

Fabrication and performance test of solid oxide fuel cells with screen-printed yttria-stabilized zirconia electrolyte membranes

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Abstract Yttria-stabilized zirconia (YSZ) membranes were deposited onto porous NiO–YSZ anode supports by screen printing. Combined with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ –YSZ composite cathode, the prepared anode-supported solid oxide fuel cells (SOFCs) were electrochemically tested. A typical SOFC with a 30- μm -thick YSZ electrolyte membrane gave the maximum power densities (MPDs) of 0.26, 0.53, 0.78, and 1.03 W/cm^2 at 650, 700, 800, and 850 °C, respectively, using hydrogen as fuel and stationary air as oxidant. Replacement of stationary air with pure oxygen flow exerted a significant positive effect on the MPDs of the cell. Using 100- and 200-ml/min oxygen as oxidants, the MPDs of the cell were enhanced 35.3% and 68.6%, respectively. Polarization analysis indicated that, at the MPD points, the electrode polarization resistances accounted for 80% of the cell total resistances.

Keywords Solid oxide fuel cells · YSZ membranes · Screen printing · Electrode polarization

Introduction

Solid oxide fuel cells (SOFCs) have drawn considerable attention in recent years because of their high efficiency, environmental friendliness, and feasibility of using hydrocarbon as fuel [1–5]. In fact, high fabrication cost is the main challenge for wide commercial applications of SOFCs. From the viewpoint of cost reduction and long-term stability, many researchers have paid attention to developing anode-supported thin electrolyte membrane SOFCs which can be operated at reduced temperature while maintaining the high performances [6, 7]. In the anode-supported thin membrane SOFC design, electrolyte membranes with a thickness of several to tens of microns were supported by porous anode substrates. Excellent power densities up to 1.5 W/cm^2 have been reported based on an anode-supported design [8, 9].

Development of cost-effective technologies for electrolyte membrane deposition is a crucial issue for fabrication of thin electrolyte membrane SOFCs [10]. Wet ceramic powder method such as electrophoretic deposition [11], spinning coating [12], slurry coating [13], spray coating [14], vacuum casting [15], and centrifugal casting [16] have been investigated to deposit dense electrolyte membranes for SOFCs application. Compared to the above-mentioned techniques, screen printing is a simple and inexpensive technology for membrane deposition. The technique has already been applied successfully in the electronic industries for integrated circuits [17]. For application in SOFCs fabrication, electrolyte powder was firstly mixed with appropriate organic vehicles to make homogeneous and stable printing ink. Then, the ink was extruded through a screen onto the anode substrate by a scraping blade. Finally, the anode substrate with printed electrolyte membrane was dried and co-fired at high temperature to densify the

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electrolyte membrane. Peng et al. [18] fabricated a dense $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ (YDC) membrane (15- μm thick) on porous NiO–YDC anode by screen printing. Based on this YDC membrane and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) cathode, they obtained a maximum power density of 0.23 W/cm^2 at $600\text{ }^\circ\text{C}$. Xia et al. [19] got a $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) electrolyte membrane with a thickness of $30\text{ }\mu\text{m}$ using a similar screen-printing technology. Combined with a SSC–SDC cathode, their fuel cell provided the maximum power densities of 0.12 and 0.4 W/cm^2 at 500 and $600\text{ }^\circ\text{C}$, respectively. Recently, Dollen and Barnett [7] prepared anode-supported yttria-stabilized zirconia (YSZ) membrane SOFCs by screen-printing technology and got a maximum power density of 1.45 W/cm^2 . Yoon et al. [20] fabricated dense YSZ electrolyte membranes by combination of screen printing and single-step co-firing. The maximum power density of 1.5 W/cm^2 was achieved.

Compared with other electrolyte materials such as doped CeO_2 and doped LaGaO_3 , YSZ possesses unique advantages including high physical and chemical stability and high mechanical properties. To date, YSZ is still the most suitable electrolyte material for commercialization of SOFCs. From the viewpoint of low cost and simplification, it is necessary to find a simple and reliable approach for fabrication of YSZ electrolyte membranes. In this study, screen printing was developed to deposit gas-tight YSZ electrolyte membranes onto porous NiO–YSZ anode supports. Combined with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM)–YSZ composite cathode, single cells were assembled and electrochemically tested.

Experimental

Starting powder preparation

NiO powder was prepared by an ammonia precipitation method. Ammonia (analytical reagent, AR) was added to $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR) solution drop by drop to obtain nickel hydroxide deposition. Magnetic stirrer was applied to alleviate aggregates in the nickel hydroxide. Then, the as-prepared deposition was aged at $70\text{ }^\circ\text{C}$ for 40 min. After washing by alcohol and drying at $105\text{ }^\circ\text{C}$, the resultant deposition was finally fired at $400\text{ }^\circ\text{C}$ for 2 h to get nickel oxide powder.

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) powder was synthesized by a citric–nitrate process. Stoichiometric amounts of $\text{Mn}(\text{NO}_3)_2$ (AR), $\text{Sr}(\text{NO}_3)_2$ (AR), and La_2O_3 (99.99%) were dissolved in diluted HNO_3 (AR) and citric acid (AR) was added as the complexant. The total molar ratio of cation to citric acid was 1/1.15. The solution was evaporated at $75\text{ }^\circ\text{C}$ to form a transparent gel. After drying at $100\text{ }^\circ\text{C}$ for 12 h, the transparent gel changed to dry gel. Finally, the dry gel was fired at $1,000\text{ }^\circ\text{C}$ for 4 h to get LSM powder.

Cell fabrication

The as-prepared NiO powder was mixed with YSZ (8 mol % Y_2O_3 –92 mol% ZrO_2 ; Tosoh Corp.) in an agate mortar for 1 h. The weight ratio of NiO to YSZ was 1:1. Additionally, 10 wt% flour was added in the anode powder as pore former. The anode powder was pressed into pellets of 13 mm in diameter and 0.5 mm in thickness under a pressure of 260 MPa. The green anode pellets were pre-sintered at $1,000\text{ }^\circ\text{C}$ for 2 h.

For printing ink preparation, YSZ powder was mixed with terpeneol–ethylcellulose media in an agate mortar for 2 h to get uniform YSZ ink. Before ink preparation, the YSZ powder was ball-milled using ethanol as media for 13 h to break the big aggregates in the powder. The YSZ ink contained 60 wt% terpeneol–ethylcellulose media and 40 wt% YSZ powder. The YSZ ink was screen-printed onto the pre-sintered NiO–YSZ anode substrates through a terylene screen. The mesh count of the screen was 165 wires/cm and the wire diameter was $30\text{ }\mu\text{m}$. The screen had an opening size of $30\text{ }\mu\text{m}$ and an open area of 25%. After printing and dried in air overnight, the anode-supported YSZ membranes were co-fired at $1,350\text{ }^\circ\text{C}$ to densify the green YSZ membranes.

The LSM–YSZ composition cathode was also applied to the sintered YSZ membranes by screen printing and then sintered at $1,200\text{ }^\circ\text{C}$ for 3 h.

Electrochemical test

Single cell was sealed onto one end of ceramic tube using silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, Shanghai, China). The electrochemical data were collected using a four-probe setup in which two Ag lines were fixed to each electrode to serve as respective current and voltage probes. Silver paste was used as current collector for both anode and cathode. The cell performance and electrochemical impedance spectra were measured using SI 1260 impedance/gain-phase analyzer in combination with SI 1287 electrochemical interface (Solartron Instruments, Hampshire, UK). The cell current–voltage (I–V) curves were tested by linear sweep voltammetry at a scanning rate of 5 mV/s . The impedances were measured in the frequency range of 910 kHz – 0.1 Hz with a signal amplitude of 10 mV under open-circuit condition. Hydrogen was used as fuel and stationary air or pure oxygen flow was used as oxidant. During electrochemical testing, flow rate of fuel or oxidant was varied to investigate the effect of gas composition on the cell performance. After the electrochemical test, the cell was fractured and observed by a Hitachi S-570 (Tokyo, Japan) scanning electron microscopy (SEM).

Results and discussion

Microstructure and cell performance

Figure 1 shows a SEM micrograph of cell with a screen-printed YSZ electrolyte membrane sintered at 1,350 °C for 4 h. It can be seen that the YSZ electrolyte membrane was crack-free with limited blink pin holes in the cross-section. The thickness of film was 30 μm. The YSZ membrane adhered well with both cathode and anode. The anode porosity was about 60% as tested using a standard Archimedes method and the porosity for cathode was estimated from the SEM photos to be about 45%.

Figure 2 presents the cell output performance using hydrogen as fuel and stationary air as oxidant. The maximum power densities of 0.26, 0.53, 0.78, and 1.03 W/cm² were obtained at 650, 700, 800, and 850 °C, respectively.

Effect of gas composition on the cell performance

To investigate the effect of cathode gas atmosphere on the performance of the cell, the hydrogen flow rate on the anode side was fixed at 100 ml/min while the cathode side was exposed to the stationary air or blew with different pure oxygen flows (100 and 200 ml/min). Figure 3 shows the effect of pure oxygen flow rate on the *I-V-P* curves of the cell. The maximum power densities (MPDs) of 1.02, 1.38, and 1.72 W/cm² were obtained when stationary air, 100-, and 200-ml/min oxygen were introduced to the cathode side, respectively. Using 100- and 200-ml/min oxygen as oxidants, the MPDs of the cell were enhanced 35.3% and 68.6%, respectively, compared with the MPD obtained from stationary air. Replacement of stationary air by pure oxygen flow means a higher oxygen concentration on the surface of the cathode. Additionally, the flowing oxygen can accelerate the gas circulation rate around/within the

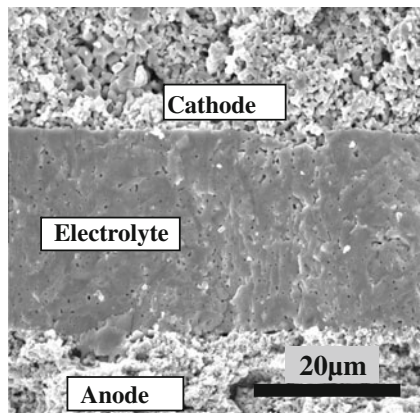


Fig. 1 SEM micrographs of cells with screen-printed YSZ membrane sintered at 1,350 °C

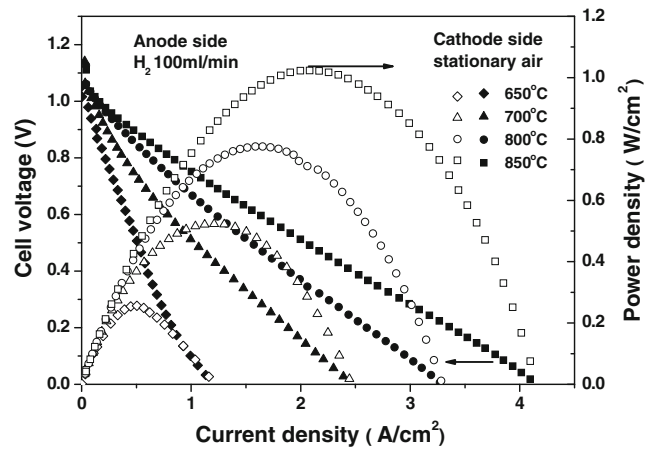


Fig. 2 Typical *I-V-P* curves for a cell with a 30-μm-thick YSZ electrolyte membrane. Hydrogen and stationary air are used as fuel and oxidant, respectively

cathode. The exhaustion of oxygen during high current discharge can be timely supplied by the flowing oxygen. The change of oxygen flow rate has no obvious influence on the open circuit voltages (OCVs) of the cell while it exerts a strong positive effect on the MPDs of the cell. On the other hand, the influence of anode gas atmosphere on the performance of the cell is negligible. These results indicated that the polarization (including both activation and concentration polarization) of cathode instead of anode controls the performance of the anode-supported SOFCs. This agrees well with Yoon’s reports regarding the anode-supported SOFCs [20].

Figure 4 shows the comparison of the impedances tested with different oxygen flow rates under open-circuit condition. The ohmic resistances (the high frequency intercept) of the cell were independent of the oxygen flow rate. The polarization resistances (the arc between the high frequency intercept and the low frequency intercept) of the cell decreased with the increasing of the oxygen flow rate.

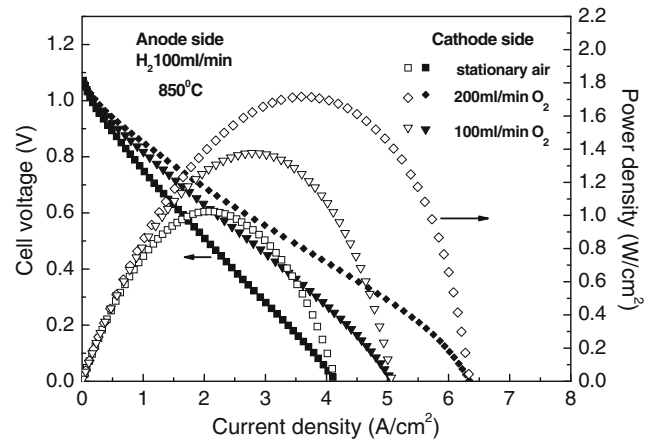


Fig. 3 Effect of oxygen flow rate on the *I-V-P* curves of the cell

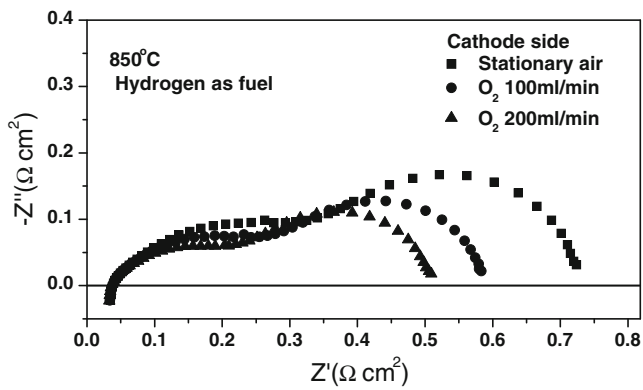


Fig. 4 Effect of oxygen flow rate on the impedances of the cell. The data are collected under open-circuit condition

It is reasonable to ascribe the reduction of the polarization resistances to the enhanced cathode performances because the impedance data were collected by a fixed hydrogen flow rate. In Yoon's report [20], the voltage losses in the cell were classified as ohmic resistance loss, activation polarization loss (mixture of anode and cathode), anode concentration polarization loss, and cathode concentration polarization loss. By fitting the current–voltage curves with suitable polarization model, the above-mentioned polarization resistances can be obtained quantitatively. They found that the majority of the activation polarization loss occurs on the cathode side. In the present paper, the electrode polarization resistances contain both anode polarization resistance and cathode polarization resistance. The ratios of electrode polarization to the total resistance of the cell under OCV condition were 94.8%, 93.7%, and 92.7% for stationary air, 100-, and 200-ml/min oxygen flow, respectively. The impedance of the cell under current loading may be different from that under OCV condition, especially for the non-linear current–voltage curves. Figure 5 shows the ratio of electrode polarization to the total resistance of the cell (η_e/η_t) under current loading. The ratio plot was derived from the current–voltage curve and the impedance data of total cell ohmic resistance. The data collected from different oxygen flow rates were plotted together for comparison. It can be seen that all the η_e/η_t values decreased gradually with the increasing of current loading from OCV condition to 4.5 A/cm². When the current loading was higher than 4.5 A/cm², the η_e/η_t values derived from 100- and 200-ml/min oxygen flow turned to be increasing, which associated with the occurrence of concentration polarization at high current discharge stage. The introduction of pure oxygen flow on the cathode side significantly reduced the cathode polarization and thus reduced the η_e/η_t values. The higher the oxygen flow rate, the lower the η_e/η_t value. It can be seen that the cathode atmosphere exerted a significant effect on

electrode polarizations from low current densities to high current densities. According to Kim's report, the effect of concentration polarization was not negligible at a very low current density, even close to the open-circuit limit [21]. The increasing of pure oxygen gas flow rate relieved the concentration polarization of cathode and thus lowered the η_e/η_t value as shown in Fig. 5. The η_e/η_t values at MPD points for stationary air, 100-, and 200-ml/min oxygen flow were 86.7%, 82.1%, and 77.6%, respectively. Accordingly, the ohmic resistance accounted for 13.3%, 17.9%, and 22.4% of the cell total resistance at these MPD points. It can be readily seen that the performances of the cell were limited by the electrode polarization, especially by the cathode polarization.

Conclusions

Anode-supported SOFCs were fabricated and electrochemically tested in this study. The YSZ electrolyte membranes were deposited onto the porous NiO–YSZ anode supports by screen-printing technique. After co-firing at high temperature, the YSZ membranes were gas-tight and suitable for application as electrolyte in SOFCs. A typical cell with a 30- μ m-thick YSZ electrolyte membrane fabricated by screen printing provided the maximum power densities of 0.26, 0.53, 0.78, and 1.03 W/cm² at 650, 700, 800, and 850 °C, respectively, using hydrogen as fuel and stationary air as oxidant. The cell performances were almost independent of the anode atmosphere. On the other hand, replacement of stationary air with pure oxygen flow exerted a significantly positive effect on the cell performances. The MPDs of 1.02, 1.38, and 1.72 W/cm² were obtained using stationary air, 100-, and 200-ml/min oxygen as oxidants on the cathode side, respectively.

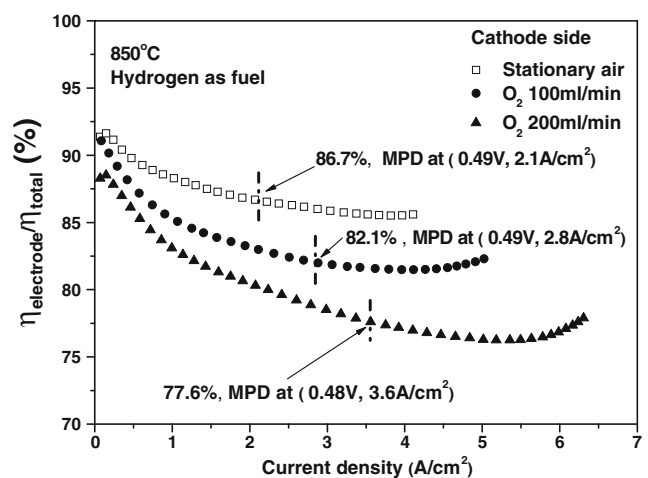


Fig. 5 Distribution of electrode polarization under current loading

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