Journal of Power Sources 290 (2015) 1–7

Contents lists available at ScienceDirect

Journal of Power Sources

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

Fabrication of micro-tubular solid oxide fuel cells using sulfur-free polymer binder via a phase inversion method

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HIGHLIGHTS

- Novel sulfur-free polymer binder was applied for PC-SOFC fabrication.
- Effect of polymer binder on anode substrate was systematically investigated.
- Influence of sulfide impurity on cell performance was analyzed.
- Power density of 0.45 Wcm^{-2} was achieved at 650 °C using PEI as polymer binder.

ARTICLE INFO

Article history:
Received 16 January 2015
Received in revised form
10 April 2015
Accepted 11 April 2015
Available online 15 May 2015

Keywords:
Micro-tubular SOFCs
Phase inversion
Polymer binder
Barium sulfate

ABSTRACT

Three sulfur-free polymer binders (ethyl cellulose (EC), polyvinylidene fluoride (PVDF), polyetherimide (PEI)) and sulfur-containing polyethersulfone (PESf) polymer binder were used to fabricate NiO −$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) anode substrates. The overall influence of polymer binder on the anode supports was evaluated. Sulfide impurity in the anode substrate was identified when sulfur-containing PESf was used as the polymer binder. Single cells based on different anode supports were characterized in anode-supported MT-SOFCs with the cell configuration of Ni-BZCYYb anode, BZCYYb proton-conducting electrolyte and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-BZCYYb cathode at 650 °C, 600 °C and 550 °C, using humidified hydrogen as fuel and ambient air as oxidant. MT-SOFCs of the anode fabricated using PEI show maximum power density of 0.45 Wcm^{-2}, 0.34 Wcm^{-2} and 0.23 Wcm^{-2} at 650 °C, 600 °C and 550 °C respectively, compared with 0.35 Wcm^{-2}, 0.27 Wcm^{-2} and 0.18 Wcm^{-2} for cells fabricated with PESf. The difference in cell performance was attributed to the phase purity of the anode fabricated by different polymer binders. Sulfur-free polymer binder PEI exhibits advantages over the commonly applied PESf and other sulfur-free polymer binders, pointing to a new direction in the fabrication of micro-tubular oxide substrates for energy conversion and storage.

1. Introduction

Recently, phase inversion method, which was initially developed by Loeb and Sourirajan for polymer membrane preparation [1], has been explored to fabricate ceramics for applications such as oxygen separation membranes [2,3] and micro-tubular solid oxide fuel cells (MT-SOFCs) [4–6]. Comparing with the conventional dry pressing or isostatic pressing method [7–9], phase inversion method can produce a unique asymmetric microstructure, where the macrovoids especially the finger-like pores generated by the phase separation process can facilitate mass transport, which is expected to decrease concentration polarization and enhance the cell performance [10]. To fabricate ceramic membrane by phase inversion method, polyethersulfone (PESf) has been a popular polymer binder, due to its excellent chemical and thermal stability as well as membrane forming properties. PESf has been employed in numerous studies for various applications [11–13]. However, recently it has been reported that PESf can introduce sulfide into ceramic samples even after high temperature sintering, especially for ceramics containing barium [14]. The formed $BaSO_4$ impurity will cause detrimental effects for the

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http://dx.doi.org/10.1016/j.jpowsour.2015.04.057
0378-7753/

application of the ceramic membrane, especially for oxygen separation [14].

Proton conducting solid oxide fuel cell (PC-SOFC) has attracted many attentions in the past decades, due to its advantages over the conventional YSZ based SOFC. On one hand, with a proton conducting electrolyte, water vapor will not be generated in the anode side and the fuel gas will not be diluted. On the other hand, the proton conductors with much higher conductivities in the intermediate temperature range can provide enhanced cell performance at lower operating temperature [15,16].

Previously, phase inversion method has also been successfully employed to fabricate tubular PC-SOFC, which based on the barium containing $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) electrolyte using PESf as polymer binder [17]. However, the potential sulfide impurity has not been investigated in that work. It is known that barium based oxide has been regarded as promising electrolyte material for PC-SOFCs [18–20]. Therefore, considering that the negative influence may be generated by sulfide impurity on anode of PC-SOFC, investigating the sulfur residue resulting from PESf and developing sulfur free polymer binder should be a necessary and inevitable task for the application of phase inversion method to fabricate PC-SOFCs.

In this work, we explore three sulfur free polymer binder candidates ethyl cellulose (EC) [21], polyvinylidene fluoride (PVDF) [22] and polyetherimide (PEI) [23] for the BZCYYb based proton conducting MT-SOFCs fabrication. BZCYYb-NiO anode supports were fabricated by phase inversion method with both sulfur containing PESf and sulfur-free polymer binders, respectively. The pre-sintered anode supports and the prepared electrolyte were examined by X-ray diffraction (XRD) and the sulfur impurity was investigated by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS). The overall performance of the sulfur-free polymer binders was examined and evaluated, and the relationship between polymer binder employed and the microstructure achieved was discussed. Based on the anode supports prepared, single cells with the cell configuration of BZCYYb-NiO/BZCYYb/$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-BZCYYb were fabricated. The cell performance was tested at 650 °C, 600 °C and 550 °C with humidified hydrogen as fuel gas and ambient air as oxidant. The correlation of polymer binder, anode support property and cell performance was discussed.

2. Experimental

2.1. Anode support fabrication and characterization

The micro-tubular anode supports were fabricated by the phase inversion method [24]. NiO (Sigma–Aldrich, USA, D (50): 1.73 μm) and $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) powders, which were synthesized by the solid state reaction method [18], were mixed together in a weight ratio of 65:35 with ethanol as milling medium, and then ball milled for more than 24 h and dried. N-methyl-2-pyrrolidone (NMP, Alfa Aesar, USA) was chosen as the solvent to dissolve PESf (Radel A-300, Ameco Performance, USA), EC (Sigma–Aldrich, USA), PVDF (*Alfa Aesar*, USA) and PEI (Sigma–Aldrich, USA) respectively to form the casting solutions. Subsequently, the prepared solid powders were dispersed into the casting solutions to prepare the homogenous casting slurry. The weight ratio of the polymer binder, solvent and ceramic powder is set to 1:7:10. The viscosity η (Pa·s) of different casting slurries was measured using a Rheometer (DHR-3, TA Instruments, USA) at the shear rate between 0.1 s^{-1} and 100 s^{-1} at 25 °C. The phase separation process is triggered using water as non-solvent into which the samples were immersed for more than 24 h to ensure a complete precipitation. Subsequently, the green tubes were dried and pre-sintered at 1000 °C for 2 h to achieve adequate mechanical strength prior to coating the electrolyte. The pre-sintered anode supports were characterized by scanning electron microscope (SEM, Zeiss Ultra plus FESEM). The materials composition of pre-sintered anode supports and the prepared electrolyte were examined by an X-ray diffractometer (D/MAX-3C) using Cu Kα radiation ($\lambda = 0.15418$ nm) with 2° min^{-1} scanning rate in the angle range from 20° to 80°. XPS analysis was also performed using a Kratos Axis Ultra DLD instrument to detect the impurity residue in samples after high temperature sintering. After the anode supports were sintered at 1400 °C for 5 h and reduced at 800 °C for 5 h, the gas permeation data was measured [11] and the porosity value was determined by the Archimedes method.

2.2. Single micro-tubular cell fabrication and characterization

Thin BZCYYb electrolyte film was fabricated by a dip-coating process [17] on the pre-sintered micro-tubes. Upon co-sintering at 1400 °C for 5 h, micro-tubular anode supports with dense electrolyte were prepared. The cathode with an area of 0.33 cm^2 was prepared by grinding $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-BZCYYb mixture powder (with a weight ratio of 1:1) with binder (V-006, Heraeus) to make the cathode slurry, brush-printing the cathode slurry on the electrolyte, and then firing at 1000 °C for 2 h. The prepared cells were tested from 650 °C to 550 °C with 40 SCCM humidified (3 vol% H_2O) hydrogen as fuel and ambient air as oxidant. The setup for the electrochemical performance measurement has been described in our previous work [4].

The microstructure and materials composition of the tested micro-tubular anode-supported cells were characterized by SEM and EDS. The current density–voltage curve (I–V curve) and the impedance spectra of cells were obtained using multi-channel VersaSTAT (Princeton Applied Research).

3. Result and discussion

3.1. Microstructure of the anode support

Among the three sulfur-free polymer binder candidates employed, PVDF can not show enough solubility in the NMP solvent when using the fixed polymer binder and solvent ratio. When using EC as the polymer binder, the prepared green sample is mechanically weak, and after sintered at 1200 °C, the sample shows small cracks, which is not suitable for the cell fabrication. For the third candidate PEI, the casting slurry shows better processing properties than the others. Therefore, by evaluating the performance of all the three sulfur-free polymer binder candidates, we select PEI for the anode support fabrication.

The microstructure of the pre-sintered BZCYYb-NiO anode supports fabricated by PESf and PEI are shown in Fig. 1 (a) and Fig. 1(b) respectively. Both of the anode supports have the typical asymmetrical microstructure generated by the phase inversion process. However, for the large finger-like pores, the geometry is different. The large finger-like pores of samples fabricated with PESf have a tortuous geometry and the individual finger-like pore tends to merge with each other when growing near the inside of the tube. In contrast, for samples fabricated with PEI, they show straight parallel distributed finger-like pores. The solubility parameter difference has been wildly used to estimate the compatibility between the materials involved in the phase inversion method and further to explain the mechanism of pore formation [25]. The value can be calculated by the formula: