDTA–citrate complexing sol-gel method. Stoichiometric amounts of Pr_6O_{11}, $Ba(NO_3)_2$ and $Co(NO_3)_2 \cdot 6H_2O$, all in analytical grade, were dissolved into dilute nitric acid. The EDTA-$NH_3 \cdot H_2O$ and citrate were added in sequence at a mole ratio of 1:1:2 for total metal ions: EDTA: citric acid under heating and stirring. A transparent gel was obtained by evaporating the water from the solution. The gel was heated at 180 and 400 °C in sequence to obtain a dark dry foam structure. The precursor was first calcined at 900 °C for 10 h to burn out organic species. The obtained powder was grounded and then sintered at 1100 °C for 10 h to obtain the desired product. The SDC and NiO powders were synthesized by a glycine-nitrate process. The anode was obtained by mixing SDC and NiO powers in a weight ratio of 60:40. The dense SDC electrolyte pellets were prepared by uniaxial mold pressing of SDC powders at 220 MPa and then sintering at 1400 °C for 10 h.

Symmetrical cell with P_{1-x}BCO|SDC|P_{1-x}BCO ($0.00 \leq x \leq 0.10$) configuration for the impedance study was fabricated by screen-printing cathode slurry onto both sides of SDC electrolyte pellet and then calcining at 950 °C for 2 h. A single-cell with P_{1-x}BCO|SDC|NiO−SDC configuration was fabricated by an electrolyte-supported technique. For comparison with other related studies, the thickness of SDC pellet used for single-cell was controlled to be 300 μm. The anode slurry was printed on one side of SDC pellet and calcined at 1250 °C for 4 h. Then the cathode slurry was printed on the other side of SDC pellet and calcined at 950 °C for 2 h. Silver was attached to the electrode surfaces using silver paste as the current collector.