



# Long-term stability of metal-supported solid oxide fuel cells employing infiltrated electrodes



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## HIGHLIGHTS

- Both temperatures and current densities affect the cell stability.
- The degradation was mainly caused by the morphological change of the anode.
- A degradation rate of  $1.3\% \text{ kh}^{-1}$  was found during the 1500 h test at  $650^\circ\text{C}$ .

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## ABSTRACT

Here, stability of the metal-supported solid oxide fuel cell (MS-SOFC) with  $\text{Ni-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (SDC) infiltrated 430L anode and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$  (LSFSc) infiltrated scandia-stabilized zirconia (SSZ) cathode is evaluated. It is found that the degradation rate defined as the voltage loss during a fixed period is faster at higher operation temperatures and larger current densities. Scanning electron microscopy (SEM) and energy dispersive X-ray spectra (EDS) analysis indicate that the degradation is mainly caused by the morphological change of the anode while metal element diffusion between Ni catalyst and 430L substrate contributes little. A 1500 h durability test measured at  $650^\circ\text{C}$  and  $0.9 \text{ A cm}^{-2}$  shows a degradation rate of  $1.3\% \text{ kh}^{-1}$  and the voltage decrease is mainly found in the initial 500 h.

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## 1. Introduction

Metal-supported solid oxide fuel cells (MS-SOFCs) using a porous alloy e.g., ferritic stainless steel as the supporting component have regained wide interest due to the advantages like lower materials cost, improved mechanical strength and enhanced tolerance to redox cycles over the traditional anode- or electrolyte-supported SOFCs [1]. Considerable progress both in fundamental and applied aspects in MS-SOFCs has been obtained in recent years. For example, micro combined heat and power (mCHP) unit based on the MS-SOFC has been demonstrated by Ceres Power [2], a plasma sprayed MS-SOFC stack delivered a power of 606 W at 42.4% fuel utilization has been put forward in the Institute of Nuclear

Energy Research in Taiwan [3], the potential of MS-SOFC for mobile applications has also been demonstrated in Plansee [4].

However, before the commercial deployment of the MS-SOFC, several critical issues should be solved. For the anode, oxidation of the porous metal substrate in the humidified hydrogen atmosphere is a problem which would increase the anode area specific resistance (ASR) due to the formation of oxide scales and the metal/oxide scale interfaces [5]. The linear increase in oxide scale growth as the porosity of the metal substrate increased has also been reported [6]. Another critical issue is the metal element diffusion between the Ni based anode and the Fe–Cr based substrate, which will inhibit the electrochemical activity of the anode and change the oxidation behavior and the coefficient of thermal expansion (CTE) of the substrate [7]. As reported, Cr and Fe were diffused to a depth of approximately  $50 \mu\text{m}$  from the STS 430 containing layer to the anode during the operation at  $800^\circ\text{C}$  for about 800 h [8]. Additionally, Ni coarsening is also a problem, especially for the

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infiltrated anode. For example, a rapid power degradation of a MS-SOFC with infiltrated Ni catalysts was found at 700 °C [9]. Our previous work also demonstrated a degradation rate of approximately 11%/100 h at 650 °C for a MS-SOFC and the degradation mainly resulted from rapid coarsening of the infiltrated nano-scale Ni catalysts [10]. Despite the issues coming from the cell anode, the poor chemical compatibility and thermal expansion compatibility between the cathodes and the traditional electrolyte materials also affect the cell stability [8,11]. For the oxidation behavior of the metal support at high temperature in air, it is difficult to sinter the traditional cathode materials such as  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  (LSM) which needs to be sintered in air at 1000–1200 °C. Sintering the cathodes in-situ at the temperature of 800–850 °C is an effective way to solve the problem while cathode materials like  $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$  (LSC) and  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF) with higher sintering capabilities are needed [12]. However, one of the drawbacks of these cathodes is the poor chemical compatibility with the zirconia-based electrolytes. For example, the maximum power density (MPD) of a MS-SOFC with  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) cathode decreased from 0.81 to 0.63  $\text{W cm}^{-2}$  after operating at 850 °C for 50 h [11]. The interaction between BSCF and yttria-stabilized zirconia (YSZ) which promotes  $\text{SrZrO}_3$  and  $\text{BaZrO}_3$  secondary phases was responsible for the degradation. Another issue of these in-situ sintered cathodes is the thermal expansion compatibility with the electrolyte materials. A MS-SOFC with  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (SSC)– $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (SDC) cathode showed rapid performance decrease after first two thermal cycles and the degradation was mainly due to the CTE mismatch between the SDC electrolyte layer and the SSC–SDC composite cathode [13]. Thermal expansion mismatch was also found to be one of the degradation mechanisms of the MS-SOFC employing NiO–SDC anode, SDC electrolyte and SSC–SDC composite cathode [14].

Preparing the electrodes by the infiltration method can circumvent the above issues while coarsening of the infiltrated nano particles is another problem [9,10,15–17]. In our previous work, a MS-SOFC comprising of Ni–SDC infiltrated 430L (16–18 wt% Cr-based ferritic stainless steel alloy) anode, YSZ electrolyte and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$  (LSFSc) infiltrated YSZ cathode was successfully fabricated [16]. Promising performance of such cell was obtained at the temperature range of 650–800 °C and short-term stability was demonstrated at 600 °C. In this study, long-term stability of this kind of MS-SOFC was further studied and effects of temperature and current density on the cell stability were evaluated.

## 2. Experimental

The cell scaffold of porous 430L support/dense scandia-stabilized zirconia (SSZ) electrolyte/porous SSZ layer was produced by the tape casting, laminating and co-firing method [16]. Commercially available 430L stainless steel powder (–400 mesh, Jing-yuan Powder Material Co., Ltd, China) and SSZ powder ( $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.1}(\text{CeO}_2)_{0.01}$ , Daiichi kigenso kagaku kogyo Co., Ltd, Japan) were used as the starting materials. The slurry for tape casting was based on ethanol solvent, containing acrylic resin dispersant, polyvinyl butyral binder, dibutyl phthalate plasticizer and other organic additives, in addition to powder. After drying, green sheets of 430L support, SSZ electrolyte and SSZ cathode backbone were laminated and co-sintered in a reducing atmosphere of 5%  $\text{H}_2$ /95%  $\text{N}_2$  at 1320 °C for 4 h. After the cell scaffold preparation,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Sm}(\text{NO}_3)_3$  and  $\text{Ce}(\text{NO}_3)_3$  aqueous solution in stoichiometric ratios (the mass ratio of SDC:Ni = 8:2) was introduced into the porous 430L support by the infiltration method. After that, the LSFSc cathode catalyst was introduced into the porous cathode backbone by infiltration of an aqueous solution

containing stoichiometric amounts of  $\text{La}(\text{NO}_3)_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Sc}(\text{NO}_3)_3$ , where citric acid was also added at a 1:1 molar ratio to metal ions (99% pure, Sinopharm Chemical Reagent Co., Ltd.). After drying, heat treatment was conducted at 850 °C in 5%  $\text{H}_2$  – 95%  $\text{N}_2$  for 2 h to convert these salts into metal oxides. The reducing atmosphere was applied to protect the 430L substrate from excessive oxidation and the low sintering temperature was chosen to avoid the possible reaction between the cathode and the electrolyte. The infiltration/heat treatment cycle was repeated to increase the amounts of the infiltrated catalysts. A single infiltration/heat treating cycle yielded a loading of  $\approx 5$  wt% for the cathode and  $\approx 3$  wt% for the anode. 30 wt% catalyst loading for the cathode and 10 wt% catalyst loading for the anode were applied as we optimized previously [18,19].

For electrochemical measurements, the single cells were sealed onto alumina tubes using the silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins) and silver current collectors were applied to both electrodes for electrical connections. Current–voltage ( $I$ – $V$ ) curves and electrochemical impedance spectra (EIS) were obtained by using an IM6 Electrochemical Workstation (ZAHNER, Germany) over the temperatures range of 600–800 °C with the cathode exposed to air and the anode to humidified (3%  $\text{H}_2\text{O}$ ) hydrogen, both at the flow rate of 100  $\text{mL min}^{-1}$ .  $I$ – $V$  curves were measured in the galvanostatic mode and EIS were collected under open circuit conditions with a 20 mV AC amplitude over the frequency range of 100 mHz–0.2 MHz. The area specific ohmic resistance ( $R_o$ ) corresponds to the high-frequency real-axis intercept and the area specific polarization resistance ( $R_p$ ) was determined by the difference of the low- and high-frequency intercepts of the impedance spectra with the real axis. For long-term stability test, the cell was operated at 600, 650 and 700 °C at different current densities with humidified (3%  $\text{H}_2\text{O}$ ) hydrogen and air. Active area of the single cell was 0.35  $\text{cm}^2$ .

Microstructures of the fuel cell were examined by scanning electron microscopy (SEM) using Hitachi S-4800-II and SU-8220 microscopes. Element distributions were analyzed using a JEOL JXA-8100 electron probe microanalyzer (EPMA).

## 3. Results and discussion

Photograph of the MS-SOFC backbone (porous 430L support/dense SSZ electrolyte/porous SSZ layer) after sintering at 1320 °C in 5%  $\text{H}_2$ /95%  $\text{N}_2$  is shown in Fig. 1(a). The cell was flat with a diameter of 1.5 cm. Fig. 1(b) shows the cross-sectional SEM micrograph of SOFC containing a porous Ni–SDC infiltrated 430L anode ( $\approx 260$   $\mu\text{m}$ ), a dense SSZ electrolyte ( $\approx 17$   $\mu\text{m}$ ) and a porous LSFSc infiltrated SSZ cathode ( $\approx 30$   $\mu\text{m}$ ). In this study, the Ni–SDC infiltrated 430L both acts as the cell support and the cell anode. The electrolyte was fully dense without obvious pores. Fig. 1(c) and (d) show a higher-magnification SEM micrograph of the Ni–SDC infiltrated 430L anode (10 wt% loading) and LSFSc infiltrated SSZ cathode (30 wt% loading), respectively. Coatings consist of nano and porous particles were well connected with the electrode backbones.

Electrochemical characteristics of the single MS-SOFC operating on humidified hydrogen fuel and air oxidant at 600–800 °C are shown in Fig. 2. Fig. 2(a) shows that the maximum power densities (MPDs) measured were 0.30, 0.53, 0.78, 1.00 and 1.22  $\text{W cm}^{-2}$  at 600, 650, 700, 750 and 800 °C, respectively. Nyquist plots of the impedance data as obtained at open circuit voltage (OCV) for the present MS-SOFC is shown in Fig. 2(b). The pure ohmic losses correspond to the high-frequency real-axis intercepts and the polarization resistances are taken by subtracting the ohmic resistances from the total resistances (low-frequency intercepts at real-axis). The pure ohmic resistance were 0.10, 0.13, 0.17, 0.24

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