Performance and long term durability of metal-supported solid oxide fuel cells

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A long term durability test is conducted on a large area 10 × 10 cm² metal-supported cell. The cell that consists of a porous nickel substrate as a support, an Lₐ₉₂ₓSnₓ₂₋ₓCrₓ₋ₓGaₓ₋ₓMₗₓ₋ₓO₃₋₉₋δ (SDC) cathode is prepared by using an atmospheric plasma spraying technology. The measured maximum output powers are 40.4, 31.2 and 22.7 W at 750, 700 and 650°C respectively. In the long term durability test, the cell voltages are measured in a constant current mode (400 mA cm⁻²) for 3000 h at 700°C. The measured I–V curves and AC impedance data are used to trace the variations of ohmic and non-ohmic resistances at different times. It is found that the dominant factors in the degradation of the tested cell are the increases of activation polarization and ohmic resistances. The tested cell is recovered and demonstrate that the heat treated process at the condition of 820°C and OCV for 4 h is effective to recover the performance of the prepared cell. Based on the measured experimental data and the post microstructure analysis, the degradation of the tested cell is mainly due to the microstructural change in the anode and micro-cracks formed at layer interfaces that have significant thermal expansion mismatches, they cause the increases of activation polarization and ohmic resistances. After the recovery process, it is found the ohmic resistance decreases.

Key-words : Metal-supported solid oxide fuel cells, Atmospheric plasma spraying, Durability, Recoverable performance

1. Introduction

Solid oxide fuel cells (SOFCs) are very promising electrochemical energy conversion devices because they have high efficiencies and emit low amounts of pollutants. However, there are still several challenges facing the commercialization of SOFC technology. Reducing operation temperature of solid oxide fuel cell would promote the commercialization of a power-generation module in terms of the manufacturing cost, lifetime, reliability, etc. Toward lowering operation temperatures, there is a tendency to shift ceramic-supported fuel cells to metal-supported fuel cells due to the potential benefits of low cost, high strength, better workability, good thermal conductivity and quicker start-up. SOFCs are typically manufactured by using wet ceramic techniques such as tape casting combined with multi-steps of high temperature (up to 1400°C) sintering to obtain dense electrolyte layers. It is difficulty to incorporate metallic substrates into the wet ceramic manufacturing processes without oxidizing the metallic substrates or significantly changing metallic substrate properties. Atmospheric plasma spraying (APS) is a fast sintering process, it allows reducing the interaction between layers of SOFC cells that can be induced during conventional high temperature sintering processes, for instance, the interaction between LSGM electrolyte layer and Ni in the anode layer. In addition to high material deposition rates, APS processes can easily control the component composition and microstructure through variation of spray parameters, hence, the atmospheric plasma spraying process has thus appeared as a promising candidate for inexpensive and fast cell production, and attracted much attention.

Long term durability is one of the most important requirements for SOFC commercialization. The recent research in solid oxide fuel cells has been devoted on the studies of cell degradation mechanisms. In the case of Ni–YSZ anodes, typical degradation phenomena are Ni agglomeration, changes in nickel surface morphology, disconnection of Ni particles, losses of anode porosity and Ni re-oxidation. These microstructural changes in anode are highly dependent on operating conditions, such as operating temperature and water vapor content in the fuel. Consequently, anode microstructure changes decrease the number of triple phase boundaries (TPBs) resulting in an increase in activation polarization. On the other hand, degradation mechanisms of the cathode are oriented to coarsening of the microstructure, decomposition, Cr poisoning and formation of an insulating phase at interfaces between electrolyte and cathode.

In the present work, in order to understand the major mechanisms affecting the durability of a large area (10 × 10 cm²) planar type metal-supported SOFC prepared by APS technology, the following long term durability test and corresponding post microstructure analysis were conducted.

2. Experimental

2.1 Apparatus

The robotic APS system primarily consists of a DC plasma spray gun (Model Triplex200, Sulzer Metco) that generates a high temperature plasma flame under atmospheric condition, a robot (FANUC Robot ARC Mate 120iB) that holding plasma
spray gun to scan substrate, a powder feeder for delivering plasma spray-able powders, a cooling system for the torch, a heater for preheating the substrate, an IR detector for measuring the temperature of the substrate and a fast CCD camera to observe trajectories of particles in the plasma flame. Figure 1 schematically depicts the experimental set-up.

2.2 Cell preparation

Figure 2 shows the commercially available agglomerated powders of LSCM, LDC-NiO, LDC, LSGM, SDC and SSC-C (SSC with ~15 wt% carbon pore former) that were deposited on the porous Ni-Fe substrate by atmospheric plasma spraying process. A porous nickel-iron substrate was fabricated by sintering and impregnating processes. A slurry was firstly prepared by mixing nickel powders with particle sizes in 90–250 μm and PVA binder. Then the slurry was poured into a mold, pressed and dried to form a green sheet. This green sheet was sintered at a temperature 1350°C for 6 h in a reducing atmosphere to form a porous nickel substrate. The finished porous nickel substrate was impregnated with the solution containing Fe₃O₄ powders with particle sizes less than 5 μm by a vacuum means. The impregnated porous nickel substrate was sintered again at a temperature 1350°C for 6 h in a reducing atmosphere. The impregnation and sintering processes were repeated until the content of Fe in the porous nickel substrate reached about 10 wt %. This home-made porous Ni-Fe substrate with ~1.2 mm in thickness was chosen as
a support. The porosity about 30% of the substrate was measured by the Archimedes method. After finishing all functional layers including anode, electrolyte and cathode layers that were coated in sequence to construct metal-supported solid oxide fuel cells, the prepared cell was heated and pressed in air for 4 h at 850°C and 500 g cm^{-2} pressure.

2.3 Cell characterization
The completed metal-supported cell was incorporated into the Corfer22 frame by laser welding the nickel-iron substrates to the Corfer22 frame and then placed in a cell performance measurement system with Solartron 1255 and Solartron 1287 for AC impedance measurement and with Prodigit 3311D DC electronic loads for power measurement. A non-sealed cell test housing is applied for measuring cell performance. Figures (a) and (b) shows the scheme of non-sealed cell test housing for measuring cell performance and the photo of prepared cell. The inert Al_{2}O_{3} ceramic material is used for housing the tested cell. Platinum grids and leads at the anode and cathode side of the cell are used to measure cell current and voltage. Thermocouples close to the anode and cathode of cell are applied to measure temperatures on both anode and cathode sides. The cell test housing located in an electric furnace is heated up to 800°C. The inert Al_{2}O_{3} ceramic tubes are used to deliver hydrogen fuel with 800 ml min^{-1} and air oxidizer with 2000 ml min^{-1} to the tested cell. The micro-structures were analyzed via SEM (Hitachi S4800) microscopes.

3. Results and discussion
3.1 Power generation of 10 × 10 cm^{2} cell
The current–voltage (I–V) and current–power (I–P) curve of the single cell at 750, 700 and 650°C are shown in Fig. 4. The 10 × 10 cm^{2} cell with effective electrode area of 72 cm^{2} shows the open circuit voltages (OCVs) are 0.99, 1.01 and 1.02 V and the remarkable electric output power of 40.4, 31.2 and 22.7 W at 750, 700 and 650°C, respectively. The output power of 40.4 W is obtained at a cell potential of 0.6 V at 750°C when the H_{2} flow rate is 9.8 mL min^{-1} cm^{-2} and the air flow rate is 24.7 mL min^{-1} cm^{-2}. Its fuel utilization efficiency at 67.44 A is 64.15%, and the conversion efficiency (LHV) is 30.5%. From these results, the 10 × 10 cm^{2} cell has shown a promising performance. Figure 5 shows the Nyquist plots of AC impedance results for the prepared cell measured from 750 to 650°C. The AC impedance curves are...
measured under the open-circuit condition by using the two-electrode configuration. The intercept with the real-axis at the high frequency represents the ohmic resistance ($R_s$) that contains resistances from the electrolyte and electrical connection wires. In this paper, the wire lead resistance is assumed to be negligible and the electrolyte ohmic resistance is dominant in $R_s$. The intercept with the real-axis at the low frequency represents the total cell resistance ($R_t$). The difference between $R_t$ and $R_s$ is the electrode polarization resistance ($R_p$) which includes charge transfer reaction and transport resistances from both anode and cathode of the tested cell. Table 1 shows the values of the ohmic resistance $R_s$, the polarization resistance $R_p$ and the total cell resistance $R_t$ ($R_t = R_s + R_p$) obtained from the measured impedance curves of the tested cell under the open-circuit condition.

### 3.2 Long-term durability test

Figure 6 shows a plot of the cell voltage at 400 mA cm$^{-2}$ as a function of time in two regions. In first 2000h long term durability test region, the cell voltage drops slowly as a function of time for every 500h durability test. After each of 500h durability tests, the heat treatment around 820°C and at OCV condition was executed on the tested cell for 4h. In the first 500h durability test, the measured voltage starts from 801 mV and ends at 789 mV. The estimated degradation rate is approximately 3% kh$^{-1}$. In the second 500h durability test that was done after the first heat treatment, the measured voltage starts from 820 mV, this implies that the tested cell is recovered at that moment. The final cell voltage of the second 500h durability test ends at 802 mV, the corresponding degradation rate of this test is 4.4% kh$^{-1}$. In the third 500h durability test that was done after the second heat treatment tests, the measured voltage starts from 817 mV, this indicates the tested cell is recovered again. The final cell voltage of the third 500h durability test ends at 802 mV, the corresponding degradation rate of the third durability test is 3.6% kh$^{-1}$. In the fourth 500h durability test that was done after the thermal cycle and third heat treatment tests, the measured voltage starts from 809 mV, this indicates the tested cell is recovered again. The final cell voltage of the fourth 500h durability test ends at 788 mV, the corresponding degradation rate of the fourth durability test is 5.2% kh$^{-1}$. After the fourth heat treatment, the voltage of the tested cell returns to 808 mV at 400 mA cm$^{-2}$ constant current density and 700°C, this show that the tested cell has greater voltage and power than those at the

### Table 1. Ohmic resistance $R_s$, total cell resistance $R_t$ and polarization resistance $R_p$ measured at different temperatures by AC impedance method

| Temperature (°C) | $R_s$ (Ω cm$^2$) | $R_t$ (Ω cm$^2$) | $R_p$ (Ω cm$^2$) |
|------------------|------------------|------------------|------------------|
| 750              | 0.137            | 0.4528           | 0.3158           |
| 700              | 0.202            | 0.5925           | 0.3905           |
| 650              | 0.319            | 0.8610           | 0.542            |

Fig. 4. I-V and I-P curves of the tested cell at 650, 700 and 750°C.

Fig. 5. Nyquist plots of AC impedance results for the tested cell measured from 650 to 750°C.

Fig. 6. Measured voltages during the durability test, thermal cycle and heat treatment for 10 x 10 cm$^2$ cell at 700°C.
beginning of the 2000 h durability test. Hence, the results in Fig. 6 show the degradation rate of tested metal-supported cell in the first 2000 h long term durability test region is about 0% kh⁻¹ and the cell performance can be recovered by the heat treatment around 820°C and at OCV condition.

After the second thermal cycle that was executed next to the first long term durability test, the OCV of tested cell drops to 1000 mV that is smaller than the OCV of 1030 mV before the second thermal cycle, it is explained that some cracks in the LSGM electrolyte are generated after the second thermal cycle and leads to some gas leakages. The second long term durability test of 1000 h was executed after the second thermal cycle. In the fifth 500 h durability test, the measured voltage starts from 785 mV and ends at 769 mV. The estimated degradation rate is approximately 4% kh⁻¹. In the sixth 500 h durability test that was done after the fifth heat treatment, the measured voltage starts from 786 mV, this implies that the tested cell is recovered again. The final cell voltage of the sixth 500 h durability test ends at 760 mV, the corresponding degradation rate of this test is 6.6% kh⁻¹. After the sixth heat treatment, the voltage of the tested cell returns to 780 mV at 400 mA cm⁻² constant current density and 700°C. Hence, the results given in Fig. 6 show the degradation rate of tested metal-supported cell in the second long term durability test is about 0.8% kh⁻¹.

Figures 7(a) and 7(b) give the Nyquist plots and Bode plots (frequency vs. imaginary part) obtained before the first 500 h durability, after the first 500 h durability test and after the first heat treatment. Figure 7(a) shows that the ohmic resistance of the tested cell increases after the first 500 h durability test, but after the first heat treatment this ohmic resistance becomes smaller than its initial value obtained before the first 500 h durability test. There are three interesting frequency ranges in these figures, namely, 0.01–10, 10–1000 and >1000 Hz. According to the literatures,¹⁵ the frequency range of 0.01–10 Hz corresponds to the energy loss from oxygen gas diffusion and adoption in the cathode electrode, the frequency range of 10–1000 Hz corresponds to the energy loss of electrode activation charge transfer, including charge transfers in the anode and cathode, and the frequency range larger than 1000 Hz dominates mainly in the energy loss from ohmic resistance of the tested cell. Comparing the results obtained before the durability test and after the first 500 h durability test, as shown in Fig. 7(b), the measured impedance imaginary values are different in these three frequency ranges, this implies that after the first 500 h durability test there are some changes in the cathode and anode microstructures, these changes could include some cracks or Ni disconnections or Ni passivation produced in the anode. Comparing the results obtained after the first 500 h durability test and after the first heat treatment, as shown in Fig. 7(b), the first heat treatment produces a negligible change of impedance imaginary values in the frequency range of 0.01–10 Hz, a minor change of impedance imaginary values in the frequency range of 10–1000 Hz and a change of impedance imaginary values in the frequency range larger than 1000 Hz, this implies that the first heat treatment generates a negligible change in the cathode microstructure and some changes in the anode microstructure. According the results shown in Fig. 7(a), these changes in the anode microstructure could include recovering some of formed cracks, or Ni disconnections, or Ni passivation in the anode of tested cell.

Figures 8(a) and 8(b) show I–V curves obtained before the first 500 h durability test, after the first 500 h durability test and after the first heat treatment. The current is divided into the low current (0–20 A) and the high current (20–50 A) regions. The results, as shown in Fig. 8(a), shows that the OCV value after the first heat treatment is larger than the OCV value after the first 500 h durability test and the OCV value after the first 500 h durability test is larger than the OCV value before the first 500 h durability test, this implies that the gas tightness of electrolyte layer is getting better during these tests. In the low current region, the slope of I–V curve relates to the activation loss of tested cell, and the results in Fig. 8(a) also show that the slope of I–V curve obtained after the first 500 h durability test is larger than the corresponding slope before the first 500 h durability test, this indicates that the activation losses in the cathode and anode increase due to the changes of cathode and anode microstructures. After the first heat treatment, the slope of I–V curve in the low current region returns about to the value obtained before the first 500 h durability test, this indicates that the heat treatment is effective to recover the activation performances of cathode and anode. In the high current region, the slope of I–V curve relates to the ohmic loss of tested cell, and the results in Fig. 8(b) show that the slope of I–V curve increases after the first 500 h durability test.
test, but after the first heat treatment this slope is smaller than the corresponding slope before the first 500 h durability test. Figure 8(b) indicates that the ohmic resistance loss is completely recovered and is smaller than the corresponding loss before the first 500 h durability test. The same process as the first heat treatment was executed at the second, the third and the fourth heat treatments. By these heat treatments, no degradation is observed for the first 2000 h long term durability test.

Figures 9(a) and 9(b) give the Nyquist plots and Bode plots obtained after the second thermal cycle, after the fifth 500 h durability test and after the fifth heat treatment. Figure 9(a) shows that the ohmic resistance of the tested cell increases after the fifth 500 h durability test, but after the fifth heat treatment this ohmic resistance becomes smaller than its initial value obtained after the second thermal cycle. Comparing the results obtained after the second thermal cycle and after the fifth 500 h durability test, as shown in Fig. 9(b), the measured impedance imaginary values are different in 10–1000 and >1000 Hz frequency ranges, this implies that after the fifth 500 h durability test there are some changes in the cathode and anode microstructures, these changes could include some cracks in the cathode and some cracks or Ni disconnections or Ni passivation produced in the anode. Comparing the results obtained after the fifth 500 h durability test and after the fifth heat treatment, as shown in Fig. 9(b), the fifth heat treatment produces a negligible change of impedance imaginary values in the frequency range of 0.01–10 Hz, a minor change of impedance imaginary values in the frequency range of 10–1000 Hz and a change of impedance imaginary values in the frequency range larger than 1000 Hz, this implies that the fifth heat treatment generates a negligible change in the cathode microstructure and some changes in the anode microstructure. According the results shown in Fig. 9(a), these changes in the anode microstructure could include recovering some of formed cracks, or Ni disconnections, or Ni passivation in the anode of tested cell.

Figures 10(a) and 10(b) show I–V curves obtained after the second thermal cycle, after the fifth 500 h durability test and after the fifth heat treatment. The current is also divided into the low current (0–20 A) and the high current (20–60 A) regions. The results, as shown in Fig. 10(a), shows that the OCV value after the fifth 500 h durability test is lower than the OCV value after the second thermal cycle and the OCV value after the fifth heat treatment is larger than the OCV values after the second thermal cycles and the fifth 500 h durability test. This implies that the gas tightness of electrolyte layer is getting worse during the durability tests and the fifth heat treatment improves the gas tightness of electrolyte layer. In the low current region as shown in Fig. 10(a), the slope of I–V curve obtained after the fifth 500 h durability test is larger than the corresponding slope after the second thermal cycle, this indicates that the activation losses in the cathode and anode increase due to the changes of cathode and anode microstructures. After the fifth heat treatment, the slope of I–V curve in the low current region is similar to the value obtained after the fifth 500 h durability test, this indicates that the heat treatment is not effective to recover the activation performances of cathode and anode. In the high current region as shown in Fig. 10(b), the
slope of I–V curve after the fifth 500 h durability test is larger than the corresponding slope after the second thermal cycle and the slope of I–V curve after the fifth heat treatment is smaller than that after the fifth 500 h durability test but is still larger than that after the second thermal cycle, these results indicate that the ohmic loss of tested cell increases after the fifth 500 h durability test and after the fifth heat treatment the ohmic loss reduces but is larger than the ohmic loss after the second thermal cycle. The same process as the first heat treatment was also executed at the fifth and the sixth heat treatments. By these heat treatments, a degradation rate about 0.8%kh⁻¹ is observed for the second 1000 h long term durability test after the second thermal cycle.

Thus, the cell performances after heat treatments in the present study are always better than the cell performances before heat treatments. These recovery phenomena are mainly due to the decreases in the ohmic resistance, this could be explained by reconnections between Ni and Ni nano particles of anode, or between nano Ni and LSCM particles, or between Ni–Fe substrate and LSCM, or a combination of them. It is noted that the obtained I–V curves and AC impedance data are consistent with each other.

3.3 Post microstructure analysis

After the tested cell had been operated for 3000 h, a post microstructure analysis was conducted to determine which components were responsible for the degradation in cell performance. Figures 11(a) and 11(b) give SEM micrographs of the anode functional layer (Ni-LDC) observed before and after 3000 h long term durability test in the same magnification, these SEM micrographs indicate that the microstructure of anode seems to have slightly changed due to the increase of porosity, the loss of some Ni percolation and particle growths after the long term durability test. Figure 12 gives the cross sectional SEM micrograph of the tested cell after 3000 h long term durability test. The obvious micro-cracks, as shown in Fig. 12, are located at the interface between the Ni–Fe substrate and the LSCM interlayer, in the Ni-LDC anode functional layer and at the interface between SSC-SDC cathode layer and the SDC barrier layer. The possible reason is attributed to the differences in thermal expansion coefficients of different components of the tested cell. As the micro-cracks develop, the electrochemical reaction sites decrease, the current paths through the cell become longer, leading to both larger activation polarization resistance and larger ohmic resistance.

Based on the obtained results of I–V curves, AC impedance data and post microstructures of the tested cell, the microstructural changes of anode and the micro-cracks at the interfaces
that have significant thermal expansion mismatches are believed to be the major sources to the cell degradation. These sources cause the increases in activation polarization resistance and ohmic resistance of the tested cell.

4. Conclusions

The electrochemical performance and long-term durability measurements are conducted on a 10 × 10 cm² planar-type metal-supported cell prepared by atmospheric plasma spraying. The cell has been tested for ~3,000 h under the conditions of 400 mA cm⁻² and operating temperature 700°C to explore its durability. The tested cell shows after the heat treatment around 820°C at OCV condition for 4 h, the voltages measured at 400 mA cm⁻² constant current density load and 700°C are back to the values that are larger than or equal to the initial cell voltage of 801 mV. These observed phenomena indicate that the performance of the tested cell is recovered by the heat treatment. It is found the decrease of ohmic resistance is the main reason for the cell performance recovery. This heat treatment process can reduce the rate of cell degradation so as to enhance the lifetime of the tested cell. The results of I–V curves, AC impedance data and post microstructures of the tested cell reveal that the dominant factors responsible for the cell degradation are the increases in activation polarization and ohmic resistances. The increases of these resistances originate mainly from the microstructural changes in the anode and micro-cracks at layer interfaces that have significant thermal expansion mismatches.

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References
1) Z. Wang, J. O. Berghaus, S. Yick, C. Decès-Petit, W. Qu, R. Hui, R. Marie and D. Ghosh, J. Power Sources, 176, 90–95 (2008).
2) M. C. Tucker, G. Y. Lau, C. P. Jacobson, L. C. DeJonghe and S. J. Visco, J. Power Sources, 175, 447–451 (2008).
3) M. C. Tucker, J. Power Sources, 195, 4570–4582 (2010).
4) R. Hui, Z. Wang, O. Kesler, L. Rose, J. Jankovic, S. Yick, R. Marie and D. Ghosh, J. Power Sources, 170, 308–323 (2007).
5) X. Zhang, S. Ohara, H. Okawa, R. Marie and T. Fukui, Solid State Ionics, 138, 145–152 (2001).
6) R. Henne, J. Therm. Spray Tech., 16, 381–403 (2007).
7) O. Kesler, Mater. Sci. Forum, 539–543, 1385–1390 (2007).
8) S. P. Simmer, M. D. Anderson, M. H. Engelhard and J. W. Stevenson, Electrochem. Solid-State Lett., 9, A478–A481 (2006).
9) A. Mai, M. Becker, W. Assenmacher, F. Tietz, D. Hathiramani, E. Ivers-Tiffee, D. Stover and W. Mader, Solid State Ionics, 177, 1965–1968 (2006).
10) F. Tietz, A. Mai and D. Stover, Solid State Ionics, 179, 1509–1515 (2008).
11) B. Iwanschitz, J. Sfeir, A. Mai and T. Hocker, International Workshop on Degradation Issues in Fuel Cells, Greece, September 19–21 (2007).
12) G. Robert, A. Kaiser, K. Honegger, E. Batawi, 5th European Solid Oxide Fuel Cell Forum, Lucerne, 116–122 (2002).
13) S. Koch, P. V. Hendriksen, M. Mogensen, Y.-L. Liu, N. Dekker, B. Rietveld, B. de Haart and F. Tietz, Fuel Cells (Weinheim, Ger.), 6, 130–136 (2006).
14) H. Yokokawa, H. Tu, B. Iwanschitz and A. Mai, J. Power Sources, 182, 400–412 (2008).
15) H. T. Lim, S. C. Hwang, Y. M. Park and I. S. Lee, Solid State Ionics, 225, 124–130 (2012).