



## Sr-rich chromium ferrites as symmetrical solid oxide fuel cell electrodes

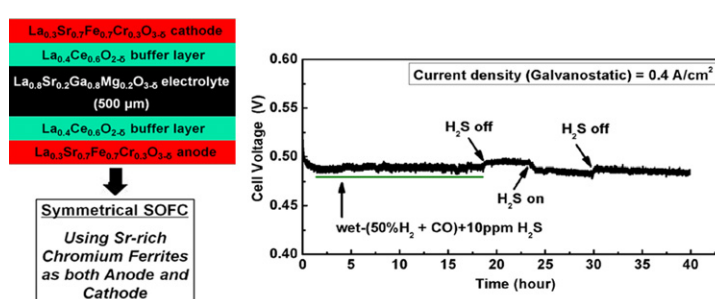
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### HIGHLIGHTS

- ▶ Cr-containing cathode shows  $R_p$  of  $0.1 \Omega \text{ cm}^2$  in air at  $800^\circ\text{C}$ .
- ▶ Sr-rich Ferrite shows far more better anode performance than La-rich Ferrite.
- ▶ Structural stability limit of LSFC-3 is down to a  $p\text{O}_2$  of  $1.9 \times 10^{-21}$  atm at  $800^\circ\text{C}$ .
- ▶ LSFC-3<sup>wet</sup>  $\rightarrow$   $\text{H}_2$ LaSrFeO<sub>4</sub>-based phase +  $\alpha$ -Fe $\rightarrow$ LSFC-3, regenerative crystal structure.
- ▶ LSFC-3 anode performs well in wet 1:1 H<sub>2</sub>:CO fuels with  $p\text{O}_2 > 1.9 \times 10^{-21}$  atm.

### GRAPHICAL ABSTRACT



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### ABSTRACT

For the first time, anodes and cathodes composed of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Cr}_x\text{O}_{3-\delta}$  (LSFC,  $x = 0-0.3$ ) are used within a symmetrical solid oxide fuel cell (SSOFC).  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM) electrolyte-supported half cells, employing  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  (LSFC-3) at both electrodes, produced electrode polarization resistances of  $0.1 \Omega \text{ cm}^2$  in air and  $0.4 \Omega \text{ cm}^2$  in wet (ca. 3% $\text{H}_2\text{O}$ )  $\text{H}_2$  at  $800^\circ\text{C}$ . Although LSFC is robust under typical SSOFC conditions at  $500^\circ\text{C}$ , *in-situ* X-ray diffraction studies at  $800^\circ\text{C}$  in reducing atmospheres show that its perovskite structure can undergo a slow,  $p\text{O}_2$ -dependent structural change, forming a LaSrFeO<sub>4</sub>-based Ruddlesden-Popper phase plus  $\alpha$ -Fe, a process which can be reversed in air at  $800^\circ\text{C}$ . For LSFC-3, this phase change occurs when the  $p\text{O}_2$  of the fuel is lower than  $1.9 \times 10^{-21}$  atm. This results in an initial power drop of ca. 30% for LSFC-3-based SSOFCs when using wet  $\text{H}_2$ , but the new anode composition still maintains a promising  $0.2 \text{ W cm}^{-2}$  cell power density over several hundred hours of operation. Extended full cell tests also show that the LSFC-3 anode performs very well in wet 1:1  $\text{H}_2$ :CO fuels ( $p\text{O}_2 > 1.9 \times 10^{-21}$  atm) that contain 10 ppm  $\text{H}_2\text{S}$ , demonstrating the excellent versatility of this electrode material.

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### 1. Introduction

Solid oxide fuel cells (SOFCs) are high efficiency energy conversion devices that also have several environmental advantages, including low to zero emission of pollutants ( $\text{SO}_x$ ,  $\text{NO}_x$  and particulates) and the generation of a clean and nearly pure stream of  $\text{CO}_2$

(no  $\text{N}_2$ ) ready for carbon capture and storage (CCS). From a cost and long-term performance perspective, there is also significant interest in developing symmetrical SOFCs (SSOFCs) using the same redox-stable materials as both the anode and cathode [1–4]. By employing identical anode and cathode compositions, the cell can be fired in a single step, hence reducing fabrication costs. Also, because conventional SOFC anodes are prone to sulfur poisoning and carbon deposition, the redox tolerance of SSOFCs allows regeneration of the anode chamber by periodic purges with steam or air, a process often employed to de-coke large-scale industrial processes [5].

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However, a key challenge in the development of SSOFC electrode materials is that they must show stable, long-term performance, while also possessing high catalytic activity and electronic conductivity over many orders of magnitude  $pO_2$  change, from a  $pO_2$  of 0.21 atm at the cathode to a  $pO_2$  of  $10^{-22}$  atm at the anode. To date, many redox-stable oxides have been evaluated as potential electrodes for SSOFCs, classified as simple perovskites ( $ABO_{3-\delta}$ ) [6,7], fluorites ( $AO_{2-\delta}$ ) [8], and perovskite-like layered compositions, such as double-perovskite ( $A_2BO_{6-\delta}$ ) [3,9]. In terms of simple perovskites, high performance Co-based perovskites are typically not stable in the presence of fuels and therefore previous work has focused more on Mn- and Fe-based perovskites [10]. Extensive work has shown that substituting the B site Mn in perovskites with Ti and Cr can result in stable, high performance anodes [11,12]. A similar strategy was used to stabilize the Fe-based perovskite,  $La_{0.75}Sr_{0.25}Fe_{0.5}Cr_{0.5}O_{3-\delta}$ , which remains a single phase in 5%  $H_2$  at 900 °C for 120 h [13]. However, as is the case for most simple perovskites, heavy doping with early transition metals leads to a significant loss of electronic and ionic conductivity, while also lowering the catalytic activity for  $O_2$  reduction on the cathode side [14].

Compared to the low Sr simple perovskites, a high Sr content in the A-site of perovskite-like phases has produced high performance ceramics that are phase stable over a wide  $pO_2$  range [15,16].  $LaSr_2Fe_{3-y}Cr_yO_{8+\delta}$  oxides, targeted as membrane materials for the partial oxidation of natural gas, have excellent ionic and electronic conductivity at oxygen partial pressures ranging from 0.5 to  $10^{-22}$  atm [17]. Recently, Fe- and Co-based double-perovskite materials, such as  $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$  have shown among the best SSOFC performances (ca.  $0.5\text{ W cm}^{-2}$ ) in  $H_2$ -air at 800 °C when employing a 0.3 mm thick  $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$  (LSGM) electrolyte support [3]. For example, a very low polarization resistances ( $R_p$ ) of 0.20–0.25  $\Omega\text{ cm}^2$  in  $H_2$  at 750–800 °C was reported for the  $LaSr_2Fe_2CrO_{8+\delta}$ – $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (GDC) composite anode [18]. Much of this work still remains in the initial stages and long-term testing under a variety of fuels and testing conditions must still be carried out.

In the present study, the high Sr content Fe-based  $La_{0.3}Sr_{0.7}Fe_{1-x}Cr_xO_{3-\delta}$  (LSFC) perovskite was selected for investigation, for the first time, as an SSOFC electrode. This was based on first increasing the electronic and ionic conductivity of a Fe-based perovskite by pushing its structural stability limit via heavy A-site substitution of La by Sr. At the extreme, it would then become structurally equivalent to the vacancy-ordered, perovskite-like, brownmillerite,  $LaSr_2Fe_3O_8$  [19], but the B site Fe should then become partially substituted by Cr to stabilize the orthorhombic perovskite and its associated high level of vacancy disorder [17]. This is because Cr has a strong preference to maintain 6-fold coordination with oxygen anions, which helps to avoid the formation of the vacancy-ordered iron–oxygen tetrahedra within the tunnels associated with layered perovskites [17]. Thus, Cr-doping can lead to a net increase, rather than a decrease, in ionic conductivity. At the same time, Cr substitution is known to increase the structural stability of  $La_{0.3}Sr_{0.7}FeO_{3-\delta}$  in reducing atmospheres [14].

This work explores the chemical (structural) stability, thermal expansion, electrical conductivity, and electrocatalytic properties of  $La_{0.3}Sr_{0.7}Fe_{1-x}Cr_xO_{3-\delta}$  (abbreviated as LSFC-0, LSFC-1, LSFC-2 and LSFC-3 for compositions with  $x = 0, 0.1, 0.2$  and  $0.3$ , respectively) over a wide range of  $pO_2$  values and temperatures. The trade-offs between these characteristics have led to the identification of the LSFC-3 material as the optimum composition for application as a SSOFC electrode. This material functions very well as a cathode and is also very good anode down to a  $pO_2$  of  $1.9 \times 10^{-21}$  atm. Even though the LSFC-3 material decomposes at a  $pO_2$  below this limit, the decomposition products (a  $LaSrFeO_4$ -based phase and  $\alpha$ -Fe) are also surprisingly active. Even more interestingly, reoxidation can

fully restore the single perovskite LSFC-3 starting material. It is shown that SSOFCs, based on LSFC-3 as both the anode and cathode, exhibit excellent long-term electrochemical performance under a variety of fuel conditions, including with exposure to a  $CO/H_2$  mixture containing 10 ppm  $H_2S$ .

## 2. Experimental

A glycine nitrate process was employed to prepare the LSFC powders. Reagent grade  $La(NO_3)_3 \cdot 6H_2O$ ,  $Sr(NO_3)_2$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Cr(NO_3)_3 \cdot 9H_2O$  and glycine were dissolved in deionized water using metal cation proportions that were based on the desired stoichiometry of each LSFC material. A 2:1 mol ratio of glycine to the total metal cation content was used. Stirred solutions were slowly heated on a hot plate until auto-ignition and self-sustaining combustion occurred. The ash was subsequently pulverized and pre-calcined at 1200 °C for 2 h in air (conditions under which single phases are generated). Powders were milled (high energy planetary ball mill, Pulverisette 5, Fritsch, Germany) in an isopropanol medium at a rotation speed of 300 rpm for 2 h using zirconia balls and were then divided into three parts, with one portion employed to investigate the material structural stability. The second portion of the LSFC powder was used for the thermal expansion and electrical conductivity measurements, while the third was employed in electrochemical testing.

The phase identification of the powders in air and dry 10%  $H_2 + N_2$  was carried out *in-situ* using a Bruker D8 Advance powder X-ray diffractometer (XRD) with a high temperature sample holder. Room temperature XRD examination of ex situ samples exposed to different fuel conditions at 800 °C for 72 h (the samples were quenched to room temperature in the same fuel environment as used at 800 °C) was also carried out. The oxygen content change in the specimens as a function of temperature was determined using thermogravimetric (TG) methods (Mettler Toledo Thermal Analysis, TGA/DSC1) at up to 900 °C in air. In order to achieve thermodynamic equilibrium during the reduction (heating) and the oxidation (cooling) of the oxide powders, a relatively low heating/cooling rate of  $2\text{ }^\circ\text{C min}^{-1}$  was used for each TG run.

For the conductivity and thermal expansion coefficient measurement, LSFC powders were uniaxially pressed into disks and cylinders under a pressure of 100 MPa (10 mm in diameter and 1 mm in thickness), followed by sintering at 1300 °C for 4 h in air. The density of the specimens was determined using the Archimedes method, giving a value of around 95%. The pellets were polished using emery paper (SiC media, 600 mesh) to ensure surface flatness and were then coated with Pt paste. The electrical conductivity was measured using the dc Van der Pauw method at 300–900 °C in both air and wet (3% $H_2O$ )–(10% $H_2 + N_2$ ). The thermal expansion measurements were conducted using cylindrical specimens (5 mm diameter and 8 mm in thickness) by heating at  $5\text{ }^\circ\text{C min}^{-1}$  between 50–900 °C in air, using a Linseis L75PT vertical dilatometer, with YSZ used as the calibration standard.

The  $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$  (LSGM, [fuelcellmaterials.com](http://fuelcellmaterials.com)) electrolyte powders were cold isostatically pressed into 35 mm pellets under a pressure of 100 MPa and pre-sintered at 1100 °C for 2 h in air to ensure adequate strength. Next, a  $La_{0.4}Ce_{0.6}O_{2-\delta}$  (LDC) buffer layer was coated onto both sides of the LSGM substrate using screen printing, followed by co-sintering at 1350 °C for 4 h. The thickness of the resulting dense electrolyte support was ca. 1 mm and 0.5 mm for the half cell and single cell studies, respectively, and the diameter was 28 mm. The LSFC powders were then screen printed symmetrically (1.0  $\text{cm}^2$  area) onto both sides of the LSGM support and fired at 1100 °C for 2 h. Au paste (C 5729, Heraeus Inc. Germany) was painted on the LSFC layers at both sides of the pellet to serve as the anode and cathode current collectors. To

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