INFLUENCE OF INTERFACIAL REACTION ON ELECTRODE PERFORMANCE AND OHMIC LOSSES

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ABSTRACT

The performance of a Sr- and Mg- doped lanthanum gallate (LSGM) electrolyte based solid oxide fuel cell is greatly affected by the interfacial reaction of electrode material with the LSGM electrolyte. The reactivity is closely related to the electrode composition and the sintering temperature. The ohmic loss is a good indicator of the reactivity (i.e., an overly-high and unequal ohmic loss between the anodic and the cathodic). The interfacial reaction also interferes with the measurement of the electrode overpotential. Care should be taken in the interpretation of measured electrode overpotentials if an interfacial reaction occurs in the cell.

INTRODUCTION

The interfacial reaction between electrolyte and electrode is closely related to the composition and morphology of the electrode starting material and electrode sintering conditions. It also plays an important role in electrode performance of solid oxide fuel cells. In searching for high performance electrodes in LSGM-based solid oxide fuel cells (1-4), we studied NiO-Sm0.2Ce0.8O1.9 (samaria-doped ceria, SDC) anodes and La0.6Sr0.4CoO3 cathodes by using starting powders prepared by spray pyrolysis (5,6). We found that ohmic losses of both NiO-SDC anode and La0.6Sr0.4CoO3 cathode increased with increase in sintering temperatures. The reaction between LSGM and NiO has already taken place at 1150°C. The reaction product could cause a complete performance loss of a NiO-LSGM anode screen printed on LSGM electrolyte when the anode was sintered at 1350°C. The LSGM shows a relatively low reactivity with Fe2O3 in comparison with Co oxide or Ni oxide. Fe2O3 mixed with 40 vol% LSGM powder as an anode starting material sintered at 1150°C demonstrates the highest initial performance (7).

In this study, we present some results related to interaction problem by changing sintering temperature and starting materials. We also report that electrode overpotential is influenced by ohmic losses. Since measured electrode overpotential (or electrochemical polarization) is generally used as a criterion in the evaluation of electrode material and fabrication conditions, care should be taken in its interpretation when electrode/electrolyte interfacial reaction occurs.
EXPERIMENTAL

Powder Preparation

Electrode powders of NiO-SDC and La$_{0.6}$Sr$_{0.4}$CoO$_3$ were prepared by aerosol spray pyrolysis method (abbreviated as sp). A detailed description of the sp preparation method is given elsewhere (5,6). We also used commercial powders of Fe$_2$O$_3$, Co$_2$O$_3$ and NiO mixed with either La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.8}$ (abbreviated as LSGM) or SDC prepared by solid state reaction method (subscripted as sr). The LSGM (sr) powder was used for the preparation of the LSGM electrolyte. Table 1 lists the chemical composition and the preparation conditions of the electrode powders and the electrolyte. The conductivity of the LSGM electrolyte at 800°C was 0.1193 S cm$^{-1}$ as measured by DC 4-probe method.

Table 1. Chemical composition and the preparation conditions of both the electrode powders and the electrolyte.

| Material  | Composition           | Preparation condition | Properties                        |
|-----------|-----------------------|-----------------------|------------------------------------|
| Cathode   | La$_{0.6}$Sr$_{0.4}$CoO$_3$ | sp method, after 24h calcination | Sphere-particle, particle size: ~1 μm in diam. |
|           | Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ | sr method, 1100°C x 10h, ball milling 24 h | Polyangular-particle, particle size: ~2 μm |
| Anode     | NiO-SDC (Ni=50vol.%) SDC= (SmO$_{1.3}$)$_{0.2}$(CeO$_2$)$_{0.8}$ | sp method, after 24h calcination | Sphere-particle, SDC sub-particles anchored on NiO core; particle size: ~1 μm in diam |
|           | NiO                   | commercially          | Particle size: ~0.8 μm |
|           | Fe$_2$O$_3$            | commercially          | Particle size: ~1 μm |
|           | Co$_2$O$_3$            | commercially          | Particle size: ~1 μm |
|           | SDC                   | sr method, 1350°C x 10h, ball milling 24 h | Particle size: 1-3 μm |
| Electrolyte| La$_{0.6}$Sr$_{0.4}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.8}$ | sr method, 1150°C x 10h, ball milling 24h, pellets:1500°C x 10h | Yellow-Brown, Perovskite-structure 0.1193 S cm$^{-1}$ (800°C) |

Single Cell Construction

An anode-electrolyte-cathode assembly was prepared on a LSGM electrolyte of 13 mm in diameter and 500 μm (or 800 μm) in thickness by screen printing, followed by sintering at a selected temperature. In order to measure the electrode polarization, a piece of platinum wire (0.3 mm in diam.) was wound around the LSGM electrolyte pellet, fixed with platinum paste, and sintered at 800°C in air for 2 hours. A soft glass ring was used as a sealing gasket to avoid the leakage of reactant gases. The assembled cell was placed in the hot zone of a vertical furnace. Air was supplied directly to the cathode side at a flow rate of 50 ml/min, while water-moistened (at 25°C) H$_2$ was fed to the anode side at the same flow rate. Pure Ar gas was used as purge gas during the startup and shutdown of the cell. Pt reference electrode was operated in pure Ar atmosphere during the test.

A steady-state polarization using the current interrupt method was implemented to investigate the cell performance and electrode polarization properties. The width of the current-off pulse applied from HC 111 current pulse generator (Hokuto Denko Ltd.) was
1.3 ms and the resulting potential responses were recorded with 54201 digitizing storage oscilloscope (Hewlett-packard) at a time display of 200 μs. The applied current was accurately monitored by 3457A ammeter (Hewlett-packard). The resistance or conductivity of the LSGM electrolytes, under the operating condition of the fuel cell, was evaluated from the ohmic drop measured in the current interruption.

RESULTS AND DISCUSSION

Influence of Electrode Sintering Temperature (Ts) on Cell Performance

Cell performance is evaluated by cell terminal voltage ($V$) or power density ($PD$) vs. the operating current density ($i$), i.e., $i-V$ or $i-PD$ curve. This could be expressed by

$$V = V_{oc} - Pa - Pc$$

or

$$PD = iV$$

where $V_{oc}$ is the open circuit voltage (about 1.090V under the tested condition of 800°C). $Pa$ stands for the anode polarization, $Pc$ for the cathode polarization.

Fig. 1 shows the $i-V$ along with $i-Pa$ and $i-Pc$ curves of the La$_{0.6}$Sr$_{0.4}$CoO$_3$ (sp) cathodes sintered at 1000°C on 500 μm-thick LSGM electrolytes coupled with NiO-SDC (sp) anode sintered at 1250°C. It can be seen that the $Pa$ and $Pc$ almost linearly increased with increasing current density ($i$) in the range of $i$ as high as 700 mA cm$^{-2}$ at 800°C; and $Pa$ is higher than $Pc$.

![Graph showing $i-V$, $i-Pa$ and $i-Pc$ curves](image)

Figure 1. $i-V$, $i-Pa$ and $i-Pc$ curves of the La$_{0.6}$Sr$_{0.4}$CoO$_3$ (sp) cathodes sintered at 1000°C on 500 μm-thick LSGM electrolytes coupled with NiO-SDC (sp) anode sintered at 1250°C.

Fig. 2 gives the influence of sintering temperatures of the anode and the cathode on the maximum power densities ($PD_{max}$) of the cells tested at 800°C. It is obvious that both

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anode sintering temperature $T_s(a)$ and cathode sintering temperature $T_s(c)$ have a great influence on $PD_{max}$ values. The cathode sintered at 1000°C appears to have the best performance, while the anode sintered at 1250°C seems optimum. The highest performance is obtained in this cell, i.e., $PD_{max} = 0.485$ W cm$^{-2}$, corresponding to about 72% theoretical value (0.670 W cm$^{-2}$).

Figure 2. Influence of sintering temperatures of the anode and the cathode on the maximum power densities ($PD_{max}$) of the cells tested at 800°C.

**Ohmic Loss and Electrode Polarization**

Cell performance loss comes from electrode polarization and ohmic loss of the electrolyte. According to our cell configuration, three kinds of ohmic loss could be measured by current interruption method, i.e., the ohmic loss between anode and the reference electrode (called as anodic ohmic loss, $iR_a$), the ohmic loss between cathode and the reference electrode (called as cathodic ohmic loss, $iR_c$), and the ohmic loss of the electrolyte (called as total ohmic loss, $iR_t$). The measured $iR_t$ values are equal to the sum of $iR_a$ and $iR_c$, i.e.,

$$iR_t = iR_a + iR_c \text{ or } Rt = Ra + Rc$$

[3]

The electrode polarization can be expressed by

for anode, $Pa = \eta_a + iR_a$ \hspace{1cm} [4]

for cathode, $Pc = \eta_c + iR_c$ \hspace{1cm} [5]

where $\eta_a$ and $\eta_c$ represents anode overpotential and cathode overpotential, respectively. $i$ is the applied current density; $R$ is the ohmic resistance; subscripts of $t, a$ and $c$ mean the total, the anode and the cathode, respectively. To minimize the possible discrepancy in the measurement at one specified current density, we use the polarization resistance, $Rp$, to make a comparison.
Table 2. Influence of cathode sintering temperatures ($T_s(c)$) on the ohmic resistance and polarization resistance.

| $T_s(c)$ / °C | $R_a$ $\Omega$ cm$^{-2}$ | $R_c$ $\Omega$ cm$^{-2}$ | $R_p(a)$ $\Omega$ cm$^{-2}$ | $R_p(c)$ $\Omega$ cm$^{-2}$ | $R_t$ $\Omega$ cm$^{-2}$ | $R_c/R_t$ | $R_p(t)$ $\Omega$ cm$^{-2}$ | $R_t + R_p(t)$ $\Omega$ cm$^{-2}$ |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------|-----------------|-----------------|
| 950          | 0.3846          | 0.1468          | 0.1475          | 0.1842          | 0.5114          | 0.2870    | 0.3317          | 0.8431          |
| 1000         | 0.3560          | 0.1471          | 0.1002          | 0.1457          | 0.5031          | 0.2944    | 0.246           | 0.7367          |
| 1050         | 0.2913          | 0.1493          | 0.1541          | 0.181           | 0.4406          | 0.3388    | 0.3201          | 0.7556          |
| 1200         | 0.3196          | 0.2316          | 0.2056          | 0.3386          | 0.6582          | 0.4201    | 0.5442          | 1.1807          |

Table 2 lists the ohmic resistance and polarization resistance of La$_{0.6}$Sr$_{0.4}$CoO$_3$ (sp) cathodes sintered at different sintering temperatures on 0.500 mm thick LSGM electrolytes coupled with NiO-SDC (sp) anode sintered at 1300°C. The cells were tested at 800°C. The cathode ohmic resistance, $R_c$, gradually increased with increase in the cathode sintering temperature, $T_s(c)$, whereas, $R_p(c)$ values show a minimum at $T_s(c)=1000°C$. The lowest $R_p(c)$ at $T_s(c)=1000°C$ is supported by the optimized microstructure of the cathode, i.e., well-bonded La$_{0.6}$Sr$_{0.4}$CoO$_3$ (sp) particles in the cathode intimately sintered on LSGM electrolyte still in a small grain size and at a high porosity (4).

Table 3. Influence of anode sintering temperatures ($T_s(a)$) on the ohmic resistance and polarization resistance.

| $T_s(a)$ / °C | $R_a$ $\Omega$ cm$^{-2}$ | $R_c$ $\Omega$ cm$^{-2}$ | $R_p(a)$ $\Omega$ cm$^{-2}$ | $R_p(c)$ $\Omega$ cm$^{-2}$ | $R_t$ $\Omega$ cm$^{-2}$ | $R_a/R_t$ | $R_p(t)$ $\Omega$ cm$^{-2}$ | $R_t + R_p(t)$ $\Omega$ cm$^{-2}$ |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------|-----------------|-----------------|
| 1200         | 0.2497          | 0.2241          | 0.203           | 0.0859          | 0.4738          | 0.5270    | 0.2889          | 0.7636          |
| 1250         | 0.2851          | 0.152           | 0.1331          | 0.1128          | 0.4371          | 0.6522    | 0.2459          | 0.683           |
| 1300         | 0.3560          | 0.14715         | 0.1002          | 0.1457          | 0.4562          | 0.7055    | 0.246           | 0.7367          |
| 1350         | 2.7796          | 0.167           | 0.5905          | 0.0257          | 2.9468          | 0.9433    | 0.6162          | 3.5628          |

Similarly, Table 3 presents the anode polarization resistance and ohmic resistance of NiO-SDC (sp) as anode sintered at temperatures of 1200, 1250, 1300, and 1350°C on the 0.500 mm-thick LSGM electrolyte coupled with La$_{0.6}$Sr$_{0.4}$CoO$_3$ (sp) cathode sintered at 1000°C, tested at 800°C. It can be seen that $R_a$ increases relatively fast with increasing $T_s(a)$ and takes the main responsibility for the cell performance loss at the higher $T_s(a)$. Due to the rapid $R_a$ increase, although the $R_p(a)$ shows the lowest value at 1300°C, the total anode polarization resistance ($R_p(a)+R_a=0.4562\Omega$ cm$^{-2}$) is higher than that of the anode sintered at 1250°C (viz., 0.4182$\Omega$ cm$^{-2}$). Similar to the cathode case, the change of $R_p(a)$ values with $T_s(a)$ can be explained as that with the increase in the sintering temperature $T_s(a)$, the sintering of electrode particles first leads to optimize electrode morphology with good particle connection and high porosity, then leads to a decrease in anode porosity and reaction area (1).
Ohmic Losses as an Indicator of Interface Reaction

The total ohmic resistance \((R_t)\) of the LSGM electrolyte of 0.500 mm thickness and 0.1193 S cm\(^{-1}\) electric conductivity should be about 0.419 \(\Omega\) cm\(^2\) if the sum of electrode layer resistance and the electrode/LSGM electrolyte interface resistance is negligible for both the anode and the cathode. However, \(R_t\) values in Tables 2 and 3 are certainly higher than 0.419 \(\Omega\) cm\(^2\). The increments of ohmic resistance are attributable to the interaction between the electrode and the LSGM electrolyte.

Generally, interaction between the electrode and electrolyte is detrimental to the ionic and/or electric conductivity at this interface region, and results in an increase in ohmic resistance. We have verified the formation of new phase, like doped-LiNiO\(_2\) in the hexagonal structure (1,3), with very low conductivity in the 1150°C co-fired powder mixture of NiO and LSGM; and also observed Ni diffusion into LSGM electrolyte at the anode side. The \(R_a\) in Table 3 shows that the interfacial reaction of NiO-SDC anode with LSGM electrolyte is favoured by increasing \(T_s(a)\). Sharp increases in both \(R_a\) and \(R_p(a)\) are observed when \(T_s(a)\) is higher than 1300°C. Meanwhile, the cathode also follows a similar pattern (see Table 2). Cobalt diffusion from the 1000°C-sintered cathode into the LSGM electrolyte was observed to reach the depth of about 3 micrometers along the cathode/LSGM interface by EDAX analysis.

Among the tested cells, \(P_a\) value is higher than \(P_c\) value, except in the cell of \(T_s(c)=1200^\circ\text{C}\) (see Table 2). It is easy to understand from Tables 2 and 3, that the main reason for \(P_a>P_c\) is because \(R_a\) is higher than \(R_c\). As a consequence, it can be proposed that the interface reaction between NiO-SDC anode and LSGM is the main cause of the cell performance loss under the tested conditions. It is necessary to control \(T_s\) at a possible low level in electrode preparation.

From Tables 2 and 3, the counter electrodes also show the variation both in polarization resistance and in ohmic resistance with the different \(T_s\), although they are prepared under the same conditions. We could not simply attribute the discrepancy to the different test. In fact, there is some correlation with the studied electrode. We calculate the ratio of \(R_a\) (or \(R_c\)) to \(R_t\) to limit the possible influence of the variation of different tests. The calculated \(R_c/R_t\) in Table 2 and \(R_a/R_t\) in Table 3 show a clear dependence on the sintering temperatures, \(i.e.,\) the interface reaction. When the asymmetric interfacial reaction takes place, the ratio of either the \(R_c/R_t\) or \(R_a/R_t\) will definitely increase.

Effects of Electrode Materials

Table 4 gives the results of three kinds of anode materials, \(v.i.z.,\) NiO, Fe\(_2\)O\(_3\) or Co\(_2\)O\(_3\), each oxide mixed with 40 vol% LSGM (sr) and sintered at 1150°C for 2 h on 0.800 mm thick LSGM electrolyte coupled with Sm\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\) (sr) cathode sintered at 1000°C for 4 h. It is obvious that the cell with Fe\(_2\)O\(_3\) anode is the best one, and the total ohmic resistance \((R_t)\) in this cell almost equals the calculated value based on the conductivity of LSGM. In their XRD patterns before the cell test, the LSGM peak was found enlarged at the (110) plane and changed greatly in the cases of Co\(_2\)O\(_3\) and NiO as anodes. While in the case of Fe\(_2\)O\(_3\) anode no obvious change happened to this LSGM intrinsic peak. This result suggests that the cell performance loss should be attributed to the reactivity between the electrode and LSGM electrolyte.
Table 4. Influence of different anode materials on cell performance.

| Anode Composition          | Operation Condition | Performance Parameters |
|----------------------------|---------------------|------------------------|
| cathode SmSrCoO₃ (sr)      | Toper. (°C) 900     |
| anode NiO, Fe₂O₃ or Co₂O₃ + 40 vol% LSGM(sr) | I (mA cm⁻²) 300 |

Effects of Electrode Powder Morphology

To understand the influence of starting powder morphology, we tested the NiO-SDC anode prepared from the powder mixture of NiO (commercially) and SDC (sr) at the same NiO:SDC ratio as NiO-SDC(sp) powder. The result is shown in Table 5. The \( iRa \) value in NiO-SDC (sp) anode is much lower than that in the NiO-SDC (sr) anode, which exhibits the advantage of using spray pyrolysis NiO-SDC powder as the anode material for the LSGM-based cell. SEM observation revealed that the NiO-SDC(sp) starting powder was in an almost perfect spherical shape about 1 μm in diameter, each agglomerated particle consisting of smaller particles, where the NiO particles are mostly closed and surrounded with dense shells of smaller SDC particles. In the case of NiO-SDC(sr) starting powder, NiO particle and SDC particle were separated from each other.

Table 5. Difference in cell performance by using Ni-SDC(sp) and Ni-SDC(sr) as anode materials.

| Anode       | LSGM Electrolyte | \( iRa \) mV | \( iRc \) mV | \( iRt \) mV | \( iRa/iRt \) mV | \( \eta_{ra} \) mV | \( \eta_{rc} \) mV | \( V_{cell} \) MV |
|-------------|------------------|--------------|--------------|--------------|-----------------|----------------|----------------|-----------------|
| Ni-SDC(sp)  | 0.500 mm         | 86           | 45.8         | 131.8        | 0.653           | 43             | 34.9           | 885             |
| Ni-SDC(sr)  | 0.510 mm         | 329          | 37           | 366          | 0.889           | 129            | -14            | 611             |

To alleviate the reactivity problem, Goodenough et al. (8) applied a SDC interlayer between Ni-based anode and LSGM electrolyte, and found this interlayer is quite effective to support their cell with high performance and long-term stability. The advantage of this kind of cell configuration may lie in the different reactivity behaviors among LSGM-NiO, LSGM-SDC and SDC-NiO. It is reported that NiO has much lower reactivity with SDC than with LSGM, even though the reactivity between LSGM and SDC could cause a decrease in conductivity of both LSGM electrolyte and SDC electrolyte (4). As a whole, the decrease in conductivity of LSGM-SDC is not crucial when the thickness of this interlayer is only few micrometers. Therefore, the advantage of NiO-SDC(sp) powder probably arises from the effective blockage of the SDC shell which prevents direct contact and reaction of NiO particles with the LSGM electrolyte.

Interpretation of Measured Ohmic Resistance and Electrode Overpotential

From Tables 4 and 5, it can be seen that the cathode performance measurement is influenced by the anode reactivity with LSGM electrolyte. The cathode overpotential (\( \eta_{ra} \)) measured by current interruption method often appears unbelievably low or even minus in the cells of high \( Ra \) value. The most probable explanation is that the effective reaction area in the anode substantially decreased by the interfacial reaction. As a result, the
applied current was not uniformly distributed inside the LSGM electrolyte between the anode and the cathode.

Based on theoretical calculations by Svensson et al (9), the measured electrode overpotential or polarization resistance can deviate significantly from the true value, if the electrolyte is thin and its conductivity is low, the electrodes are not symmetrically placed on the surface of the electrolyte and electrode kinetics is fast. Since a deviation could be caused by the interface reaction between electrode and electrolyte, i.e., by a non-uniform current distribution at the electrode, care should be taken in the interpretation of measured electrode overpotentials in a cell with electrode/electrolyte interfacial reaction.

CONCLUSIONS

The performance of an LSGM-based SOFC is greatly affected by the reactivity of electrode material with the LSGM electrolyte. The reactivity between the electrode and the LSGM electrolyte is closely related with the sintering temperature, the composition, and the morphology of electrode starting powder. It is found that the ohmic loss is a good indicator of the reactivity (viz., an overly-high and unequal ohmic loss between the anodic and the cathodic), and the measured electrode overpotential will be influenced by the reactivity as well. Care should be taken in the interpretation of measured electrode overpotentials for a cell with electrode/electrolyte interfacial reaction.

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