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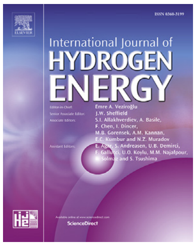

Fabrication of integrated BZY electrolyte matrices for protonic ceramic membrane fuel cells by tape-casting and solid-state reactive sintering

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ABSTRACT

Integrated porous/dense/porous tri-layer $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY) electrolyte asymmetrical matrices were designed for protonic ceramic membrane fuel cells (PCMFCs) and fabricated by multilayer tape-casting and solid-state reactive sintering. The effects of pore-former, sintering aid and sintering program on the microstructure of integrated electrolyte matrices (IEMs) were studied. Graphite and NiO were appropriate pore-former and sintering aid, respectively, and an accelerated heating program was more desirable. The conductivities of the IEM with designed microstructure in different atmospheres were measured by AC impedance spectroscopy at 400–600 °C. The highest conductivity of 6.9×10^{-3} S cm^{-1} at 600 °C was obtained in wet air atmosphere, and the corresponding activation energy was 0.602 eV. Gas-tightness of the IEM was confirmed by a stable open circuit voltage (OCV) of 0.97 V at 600 °C from a button fuel cell with impregnated NiO anode and $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY) cathode. These indicate that the fabricated BZY-based IEM has great potential for PCMFC application.

Introduction

Reducing the operating temperature of solid oxide fuel cells (SOFCs) from high range (800–1000 °C) to intermediate range (600–800 °C) and low range (400–600 °C) has become the developing trend of SOFC technology [1,2]. Over the past decade, considerable progress has been achieved on the development of low temperature SOFCs by ceramic membrane technology based on typical yttria-stabilized zirconia (YSZ) electrolyte [3] or alternative electrolytes with higher ionic conductivity at low temperatures [4–8], combining with high-performance electrodes [9,10], as well as optimized microstructure [11,12]. In particular, the nano- and composite technologies can strengthen interfacial conduction thus greatly enhance electrolyte conductivity and improve fuel cell performance at significantly lower temperatures, which help to develop next generation fuel cell technology for commercialization [13–15]. Compared with traditional oxygen-ion conducting SOFCs, proton conducting SOFCs take the advantages of low activation energy for proton migration in oxides and of water formation at cathode side, offering adequate proton conductivity for low temperature operation and leading to higher cell efficiency by avoiding fuel dilution with water [16]. Particularly in hydrocarbon fuel operation, the latter show higher fuel conversion than the former because of direct proton removal from the fuels and higher carbon-

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coking resistance [17]. Therefore, proton conducting ceramic membrane SOFCs, i.e. protonic ceramic membrane fuel cells (PCMFCs) are more suited for low temperature operation.

Proton-conducting acceptor-doped barium cerate and barium zirconate based perovskite materials have been widely investigated as electrolytes for PCMFCs. PCMFCs based on doped $BaCeO_3$ electrolyte membranes have shown promising performances at low temperatures [18,19] but the poor chemical stability of $BaCeO_3$ against H_2O and CO_2 deteriorates the long-term stability which hinder their practical application [16]. In contrast, PCMFCs based on doped $BaZrO_3$ electrolyte membranes have received wider attention due to their excellent chemical stability and high proton conductivity, although the performances are inferior to those of $BaCeO_3$ based PCMFCs up to now. Indeed, 20 mol% Y-doped $BaZrO_3$ (BZY) shows the largest bulk proton conductivity and lowest activation energy below 500 °C in comparison with Y-doped $BaCeO_3$ (BCY), Gd-doped CeO_2 (GDC) and Sr and Mg doped $LaGaO_3$ (LSGM) [20]. The main problem of BZY is the difficult sintering due to its refractory nature that makes the fabrication of dense electrolyte membranes having large grain size difficult, leads to low density of sintered samples and a large volume of highly resistive grain boundaries, resulting in quite low total proton conductivity [16]. The grain boundary resistance can be reduced by sintering at extreme high temperatures [21]. However, high sintering temperature with a long soaking time can lead to Ba evaporation, thus lowering conductivity [22]. Moreover, the high sintering temperature required to prepare dense BZY electrolyte membrane in electrode-supported PCMFCs may cause ingredient and porosity losses in the electrodes or unfavorable electrode/electrolyte interface reactions or interface delamination induced by thermal stress, which will deteriorate cell performance.

Several attempts have been made to improve the sinterability of BZY including the addition of sintering aids [23,24], composition modification by co-doping [25–27], synthesis of ultrafine BZY powders [28], and utilization of new sintering methods [17,29]. All these efforts are proved to be efficient to reduce the sintering temperature, enhance the sintered density, and maintain high proton conductivity, facilitating the preparation of dense BZY electrolyte membrane on porous electrode substrate. Another strategy is adopting new cell configuration based on integrated electrolyte matrix (IEM) with porous/dense/porous tri-layer structure. Highly active electrodes can be produced by ion-impregnation after the well-architected IEM has been established. This cell design has been successfully applied on YSZ [30] and LSGM [31,32] based intermediate-to-low temperature SOFCs.

Here we propose a novel strategy to develop BZY-based PCMFC for low temperature operation in which integrated BZY electrolyte matrix is fabricated by multilayer tape-casting and solid-state reactive sintering. This strategy facilitates the cost-effective scale-up of single cell and allows the preparation of active electrodes in the established IEM by ion-impregnation process. In this study, the effects of pore-former and sintering aid in electrolyte slurry and sintering program on the microstructure of the integrated BZY matrix were investigated and the electrical behaviors of the integrated BZY matrix with designed microstructure in different atmospheres were studied. A button cell was also constructed and the OCV was measured to evaluate the gas-tightness of the integrated BZY matrix.

Experimental

Slurry preparation and tape casting

The integrated $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY) electrolyte matrices were fabricated by multilayer tape-casting and solid-state reactive sintering. The precursor powders were the raw powders ($BaCO_3$, ZrO_2, Y_2O_3), sintering aid (NiO, ZnO or CuO), with or without pore-former (starch or graphite) for porous electrolyte layer (PEL) or dense electrolyte layer (DEL). The composition of the slurries for PEL (named PEL-slurry) and DEL (named DEL-slurry) is shown in Table 1 and a schematic diagram of slurry preparation and tape casting process is shown in Fig. 1.

The appropriate slurries were prepared by a two-step ball milling process. In the first step, all raw powders and sintering aid with or without pore-former were homogeneously dispersed in the mixed solvents of ethanol and acetone (3:2 in volume ratio). Meanwhile, triethanolamine was served as dispersant and the optimum dosage was 5 ml/100 g determined by settlement experiment. In the second step, polyethylene glycol (PEG) and dibutyl phthalate (DBP) (1:1 in volume ratio) were added as plasticizers and polyvinyl butyral (PVB) was added as binder to obtain the slurry with proper rheological properties.

Prior to tape-casting, the slurries were de-aired by vacuum treatment for 40 min. The tape-casting process included three steps. First, the de-aired PEL-slurry was casted on the Mylar membrane at the blade height of 4 mm to form thick PEL green tape with a casting speed of 0.1 m min^{-1}, then dried in air at room temperature for 48 h. Next, the blade height was placed 0.3 mm higher than the dried thick PEL green tape, and then the de-aired DEL-slurry was casted on the dried thick PEL green tape with a casting speed of 0.2 m min^{-1} and dried for 24 h to obtain a thin DEL green tape. Finally, the de-aired PEL-slurry was casted on the thin DEL green tape with a casting speed of 0.2 m min^{-1} and dried for 24 h to complete the integrated electrolyte matrix (IEM) green tape with a thin PEL green tape. The final thickness of the IEM green tape was 2 mm.

In addition, de-aired DEL-slurry containing different sintering aid was casted separately on the Mylar membrane at the blade height of 2.5 mm to form thick DEL green tape with a casting speed of 0.1 m min^{-1} and dried for 48 h. While the de-aired PEL-slurry containing different pore-former was casted separately on the Mylar membrane at the blade height of 4 mm to form thick PEL green tape with a casting speed of 0.1 m min^{-1} and dried for 48 h.

Sintering process

All the green tapes were cut into discs with a diameter of 20 mm. These discs were sandwiched between two pieces of corundum plate isolated by BZY powder synthesized by a solid-state reaction method [33]. Next, the discs were sintered at 1500 °C in air for 10 h. Different sintering programs were set up with a uniform heating rate of 0.5, 1 and 2 °C min^{-1} from

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