Journal of Power Sources 404 (2018) 73–80

Contents lists available at ScienceDirect

Journal of Power Sources

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

Cyclic polarization enhances the operating stability of $La_{0.57}Sr_{0.38}Co_{0.18}Fe_{0.72}Nb_{0.1}O_{3-\delta}$ oxygen electrode of reversible solid oxide cells

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HIGHLIGHTS

- LSCFN oxygen electrode assembled on barrier-layer-free Y_2O_3—ZrO_2 electrolyte.
- Reversible operation of LSCFN electrode during cyclic polarization for 240 h.
- Mitigated Sr surface segregation and accumulation by cyclic polarization.
- Enhanced operating stability in a longer cyclic time period.

ARTICLE INFO

Keywords:
Reversible solid oxide cells
LSCFN oxygen electrode
Cyclic polarization
Sr surface segregation
Performance recovery

ABSTRACT

Reversing the direction of polarization current is essential for reversible solid oxide cells technologies, but its effect on cobaltite based perovskite oxygen electrodes is largely unknown. Herein, we report the operating stability and microstructure at the electrode/electrolyte interface of $La_{0.57}Sr_{0.38}Co_{0.18}Fe_{0.72}Nb_{0.1}O_{3-\delta}$ (LSCFN) oxygen electrodes assembled on barrier-layer-free Y_2O_3—ZrO_2 electrolyte under cyclic anodic/cathodic polarization mode at 0.5 A cm^{-2} and 750 °C. During the cyclic polarization, the electrocatalytic activity of LSCFN electrode is drastically deteriorated in cathodic mode, but the performance loss is largely recoverable in anodic mode. This is due to the fact that the surface segregation of Sr and accumulation at the electrode/electrolyte interface by cathodic polarization can be remarkably mitigated by anodic polarization. The time period in each cycle plays a key role in determining the accumulation of Sr species at the electrode/electrolyte interface. A full cell operating in a time period of 12 h fuel-cell/12 h electrolysis is reversible for a duration of 240 h, in contrast to the performance degradation in a shorter time period of 4 h fuel cell/4 h electrolysis. The present study sheds lights on applying cobaltite based perovskite oxygen electrodes on barrier-layer-free YSZ electrolyte for reliable solid oxide cells.

1. Introduction

Reversible solid oxide cells (SOCs) are a promising energy storage and regeneration device capable of running in solid oxide fuel cell (SOFC) mode and solid oxide electrolysis cell (SOEC) mode [1–4]. Perovskite based oxides such as $La_{0.8}Sr_{0.2}MnO_{3+\delta}$ (LSM) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) are most commonly used oxygen electrodes, which however suffer from performance degradation and structural destruction during operation in electrolysis mode [5,6]. For example, in electrolysis mode LSM electrode is frequently observed to delaminate from the electrolyte, leading to failure of the SOC system [7–11]. On the other hand, the structural destruction of LSM electrode in the electrolysis mode can be eliminated by operating in cyclic fuel cell/electrolysis mode of SOCs [12–16].

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https://doi.org/10.1016/j.jpowsour.2018.10.009
Received 12 July 2018; Received in revised form 18 September 2018; Accepted 6 October 2018
0378-7753/

Compared to the LSM electrode that possesses predominantly electronic conductivity with negligible ionic conductivity [17,18], LSCF electrode with mixed ionic/electronic conductivity (MIEC) exhibits much better electrocatalytic activity for the oxygen reduction and evolution reactions (ORR and OER) [19,20]. On the other hand, Sr in the A-site of LSCF perovskite structure tends to undergo surface segregation at the operating temperatures of SOCs (600–800 °C), occupying the active surface for the ORR and OER [21–27]. In addition, the segregated Sr species is highly mobile and can distantly migrate a few micrometers across the Gd-doped ceria (GDC) barrier layer (dense or porous), forming resistive $SrZrO_3$ phase at the GDC/YSZ interface [28–30]. The electrochemical polarization applied under the cell's operating conditions also has a close impact on the distribution of surface Sr species [31–34]. Vovk et al. [35] studied the $La_{0.5}Sr_{0.5}CoO_3$ (LSC) surfaces under electrochemical polarization using an *in situ* X-ray photoelectron spectroscopy (XPS) technique and observed enrichment of Sr on the LSC surface. Consistently, Baumann et al. [36] reported that cathodic polarization led to increase of surface Sr and Co on the LSCF film, but the surface composition is unchanged by anodic polarization. Mutoro et al. [37] *in situ* probed surface composition of LSC film using synchrotron XPS and observed reversible surface composition changes by electrochemical polarization, that is, the segregation of Sr on LSC surface under cathodic polarization can be reduced under anodic polarization. On the contrary, Laurencin et al. [31] reported the LSCF-GDC composite oxygen electrodes degraded faster in anodic mode than in cathodic mode.

Nevertheless, compared to the extensively investigated Sr surface distribution by either cathodic or anodic polarization, the effect of periodically reversing polarization current under practical operating conditions of SOCs is scarcely known. Recently, Barnett group [38] studied the effect of reversing current on symmetrical LSCF electrodes using GDC electrolyte in a current range of 0.7–1.5 A cm^{-2}. They observed faster performance degradation under a higher current and attributed it to the increased amount of surface segregated Sr under the influence of polarization current [38]. However, it is not clear whether the cyclic polarization is beneficial or detrimental to the LSCF electrodes.

We have recently fabricated LSCF electrode on barrier-layer-free YSZ electrolyte using a direct assembly approach without conventional high temperature sintering and investigated in detail the effect of direction of polarization current on Sr surface segregation and accumulation at the electrode/electrolyte interface as well as on the electrode's operating stability [39–41]. The results have shown that the electrode performance and stability is drastically deteriorated by applying the cathodic polarization, but is significantly enhanced under the influence of anodic polarization. The underlying mechanism as indicated by the elemental analysis is that Sr surface segregation is favoured by cathodic polarization, but is suppressed by anodic polarization [39,41]. Thus we hypothesize that the Sr surface segregation due to cathodic polarization may be mitigated or even eliminated by anodic polarization. Herein, we report our investigation on the effect of cyclic polarization on the operating stability of A-site deficient $La_{0.57}Sr_{0.38}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (LSCFN) electrode on barrier-layer-free zirconia electrolyte. Adoption of A-site deficiency and/or doping high valence cations such as Nb in the B-site of perovskite structure have been demonstrated to remarkably reduce the Sr surface segregation and enhance the structural stability of LSCF [42–47]. The results demonstrate that the cyclic polarization has a beneficial effect on enhancing the operating stability of the LSCFN oxygen electrodes of SOCs.

2. Experimental

2.1. Synthesis of electrodes and fabrication of cells

A-site deficient $La_{0.57}Sr_{0.38}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (LSCFN) oxygen electrode powder was synthesized using a modified Pechini approach. $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $C_4H_4NNbO_9{\cdot}xH_2O$, citric acid (CA), ethylenediaminetetraacetic acid (EDTA) and 28% ammonia solution in reagent grade were dissolved in a beaker. Metal ions/CA/EDTA was in a molar ratio of 1:1.5:1. The aqueous solution was magnetically stirred on a hot plate till gelation took place. The gel was thoroughly dried at 180 °C in an oven for 12 h, forming foam-like ash. The ash was ground and calcined at 900 °C in air for 2 h to form LSCFN phase. The as-prepared LSCFN powder was blended with an ink vehicle (4 wt% ethyl cellulose dispersed in 96 wt% terpineol) in a mass ratio of 7:3 using an agate mortar and pestle to obtain the LSCFN ink.

YSZ electrolyte pellets and thin films were fabricated for the LSCFN electrodes. YSZ pellet samples were prepared by die pressing YSZ powder (TZ-8Y, Tosoh) at 200 MPa, and densified by sintering at 1450 °C in air for 5 h. The diameter and thickness of as-sintered YSZ pellets were 18 mm and 0.8 mm, respectively. YSZ electrolyte thin films were deposited on Ni-YSZ hydrogen electrode substrates using slurry spin coating. In the hydrogen electrode, NiO (J.T. Baker), YSZ and tapioca as pore-former were mixed in a mass ratio of 40:40:20. The premixed powder was compacted in a stainless steel die (ID 18 mm) and pre-sintered at 1000 °C in air for 2 h to burn off the pore-former and attain certain mechanical strength. A hydrogen electrode functional layer (HEFL) with identical NiO and YSZ mass ratio of 50:50 was spin coated on the hydrogen electrode. The absence of pore-former in the HEFL maximizes the active reaction site. The thickness of hydrogen electrode substrate, HEFL and YSZ film was 800, 14 and 7 μm, respectively. Detailed fabrication procedures are available elsewhere [48,49].

The LSCFN ink was screen printed to the YSZ pellets and thin films, followed by drying at 100 °C for 2 h without additional pre-sintering at high temperatures. Prior to the coating of LSCFN ink on the half cells, Pt ink (Gwent Electronic Materials Ltd) was screen printed on one side of the YSZ pellets as counter and reference electrodes and sintered at 1100 °C in air for 2 h [50]. In the case of half-cell test using YSZ pellets, Pt mesh as current collector was placed on the oxygen electrodes, while for the full cell test using YSZ thin films, Pt ink as current collector was painted on the electrode surface and heat-treated at 150 °C for 2 h. The surface area of oxygen electrodes was 0.5 and 0.25 cm^2 for half cells and full cells, respectively.

2.2. Electrochemical characterisation

Half cells were placed in a vertical tube furnace and exposed to atmospheric air. In the case of full cells, the cells were mounted on one end of an alumina tube and sealed using a ceramic sealant (Ceramabond 552, Aremco Products Inc.). The hydrogen electrode was reduced in H_2 at 750 °C for 1 h, which is adequate to convert NiO to Ni [51]. During the electrochemical testing, the hydrogen electrode was flowed with H_2 or $H_2 + CO_2$ at a rate of 50 ml min^{-1} and the oxygen electrode was open to atmospheric air. Polarization performance such as galvanostatic stability curves and impedance spectra was characterized under a current density of 0.5 A cm^{-2} and 750 °C in cathodic mode (fuel cell mode), anodic mode (electrolysis mode) and cyclic mode (switching between fuel cell mode and electrolysis mode) using a Gamry Potentiostat (Reference 3000). Impedance spectra were measured in a frequency range of 100 kHz–0.1 Hz with a signal amplitude of 10 mV under open circuit. The tests were repeated at least twice to ensure the reproducibility.

2.3. Microscopic and spectroscopic characterizations

The crystal phase of as prepared LSCFN powder was characterized using a Bruker D8 Advance X-ray diffractometer (XRD) with a Cu Kα X-ray source. The morphology of LSCFN powder and microstructure of LSCFN oxygen electrode were characterized using Zeiss Neon 40EsB scanning electron microscopy (SEM). The oxygen electrodes were also