



Short communication

Testing of a cathode fabricated by painting with a brush pen for anode-supported tubular solid oxide fuel cells

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ARTICLE INFO

Article history:

Received 29 June 2009

Accepted 30 June 2009

Available online 8 July 2009

Keywords:

Solid oxide fuel cell

Tubular

Anode-supported

Dip-coating

Composite cathode

Painting

ABSTRACT

We have studied the properties of a cathode fabricated by painting with a brush pen for use with anode-supported tubular solid oxide fuel cells (SOFCs). The porous cathode connects well with the electrolyte. A preliminary examination of a single tubular cell, consisting of a Ni-YSZ anode support tube, a Ni-ScSZ anode functional layer, a ScSZ electrolyte film, and a LSM-ScSZ cathode fabricated by painting with a brush pen, has been carried out, and an improved performance is obtained. The ohmic resistance of the cathode side clearly decreases, falling to a value only 37% of that of the comparable cathode made by dip-coating at 850 °C. The single cell with the painted cathode generates a maximum power density of 405 mW cm⁻² at 850 °C, when operating with humidified hydrogen.

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1. Introduction

The solid oxide fuel cell (SOFC) is a completely solid device that converts the chemical energy of fuels to electricity by electrochemical oxidation. It has emerged as one of the most important power generation devices because of its high energy conversion efficiency, low noise and low pollution [1–3], and its ability to be used with many different fuels [4]. There are two main designs of SOFC: planar and tubular. Tubular SOFCs have many advantages [5–8] such as the ease of sealing, and their ability to endure the thermal stress caused by rapid heating up to the operating temperature, as reported by Kendall and Palin [6] and Yashiro et al. [7] for micro-tubular SOFCs. Tubular SOFCs can therefore be expected to be used for co-generation and transportation applications. The ohmic resistance of the cathode/electrolyte interface dominates the total ohmic resistance of the anode-supported tubular SOFCs [9]. Accordingly, the cathode needs to be optimized first in order for the SOFC to have the potential for commercial application at intermediate temperatures.

Sr-doped lanthanum manganate La_{1-x}Sr_xMnO₃ (LSM) is the classic cathode material for high-temperature solid oxide fuel cells (SOFCs) because of its good properties, such as electrical conductivity, catalytic activity for oxygen reduction, thermal and chemical stability at high temperature, and compatibility with electrolytes such as yttria-stabilized zirconia (YSZ) and doped ceria (DCO) [10].

However, LSM exhibits negligible ionic conductivity and high activation energy for oxygen dissociation, so there is some limitation in the use of pure LSM in cathodes for SOFCs operating at intermediate temperatures (600–800 °C). The LSM-based composite cathode is one where an ionic conductor is added to the LSM, leading to a significant decrease in the polarization resistance. For instance, Murray and Barnett [11] reported that at 700 °C, the polarization resistance is 7.28 Ω cm² for a pure LSM cathode but 2.49 Ω cm² for a LSM-YSZ composite cathode.

Cathode fabrication is a major focus for improving performance and reducing cost. Many methods for fabricating cathodes for anode-supported tubular SOFCs have been reported in recent years including dip-coating [9,8,12–15], atmospheric plasma-spraying [16,17], and the doctor-blade method [18]. However, they have a number of shortcomings. For example, with the dip-coating method it is difficult to control the thickness or weight of the cathode and the atmospheric plasma-spraying method requires high investment in large equipment and has complicated fabrication processes.

In this study, we describe painting of the cathode by a brush pen, a new method for fabricating the cathode of anode-supported tubular SOFCs. It has many advantages over conventional processes such as dip-coating, plasma-spraying and the doctor-blade method. First of all, it needs no large equipment or significant control of ambience conditions so the fabrication cost is very low. Secondly, it is a simple fabrication process and easy to carry out. Thirdly, it is easy to control the thickness or weight of the cathode. Finally, it can be applied to both laboratory and industry scale by reason of the advantages listed above.

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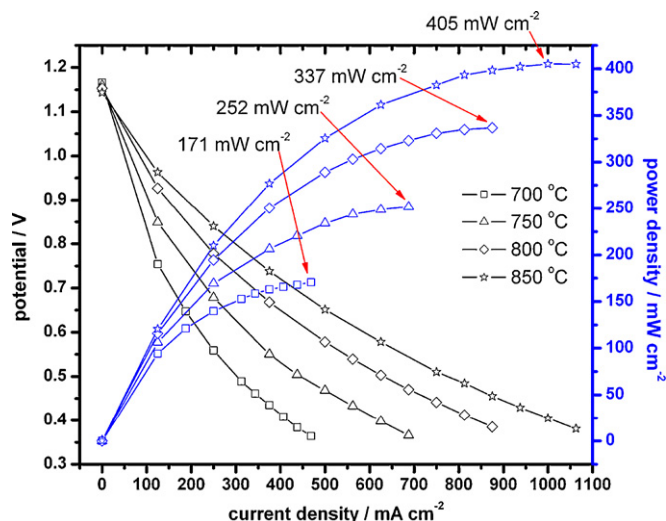


Fig. 1. The typical curves for potential and power density versus the current density for the tubular SOFC with a painted cathode at different temperatures while running on humidified hydrogen.

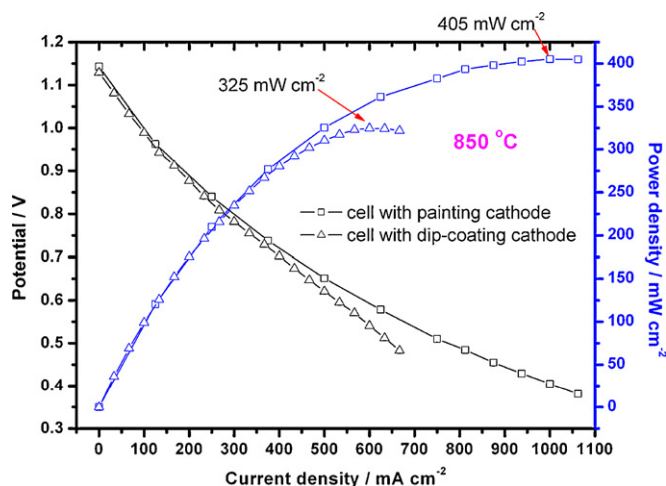


Fig. 2. The comparison of the I - V and I - P curves for tubular cells using cathodes prepared by the two methods at 850 °C while running on humidified hydrogen.

2. Experimental

2.1. Fabrication of tubular SOFCs

The anode-supported thin electrolyte tube, consisted of a NiO-YSZ anode support tube, a NiO-Zr_{0.89}Sc_{0.1}Ce_{0.01}O_{2-x} (ScSZ, scandia-stabilized zirconia, Daiichi Kigenso Kagaku Kogyo, Japan) (NiO-ScSZ) anode functional layer, and a ScSZ electrolyte film, was first obtained using dip-coating and co-sintering techniques [9]. The length of the tube was approx. 10.8 cm and the outside diameter of the tube was approx. 1.0 cm.

Next, the anode tube with electrolyte was painted with cathode ink by a brush pen. The cathode ink consisted

Table 1
Maximum power densities (MPD), ohmic resistances (R_{Ω}) and electrode polarization resistances (R_E) of cell and cathode of the anode-supported tubular SOFC at 850 °C using a painted cathode compared to those with a dip-coated cathode.

	MPD (mW cm ⁻²)	R_{Ω} of cell (Ω cm ²)	R_E of cell (Ω cm ²)	R_{Ω} of cathode (Ω cm ²)	R_E of cathode (Ω cm ²)
Dip-coated cathode	325	0.72	0.80	0.62	0.68
Painted cathode	405	0.32	1.86	0.23	1.46

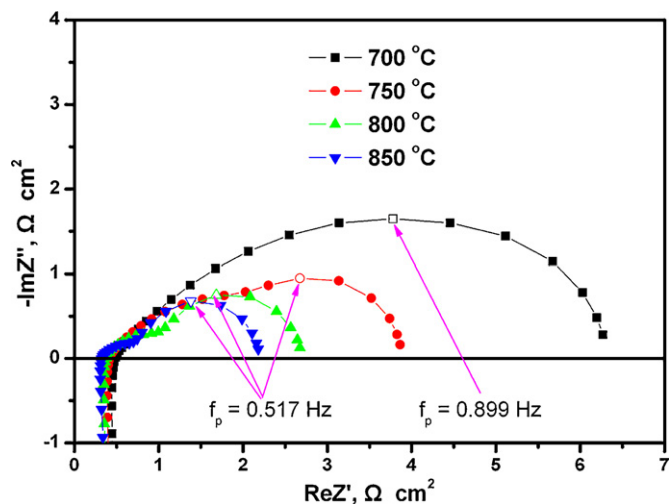


Fig. 3. AC impedance spectra for the cell with a painted cathode under open circuit at different temperatures using humidified H₂ as fuel and O₂ as oxidant.

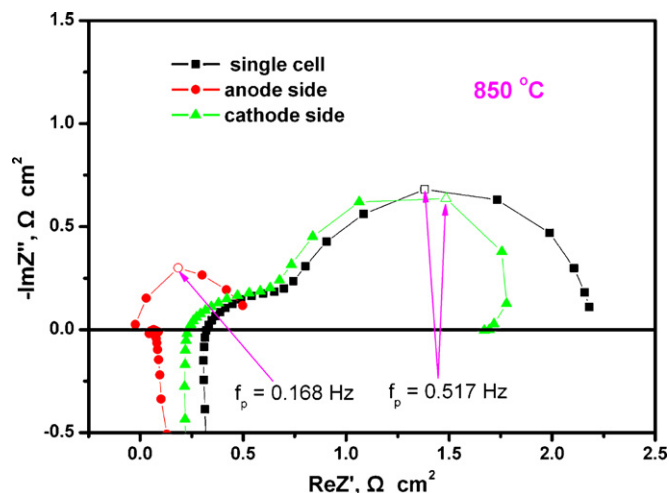


Fig. 4. AC impedance spectra for the single cell, the anode side and the cathode side under open circuit at 850 °C using humidified H₂ as fuel and O₂ as oxidant.

of (La_{0.8}Sr_{0.2})_{0.98}MnO₃ (LSM, lanthanum strontium manganite, Inframet Advanced Materials, CT, USA) and ScSZ powder, and terpineol, ethyl-cellulose and other organic ingredients. After painting the cathode ink, the tube was dried in air and sintered at 1200 °C for 2 h in air to complete a cell. The area of the cathode was approximately 10.0 cm².

2.2. Cell performance test

Tubular SOFC tests were carried out in a single-cell test setup, whose details are reported elsewhere [9]. Humidified hydrogen was used as fuel and oxygen was used as the oxidant. The fuel and oxidant flow rates were controlled at 180 mL min⁻¹ and 120 mL min⁻¹, respectively. The current-voltage (I - V) curves and electrochemical

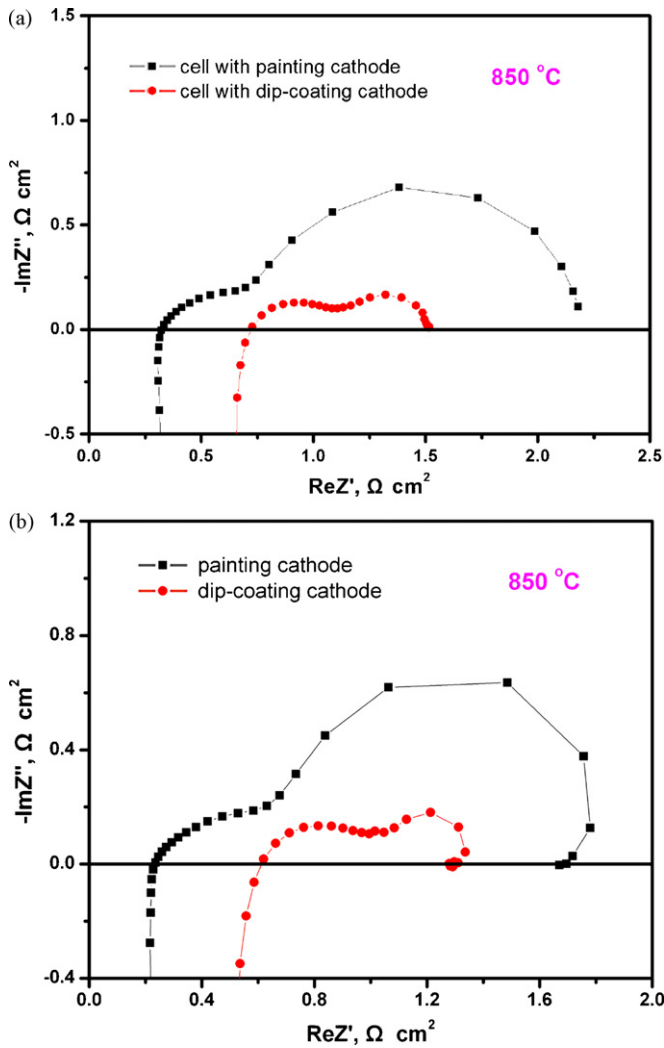


Fig. 5. The comparison of AC impedance spectra under open circuit at 850 °C for (a) the single cells, and (b) the cathode sides, with cathodes prepared by the two methods.

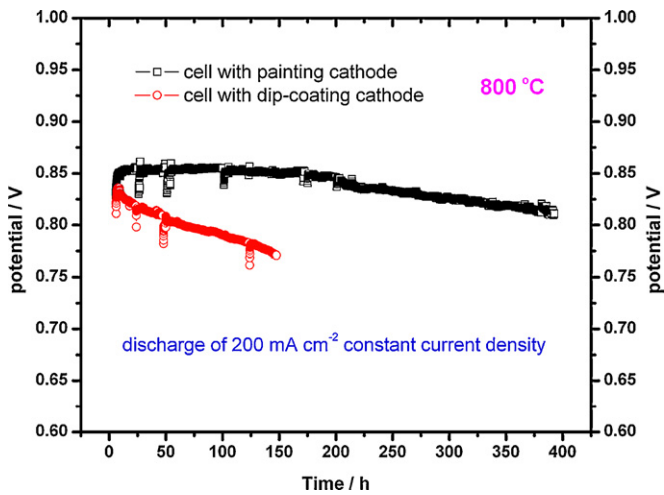


Fig. 6. The voltage change of the cell with a painted cathode during a long duration discharge at a current density of 200 mA cm⁻² at 800 °C compared to that of a cell with a dip-coated cathode.

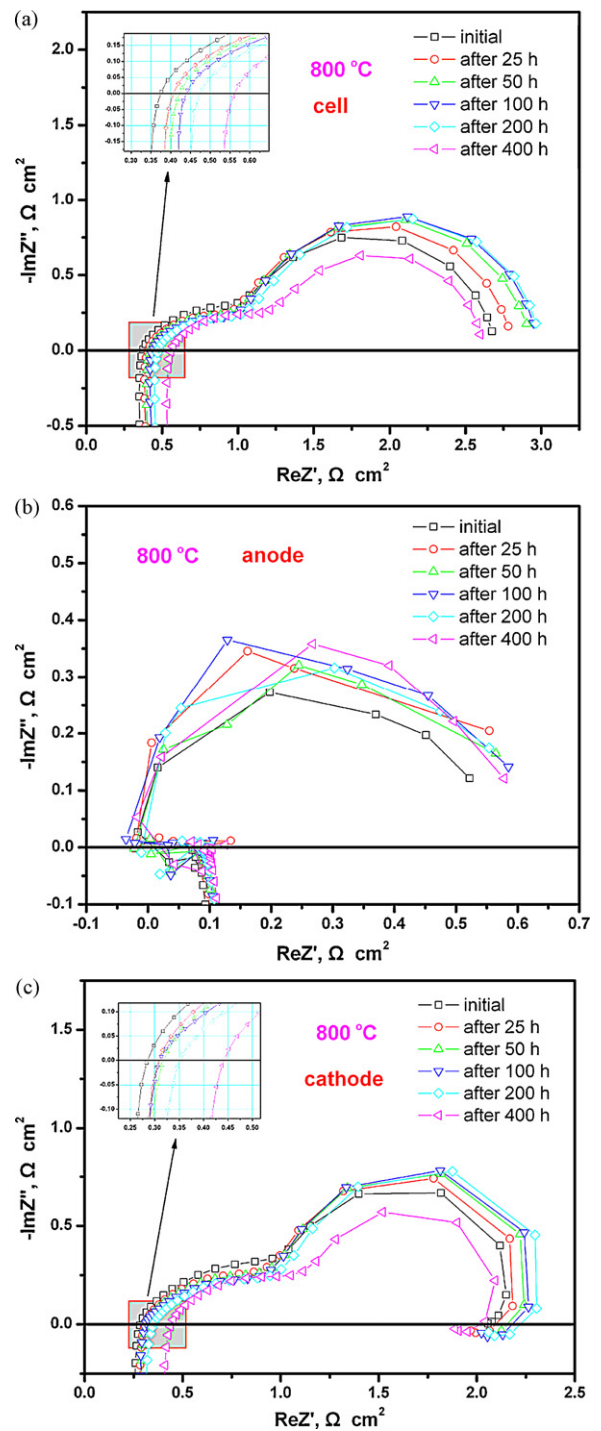


Fig. 7. AC impedance spectra for (a) the single cell, (b) the anode side and (c) the cathode side under open circuit at 800 °C after different discharge times.

impedance spectra (EIS) were obtained to evaluate the performance of the cell. The *I*–*V* curves were obtained by the volt–ampere method. The EIS were obtained using an Electrochemical Workstation IM6ex (Zahner, GmbH, Germany). The impedance spectra of the electrochemical cell were recorded under open circuit, with an amplitude of 20 mV, in the frequency range 0.03 Hz to 100 kHz. At the same time, the EIS of the anode to reference cathode and the cathode to reference cathode were measured under open circuit. The measurements were carried out at 700–850 °C, in steps

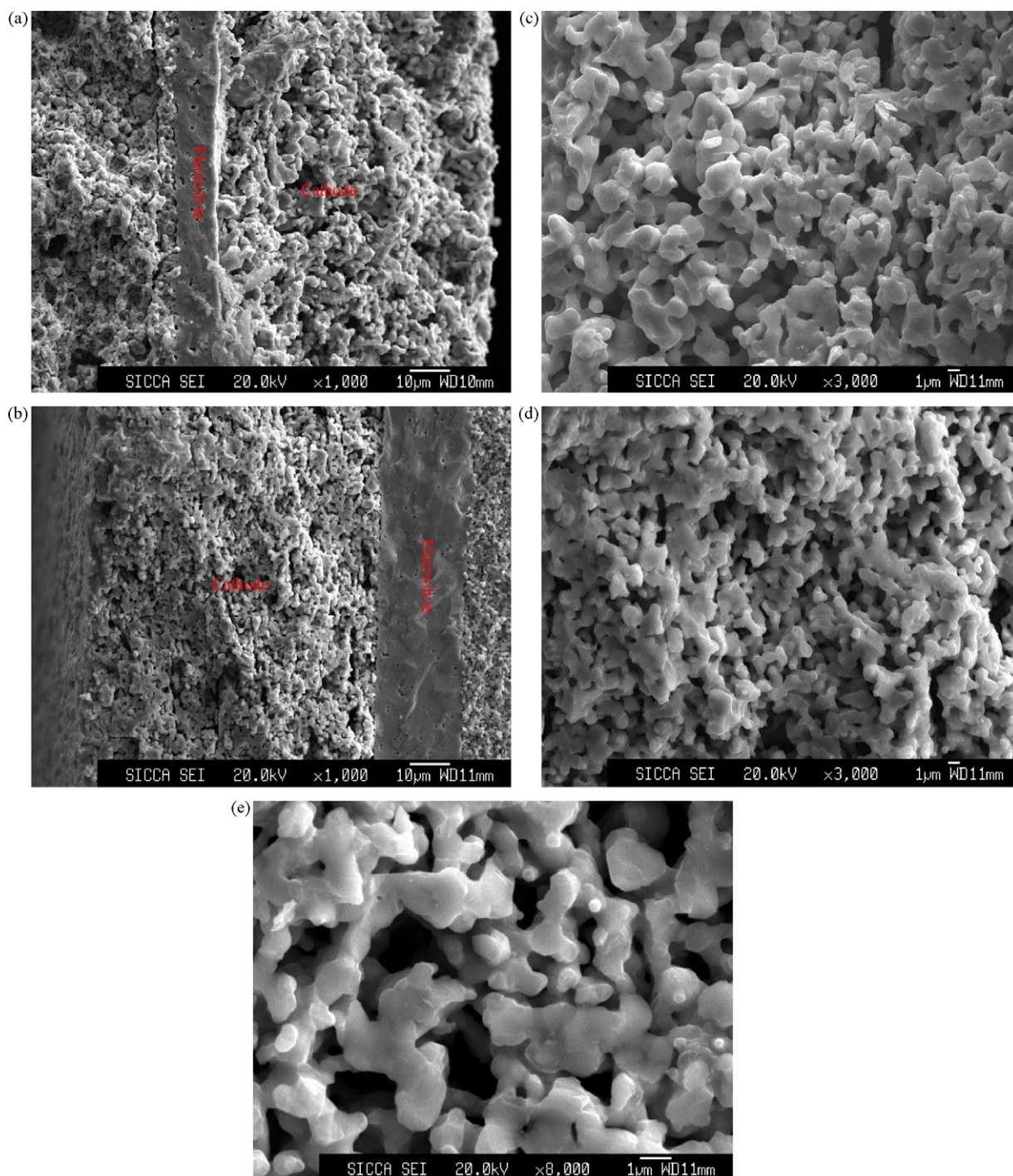


Fig. 8. SEM micrographs of (a) the dip-coated cathode after cell testing, (c) the painted cathode before cell testing, and (b, d, e) the painted cathode after cell testing.

of 50 °C. The ohmic resistances (R_{Ω}) were estimated from the high frequency intercepts with the real axis and the overall electrode polarization resistances (R_E) were directly measured from the differences between the low and high frequency intercepts with the real axis.

The long-time stability testing for the tubular SOFC was carried out at a current density of 200 mA cm⁻² at 800 °C. The electrochemical impedance spectra under open circuit of the cell, the anode side and the cathode side, were recorded after different times.

In order to study the microstructure of the cathode, scanning electron microscope (SEM) images of a cross section of the cathode

were observed with an electron probe microanalyzer (EPMA, JXA-8100, JEOL) before and after the cell operation.

3. Results and discussion

3.1. Electrochemical performance of anode-supported tubular SOFC

Fig. 1 shows typical curves for potential and power density versus the current density for the anode-supported tubular SOFC with a painted cathode at different temperatures while

running on humidified hydrogen. It can be seen that the anode-supported tubular cell with an effective area of approximately 10 cm^2 produced a good performance, with maximum power densities of 405, 337, 252 and 171 mW cm^{-2} at 850, 800, 750 and 700°C , respectively. This performance was clearly improved with respect to that of a previous cell using a dip-coated cathode [9]. A comparison of the I - V and I - P curves for tubular cells using cathodes prepared by the two methods, while running on humidified hydrogen at 850°C , is shown in Fig. 2. A comparison of other performance data for the two cells is given in Table 1.

The AC impedance spectra for the cell at different temperatures using humidified hydrogen and oxygen as the working gases under open circuit are shown in Fig. 3. The ohmic resistances and the polarization resistances increased as the temperature decreased. The ohmic resistances were 0.32, 0.38, 0.42, and $0.48\ \Omega\text{ cm}^2$ at 850, 800, 750 and 700°C , while the electrode polarization resistances were 1.86, 2.30, 3.44, and $5.79\ \Omega\text{ cm}^2$, respectively. Fig. 4 shows the AC impedance spectra for the single cell, the anode side and the cathode side under open circuit at 850°C . The ohmic resistances and polarization resistances of the single cell, the anode side and the cathode side were, respectively, 0.32 and $1.86\ \Omega\text{ cm}^2$, 0.08 and $0.42\ \Omega\text{ cm}^2$, and 0.23 and $1.46\ \Omega\text{ cm}^2$. The ohmic resistance of the cathode side had clearly decreased but the polarization resistance under open circuit had significantly increased compared with that of dip-coated cathode, as can be seen from Table 1 and Fig. 5. This indicates that the maximum power density greatly depends on the ohmic resistance of the cell. The relatively large polarization resistance may decrease sharply during discharge, owing to the current effect of the LSM-based cathode [9]. From Fig. 5 it also can be seen that the high frequency arcs of the two cells with different cathodes were almost the same, but their low-frequency arcs, which correspond to mass transport processes, were very different. The different micro-structure of the cathodes, which can be seen from Fig. 8, may be the reason.

3.2. Long term stability testing of the tubular SOFC

Fig. 6 shows the voltage change of the cell with a painted cathode during a long duration discharge at a current density of 200 mA cm^{-2} at 800°C compared to that of a cell with a dip-coated cathode. It can be seen that the voltage of the cell with the painted cathode was much more stable than that of a cell with a dip-coated cathode. It increased slightly in the first 50 h, and then remained almost constant over the following 150 h. However, the voltage decreased slowly after 200 h. The reason can be seen by inspection of Fig. 7.

Fig. 7 shows the AC impedance spectra for (a) the single cell, (b) the anode side, and (c) the cathode side under open circuit at 800°C after different discharge times. In Fig. 7, we can see that the ohmic resistance of the cell increased continuously over the test period, and its polarization resistance, especially the low-frequency arc corresponding to the mass transport process, increased slowly to 100 h, and then tended to remain constant, decreasing slightly after 200 h. The change of ohmic resistance and polarization resistance of the cathode in the test time were similar to those of the complete cell. However, the resistance at the anode side did not change. This indicates that the degradation of cell was mainly due to the aging of cathode. This was probably due to the unsealed setup used for testing, which leads to burning of the unused H_2 and O_2 at the mouth of the tubular cell. The unburned H_2 and the by-product H_2O , may diffuse to the cathode and destroy its structure.

3.3. Microstructural characteristics of the cathode

Fig. 8 shows SEM micrographs of (a) the dip-coated cathode after cell testing, (c) the painted cathode before cell testing and (b, d, e) the painted cathode after testing. From Fig. 8(a) and (b), we found that both cathodes had a porous structure, and their thicknesses were both approximately $70\ \mu\text{m}$. However, the painted cathode combined better with the electrolyte and had more uniform grains than the dip-coated cathode. On the other hand, the dip-coated cathode had a higher porosity, which was advantageous for the transportation of oxygen, so resulted in a smaller low-frequency arc in the AC impedance spectra. The different micro-structures of the two cathodes were probably caused by the different solvents. The ink for the painted cathode with terpineol solvent was more viscous than the slurry used for dip-coating with ethanol solvent, so the cathode ink was more uniform and made the cathode combine better with the electrolyte, which resulted in a smaller ohmic resistance at the interface between the cathode and electrolyte. From Fig. 8(c) and (d), it can be seen that the grains in the painted cathode were distributed over two dimension scales. The larger grains, with an average size of approximately $2\text{--}3\ \mu\text{m}$, were ScSZ grains, which can conduct oxygen ions. The smaller grains, with average size approximately $0.5\text{--}1\ \mu\text{m}$ were LSM grains, which were electronic conductors. The micro-pores, ScSZ grains and the LSM grains constitute a three-phase boundary, in which the oxygen was dissociated.

4. Conclusions

A cathode for an anode-supported tubular SOFC has been successfully fabricated by a method consisting of painting with a brush pen. The cell was tested at intermediate temperatures (below 850°C). The single tubular cell, with cathode area approximately 10.0 cm^2 , generated 405, 337, 252 and 171 mW cm^{-2} at 850, 800, 750, and 700°C , respectively, with humidified hydrogen and oxygen as the working gases. The AC impedance spectra for the cell indicated that the ohmic resistance of the cathode side had clearly decreased compared to that of the dip-coated cathode. Further work is currently being undertaken in order to achieve a better performance of the anode-supported tubular SOFC.

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