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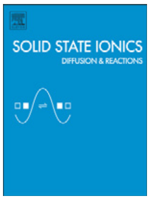

Effect of strontium concentration on sulfur poisoning of LSCF cathodes

Fangfang Wang *, Katsuhiko Yamaji, Do-Hyung Cho, Taro Shimonosono, Haruo Kishimoto, Manuel E. Brito, Teruhisa Horita, Harumi Yokokawa

Fuel Cell Group, National Institute of Advanced Industrial Science and Technology, Higashi, 1-1-1, AIST Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT

Sulfur poisoning behavior of LSCF cathodes with different Sr contents, $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$, LSCF6428 and $(La_{0.8}Sr_{0.2})(Co_{0.2}Fe_{0.8})O_3$, LSCF8228, was investigated at $T = 800$ °C in air with 1 ppm SO_2. The sulfur distribution of the cathodes was derived from the SEM/EDX mapping and was identified due to the $SrSO_4$ formation. Although this $SrSO_4$ formation can be recognized as the oxidative reaction, this took place mainly in the vicinity of the electrolyte/cathode interfaces where the electrochemical reaction occurs and therefore the oxygen potential is lowered due to the over-potential. Moreover, the width of the $SrSO_4$ formation was wider in LSCF6428 than in LSCF8228. These features suggest that the $SrSO_4$ formation is governed mainly by some kinetic factors in the electrochemical oxygen reduction; roles of oxide ion vacancies, the presence of dissociated oxygen, and the thermodynamic activity of SrO are discussed in relation to the $SrSO_4$ formation.

1. Introduction

Recent investigation on durability of solid oxide fuel cell (SOFC) stacks in real operation environment has revealed that the cathode is contaminated with sulfur [1]. In order to improve the durability/reliability of SOFC stacks/modules, therefore it is important to investigate possible effects of sulfur impurities on cathode performance. So far, only a few groups have focused on the sulfur poisoning effects of several different cathode materials [2–7]. In our previous results, sulfur poisoning effects for different perovskite cathodes $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF6428), $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC), and $(La_{0.85}Sr_{0.15})_{0.95}MnO_3$ (LSM) were examined experimentally. From these results, we extracted the fact that the sulfur poisoning effect depends on the thermodynamic activity of SrO in the cathode materials [4].

In the lanthanum strontium cobaltite ferrite $(La,Sr)(Co,Fe)O_3$ (LSCF) cathode, the Sr content will affect its physicochemical properties [8–10] such as the ionic/electronic conductivity and the lattice structure; in addition, the thermodynamic activity of SrO must depend of the Sr content. These features imply that for the LSCF cathodes, the Sr content may affect sulfur poisoning. To further investigate the effect of the Sr content on sulfur poisoning in LSCF cathodes, two compositions namely $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ (LSCF6428) and $(La_{0.8}Sr_{0.2})(Co_{0.2}Fe_{0.8})O_3$ (LSCF8228) were examined in the present investigation. Discussions will be thus made on the relation of the $SrSO_4$ formation mechanism to the electrochemical oxygen reduction mechanism.

2. Experimental

Powders of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC10, Anan Kasei Co. Ltd., Japan) were shaped into disks with CIP at 390 MPa. The disks were sintered at 1400 °C for 5 h. Powders of LSCF6428 or LSCF8228 (AGC Semi Chemical Co. Ltd., Japan) were applied as cathode ($\phi = 10$ mm, $t = 26$ μm) on the polished surface of a GDC10 electrolyte ($\phi = 17.5$ mm, $t = 1$ mm) by the screen printing method and fired at 1200 °C for 2 h. A Pt counter electrode was fired on the opposite surface of the electrolyte. A Pt reference electrode was attached on the edge of the electrolyte. Platinum meshes were pushed onto the respective electrodes as a current collector. In this work, a symmetrical half-cell was tested between double alumina tubes; a glass seal was used for the cathode side in order to avoid leakage of SO_2 gas. The operation temperature was set at 800 °C. During cell tests, dry air or dry air containing 1 ppm SO_2 was fed to the cathode at a flow rate of 50 cm^3/min and dry air was also fed to the counter electrode. The cells were operated using a potentio/galvano stat (electrochemical interface, Solartron Analytical, SI-1287) and an impedance analyzer (impedance/gain-faze analyzer, Solartron Analytical, SI-1260) at a fixed voltage of -0.2 V (vs. air reference electrode) to the cathode. A test was initiated by feeding air to the cathode until the current became constant, and then 1 ppm SO_2 was fed to the cathode. The cathodes before and after the cell tests were investigated by X-ray powder diffraction (XRD, Ultima IV, Rigaku Co., Japan), scanning electron microscopy (FE-SEM, JSM-7001, JEOL, Japan) and energy dispersive X-ray analysis (EDX, INCA, Oxford, England).

3. Results and discussion

Fig. 1 shows the relative current to the initial value (I/I_0) of cells with the LSCF8228 and the LSCF6428 cathodes. For the LSCF6428

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* Corresponding author. Tel.: +81 29 861 3387; fax: +81 29 861 4540.
E-mail address: wan.fangfang@aist.go.jp (F. Wang).

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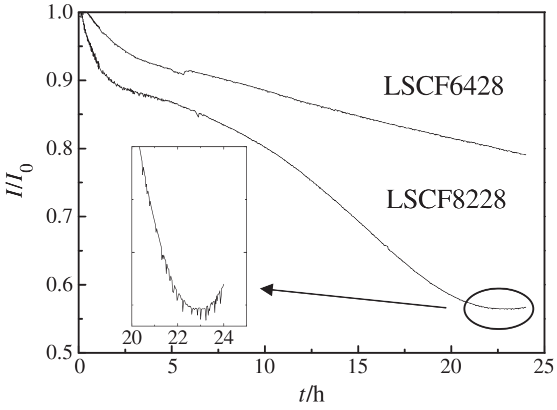

Fig. 1. Degradation of the current in relation to the initial current (I/I_0) of cells with LSCF8228 and LSCF6428 cathodes during exposition to 1 ppm SO_2 at 800 °C for 24 h at a fixed voltage of −0.2 V. Inset: enlarged detail.

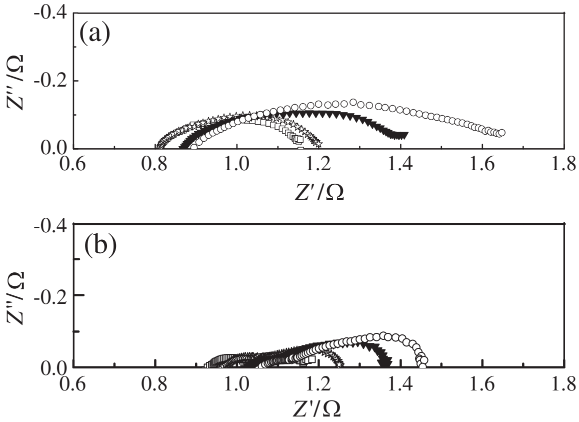

Fig. 2. Nyquist plots of the ac-impedance spectra for (a) LSCF8228 and (b) LSCF6428 cathodes tested in 1 ppm of SO_2 under −0.2 V, respectively.

cathode, the degradation became gradually significant with increasing time. On the other hand, for the LSCF8228 cathode, the I/I_0 value initially decreased but after about 23 h showed an upward recovery (inset of Fig. 1). Compared with the LSCF6428 cathode, the LSCF8228 cathode showed more rapid performance degradation.

Fig. 2 shows the Nyquist plots of the ac-impedance spectra for the LSCF8228 and the LSCF6428 cathodes under −0.2 V. Both cathodes exhibited increase in ohmic and polarization resistances with time. The larger increase in polarization resistance for the LSCF8228 cathode corresponds to the faster performance degradation. Moreover, the different shape of the Nyquist plots for two cathodes suggests some difference in poisoning behavior.

Sulfur distributions over a layer of the LSCF8228 and the LSCF6428 cathodes are shown in Fig. 3(a) and (b), respectively. Apparently, the sulfur concentrated mainly in the vicinity of cathode/electrolyte interfaces for the two cathodes. The sulfur deposited region was about 4 μm wide near the interface for LSCF8228, while it was about 15 μm wide for LSCF6428. Element distributions at the interface region were examined in a more detailed manner. The EDX results shown in Fig. 4 indicate that the reaction compounds are essentially the same between two cathodes, that is, $SrSO_4$ and $CoFe_2O_4$.

To check the performance recovery observed in the LSCF8228 cathode, the test was made for a longer period of time. Fig. 5 shows SEM images and EDX mapping of LSCF8228/GDC10 interface for 120 h. As shown in Fig. 5(a) and (b), a number of particles with white contrast were observed around the interface, and they were identified as Pt particles using EDX mapping [Fig. 5(c)]. This confirms that the observed performance improvement for the LSCF8228 cathode can be attributed to the Pt particles that are evaporated as PtO_2(g) as a result of the reaction of Pt mesh/wire with oxygen and are transported to be deposited at the electrochemically active sites in a similar manner to Pt deposition in the LSM cathode. Usually the over-potential of the LSCF cathode is small and the electrochemically active sites are distributed over a wide region; this Pt deposition is seldom observed. In the present case of the LSCF8228 cathode, the degradation due to the $SrSO_4$ formation in the active site region shifts the over-potential value and related distribution of active sites to those similar to the TPB mechanism in the LSM cathode.

In order to understand the difference in the sulfur poisoning between the two cathodes, it should be necessary to compare first the electrochemical performance between them. The electrochemical performance is determined by the ionic conductivity and the surface reaction rate for the oxygen reduction. For both properties, the oxide ion vacancy plays important roles. For the LSCF6428 cathode, when the vacancy concentration is higher, the ionic conductivity is higher [8,11] and the electrode resistivity is smaller as shown in Fig. 2. The electrochemically active region is therefore expected to be extended to a wider area from the interface towards the cathode surface for higher Sr content, namely for LSCF6428. These features can be compared with the observed features for the $SrSO_4$ formation and sulfur poisoning. Since sulfur is observed in the vicinity of the LSCF/GDC interface, it is suggested that the $SrSO_4$ formation takes place preferentially at the electrochemically active sites. Usually, the $SrSO_4$ formation proceeds as follows:

$$SrO + SO_2 + 0.5O_2(g) = SrSO_4.$$

Although this is an oxidative reaction, this took place at those active sites which should be at lower oxygen potential due to the

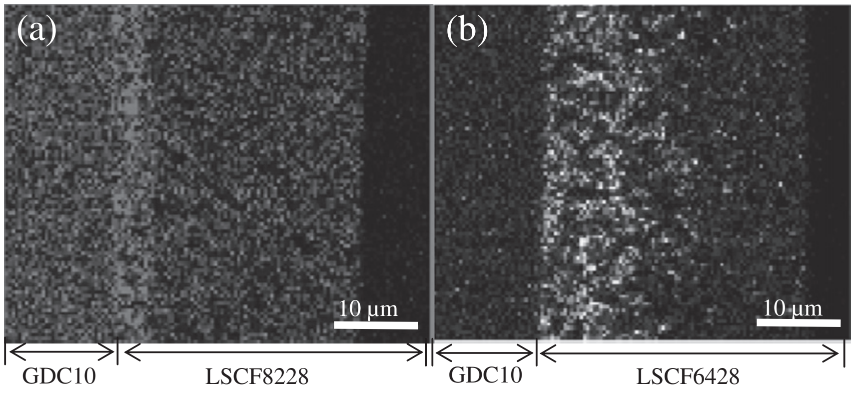

Fig. 3. Sulfur distribution over a cathode layer. (a) LSCF8228 and (b) LSCF6428 cathodes after exposure to 1 ppm SO_2 for 24 h.