Journal of Power Sources 363 (2017) 304–310

Contents lists available at ScienceDirect

Journal of Power Sources

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

Solvent effects on the morphology and performance of the anode substrates for solid oxide fuel cells

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HIGHLIGHTS

- Solvent is a key factor to affect the anode microstructure.
- Anode microstructure evolution is explained by the solubility parameters.
- The maximum power density of 719.2 $mWcm^{-2}$ is achieved at 750 °C.
- NMP is a promising solvent to fabricate high-performance solid oxide fuel cells.

ARTICLE INFO

Article history:
Received 25 April 2017
Received in revised form
22 July 2017
Accepted 27 July 2017

Keywords:
Solid oxide fuel cells
Phase inversion tape casting
Solvent
Anode substrate

ABSTRACT

Solvents effects on the microstructure of anode substrates as well as the electrochemical performance of the respective cells are systematically evaluated. The solubility parameters are used to interpret the relationship between the rheological properties of phase inversion slurries and pore formation mechanism of the anode substrates. When N-methyl-2-pyrrolidone (NMP) is chosen as the solvent, a dual-layered anode substrates with hierarchically oriented pores is achieved, while a sponge-like homogeneous anode substrate is obtained using dimethyl sulfoxide (DMSO) as the solvent, indicating that solvent is a key factor to affect the anode substrate microstructure. Two-dimensional and three-dimensional microstructures of the anode substrates prepared using NMP are analyzed by scanning electron microscopy and X-ray microscopy, respectively. Solid oxide fuel cells (SOFCs) with different microstructured anode substrates are prepared, and the maximum power density is significantly enhanced from 320.3 to 719.2 $mWcm^{-2}$ by varying the anode substrate from homogeneous sponge-like microstructure to dual-layered microstructure, revealing that the finger-like macro-voids layer can facilitate H_2-H_2O mass diffusion, while the thin sponge-like pores layer can serve as anode functional layer and provide sufficient active reaction sites for H_2 oxidation. This study demonstrates that NMP is a promising solvent to fabricate hierarchically oriented anode for high-performance SOFCs application.

1. Introduction

Solid oxide fuel cell (SOFC) is a highly effective energy conversion device, which can directly convert chemical energy in the fuel into electrical power [1–4]. Due to its fuel flexibility, high energy conversion efficiency and low emissions of toxic pollutants, SOFC has been considered as one of the most feasible and environmentally friendly energy conversion technologies. SOFCs are all solid-state devices with a sandwich assembly, consisting of porous cathode and anode attached on either side of the dense electrolyte. Anode-supported, electrolyte-supported and cathode-supported

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http://dx.doi.org/10.1016/j.jpowsour.2017.07.110
0378-7753/

SOFCs have been developed to meet the requirements for specific applications. Among these different cell configurations, anode-supported SOFC has received increasing attentions because of its lower ohmic resistance as well as its better mechanical strength [5–7]. Recently, tape casting method has been used for the fabrication of the anode substrates for practical SOFC applications [8–12], however, anode with high porosity and low tortuosity, which is believed to facilitate mass transport, is not easy to be achieved by using the conventional tape-casting method. Therefore, developing a novel method which can effectively fabricate the anode supports with higher porosity and lower tortuosity has been an important endeavor for SOFCs.

Phase inversion tape casting method, which combines phase inversion process and tape casting process, has recently been introduced to fabricate ceramics with hierarchically oriented pore microstructure for various applications such as oxygen separation membranes [13–15], SOFCs [16–19] and solid oxide electrolysis cells (SOECs) [20]. In this process, the phase-inversion slurry consisting of polymer binder, solvent, additive and ceramics powders is tape-casted on a Mylar polymer film, and then immersed into a nonsolvent coagulation bath, where the phase inversion process occurs spontaneously, resulting in the precipitation of the slurry because of the interchange/interaction of solvent and nonsolvent, and finally forming an asymmetric membrane. The phase inversion membrane formation mechanism has been previously studied by different groups [16–19], and it has been found that the membrane microstructure is highly affected by the choice of the polymer binder, solvent, additive, ceramics powers, nonsolvent coagulant and other preparation parameters. Kim et al. studied the effect of solvents including dimethyl formamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) on the phase behavior and morphology of the polyimide (PI) membrane [21], showing that the formation of finger-like macro-voids became more vigorous when NMP system was chosen as the solvent instead of DMF and DMSO systems. Yeow et al. utilized four solvents of NMP, DMF, N,N-dimethylacetamide (DMAc), and triethylphosphate (TEP) to prepare asymmetric poly(vinylidene fluoride) (PVDF) membranes [22], and found that the morphologies of the membranes were significantly influenced by the solvents, which was attributed to the different mutual affinities between the solvents and non-solvents. However, the previous studies only investigated the solvent effects on the microstructures of polymer membranes such as PI and PVDF. For the ceramics membrane fabrication, NMP is almost exclusively used as the solvent while other solvents are seldom explored [13,16,18,23,24]. Our previous study indicated that the solid loading of ceramics powders had significant influence on the rheological properties of the phase inversion slurry and the membrane microstructure [23], implying that some rules of the microstructure evolution in the polymer membranes may sharply change during the fabrication of the ceramic membranes.

To better understand the solvent effects on the microstructure of the anode substrates and tailor optimal anode microstructure for SOFC application, the correlation between the anode microstructure and solvent as well as the solvent effects on the pore formation and morphologies of the membranes should be systematically investigated. Therefore, in this study, the effects of five commonly used solvents (NMP, DMSO, DMAc, DMF and TEP) on the rheological properties of the phase inversion slurries and morphologies of the anode substrates prepared by phase inversion tape casting method were investigated. Moreover, SOFCs with three different microstructured anodes were fabricated and evaluated.

2. Experimental

2.1. Materials

Composite anode powders were obtained by planetary ball-milling commercial NiO powders (JT Baker, USA) and YSZ powders (TZ-8Y, Tosoh Corporation, Japan) with a weight ratio of 6:4 in ethanol for 2 h and then drying at 80 °C overnight prior to use. $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3-\delta}$ (LSM) powders were synthesized by a glycine assisted combustion method. Polyethersulfone (PESf, Veradel 3000P) was purchased from Solvay Specialty Polymers Inc, USA. NMP, DMSO, DMAc, DMF, TEP, and polyvinylpyrrolidone (PVP, K30, CP) were purchased from Sigma-Aldrich, USA. Tap water was used as the coagulant for preparation of anode substrates, and all preparation processes were done at 25 °C.

2.2. Preparation and rheological properties of the phase inversion slurries

Five different phase inversion slurries were prepared by dissolving 1 g PVP and 4 g PESf into 24 g solvents (NMP, DMSO, DMAc, DMF and TEP) solution prior to the addition of 40 g NiO-YSZ composite anode powders. For simplification, the five perspective slurries were denoted as S_{NMP}, S_{DMSO}, S_{DMAc}, S_{DMF} and S_{TEP}, respectively. The slurries were ball-milled for 2 days. The rheological properties of the five slurries were measured by Discovery HR-3 (DHR-3) Rheometer (TA Instruments Co., USA) at 25 °C, and the measurements were performed by stepping up to high shearing rates from 0.1 to 100 s^{-1} after pre-shearing the slurries for 30 s.

2.3. Preparation and characterization of anode substrates

NiO-YSZ anode substrates were fabricated using the phase inversion tape casting method. In the preparation process, after being degassed for 10 min by a vacuum pump, the phase inversion slurries were casted onto carrier Mylar polymer films by a doctor blade with a gap height of 0.7 mm to form nascent anode substrates, and then immersed into the nonsolvent bath (tap water bath) for 24 h to fully remove traces of solvents and allow for completion of solidification. Finally, the anode substrates were taken out of the water bath and dried in air for one week.

To evaluate their gas permeabilities, electrical conductivities and porosities, the green NiO-YSZ anode substrates were first heated to 600 °C and maintained for 2 h to remove PESf and PVP, then to 1430 °C and held for 5 h, and subsequently reduced at 800 °C for 5 h in the humidified H_2 (3 vol% H_2O) to form Ni-YSZ anode substrates for the test of physical properties. During the heat-treatment, both the heating and cooling rates were fixed at 2 °C min^{-1}. The gas permeabilities of the samples were measured using a home-made setup similar to that described in Ref. [25]. The electrical conductivities and porosities were performed using the four-probe method and the Archimedes method in water [26–28], respectively.

2.4. Fabrication and characterization of single cells

To achieve sufficient mechanical strength for assembling the single cells, the green anode substrate tape was first punched into pellets with a diameter of about 16 mm, and then heated to 600 °C with a dwell time of 2 h, and finally to 1200 °C with a dwell time of 2 h. YSZ slurry was drop-coated on the pre-heated anode substrates, followed by co-sintering at 1430 °C with a dwell time of 5 h to obtain thin YSZ electrolyte films. The cathode inks consisting of 50 wt% YSZ and 50 wt% LSM were screen-printed on the YSZ electrolyte, and then fired at 1100 °C for 2 h. Gold (Au) paste was