

Correlation between degradation of cathode performance and chromium concentration in (La,Sr)MnO₃ cathode

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ABSTRACT

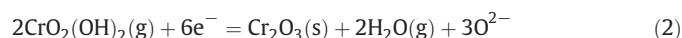
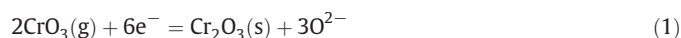
The relationship between the Chromium (Cr) concentration in the porous (La,Sr) MnO₃ (LSM) cathode and the polarization resistance was examined at accelerated Cr poisoning conditions. By supplying Cr vapor ($p(\text{Cr}) \sim 10^{-8}$ atm) to the porous LSM cathode the polarization resistances were increased significantly. Secondary ion mass spectrometry (SIMS) analysis of the LSM cathode suggested that an increase of Cr concentration levels both at the surface and at the triple phase boundary (TPBs) under polarization. The precise Cr concentration in the porous LSM cathode was successfully determined by SIMS to be in the orders of 0.0001–1 wt.% levels. The deposited Cr at the TPB effectively reduced the cathode performance under polarization; and the deposited Cr concentration at the TPB was above 1 wt.% in the Cr-poisoned cells. The polarization resistance increased with the Cr-concentration at the TPBs as well as at the cathode surface areas.

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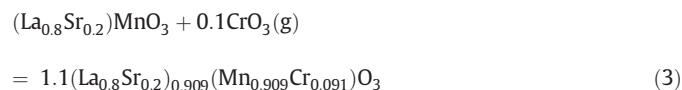
1. Introduction

Among the many degradation factors of Solid Oxide Fuel Cells (SOFCs), impurities in the air deteriorate the cathode performance in long-term operations. One of the critical issues is the Cr-poisoning, that is Cr deposition and reaction at active sites during cathodic reaction (oxygen reduction) [1–13]. Usually, metallic components in the SOFC stacks, such as interconnects, manifold, gas supply tubes, etc. can generate Cr vapors. Even though the vapor pressures of Cr (e.g. CrO₃(g) or Cr₂(OH)₂(g)) are lower than $p(\text{CrO}_3) = 10^{-8}$ atm at 1073 K [14–16], Cr can deposit and react at the active sites of the cathode, decreasing the cathode performance. So far, many studies have been made on the Cr-poisoning, and two important reaction mechanisms were considered: i) the Cr deposition at the gas/cathode/electrolyte interfaces (hereafter triple phase boundary, TPB), and ii) the chemical reaction of Cr on the cathode surface.

For the TPB mechanism, hexa-valence (Cr⁶⁺) chromium containing vapors are transported towards and deposited at the TPB induced by the chemical potential gradient of oxygen. The Cr⁶⁺ vapors can be reduced to Cr³⁺ to form Cr₂O₃ at the TPBs by the following reactions:



Another Cr-poisoning mechanism is the chemical reaction with cathode. Thermodynamic calculation has shown the chemical reactivity of different candidate materials with Cr [17]. In the case of La_{0.8}Sr_{0.2}MnO₃ (LSM), the chemical reactivity with Cr is small and SrCrO₄ formation has not been reported. However, there might be some substitution of Cr in the Mn-site of (La,Sr) MnO₃ found in the following equation according to the reference of [17]:



Although the above reaction is believed to occur at the LSM surface area, there are almost no reports on the formation of (La, Sr)(Mn,Cr)O₃. The determination of (La,Sr)(Mn,Cr)O₃ phase in the LaMnO₃ has proven to be difficult because of the similarity of perovskite structures and the small amounts of (La,Sr)(Mn,Cr)O₃ formation in the (La,Sr) MnO₃ cathodes. Instead of formation of (La,Sr)(Mn,Cr)O₃, (Mn, Cr)₃O₄ spinel formation was reported by some authors [3,9]. Needless to say, this reaction also decreases the cathode performance.

As it was said above, many reports proposed the reaction mechanism and possible reaction of Cr with (La,Sr) MnO₃ based cathode materials. To estimate the long-term durability of cathodes, it is important to know the relationship between the amounts of Cr in the cathodes and the performance of (La,Sr) MnO₃ based cathodes. Recently, an excellent study has been made on the relationship between the amounts of Cr

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deposited in the cell or in the stack [18] under several operating conditions. There was no clear correlation between the amounts of Cr and the cathode performance. The Cr deposition and decreasing in cathode performance seems to be difficult to correlate because of low Cr concentration inside the cathodes (lower than 0.1 wt.% = 1000 wt ppm level) and there is no information available on distribution of Cr in the depth direction. In order to overcome the difficulty in the detection limit of low Cr concentration and to clarify the amounts of Cr condensed in the cathodes, we have applied secondary ion mass spectrometry (SIMS) [19,20] after exposure to Cr vapors. Low concentration levels (lower than 0.1 wt.%) of Cr in the porous cathodes were successfully detected by the SIMS technique and corresponding distribution of Cr in the depth direction. In our previous report, the precise Cr concentration was not determined because of difficulty in the detection of Cr concentration arising from porous structures [20]. The purpose of this study is to clarify the relationship between the amounts of Cr deposition in the cathodes and the electrochemical performances of (La,Sr) MnO₃. For that purpose, intentionally Cr-added porous LSM standard was prepared and SIMS signal counts were measured at the same experimental condition. We report SIMS depth profiles with precise concentration and the distribution of Cr in the porous (La,Sr) MnO₃ cathode under cathodic polarization.

2. Experimental

2.1. Samples

The cathode materials examined were (La_{0.8}Sr_{0.2})_{0.95}MnO₃ (A-side deficient (La,Sr) MnO₃, hereafter denoted as LSM), purchased from Powlex Co. Japan. The X-ray diffraction patterns showed that the LSM powders were a single phase without any impurities (no XRD peaks other than LSM). As an electrolyte, Gd₂O₃ doped CeO₂ (Gd_{0.1}Cr_{0.9}O_{1.95} (GDC)) was adopted to avoid chemical reaction with cathodes. The GDC pellets were sintered at 1673 K for 5 h in the air to obtain the sintered dense pellets (20 mm in diameter and 1 mm in thickness). The LSM powders were screen printed on the GDC pellets, and fired at 1473 K. The geometric electrode area is 0.785 cm² and the thickness of porous cathode was 30–32 μm. The microstructures of cathodes have open pores for gas diffusion. The grain size of LSM is 1–2 μm in diameter. A rough estimation of the porosity from the SEM images gives about 55% of porosity in the LSM cathodes.

For the determination of Cr concentration in the porous LSM cathode, Cr₂O₃ was intentionally added to the LSM powders and then screen printed on the GDC. SIMS depth profiles were measured at the different Cr concentrations. The concentrations of Cr were 0.56 wt.%, 1.12 wt.%, and 2.21 wt.% (0.00125 mol%, 0.0025 mol%, and 0.005 mol%) in the LSM cathodes.

2.2. Cr poisoning under simulated fuel cell test conditions

Fig. 1 shows schematic diagram of Cr poisoning experiment under simulated cathodic polarization: oxidized Cr/Pt-mesh/cathode/GDC/Pt-paste-Pt-mesh. The cathode/GDC/Pt samples were set in the air atmosphere (air flow rate of 50 ml/min). The working electrode was porous LSM and the counter electrode was platinum paste electrode. The reference electrode was platinum on the side wall of the GDC sample pellet. A platinum mesh current collector was put on the porous cathode material surface. Pre-oxidized Cr metal (Cr₂O₃ formed on a Cr surface) was placed onto the Pt-mesh current collector to avoid direct contact between Cr₂O₃ and cathodes. In this way, only Cr vapors are supplied to the cathode surface. The test temperature was 1073 K for all the experiments. Air ($p(\text{O}_2) = 0.21$ atm) was humidified at 283 K (10 °C). At this experimental condition, the estimated Cr vapor pressure was $p(\text{CrO}_3) = 10^{-8}$ atm from the reference data (references of [14]–[16]).

The DC polarization and AC impedance were measured to estimate the electrochemical properties of cathode. The cathodic polarization was applied between the working electrode and the reference electrode. The set voltages were changed from –0.05 to –0.3 V versus the reference in an air atmosphere (no fuel flow condition). Under constant cathodic polarization, the polarization resistance was measured from the AC impedance arcs. The degradation of cathode performance was estimated from the increase of polarization resistances. The operation time was 50–300 h in air.

2.3. Post analysis of Cr distribution and concentration

After exposure to Cr vapors under cathodic polarization, the distributions and the concentration of Cr in the LSM cathodes were measured by SIMS depth analysis (Cameca/AMETEK ims-7f). The depth profiles of SIMS were measured by sputtering with an O₂⁺ primary beam. The secondary M⁺ ions were measured as a function of depth. The secondary ion intensity of each M⁺ was converted to the

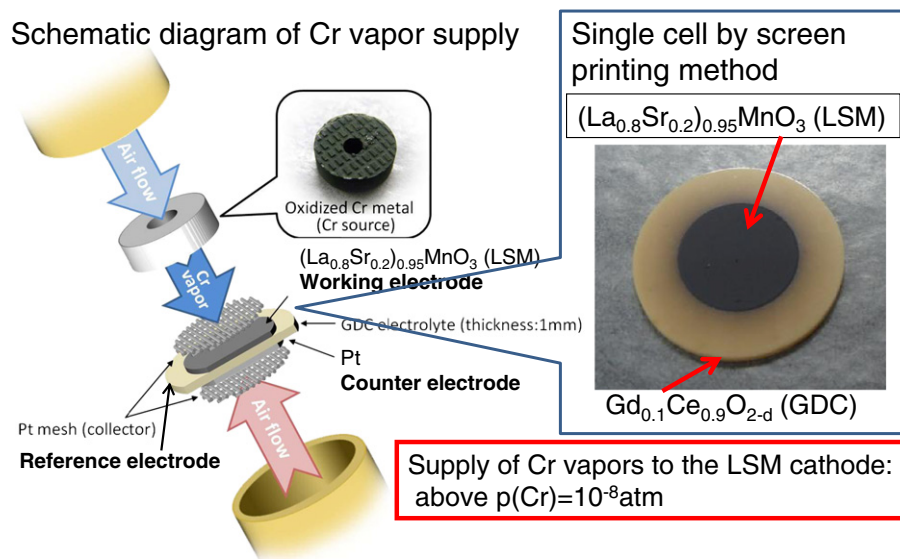


Fig. 1. Schematic diagram of experimental configuration for Cr-poisoning test and single cell. Testing temperature is 1073 K in air.

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