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Short communication

Low-temperature protonic ceramic membrane fuel cells (PCMFCs) with $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ cubic perovskite cathode

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ABSTRACT

The $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ (SCS) composite oxide with cubic perovskite structure was synthesized by a modified Pechini method and examined as a novel cathode for protonic ceramic membrane fuel cells (PCMFCs). At 700 °C and under open-circuit condition, symmetrical SCS cathode on $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) electrolyte showed low polarization resistances (R_p) of 0.22 Ωcm^2 in air. A laboratory-sized tri-layer cell of NiO–BZCY7/BZCY7/SCS was operated from 500 to 700 °C with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant. A high open-circuit potential of 1.004 V, a maximum power density of 259 mW cm^{-2}, and a low polarization resistance of the electrodes of 0.14 Ωcm^2 was achieved at 700 °C.
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1. Introduction

The development of solid oxide fuel cells (SOFCs) has reached its new stage characterized with thin electrolytes on porous electrode support, in which the most important fabrication techniques developed are almost all concerned with inorganic membranes, and so can be named as ceramic membrane fuel cells (CMFCs) [1]. Protonic ceramic membrane fuel cells (PCMFCs) based on proton-conducting electrolytes may exhibit more advantages than CMFCs based on oxygen-ion electrolytes in many respects, such as low activation energy [2] and high energy efficiency [3].

There is now considerable interest in proton-conducting oxide electrolytes for PCMFCs. Many perovskite-type oxides show high proton conductivity in a reducing atmosphere. One of the major challenges for this type of proton conductor is a proper compromise between conductivity and chemical stability. Zuo et al. [4] reported a new composition, $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) that exhibited both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation. BZCY7, at temperatures below 550 °C, displayed the highest ionic conductivity of all known electrolyte materials for SOFC applications.

The development of proper cathode materials for PCMFCs in order to improve materials compatibility and reduce costs remains a challenge. Many simple perovskite-type mixed ionic–electronic conductors such as doped $LaCoO_3$ [5], $BaCoO_3$ [6] or $LaFeO_3$ [7] have been extensively studied as possible cathodes, however not much attention has been paid to the perovskite structures such as doped $SrCoO_3$. Recently, Aguadero et al. [8] have prepared a novel $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ perovskite, and shown its potential use as a MIEC in SOFCs. We have evaluated the performance of this material working as a cathode in SOFCs based on oxide ion conductors (SDC) [9]. In this work, the $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ cubic perovskite synthesized by a modified Pechini method was examined as a new cathode for PCMFCs based on proton BZCY7 electrolyte.

2. Experimental

The $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ (SCS) powder was synthesized by Pechini method. Stoichiometric amounts of commercial Sb_2O_3, $SrNO_3$, $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in a citric acid aqueous solution containing some drops of HNO_3. The solution was slowly evaporated, leading to an organic gel, which was dried at 120 °C and slowly decomposed at temperatures of up to 600 °C. A black phase-pure SCS powder was obtained after calcinating the precursor

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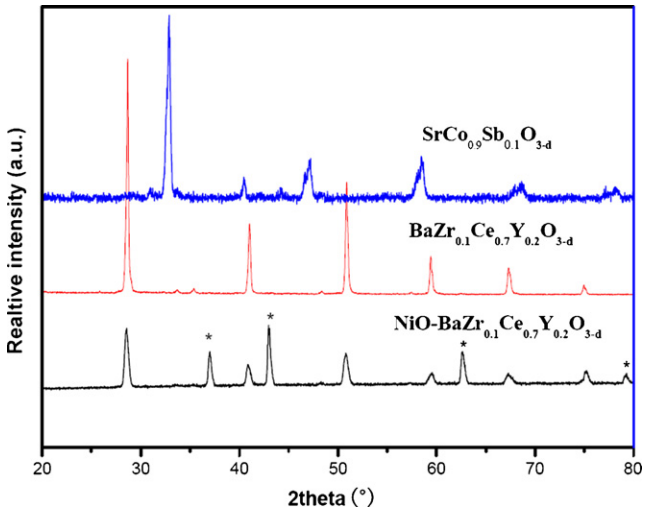

Fig. 1. X-ray diffraction patterns of (a) the $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ (SCS) powder, the bi-layer of (b) BZCY7 membrane and (c) NiO–BZCY7 anode substrate (*: NiO).

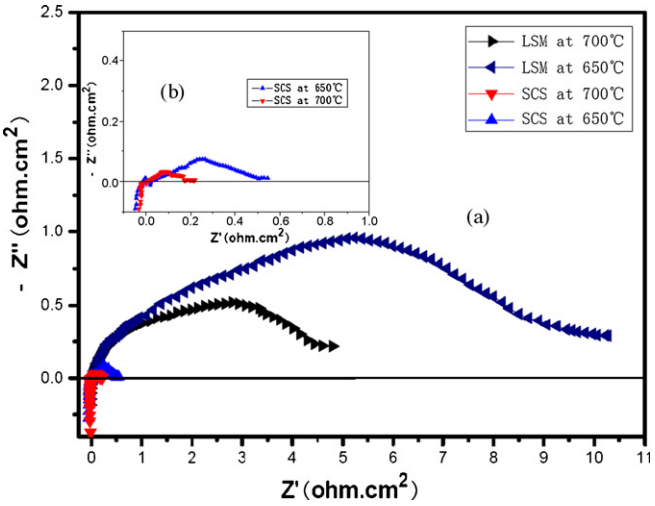

Fig. 2. Comparison of the impedance spectra for (a) the $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) cathode and (b) the $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ (SCS) cathode in air.

at 1000 °C for 10 h. The $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) powders were synthesized by a modified Pechini method with citrate and ethylenediamine tetraacetic acid (EDTA) as parallel complexing agents. Y_2O_3 was dissolved in nitric acid first, and calculated amounts of $Ba(NO_3)_2{\cdot}9H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}4H_2O$ were dissolved in EDTA–NH_3 aqueous solution. After agitation for a certain time, a proper amount of citric acid was introduced, with the molar ratio of EDTA:citric acid:total of metal cations controlled at around 1:1.5:1. The solution was heated under stirring, converted to a viscous gel and ignited to flame, resulting in the ash. The resulting ash-like material was afterwards calcined in air at 1100 °C for 5 h. Fine SCS powder was mixed thoroughly with a 6 wt% ethylcellulose–terpineol binder to prepare the cathode slurry, which was then painted on both sides of dense BZCY7 pellets, forming SCS/BZCY7/SCS symmetric cells. The cathodes were calcined at 1000 °C for 3 h in air. For comparison, a conventional $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) cathode was also fabricated (calcined at 1150 °C for 3 h) and characterized.

The anode-supported BZCY7 bi-layer (Ø15 mm) was prepared by a dry-pressing method. NiO + BZCY7 + corn starch mixture (60%:40%:20% in weight) was pre-pressed at 200 MPa as substrate about 0.95 mm. Then the anode functional layer (mixture of NiO + BZCY7, NiO:BZCY7 = 50%:50%) was pressed onto the substrate. Finally loose BZCY7 powder, calcined at 1100 °C for 5 h to form a pure perovskite oxide, was uniformly distributed onto anode substrate, co-pressed at 250 MPa and sintered subsequently at 1400 °C for 5 h to densitify the BZCY7 membrane. The cathode slurry was then painted on BZCY7 electrolyte films, and sintered at 1000 °C for 3 h in air to form cells.

The phase identification of the prepared SCS powders was studied with the powder X-ray diffraction by Cu K radiation (D/Max-gA, Japan). For electrochemical measurements, a silver paste was painted on the surfaces of SCS/BZCY7/SCS symmetric cells as a current collector. Electrochemical impedance spectroscopy (EIS) was measured by a frequency response analyzer (Chi604c, Shanghai Chenhua) in the temperature range of 600–800 °C in air. Single cells were tested from 550 to 700 °C in a home-developed cell testing system with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant, respectively. The flow rate of fuel gas was about 40 ml min^{-1}. The cell voltages and output current of the cells were measured with digital multi-meters (GDM-8145). AC impedance spectroscopy (Chi604c, Shanghai Chenhua) was performed on the cell under open-current conditions from

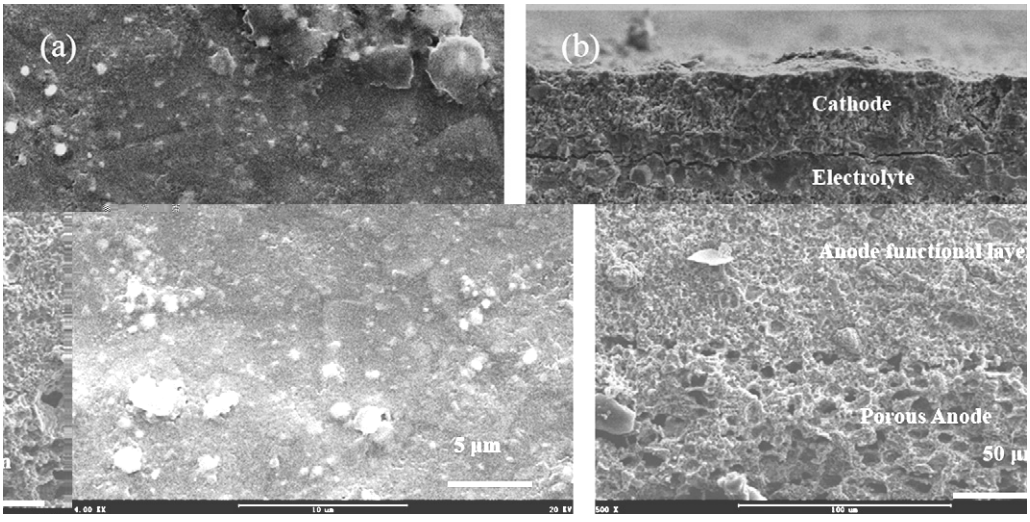

Fig. 3. SEM micrographs of as-prepared cells after testing: (a) the surface of BZCY7 electrolyte and (b) the cross-section of tri-layer cell of NiO–BZCY7/BZCY7/SCS.