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Long term behaviors of $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ as cathodes for solid oxide fuel cells

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Kathy Lu*, Fengyu Shen

Department of Materials Science and Engineering, Virginia Tech, 211B Holden Hall, Blacksburg, VA 24061, USA

ABSTRACT

This work studies the electrochemical performance and stability of $La_{0.8}Sr_{0.2}MnO_3$ (LSM) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathodes in a AISI441 interconnect/cathode/YSZ electrolyte half-cell configuration at 800 °C for 500 h. Ohmic resistance and polarization resistance of the cathodes are analyzed by deconvoluting the electrochemical impedance spectroscopy (EIS) results. The LSM cathode has much higher resistance than the LSCF electrode even though the respective cathode resistance either decreases or stays stable over the long term thermal treatment. During the 500 h thermal treatment, dramatic elemental distribution changes influence the electrochemical behaviors of the cathodes. Chromium diffusion from the interconnect into the LSM electrode at triple phase boundaries (TPBs) leads to segregation of Sr away from La and Mn. For the LSCF cathode, Sr and Co segregation is dominant. The fundamental processes at the TPBs are proposed. Overall, LSCF is a much preferred cathode material because of its much smaller resistance for the 500 h thermal treatment time.

Introduction

Solid oxide fuel cells (SOFCs) hold the greatest promise as a clean power generation device because of a combination of high efficiency, high energy and power densities, and fuel flexibility. Applications include on-board auxiliary power units, mobile power generators, and stationary power generation [1—5]. Miniaturized SOFCs are desired for powering long duration devices and remote communication electronics [6]. However, several technical issues need to be addressed in order to fully realize the promise of SOFCs. The most serious problem is the inte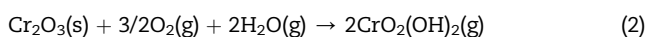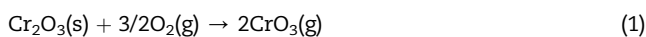rfacial reaction and degradation at the cathode/electrolyte interface, mostly as a result of Cr species diffusion (gas and solid state) from the interconnect [7].

Many materials have been studied as the cathodes, including $(La_{1-x}Sr_x)_nMnO_{3-\delta}$ [8], $(La_{1-x}Sr_x)_nCo_{1-y}Fe_yO_{3-\delta}$ [9], $La_2NiO_{4+\delta}$ [10], $PrBaCo_2O_{5+\delta}$ [11], $La_{0.995}Ca_{0.005}NbO_4$ [12], $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ [13], $Ce_{0.9}Gd_{0.1}O_{1.95}$ [14], and so on. Among them, LSM and LSCF are the most promising and mature cathode candidates. They are conductive perovskite ABO_3 ceramics. For LSM, La and Sr occupy A-sites and Mn occupies B-sites; it is a widely used cathode material due to its chemical compatibility with yttria-stabilized zirconia (YSZ) electrolyte [15]. However, LSM is predominantly an electronic conductor ($\sim$200 S cm^{-1} electronic conductivity [16]) with very

poor ionic conductivity (4×10^{-8} S cm^{-1} [17]); oxygen reduction reaction occurs mainly at the tripe phase boundary (TPB) area with severe limitation on SOFC powder density. For LSCF, La and Sr occupy A-sites and Co and Fe occupy B-sites. The material exhibits much higher ionic and electronic conductivities (257—412 S cm^{-1} between 450 and 900 °C [18]) due to fewer surface oxygen vacancies [19]; oxygen reduction reaction occurs throughout the electrode [20,21]. Doping of cobalt lowers cathode polarization resistance because both ionic and electronic conductivities can be enhanced [22—24].

Both LSM and LSCF cathodes can be poisoned by chromium species which diffuse from the interconnects at high operating temperatures. The diffusion can be through vapor phase or solid state. Most of the understanding was obtained based on dry air cathode environment even though moisture can play an important role in the reactions. Chromia-forming alloys produce different gaseous chromium species in dry air and moist air and the reactions are as follows [25,26]:

$$Cr_2O_3(s) + 3/2O_2(g) \rightarrow 2CrO_3(g) \quad (1)$$

$$Cr_2O_3(s) + 3/2O_2(g) + 2H_2O(g) \rightarrow 2CrO_2(OH)_2(g) \quad (2)$$

It has been claimed that the Mn species from the LSM cathode induces the deposition of the Cr species under cathodic polarization at high temperatures by forming Cr—Mn—O nuclei [27—29]. This process prohibits electrons from entering the cathode and causes an increase in cathode resistance. LSCF, on the other hand, is reported to be more Cr-tolerant due to the lack of Mn species that interacts with the Cr species [30,31]. Because of the higher ionic conductivity, LSCF cathodes are also adequate alternatives to LSM cathodes at lower temperatures. However, the long term performance of LSM and LSCF cathodes has not been compared and their fundamental interaction mechanisms with Cr species under the same testing conditions are not clear.

In this study, LSM and LSCF cathodes are fabricated in order to study the interconnect/electrode/electrolyte half-cell performance and interfacial reaction and degradation with YSZ and AISI 441 alloy serving as the electrolyte and the interconnect, respectively. The gas diffusion process is not directly measured but the interfacial reaction is believed to be a combined result of vapor phase diffusion and solid state diffusion from the interconnect to the electrolyte. The electrochemical performance and the microstructure/composition evolution of the LSM and LSCF cathodes during the thermal treatment are examined. Based on these efforts, the cathode degradation mechanisms for these cathodes are proposed and the enhanced performance for the LSCF cathode is explained.

Experimental procedures

Synthesis of LSM and LSCF powders

In this work, perovskite LSM and LSCF powders were synthesized by an identical solid state reaction process [32]. SrCO$_3$ (99.9%, Sigma Aldrich, St. Louis, MO), La$_2$O$_3$ (99.98%, Alfa Aesar, Ward Hill, MA), MnCO$_3$ (99.9%, Alfa Aesar, Ward Hill, MA), Co$_3$O$_4$ (Alfa Aesar, Ward Hill, MA), and Fe$_2$O$_3$ (Sigma—Aldrich, St. Louis, MO) at designed composition ratios were mixed. The mixed powders were ball-milled overnight and then sintered at 1400 °C for 15 h with a heating and cooling rate of 5 °C/min. The resulting powders were ball-milled overnight again to reduce the particle sizes, and a second sintering process at 1400 °C for 5 h was carried out with the same heating and cooling rate. The prepared powders were then ball-milled for 3 days to further reduce the particle sizes and improve the performance of the resulting cathodes.

Assembly of AISI 441/LSM/YSZ and AISI 441/LSCF/YSZ tri-layers

The LSM and LSCF powders (56.8 wt%), respectively, were mixed and ball-milled with microcrystalline cellulose (pore forming agent, 5.7 wt%, Spectrum, Gardena, CA), ethyl cellulose (binder, 1.1 wt%, Acros Organics, New Jersey), and α-terpineol (solvent, 36.4 wt%, Sigma—Aldrich, St. Louis, MO) for 1 h to make pastes for screen printing. The prepared pastes were screen printed on 8 mol% YSZ (Nextech Materials, Lewis Center, OH) substrates, using a #330 mesh. The screen printed pastes were square-like with ~0.5 cm^2 area. The LSM/YSZ and LSCF/YSZ couples were kept at 200 °C for 3 h and at 400 °C for 1 h to burn out the binder, pore-forming agent, and solvent. Afterward, these bi-layers were sintered at 1150 °C for 2 h, with a heating and cooling rate of 1 °C/min. The thickness of the LSM and LSCF electrodes after sintering was ~30 μm, measured through scanning electron microscopy (SEM) images.

AISI 441 ferritic stainless steel pieces (ATI Allegheny Ludlum Corporation, Brackenridge, PA) were used as the interconnect material and were cut into rectangular substrates (area: 10×10 mm^2). In order to remove the oxidized layer (if any) and obtain a scratch free flat surface, the steel pieces were polished to optical finish, and ultrasonically cleaned with water and ethanol. The polished AISI 441 alloy piece was placed on the LSM electrode or LSCF electrode side of the LSM/YSZ and LSCF/YSZ bi-layers and the configuration of the tri-layer was shown in our previous paper [33].

Thermal treatment under current load

In order to investigate the electrochemical behaviors of the LSM and LSCF cathodes, AISI 441/LSM/YSZ and AISI 441/LSCF/YSZ tri-layers were heated to 800 °C, using a tube furnace (1730-20 HT Furnace, CM Furnace Inc. Bloomfield, NJ) in dry air environment. Afterward, the tri-layers were cathodically polarized under a constant current density of 200 mA cm^{-2}, using a potentiostat (VersaSTAT 3, Princeton Applied Research, Oak Ridge, TN). A platinum mesh was placed in-between the cathode and the AISI 441 interconnect to optimize the current distribution, and the electrodes were connected by Pt wires along with Pd paste. The electrochemical impedance spectroscopy (EIS) testing program used was a multi-loop process. In each loop, EIS test was carried out from 100 kHz to 0.025 Hz. The amplitude was 10 mV. After that, a current density of 200 mA/cm^2 was applied to mimic the