

NaCl Effect on SOFC Cathode

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Abstract—The fact that NaCl in air has induced degradation of cathode has been investigated for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF). Cell performance was measured by volatilizing NaCl into the air supplied to the cathode at a constant current density of 200 mA cm^{-2} up to 100 h. At 800 °C, an exposure to 30 ppm NaCl caused negligible degradation of LSCF cathode at least for 100 h, yet degradation became obvious with increasing NaCl concentration. Slight change in the composition of the cathode materials was observed which may lead to the gradual degradation of cell performance. In addition, cell performance degradation was compared between 700 °C to 900 °C, being poisoned by 30 ppm NaCl. The LSCF cathode showed slightly poor tolerance of NaCl at 700 °C due to the decomposition of the cathode material. The long-term influence of NaCl on cathode performance should be done to clarify.

Keywords-fuel cell, NaCl, cathode.

I INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) are considered to be a promising power generation system due to their potential advantages with respect to high energy conversion efficiency, environmental compatibility and/or multi-fuel capability. Its high-temperature operation (500°C~1000°C), however, makes it necessary to use heat-resistant materials and to take longer time for start and stop process in power generation than lower temperature operation. Disadvantages such as chemical instability between different components of cells and sintering of electrode materials may appear, and cell performance degradation during a long-range operation would become one of the most important technological issues.

As the technology is developing towards commercialization, it is necessary to consider the operating environments in which SOFC will be used. Ambient air will be supplied as oxidant in the real application of SOFCs. The ambient air may contain various impurities, which may affect performance or durability of fuel cells. Such impurities may come from vehicles and industry exhausts, dust from human life, natural contaminants etc.

Improvement of long-term durability is one of the major issues towards SOFCs commercialization. Various degradation mechanisms, however, may appear such as chemical instability between different components of cells

and sintering of electrode materials especially during a long-range operation at high temperatures. These degradations mainly come from several sources as follows:

1. Fuel contamination sources (Anode): One overwhelming advantage of SOFC (and MCFC) over the other types of fuel cells lies in the possibility of internal reforming, which means that it is possible to use practical hydrocarbon fuels ((e.g., natural gas, liquefied petroleum gas (LPG), kerosene, coal-derived syngas, biogas, alcohol, gasoline etc.) Yet problem arises consequently: minor constituents involved in these fuels can cause fatal degradation of cell performance or affect overall SOFC system durability. Researchers have detected anode performance degradation by such impurities as H_2S etc. [1] and the chemical degradation phenomena of Ni-based anode materials in his doctoral dissertation [2].

2. System: In addition to the fuel contaminants mentioned above, some trace amounts of system components can also cause fuel cell degradation, for example, inlet/outlet manifold, thermal insulating materials, metallic gas supply pipes, sealing gasket and so on. It is well known that typical stainless steel (e.g. SUS 430) contains a small amount of S, P, Si. Some researchers have reported the chromium diffusing from alloy separator to cathode and leading to cathode degradation [3]. Furthermore, several impurities such as Na and Si in cells were detected after several thousand-hour operations in real SOFC stacks, whose sources are considered to be system components exposed at high temperatures for long periods of time [4, 5].

3. Air contamination sources (Cathode).

Air is the most practical and economical oxidant to feed the fuel cell stack. However, air pollutants, namely nitro oxides (NO_x , including NO and NO_2), sulfur oxides (SO_x , including SO_2 and SO_3), carbon dioxide (CO_2), ozone and other organic chemical species (such as benzoic compounds) contaminate the fuel cell, resulting in possible performance degradation [6, 7].

Already, air pollution is a major issue in an increasing number of megacities around the world, and new policies to address urban air pollution are likely to be enacted in many developing countries irrespective of the participation of these countries in any explicit future climate policies.

It is necessary to clarify the influence of these trace impurities and to propose the strategies in impurity-tolerant SOFC materials selection considering these latent threatening for SOFC performance and durability. Yet although the contamination effects of trace impurities in air on SOFC performance have been substantially investigated, the corresponding contamination mechanisms are not well understood, mainly due the lower priority of contamination problems in fuel cell R&D[8], and also partially due to the complexity of the contamination processes. The complexity may arise from the following reasons: (1) cathode reaction is complex and predominating parameters remain unclear;(2) the influence of crystal/surface structure on electrochemical reactions has not yet been clarified; (3) quantitative relationship between factors, such as temperature, electrochemical reaction rate, degradation rate has not been clarified; (4) difference between short-term and long-term of reaction and degradation mechanisms in SOFC cathodes have not yet been clarified [9].

The scope of this paper is on the chemical degradation of SOFC cathodes induced by typical contaminants in the ambient air (such as NaCl), including fundamental degradation mechanisms and concentration threshold. The work has been completed by the measurement of cell performance and long-term durability to clarify the degradation behaviour as well as the observation and analysis on the changes in microstructure and composition of cathode materials to clarify the poisoning mechanisms of each contaminant. These could offer valuable information to overview chemical degradations from the system viewpoint and could develop strategy to realize durable SOFCs.

II EXPERIMENTAL

LSCF cathode was used as the cathode of electrolyte-supported cell in this study. The photograph of anode and cathode side of a single cell is shown in Figure 1.

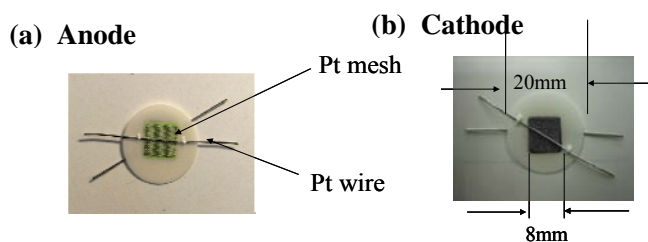


Figure 1. Photograph of single cell of (a) Anode; (b) Cathode.

The preparation of electrode materials and experimental procedures were described as follows. Anode powders were prepared by mixing NiO (>99.9%) and ScSZ with a specific ratio in ethanol via ball-milling for 24 hours. The use of ScSZ in the cermet anode can enhance electrochemical performance since ScSZ has rather higher ionic conductivity (ScSZ: 2.5×10^{-1} S/cm, YSZ: 1.0×10^{-1} S/cm at 1000°C). After drying the resulting suspension, anode pastes were prepared by blending the anode powders with organic binders (α -terpineol mixed with ethylcellulose) and then homogenized using three-roller grinding mills. Anode layers were screen-printed on ScSZ electrolyte plates with a

thickness of 200 μm and a diameter of 20 mm, followed by sintering in air at 1300°C for 3 hours. The anode layer is composed of two layers: the weight ratio of the first layer as a functional layer and the second layer mainly as a current collector as well as a reforming catalyst layer. The mask with a thickness of 30 μm for screen printing and a commercially available kit was modified in our laboratory as a screen printer in this study.

For the LSCF cathode, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (GDC) (>99.9%) layer was firstly screen-printed on the counter side of the ScSZ electrolyte plate as a protecting layer, followed by sintering in air at 1300°C for 3 hours with the counter Ni-ScSZ anode. It is noted that the thickness of the GDC layer is ca. 5 μm , ensuring its lower ohmic loss. Because GDC has a higher ionic conductivity while its electronic conductivity is low. Consequently $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) (>99.9%) powder was used for the LSCF cathode and screen-printed on the GDC layer, followed by sintering at 900 °C for 5 hours in air. For the simplicity of the cathode structure and interfacial ohmic loss, only one layer of LSCF was used as the functional layer.

After cell was heated up to the operating temperature by an electric furnace, 3 vol% humidified H_2 and air were supplied to the anode and the cathode, respectively, for about 1 hour. The gas flow rates were set to be 150 cc/ min by mass flow controllers. Subsequently, I-V characteristics were measured and then cell voltages were measured at a constant current density of 200 mAcm^{-2} for at least 1 hour to ensure the stabilization of cell performance before the NaCl poisoning tests.

For supplying sodium chloride to the cathode gas, NaCl (s) powder was volatilized by another electric furnace at predetermined temperatures, as schematically shown in Figure 2.

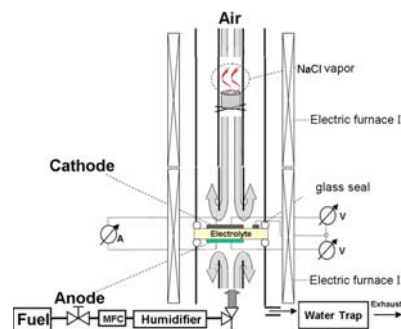


Figure 2. Experimental setup for NaCl poisoning tests.

The concentration of NaCl in the “poisoned” air was estimated by a thermogravimetry (TG) simulating the cell operating conditions. The weight change of NaCl at 700 °C for 100 h was shown in Figure 3 and the concentration of NaCl in the air was calculated from this result. Note that the actual concentration of NaCl in air near coastal regions is ca. 1 ppm, which varies according to e.g. the wind speed. In this study 30 ppm and 600 ppm NaCl(g) were supplied to the cathode to investigate whether the poisoning effect could be accelerated at 800 °C. Change in the cell performance at a constant current density of 200 mAcm^{-2}

was measured for 100 h between 700 °C and 900 °C to clarify the influence of operating temperature. During experiments, cathode-side IR loss and cathodic polarization were simultaneously measured by the current interruption method to specify the major contribution in cell degradation.

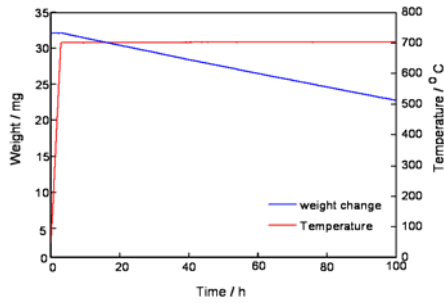


Figure 3. Weight change of NaCl powder measured by the thermogravimetry in air.

III RESULTS AND DISCUSSION

Influence of 30 ppm NaCl in air on the cell voltage with the LSCF cathode measured at different operating temperatures is shown in Figure 4. For the case of 900 °C, cell voltage dropped by ca. 5 mV within 100 hours. The cell voltage drop increased to ca. 40 mV at 800 °C and 70 mV at 700 °C, which means that the poisoning effect by NaCl on the cell performance increases with decreasing temperature. In addition, the performance degradation mainly came from cathode-side IR loss.

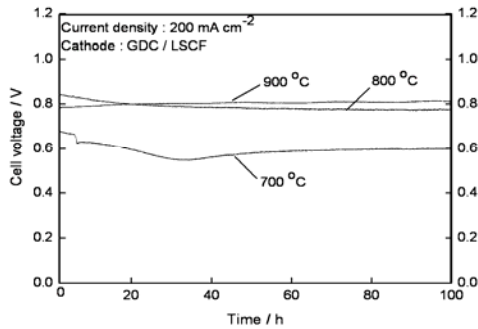


Figure 4. Influence of 30 ppm NaCl in air on the cell performance with the LSCF cathode at different temperatures at the constant current density of 200 mA cm⁻² up for 100 h.

From the FESEM images of the LSCF surface with and without NaCl poisoning at different temperatures shown in Fig.5, change in cathode morphology was observed that is the particle condensed slightly after being poisoned by NaCl, compared to the one without poisoning.

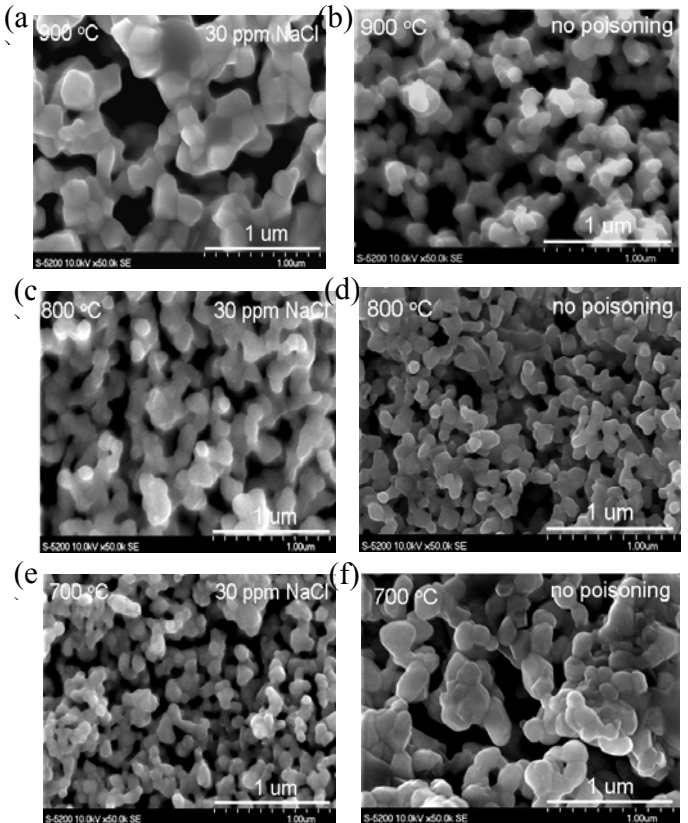


Figure 5. FESEM images of the surface of the LSCF cathode after the galvanostatic measurements with and without NaCl poisoning at different temperatures.

For the case of 600 ppm NaCl poisoning on the LSCF cathode, the rate of cell voltage drop by 600 ppm NaCl was nearly the same as 30 ppm NaCl at 800 °C, as shown in Figure 6. In addition there was no difference in cathode-side IR loss and cathodic polarization between the two cases.

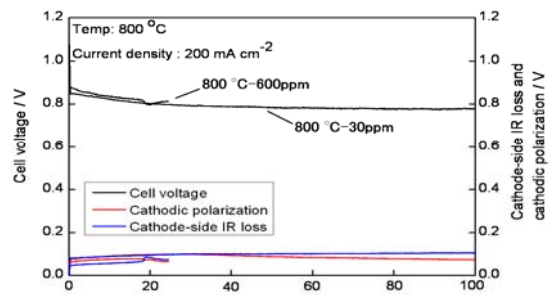


Figure 6. Influence of NaCl on the cell performance with the LSCF cathode at the current density of 200 mA cm⁻² up to 24 h at 800 °C.

IV CONCLUSIONS

In NaCl poisoning effect on the the LSCF cathode may come from partial substitution of Sr²⁺ with Na⁺ accompanied by the formation of SrO, and nonnegligible

effect appeared at 700 °C for the LSCF cathode. In addition, the formation of SrO exhibited dependency on NaCl concentration. The fact implied that the accelerated degradation may appear after long-term operations. On the other hand, the dependency of NaCl concentration on cell performance was weak for the cathode, LSCF, at 800 °C conducted by short-term experiments of 24 hours. Further study should be done to detect the longer term durability and clarify the overall mechanism of the NaCl poisoning effect.

V ACKNOWLEDGEMENTS

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