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Large-area solid oxide cells with $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ infiltrated oxygen electrodes for electricity generation and hydrogen production

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Abstract

Infiltration is an effective way to improve the performance of the oxygen electrode for solid oxide cells (SOCs). Most studies on infiltrated SOC are carried out on button cells with a small active area. Here, we report on the preparation of large-area fuel-electrode-supported SOC with a $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) infiltrated gadolinia-doped ceria (CGO) oxygen electrode. The electrochemical performance of the resulting SOC is examined at $4 \times 4 \text{ cm}^2$ level (active area). The cell delivers a power density of 1.08 W cm^{-2} at 0.6 V and 750 °C in fuel cell mode with high fuel and oxygen utilization of 52 and 57 %, respectively; in electrolysis mode, the current density reaches 1.07 A cm^{-2} at 1.3 V and 750 °C with a steam utilization of 60%. Additionally, the

influence of feed gas composition on cell performance and the short-term durability of the cell in electrolysis mode are studied. Electrochemical impedance spectroscopy (EIS) results and the post-test microstructural characterization demonstrate that there is no visible degradation of the LSC infiltrated CGO oxygen electrode after the durability test. These results highlight the potential of large-scale production of high-performance SOCs by designing nanostructured electrode via infiltration.

Keywords: Reversible solid oxide cell; Oxygen electrode; Infiltration; Nanostructure; Durability

1. Introduction

Affordable large-scale energy storage is essential for a sustainable energy future with a rising share of solar and wind-based intermittent electricity generation [1]. Solid oxide cells (SOCs) is a promising technology in this context. They can be operated either in electrolysis mode to convert surplus electricity from these renewable sources into chemical energy stored in various fuels such as H₂ and/or CO, or in fuel cell mode to generate electricity using the fuels produced [2-4]. One of the key factors limiting the performance of SOCs is the rate of the oxygen electrode reaction processes, i.e., the oxygen reduction reaction (ORR) in fuel cell mode and the oxygen evolution reaction (OER) in electrolysis mode, particularly at temperatures ≤ 750 °C. The most well studied oxygen electrode material is strontium-doped lanthanum manganite (LSM)/yttria-stabilized zirconia (YSZ) composite. However, SOCs with LSM/YSZ electrodes have limited performance at reduced temperatures; at 750 °C, most such cells were reported to show power densities of 0.3-0.65 W cm⁻² at a voltage of 0.7 V in fuel cell mode and current densities of 0.2-0.5 A cm⁻² at 1.3 V in electrolysis mode [5-9].

Accordingly, mixed ionic-electronic conducting (MIEC) oxides, such as La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} (LSCF) [10, 11], La_{0.6}Sr_{0.4}CoO_{3- δ} (LSC) [12], Sm_{0.5}Sr_{0.5}CoO_{3- δ} (SSC) [13], Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) [14], PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+ δ} (PBSCF) [15], Pr₂NiO_{4+ δ} (PNO) [16] and Pr₆O₁₁ [17] have been employed as alternative oxygen electrode materials, resulting in improved performance. Solution infiltration, also known as impregnation, has drawn increasing interests for preparing these MIEC type electrodes [18-21]. In the infiltration process the active electrocatalysts are introduced into a porous backbone at relatively low temperatures. Typically, the maximum firing temperature for the infiltrated electrode is now

the temperature of cell operation. Issues of chemical reactivity and thermal expansion mismatch of such MIEC oxides with the other cell components can be alleviated. The resulting electrodes with nano-scale catalysts have shown improved catalytic activity for the ORR/OER. For example, a power density of 0.78 W cm^{-2} at 0.7 V in fuel cell mode and a current density of 0.98 A cm^{-2} at 1.3 V in electrolysis mode were reported on a cell with LSCF infiltrated YSZ oxygen electrode at $750 \text{ }^{\circ}\text{C}$ [22]. Even better performance was reported on a cell using LSCF/gadolinia-doped ceria (CGO) composite electrode infiltrated with SSC nano-catalysts, exhibiting a power density of 1.39 W cm^{-2} at 0.7 V in fuel cell mode and a current density of 1.80 A cm^{-2} at 1.3 V in electrolysis mode [23].

However, most reports of infiltrated SOC were carried out on laboratory-scale button size cells with active areas less than 2 cm^2 . The performance of such button cells does not necessarily represent the performance of corresponding large-area, commercially relevant cells due to complexities related to the scale up of the manufacture and the influence of operating conditions such as increased gas utilization and non-isothermal operation. There have been only limited reports of successful manufacture of large-area cells using infiltration. In one exception, Jiang et al. reported a fuel-electrode-supported planar SOC with an active area of $9 \times 9 \text{ cm}^2$ and an LSCF infiltrated YSZ oxygen electrode [24]. This SOC was investigated for fuel cell operation, displaying a power density of 0.42 W cm^{-2} at 0.7 V and $750 \text{ }^{\circ}\text{C}$. More recently, we have developed two types of fuel-electrode-supported SOC in size of $13 \times 13 \text{ cm}^2$ with either an LSC infiltrated YSZ oxygen electrode or a $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$ (LNC) infiltrated YSZ oxygen electrode and evaluated their performance for fuel cell operation at $4 \times 4 \text{ cm}^2$ level (active area) [25]. Even though a CGO coating was infiltrated into the YSZ backbone prior to infiltrating LNC electrocatalysts, the formation of poorly conducting zirconate phases ($\text{La}_2\text{Zr}_2\text{O}_7$ or SrZrO_3) at the

interface between the electrocatalyst and YSZ backbone (where the CGO covering is not complete) was observed for 1300 h operation in fuel cell mode at 700 °C, 0.5 A cm⁻². In this work, 12.5 × 12.5 cm² fuel-electrode-supported half cells with porous CGO backbones at the oxide electrode side are produced by scalable and cost-effective processes of tape-casting, lamination, and co-sintering, and then an LSC precursor solution is infiltrated into the CGO backbones to prepare nanostructured LSC-CGO oxygen electrode. A CGO backbone is applied instead of YSZ as CGO has good chemical compatibility with most of the preferred perovskite electrocatalysts (including LSC) and higher ionic conductivity than YSZ. The prepared planar SOCs are investigated at 4 × 4 cm² level (active area) both in fuel cell mode and electrolysis mode. The durability of the cell in the electrolysis mode is investigated under a constant current density of 0.5 A cm⁻² at 750 °C.

2. Experimental

2.1. Cell preparation

The 12.5 × 12.5 cm² fuel-electrode-supported cells with a configuration NiO/YSZ support | NiO/YSZ fuel electrode | YSZ electrolyte | CGO barrier | CGO backbone were produced by laminating and co-sintering tape-cast green tapes at 1315 °C. The tape-cast slurries were prepared by two steps ball milling. In the first step, the ceramic powders were dispersed and milled in Ethanol with PVP as dispersant. The ball milling was performed in a plastic container with zirconia milling balls for 3 days. In the second step, PVB binder solution was added and mixed for 1 day. The green tapes of NiO/YSZ support, NiO/YSZ fuel electrode and CGO backbone were prepared by single layer tape-casting while tapes of YSZ electrolyte and CGO

barrier were prepared via a multilayer tape casting (MTC) process [26]. The CGO backbone tape was prepared with the addition of 60-70 % pyrolyseable pore formers in the tape-cast slurry to obtain sufficient porosity after sintering. The volume ratio of Ni to YSZ in the Ni/YSZ support and electrode was controlled to be 40/60 after the reduction of NiO [27].

Afterwards, LSC catalyst was coated on the internal surfaces of the porous CGO backbone via the infiltration technique, as reported previously [21, 25]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved into deionized water to prepare the corresponding nitrate solutions, respectively. $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Co}(\text{NO}_3)_3$ solutions were mixed in a molar ratio of 3:2:5 to obtain 0.5 M LSC precursor solution. Note that the surfactant Pluoronic® P123 (1.7 wt. %) was added into the LSC precursor solution to improve wetting/penetration of the structure, thus ensuring a uniform dispersion of infiltrate [25]. The LSC solution was dropped onto the surface of the CGO backbone and spread over the entire surface. The solution sucked into the pores of the backbone driven by capillary forces. A sufficient amount of solution was dropped to ensure that the pores of the backbone were completely filled. The surplus solution was removed from the surface with a sponge. The infiltrated samples were then calcinated at 350 °C in air for 15 min with a heating/cooling rate of 5 °C min⁻¹. The infiltration/calcination processes were repeated 9 times to get a loading of ~1300 mg of LSC catalysts per 1 cm³ CGO scaffold. After the infiltration, the cells were cut into pieces of 5.3 × 5.3 cm² to fit the in-house constructed cell test houses. Finally, an LSC layer in size of 4 × 4 cm² was screen printed onto the oxygen electrode to enhance the current collection.

2.2. Electrochemical characterization

The electrochemical performance and durability of the prepared cells were investigated using in-house constructed test rigs. In each test, a cell was mounted onto an alumina housing and sealed with a gold frame, as described in previous work [28]. The cells were heated to 800 °C with a heating rate of 1 °C min⁻¹ and with pure Ar fed to the fuel electrode and dry air to the oxygen electrode. Afterwards, the cells were held at 800 °C for 4 h with the fuel electrode first fed with 9%H₂-91%Ar for 2 h, followed by another 2 h in 4%H₂O-96%H₂ to fully reduce all NiO to Ni and form a percolating network. Meanwhile, the oxygen electrode was treated with air to enable the infiltrates to form the desired LSC crystalline phase. The electrochemical performance of the cells was evaluated at 800–700 °C under varying gas feeds to the electrodes, but the flow rates of gases in the fuel and oxygen electrodes were kept at 24 l h⁻¹ and 50 l h⁻¹, respectively. Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Solartron 1255 frequency response analyzer in combination with a measurement resistor, at frequencies from 0.0968 to 96850 Hz with an amplitude of 3.75 mA cm⁻². The durability of the cell was evaluated in electrolysis mode at 750 °C under a constant current density of 0.5 A cm⁻², with 13.4 l h⁻¹ 90%H₂O-10%H₂ fed to the fuel electrode and 50 l h⁻¹ pure O₂ to the oxygen electrode. EIS data were recorded every 20 h during the durability test under the current of 0.5 A cm⁻². All of EIS data analyses were carried out using the Python-based software Ravdav [29].

2.3. Microstructure characterization

The cell structure was examined using scanning electron microscopy (SEM) in a Zeiss Merlin microscope. Both polished and fractured cross-sections of the cells were prepared for SEM characterization, corresponding to the SEM micrographs shown in Fig. 1 and Fig. 8, respectively. SEM image analysis was carried out with ImageJ software. In order to check the phase composition of the infiltrates deposited on the CGO backbone, powders synthesized by

calcinating the above LSC infiltrate solution at 800 °C for 4 h were examined at room temperature using X-ray diffraction (XRD, Bruker D8 Rigaku, CuK α radiation) with a scanning range of 20–80° and a step size of 0.01°.

3. Results and discussion

3.1. Microstructure

Fig. 1a and Fig. S1 show the typical cross-sectional SEM micrographs of the fuel-electrode-supported cell prior to infiltration of LSC catalysts. The cell consists of a Ni/YSZ support (~ 300 μm), a Ni/YSZ fuel electrode (~ 15 μm), a YSZ electrolyte (~ 5 μm), a CGO barrier layer (~ 6 μm), and a porous CGO backbone (~ 25 μm). There is good adherence between different layers as no obvious delamination or crack is observed. The YSZ electrolyte is fully dense while some closed pores are observed in the CGO barrier layer. The CGO backbone for infiltration has a uniform porous microstructure with a porosity of ~ 55 % and an average pore size of ~ 1.3 μm , estimated based on counting black and gray pixels of the micrograph, which refer to pores and CGO grains, respectively (Fig. 1a and 1b).

Fig. 1. Cross-sectional SEM images of (a) a fuel electrode-supported cell prior to the infiltration of LSC (inset showing the photograph of this cell in size of $12.5 \times 12.5 \text{ cm}^2$), (b) porous CGO backbone, and (c) CGO backbone infiltrated with LSC catalysts. (d) Photograph showing the as-prepared planar cell for testing.

The LSC infiltrated CGO oxygen electrode is prepared by infiltration of LSC catalysts and calcination at 800°C , and its microstructure is shown in Fig. 1c and Fig. S2, where the interconnected and nanoporous LSC coatings are well deposited on the internal surfaces of the porous CGO backbone. Formation of LSC in the coatings is confirmed by XRD pattern of powders, synthesized by calcinating the infiltrate solution at 800°C (Fig. 2). In addition to LSC, second phases including $(\text{La}_{2-x}\text{Sr}_x)\text{CoO}_4$, SrCO_3 , and Co_3O_4 were detected. Similar secondary

phases of LSC infiltration have also been observed by Samson et al. [30], even though a higher calcinating temperature of 900 °C was applied. Note that secondary phases of $(\text{La}_{2-x}\text{Sr}_x)\text{CoO}_4$ [31] and Co_3O_4 [30] have been demonstrated with electrochemical activity when applied as catalysts for oxygen electrodes. Hence secondary phases may not necessarily be detrimental to the electrochemical reactions. In addition, a 100% phase pure LSC infiltrate may not necessarily provide the best electrochemical performance if this has to be achieved via calcination at high temperature with coarsened catalyst particles. In the current work, a calcination temperature of 800 °C was eventually chosen based on the findings from Samson et al. [30]. Fig. 1d shows a photograph of the as-prepared planar cell that has been cut into the size of $5.3 \times 5.3 \text{ cm}^2$, with a screen-printed $4 \times 4 \text{ cm}^2$ LSC contact layer on top of the LSC infiltrated CGO oxygen electrode.

Fig. 2. XRD pattern of the LSC powders calcinated at 800 °C.

3.2. Electrochemical performance

The electrochemical performance of the as-prepared cells was evaluated both in fuel cell mode and electrolysis cell mode. The active area of the cells is $4 \times 4 \text{ cm}^2$ (the edges are used for sealing, as described in Experimental). Fig. 3a shows typical polarization curves of cell voltage and power density versus current density (I - V - P curves) of fuel cell operation, measured at 700–800 °C with 4% H_2O -96% H_2 fed to the fuel electrode and dry air to the oxygen electrode. The open circuit voltages (OCVs) range between 1.050 V at 800 °C and 1.069 V at 700 °C, and are within 35 mV off the calculated Nernst potentials (1.085 V at 800 °C and 1.104 V at 700 °C). Under a voltage output of 0.6 V, the cell delivers power densities of 1.34, 1.08, and 0.70 W cm^{-2} at 800, 750, and 700 °C, respectively. Unlike most of the previous SOC studies, in which the power densities are reported on button cells with active areas less than 2 cm^2 and gas utilization lower than 10 %, the here-reported power densities are accompanied with significant fuel and oxygen utilization, e.g., 65 and 71 % at 800 °C, 52 and 57 % at 750 °C, and 34 and 37 % at 700 °C, respectively (Fig. 2b). A high gas utilization is required for practical application and leads to lower power out than with negligible utilization due to the loss of Nernst potential along the fuel flow. The effect of fuel utilization on cell performance was further illustrated by feeding H_2O - H_2 mixtures with varying H_2O to H_2 ratios. The OCV decreases from 1.060 to 0.947 V with decreasing H_2 content from 96% to 50% in accordance with the tendency of the calculated Nernst potentials that decreasing from 1.095 V to 0.957 V (Fig. 3c). At a voltage of 0.6 V, power densities decrease from 1.08 to 0.78 W cm^{-2} , corresponding to a fuel utilization of 52 % and 72 %, respectively (Fig. 3d).

Fig. 3. Performance in fuel cell mode. Voltage and power density versus current density measured (a) at different temperatures with 4% H₂O-96% H₂ fed to the fuel electrode and dry air to the oxygen electrode, and (c) at 750 °C with different H₂O-H₂ gas mixtures fed to the fuel electrode and dry air to the oxygen electrode. (b, d) Corresponding fuel utilization and oxygen utilization at an operating potential of 0.6 V on the performance shown in (a) and (c).

Fig. 4a shows the voltage versus current density (I - V) curves in electrolysis mode for H₂ production, measured at 700–800 °C with 50% H₂O-50% H₂ fed to the fuel electrode and dry air to the oxygen electrode. The OCVs at different temperatures are all within 10 mV of the calculated Nernst potentials. At an electrolysis voltage of 1.3 V, current densities of 1.37, 1.07, and 0.69 A cm⁻² are obtained at 800, 750, and 700 °C, respectively, which correspond to the H₂

production rates of 9.53, 7.45, and 4.80 ml min⁻¹ cm⁻², respectively, calculated using Faraday's law. These H₂ production rates are achieved with steam utilization of 76 %, 60%, and 38%, respectively, and the hydrogen content in the outlet gas reaches 88 %, 80%, and 69%. At 800 °C, a significantly nonlinear increase in the voltage at high current densities is observed, which is attributed to the effect of growing concentration polarization because of the steam starvation in the fuel electrode under high steam utilization [32, 33].

The electrolysis performance was also investigated under different gas feeds to the fuel and oxygen electrodes at 750 °C. As shown in Fig. 4c, increasing the H₂O content from 20 % to 50 % leads to a decrease in OCV of 54 mV. The cell exhibits a current density of 0.64 A cm⁻² at 1.3 V with 20%H₂O-80%H₂ fed to the fuel electrode. This performance is strongly limited by the concentration polarization due to the high steam utilization of 86 %, and the corresponding hydrogen content in the outlet gas is as high as 97% (Fig. 4d). By increasing H₂O content to 50%, the concentration polarization is significantly reduced, resulting in an increase in current density of 67 % (i.e., 0.43 A cm⁻²) at 1.3 V. Fig. 4c also shows that the OCV increases 25 mV when the gas in the oxygen electrode is changed from air to pure O₂, and the current density at 1.3 V has a slight increase of 2 % (i.e., 0.02 A cm⁻²). Hence, the decreased driving force due to the increased OCV is fully compensated for by improved electrode performance in pure O₂. One should note that in principle for technical use, O₂ purge at the oxygen electrode is not likely to be a preferred mode of operation. Either no purge should be applied – “oxygen production mode” or for safety reasons steam, N₂ purge could be considered depending on whether the produced oxygen will be used or discarded. The results show that electrolysis performance is more sensitive to the H₂O content in the fuel electrode and the corresponding steam utilization and less sensitive to the

oxygen content in the oxygen electrode, as expected both from the relative thickness of the electrodes and the form of the Nernst expression.

Fig. 4. Performance in electrolysis cell mode. Voltage versus current density measured (a) at different temperatures with 50% H_2O -50% H_2 fed to the fuel electrode and dry air to the oxygen electrode, and (c) at 750 °C with varying gas feeds to the electrodes. (b, d) Corresponding gas composition at the outlet and overall steam utilization at an operating potential of 1.3 V on the performance shown in (a) and (c).

Fig. 5a-e shows the Nyquist plots of EIS data recorded under OCV condition in the temperature range of 700–800 °C with different gas feeds. The intercept with the real axis at high frequency in the Nyquist plot represents the ohmic resistance (R_{ohm}), and the difference between the high and low frequency intercepts represents the total electrode polarization resistance (R_p). R_{ohm} is almost unaltered with the change of gas feeds, and they are around 0.11, 0.16, and 0.25 $\Omega\text{ cm}^2$ at 800, 750, and 700 °C, respectively. These R_{ohm} are much greater than the expected resistances for 5 μm thick YSZ electrolyte and 6 μm thick CGO barrier here. At 700 °C, the observed R_{ohm} of 0.25 $\Omega\text{ cm}^2$ is 5 times the expected ($\sim 0.05\text{ }\Omega\text{ cm}^2$) based upon the ionic conductivities of 0.02 S cm^{-1} for YSZ and 0.03 S cm^{-1} for CGO [34]. This can be attributed to the interdiffusion of elements at the YSZ electrolyte – CGO barrier interface during the co-sintering process at 1315 °C leading to the formation of solid solution phases with lower ionic conductivity [35–37]. Furthermore, R_{ohm} actually constitute 29–40 % and 56–60 % of the overall resistances of the EIS data shown in Fig. 5a and 5c, respectively. These results suggest that there is room for further improvement of the cell performance by limiting the YSZ – CGO interdiffusion via, e.g., lowering the sintering temperature, or more preferably sintering the half-cell (NiO/YSZ support | NiO/YSZ fuel electrode | YSZ electrolyte) first and then sintering CGO barrier and porous CGO layer at lower temperature, such as 1200 °C.

For 4% H_2O -96% H_2 fed to the fuel electrode and air to the oxygen electrode, the R_p values are 0.26, 0.30, and 0.38 $\Omega\text{ cm}^2$ at 800, 750, and 700 °C, respectively (Fig. 5a). These R_p values are lower than those of our previously reported Ni/YSZ fuel electrode supported cell with a thin YSZ electrolyte, a CGO barrier layer applied by pulsed vapor deposition (PVD), and a screen printed LSC/CGO oxygen electrode [38], showing R_p values of 0.44 $\Omega\text{ cm}^2$ at 750 °C and 0.59 $\Omega\text{ cm}^2$ at 700 °C under same gas conditions (Fig. S3). The R_p values are also lower than many of

those previously reported for other cells with Ni/YSZ fuel electrodes and using different oxygen electrodes, e.g., $0.43 \Omega \text{ cm}^2$ at 750°C for the commonly used LSCF/CGO composite [23], $0.78 \Omega \text{ cm}^2$ at 700°C for SSC infiltrated YSZ [39], and $0.44 \Omega \text{ cm}^2$ at 700°C for $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$ (LNC) infiltrated YSZ [21]. Furthermore, the R_p values are comparable to those reported recently for high-performance cells using $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) infiltrated LSCF/CGO composite (e.g., $0.28 \Omega \text{ cm}^2$ at 750°C) [23] and $\text{SrTi}_{0.3}\text{Fe}_{0.63}\text{Co}_{0.07}\text{O}_{3-\delta}$ (e.g., $0.27 \Omega \text{ cm}^2$ at 750°C) [40]. With increasing the H_2O content from 4 % to 50 %, the R_p decreases pronouncedly at corresponding temperatures (Fig. 5c and 5e), to 0.09, 0.12, and $0.18 \Omega \text{ cm}^2$, respectively. The observed R_p of $0.18 \Omega \text{ cm}^2$ at 700°C is also lower than those reported for Ni/YSZ fuel-electrode-supported cells using different oxygen electrodes under the same condition, including LSCF/CGO composite ($0.33 \Omega \text{ cm}^2$) [10], SSC infiltrated YSZ ($0.66 \Omega \text{ cm}^2$) [39], $\text{Nd}_2\text{NiO}_{4+\delta}$ (NNO) infiltrated $\text{Zr}_{0.88}\text{Sc}_{0.22}\text{Ce}_{0.01}\text{O}_{2.11}$ (SSZ) ($0.51 \Omega \text{ cm}^2$) [41], and LSCF infiltrated YSZ ($0.20 \Omega \text{ cm}^2$) [22]. These EIS results demonstrate the high performance of the LSC infiltrated CGO oxygen electrode, and that this electrode is very suitable for the purpose.

To clarify the type of electrode processes and their contributions to R_p , the method based on calculating the distribution function of relaxation times (DRT) was applied in the EIS analysis. Fig. 5b, 5d, and 5f show the DRT plots calculated from the EIS data shown in Fig. 5a, 5c, and 5e, respectively. These DRT plots have a set of five distinct peaks denoted P1 to P5 from high to low frequency. Each peak represents an electrode process, and its integral area is a measure of the resistance of that process. Evidently from Fig. 5b and 5d the processes associated with P1 to P3 are characterized by a pronounced thermal activation while P4 and P5 are not sensitive to temperature. This strongly indicates that P1 to P3 correspond to the chemical and electrochemical processes in the electrodes and P4 and P5 are related to gas diffusion and

conversion [42]. Fig. 5f shows that P2, P4, and P5 are very sensitive to the ratio of H_2O to H_2 in the fuel electrode compartment while they are almost independent of gas change in the oxygen electrode. Thus, P2 is most likely associated with charge transfer processes at the triple phase boundaries (TPBs) of the fuel electrode; P4 represents the gas diffusion and the major contribution of P4 is from the fuel electrode; P5 is the gas conversion impedance in the fuel electrode [27, 43]. Furthermore, P1 is independent of any gas changes, and it is likely associated with the transport of oxygen anions through the ionic conducting networks in the electrodes [27, 43, 44]. Since the present cell has a highly ionic conducting CGO backbone based oxygen electrode, the major contribution of P1 is from the fuel electrode that has a YSZ network. The change of gas in the oxygen electrode compartment from air to pure O_2 leads to a change in P3, indicating that P3 is likely related to the charge transfer processes of oxygen incorporation/evolution at the active sites of the oxygen electrode [27, 45]. The DRT results suggest that for the present cell with the Ni/YSZ fuel electrode and the nanostructured LSC infiltrated CGO oxygen electrode, the resistance of the fuel electrode dominates the total R_p while the resistance of oxygen electrode is much smaller.

Fig. 5. Nyquist plots of EIS data recorded under OCV (a) at different temperatures with 4% H_2O -96% H_2 fed to the fuel electrode and dry air to the oxygen electrode, (c) at different temperatures with 50% H_2O -50% H_2 fed to the fuel electrode and dry air to the oxygen electrode, and (e) at 750 °C with varying gas feeds to the electrodes. (b, d, f) Corresponding DRT plots of EIS data shown in (a), (c) and (e).

3.3. Durability

The durability of the cell was evaluated under electrolysis condition with a constant applied current density of 0.5 A cm^{-2} , and 90% H_2O -10% H_2 fed to the fuel electrode and pure O_2 to the oxygen electrode. Fig. 6a shows the evolution of cell voltage with time and the trend of cell degradation. Only 86 h of durability data is shown, because the test was terminated involuntarily after 86 h due to a malfunction in the H_2 supply, which led to the redox of the Ni/YSZ support thus damaging the cell structure. The degradation rate increases from ~ 0.3 to $\sim 0.6 \text{ mV h}^{-1}$ in the first 30 h, then decreases towards $\sim 0.1 \text{ mV h}^{-1}$ in the following 50 h.

Fig. 6b shows the Nyquist plots of the EIS data recorded under current during the durability test. The almost unaltered R_{ohm} and the pronouncedly increased R_p shows that the cell degradation processes occur mainly on the electrodes. Between each two of the spectra measured at every 20 h, the R_p of EIS data recorded at 20 h and 40 h exhibits the largest difference, in agreement with the evolution of degradation rate shown in Fig. 6a. Furthermore, among the five peaks of the DRT plots shown in Fig. 6c, P2 increases significantly, implying that the major degradation is from the Ni/YSZ fuel electrode. This degradation of Ni/YSZ fuel electrode during electrolysis operation has also been reported previously [38, 46-48]. It is difficult to precisely determine the evolution of the resistance of the LSC-CGO oxygen electrode (P3), because the oxygen electrode impedance is relatively small and with respect to time constants it is overlapping with P2.

Fig. 6. Durability for steam electrolysis. (a) Evolution of cell voltage during short-term test under a constant current density of 0.5 A cm⁻² at 750 °C with 90%H₂O-10%H₂ fed to the fuel electrode and pure O₂ to the oxygen electrode. (b) Nyquist plots and (c) DRT plots of EIS data recorded under 0.5 A cm⁻² during durability test.

These EIS data were further fitted with an equivalent circuit model shown in Fig. 7a. The model consists of four constant phase elements (RQ) and a modified Gerischer element (G), matching to the five different processes seen by DRT analysis, along with the R_{ohm} and an inductor (L) [38, 44]. The fitting results are shown in Fig. 7b,c, Fig. S4 and Table S1. The fitted spectra of EIS data measured at 0 h and 80 h are shown in Fig. 7b as examples. Fig. 7c summarizes the resistance values for each circuit element obtained from the fits. The value of R_3

(corresponding to the Gerischer element in the circuit model and the resistance of P3 of which includes the oxygen evolution steps at active sites in the oxygen electrode, $R_{\text{LSC-CGO}}$) is only $0.010 \, \Omega \, \text{cm}^2$ initially, demonstrating the high activity of the LSC infiltrated CGO oxygen electrode for the OER. Furthermore, the R_3 has an increase of $0.002 \, \Omega \, \text{cm}^2$ in 80 h, contributing to less than 3% of the increase of ASR of cell ($0.082 \, \Omega \, \text{cm}^2$). While the increase of R_1 (corresponding to the resistance for P1 of transport of oxygen anions, R_{ion}) and R_2 (corresponding to the resistance for P2 including the steam splitting processes at the TPBs of the fuel electrode, $R_{\text{Ni/YSZ TPB}}$) are $0.009 \, \Omega \, \text{cm}^2$ and $0.046 \, \Omega \, \text{cm}^2$, respectively, and contributes to $\sim 70\%$ of the increase of ASR of cell. Albeit being encompassed with some uncertainty of fitting due to overlapping time scales, these results further confirm that the degradation of the cell is mainly from the Ni/YSZ fuel electrode, and demonstrates that also after 80 h the contribution from the LSC-CGO oxygen electrode is negligible. SEM micrographs of the LSC-CGO oxygen electrode before and after durability test are shown in Fig. 8. No obvious growth of the LSC nanoparticles is observed, consistent with the EIS results. It is worth noting that recently some encouraging progress has been made in insight into the degradation mechanism of Ni/YSZ fuel electrode during electrolysis and exploring strategies to reduce this degradation [27, 49-53]. For example, our laboratory has found that the durability of Ni/YSZ fuel electrode can be significantly enhanced either by optimizing the microstructure of electrode [27] or modifying the electrode with CGO electrocatalysts [49, 50].

Fig. 7. (a) Equivalent circuit model for CNLS fit. (b) CNLS fits of EIS data recorded at 0 h and 80 h of durability test under 0.5 A cm^{-2} at 750°C with $90\% \text{H}_2\text{O}$ - $10\% \text{H}_2$ fed to the fuel electrode and pure O_2 to the oxygen electrode. (c) Resistances from the fitting results.

Fig. 8. Cross-sectional SEM images of LSC infiltrated CGO oxygen electrode for (a) before, and (b) after the durability test.

Conclusion

In summary, we demonstrated the feasibility of preparing large-area SOCs by conventional ceramic processing techniques involving infiltrating LSC electrocatalysts into a pre-fired CGO porous backbone. The cell was examined at $4 \times 4 \text{ cm}^2$ level (active area). In fuel cell mode, at a voltage of 0.6 V, the cell delivered power densities of 1.34, 1.08, and 0.70 W cm^{-2} at 800, 750, and 700 °C, respectively. These power densities were obtained with fuel and oxygen utilization of 65 and 71 % at 800 °C, 52 and 57 % at 750 °C, and 34 and 37 % at 700 °C, respectively. In electrolysis mode, the current densities at 1.3 V reached 1.37, 1.07, and 0.69 A cm^{-2} at 800, 750, and 700 °C, respectively, corresponding to steam utilization of 76 %, 60%, and 38%. The EIS results suggest that the LSC infiltrated CGO oxygen electrode has excellent activity for both the ORR and the OER and its durability when operated at 0.5 A cm^{-2} for steam electrolysis is good. The $R_{\text{LSC-CGO}}$ is only $0.010 \Omega \text{ cm}^2$ initially, and it has an increase of $0.002 \Omega \text{ cm}^2$ in 80 h, contributing to less than 3% of the increase of ASR of cell ($0.082 \Omega \text{ cm}^2$). The performance of the present cell is limited primarily by ohmic resistance and the resistance for electrochemical processes in the fuel electrode, of which the latter is responsible for the resistance degradation seen over the short durability test. Future work will focus on reducing the ohmic resistance and the fuel electrode polarization resistance, to improve both the cell performance and long-term durability.

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