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Effects of Processing Variables on Formation of Thin Electrolyte Films for Solid Oxide Fuel Cells

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Abstract

Effects of processing variables on formation of thin 8YSZ electrolyte films on porous screen-printed anode/Ni-NiAl\textsubscript{2}O\textsubscript{4} supports are presented in this paper. The screen-printed support design was Ni-8YSZ functional anode (thickness ~5 \textmu m) on the thick NiO-NiAl\textsubscript{2}O\textsubscript{4} composite (1:1 weight ratio) based support. Average pore size and porosity of the anode functional layer was made to be around 1.1 \textmu m and 37\% respectively. 8YSZ electrolyte layer was fabricated via an electrophoresis deposition with variations of voltage (10, 20, 30 V) and deposition time (20, 30, 40 s). It was shown that at 10 V for 20 s, the thin layer was only loosely deposited while adjusting the voltage to 20 V resulting in a smooth film surface. Further increasing the voltage to 30 V gave an adverse result. However, these films were not yet densified after co-sintering and reduction in H\textsubscript{2} atmosphere. Further attempt was done by increasing the deposition time to 30 s at 20 V. This resulted in a densely packed microstructure arrangement. Further increasing the deposition time to 40 s gave rise to layer cracking. Electrical performance of the cells was measured at the temperature range of 500-800 \textdegree C under H\textsubscript{2}/O\textsubscript{2} atmosphere. The highest power density obtained was 70 mW/cm\textsuperscript{2}. Impedance spectroscopy analysis indicated the ohmic resistance of 6 \Omega\cdot cm\textsuperscript{2} while the total resistance was found to be 49 \Omega\cdot cm\textsuperscript{2}.

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1. Introduction

Solid oxide fuel cells (SOFCs) are the electrochemical devices that produce clean electrical energy from chemical energy stored in the fuels, primarily hydrogen and hydrocarbon [1,2]. SOFCs could be used with a variety of fuels and also showed promising conversion efficiency, so a great deal of development and research on this type of fuel cell has been undertaking [3,4].

SOFCs configuration is based on sandwiching the dense electrolyte between the anode and cathode whose mixed conduction modes between electronic and ionic are highly required. In the conventional anode support design, a conducting metal, typically Ni, is mixed with the electrolyte powder in order to reduce the thermal stress and also to enhance the electronic conduction. Attempts to use external supports in order to reduce the thickness of the expensive anode, which in turn gave rise to lower polarization of the anode layer were reported [5-6]. Metal such as stainless steel were reported to be a promising external support as it is cheap and does not require complicated fabrication technique [5]. However, thermal mismatching between the metal support and the cermet anode layer was the concerns as cyclic operation may result in thermal stress and layer cracking. The use of ceramic support such as alumina was found to result in a dense interlayer which was harmful to gas diffusion to the next layer [6].

Fabrication of dense electrolyte layers could be achieved by many methods such as tape casting, sol-gel, vapor phase, and screen-printing. These methods presented some drawbacks. Electrophoresis deposition was the technique used for fabrications of thin layers using a simple apparatus [7]. Very thin layers with a thickness of less than 10 micrometer could be fabricated. In this method, stable slurry of the material to be deposited was prepared. Particle size homogeneity of the powder played an important role in controlling microstructure arrangement of the final products [8].

In this paper, the use of an external support was reported. This support was prepared from the mixed powers between alumina and NiO. The powders were mixed in a proportion to form pre-designed conducting Ni/NiAl2O4 cermet after firing and reduction in hydrogen. The anode layer was then coated on using a screen-printing method. Solid contents of the anode paste were adjusted to give the surface quality suitable for the electrolyte coating. Fabrication of the electrolyte layer using an electrophoresis deposition was studied. Effects of the fabrication conditions, coating time and voltage, on the coating layers were examined. Electrical performances of the single cells were measured at the temperature range of 500-800 °C under H2/O2 atmosphere.

2. Methodology

The designed final weight ratio between NiO and NiAl2O4 was 1:1. The weighed NiO and Al2O3 powders were mixed in a vibrational mill before being sieved and uniaxially pressed to form cylindrical supports. The supports were then fired at 1400°C for 1 h before prior to reduction at 750-800 °C in H2 atmosphere. Phase evolution was monitored using an X-ray diffraction technique (PANalytical, X-Pert PRO MPD) with a step size and time per step of 0.0167 and 5.08 seconds respectively. Microstructure was examined using a SEM (JEOL, JSM-5410LV). Both secondary and back-scattered images were recorded. Porosity of the substrate was measured based on the Archimedes water absorption method.

Electrical conductivity was measured using a 4-point probe method. The sample was cut and ground into a 9×4×1 mm-bar and coiled with 4 platinum (Pt) wires. In order to enhance the contacts between the wire and the sample, Pt paste was applied and annealed at 1050 °C for 1 h. Bending strength was examined based on a ball-on-ring technique using a UTM (Instron, 556). The bending strength was calculated according to ASTM C1499. For fabrication of the cells, the NiO-8YSZ anode paste (NiO-8YSZ powder mixed with polyvinylbutyral in terpenol) was applied on the support pre-fired at 1000 °C using a screen-printing technique. Solid contents of the anode paste were varying from 60, 70 and 80%.
The anode printed support was then co-sintered at 1000 °C for 1 h. The screen-printed supports were then coated with carbon to enhance conductivity before being placed on a copper plate attached in the negative side during the electrophoresis deposition. Stainless steel was used as an inert positive electrode. The electrolyte slurry concentration was 10 g/L. The deposition was performed with variations of voltage from 10, 20, 30 V and deposition time of 20, 30, 40 s. To further observe quality of the electrolyte films, the layered samples were co-sintered at 1400 °C for 1 h and reduced at 800 °C in H₂ atmosphere. Microstructure of the layers and top surface were examined using the SEM. Cell performance was measured at the temperature range of 500-800 °C under H₂/O₂ atmosphere. Pt mesh was attached onto the cathode side using the Pt paste while Pt wire was used as the cathode and also the current collector. Polarisation of the cells was examined using an impedance spectroscopy (Solartron IS 1260) with a voltage and frequency range of 100 mV and 0.1-500 kHz respectively.

3. Results and discussion

XRD analysis (result is now shown) indicated that the fired support contained mixed phases of NiO and NiAl₂O₄ only. After reduction at 750 °C, there appeared reflections according to Ni while NiO peaks were still observed, suggesting that some of the NiO phase had transformed into Ni. Reflections according to the NiO had disappeared after reduction at 800 °C suggesting that this condition was suitable to use. This support showed porosity of 32%, flexural strength of 80 MPa and conductivity at 800 °C of 1300 S·cm⁻¹.

Effects of solid contents on surface quality of the screen printed NiO-8YSZ anode layers were compared in Fig 1 It was found that the paste with 60% solid content was too running so the surface connectivity was too low. Increasing the solid content of the paste to 70%, the surface became smooth with good connectivity of solid particles when dried. The past with 80% solid content was too viscous and the solid particles were clustered resulting poor surface quality anode. So the solid content selected was 70%. The screen-printed anode layer contained porosity of around 30%, with a layer thickness of 5 μm after reduction.

![Fig 1. Comparative surface of anode layers screen printed using the anode pasts with (a) 60%, (b) 70% and (c) 80% solid contents.](image)

8YSZ electrolyte slurry was then deposited onto the anode layer. The deposition process was performed with variations of voltages from 10 to 20 and 30 V for 20 s (Fig 2). It was shown that at 10 Vs, the thin layer was only loosely deposited with some uncoated areas. Adjusting the voltage to 20 V resulted in a smooth film surface with a denser packing of solid particles. Further increasing the voltage to 30 V gave an adverse result. After drying, surface cracking and peeling were observed. As the voltage was increased, the particle mobility was thus enhanced so the thickness of the films increased rapidly. During drying, large shrinkage of the thick electrode layer thus gave rise to internal stress and finally
cracking. SEM images of the half cells after co-sintering and reduction are shown in Fig 3. It was observed that both 10 and 20 V used were still insufficient to produce high quality electrolyte films so further attempts to improve the film quality was done by varying deposition time to 30 and 40 s (Fig 4). The half cells were then co-fired and reduced prior to examination with SEM (Fig 5). The result showed that increasing the deposition time to 30 s, a smooth electrolyte film surface was obtained. Increasing deposition time to 40 s, the anode and the electrolyte layers became almost undistinguishable as the electrolyte was porous and unsintered.

![Fig. 2. Quality of the electrolyte coatings with the use of EPD voltage at (a) 10, (b) 20 and (c) 30 V for 20 s. The uncoated area is marked in (a) due to the low deposition voltage.](image)

Electrical performance of the cells was measured at the temperature range of 500-800 °C under H2/O2 atmosphere. Pt was used as the cathode material and current collector. The highest power density obtained at 800 °C was 70 mW/cm² (Fig 6). Impedance spectroscopy analysis indicated the ohmic resistance of 6 Ω·cm² while the total resistivity was found to be 49 Ω·cm². The large contribution from electrode polarization was responsible for the total resistivity.

![Fig. 3. SEM images of the EPD electrolyte on the anode/supports. The deposition was performed for 2 s at (a,b) 10 V and (c,d) 20 V.](image)
Fig. 4. Quality of the electrolyte coatings with the use of EPD voltage at 20 V for (a) 20, (b) 30 and (c) 40 s.

Fig. 5. SEM images of the EPD electrolyte on the anode/supports. The deposition was performed at 20V for (a,b) 30 s and (c,d) 40 s.

4. Conclusion

Fabrication of thin electrolyte 8YSZ films on the anode-printed conducting substrates was achieved. It was found that the EPD processing parameters played an important role to the quality of the final films. The optimum condition found was found to be at 20V for 30 seconds, based on the 10 g/L slurry. The optimum power density of cell obtained at 800 °C was 70 mW/cm².

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Fig. 6. Electrical performance of the cells measured at 500-800 °C.

References