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A robust high performance cobalt-free oxygen electrode $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$ for reversible solid oxide electrochemical cell

Ning Zhou, Yi-Mei Yin*, Jingcheng Li, Lei Xu, Zi-Feng Ma

Institute of Electrochemical & Energy Technology, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

HIGHLIGHTS

- $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$ (LSFCN) is evaluated as oxygen electrode for RSOCs.
- The LSFCN shows high performance and stability in fuel cell and electrolysis modes.
- An electrolysis current density of 0.85 A cm^{-2} is achieved at 750 °C under 1.3 V.
- No degradation is observed after 50 h electrolysis operation under 1.60 V at 800 °C.

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ABSTRACT

A novel cobalt-free perovskite oxide $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$ (LSFCN) has been synthesized and evaluated as oxygen electrode for reversible solid oxide electrochemical cells (RSOCs). The performance and stability of the LSFCN based RSOCs have been characterized in fuel cell and electrolysis modes, and the reversibility of the cells has been proven. In FC mode, the cell exhibits the maximum power density of 1.10 Wcm^{-2} at 800 °C, and a stable output under 0.7 V at 700 °C during 108 h. The performance and stability of the cell in electrolysis mode are also remarkable. An electrolysis current of 0.85 A cm^{-2} is achieved at 750 °C with an applied voltage of 1.3 V, and no degradation as well as delamination are observed for the cell after 50 h electrolysis under voltage of 1.60 V (~1.27 A cm^{-2}) at 800 °C. The high performance of the LSFCN at both cathodic and anodic conditions may be attributed to the inherent high electrochemical activity of copper-iron based perovskites; and the incorporation of Nb^{5+} cations into perovskite lattice is responsible for the stability of LSFCN, which leads to the more stable crystal structure, lower thermal expansion coefficient and the reduced Sr segregation at surface.

1. Introduction

Reversible solid oxide electrochemical cells (RSOCs) are anticipated to have important applications in future large-scale regenerative energy storage [1,2] by storing electricity (electrolysis mode) produced from solar cell or wind as relatively inexpensive chemical fuels (SOEC mode), and generating power in reverse processes by consuming those fuels when necessary (fuel cell mode). In electrolysis mode, applying high current density (≥1 A) on RSOCs is desirable, because high current density will promote cells to be operated in thermos-neutral or exothermal mode with possible utilization of excessive ohmic heat from nonelectrical sources to sustain the operating temperature. This will improve the round trip energy storage efficiency of RSOC in a charge/discharge circle [3,4]. However, the degradation rate of RSOCs in electrolysis mode is typically higher than that in fuel cell mode [5], especially, a severe degradation occurs at high current densities in electrolysis process, limiting the development and application of RSOC [6,7]. Microstructure deterioration near the oxygen-electrode/electrolyte interface has been widely reported as the major type of the degradation, which are believed to be caused by the very high internal oxygen pressure resulting from the high anodic overpotential and cation migration of the most commonly used oxygen electrodes, such as $La_{1-x}Sr_xMnO_3$(LSM) and La-Sr-Co-Fe oxide-based perovskites (LSCoF), under high anodic polarization [4–7].

Many efforts have been devoted to mitigate the microstructural

* Corresponding author.
E-mail address: yimei@sjtu.edu.cn (Y.-M. Yin).

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damage [5] by decreasing polarization resistance of oxygen electrode through modifying the cobalt-iron based perovskite oxides [8] and exploring excess oxygen tolerant electrode with layered perovskite structure [9,10], however, few of them can simultaneously satisfy the requirements for high performance and durability at SOEC mode [11]. Therefore, exploring more active and durable oxygen electrode materials for reversible operation is still an outstanding challenge.

In previous works [12–16], copper-iron based mixed ionic-electronic conductors (MIECs) with perovskite structure $Ln_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (Ln = La, Pr, Nd) have been found to have high catalytic activity for oxygen reduction reaction (ORR) (fuel cell mode) and reduced thermal expansion coefficient (TEC) in comparison with their cobalt-based counterparts as cathode of SOFC. However, the electrochemical activity and stability of these materials for oxygen evolution reaction (OER) in electrolysis mode are still doubtful due to its oxygen deficient perovskite structure which is not very flexible in maintaining phase integrity in both oxygen-excess (electrolysis mode) as well as in oxygen-deficient (fuel cell mode) conditions [9]. It has been reported that Nb doping can stabilize the perovskite structure of oxides, such as $SrCoO_{3-\delta}$ [17], $SrTiO_3$ [18], $BaCo_{0.7}Fe_{0.3-x}Nb_xO_{3-\delta}$ [19] and $Ba_{0.9}Co_{0.5}Fe_{0.4}Nb_{0.1}O_{3-\delta}$ [11], due to the incorporation of high oxidation state of Nb^{5+} cations. The stabilizing effect of Nb^{5+} cations for perovskite structure has been considered as the decrease of the number of oxygen vacancies (δ) or electronic holes (Co^{4+}) [17], or introduction of oxide anions (excess oxygen) or cation vacancies (for example, Sr vacancies) to compensate the positive charge and to stabilize the perovskite structure [18]. In the meantime, the ionic mobility of the $BaCo_{0.7}Fe_{0.3-x}Nb_xO_{3-\delta}$ oxides was improved by Nb doping possibly through lowering the migration barrier of oxygen ion in lattice [19]. Similarly, the oxygen permeability of $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ has also been observed to be enhanced by Nb substitution for Co [17]. Therefore, in this paper, Nb is used to partially substitute Cu of $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.0.2}O_{3-\delta}$ (LSFC) to prepare $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$ (LSFCN), then the properties and performances of LSFCN as oxygen electrode of RSOCs in both fuel cell mode and electrolysis mode are investigated, including structure stability, surface chemistry, thermal expansion coefficient (TEC), conductivity, and electrochemical performance as well as stability in both cathodic and anodic conditions.

2. Experimental

2.1. Material synthesis and characterization

$La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$ (LSFCN) precursor was synthesized using a solid-state reaction method as we previously reported for other copper-iron perovskites [20]. Initially, stoichiometric amounts of La_2O_3, $SrCO_3$, Fe_2O_3, CuO and Nb_2O_5 powders were mixed and ball milled for 24 h in a planetary ball miller (Instrument Company affiliated to Nanjing University, QM-3SP2), followed by uniaxial pressing the resulting powders at a pressure of 4 MPa to form pellets. The pellets were calcined in air at 1100 °C for 10 h, subsequently grounded to obtain LSFCN final powders. The crystal structures of the powders in various atmospheres were characterized by X-ray diffraction (XRD) measurements performed on an X-ray diffractometer (Rigaku D/max-2200/PC) with a Cu Ka radiation, λ = 0.15415 nm. X-ray Photoelectron Spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV) and binding energy was calibrated using the containment carbon (C 1s = 284.6 eV). The deconvolution of the XPS spectra was completed using the XPS Peak 4.1 software.

Thermal expansion coefficient (TEC) of LSFCN was measured in air using a horizontal pushrod Netzsch DIL 402 PC dilatometer from room temperature to 900 °C at a heating rate of 5 °C min^{-1} with Al_2O_3 as reference. For TEC measurement, cylinder bars with a dimension of Φ = 8 mm × 15 mm were used. The bar was fabricated by uniaxial pressing LSFCN powders at a pressure of 200 MPa, followed by firing at 1200 °C for 5 h. The temperature dependence of electronic conductivity in air was measured on rectangular bars with a dimension of 4 × 4 × 15 mm from room temperature to 900 °C via four-terminal DC technique using a digital sourcemeter (Keithley 2420).

2.2. Electrochemical testing

Electrochemical performance of LSFCN in SOFC mode was evaluated by a symmetric half cell and an anode-supported full cell with the configuration of LSFCN|SDC|LSFCN and Ni-YSZ|YSZ|SDC|LSFCN, respectively. The half cell was prepared according to our previous procedure [20,21] by screen-printing LSFCN ink onto both sides of SDC pellet and sintered at 900 °C for 2 h. Electrochemical impedance spectra (EIS) were collected via AC impedance method using Zahner IM6eX electrochemical workstation on the cells under open circuit voltage (OCV) in temperature range of 600–800 °C at 50 °C interval after cell stabilization for 15 min at each testing temperature. An AC signal with 10 mV amplitude and a frequency range from 0.01 Hz to 10^6 Hz was applied for the EIS measurements.

The full cell was fabricated based on the commercial half-cell Ni-YSZ|YSZ with a thick anode-supporting layer (~300 μm) and dense YSZ electrolyte layer (~14 μm) purchased from NIMTE (Ningbo Institute of Material Technology & Engineering, Chinese Academy of Science). The SDC ink was screen-printed onto the YSZ electrolyte and sintered at 1250 °C for 2 h to form a protection interlayer with the thickness of ~10 μm. Then the LSFCN ink was screen-printed on the SDC interlayer and sintered at 900 °C for 2 h. The thickness and active area of the oxygen electrode are ~30 μm and ~0.28 cm^2, respectively. The current-voltage (I-V) curves of the cells were collected by a four-probe configuration. The fuel electrode side was fed by humidified hydrogen with 3 vol % H_2O at the flow rate of 60 ml min^{-1}, while the oxygen electrode was exposed to static air as oxidant. The stability of the cells was tested under a voltage of 0.7 V at 700 °C. During the test, the gas flow rate of wet H_2 (~3% H_2O) as the fuel was controlled at 40 ml $min^{-1}$and static air was used as the oxidant.

The setup for SOEC operation has been described previously [8], N_2 at a flow rate of 80 ml min^{-1} was used as a carrier gas which was saturated in a water bath at 80 °C. The carrier gas was fed to the hydrogen electrode (cathode) chamber, and the anode LSFCN was exposed to static air. To maintain the reducing atmosphere, hydrogen with a flow rate of 10 ml min^{-1} was introduced into the hydrogen electrode. The absolute humidity (AH, the vol% of humidity in the total gas volume) was about 50 vol% in the electrolysis process. I-V curves are recorded from OCV to OCV ±1 V with a voltage sweeping speed of 0.03 V^{-1}. The stability of the cell was tested using a DC Electronic Load under a posed voltage of 1.6 V at 800 °C.

3. Results and discussion

3.1. Structural stability of LSFCN in various atmospheres

X-ray diffraction measurements are conducted for LSFCN and LSFC powders fired respectively in air, pure O_2 and 5% H_2-Ar at 900 °C for 10 h to examine the structural stability of the samples in oxygen-rich and oxygen-deficit atmospheres. Fig. 1a and b shows the XRD patterns of LSFCN and LSFC powders, respectively. Cubic