ARTICLE IN PRESS

SOSI-13296; No of Pages 7

Solid State Ionics xxx (2014) xxx-xxx



Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Comparison of chromium poisoning among solid oxide fuel cell cathode materials

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ARTICLE INFO

Article history: Received 17 May 2013 Received in revised form 12 December 2013 Accepted 29 January 2014 Available online xxxx

Keywords: SOFC Cathode Chromium Poisoning Polarization

ABSTRACT

Chromium poisoning phenomena of solid oxide fuel cells (SOFCs) were investigated using ($La_{0.8}Sr_{0.2}$) $_{0.98}MnO_3$ (LSM), $Pr_{0.8}Sr_{0.2}MnO_3$ (PrSM), $Nd_{0.8}Sr_{0.2}MnO_3$ (NdSM), and $Br_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) for the cathode materials and yttria-stabilized zirconia (YSZ) as the electrolyte material at 700 °C under constant cathode polarization conditions. Deposition of chromium increased with increasing cathode polarization similarly for the four cathodes, although position of the deposition was different for the BSCF cathode. Chromium deposited near the cathode/electrolyte interface for the LSM cathode, the PrSM cathode and the NdSM cathode. Chromium deposition on the surface of the zirconia electrolyte was observed for the PrSM cathode and the NdSM cathode as previously observed in the LSM cathode. Oxygen deficiency in the deposited chromium on the surface of the zirconia electrolyte was also observed, thus the reaction mechanism of chromium vapor with the oxygen vacancy induced by cathode polarization was supported. The oxygen vacancy on the surface of the zirconia electrolyte seemed to be generated via metal oxides such as manganese oxide or neodymium oxide segregated from the cathode materials. Chromium deposited on the surface of the BSCF cathode. Cathode polarization seems to increase reactivity of BSCF and enhance trapping of chromium vapor near the cathode surface.

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1. Introduction

Among several degradation factors in solid oxide fuel cells (SOFCs), chromium poisoning of cathodes has been one of the major concerns for practical use [1,2]. The degradation originates from a vaporization of chromium from the surface of metallic components such as interconnects, manifolds and gas supply tubes. The chromium vapor deposits at the electrochemically active sites during operation, resulting in a degradation of cathode performance [3–5]. It was revealed that cathode polarization (overpotential) affects the chromium poisoning kinetics for the cathode consisting of lanthanum strontium manganite (LSM), by which it was concluded that the decrease in oxygen activity in the cathode accompanied by the electrode reaction could be the driving force of the deposition of chromium [5]. In our recent study, chromium deposition was compared among three cathodes using (La_{0.8}Sr_{0.2})_{0.98}MnO₃ (LSM)-zirconia composite, LaNi_{0.6}Fe_{0.4}O₃ (LNF) or La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) [6,7]. Chromium deposition near the cathode/electrolyte interface was facilitated similarly for the three cathodes under large cathode polarization of more than 200 mV, although the deposition

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0167-2738/\$ – see front matter © 2014 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ssi.2014.01.047 was located near the cathode surface for the LSCF cathode under small cathode polarization of less than 200 mV.

In this study, the chromium poisoning phenomena were studied using different cathode materials, $\rm Pr_{0.8}Sr_{0.2}MnO_3~(PrSM), Nd_{0.8}Sr_{0.2}MnO_3~(NdSM)~$ and $\rm Br_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3~(BSCF)~$ under constant cathode polarization conditions. Cathode polarization was regulated to the predetermined values from 100 mV to 300 mV, and distribution of the chromium deposition were analyzed after cooling the cell by keeping the cathode polarization. Mechanism of the chromium deposition was discussed especially for the LSM cathode, the PrSM cathode and the NdSM cathode focusing on the surface of zirconia electrolyte, considering microscopic distribution around the boundary of the zirconia surface and the deposited chromium.

2. Experiments

Electrolyte plates made of 8 mol% Y_2O_3 –92 mol% ZrO_2 (YSZ) with a thickness of 200 μ m and a diameter of 20 mm were used. A mixture of 56 wt.% NiO and 44 wt.% ScSZ (Sc $_2O_3$ – 1 mol% Ce O_2 – 89 mol% Zr O_2 , Daiichi Kigenso Kagaku, JP) was used for the anode material. Anode was printed on the electrolyte plate and sintered at 1300 °C for 3 h. Four kinds of cathode materials, (La $_{0.8}$ Sr $_{0.2}$) $_{0.98}$ MnO $_3$ (LSM), Br $_{0.5}$ Sr $_{0.5}$ Co $_{0.8}$ Fe $_{0.2}$ O $_3$ (BSCF), Pr $_{0.8}$ Sr $_{0.2}$ MnO $_3$ (PrSM), and Nd $_{0.8}$ Sr $_{0.2}$ MnO $_3$ (NdSM) were used, and they were printed on the other side of the electrolyte plate and sintered. Heat-treatment condition was

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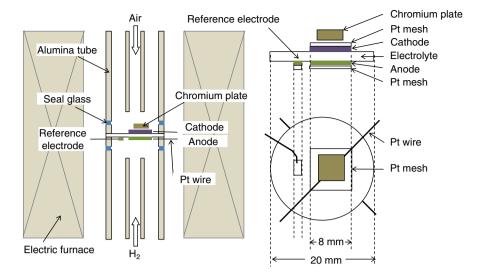


Fig. 1. Schematic of the cell test configuration.

 $1200~^\circ\text{C}-4~\text{h}$ for LSM, PrSM, and NdSM, and $1100~^\circ\text{C}-5~\text{h}$ for BSCF. Electrode area was 8 mm \times 8 mm (0.64 cm²). Pt mesh was used as the current collector. Reference electrode was placed on the anode side as shown in Fig. 1. For the experiment of chromium poisoning, a chromium plate with 5 mm \times 5 mm \times 1 mm in size was placed on the current collector of cathode side. The chromium plate did not contact directly with the cathode.

The cell was set in the cell test equipment as schematically shown in Fig. 1 and heated by the electric furnace up to 850 °C in 4 h to soften the glass seal, and was cooled down to the operating temperature of 700 °C in 1 h. Cell performance was measured at 700 °C by feeding air (0.15 l/min, 0.1 MPa) to the cathode and hydrogen to the anode (0.15 l/min,

0.1 MPa). The air used in this study was a compressor air (0.7–0.85 MPa, 5–15 °C). The water vapor pressure in the cathode gas ranges from 100 Pa to 240 Pa, which was estimated from the saturated water vapor pressure in the compressor. The surface of the chromium plate oxidizes in the cell operating condition, and chromium vaporizes by the following reactions.

$$Cr_2O_3(s) + 3/2\ O_2(g) = 2\ CrO_3(g) \eqno(1)$$

$$Cr_2O_3(s) + 3/2 O_2(g) + 2 H_2O(g) = 2 CrO_2(OH)_2(g).$$
 (2)

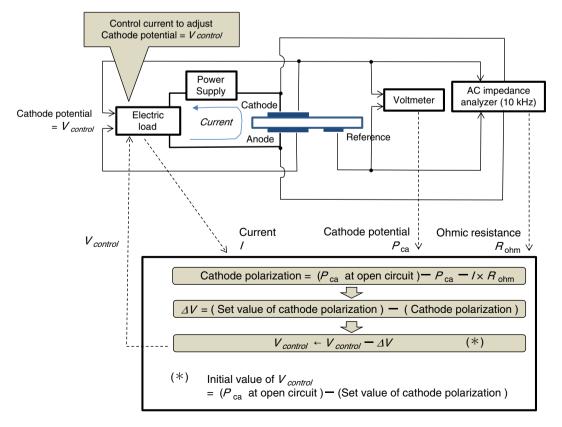


Fig. 2. Feedback control system of the cell test to keep cathode polarization constant.

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