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Suppressed Sr segregation and performance of directly assembled $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ oxygen electrode on Y_2O_3-ZrO_2 electrolyte of solid oxide electrolysis cells

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HIGHLIGHTS

- LSCF electrode is directly assemble on barrier-layer-free YSZ electrolyte of SOECs.
- Directly assembled LSCF oxygen electrode shows high performance and stability.
- Anodic polarization induces the LSCF electrode/YSZ electrolyte interface formation.
- Sr segregation and migration is inhibited under SOEC operation conditions.

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ABSTRACT

Active and stable oxygen electrode is probably the most important in the development of solid oxide electrolysis cells (SOECs) technologies. Herein, we report the successful development of mixed ionic and electronic conducting (MIEC) $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) perovskite oxides directly assembled on barrier-layer-free yttria-stabilized zirconia (YSZ) electrolyte as highly active and stable oxygen electrodes of SOECs. Electrolysis polarization effectively induces the formation of electrode/electrolyte interface, similar to that observed under solid oxide fuel cell (SOFC) operation conditions. However, in contrast to the significant performance decay under SOFC operation conditions, the cell with directly assembled LSCF oxygen electrodes shows excellent stability, tested for 300 h at 0.5 A cm^{-2} and 750 °C under SOEC operation conditions. Detailed microstructure and phase analysis reveal that Sr segregation is inevitable for LSCF electrode, but anodic polarization substantially suppresses Sr segregation and migration to the electrode/electrolyte interface, leading to the formation of stable and efficient electrode/electrolyte interface for water and CO_2 electrolysis under SOECs operation conditions. The present study demonstrates the feasibility of using directly assembled MIEC cobaltite based oxygen electrodes on barrier-layer-free YSZ electrolyte of SOECs.

1. Introduction

Renewable energy sources such as solar energy and wind power are essential to supply sustainable energy for the future but requires efficient and cost-effective storage of renewable electricity due to the intermittent nature of electricity generation from solar and wind [1,2]. Solid oxide electrolysis cells (SOECs) are an energy storage device capable of storing electrical energy generated from intermittent renewable sources into chemical energy of fuels such as hydrogen, synthesis gas and methane [3–9]. In SOECs, Ni based hydrogen electrode, yttria-stabilized zirconia (YSZ) electrolyte and manganite or cobaltite based perovskite oxygen electrodes such as $(La,Sr)MnO_{3+\delta}$

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(LSM) and (La,Sr)(Co,Fe)$O_{3-\delta}$ (LSCF) are the most extensively investigated materials. Mixed ionic and electronic conducting (MIEC) LSCF based perovskite oxides possess a high oxygen vacancy concentration and ion mobility several orders of magnitude higher than that of LSM, therefore, LSCF based electrodes show a much better electrocatalytic activity for the oxygen evolution reaction (OER) of SOEC than LSM [10–13]. However, one of the critical issues of developing durable and reliable SOECs is the significant degradation of oxygen electrodes under the anodic polarization conditions [14–18]. To use LSCF-based oxygen electrodes on YSZ electrolyte, a ceria based barrier layer needs to be used to prevent the interfacial reaction between cobaltites and YSZ [19].

In the case of MIEC cobaltite based electrodes such as (La,Sr)$CoO_{3-\delta}$ (LSC) and LSCF, Sr surface segregation is a major issue in the performance degradation [20–31]. Oh et al. [22] reported the formation of SrO precipitates on the surface of LSCF dense samples after heat-treatment at 600-900 °C and the precipitated Sr increased with the increase of temperature and oxygen partial pressure. We studied the chromium deposition on LSCF electrode in contact with a Fe-Cr interconnect and observed the formation of $SrCrO_4$ on the surface of LSCF electrode under open circuit conditions, induced by the segregated SrO under open circuit [32]. Simner et al. [20] observed the formation of ~ 50 nm thick SrO layer on the surface of LSCF grains after the cell was tested at 750 °C for 500 h under solid oxide fuel cell (SOFC) mode. Sr segregation and diffusion also occurred significantly during the high temperature sintering of LSCF electrode on Gd-doped ceria (GDC) electrolyte and between LSCF and GDC barrier layer [33]. The segregated SrO layer occupies the active sites for the oxygen reduction/evolution reactions and thus dramatically reduces the electrocatalytic activity of the electrode. Moreover, the surface segregated Sr species are also reactive with contaminants such as volatile chromium species from the stainless steel interconnect and sulphur dioxide from the air stream, leading to a decrease of the electrocatalytic activity of the oxygen electrodes [34–36].

Electrochemical polarization has a significant effect on the Sr surface segregation and migration, however, there are considerable discrepancies regarding the role of polarization in the Sr segregation. Under the cathodic polarization, it has been extensively reported that Sr segregation occurs on the surface of porous LSCF electrodes and the segregated Sr tends to migrate across the ceria barrier layer to react with the YSZ electrolyte, forming the insulating $SrZrO_3$ phase [20,37]. Vovk et al. [38] studied the $La_{0.5}Sr_{0.5}CoO_3$ (LSC) thin film electrode surface using *in situ* X-ray photoelectron spectroscopy (XPS) and observed the increase of Sr/(La + Co) ratio at the surface by 5% after cathodic polarization. Mutoro et al. [39] observed the increase of Sr and decrease of Co on the LSC thin film under cathodic polarization using *in situ* synchrotron-based XPS, and the compositional change on the surface was reversed by switching to anodic polarization. Under the anodic electrolysis mode, Sr diffusion and formation of $SrZrO_3$ on YSZ surface has also been observed [19,40,41]. Baumann et al. [42] reported the dc bias induced activity enhancement of LSCF dense thin film microelectrodes due to the increase of surface Sr and Co by cathodic polarization, but observed no change in the surface composition of the LSCF film with the anodic polarization. This implies that the Sr surface segregation would not be favourable under the anodic polarization conditions as compared to that under cathodic polarization conditions. On the other hand, Laurencin et al. [43] studied the stability of Ni-YSZ supported YSZ electrolyte cells with GDC barrier layer and LSCF-GDC composite oxygen electrode in fuel cell and electrolysis modes at 850 °C for over 1000 h and found that the degradation rate was higher in the electrolysis mode than that in the fuel cell mode, and this was attributed to the promoted diffusion of Sr species to the YSZ surface under the anodic polarization conditions, leading to the formation of excess $SrZrO_3$ phase.

Herein, we discovered for the first time that LSCF perovskite oxides on barrier-layer-free YSZ electrolyte using the direct assembly technique [44–47] can be utilized as highly active and stable oxygen electrodes of SOECs, achieving excellent cell performance and stability at 750 °C for 300 h under the SOEC operation conditions. This is in contrast to the rapid decay and degradation of LSCF electrodes on YSZ electrolyte under SOFC operation conditions [46]. The fundamental reason is the inhibited Sr segregation of LSCF under the influence of anodic polarization.

2. Experimental section

2.1. Fabrication of YSZ electrolyte cells and direct assembly of electrodes

NiO-YSZ hydrogen electrode-supported YSZ electrolyte cells were fabricated by slurry spin coating technique [48,49]. NiO (J.T. Baker), 8 mol% Y_2O_3-ZrO_2 (YSZ, Tosoh) and tapioca in a mass ratio of 5:5:2.5 were mixed in a ball mill for 24 h. The mixed powder was compacted in a stainless steel die with an internal diameter 18 mm and pre-sintered at 1000 °C for 2 h to form the hydrogen electrode substrates. The hydrogen electrode functional layer with NiO:YSZ mass ratio of 5:5 and YSZ thin film were prepared on the hydrogen electrode substrates using a spin coater (VTC-100, MTI), followed by sintering at 1450 °C in air for 5 h.

Half cells with a three-electrode configuration were also prepared. YSZ electrolyte pellets were prepared by die pressing and sintering at 1450 °C in air for 5 h. The sintered YSZ pellets were 18 mm in diameter and 0.8 mm in thickness. Pt ink (Gwent Electronic Materials Ltd) was painted on one side of the electrolyte pellet as the counter and reference electrodes and sintered at 1100 °C in air for 2 h. The gap between the counter electrode and ring-shaped reference electrode was 3 mm. The validity of the cell configurations with three electrode arrangement has been discussed in detail in a previous report [50].

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) powder was prepared using a modified Pechini method. The starting chemicals were $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa-Aesar), $Sr(NO_3)_2$ (99%, Sigma-Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (98.0–102.0%, Alfa-Aesar), $Fe(NO_3)_3 \cdot 9H_2O$ (98%, Chem Supply), citric acid (99.5%, Chem Supply), ethylenediaminetetraacetic acid (EDTA, 99%, Acros Organics) and ammonia (28%, Ajax Finechem). The molar ratio of metal ions/citric acid/EDTA was 1:1.5:1 and the resultant powder was calcined at 900 °C in air for 2 h. The LSCF powder was mixed with an ink vehicle (Fuel Cell Materials) in a mass ratio of 5:5. The ink was prepared on the YSZ electrolyte side of the cells using screen-printing and dried at 100 °C for 2 h in an oven. The effective areas of the LSCF oxygen electrodes were 0.25 and 0.50 cm^2 for full cells and half cells, respectively. In the case of fuel electrode supported electrolyte film full cells, Pt ink was painted on the electrode surface as the current collector and heat-treated at 150 °C for 2 h, while for half cells, Pt mesh instead of Pt ink were placed on the electrode surface as current collector. The cells with as-prepared LSCF oxygen electrodes were placed in a fuel cell test station and heated to a test temperature for electrochemical measurement without a pre-sintering step at high temperatures.

2.2. Electrochemical tests

The fuel electrode supported YSZ electrolyte film cells were sealed on alumina tubes using a ceramic sealant (Ceramabond 552, AREMCO Products Inc), solidified at room temperature for 12 h, and heat-treated to 750 °C at a heating rate of 5 °C min^{-1} using nitrogen as safe gas in the hydrogen electrode. The nitrogen was switched to hydrogen, and the hydrogen electrode was reduced at 750 °C for 1 h. The complete conversion of NiO into metallic Ni in the composite hydrogen electrodes during the reduction process was indicated by the observed high open circuit voltage (OCV) of > 1.1 V. Hydrogen flow rate at the hydrogen electrode was 50 ml min^{-1} and the oxygen electrode was exposed to open air. H_2O + H_2 or $CO_2 + H_2$ mixed gas at a total flow rate of 50 ml min^{-1} was supplied for testing under electrolysis mode. Polarization performance was measured using a Gamry Reference 3000