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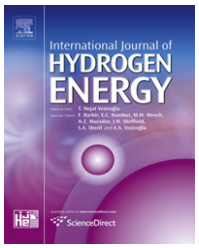

A fundamental study of chromium deposition and poisoning at $(La_{0.8}Sr_{0.2})_{0.95}(Mn_{1-x}Co_x)O_{3\pm\delta}$ ($0.0 \leq x \leq 1.0$) cathodes of solid oxide fuel cells

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ABSTRACT

Fundamental understanding of the chromium deposition and poisoning is very important in the development of intermediate temperature solid oxide fuel cells (IT-SOFCs) based on metallic interconnect. In this paper, chromium deposition and poisoning at the $(La_{0.8}Sr_{0.2})_{0.95}(Mn_{1-x}Co_x)O_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$) cathodes are systematically studied in the presence of a chromia-forming metallic interconnect under SOFC operation conditions. The results show that as the B-site Mn is substituted by Co, electrochemical activity of the cathodes for the O_2 reduction reaction increases due to the increased oxygen exchange coefficient and oxygen diffusion coefficient as a result of the increased oxygen vacancies of the LSMC perovskite. However, in the presence of a chromia-forming metallic interconnect, chromium deposition on the electrolyte surface in contact with the LSMC electrode decreases while on the electrode surface it increases as Co content in LSMC increases from 0.0 to 1.0. On the other hand, the chromium poisoning effects as measured by the increase in the overpotential and electrode polarization resistance are most pronounced for the LSMC cathode with $x = 0.4$. The occurrence of the maximum chromium poisoning is most likely due to combined poisoning effect of the Cr deposits at the electrode surface and electrolyte surface on the kinetics of the O_2 reduction reactions. The results clearly indicate that the increase in the electrochemical activity of the cathode does not necessarily lead to the reduction in the chromium deposition. Rather, the changes in the electrochemical activity of the LSMC cathodes simply change the distribution pattern of chromium deposition on the electrode and electrolyte surface. Chromium deposition at LSMC cathode is closely related to the chemical affinity and stability of the manganese and strontium species, which depends significantly on the Co/Mn ratio at the B-site of the LSMC perovskite.

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1. Introduction

Fuel flexibility, high efficiency, low greenhouse gas emission and production of high quality heat make solid oxide fuel cells (SOFCs) attractive energy conversion technology for future electricity power generation. To improve the stability, reliability and to reduce the production cost, it is necessary to reduce the operating temperature from conventional 1000 °C to

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intermediate temperature ranges of 700–900 °C [1–3]. One significant advantage of intermediate temperature solid oxide fuel cells (IT-SOFCs) lies in the use of metallic interconnect materials with higher electronic conductivity, better mechanical property, higher thermal conductivity, better workability and lower cost, as compared to lanthanum chromite perovskite-based ceramic interconnect materials [4–9]. The most widely developed and studied metallic interconnect materials are the chromia-forming alloys due to their good thermal properties, high corrosion resistance at high temperature and conductive chromium oxide scales. However, on the cathode side, chromium oxide, Cr_2O_3, can further react with oxygen and moisture to form various gaseous hexavalent Cr species such as CrO_3 and $CrO_2(OH)_2$ under the operating temperatures of SOFCs [10,11]. The volatility can be further enhanced if there is presence of any alkali metals in sealing glasses due to the formation of even more volatile species [12]. The gaseous chromium species from the interconnect would migrate through the cathode and deposit in the form of low valence chromium (III) species either at the electrode/electrolyte interface, inside the bulk of the electrode and/or on the electrode surface. The accumulation of Cr deposits eventually leads to a serious polarization loss of the cathode and performance degradation of the cell [13–19]. The chromium deposition and poisoning is a critical issue for the application of metallic interconnect materials in IT-SOFCs [17,20].

Fundamental understanding of the chromium deposition and poisoning of the cathode materials is vital for the development of Cr-tolerant cathodes or better preventive measures to enhance the long-term stability of SOFCs [21,22]. However, despite the numerous studies on the chromium deposition and poisoning processes on the SOFC cathodes, there are still considerable disagreements on the mechanism and processes of the chromium deposition and poisoning on the cathodes for the O_2 reduction reaction. Badwal et al. [19] investigated stacks operated between 900 and 1000 °C with air oxidant and 97%H_2/3%H_2O fuel using high chromium alloy (Plansee) as interconnect. Cell performance declined rapidly and manganese chromium spinel $(Mn,Cr)_3O_4$, was observed in the (La,Sr)MnO_3 (LSM) cathode. The degradation of Cr species is considered to be closely related to the oxygen activity at the electrode/electrolyte interface [19]. In another words, the deposition of Cr is driven by the electrochemical reduction of gaseous Cr species to solid Cr_2O_3 phase in competition with the O_2 reduction reaction [16,19,23–25]. Hilpert et al. [10] discussed the thermodynamics of the volatile chromium species and the results indicate that the electrochemical reduction of the high valent chromium species and the O_2 reduction reaction are thermodynamic compatible under the SOFC operation conditions. Chromium deposition on the Y_2O_3–ZrO_2 (YSZ) electrolyte surface and in the LSM cathodes was also observed by others [16,18,23].

A detailed study of the chromium deposition on the LSM cathode found that at the initial stages of the O_2 reduction reaction in the presence of Fe–Cr alloy interconnect, chromium deposition does not occur preferentially at the three phase boundaries at the LSM electrode/YSZ electrolyte interface region, and in fact the chromium deposition is random, simply filling the space between the LSM grains with the increase in the cathodic polarization time [26]. Wang and Fergus [27] studied the chromium deposition at a Pt electrode on undoped and Mn-doped YSZ electrolyte. The results show the significantly higher chromium deposition on the Mn-doped YSZ electrolyte surface, indicating that the presence of manganese species promotes the chromium deposition. On the other hand, Konysheva et al. [15] found that the chromium deposition increases with the polarization current and chromium deposition in the LSM electrode also occurs in open circuit (i.e., no polarization current).

In addition to the LSM cathodes, chromium deposition and poisoning were also studied on other cathode materials, including (La,Sr)$(Co,Fe)O_3$ (LSCF), (La,Sr)FeO_3 (LSF), (La,Ba)$(Co,Fe)O_3$ (LBCF) and La$(Ni,Fe)O_3$ (LNF) [15,28–35]. In the case of LSCF cathode, chromium deposition occurs predominantly on the surface of the LSCF cathode, forming $SrCrO_4$ [15,32]. In the case of LNF cathode, significant chromium deposits were not observed either at the LNF cathode/electrolyte interface region or on the LNF electrode surface [34,36]. The results clearly show that chromium deposition and poisoning strongly depend on the chemistry of the cathode materials. However, a direct comparison of the chromium deposition and poisoning behavior on different cathode materials is difficult due to the fact there are significant variations in the materials composition, microstructure and test conditions conducted in different research laboratories.

LSCF perovskites are well known mixed oxygen ion and electron conductors (MIEC) [37,38], while LSM is a typical electronic conductor with negligible ionic conductivity [39–41]. De Souza and Kilner [42,43] studied in details the oxygen transport properties in $La_{1-x}Sr_xMn_{1-y}Co_yO_{3\pm\delta}$ (LSMC) perovskites and showed that the oxygen surface exchange coefficient, k*, and the oxygen tracer diffusion coefficient, D*, generally increases with the Co content in the B-site of LSMC perovskite. Oxygen vacancies play a major role in the strong relationship between the oxygen transport parameters, k* and D*, acceptor-dopant concentration and the Mn/Co ratio. As the Co content at the B-site increases from 0.0 to 1.0, the LSMC materials change from a pure electronic conductor to a MIEC with $La_{1-x}Sr_xCoO_{3-\delta}$ displaying the highest oxygen diffusion coefficient and $La_{1-x}Sr_xMnO_{3+\delta}$ displaying the lowest oxygen diffusion coefficient. Thus, the LSMC system such as $(La_{0.8}Sr_{0.2})_{0.95}(Mn_{1-x}Co_x)O_{3\pm\delta}$ (LSMC, $0.0 \le x \le 1.0$) would be an ideal model system to investigate the fundamental relationship between the Cr deposition and poisoning and the electrocatalytic activity (i.e., oxygen surface exchange and diffusion coefficients) of LSMC cathodes under SOFC operation conditions.

2. Experimental

Gadolinium-doped ceria ($Gd_{0.2}Ce_{0.8}O_2$, GDC) synthesized by a solid state reaction method was used as the electrolyte. Stoichiometric amounts of CeO_2 (99.9%, Sigma–Aldrich) and Gd_2O_3 (99.9%, Sigma–Aldrich) were mixed and ball-milled in iso-propanol with yttria-stabilized zirconia medium for 24 h. After drying, the mixture was uniaxially pressed into disks and sintered at 1600 °C for 6h in air to form the electrolyte pellets. The GDC electrolyte pellets were ~1 mm in thickness and ~20 mm in diameter.

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