

Passivation and Activation of SOFC Nanostructured Cathodes

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For a solid oxide fuel cell, performance is largely determined by the cathode properties, particularly at low operating temperatures (<700°C). Extensive cathode studies have made great strides in reducing the polarization resistance (R_p) in many systems. This has led to reduction of fuel cell operating temperature to allow use of stainless steel as interconnect, and thus reduce cost. However, our studies showed a significant increase of R_p over time when samples were kept at low temperature and open circuit voltage. We have systematically investigated these passivation phenomena in LaSrMnO₃, LaSrCoFeO₃ and BaSrCoFeO₃ systems. On the other hand, R_p was reduced significantly by a high temperature annealing, close to the initial value and sometimes series resistance (R_s) could be recovered completely. Cation diffusion and defect disordering are considered to be the main contributors to passivation and activation.

Introduction

Reduction of the operation temperature in an SOFC system is vitally important in reducing cost of, which is necessary for commercialization of this technology. This is particularly true for small stacks for distributed combined heat and power system. Mass production of units requires cheap material components. Keeping the performance, i.e. the same power density at a lower temperature as it was with previous cells at higher temperatures, calls for reduced resistive losses both from electrolyte and electrodes. Reducing the electrolyte thickness is one way to decrease the resistance from electrolyte (1); another is to use other electrolytes with higher ionic conductivity than yttria stabilized zirconia (YSZ) such as Ce_{1-x}Gd_xO₂ (CGO) (2), La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85} (LSGM) (3) or Zr_{1-x}Sc_xO₂ (1). There are problems associated with Ce_{1-x}Gd_xO₂ and LSGM such as electronic conductivity in reducing atmosphere for Ce_{1-x}Gd_xO₂ (2), and reaction with electrodes for LSGM (4). Thus, zirconia based electrolytes are still preferred by most SOFC developers.

Many studies show that cathode polarization is the major contribution to the total loss in a cell. High percentage losses come from the cathode when the operation temperature is in the range of 500-700°C. There are good examples for (La_{1-x}Sr_x)_yMnO₃ (LSM) composite cathode developments, which have led to good electric performance of the anode supported cells operating at 750°C (5-7). In recent years, studies of the (La,Sr)(Co,Fe)O₃ (LSCF) have been popular in cathode research toward to intermediate

temperatures (8-14). By making the composite $(\text{La}_{0.6}\text{Sr}_{0.4})_{1-x}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ cathodes, we have achieved R_p of $0.19 \Omega\text{cm}^2$ at 600°C and $0.026 \Omega\text{cm}^2$ at 700°C on the CGO electrolyte (14). Recently, Shao and Haile measured remarkably low polarization resistances in the cathode of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) on 15 mol% samaria-doped ceria (SDC) which were $0.055\text{-}0.071 \Omega\text{cm}^2$ at 600°C (15). However, our studies have shown a significant increase of R_p over time when the samples were kept at low temperature and open circuit voltage. In this work, these passivation phenomena were systematically investigated in LSM, LSCF and BSCF systems. A short high temperature treatment was found to reduce the R_p significantly and some times recover the R_s completely. Gerischer type impedance was used to analyze such passivation and activation phenomena. Such passivation and activation phenomena are discussed and explained.

Experimental

Symmetric electrode cells were prepared to study the electrochemical properties of the LSM/YSZ on YSZ, LSCF/CGO on YSZ, and BSCF/CGO composite cathodes on CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$) electrolyte. Electrolyte substrates in $5\times 5 \text{ cm}^2$ size were produced using tape casting. The thickness was approximately $200 \mu\text{m}$. The cathode specifications of LSM and LSCF and processing parameters can be found in references 7 and 14, respectively. For the BSCF system, cathodes were made using the composition 50wt% $(\text{Ba}_{0.5}\text{Sr}_{0.5})_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($x=0.05$ and 0.1) + 50wt% CGO. Cathode material $(\text{Ba}_{0.5}\text{Sr}_{0.5})_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ was made by Glycine-Nitrate method. The raw powders were calcined at 850°C for 2 hours. The symmetric samples were made by spraying composite cathode slurry on both sides of the electrolyte. The slurry consisted of cathode powder, binder, dispersant and organic solvent. After spraying all symmetric cells were sintered at 850°C to 1200°C for 2 hours. The cathode thickness is $10\text{-}20 \mu\text{m}$ after sintering. In the final preparation step the samples were cut into approximately $0.4\times 0.4 \text{ cm}^2$ from the $5\times 5 \text{ cm}^2$ plates and then randomly selected for the impedance measurement. The samples were coated with Pt-paste for current collector purpose before the samples were put into a furnace for impedance measurements. The measurement temperatures ranged from 500 to 800°C . Our test rig has 4 positions for sample testing at the same temperature which allows us to know the reliability of our results based on 4 samples at each of the experimental conditions. Electrochemical measurements were performed on these symmetric cells using a Solartron 1260 frequency response analyzer. The impedance spectra were obtained at the open circuit voltage (OCV) in a frequency range of 0.1 Hz - 1 MHz . The R_p and R_s were extracted from the spectra using EQUIVCRT. The microstructures of the symmetric cells were examined by a low-vacuum scanning electron microscope (Jeol LV5310). Because most samples were sintered at low temperature $<1000^\circ\text{C}$, the grain size is around 200 nanometers with size distributed from 50 to 500 nanometers.

Results and Discussion

For the study of a LSM/YSZ composite cathode, $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_3/8\text{YSZ}$ on 8YSZ electrolyte was used. Figure 1 shows the increase of R_p over time for this system when the samples were kept at 650°C and open circuit voltage. From 120 hours to 480 hours, the R_p increased almost 50%. After annealing at 850°C for 24 hours, the R_p was

reduced almost to its original value. The fact that the loss of performance was recoverable means that it was not caused by sintering or chemical reaction of the components.

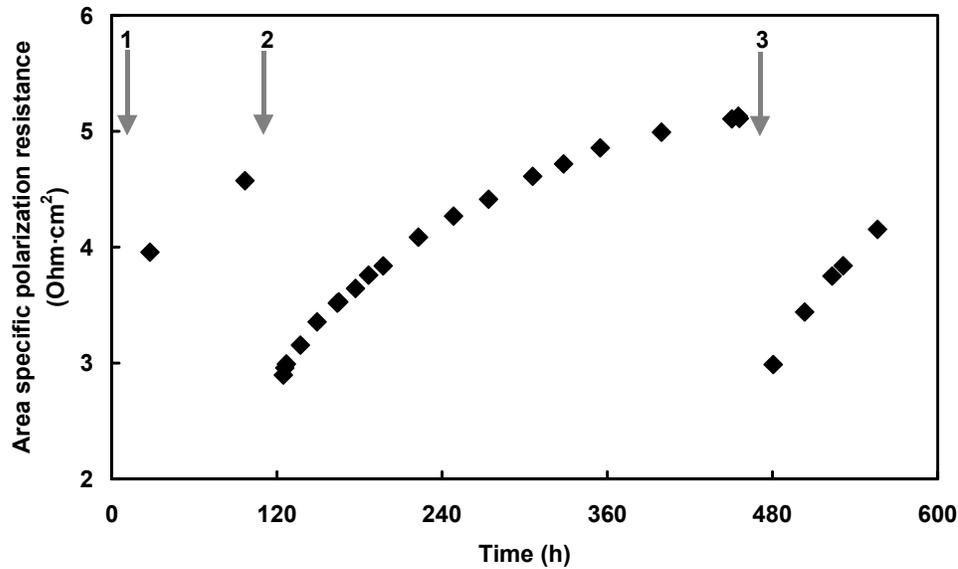


Figure 1. Area specific polarization resistance at 650°C for a composite $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_3/8\text{YSZ}$ cathode versus time after equilibration for 24 hours, indicated by the arrows, at higher temperatures (arrow 1 : 750°C; arrows 2 and 3: 850°C).

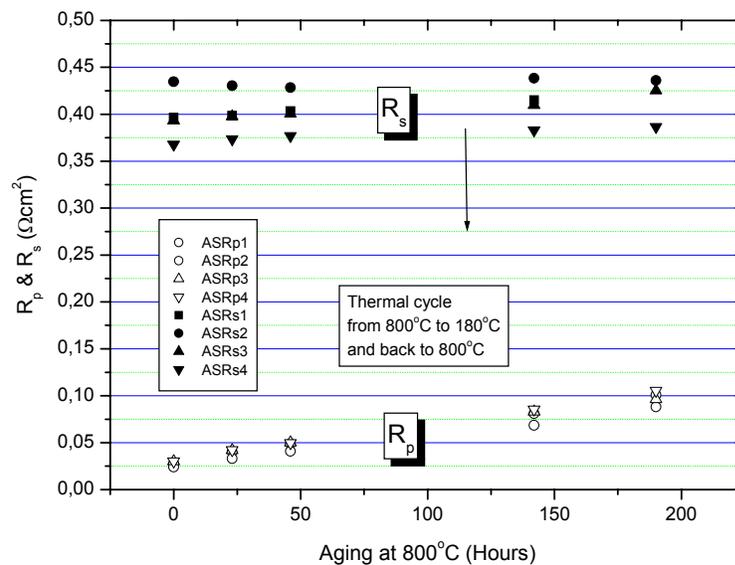


Figure 2. R_p and R_s versus time when symmetric samples of LSCF/CGO on CGO were kept at 800°C.

Regarding LSCF/CGO on YSZ, a reaction between LSCF and YSZ was deduced from the impedance measurements according to the previous work published by Chen, et al. (16). The values of R_p and R_s increased rapidly at 800°C for only a few hours in their experiment and were interpreted as suggesting a chemical reaction between LSCF and YSZ. However, our results show modest increase of the R_p and no obvious increase of R_s as shown in Figure 2. This suggests that the increase of the cathode polarization resistance is not due to a reaction between cathode and electrolyte. Our SEM observation did not show any reaction products originating from a reaction between LSCF and YSZ after 180 hours test at 800°C. This phenomenon is now considered to be a kind of passivation.

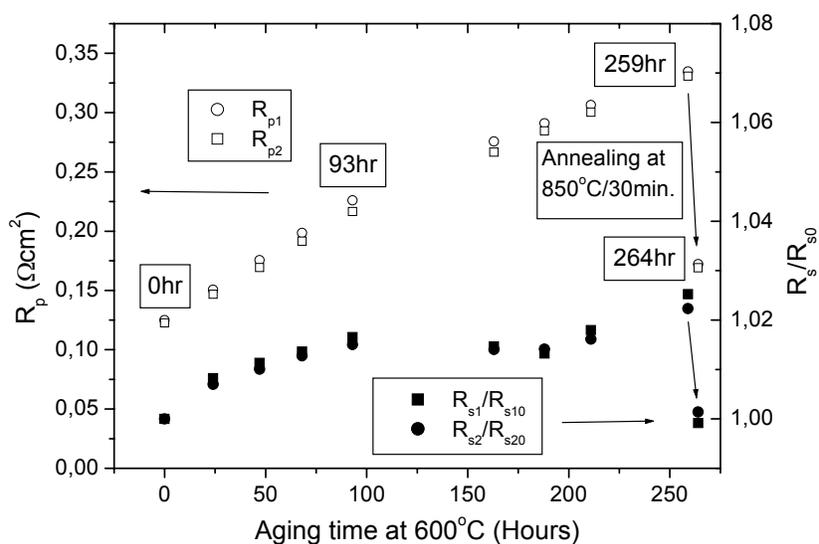


Figure 3. R_p and R_s/R_{s0} as a function of aging time at 600°C for $BS_{0.95}CF$ cathode. R_{s0} is R_s at 0 hour. The indicated black squares refer to the impedance spectra shown in Figure 4.

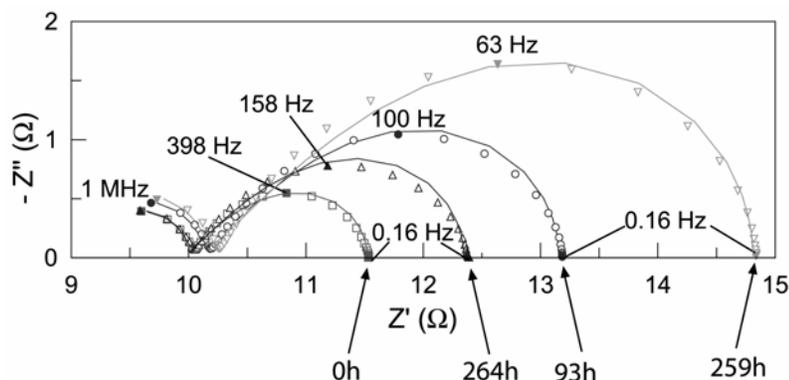


Figure 4. Impedance spectra at 600°C and OCV on cathode $BS_{0.95}CF$. The closed symbols present the summit, start and end frequencies.

Long term stability has been found to be a severe problem when the samples were kept at a low temperature, i.e. <700°C; therefore we have made a detailed study on BSCF system. Annealing at 600°C was examined with samples of BS0.95CF/CGO, and results are shown in Figures 3 and 4. Within almost 250 hours, the R_p increased significantly from 0.12 to 0.33 Ωcm^2 , while the R_s increased only as little as 2 %. We have reported the similar phenomenon in a $(\text{La}_{0.6}\text{Sr}_{0.4})_{1-x}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathode (14). We attributed such R_p increases to the cathode sintering in that paper. However, the degradation mechanism looks much more complicated. Significant increase of R_p accompanied with no or a slight change of R_s in an isothermal annealing was also observed in an LSM cathode (17).

In order to find whether such changes are irreversible, a heat treatment at high temperature was applied to activate the cathode. The samples were annealed at 850°C for 30 minutes, and then cooled down to 600°C, and the area specific resistances were measured again. The R_p values had decreased from 0.33 to 0.17 Ωcm^2 , while the R_s values were reduced to original start value. There are many reports about electrochemical activation by cathodic dc bias (12,18). Impedance spectra are shown in Figure 4 for one of the BSCF samples. The spectra show two arcs. The high frequency arc of the impedances spectra did not change much and may be attributed to electrolyte grain boundary or measurement equipment errors due to very high frequency of up to 10^6 Hz. However, the low frequency arc did change significantly. The summit frequency increased from 398 Hz to 63 Hz after aging at 600°C for 11 days.

Impedance spectra recorded on composite cathode electrodes are typically modeled by a Gerischer element (19-21). The impedance response from a Gerischer element can be written as

$$Z_{\text{Ge}} = \frac{Z_0}{\sqrt{k + j\omega}} \quad (1)$$

where Z_0 is a resistance and k is a rate constant. The impedance spectra in Figure 4 were modeled by an equivalent circuit shown in Figure 5. R_s is the electrolyte series resistance. R_1 is a resistance and C_1 is a capacitance. (R_1C_1) models the high frequency arc. The low frequency arc is modeled by the Gerischer element GE_2 . The lines in figure 4 are least square fits using the model in Figure 5.

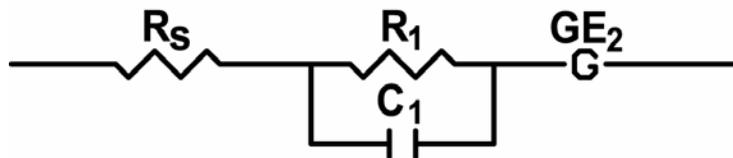


Figure 5. Equivalent circuit model used to fit the impedance spectra.

For each spectrum in Figure 4, the element values are shown in Table I.

Table I. Natural logarithm to parameter change.

0 h	R_s : 9.2 Ωcm^2	R_1 : 0.75 Ωcm^2	C_1 : 0.19 $\square\text{F}$	Z_0 : 53 \square	k : 1100 s^{-1}
93 h	0.00	0.20	-0.27	-0.03	-1.41
259 h	-0.01	0.30	-0.50	0.14	-1.92
264 h	0.00	0.03	-0.01	-0.14	-1.13

E.g. values for R_s is given as $\ln\{R_s/R_s(0\text{h})\}$

For a composite electrode the Gerischer impedance can be interpreted as (22)

$$Z_{Ge} = \frac{\sqrt{r_s/c_p}}{\sqrt{(r_p c_p)^{-1} + j\omega}} \quad (2)$$

where r_s are the area specific ionic resistance (O^{2-} in CGO) + electronic resistance (e^- in BSCF) per unit length perpendicular to the electrolyte surface in the electrode. c_p is the double layer capacitance at the two phase boundary and r_p is the ion transfer resistance at the TPB. Both c_p and r_p are volume specific with respect to the BSCF/CGO electrode. From Table 1 it is seen that Z_0 is virtually constant throughout the test, compared with the changes of $k = (r_p c_p)^{-1}$. This indicates that only r_p , the resistance associated with the reaction at the TPB, changed when the electrode passivated. Otherwise r_s and c_p should be proportional, which is unlikely. The fact that r_s is constant indicates that the CGO network structure in the composite cathode does not change when the electrode passivates. This would also be very unlikely, since the electrode can be reactivated by annealing, as discussed below.

Figure 6 shows long term test on the samples with cathode composition of BS0.9CF at 700°C. Similar to as Figure 3, the R_p increased significantly and R_s only increased slightly. R_p decreased when the atmosphere was changed from air to oxygen at around 400 hours. A large drop of R_p happened when the sample was heat treated at 850°C for 30 minutes. We observed the R_p gradually moved back to the value at the start before high temperature treatment and to an even higher value. R_s showed similar tendency, but on a much smaller scale. This could be repeated as shown in the Figure 6. At 1100 hours, we repeated the treatment and it showed similar recovery and deterioration. The recoveries became less complete. We could not see the saturation of the R_p at even 1600 hours. The R_p of 0.2 Ωcm^2 at that time was a factor of 10 higher than the initial value of 0.02 Ωcm^2 .

It is complicated to explain the mechanism of the passivation and activation phenomena. Here we try to make some discussions. At the beginning when we cool the sample from high temperature to low temperature, for example from 850°C to 650°C, the sample state in terms of oxygen vacancies content, disorder and mobility may be kept at least partially on the level of the equilibrium at the high temperature. This will keep a high oxygen exchange rate at the active three phase boundary. Such effect may be

significant particularly for nano-structured cathode that was produced at relative low sintering temperature. Because nano-sized three phase boundary has short pass ways for oxygen ion movement and diffusion. During measurement of R_p , the sample is not completely at equilibrium, and R_p is lower than the equilibrium value. During the dwell period, the cation may diffuse and defect ordering takes place, and by this the oxide vacancies are immobilized, which in turn decreases the oxygen exchange rate. This seems to be consistent with the time constant of the change, and with the fact that a short heat treatment at a higher temperature restores the initial defect disorder (sets the oxide vacancies free) reducing the R_p .

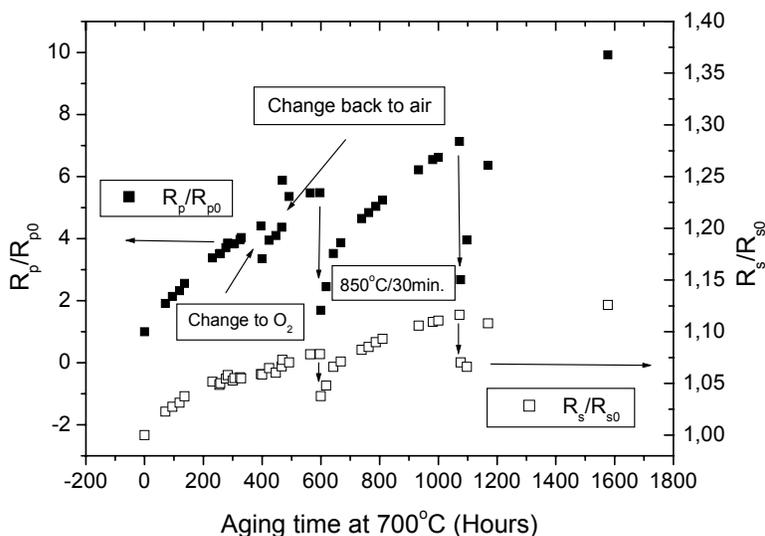


Figure 6. Normalized R_p and R_s as a function of time at 700°C for $BS_{0.9}CF$ cathode.

It is important to understand the passivation and activation phenomena when we want to lower the operating temperature. It is also important in guiding the process of electrode optimization. Experiments that will give some further indications of the detailed nature of the passivation problem are needed, e.g. more measurements on samples under current.

Summary

We have investigated the passivation phenomena in LSM, LSCF and BSCF systems. For example, one set of the samples from the $(Ba_{0.5}Sr_{0.5})_{0.95}Co_{0.8}Fe_{0.2}O_3$ system showed that R_p increased nearly 3 times from 0.12 to 0.33 Ωcm^2 after 10 days at 600°C, while R_s of the same symmetric cell only increased 2.5 % from 1.53 to 1.57 Ωcm^2 . Further, an increased temperature of 850°C for 30 minutes reduced the R_p at 600°C to 0.17 Ωcm^2 and R_s back to 1.53 Ωcm^2 . A Gerischer type impedance was used to analyze such passivation and activation phenomena. It indicates a significant reduction of the activity at the active three phase boundary length during passivation. On the other hand, short high temperature heat treatment may help adhesion between cathode and electrolyte as illustrated by the R_s decrease and may be partly responsible for the activation. A short heat treatment at a higher temperature restore the initial defect disorder (sets the oxide

vacancies free) and keeps this state for some time at the low temperature and may lead to increased oxygen exchange and therefore activation. Cation diffusion is necessary for the ordering at low temperature.

Acknowledgments

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