Short communication

Metal-supported solid oxide fuel cell operated at 400–600 °C

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Abstract

A metal-supported SOFC with a samarium doped ceria (SDC)/scandia-stabilized zirconia (ScSZ) bilayer electrolyte was fabricated by a combination of pulsed laser deposition (PLD) and wet ceramic processes. The cell performance and aging characteristics during operation were analyzed by both AC impedance spectroscopy and current-voltage measurements in the temperature range from 400 °C to 600 °C. The power generation characteristics of this metal-supported SOFC at low temperatures should allow for rapid start-up and help to reduce the performance deterioration seen in high temperature SOFCs due material oxidation and instability. In this paper, our early research results are presented.
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1. Introduction

Metal-supported SOFCs offer many advantages over conventional electrode- and electrolyte-supported SOFCs and have been recognized as a promising alternative to traditional structures. Due to good thermal conductivity and ductility of the metallic substrate, metal-supported SOFCs may both improve thermal shock resistance, and alleviate internal temperature gradients. Switching from ceramic to metal supports also allows the use of conventional metal joining and forming techniques and could significantly reduce the material and manufacturing costs of SOFC stacks.

Despite these potential merits, processing challenges have seriously impeded the developments of metal-supported SOFCs. For example, densification of the electrolyte layer requires high sintering temperatures (usually above 1200 °C). Sintering at such high temperatures, however, will lead to serious oxidation of the metallic substrate. Therefore, only a few advances on metal-supported SOFCs, such as vacuum plasma spray processing at the Aerospace Research Center and Space Agency (DLR) [1–3], atmospheric plasma spray processing at Jülich [4],

high temperature sintering in reducing atmospheres at Lawrence Berkeley National Laboratory (LBNL) [5,6], etc. have been achieved through these processes.

So far, most metal-supported cells have been operated at −800 °C or higher. This temperature range introduces serious oxidation of the metal substrate during long-term operation and requires a longer warm-up period. Ceres Power and Imperial College in the UK have achieved what is expected to be commercially viable performance of metal-supported SOFCs of 140 mW cm^{-2} at 570 °C [7,8]. As reported in these sources, the gadolinium oxide-doped ceria (GDC) electrolyte layer was fabricated using an electrophoretic deposition (EPD) process and sintered in air at temperatures as low as 1000 °C. Both cell and short stack durability have been demonstrated during 2500–3000 h of operation on reformed fuels and with over 500 rapid thermal cycles. These metal-supported cells, however, show much lower open circuit voltages since the thin GDC electrolyte layer exhibits high electronic leakage current due to the mixed electronic and ionic conductivity under normal SOFC operating conditions. An interlayer consisting of a pure ionic conductor with high conductivity is required to prevent the electronic current, in order to improve the cell efficiency. For this reason, SOFCs with a bi-layer electrolyte and anode-supported structure have widely been reported with Sr- and Mg-doped LaGaO$_3$ (LSGM)/La$_2$O$_3$ doped ceria (LDC) [9], LSGM/SDC

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[10], ScSZ/GDC [11] and yttria-stabilized zirconia (YSZ)/SDC [12]. In this study, a metal-supported SOFC with SDC/ScSZ bilayer electrolyte was fabricated and the cell performance was investigated at low operating temperatures (400–600 °C).

2. Experimental

Commercially available SS430 metallic substrates were adopted in this study and their porosity was measured by the Archimedes method. On the substrate, a NiO-SDC anode layer (70 μm thick, mixed with a sintering additive), and an anode functional layer (AFL, 20 μm thick) were consecutively deposited by spin coating. The thin ScSZ electrolyte layer (2 μm) and SDC electrolyte layer were fabricated by pulsed laser deposition (PLD), followed by sintering at 850 °C, which resulted in a dense SDC layer (20 μm). The deposition methods of the ScSZ and SDC layers by PLD in these experiments remain as reported in our previous work [13]. An $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSCo)-SDC (75:25) composite cathode was then fabricated on the surface of the SDC layer by screen-printing with a thickness of 25 μm. The metal-supported cell obtained from this process was mounted on an alumina tube using Ceramabond 552 (Aremco). Pt meshes were used as current collectors in both the anode and cathode chambers. The cell was heated to 800 °C at 3 °C min^{-1} to sinter the cathode for 30 min and then cooled down at 2 °C min^{-1} successively to 600 °C, 550 °C, 500 °C, 450 °C and 400 °C. At each temperature, AC impedance and current-voltage curve measurements were performed twice at 10-min intervals using moist hydrogen as the fuel and dry air as the oxidant. The cell impedance spectra were measured in the frequency range of 100 kHz–0.1 Hz under open circuit voltage (OCV) conditions using a Solartron 1260 frequency response analyzer (FRA) connected to a Solartron 1480 A potentiostat. Power generation characteristics were measured using a Solartron 1480 A potentiostat with a slew rate of 4 mV s^{-1} from the OCV to 0.3 V. In order to simplify the analysis, the polarization resistance was not separated into the charge transfer resistance and the surface diffusion resistance [14]. After testing, the cell was mounted in an epoxy, and then polished with different diamond slurries for scanning electron microscopy (SEM) analysis. The microstructure was observed using a scanning electron microscope (Hitachi S-3500N).

3. Results and discussion

Fig. 1 gives the microstructure of the polished cross-section of the metal-supported SOFC (×350 magnification). Porous SS430 stainless steel was chosen as the metallic substrate and its porosity was measured by the Archimede method, showing a value of 22 vol.% for the as-received samples. This is obviously lower than the expected porosity of approximately 40 vol.%, required by gas diffusion in the SOFC anode. Therefore, it is expected that the polarization loss may be reduced with further optimization. The low porosity of the metallic substrate, however, is beneficial for the consecutive deposition of the membrane-electrode assembly (MEA). Both the anode layer and the anode functional layer (AFL) show the desired porous microstruc-
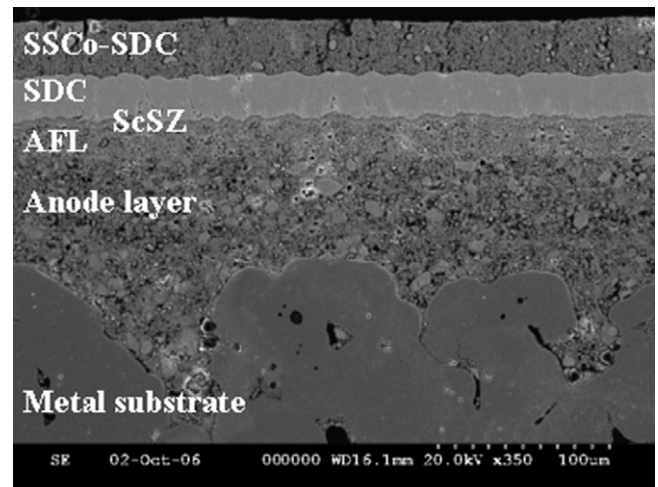

Fig. 1. Cross-sectional SEM image of the metal-supported SOFC after testing (×350).

ture. The anode layer has a larger pore size and rough internal microstructure, which is beneficial for the gas diffusion. The AFL shows a much finer microstructure, extending the electron-oxygen ion-gas boundary length (triple phase boundary length, TPBL). Higher magnification SEM image (Fig. 2, ×2000 magnification) of the polished cross-section indicates that the SDC layer fabricated by PLD, followed by low-temperature sintering is completely dense. No macro cracks or continuous pores can be found. Densification of electrolyte layer takes place at temperatures as low as 850 °C in an air atmosphere. This is an important technical breakthrough for the fabrication of metal-supported SOFCs since at this temperature, the oxidation of the metallic substrate can largely be avoided, although not completely. To our knowledge, this is the lowest sintering temperature reported for the densification of the electrolyte layer. Moreover, the low temperature densification restrains the particle growth in both the electrolyte and anode layers such that a finer inner structure and more active sites can be obtained after sintering. How-
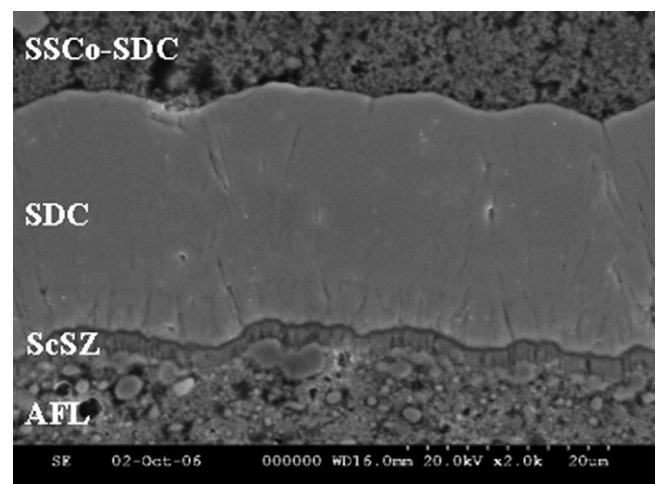

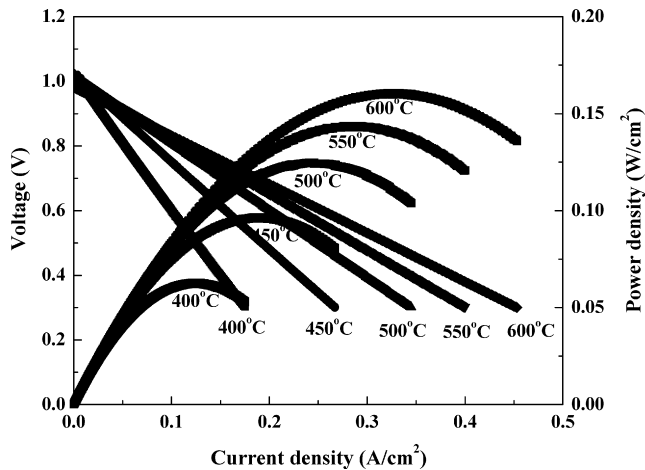Fig. 2. Cross-sectional SEM image of the metal-supported SOFC after testing (×2000).

Fig. 3. Cell performance at different temperatures from 400 to 600 °C.

Fig. 4. Resistance analysis of the cell under different temperatures.

ever, the ScSZ layer deposited by PLD, is not continuous, and therefore the SDC layer may not be completely protected from reduction.

Fig. 3 shows the power generation characteristics of the metal-supported SOFC operated between 400–600 °C. The open circuit voltage (OCV) varies between 1.00–1.03 V, much higher than that of a cell with thin SDC single layer electrolyte. ScSZ shows pure oxygen ionic conductivity and is almost completely insulating for electronic current, which prevent the electronic current leakage between the anode and cathode due to the partial reduction of Ce^{4+} to Ce^{3+}. The OCV value obtained, however, is still lower than the theoretical value of 1.20 V, likely due to both the thickness and non-uniform nature of the ScSZ layer formed by PLD. Therefore, we conclude that in these experiments, the ScSZ layer does not completely prevent the electronic current leakage.

The maximum power densities of the metal-supported cell fabricated in this work are 0.063 W cm^{-2}, 0.097 W cm^{-2}, 0.125 W cm^{-2}, 0.144 W cm^{-2}, and 0.161 W cm^{-2} at the operation temperatures of 400 °C, 450 °C, 500 °C, 550 °C and 600 °C, respectively. This cell performance is promising considering the temperature range and the early stage of development of this technology. We expect that the cell OCV and power generation characteristics can be further improved by a systematic optimization of materials, their microstructure and the fabrication processes.

Fig. 4 shows the variation of cell resistances at different temperatures. With decreasing operating temperatures, both the polarization resistance and ohmic resistance increase significantly. The polarization resistance increases approximately nine times from 0.15 Ohm cm^2 to 1.37 Ohm cm^2 during temperature decrease from 600 °C to 400 °C. This means that the SSCo cathode, usually adopted for operation above 600 °C, shows unsatisfactory electrochemical performance in this temperature range. More active electrodes, such as $Ba_{0.8}Sr_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$, may be a better alternative for SOFCs operating below 600 °C. At the same time, the microstructure of the metallic substrate, anode and cathode should be carefully optimized, focusing on low temperature operation.
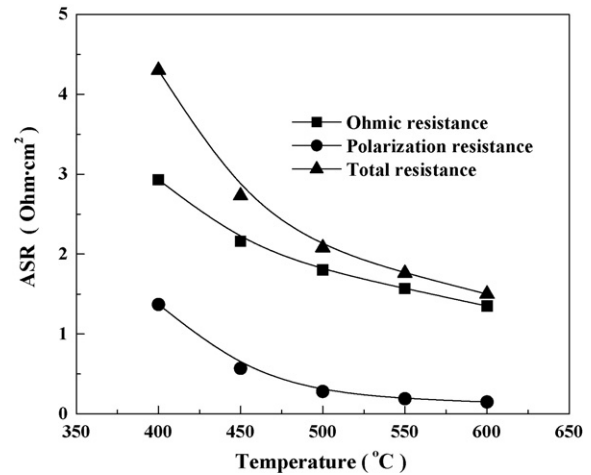
However, the polarization resistance was not the main contributor to the loss of cell voltage even at operating temperatures as low as 400 °C. The main loss of cell voltage was the ohmic resistance, which increases from 1.35 Ohm cm^2 at 600 °C to 2.93 Ohm cm^2 at 400 °C. This value is obviously higher than the calculated value (1.43 Ohm cm^2) determined from the thicknesses and theoretical conductivities of SDC (2.0×10^{-3} S cm^{-1}, 400 °C) and ScSZ (4.7×10^{-4} S cm^{-1}, 400 °C) layers. It was also observed that Pt mesh, which was used as current collector for these experiments, is too rigid for low temperature operation. Other current collecting layers with higher ductility would be beneficial for better interfacial contact, and therefore lower ohmic loss.

Fig. 5 shows the trend of the ohmic resistance and polarization resistance when the cell is operated at 500 °C. The polarization resistance increased over the 11-day test period, indicating a slow change in the electrodes microstructure. It is hypothesised that the sintering additive, which remained after firing the cell at 850 °C and is enriched at the metal/anode interface, may evaporate during the first 3 days of operation. This would explain why the ohmic resistance shows a significant decrease within
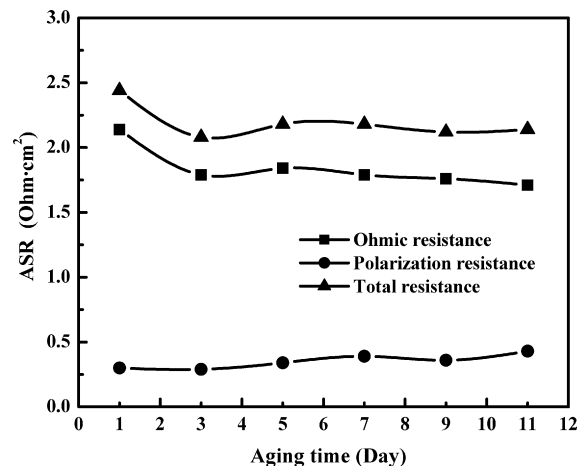

Fig. 5. Analysis of polarization resistances from different cell components as a function of time.
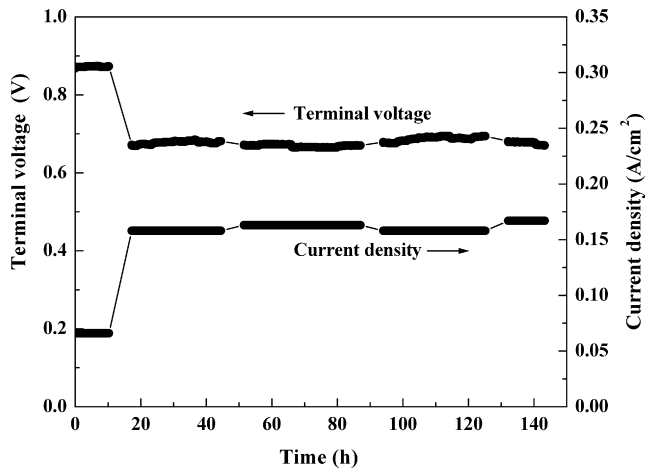
Fig. 6. Performance stability of the metal-supported SOFC under 500 °C operation.

the first 3 days. Another possibility is that plastic deformation (creep) of both the Pt mesh and SS430 substrate occurs at the operating temperature, resulting in better interfacial contact over time. It was observed that the cell interfaces become better at the beginning of the test. After this initial improvement, the cell performance is stable during the short aging period as indicated in Fig. 5. The corresponding OCV and maximum power density are also very stable in this period. Further study is required to determine the mechanisms involved in these processes.

Fig. 6 gives the performance stability of the metal-supported SOFC under a constant current at 500 °C. The operating current density was kept at 0.068 A cm^{-2} with a terminal voltage of 0.88 V for the first 10 h and then increased to 0.16 A cm^{-2} with a terminal voltage of 0.69 V for the rest of the test. Generally speaking, the cell performance was relatively stable over the test period. This is consistent with the measured change of area specific resistance (ASR), as shown in Fig. 5. Therefore, the low operating temperature of 500 °C may not bring about interfacial reactions, electrode aging or serious oxidation of the metallic substrate due to slow reaction kinetics.

4. Conclusions

A metal-supported solid oxide fuel cell (SOFC) with an SDC/ScSZ bi-layer electrolyte was fabricated using the combination of PLD and wet ceramic processes followed by low-temperature firing. The cell shows promising performance between 400 and 600 °C. However, the ohmic loss of the cell was still significant as was the polarization loss. The ohmic resistance and polarization resistance could be reduced significantly through optimization of both the microstructures and fabrication processes used in the metal-supported SOFCs. Further research will focus on the optimization of metal–substrate porosity, electrode microstructure, interfacial resistance, and electrolyte thickness.

Acknowledgement

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