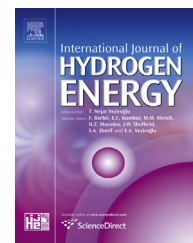




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Long term stability of porosity gradient composite cathode controlled by electro-static slurry spray deposition

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ABSTRACT

Proton conducting fuel cells (PCFCs) have attracted much attention due to the lower activation energy of proton transport at intermediate temperatures. The cathode of PCFCs has been studied for enhancement of cell performance. Unlike solid oxide fuel cells (SOFCs), the product of chemical reaction, H_2O , is generated in the cathode region. Generally, as the structure of the PCFC cathode is denser than the anode of SOFC, the vapor is not easily emitted outside of the cathode, and this remaining vapor in the isolated cathode structure has a negative effect on cell performance. In this work, a gradient porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)/ $BaCe_{0.7}Zr_{0.15}Y_{0.15}O_{3-\delta}$ (BCZY) composite cathode was developed for fuel cells based on the BCZY electrolyte using an electrostatic spray slurry deposition method. The cathode porosity and deposited powder size gradually increased in the direction away from the electrolyte-electrode. The results indicate that the structure of the porosity gradient cathode might enhance the long-term stability in proton conducting fuel cells.

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Introduction

Reduction of the operating temperature is a critical means of improving the commercialization of solid oxide fuel cell (SOFC) technology. Therefore, intermediate-temperature solid oxide fuel cells have attracted considerable attention worldwide for their high efficiency and low environmental impact. They are widely viewed as having an important role in the hydrogen fuel economy [1–3]. However, lowering the working temperature of SOFCs causes large overpotential at the electrode–electrolyte interface [4–6].

Proton conductors have received increasing research focus because of their advantages such as low activation energy and

high energy efficiency [7]. During the past two decades, perovskite oxide materials have been a focus of research, in which trivalent rare earth elements have been added as dopants to introduce oxygen vacancies [8–10]. Although proton conducting SOFCs (PCFC) can operate at lower temperatures compared to traditional oxide ion conducting SOFCs, the performance to date of proton conducting SOFCs is still lower than that of optimized oxide ion conducting SOFCs.

A major challenge for this type of proton conductors is chemical stability because electrolyte materials easily decompose when exposed to CO_2/H_2O atmosphere in practical environments [11–13]. With increasing load, the proton-conducting fuel cell produces water vapor on the cathode side. The high air flow usually removes this product outside.

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However, when operation is long-term, the trapped vapor in the isolated cathode structure impedes the remaining high performance because of the reduction of the length of the triple phase boundaries (TPBs). Also, this remaining vapor sometimes reacts to electrolyte and causes undesirable secondary phases.

In this work, a cathode with a porosity gradient structure is introduced to solve the aforementioned problems and to maximize the stability of proton conducting fuel cells in long-term operation. To realize this structure of composite cathode, an electrostatic slurry spray deposition (ESSD) technique with substrate rotation was applied. The ESSD utilizes electrostatic spraying of slurries containing powders and organic additives for slurry stabilization and rheological control [14]. This deposition method has several advantages; high deposition rate, stability of the crystal phase, much less crack formation, and better adhesion to the substrate caused by deposition condition at room temperature. The ESSD with a substrate rotation method can deposit two materials simultaneously with independent control of the flow rates [15]. The composite cathodes fabricated in this work were designed to pore former contents, which gradually increased in the direction away from the electrolyte/cathode interface. The fabricated cathodes showed good adhesion with the electrolyte and significantly improved the electrochemical performance of a single cell.

Experimental

Electrolyte $\text{BaCe}_{0.7}\text{Zr}_{0.15}\text{Y}_{0.15}\text{O}_{3-\delta}$ (BCZY) powders were prepared by a citric acid-nitrate sol-gel method. NiO-BCZY anode supports with 1 wt.% carbon black as a pore former, were pressed into a disc 1 mm in thickness and 25 mm in diameter. The prepared BCZY slurry was deposited on the NiO-BCZY anode pellet without pre-sintering by the ESSD method. The electrolyte deposited half-cell was co-sintered with the anode at 1450 °C for 2 h.

The cathode was fabricated using the ESSD method with a rotating stage, as shown in Fig. 1(a). The first slurry was prepared by mixing BCZY and LSCF in a weight ratio of 4:6 with isopropyl alcohol (IPA). The second slurry was a pore former, super P carbon black, mixed in IPA solution. Two separate slurries of BCZY/LSCF and the pore former were contained into separate slurry reservoirs connected to spray nozzles. A polyvinyl pyrrolidone (PVP) of 0.2 wt.% as a dispersant was dissolved in the solvents.

A cathode area of 1 cm² was deposited by the ESSD technique from the aforementioned slurries on the rotating stage. The rotating speed of the disk was 4 RPM. The flow rate of the BCZY/LSCF slurry was 5 ml/h and that of the pore former slurry was changed from 2 ml/h to 8 ml/h. The expected structure is schematically shown in Fig. 1(b). Subsequently, the deposited cell was sintered at 1050 °C for 2 h in air.

An electrolyte-supported symmetric cell was fabricated for characterization of the cathodes. The BCZY powders with 1 wt.% NiO as a sintering aid were pressed into a pellet 1 mm in thickness and 25 mm in diameter. The cathode layers were deposited on both sides of the electrolyte pellet by the aforementioned method.

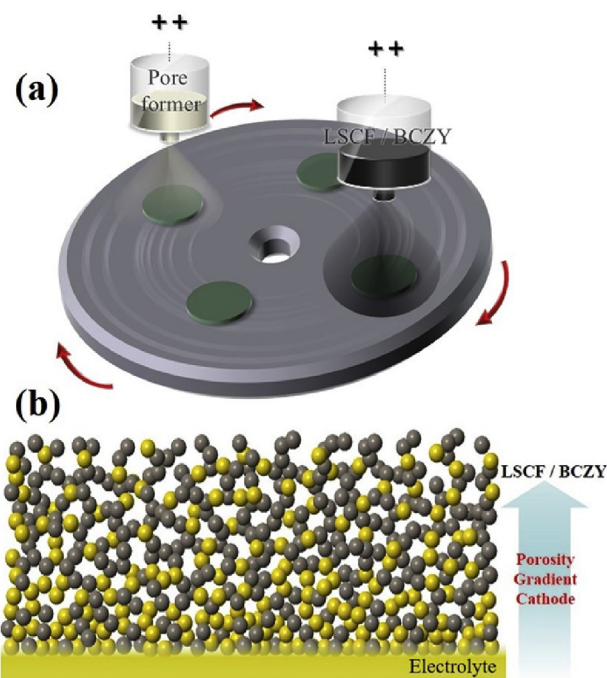


Fig. 1 – (a) Illustration of the ESSD system with a rotating substrate and (b) schematic diagram of the porosity gradient composite cathode.

An image analyzer (Image-Pro plus and Image J software) was used to verify the porosity gradient. A scanning electron microscope was used to observe the microstructure of the cells before the full cell test. Electrochemical measurements of single cells were performed from 550 to 700 °C with humidified hydrogen (~3% H₂O) as fuel and static air as the oxidant. The impedance spectra were recorded under open circuit conditions (OCV) using a 20 mV amplitude AC signal over a frequency range of 1 MHz to 0.1 Hz at temperatures ranging from 550 °C to 700 °C. The I–V curve and impedance tests were performed at intervals of 50 °C, and all data were taken 1 h after the desired temperature was reached. The cell performance was measured with a Potentiostat/Galvanostat (Solartron 1287) coupled with a 1260 frequency response analyzer using Corr-Ware and Z-Plot software. The voltage–current curves were recorded by the DC Electronic Load at a scanning rate of 20 mV s⁻¹.

Results and discussion

Fig. 2 shows a cross-sectional scanning electron microscope images of the porosity gradient and conventional cathode with a thickness of ~25 μm. Also, Fig. 2(a) reveals the difference in the porosity ratio measured by the image analyzer; the cathode porosity consists of a gradually increasing pore ratio from the underlying dense electrolyte to the current collector on the top. At the interface to the electrolyte, area-I, the cathode porosity was about 24%. On the other hand, at the top of the cathode, area-III, the porosity of the cathode was about 38% to enable better air diffusion and rapidly escape of vapor from inside the cathode. The lower porosity layer helped not

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