



Niobium doped lanthanum calcium ferrite perovskite as a novel electrode material for symmetrical solid oxide fuel cells



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HIGHLIGHTS

- $\text{La}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (LCFNb) was used as symmetrical SOFC electrodes.
- LCFNb is high stable and activated in reducing and oxidizing atmospheres.
- The catalytic activity of LCFNb for H_2 oxidation is better than O_2 reduction.
- Maximum power density of 528 mW cm^{-2} in H_2 was obtained at 850°C .
- Short-term stability in H_2 , CO and syngas for 50 h were achieved.

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ABSTRACT

Development of cost-effective and efficient electrochemical catalysts for the fuel cells electrode is of prime importance to emerging renewable energy technologies. Here, we report for the first time the novel $\text{La}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (LCFNb) perovskite with good potentiality for the electrode material of the symmetrical solid oxide fuel cells (SSOFC). The $\text{Sc}_{0.2}\text{Zr}_{0.8}\text{O}_{2-\delta}$ (SSZ) electrolyte supported symmetrical cells with impregnated LCFNb and LCFNb/SDC ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$) electrodes achieve relatively high power outputs with maximum power densities (MPDs) reaching up to 392 and 528.6 mW cm^{-2} at 850°C in dry H_2 , respectively, indicating the excellent electro-catalytic activity of LCFNb towards both hydrogen oxidation and oxygen reduction. Besides, the MPDs of the symmetrical cells with LCFNb/SDC composite electrodes in CO and syngas (CO: $\text{H}_2 = 1:1$) are almost identical to those in H_2 , implying that LCFNb material has similar catalytic activities to carbon monoxide compared with hydrogen. High durability in both H_2 , CO and syngas during the short term stability tests for 50 h are also obtained, showing desirable structure stability, and carbon deposition resistance of LCFNb based electrodes. The present results indicate that the LCFNb perovskite with remarkable cell performance is a promising electrode material for symmetrical SOFCs.

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1. Introduction

Recent years have witnessed remarkable growing interests in solid oxide fuel cells (SOFCs) research due to their distinctive advantages of high energy conversion efficiency, low emission of greenhouse gases and wide fuel flexibility [1–4]. Among all types of

SOFCs, a new concept of symmetrical SOFC (SSOFC) with identical material compositions for both electrodes has been attracting increasing attentions due to its potentials for simplifying fabrication processes, lowering production costs, improving thermo-mechanical compatibility between the electrolyte and the electrodes, and easy cleanup of the coking and sulfur poisoning by briefly reversing the gas flow to remove the possible carbon deposition and sulfur adsorption on the anode side [1,5–7].

Requirements for the SSOFC electrode materials are rather strict. High electrical conductivity and structural stability in both oxidizing and reducing atmospheres, good electrochemical catalytic activities for both oxygen reduction and fuel oxidation, and

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reasonable carbon resistance and sulfur de-poisoning abilities are necessary for an ideal electrode material [1,8]. To date, however, only a few numbers of materials have been proposed as possible electrodes for SSOFC, most of which are perovskite or double perovskite materials, such as: $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.97}\text{O}_3$ [9], $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ [5,10,11], $\text{La}_{0.3}\text{Sr}_{0.7}\text{Cr}_x\text{Fe}_{1-x}\text{O}_3$ [12], $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{Fe}_x\text{O}_3$ [13], $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ [14,15], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Sc}_{0.1}\text{O}_3$ [6], $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ [16,17], $\text{Sr}_2\text{Co}_{1+x}\text{Mo}_{1-x}\text{O}_6$ [18], $\text{Sr}_2\text{Fe}_{1.5-x}\text{Co}_x\text{Mo}_{0.5}\text{O}_6$ [19], $\text{SrFe}_{0.75}\text{Zr}_{0.25}\text{O}_3$ [20], $\text{La}_{0.6}\text{Sr}_{1.4}\text{MnO}_4$ [21] et al.

As listed above, the Fe based perovskite and double perovskite oxides play important roles in the selection of the potential materials for SSOFC electrode. Recently, $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ (LCF) perovskite ceramic with low cost has been reported to be an effective and energy-saving oxygen ion transfer membrane for syngas production from CH_4 due to its advantages of high oxygen-ion conductivity and phase stability in both oxidizing and reducing atmospheres [22,23]. However, there is certainly a concern about the possible problem of chemical instability of LCF under the rigorous reducing condition in the anode side since Fe based perovskite in the anode compartment of a SOFC is reported to be not stable enough due to the very low oxygen partial pressure under the anode operating conditions [24,25]. Considering that the stability of ABO_3 perovskite could be enhanced by substituting the B-site cation with another transition metal ion with a higher valence [26–28], Fe^{3+} ions in the LCF can be partially substituted by Nb^{5+} ions to form the novel $\text{La}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (LCFNb) perovskite due to their similar ionic radii (0.0645 nm for Fe^{3+} vs. 0.064 nm for Nb^{5+}), with respect to improving the chemical stability of LCFNb for SOFCs applications.

In this paper, the Fe-based perovskite $\text{La}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ as a novel electrode material for symmetrical SOFC is discussed. The SSOFC backbone was fabricated by lamination method with the dense SSZ ($\text{Sc}_{0.2}\text{Zr}_{0.8}\text{O}_{2-\delta}$) electrolyte film sandwiched between two porous SSZ layers. The electrode surface areas and triple-phase boundary lengths were substantially increased via the impregnation of LCFNb precursor. The composite electrode with additional SDC ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$) precursor infiltrated into the LCFNb electrode was also fabricated and tested. The obtained results demonstrate that the LCFNb perovskite has good structural stability, carbon deposition resistance and remarkable catalytic activities in both anode and cathode conditions, making LCFNb a promising electrode candidate for symmetrical SOFCs.

2. Experimental details

2.1. Cell fabrication

The $\text{La}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (LCFNb) and SDC ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$) precursors were both prepared by a conventional citrate-nitrate method [29–31], by which stoichiometric amounts of the raw materials (Analytical grade, all from Aladdin Reagent Corp.) were successively weighted and dissolved in deionized water to form the desired solutions. More specifically, stoichiometric amount of Niobium (V) oxalate hydrate ($\text{C}_{10}\text{H}_5\text{NbO}_{20}\cdot 6\text{H}_2\text{O}$) was weighted, dissolved in deionized water through complexation with citric acid (CA) in one beaker (Solution A), while stoichiometric amounts of the $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ chemicals were weighted, dissolved in another beaker (Solution B) by deionized water. Then, the Solution B was dropped into Solution A under the constant and vigorous magnetic stirring to avoid any possible hydrolysis reactions. As to the SDC precursor, stoichiometric amounts of CA, $\text{Sm}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ were weighted and dissolved in deionized water in any sequence. In both cases, the complexing capability of citric acid was used at a mole ratio 1.8:1 of

CA to total metal ions. The final concentrations of the precursors were both about 0.5 mol/L. The as-prepared LCFNb and SDC precursors were transparent and can be kept stable up to two months at room temperature.

The commercial SSZ powder ($\text{Sc}_{0.2}\text{Zr}_{0.8}\text{O}_{2-\delta}$, Tianyao, China) was ball-milled thoroughly with ethanol solvent and polyvinyl butyral (PVB) binder for 48 h to prepare the electrolyte slurry, while additional graphite was introduced as pore formers to prepare the electrode slurry simultaneously. The dense electrolyte film and porous electrode layer were tape cast, sliced and laminated into disks with a 'porous–dense–porous' sandwich structure using the as-prepared slurries. The sandwiched tri-layers were subsequently sintered at 1550 °C for 4 h in air. The porosity of the porous electrode layer was estimated to be around 69% by calculating its volume and weight. The effective electrode areas for all the as-prepared cells were 0.31 cm².

The as-prepared tri-layer wafers were then impregnated with the aqueous solution containing 0.5 M LCFNb or SDC precursor solution in the two porous electrode sides, followed by a heat-treatment at 450 °C for five minutes. The loadings of LCFNb and SDC were measured with an electronic balance and the infiltration procedure was repeated by turns. The final weight increments of LCFNb and SDC were about 40 wt.% and 25 wt.% with respect to the whole weight of the porous layer, respectively. Finally, the cells with impregnated electrodes were sintered at 850 °C for 2 h. The obtained electrodes after infiltration were abbreviated as LCFNb or LCFNb/SDC hereafter for convenience.

2.2. Characterization

The as-prepared single cell was sealed with ceramic adhesive (Ceramax 552, Aremco products, USA) onto one end of the alumina ceramic tube. Silver paste (DAD-87, Shanghai Research Institute of Synthetic Resin, China) was used as the current collector for the electrodes. A tubular furnace (SK-G08123K, Tianjin Zhonghuan, China) was utilized to heat the cells. Before testing, the assembled SOFC was first heated to 650 °C and fed with H_2 to ensure proper function. After the open circuit voltage (OCV) was stabilized for one hour in H_2 at the target temperatures, the impregnated cell was electrochemically characterized. The H_2 gas flow was then switched to CO or syngas ($\text{CO}:\text{H}_2 = 1:1$) if necessary and the cell was tested again before the temperature was elevated to the next temperature. The anode fuel gas was fixed at a flow rate of 30 sccm with a mass flow controller (Alicat, USA), while the cathode was exposed to ambient air during all the tests.

The electrochemical performance characterization was performed at the temperatures ranging from 650 to 850 °C at 50 °C intervals by using an Arbin MSTAT4 electrochemical workstation (Arbin Corporation, USA) with a four-probe setup. The electrochemical impedance spectrum (EIS) was conducted using an AC signal amplitude of 10 mV at open circuit voltage with the impedance frequency ranging from 1 MHz to 0.01 Hz.

To evaluate the crystallization property of the LCFNb, part of the LCFNb precursor solution was calcined at 850 °C in air for 2 h and detected by the X-ray diffraction (XRD) technique. The powders of LCFNb, SDC and SSZ were also ball milled thoroughly and reduced in pure hydrogen for 4 h at 850 °C to assess the possible harmful reaction between them. The XRD patterns were recorded with a conventional X-ray powder diffractometer (PANalytical, operating at 40 kV and 30 mA using $\text{CuK}\alpha$ radiation, scanning in the 2 θ range of 10–70°). The microstructures of the cell before and after testing were observed with a scanning electron microscope (SEM, Hitachi SU8010, Japan) coupled with Oxford energy-dispersive X-ray spectroscopy (EDS, Oxford X-MAX 50 mm², UK).

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