Research on a low temperature reversible solid oxide cell

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In this study, two-electrode-supported solid oxide cells with the structure of “Ni-Sm doped CeO2 infiltrated porous La0.9Sr0.1Ga0.8Mg0.2O3 (LSGM) | dense LSGM | SmBa0.5Sr0.5Co2O5 infiltrated porous LSGM” are fabricated. Fuel cell and steam electrolysis performance at different operating temperature (450–600 °C) for different steam content are tested, and reaction mechanism discussed. In the fuel-cell mode, the maximum power density reaches 1.817, 1.345, 0.801 and 0.342 W cm−2 at 600, 550, 500, and 450 °C, respectively. In electrolysis mode, current density at 1.3 V in 70% H2O + 30% H2 stream is 2.472, 1.616, and 0.727 A cm−2 at 600, 550, and 500 °C, respectively. The durability of the cell is tested for over 351 h.

Introduction

Reversible solid oxide cells (SOC) [1] can be operated in both electrolysis mode (SOEC: to store electricity energy with chemical fuels) and fuel-cell mode (SOFC: to convert fuels into electricity), which is considered as a promising energy storage technology [2–5] to balance the supply-demand mismatch for electricity from renewable energy such as solar and wind energy. Conventional SOFC using Yttria stabilized Zirconia (YSZ) as the electrolyte and Sr-doped LaMnO3 (LSM) as the air electrode is called as high temperature SOFC, because the YSZ can only meet sufficient ionic conductivity, 0.1 S/cm, at around 1000 °C. So high an operating temperature severely limited the selection of component materials and hindered the commercialization of this technology [6].

Recently, there is a trend to reduce the operating temperature of SOCs into the so-called low temperature (LT) range (lower than 650 °C) for the following reason: at first, if the operating temperature could be decreased down to 500–600 °C, many waste heat sources in industry such as steel manufacturing or those from various combustors could be used for SOEC [7]; secondly, Fischer-Tropsch synthesis reaction [8,9] for directly synthesis of CH4 [3] can be possible when stable electrolysis of CO2 [10–12] can be realized on LT-SOCs; third, cheaper cost of components such as separators of SOC at low temperature would reduce the system cost [13]. For this purpose, however, the ohmic resistance and polarizations should be reduced by fine design of the cells and careful selection of materials.

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La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-0.5(x+y)}$ (LSGM) has sufficient ionic conductivity at reduced temperatures; it is stable and has no electronic conductivity in both oxidizing and reducing atmospheres. Because of such advantages, LSGM has been known as a very promising electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFC) [14–16] and solid oxide electrolysis cells (IT-SOEC) [17]. In contrast, Sm-doped ceria (SDC) or Gd-doped ceria (GDC) is not a good electrolyte for its partial reduction in reducing atmospheres, although it has comparable ionic conductivity as LSGM and is widely used as a barrier layer or a component in electrode materials [18]. In the temperature range lower than 650 °C, the thickness of LSGM film is expected to be reduced, and then electrode supported LSGM film, especially which supported from both sides, is the ideal choose. In this case, however, the thickness of electrodes increases from normal scale, and the risk of concentration polarization becomes the main concern; there are many model simulation works in the literature which reveal the importance of controlling the diffusion resistance [19–21].

Ni electrode has excellent activity and is a good catalyst for the H$_2$ formation during water splitting [22]. To avoid its re-action with LSGM and sintering at high manufacturing temperature, Ni is expected to be infiltrated into pre-sintered porous LSGM skeleton. The obtained nano-particles of Ni have high activity, but its sintering is the main reason of degradation. In our previous study, it has been confirmed that Ni-SDC infiltrated LSGM electrode is more stable and catalytically more active than Ni infiltrated LSGM electrode [23].

SmBa$_{0.5}$Sr$_{0.5}$Co$_2$O$_5$ is demonstrated a good cathode material, it has high conductivity and shows small area specific resistance (ASR) at intermediate temperatures [24]. And the recent studies show that infiltrated SmBa$_{0.5}$Sr$_{0.5}$Co$_2$O$_5$ has even higher catalytic activity and lower ASR [25].

Above materials have been widely studied in literature, but the assembly of them was mainly studied in the SOFC mode; the performance and its stability in SOEC mode is interesting. In the present work, two-electrode mode (FC mode) and electrolysis cell mode (EC mode). DC polarization (I–V) curves and Electrochemical impedance spectra (EIS) were measured at 450, 500, 550 and 600 °C, while a stream of H$_2$/H$_2$O mixture with different ratio (with the total flow rate being 100 sccm) was supplied to the Ni-SDC-LSGM hydrogen electrode and air supplied to the SBSC-LSGM oxygen electrode (flow rate 100 sccm).

**Electrical impedance spectroscopy (EIS) testing was performed using an IM6 Electrochemical Workstation (ZAHNER, Germany) between 10$^5$ and 10$^{-1}$ Hz, with a 20 mV perturbation under open-circuit conditions. The ohmic resistance (R$_o$) was obtained from the value of the high frequency intercept. The electrode polarization resistances (R$_p$) were measured by the differences between the high and low frequency intersections of the impedance spectrum on the real axis (Z real axis).**

### Experimental

**Cell fabrication and characterization**

The scaffold of the symmetrical cells with tri-layer structures of “porous LSGM | dense LSGM | porous LSGM” was fabricated by laminating one dense LSGM green tape and two porous LSGM green tapes on both sides with subsequent co-firing at 1380 °C for 4 h. The green tape for LSGM dense layer was prepared by tape casting technology. For this purpose, commercial LSGM powder was weighted and ball milled for 12 h, in the mixture of xylene and butyl acetate, with triethanolamine as dispersant. Then polyvinyl butylar (PVB) as binder, polyethylene glycol and dibutyl phthalate as plasticizer were added. The mixture was ball milled for 8 h to get the slurry, which was degassed in vacuum for 5 min, and tape casted on PET tape, following with drying at 50 °C, to get the green tape for the dense LSGM electrolyte film. As for the porous LSGM tape, similar procedure was adopted, but graphite as pole former was added to LSGM powder with the weight ratio being 1:5. During tape casting, the height of blade was 75 μm for the dense layer but 300 μm for the porous layer. During laminating of the green tapes, they were pressed under 3000 psi at 75 °C, and the hold time was 20 min. The green tri-layer tape of “porous LSGM | dense LSGM | porous LSGM” was cut to plates of 14 mm in diameter, and then sintered in air at 1380 °C for 4 h to get the LSGM skeleton of the symmetrical cells with ~20 μm thick dense LSGM electrolyte film in the middle.

For the preparation of SmBa$_{0.5}$Sr$_{0.5}$Co$_2$O$_5$(SBSC) electrode, solution for infiltration was prepared by weighting commercial Sm(NO$_3$)$_3$ · 6H$_2$O, Ba(NO$_3$)$_2$, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$ · 6H$_2$O (all of them are AR grade in purity) and dissolving them into deionized water. Citric acid was added and its molar ration to the total metal ion was 1.2:1, the concentration of the solution was controlled to be around 0.5 mol L$^{-1}$. The solution was infiltrated into the porous LSGM layer, following by heat treatment at 500 °C for decomposition of the nitrates. This process was repeated several times until the final SBSC phase would be 20 w% in the porous electrode. The previous work in our group shows that 21 w% SBSC infiltrated LSGM skeleton gives the lowest polarization as a SOFC cathode [25]. The final heat treating temperature was selected as 900 °C (for 2 h), because samples treated independently at this temperature showed pure SBSC phase, while those treated at temperatures bellowing 850 °C showed XRD pattern of SrCoO$_3$ as impurity.

For the preparation of Ni-SDC electrode, similar procedure was adopted, but the start materials were Sm(NO$_3$)$_3$ · 6H$_2$O, Ce(NO$_3$)$_3$ · 6H$_2$O, and Ni(NO$_3$)$_2$ · 6H$_2$O (also AR grade), the calculated Ni ratio in Ni/SDC mixture was 70 w%, the weight ration of infiltrated active substance in the final electrode was controlled to be 20 w%, and the final treating temperature of the infiltrated Ni/SDC mixture was selected as 850 °C.

The morphologies of the cell configuration and infiltrated particles were characterized by scanning electron microscope (SEM, Hitachi S-4800-2).
Durability test

The durability of the cell was studied at 500 °C in both EC mode and FC mode, with 30% H₂–70% H₂O mixture for EC mode and 97% H₂–3% H₂O mixture for FC mode (total flow rate: 100 sccm) supplied to the Ni-SDC-LSGM hydrogen electrode and air supplied to the SBSC-LSGM oxygen electrode (flow rate 100 sccm). The cell was first operated at −0.6 A cm⁻² (EC mode) for 206 h and then at 0.4 A cm⁻² (FC mode) for 85 h and finally at −0.6 A cm⁻² (EC mode) for 60 h.

Results and discussion

Fig. 1 (a) presents SEM image of the “porous LSGM| dense LSGM| porous LSGM” structure. The thickness of the porous LSGM layer and dense LSGM layer are 210 and 16 μm, respectively. Fig. 1 (b) and (b’) show the SEM image of Ni-SDC-LSGM hydrogen electrode, while Fig. 1 (c) and (c’) are for the SBSC-LSGM oxygen electrode, respectively. The micrograph shows that SBSC and Ni-SDC particles are evenly distributed on the surface of the LSGM skeleton with the particle size being 50–200 nm. Based upon mercury porosimetry measurements prior to catalyst infiltration, the porous LSGM layer has an overall porosity of 50% with pore size around 5 μm. After infiltration and reduction, the porosity of the Ni-SDC-LSGM electrode is estimated to be around 39%.

Fig. 2 — I–V curves and power densities in SOFC mode measured at 450–600 °C with 3% H₂O–97% H₂ as fuel and air as oxidant.
As is shown in Fig. 2, the maximum power density is 1.817, 1.345, 0.801 and 0.342 W cm\(^{-2}\) at 600, 550, 500, 450 °C, respectively.

As is shown in Fig. 3, the electrochemical impedance spectra of the SOCs above 500 °C are composed of two overlapping depressed arcs reflecting physical and/or chemical processes associated with the electrode reactions [26,27]. The EIS consist of two dominant arcs with summit frequencies of \(10^2\)–\(10^3\) Hz (mid-frequency) and \(10^{-1}\)–\(10\) Hz (low-frequency). The mid-frequency arcs, usually associated with the surface kinetics, decrease with the increase of temperature. At 450 °C, an obvious arc is observed at very high frequency, showing a different reaction mechanism. 450 °C may be too low and grain boundary resistance may become obvious.

The low-frequency arcs decreased with the temperature increasing from 450 to 500 °C and then increased with increasing temperature from 550 to 600 °C. The former is due to the increase of electrodes’ activity, the latter, however, may have another reason. Since low frequency is attributed to gas phase diffusion, the increase of low-frequency arc can be explained by the insufficient supply of H\(_2\)O on the hydrogen electrode or O\(_2\) on the oxygen electrode. The measurement was done at OCV with fixed 20 mV perturbation; the electrodes’ activity and exchange current density will increase with increasing temperature. A larger exchange current density may cause more obvious diffusion polarization at low frequency. This may explain the abnormal increase of the low frequency arc above 500 °C.

Fig. 4 shows i-V curves for the SOC in H\(_2\)/H\(_2\)O mixtures at 500, 550, 600 °C. The gas mixtures used were 3% H\(_2\)O + 97% H\(_2\), 50% H\(_2\)O + 50% H\(_2\), and 70% H\(_2\)O + 30% H\(_2\), respectively. Data are recorded for operation in both electrolysis mode (negative current) and fuel-cell mode (positive current).

As is shown in Fig. 4(a–c), the OCV decreases as the steam ratio increases, which can be predicted from the Nernst Equation for the hydrogen-oxygen-steam system.

\[
E = E_0 - \frac{RT}{nF} \ln \left( \frac{y_{H_2}y_{O_2}^{1/2}}{y_{H_2O}} \right) \left( \frac{P}{P_{std}} \right)^{-1/2}
\]

where \(E_0\) is the Nernst potential at standard state, R is the gas constant (J mol\(^{-1}\) K\(^{-1}\)), T the temperature (K), n the number of electrons transferred per molecule of steam electrolyzed, F the Faraday’s constant (J V\(^{-1}\) mol\(^{-1}\)), P the test pressure (kPa), \(P_{std}\) the standard atmospheric pressure (kPa), and \(y_{H_2}\), \(y_{O_2}\) and \(y_{H_2O}\) are mole fractions of hydrogen, oxygen and water vapor, respectively.

For FC mode, the cell performance depends slightly on H\(_2\)O concentration, indicating the Ni-SDC infiltrated electrode possess sufficient stability and catalytic activity under high H\(_2\)O concentration.

As shown in the Fig. 4, the voltage data vary linearly with the current density up to a value (limiting current density) that depends on the temperature and the inlet H\(_2\)O concentration. At 500 °C, as is shown in Fig. 4 (a), the i-V scan is fairly linear from 2 A cm\(^{-2}\) in the FC mode, through the OCV, to –2 A cm\(^{-2}\) in the EC mode in all H\(_2\)O concentrations. However, as temperature rises to 550 °C and 600 °C, shown in Fig. 4 (b) and (c), limiting current is observed in the SOEC mode for H\(_2\)O.

Fig. 4 – I–V curves measured with various H\(_2\)O concentrations in the fuel while air is flowing on the SBSC electrode: (a) 500 °C; (b) 550 °C; (c) 600 °C.
concentration of 3 and 50%, i.e. the I-V curves were approximately linear at low current density, but a rapid increase in cell voltage occurs at high current density. The limiting current densities increases for higher water concentrations, and then disappears as H₂O concentration rises to 70% at 550 °C but not fully disappears at 600 °C, which can be explained by the concentration polarization occurring at high current density, where H₂O diffusion becomes the rate limiting step.

Fig. 5 shows the Nyquist and Bode plots for different H₂O concentration at 500, 550 and 600 °C. The EIS consist of two dominant arcs with summit frequencies being 10⁻⁵ - 10⁻¹ Hz (mid-frequency) and 10⁻¹ - 10⁻¹ Hz (low-frequency). The mid-frequency arcs decrease with the increase of H₂O concentration and temperature, while the low-frequency arcs increase with the decrease of H₂O concentration and the increase of temperature. The mid-frequency arcs are significantly influenced by temperature but slightly by H₂O concentration. However, the low frequency arcs strongly depend on H₂O concentration. Since the mid-frequency arc is usually associated with the surface kinetics and low frequency is attributed to gas phase diffusion. EIS results confirmed that water diffusion becomes rate limiting as is also shown in Fig. 3 at high current density. Ro increases with increasing H₂O concentration at all the tested temperatures, which may be caused by the partial oxidation of Ni to NiO.

The durability of the cell was examined after the initial performance characterization. As shown in Fig. 6, reversible operation between electrolysis mode (−0.6 A cm⁻²) and fuel cell mode (+0.4 A cm⁻²) were performed. The current density of −0.6 A cm⁻² gives a cell voltage close to the thermo-neutral voltage for steam electrolysis [3].

The cell voltage increased by about 45 mV (from 1.306 V to 1.351 V) during the first 206 h of electrolysis mode at −0.6 A cm⁻², which corresponds to a degradation of 1.7% 100 h⁻¹. During the next 85 h (from 206 h to 291 h) in fuel cell mode at 0.4 A cm⁻², a decrease in cell voltage of 69 mV (from

![Fig. 5](image1.png) EIS measured under OCV at 450–600 °C with various H₂O concentration in the fuel: (a–c) Nyquist and (a’–c’) Bode plots.

![Fig. 6](image2.png) Variation of (a) Voltage vs time and (b) impedance components vs time.

0.761 V to 0.692 V) or 10.7% 100 h⁻¹ was observed. During the last stage of electrolysis mode over 60 h (from 291 h to 361 h) at −0.6 A cm⁻², the voltage increased 97 mV (from 1.282 V to 1.379 V), which corresponds to a degradation of 12.6% 100 h⁻¹.

Fig. 6 (b) shows the EIS measurements recorded throughout the galvanostatic tests at OCV. The \( R_0 \) increased 0.066 \( \Omega \) cm⁻² (from 0.231 to 0.297 \( \Omega \) cm⁻²), 0.059 \( \Omega \) cm⁻² (from 0.319 to 0.378 \( \Omega \) cm⁻²), and −0.004 \( \Omega \) cm⁻² (from 0.386 to 0.382 \( \Omega \) cm⁻²), respectively for the three steps in the corresponding tested mode in Fig. 6 (a), with the corresponding degradation rate being 13.87%, 21.8% and −1.7% per 100 h, respectively. The whole \( R_0 \) degradation rate was 18.6%.

\[ R_p \] increased for 0.131 \( \Omega \) cm⁻² (from 0.199 to 0.330 \( \Omega \) cm⁻²), 0.011 \( \Omega \) cm⁻² (from 1.024 to 1.035 \( \Omega \) cm⁻²), and 0.07 \( \Omega \) cm⁻² (from 0.282 to 0.352 \( \Omega \) cm⁻²), respectively, with the corresponding degradation rate being 31.9%, 1.2% and 41.3% per 100 h, respectively.

In order to understand the reason of degradation, we compared the SEM image of the electrodes before and after the durability test. As is shown in Fig. 7, the left pictures (a1, b1, c1, and d1) show the microstructure of electrodes before the test, while right pictures (a2, b2, c2, and d2) show those after the test. Obvious sintering phenomena are observed for both the hydrogen electrode and the oxygen electrode. Although the

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Fig. 7 – SEM images of the cell before and after the stability test: (a1)Ni-LSGM (b1)Ni particles (c1)SBSC-LSGM (d1)SBSC particles; (a2)Ni-LSGM (b2)Ni particles (c2)SBSC-LSGM (d2) SBSC particles.

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active substances keep close contact to the LSGM skeleton, they form relatively dense layers to cover the LSGM particles. Densification of the active layers would reduce the triple phase boundary; some cracks also appear on the SBSC layer in picture c2. The structure change can explain the increase of both $R_0$ and $R_p$ in Fig. 6. A nature material paper from Christopher Graves et al. reported that degradation of SOEC can be reduced by repeating shift operations between SOFC and SOEC mode, [2] and the result is observed for the cells of the type Ni–YSZ | YSZ | LSGM–YSZ. But in our case, different result is obtained due to the difference in degradation mechanism.

For further work, it seems that main effort should be paid to prevent the sintering of the infiltrated particles, especially for SBSC.

**Conclusions**

We have developed two-electrode-supported LT-SOC with the structure “Ni-SDC infiltrated porous LSGM | dense LSGM | SBSC infiltrated porous LSGM”. Excellent performance is shown for both SOFC and SOEC mode. However, a short-term test runs over 206 h in EC mode (0.6 A cm$^{-2}$, 85 h in FC mode (0.4 A cm$^{-2}$) and then 60 h in EC mode (0.6 A cm$^{-2}$) showed a quite fast degradation due to sintering of both Ni and SBSC particles.

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