INVESTIGATION OF LSM CATHODE ACTIVATION UNDER POLARIZATION

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ABSTRACT

The activation of \((\text{La}_{0.98}\text{Sr}_{0.02})\text{MnO}_3\) cathodes on thick 8YSZ wafers was studied by galvanostatic current interruption. The activation phenomenon leading to a 10-fold decrease in the oxygen reduction overpotential was observed to be reversible at 800°C. This contradicts previous explanations based on non-reversible processes.

INTRODUCTION

Strontium-doped lanthanum manganese oxide \((\text{La}_{1-x}\text{Sr}_x\text{MnO}_3)\) is the common cathode material for high temperature solid oxide fuel cells (SOFCs). During the first 4-6 h of operation under cathodic polarization, the overpotential at the cathode-electrolyte interface decreases dramatically. This effect has been observed by other research groups (1-4). Despite the number of studies of this phenomenon, no consistent explanation or interpretation has emerged. The change in the triple phase boundary length (3, 5), the creation of oxygen ion vacancies at the LSM surface (1), the change of surface composition of the LSM grains (2), and the elimination of inhibiting phases nucleated during fabrication coupled with Mn diffusion into the electrolyte (4) have all been suggested as possible causes. The importance of the phenomenon is that it leads to a 10-fold decrease in cathodic overpotential with time. Its peculiarity is that the time constant of the change is on the order of hours under current bias. Although this phenomenon has been studied previously, our experimental set up allows an original approach to the problem which leads to the elimination of some assumptions. This paper focuses on our experimental procedure, the analysis of our results of the cathode activation phenomenon and a discussion of the explanations previously published.

EXPERIMENTAL PROCEDURE

Galvanostatic Current Interruption (GCI) and Electrochemical Impedance Spectroscopy (EIS)

It is well established that electrochemical impedance spectroscopy (EIS) is an extremely powerful experimental technique for studying electrode behavior as it allows resolution of individual processes at individual electrodes with very minimal perturbation (6) provided that a well placed reference electrode is used (4).
Galvanostatic current interruption (GCI) presents the advantage of versatility. A sampling time less than 200 microseconds allows one to separate ohmic losses from electrochemical process losses (overpotentials), through an electrode-electrolyte interface. With a current interruption transient close to microsecond, the spectral resolution of GCI is equivalent to a ~1 MHz to 0 Hz impedance response, well within the range of what is generally used for EIS measurements.

GCI does not compete with EIS in process resolution as a single 200 microsecond sampling presents a much greater noise than an EIS frequency sweep and therefore the extraction of time constants from a GCI transient is not practical. However GCI allows one to extract the ohmic losses from the rest of the reference to working electrode potential difference in an extremely short sampling time, whereas the same information is held in the intercept of high frequency and low frequency response in EIS.

GCI, coupled with a computerized monitoring of the overpotential and dynamic control of the current bias allows performing experiments at constant overpotential and therefore characterizing processes eventually driven by the potential “step” at the cathode-electrolyte interface.

**Sample Geometry and Reference Electrode Placement**

When using pellet electrolytes, it has been shown that the choice of electrolyte thickness and working to reference electrode distance is of paramount importance for proper interpretation of results for EIS studies (7, 8) as working to counter electrode cannot be perfectly aligned, leading to discrepancies in the observed overpotentials.

Following previously published modeling of geometric requirements for reference electrode placement (8), it is possible to evaluate the experimental error associated with our sample geometry. The maximum observed misalignment of counter and working electrode on our cells was of the order of 100 µm and the resulting uncertainty on the observed overpotential is therefore less than +/-5%.

**Test Description**

Our experimental testing was applied in one of three modes:

**Cathode activation under constant current.** GCI is used to monitor the overpotential with time under a constant current bias.
Cathode activation under constant overpotential. GCI is used to monitor the overpotential at a higher sampling rate, and the applied current load is constantly adjusted to maintain a constant overpotential with time.

Cathode relaxation. No current is applied. Every 10 to 30 minutes, a constant current is applied for 5 seconds and GCI is performed to extract the overpotential value.

This allows monitoring of the reversing transient of the cathode with time after polarization either at constant current or constant potential.

Cathode Fabrication

The test cathodes were fabricated by screen printing 3 layers of LSM slurry with a drying step at 300°C for 10 minutes after each. Sintering was done at 1200°C for 1 h in air. The resulting porous cathode was approximately 15 microns thick as shown on figure 2.

Pt paste screen printed and cured at 850°C comprised the current collector, counter electrode and reference electrode. All contacts were through a Pt mesh and 0.5 mm diameter shielded Pt wires.

Table 1. Screen printing slurry composition.

| Component                  | Amount   |
|----------------------------|----------|
| (La₀.₈Sr₂)₀.₀₉MnO₃ powder  | 25.000g  |
| (4.13 m²/g, Praxair)       |          |
| Carbon                     | 1.350g   |
| Binder                     | 28.580g  |
| Terpineol                  | 200 drops|

Figure 2. SEM observation of the YSZ-LSM-Pt cross section.

EXPERIMENTAL RESULTS AND DISCUSSION

Overpotential Stabilization in Galvanostatic Operation

It was found that the cathodic overpotential decrease from 680 mV to less than 100 mV under polarization at 714 mA/cm² current density. This behavior has been observed in other studies. Upon relaxation, the overpotential returned to more than 90% of its original value. It can be seen in figure 3 that the first activation cycle ends with a small increase in the overpotential, which is believed to be due to other degradation mechanisms. If so, the activation-relaxation feature could be considered 100% reversible. This contradicts some previous reports (9) and the disagreement may be explained by the need for the cathode...
to be maintained at 800°C for more than a 100 h to observe the reversibility, which would not have likely been done if monitoring of the overpotential during relaxation was not possible at the same time.

This presents a clear contradiction with all explanations previously given involving non-reversible changes. Indeed, a change in the triple phase morphology does not seem to be a possible explanation as it would lead to a permanent change of the cathode catalytic activity. Furthermore, the migration of Mn ions through the electrolyte driven by a chemical potential gradient is not reversible and hence would not provide a satisfactory reason for the catalytic activity change. It is very unlikely that the formation and elimination of La2Zr2O7 at the LSM-YSZ interface would be reversible at 800°C, as the interface is supposed to be stable under no polarization at that temperature. Although the elimination of the La2Zr2O7 phase during the first cycle may constitute the initial non-reversible part of the signal, the proportion of active sites poisoned by the presence of La2Zr2O7 would also have to be close to 90% to explain such a dramatic change in the catalytic activity upon polarization, which is not what is experimentally observed with our LSM composition and a 1200°C sintering temperature (4).

The time scale of an overall experiment prevents one from comparing the constant current polarization transients. Figure 4 shows a comparison of the three activation cycles. The overpotential change has been normalized for greater clarity. It is clear that the first activation presents a different behavior than subsequent ones. If we attribute the initial difference to permanent changes within the cathode this is another possible explanation for the difference between first and subsequent cycles. Similarly the cathode relaxation kinetics are different between first and subsequent cycles (Figure 5).

Since porous platinum is used as a current collector layer, the influence of platinum on the electrochemical behavior of the cathode was also verified. A pure platinum electrode was characterized and showed a greater overpotential than our LSM cathode. Furthermore, no activation/relaxation behavior was observed for the pure platinum cathode.
Figure 4. Normalized change of the overpotential under constant current (714 mA/cm²) at 800°C in air. The actual starting and finishing overpotential values are given in figure 3.

![Normalized change of the overpotential](image)

**Figure 5.** Cathode overpotential during relaxation when the current is off and the cell maintained at 800°C after complete activation.

**Constant Overpotential Experiment**

In this type of experiment, the overpotential was maintained constant by continually readjusting the current bias and measuring the resulting overpotential by current interruption. This experiment differs from a classic potentiostatic experiment as the overpotential and not the overall working to counter electrode potential is maintained constant. Figure 6 shows the resulting change in area specific resistance of the cathode under a constant overpotential of 160 mV. Since this is the overpotential ultimately reached under constant current (cycle 2 and 3), the same final activated state is expected to be achieved.

![Cathode overpotential during relaxation](image)
The degree of activation of the cathode under constant overpotential was consistently lower than the galvanostatic one. This is a clear indication that the change is driven by the overpotential across the interface and not by the passage of the current or an eventual local heating of the triple phase boundary. Indeed in the galvanostatic mode the driving force would be always greater than 160 mV and would reach the equilibrium activated state relatively fast, whereas in the constant overpotential mode, the driving force would become infinitely small as the cathode approached its equilibrium activated state, therefore greatly increasing the time to recover complete activation.

It was not possible to assign a simple linear or parabolic law to the relaxation or constant overpotential activation kinetics, contrarily to previous results (1). Therefore it is not possible to decide between the diffusive or non-diffusive nature of the change occurring within the cathode under polarization. Furthermore, since a linear relation between the cathode physical change and its increase in catalytic activity is very unlikely, even if the process was diffusion controlled, there would be little chance that the resulting change in overpotential with time follows a parabolic law.

A current induced change hypothesis is refuted by our study of the temperature change of the cathode with current bias (figure 7). A 5 degree rise was observed in the first 100 s of the tests. This is in the same range as what was observed in previous studies (10). It is unlikely that such a temperature rise could lead to a dramatic morphology change of the triple phase boundary. It is also important to note that to accurately measure the temperature dependant catalytic activity of the cathode under a current bias, it is necessary to reach thermal equilibrium within the cell before taking a measurement.

**Current Voltage Characteristic of the Cathode**

Our cathode was characterized in the 0 to 1000 mA/cm² and 550°C to 800°C range and compared to other published LSM catalytic activities (figure 8). For each point, the overpotential stability with time was verified. Our results are consistently below those found elsewhere (11-14). This could be explained by the fact that for each point enough time was given for the activation process to be completed before taking the measurement.
Figure 7. Temperature rise of the cathode measured by a thermocouple in direct contact with the current collection layer. The bias is applied at $t = 0$.

Figure 8. Current-voltage characteristics of the cathode. The derived area specific resistance is close to 0.2 $\Omega \cdot cm^2$ at 800°C and 1 A/cm².

Figure 9. Comparison of the present study with previously published results.
as well as by our use of a Pt current collector rather than a thick porous LSM layer. Figure 9 provides a comparison of the studied cathode to equivalent ones found in the literature.

CONCLUSIONS

The activation of a classical LSM cathode under polarization was studied using a galvanostatic current interruption technique. The major conclusion of this work is that the activation of the LSM cathode under polarization is reversible. This leads us to conclude that the change must be either the destruction of an inhibiting layer at the grain surface (2) or the formation of surface oxygen vacancies upon polarization (1). Although the bulk ionic conductivity of LSM is rather poor, its catalytic activity, including adsorption and charge transfer abilities would evidently be influenced by a change in surface composition. It is clear that the long term stability of the observed overvoltages must be monitored when characterizing SOFC cathodes as the potential drop at the interface itself can induce changes in the cathode properties and the current bias across the interface can induce local heating resulting in a significant cathode temperature increase.

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