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Influence of water vapor on long-term performance and accelerated degradation of solid oxide fuel cell cathodes

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ABSTRACT

The influence of water vapor in the air on the performance and durability of solid oxide fuel cell (SOFC) has been investigated for the-state-of-the-art cathodes, $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF). Durability experiments were carried out at 800 °C up to 1000 h with various water vapor containing-air fed to the cathode side. Both types of cathode materials were basically stable under typical water vapor concentrations in the ambient air. Degradations could be accelerated at much higher water vapor concentrations, which could be associated with the decomposition of the cathode materials. Temperature dependence of this degradation was analyzed between 700 °C and 900 °C under 10 vol% water vapor concentration, which showed that the effect of water vapor depends strongly on the temperature and led to a severe degradation at 700 °C within a short time period for both cathode materials.

1. Introduction

Solid oxide fuel cell (SOFC) is regarded as an energy device with several advantages, such as high electrical efficiencies, low-emission of SO_x and NO_x and possibility of internal reforming. SOFC is expected to be used as a practical energy system for co-generation, distributed power generation and transportation applications [1–3]. 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. Improvement of long-term stability of SOFC is one of the major issues of this technology and research efforts are being made to clarify the mechanisms of cell performance degradation and to improve durability effectively.

There are various impurities contained in the gas supplied to cells which could lower the SOFC performance. Influence of H_2S, which is a major impurity in hydrocarbon based fuels, on the anode performance has been discussed so far [4]. As for the cathode, humidification effect has been investigated and it was reported that nano-sized particles appeared between the LSM/YSZ interface [5]. Yet very limited information has been obtained about the influence of humidity, on the cathode performance especially with respect to the long-term durability of SOFCs.

Here we are focusing on the degradation by water vapor with respect to concentration and operating temperature, on the performance and durability of SOFC cathodes. Changes in electrode performance and cathode microstructure and composition by the effect was studied and analyzed to reveal the degradation mechanism of LSM and LSCF based cathodes.

2. Experimental procedures

Electrolyte-supported cells are used in this study. Electrolyte plates made of 10 mol% Sc_2O_3–1 mol% CeO_2–89 mol% ZrO_2 (abbreviated by ScSZ, Daiichi Kigenso Kagaku Kogyo) with the thickness of 200 μm were selected. Mixture of 56 wt% NiO and 44 wt% ScSZ was used for the anode material. The cathodes in this study had double layer structures. Mixture of $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM) (>99.9%, Praxair, CT, USA) and ScSZ with a weight ratio of 1:1 was applied as a functional layer (first layer), and coarse LSM powder (calcined at 1400 °C for 5 h and ball-milling 24 h) with the particle size of 10–20 μm was used as a current collecting layer (second layer) for LSM cathode. The anode and LSM cathode layers were screen-printed on the electrolyte plates followed by sintering at 1300 °C for 3 h and at 1200 °C for 5 h, respectively. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) (>99.9%, Praxair, CT, USA) was used for LSCF cathode and it was sintered at 900 °C on the $Ce_{0.9}Gd_{0.1}O_2$ (GDC) (>99.9%, Rhodia, Tokushima, Japan) layer which had been already sintered on the electrolyte plate at 1300 °C as a protecting layer. Electrode area was 8 mm × 8 mm and Pt mesh was used as the current collector.

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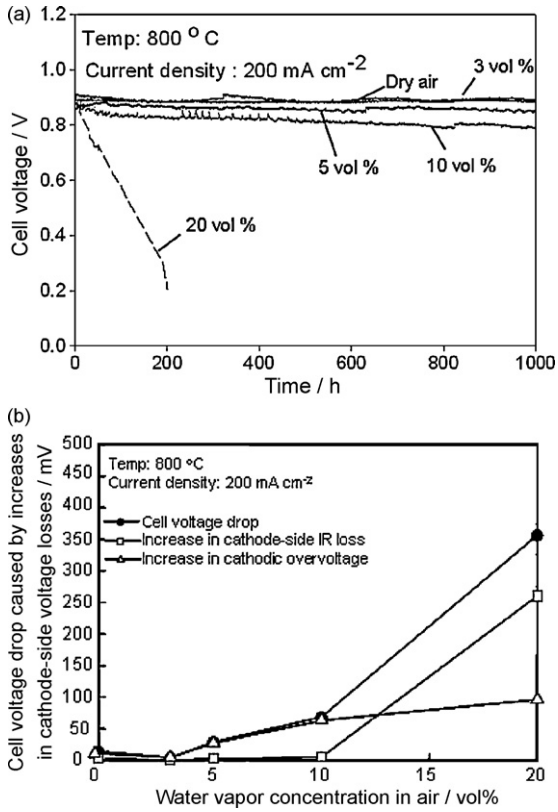

Fig. 1. (a) Cell voltage measured at 800 °C under the constant current density of 200 mA cm^{-2} showing the influence of water vapor in air on the performance of LSM cathode; (b) cell voltage drop, increase in cathode-side IR loss, and increase in cathodic overvoltage during 200 h.

For electrochemical characterizations, 3 vol% humidified H_2 was supplied to the Ni-ScSZ anode, and humidified air (3, 5, 10 and 20 vol%) was supplied to the cathode to clarify the dependence of cell durability on water vapor concentration. Note that the saturated concentration of water vapor at room temperature is ca. 3 vol% and these experiments at higher water vapor concentrations were conducted as acceleration tests to understand degradation phenomena. Cell voltages under open circuit condition and under a constant current density of 200 mA cm^{-2} were measured for 1000 h at 800 °C. In order to clarify the dependency of operating temperature on cell performance, experiments were conducted between 700 °C and 900 °C up to 200 h with 10 vol% humidified air supplied to the cathode. During experiments, cathode-side IR loss

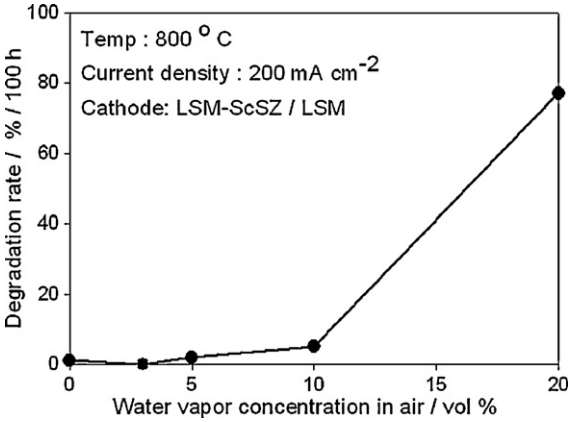

Fig. 2. Influence of water vapor in air on the degradation rate of the cell with LSM cathode within 200 h.

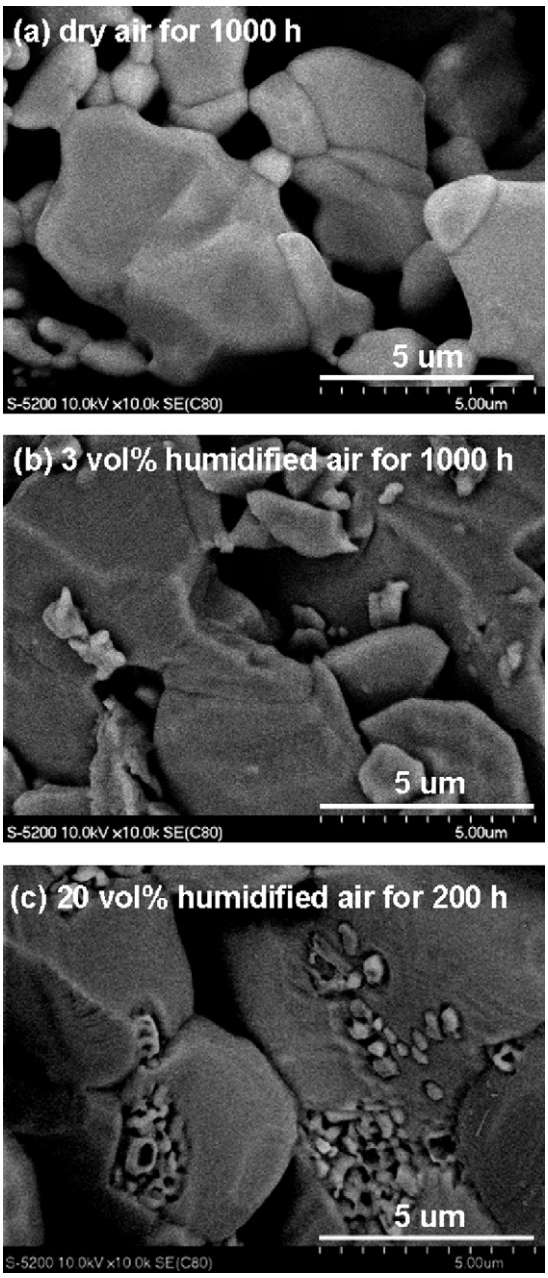

Fig. 3. FESEM images of LSM particles in the current collecting layer after operation in (a) dry air for 1000 h, (b) 3 vol% humidified air for 1000 h, and (c) 20 vol% humidified air for 200 h, at 800 °C.

and cathodic polarization were measured by the current interrupt method to detect the major origin of cell voltage degradation.

FESEM-EDX (Field Emission Scanning Electron Microscope-Energy Dispersive X-ray analysis, S-5200, Hitachi), STEM-EDX (Scanning Transmission Electron Microscope, HD-2300A, Hitachi) and X-ray diffraction (XRD with Cu Kα radiation) (Rigaku RINT Ultima III, Japan) were applied to investigate changes in cathode microstructure and composition after cell performance tests.

3. Results and discussion

3.1. Dependency of cell performance and durability on water vapor concentration

3.1.1. LSM cathode

Fig. 1 shows the influence of water vapor on cell performance with the LSM cathode. Dependency of cell voltage on water vapor