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High performance $\text{La}_{0.3}\text{Ca}_{0.7}\text{Cr}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ air electrode for reversible solid oxide fuel cell applications

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ARTICLE INFO

Article history:

Received 5 October 2014

Received in revised form

21 November 2014

Accepted 22 November 2014

Available online 19 December 2014

Keywords:

Reversible solid oxide fuel cells

Air electrode

Mixed conducting oxides

Oxygen reduction

Oxygen evolution

Electrocatalysis

ABSTRACT

A novel mixed-conducting perovskite oxide ($\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, LCFCr), prepared using the combustion method, has been developed as a new air electrode material for reversible solid oxide fuel cells (RSOFCs) applications. XRD analysis showed that the LCFCr powder is a pure crystalline phase with an orthorhombic perovskite structure and that its thermal expansion coefficient matches closely with several commonly used solid electrolytes, while TEM analysis confirmed the high purity of the LCFCr powders. The electrochemical activity of LCFCr, screen-printed on a gadolinium doped ceria electrolyte, towards both the oxygen reduction (ORR) and oxygen evolution (OER) reactions, was examined at 600–800 °C in stagnant air using a symmetrical RSOFC configuration. Under open circuit conditions, LCFCr showed a very low polarization resistance (R_p) of only 0.07 $\Omega \text{ cm}^2$ at 800 °C, comparable to some of the best-performing oxide materials reported by others. The LCFCr air electrode was also found to be very stable, with very little loss in performance and no interfacial damage observed, even after 100 h at a 0.4 V (OER) and –0.4 V (ORR) overpotentials.

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Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that can convert chemical energy into electrical energy with very high efficiency. SOFCs also have several other advantages over combustion-based technologies, such as fuel flexibility (H_2 , hydrocarbon-based fuels such as CH_4 , CO , etc.), low emission of pollutants (SO_x and NO_x), and serve to capture CO_2 from the

anode exhaust stream in high purity form, already separated from N_2 .

A typical SOFC consists of a dense electrolyte and two porous electrodes, the anode and the cathode. As part of the efforts to develop new energy conversion systems, there is great interest in reversible fuel cells, particularly reversible solid oxide fuel cells (RSOFCs). RSOFCs are single-unit, all-solid-state, electrochemical devices that can operate in both

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<http://dx.doi.org/10.1016/j.ijhydene.2014.11.127>

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the fuel cell (SOFC) and electrolysis (SOEC) mode, thus acting as flexible energy conversion and storage systems, particularly to store intermittent renewable energy, such as wind or solar. The most common degradation and cell failure issue for RSOFs arises at the air electrode when the cell is operating in the electrolysis mode (oxygen evolution at the air electrode). This is due to delamination of the electrocatalytic material from the electrolyte. Although the delamination mechanism is not fully understood, several processes have been postulated, including high oxygen pressure development, morphological changes in air electrodes, and electrolyte grain boundary separation [1–5]. Therefore, in this work, one of the main emphases is on the development of a mixed conducting oxide (MIEC) that can withstand electrolysis conditions without delamination, while also exhibiting superior oxygen evolution and reduction activities.

To date, the most common materials used in RSOFs are essentially the same as those used for SOFC, namely yttria stabilized zirconia (YSZ) as the electrolyte, a Ni-YSZ cermet as the fuel electrode, and a $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM)-YSZ composite as the air electrode. The search for higher performance electrode and electrolyte materials for RSOFs has been a key focus of research in recent years, with a particular emphasis on the development of new air electrodes. This has included the development of mixed ionic-electronic conductors (MIECs), such as Fe-based perovskites e.g., $\text{SrFeO}_{3-\delta}$, and the use of a variety of cation dopants in both the A and B-sites [6–9]. As an example, LaCrO_3 and its doped variants are good candidates for application as interconnect materials and cathode materials in SOFCs [10]. Other high performance air electrode materials include $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), which has exhibited a low polarization resistance (R_p) of $0.18 \Omega \text{ cm}^2$ at 800°C [11], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ (LSFCu), which has demonstrated a very low R_p of $0.07 \Omega \text{ cm}^2$ [12], and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) (2), which has exhibited a polarization resistance of $0.3 \Omega \text{ cm}^2$ at 800°C [13].

Recently, Chen et al. [14] have shown very good catalytic activity for both H_2/CO oxidation and O_2 reduction using the same MIEC material at both electrodes, i.e., $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr), used for the first time as an SOFC electrode. The selected stoichiometry of the material was based on increasing the electronic and ionic conductivity of a Fe-based perovskite by heavy A-site substitution of La by Sr. As well, the partial substitution of Fe at the B-site by Cr was done to stabilize the orthorhombic perovskite and its associated high level of vacancy disorder [15].

Usually, MIECs are synthesized by solid-state reactions, where the process involves multiple heating ($\geq 1200^\circ\text{C}$) and regrinding steps to help overcome the solid-state diffusion barrier [16]. Some of the traditional methods by which MIECs have been prepared include the sol–gel method [6], the EDTA citrate complexing process [12], the auto-ignition process [7], the Pechini method [9], and most commonly, by using combustion methods [14].

In the present study, the focus is on measuring the performance of a derivative of LSFCr, i.e., $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr), synthesized by the combustion method. The A-site of the perovskite was doped with Ca instead of Sr, as Ca has a smaller ionic radius than Sr and hence we were expecting to decrease the thermal expansion coefficient of the MIEC to more

closely match that of the gadolinium doped ceria (GDC) electrolyte. Several previous studies [17,18] have shown that of perovskite materials decreases as the A-site cation size is decreased, which inspired us to replace Sr with Ca (smaller ion) in our perovskite-based chromium ferrites. While the thermal expansion data for perovskites reflects both physical and chemical expansion processes, the chemical expansion due to oxygen loss should dominate the thermal expansion behavior at high temperatures. The partial substitution of Ca for Sr may also enable the introduction of structural inhomogeneities, as calcium doping of LaFeO_3 is known to promote oxygen-vacancy ordering [19,20]. We were also hoping to maintain the excellent electrochemical properties of LSFCr, despite the replacement of Sr with Ca. Consistent with these objectives, LCFCr/GDC/LCFCr symmetrical half cells, operated at $600\text{--}800^\circ\text{C}$ in stagnant air, were found to exhibit excellent electrochemical performance and long term durability, similar to our previously studied LSFCr material [8]. Electrochemical measurements have shown polarization resistances of only 0.07, 0.34, 0.71, 1.6 and $4 \Omega \text{ cm}^2$ at 800, 750, 700, 650 and 600°C , respectively.

Experimental methods

Material synthesis and characterization

$\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr) powders were synthesized by the combustion method. The metal nitrates were mixed in stoichiometric proportions and dissolved in deionized water. A 2:1 mole ratio of glycine to the total cation content was used. Solutions were slowly stirred on a hot plate until auto-ignition and self-sustaining combustion occurred. Then the sample was calcined in air at 1200°C .

X-ray diffraction (XRD) patterns of all of the samples synthesized in this work were collected using a Philips X'Pert PRO ALPHA1 of Panalytical B.V. diffractometer with $\text{Cu K}\alpha_1$ monochromatic radiation ($\lambda = 1.54056 \text{ \AA}$). The diffractometer was equipped with a primary curved Ge111 primary beam monochromator and a speed X'Celerator fast detector, operating at 45 kV and 40 mA. XRD patterns were collected in the 2θ range of $5\text{--}120^\circ$ at room temperature with a step size of 0.017° and 8 s counting time in order to ensure sufficient resolution for structural refinement.

Powder X-ray Thermo-diffraction patterns were collected on an X'Pert PRO MPD diffractometer with a high temperature reactor chamber Anton Paar HTK1200 camera, using $\text{Cu K}\alpha$ radiation. The measurements were carried out at between room temperature and 1100°C . The standard working conditions were a 2θ range of $10\text{--}70^\circ$ with an angle step size of 0.033° and a 25 s counting time. Sample was heated to the target temperatures at a ramp rate of $5^\circ\text{C}/\text{min}$ and stabilized in air for 40 min prior to the measurements. After that, the sample was cooled to RT and XRD patterns were acquired again in order to determine the phase stability of the LCFCr material under heating and cooling conditions.

Fullprof Software was employed to carry out structural refinements from conventional XRD patterns using the Rietveld method. This method of refining the powder diffraction data was used to determine the crystal structure. Zero shift, lattice parameters, background, peak width, shape and

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