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Stability study of cermet-supported solid oxide fuel cells with bi-layered electrolyte

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ABSTRACT

Performance and stability of five cermet-supported button-type solid oxide fuel cells featuring a bi-layered electrolyte (SSZ/SDC), an SSC cathode, and a Ni-SSZ anode, were analyzed using polarization curves, impedance spectroscopy, and post-mortem SEM observation. The cell performance degradation at 650 °C in H_2/air both with and without DC bias conditions was manifested primarily as an increase in polarization resistance, approximately at a rate of $2.3\,\mathrm{m\Omega\,cm^2\,h^{-1}}$ at OCV, suggesting a decrease in electrochemical kinetics as the main phenomenon responsible for the performance decay. In addition, the initial series resistance was about ten times higher than the calculated resistance corresponding to the electrolyte, reflecting a possible inter-reaction between the electrolyte layers that occurred during the sintering stage. *In situ* and *ex situ* sintered cathodes showed no obvious difference in cell performance or decay rate. The stability of the cells with and without electrical load was also investigated and no significant influence of DC bias was recorded. Based on the experimental results presented, we preliminarily attribute the performance degradation to electrochemical and microstructural degradation of the cathode.

1. Introduction

The benefits of ceria as an electrolyte material in solid oxide fuel cells include higher ionic conductivity and better compatibility with the high performance mixed ionic and electronically conductive (MIEC) cathode materials than the conventional zirconia-based electrolytes. However, these benefits of ceria-based electrolytes are partially offset by its considerable electronic conductivity under certain operating temperature and atmospheric conditions. This phenomenon results in an electronic current flowing across the electrolyte, leading to a reduction in open circuit voltage, fuel utilization, and electrical efficiency [1]. One way to alleviate this problem is to coat the ceria-based electrolyte with a thin layer of stabilized zirconia, thus blocking the flow of electrons [2]. For example, Yahiro et al. [3] added a thin (1.5 μm) protective layer of yttria-stabilized zirconia (YSZ) on the fuel side of a yttria-doped ceria electrolyte (1.5 mm) supported solid oxide fuel cell (SOFC), increasing the open-circuit voltage (OCV) and enhancing power density. This type of cell is commonly called a bi-layered electrolyte SOFC. Using an anode supported cell structure with thin YSZ/samaria-doped ceria (SDC) bi-layered electrolyte deposited by electrophoretic deposition [4] and by conventional wet processing [5], a peak power density of $0.6\,\mathrm{W\,cm^{-2}}$ at 700 °C has been reported. Recently, we demonstrated higher performance of cells with scandia-stabilized zirconia (SSZ)/SDC bi-layered electrolytes. We obtained a peak power density of $0.85\,\mathrm{W\,cm^{-2}}$ and an OCV of 1.02 V at 700 °C using a combined tape casting, screen printing and co-firing technique [6], and a peak power density of $0.95\,\mathrm{W\,cm^{-2}}$ and an OCV of 1.04 V at 600 °C using pulsed laser deposition [7]. Although the bi-layered electrolyte cell strategy has successfully prevented internal shorting in ceria-based electrolyte cells and has enabled compatibility with high-performance MIEC cathodes [8], cell performance stability has scarcely been reported in the literature. In the present contribution, we study performance and stability of cermet-supported button cells with bi-layered SSZ/SDC electrolytes.

2. Experimental procedure

2.1. Button cell preparation and testing

Table 1 shows the cell materials and the geometrical characteristics of our cells. Details of the cell preparation were given elsewhere [6]. Five cells of the same composition and the same anode and

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Table 1
Cell materials, thicknesses, and processing conditions

Cell component	Material	Thickness [μm]	Process	Firing condition
Cathode	$Sm_{0.5}Sr_{0.5}CoO_{3-y}$ (SSC)	40–50	Stencil printing	Cells A, B and C: *in situ* at 650 °C for 1.5 h; Cells D and E: *ex situ* at 1000 °C for 2 h
Electrolyte	$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)	5 ± 1		
	$Sc_{0.2}Ce_{0.01}Zr_{0.79}O_{1.9}$ (SSZ)	3 ± 1	Screen printing	1400 °C, 2 h
Anode	NiO–SSZ	10–15		
Substrate	NiO–YSZ	800–1000	Tape casting	

Table 2
Testing characteristics of the five bi-layered electrolyte button cells

Cell #	Time elapsed until each EIS measurement [h]	Remarks	
A	0, 0.33, 6, 6.84	Excursion to 800 °C between 0.33 and 6 h. Held at 0.75 V while not measuring EIS.	Performance evaluation
B	0, 0.33, 90, 115, 138, 144	Excursion to 1000 °C between 138 and 144 h.	Constant voltage, then no current (see Table 4)
C	1, 53, 150, 216, 218, 306	Held at 0.5 A cm^{-2} for 150 h, then OCV for 156 h.	Constant current
D	0, 0.16, 2, 89	Held at OCV throughout the test.	No current
E	0, 100	Held at 0.70 V throughout the test.	Constant voltage

electrolyte fabrication process, and cathode deposition process, were labelled A, B, C, D and E in this report. After deposition of the cathode layer, cells A, B, and C were mounted on a test jig and were heated at 5 °C min^{-1} to 650 °C and held for the reduction of the anode layer along with the *in situ* sintering of the cathode layer. The hydrogen partial pressure on the anode side was gradually increased (10, 20, 40, 60, and 100% H_2, balance N_2, at 15 min intervals) to reduce the NiO to Ni. The anode reduction and cathode *in situ* sintering time was approximately 1.5 h. The anode fuel stream, with a flow rate of 100 ml min^{-1}, passed first through a bubbler humidifier before entering the anode chamber, while ambient air (100 ml min^{-1}) flowed on the cathode side. In cells D and E, the cathode was pre-fired *ex situ* at 1000 °C for 2 h, and then coated with a wet layer of SSC to ensure good electrical contact against the current collecting mesh. In all cells, the cathode geometrical area was 0.5 cm^2. Impedance measurements were performed at 650 °C at OCV with a perturbation amplitude of 50 mV. The frequency ranged from 0.1 Hz to 100 kHz, with 10 data points per decade. Polarization and impedance were measured over time at 650 °C, with an intermediate excursion to 800 °C in cell A and to 1000 °C in cell B, and a pre-test excursion to 700 °C in cells D and E. Table 2 indicates the testing characteristics.

3. Results and discussion

3.1. Test results

Figs. 1–13 show the DC and impedance behaviour of the five cells, taken at different times after anode reduction. The cell performance showed deterioration at times longer than 7 h, primarily manifested as an increase in polarization resistance near OCV. Cell C also showed a 20% increase in series resistance.

3.1.1. Cell A

This cell was not subjected to stability testing. It was tested with the purpose of measuring the cell performance at different temperatures and the performance evolution during the initial several hours after the anode reduction process at 650 °C. During the 0.33–6 h period, the cell was heated up to 800 °C and cooled down to 550 °C at 50 °C intervals, measuring the polarization curve at each temperature. The detailed cell performance results and microstructure analysis have been published previously [6]. Table 3 gives a brief summary of the cell performance as a function of temperature. The cell reached a peak power density of 1.8 W cm^{-2} at 800 °C, and of 0.5 W cm^{-2} at 650 °C with OCV ranging from 0.99 to 1.04 V over the 550–800 °C temperature range.

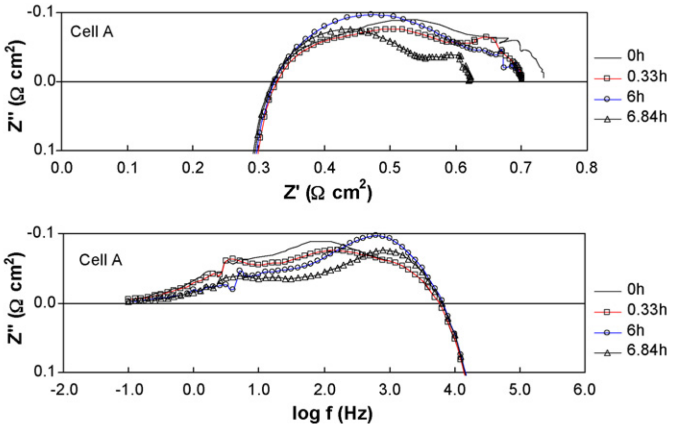

Fig. 1. Nyquist plot of the impedance evolution of cell A, tested at OCV at 650 °C. (Top) Nyquist plot. (Bottom) Imaginary impedance vs. frequency. The legend on the right indicates the time in hours elapsed since the beginning of the test. Between 0.33 and 6 h, the cell temperature was increased up to 800 °C and decreased back to 650 °C.

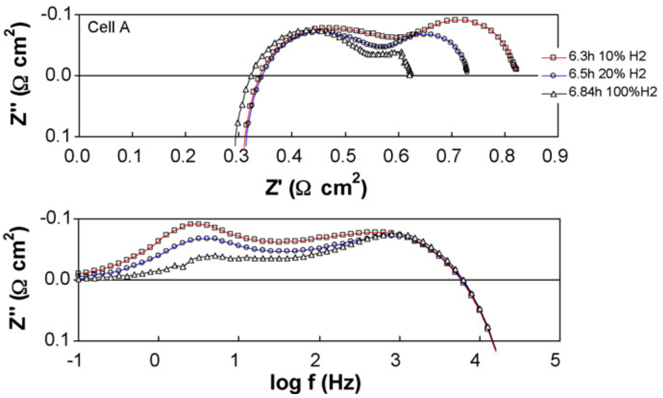

Fig. 2. Influence of H_2 dilution on the cell impedance. (Top) Nyquist plot. (Bottom) Imaginary impedance vs. frequency. The low frequency process shows a strong dependence on hydrogen activity, and thus we attribute it to the anode. Testing conditions: 650 °C, OCV, 10, 20 and 100% H_2, balance N_2/air (total gas flow rates for both anode and cathode are 100 ml min^{-1}).