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# Novel LaFe<sub>2</sub>O<sub>4</sub> spinel structure with a large oxygen reduction response towards protonic ceramic fuel cell cathode<sup> $\star$ </sup>

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# ABSTRACT

Highly active and stable electrocatalysts are mandatory for developing high-performance and longlasting fuel cells. The current study demonstrates a high oxygen reduction reaction (ORR) electrocatalytic activity of a novel spinel-structured LaFe<sub>2</sub>O<sub>4</sub> via a self-doping strategy. The LaFe<sub>2</sub>O<sub>4</sub> demonstrates excellent ORR activity in a protonic ceramic fuel cell (PCFC) at temperature range of 350–500 °C. The high ORR activity of LaFe<sub>2</sub>O<sub>4</sub> is mainly attributed to the facile release of oxide and proton ions, and improved synergistic incorporation abilities associated with interplay of multivalent Fe<sup>3+</sup>/Fe<sup>2+</sup> and La<sup>3+</sup> ions. Using LaFe<sub>2</sub>O<sub>4</sub> as cathode over proton conducting BaZr<sub>0.4</sub>Ce<sub>0.4</sub>Y<sub>0.2</sub>O<sub>3</sub> (BZCY) electrolyte, the fuel cell has delivered a high-power density of 806 mW/cm<sup>2</sup> operating at 500 °C. Different spectroscopic and calculations methods such as UV–visible, Raman, X-ray photoelectron spectroscopy and density functional theory (DFT) calculations were performed to screen the potential application of LaFe<sub>2</sub>O<sub>4</sub> as cathode. This study would help in developing functional cobalt-free ORR electrocatalysts for low temperature-PCFCs (LT-PCFCs) and solid oxide fuel cells (SOFCs) applications.

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1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical conversion technology to convert the chemical energy of  $H_2$  or hydrogen-rich fuels into electrical energy in a clean and efficient way.<sup>1</sup> The unique potential of combined heat and power applications, and no need of expensive noble-metal catalysts make SOFCs more

attractive in developing energy conversion devices.<sup>2</sup> However, the high operating temperature (600–800 °C) required by SOFCs causes material challenges and makes the technology more complex.<sup>3</sup> Therefore, an operating temperature below 600 °C would be preferred to enable cheaper current collectors, shorten the start-up time, and to open new venues for applications.<sup>4</sup> The high temperature is essential to achieve enough ionic conductivity of the yttrium doped zirconia (YSZ) electrolyte and oxygen reduction reaction (ORR) activity of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> cathode.<sup>5–7</sup> Therefore, the intensive efforts of scientists have been turned to develop advanced low temperature SOFCs (LT-SOFCs) electrolytes and cathodes. But currently, it appeared to be a serious challenge due to high saturation.<sup>8,9</sup>

In this regard, protonic ceramic fuel cells (PCFCs) have emerged potentially as an alternative to SOFCs over the last decade. The PCFCs displayed more advantages over SOFCs due to low activation energy required by protons (0.3–0.6 eV) than that of oxide ion-

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conducting electrolyte; 0.7–1.0 eV, which is important to lower the operating temperature for cheap production and also extend the life span.<sup>10</sup> Although PCFCs exhibit a high-power density of greater than 1000 mW/cm<sup>2</sup> at a temperature above 600 °C, a very sharp performance decrease has been noted by reducing further the operating temperature, e.g., to 500 °C<sup>11,12</sup>. The possible reason associated with sharp decrease of performance with lowering operational temperature could be lack of suitable cathodes that could endorse the associated species, like H<sup>+</sup> and O<sup>2–</sup>, via promoting the ORR activity.<sup>13</sup> Since the reaction mechanism of PCFCs cathodes is different, the rational design of using SOFCs cathodes directly for PCFCs is not suitable. Even though this approach was extensively used during early stage of developing PCFCs, such as to use  $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$  (LSCF),  $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_3$  (BSCF),  $Pr_{1-x}Ba_xCOO_3$  and  $BaCo_xFe_{1-x}O_{3-\delta}$  into PCFCs.<sup>14–16</sup>

The materials with triple charge conducting (TCC) properties  $(e^{-}/H^{+}/O^{2-})$  are considered ideal cathodes for PCFCs, and it can extend the TPBs (triple phase boundaries) reaction zones for the gas beyond electrode-electrolyte zone and minimize the cathodic over-potential.<sup>17,18</sup> Most of the cathodes are developed by focusing on cobalt-containing perovskite-oxide. BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Zr<sub>0.1</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> (BCFZY) is one of the TCC high-performing PCFCs cathode, which exhibited a relatively high power density (460 mW/cm<sup>2</sup>) at low operating temperature of 500 °C<sup>13</sup>. PrBa<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>1.5</sub>Fe<sub>0.5</sub>O<sub>5+δ</sub> (PBSCF) is another cathode that exhibits high proton defects molar fraction (0.017) at 600 °C<sup>19</sup>. Moreover,  $Sr_2Sc_{0.1}Nb_{0.1}Co_{1.5}Fe_{0.3}O_{6+\delta}$ (SSNCF) cathode was developed for hybrid ion-conducting electrolytes that can be operated below 700 °C<sup>20</sup>. However, Cocontaining cathodes show higher performance, but have several drawbacks, as a result it is highly demanded to develop Co-free cathodes for sustainable energy future due to resource scarcity and high cost of Co. In this context,  $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_{3-\delta}$  (LSMN; x = 0.1 and 0.3) was developed as a PCFC cathode, and aliovalent  $\mathrm{Ni}^{3+}$  substitution of  $\mathrm{Mn}^{4+}$  significantly improves the hydration capacity of LSM.<sup>21</sup>

However, Fe-based electrocatalysts for SOFCs/PCFCs are more attractive because of their abundance, nontoxicity, stable behavior in oxidizing environments, and good ORR electrocatalytic activity.<sup>22</sup> Among the Fe-based oxides, lanthanide-based  $FeO_{3-\delta}$  perovskite presents attractive oxygen permeation flux and fast oxygen surface exchange kinetics. However, for practical applications, pure Febased perovskite cathodes are not such an active candidate as compared to Co-containing cathode, and it needs cation-doping to stabilize the cubic lattice in a controlled manner of disordered oxygen vacancies, such as  $Ba^{3+}$ ,  $Sm^{3+}$ ,  $Sr^{2+}$  and  $Ca^{2+}$  at A-site and  $Nb^{5+}$ ,  $Ta^{5+} Sn^{4+}$ ,  $Sb^{3+}$ ,  $In^{3+}$ , and  $Ni^{2+}$  over B-site.<sup>23</sup> On the other hand, self-reduction or reducing oxide materials by exposing to reducing atmosphere is widely used to realize the self-doping. For example, TiO<sub>2</sub> and CeO<sub>2</sub> (TiO<sub>2-x</sub> and CeO<sub>2-x</sub>) contain mixed valence states of Ti<sup>4+</sup>/Ti<sup>3+</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup>, and create abundant oxygen vacancies.<sup>24,25</sup> Therefore, these results demonstrate that it is possible to fabricate new structures to realize this strategy. Therefore, in this work, despite from the conventional doping approach, we have developed a novel spinel structure using lanthanide rare earth element as PCFCs cathode, which shows excellent strength of LaFe<sub>2</sub>O<sub>4</sub> structure toward self-doping ( $Fe^{3+}/Fe^{2+}$  and La<sup>3+</sup>) that can help to improve ORR performance without any external ions doping. We have carried out both experimental measurements and theoretical calculations to build a combined description for ORR electrocatalytic properties of LaFe<sub>2</sub>O<sub>4</sub> for PCFCs cathode. The synthesized LaFe<sub>2</sub>O<sub>4</sub> cathode exhibits significantly high and stable electrochemical performance at LTs operation of 400-500 °C. This study determines a successful development of LaFe<sub>2</sub>O<sub>4</sub> cathode and provides some interesting insight into its ORR mechanism.

#### 2. Material synthesis and characterization

#### 2.1. Material synthesis

The spinel structured LaFe<sub>2</sub>O<sub>4</sub> ferrite powders were synthesized with a sol-gel method. Firstly, 0.1 mol of ethylenediaminetetraacetic acid (EDTA) was dissolved in de-ionized water and NH<sub>3</sub> was used to set the pH of the solution to 7.0 and make the solution transparent. Moreover,  $La(NO_3)_2 \cdot 6H_2O$  and  $Fe(NO_3)_2 \cdot 9H_2O$ (99.98%, Alfa Aesar) in a 1:2 molar ratio were dispersed into the above solution. In addition, 0.1 mol of C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> was added into the solution as a chelating agent.<sup>22</sup> Afterward, continue stirring at 240 r/min and heating at 80 °C, brownish gel was obtained from the solution. The next important step was ageing the gel and drying process; the gel was kept for 24 h for ageing and then dried in a vacuum oven at 200 °C. Moreover, powder samples were subjected to heat treatment at 850 °C for 8 h. In addition, BaZr<sub>0.4</sub>Ce<sub>0.4</sub>Y<sub>0.2</sub>O<sub>3</sub> (BZCY) electrolyte was prepared using BaCO<sub>3</sub> (Alfa Aesar 99.98%), ZrO<sub>2</sub> (Alfa Aesar 98%), CeO<sub>2</sub> (Alfa Aesar 99.98%), and Y<sub>2</sub>O<sub>3</sub> (Alfa Aesar 99.99%). The precursors were ball-milled in ethanol for 24 h and afterward dried at 150 °C to obtain precursors of BZCY powders and followed by sintering at 1100 °C for 10 h with a ramp step of 10 °C/min.<sup>17</sup>

#### 2.2. PCFCs fabrication

PCFCs device was fabricated by the solid-state dry pressing method. In detail, the prepared LaFe<sub>2</sub>O<sub>4</sub> was used as cathode, NCAL  $(Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta})$  was purchased from Bamo Sci. & Tech. Joint Stock Ltd. as anode, and synthesized BZCY was used as electrolvte.<sup>19,25</sup> In the first step, the powders of LaFe<sub>2</sub>O<sub>4</sub> and NCAL were individually mixed in Terpinol in a mass ratio of 0.9:0.1 to prepare their slurries. Approximately 0.20 g slurry of each LaFe<sub>2</sub>O<sub>4</sub> and NCAL was brushed onto one side of Ni-foam of 13 mm size having cylindrical shape with a thickness of 2 mm. The brushed Ni-foam with LaFe<sub>2</sub>O<sub>4</sub> and NCAL powders was followed by being desiccated at 120 °C for 2 h. To prepare solid PCFCs, one piece of dried Ni foam NCAL was placed in a steel mold, followed via 0.25 g of BZCY electrolyte powder and Ni-foam coated LaFe<sub>2</sub>O<sub>4</sub> one by one and meanwhile pressed at 220 MPa to obtain the three-layer fuel cell device with active area of 0.64 cm<sup>2</sup>. Moreover, fuel cells were preheated at 550 °C for 2 h for densification of the electrolyte layer before electrochemical measurements.

# 2.3. LaFe<sub>2</sub>O<sub>4</sub> characterization

The structural characterization of LaFe<sub>2</sub>O<sub>4</sub> was performed using X-ray diffraction (XRD) patterns (Bruker D8, Germany) with Cu Ka radiation ( $\lambda = 0.154$  nm). The high-resolution transmission microscope (Tecnai G2 F30 S-TWIN 300 kV/FEG HR-TEM FEI USA) was used for structural analysis at crystal-level, chemical conformation and surface morphology, respectively. The performance of fabricated single PCFCs was evaluated using humidified hydrogen (typically 98% H<sub>2</sub> and 2% H<sub>2</sub>O at 20 °C) and atmospheric air as fuel and the oxidant, respectively. The flow rates of  $H_2$  and air were set to 100-120 mL/min, respectively. IT 8500 (Itech Electronics Jiangsu, China) dc electronic load was used to record fuel cell's performance data. Gamry Reference 3000 (pine instruments U.S) was used to measure electrochemical impedance spectra of the PCFCs in the open-circuit voltage conditions in H<sub>2</sub> and air in 0.1-1 MHz frequency range. The 10 mV of dc signal was applied to record the data. ZSIMPWIN software was used to fit EIS data for model circuiting of EIS spectra of PCFCs. The UV-visible absorbance spectra of LaFe<sub>2</sub>O<sub>4</sub> were measured using an UV-vis 3600

spectrophotometer. To calculate the oxygen non-stoichiometry ( $\delta$ ) value of LaFe<sub>2</sub>O<sub>4</sub>, a simultaneous thermal analyzer 449F3 Netzsch was used to measure thermo-gravimetric analysis and differential scanning analysis in N<sub>2</sub> and O<sub>2</sub> atmospheres in the temperature range of 30–600 °C According to the TGA data, the oxygen non-stoichiometry ( $\delta$ ) of samples at various temperatures was calculated using the following equation<sup>26,27</sup>:

$$\delta = \frac{M_0}{15.999} \left( 1 - \frac{m}{m_0} \right) + \delta_0 \tag{1}$$

where  $m_0$  is the initial weight and m is the final weight of the sample at final temperatures of TGA measurements.  $M_0$  is molar mass of LaFe<sub>2</sub>O<sub>4</sub> at room temperature and 15.999 is the atomic weight of oxygen atoms.  $\delta_0$  is the oxygen non-stoichiometry at room temperature calculated by iodometric method at room temperature. An NT-MDT Raman spectrometer (Russia) was used to conduct a structural analysis of LaFe<sub>2</sub>O<sub>4</sub> powders for pristine and post measurements using a solid laser excitation energy source with 532 nm and 20 mW laser power. Physical Electronics Quantum 2000 X-ray photoelectron spectroscopy was used to collect surface and chemical properties using Al K $\alpha$  X-ray source. The peak 41 software was used to examine and fit the obtained XPS data.

# 2.4. Ab initio calculations

The theoretical investigation on preparing LaFe<sub>2</sub>O<sub>4</sub> was performed with spin-polarization with the DFT + U method. The cubic structure of LaFe<sub>2</sub>O<sub>4</sub> (a = b = c = 0.06551 nm and  $\alpha = \beta = \gamma = 60^{\circ}$ ) with space group F4-3*m* was optimized using Cambridge serial total energy package (CASTEP) on Materials Studio 8.0. The exchange function of the ion-electron was preserved with projector augmented-wave potentials and generalized gradient approximation (GGA) with the method of Perdew–Burke–Ernzerhof. The plane waves cut-off energy of 720 eV was used for calculations.<sup>28</sup> The convergence iteration error of 10<sup>-5</sup> for each atom was used to self-consistently solve Kohn–Sham equation. A unit cell of  $3 \times 3 \times$ 3 of LaFe<sub>2</sub>O<sub>4</sub> structure with grid *k*-point Brillouin zone having 111 atoms (O = 63, Fe = 40 and La = 8) was built for this study.

Pseudo atomic calculations were performed on La (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 3d<sup>10</sup>, 4s<sup>2</sup>, 4p<sup>6</sup>, 4d<sup>10</sup>, 5s<sup>2</sup>, 5p<sup>6</sup>, 5d<sup>1</sup>, 6s<sup>2</sup>), Fe (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3d<sup>6</sup>, 4s<sup>2</sup>), and O (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>4</sup>).  $U_{\text{eff}} = U - J = 4.3$  and J = 0 was set to provide more accuracy for the calculations. The vacancy formation energy ( $E(V_{O})$ ) was calculated as:

$$E\left(\ddot{\mathsf{V}}_{\mathsf{O}}\right) = E_{\mathsf{tot}}\left(\mathsf{V}_{\mathsf{O}}^{\mathsf{q}}\right) - E_{\mathsf{tot}}(\mathsf{ideal}) + \mu + q(E_{\mathsf{F}} + E_{\mathsf{val}} + \Delta V) \tag{2}$$

where  $E(V_O)$  is the oxygen vacancy formation energy,  $E_{tot}(V_O^q)$  is the total energy of the superlattice in charge state q, where q = 0 for a neutral oxygen vacancy.  $E_{tot}(ideal)$  is total energy of ideal LaFe<sub>2</sub>O<sub>4</sub> superlattice. And  $\mu$  is the chemical potential of oxygen. The  $E_F$  is orientation of the Fermi level of LaFe<sub>2</sub>O<sub>4</sub>.  $E_{val}$  refers to the valence-band maximum position of the ideal superlattice.  $\Delta V$  is the electrostatic potential of the defective LaFe<sub>2</sub>O<sub>4</sub> super-lattice.

#### 3. Results and discussion

#### 3.1. Structural and compositional study

Fig. 1(a) shows the measured and calculated XRD pattern of LaFe<sub>2</sub>O<sub>4</sub> in  $2\theta$  range from 10° to 80°. The core peaks of the diffraction pattern of LaFe<sub>2</sub>O<sub>4</sub> structure are located at  $2\theta$  of 18°, 30°, 34°, 36°, 42°, 52°, 56°, 62°, 65° and 78°, which can be indexed to the (111), (220), (311), (222), (400), (422), (511), (440), (620) and (533)

planes, respectively, corresponding to the Fm-3m (22–1086) space group with a lattice constant of 0.65251 nm.<sup>29</sup> No extra peaks rather than the cubic phase were observed indicating a pure singlephase crystalline structure of LaFe<sub>2</sub>O<sub>4</sub>. Moreover, Fig. 1(b) shows the Rietveld refinement of the XRD measured data, where red empty circles represent the observed data and the black solid line shows the experimental data. Whereas, the differences between the observed and experimental data are presented by solid blue line yielding factor of ( $\mathscr{X}^2 \leq 3.8\%$ ). The cubic structure and higher lattice parameter compared to perovskite structure (LaFeO<sub>3</sub>) may lead to unique properties of LaFe<sub>2</sub>O<sub>4</sub> structure. Moreover, the crystallographic structure of LaFe<sub>2</sub>O<sub>4</sub> is confirmed by HRTEM. The HRTEM images of LaFe<sub>2</sub>O<sub>4</sub> are shown in Fig. 1(c, d). The *d*-spacing values calculated by using a digital micrograph are 0.22, 0.24 and 0.28 nm, which correspond to (220), (311) and (111) planes, respectively.

Fig. 2(a) displays HRTEM image of the LaFe<sub>2</sub>O<sub>4</sub> sample, with significant particle dispersion, which shows morphology with homogeneous and fine particles. The average particle size calculated is about 140 nm. Moreover, elemental composition and their distribution at particle-level measured by energy dispersive assisted by HRTEM are shown in Fig. 2(b–f). Fig. 2(b) shows the high angular, dark field imaging (HAADF) graph of LaFe<sub>2</sub>O<sub>4</sub>. Fig. 2(c–e) show the mapping image of the elements in LaFe<sub>2</sub>O<sub>4</sub>, where the homogenous chemical concentration of each individual identity such as La, Fe and O is shown to be well controlled and manipulated. Fig. 2(f) shows the atomic ratio image of each species in LaFe<sub>2</sub>O<sub>4</sub>. The peaks for Fe K $\alpha$ , K $\beta$  and Fe L, show different Fe isotopes on the surface as shown by EDX image in Fig. 2(f), which could help our self-doping strategy in the LaFe<sub>2</sub>O<sub>4</sub> structure.

# 3.2. Electrochemical performance of PCFCs

The electrochemical performance of the prepared LaFe<sub>2</sub>O<sub>4</sub> as a cathode over BZCY electrolyte and NCAL anode was evaluated in a PCFCs using H<sub>2</sub> and air as fuel and oxidant. Fig. 3(a) displays typical current-voltage (I-V), and their corresponding power density (I–P) characteristic curves of fuel cell measured at 400–500 °C. The obtained OCV (open circuit voltage) of 1.1 V and the maximum power density ( $P_{max}$ ) of 806 mW/cm<sup>2</sup> at 500 °C using LaFe<sub>2</sub>O<sub>4</sub> cathode show excellent ORR electrocatalytic activity. Moreover, the LaFe<sub>2</sub>O<sub>4</sub> cathode even displays good fuel cell performance at low operating temperatures such as 450 and 400 °C as shown in Fig. 1(a), where peak power densities of 595 and 218 were achieved, respectively. Fig. 3(b) presents the cross-section SEM image of the fuel cell device. The high electrochemical performance of LaFe<sub>2</sub>O<sub>4</sub> over other Fe-doped or the state-of-the-art Co-containing cathodes suggests the vital role of self-doping of Fe ions in LaFe<sub>2</sub>O<sub>4</sub> structure, leading to lower barrier for proton transport and oxygen ions<sup>12,19</sup>. During the electrochemical process, alteration of Fe<sup>3+</sup>/Fe<sup>2+</sup> ions, acting as self-doping could facilitate the intercalation of protons for the faster transport. Moreover, LaFe<sub>2</sub>O<sub>4</sub> shows stable operation, suggesting that the stoichiometric of LaFe<sub>2</sub>O<sub>4</sub> kinetically favors the heterolytic dissociation of molecular oxygen and as well forms Fe-H and OH species, where the resulting Fe-H further changes to the thermodynamically more stable OH species, along with the reduction of  $Fe^{3+}$  to  $Fe^{2+}$ , hence, besides the high performance of the fuel cell it also showed stable operation over short period of 150 h (Fig. 3(c)). It further suggests that the presence of oxygen vacancies  $(V_0^{\cdot \cdot})$  on LaFe<sub>2</sub>O<sub>4</sub> due to self-doping not only facilitates the ORR but also enhances its stability as reported for  $Ti^{4+/3+}$ .

Furthermore, EIS was carried out at the temperature range of 350-500 °C along with electrochemical performance measurement under OCV conditions and the results are shown in Fig. 3(d). The model circuit  $R_0 - (R_1 - \text{CPE}_1) - (R_2 - \text{CPE}_2)$  that fits to EIS



**Fig. 1.** (a, b) The measured XRD and crystal structure of LaFe<sub>2</sub>O<sub>4</sub> and Rietveld refinement of the measured XRD data using Prof–Suit software to verify the experimental data; (c, d) Crystal structure planes and selected area electron diffraction (SAED) pattern of LaFe<sub>2</sub>O<sub>4</sub> powders obtained by HRTEM.



Fig. 2. (a) Morphology of prepared LaFe<sub>2</sub>O<sub>4</sub> powder by HRTEM image; (b) HAADF image of LaFe<sub>2</sub>O<sub>4</sub>; (c-e) Elements mapping of each individual element such as La, Fe and O into LaFe<sub>2</sub>O<sub>4</sub>; (f) Energy depressive spectrum (EDS) obtained from HAADF image.



**Fig. 3.** (a) Typical current (*I*)–voltage (*V*) and *I*–*P* characteristics curve using LaFe<sub>2</sub>O<sub>4</sub> cathode with BZCY electrolyte at 350–500 °C; (b) Cross-sectional SEM images of anode supported tri-layer layer after online sintering and fuel cell test with layers of LaFe<sub>2</sub>O<sub>4</sub> cathode, BCZY electrolyte and NCAL anode; (c) Voltage characteristics curve for cell at 110 mA for 150 h at 500 and 450 °C; (d) Electrochemical impedance spectra of fuel cell at different temperatures from 350–500 °C.

results suggests very low charge transfer resistance ( $R_1$ ) and mass transport resistance ( $R_2$ ) for cell based LaFe<sub>2</sub>O<sub>4</sub> cathode.<sup>31</sup> The low charge transfer resistance at the interface of electrolyte/electrode for cell may be determined by value capacitance ( $C_i$ ):

$$C_{i} = \frac{(R_{i}Q_{i})^{1/n}}{R_{i}}$$
(3)

where  $R_i$  is the resistance corresponding to constant phase element  $Q_i$  and frequency power n (0 < n < 1).<sup>32,33</sup> The low energy barrier for proton and oxygen ions could be another reason for low mass and charge transfer losses of LaFe<sub>2</sub>O<sub>4</sub> cathode.<sup>34</sup> The cell's charge transfer resistance  $(R_1)$  of 0.09 is determined by a space charge capacitance of  $5.713\times10^{-5}$  F. Whereas the mass transfer resistance  $(R_1)$  is 0.62  $\Omega$  · cm<sup>2</sup> and its space charge capacitance is 7.601  $\times$  $10^{-5}$  F for EIS data at 500 °C. This suggests that lower space charge capacitances  $(C_1, C_2)$  would help to lower  $R_1$  and  $R_2$  to break down the charge accumulation layer at their interfaces that can likely minimize charge transfer resistance. However, this led to high ionic conductivity which could be the only reason for small charge transfer resistance. Unfortunately, most often oxygen vacancies are virtually immobile in simply doped oxide materials at low temperatures of interest for applications.<sup>35</sup> Alternatively, mobile protons can be introduced by a proton conducting electrolyte with the oxygen vacancies to enhance ORR activity and TPBs of LaFe<sub>2</sub>O<sub>4</sub> cathode. To further identify ORR characteristics, EIS in a symmetrical cell configuration of LaFe<sub>2</sub>O<sub>4</sub> electrodes was examined over BZCY electrolyte at 550 °C in dry and humified air. Fig. S3 shows Nyquist plots of the EIS spectra, where area-specific resistance (ASR) reflects the overall catalytic activity of cathodes, and low ASR character of LaFe<sub>2</sub>O<sub>4</sub> cathode in dry air indicates high ORR characteristic. The ionic transfer number in LaFe<sub>2</sub>O<sub>4</sub> in dry and wet air was calculated using electromotive force method (E.M.F) using<sup>36</sup>:

$$t_i = 1 - \frac{\text{ASR}_{\text{LFO}}}{\text{ASR}_{\text{T}}} \left(1 - \frac{V_{\text{oc}}}{E_{\text{N}}}\right) \tag{4}$$

where ASR<sub>T</sub> is the total area specific total resistance obtained from low-frequency intercept with the real axis of the impedance data on a Nyquist plot,  $V_{oc}$  the OCV, and  $E_N$  the Nernst potential. For optimized electrode conditions, ionic transfer number of LaFe<sub>2</sub>O<sub>4</sub> in wet determined by the E.M.F. method is greater than 0.58 at 500 °C, while in wet air is 0.7. However, this shows that proton dominant ionic conductivity could be the only reason for small charge and mass transfer resistance in wet air.

# 3.3. Thermal and spectroscopic studies

The optical spectra of LaFe<sub>2</sub>O<sub>4</sub> measured by UV-visible are presented in Fig. 4(a). The direct band gap measured using Taucplot is inserted in Fig. 4(a).<sup>37</sup> The band gap of 1.94 eV shows that its value is much lower thank that of the Fe-based perovskite-based structure and could help to provide superior electrocatalytic for ORR. TGA–DSC curves of LaFe<sub>2</sub>O<sub>4</sub> catalyst in air and N<sub>2</sub> atmosphere from room temperature to 600 °C are shown in Fig. 4(b). As can be seen, a slight weight gain in  $N_2$  (0.1%) and air in the starting point was observed which is due to the buoyancy effect of air. While, the LaFe<sub>2</sub>O<sub>4</sub> starts to be thermally reduced and release the lattice oxygen in the form of the oxygen vacancies in air at temperature above 400 °C. The mass change (loss) progressively increases through temperature and grasped the value to 2.5% at 600 °C, while  $\delta$  value calculated using Eq. (1) is 0.28.<sup>38</sup> The  $\delta$  value at room temperature ( $\delta_0$ ), determined by iodometric titration, was 0.08 for the as-synthesized sample and it gradually increases with temperature and reaches a value of 0.36 at 600 °C, which may correspond to the thermally reduction of Fe ions from Fe<sup>4+</sup> to Fe<sup>3+</sup> and



**Fig. 4.** (a) UV-visible absorbance spectra and Tauc plot of UV-visible spectrum in insert; (b) TGA/DSC of prepared LaFe<sub>2</sub>O<sub>4</sub> in N<sub>2</sub> and O<sub>2</sub> atmosphere; (c) Raman spectra of pristine LaFe<sub>2</sub>O<sub>4</sub> and after electrochemical performance measurements.



Fig. 5. X-ray photoelectron spectroscopy (XPS) of LaFe $_2O_4$  and corresponding high-resolution XPS spectra of La 3d (a), Fe 2p (b) and O 1s (c) spectra.

Fe<sup>3+</sup> to Fe<sup>2+</sup> and hence the formation of oxygen vacancies. The  $\delta$  value for LaFe<sub>2</sub>O<sub>4</sub> in O<sub>2</sub> is much higher than that in N<sub>2</sub> atmosphere (0.36–0.20). The increase in  $\delta$  value in O<sub>2</sub> provides an evidence of online ORR activity and could be due to thermal reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, and loss of lattice oxygen which acts as self-doping enhances the oxygen vacancies in the lattice sites.<sup>39</sup> However,  $\delta$  value of LaFe<sub>2</sub>O<sub>4</sub> at this elevated temperature (600 °C) is comparable to or even higher than state-of-the-art developed cathodes.<sup>39,40</sup> These results show that more oxygen vacancies in LaFe<sub>2</sub>O<sub>4</sub> as amples in O<sub>2</sub> atmosphere as compared to N<sub>2</sub> gives the highest  $\delta$  value and provide direct evidence towards its excellence for ORR activity. The DSC (differential scanning calorimetry curve shows no obvious thermal effects, indicating that there are no 1st order phase transitions.

Moreover, Raman spectroscopy was employed for further structural characterization of pristine LaFe<sub>2</sub>O<sub>4</sub> powders and after electrochemical performance measurements for comparison. Fig. 4(c) displays specific Raman shifts bands centered at 220, 289, 418, 773 and 1307 cm<sup>-1</sup> that link to the stretching vibrations of  $T_{1g}$  (1),  $T_{1g}$  (2) and  $A_{1g}$  (1) and  $A_{1g}$  (2).<sup>41</sup> Two major differences in pristine LaFe<sub>2</sub>O<sub>4</sub> and powders after electrochemical test is red shift. The red shift in phonon mode and difference in the relative intensity of these two vibration modes  $A_{1g}$  (1) and  $A_{1g}$  (2). The incorporation of protons in LaFe<sub>2</sub>O<sub>4</sub> during electrochemical performance may soften the vibrational modes to create oxygen vacancies. This softening resulted in the red shift of vibrational mode to 0.5 cm<sup>-1.42</sup>

Fig. 5 shows XPS results with high resolution scan of individual element and full survey XPS spectra for pristine LaFe<sub>2</sub>O<sub>4</sub> sample and after electrochemical performance measurements. The focused chemical state of La 3d (Fig. 5(a)), Fe 2p (Fig. 5(b)) and O 1s bands (Fig. 5(c)) of pristine LaFe<sub>2</sub>O<sub>4</sub> and after test are shown in respective figures. Whereas, La 3d XPS spectra clearly show the chemical shifting towards higher binding energy after fuel cell testing. Moreover, the oxidation states of Fe 2p should have dominant impact on the charge transportation and ORR activity of LaFe<sub>2</sub>O<sub>4</sub>; while, the change in peak positions of Fe<sup>3+</sup> and Fe<sup>2+</sup> can clearly be observed.

The peaks of Fe 2p ( $Fe^{3+}$  and  $Fe^{2+}$ ) assigned to LaFe<sub>2</sub>O<sub>4</sub> after testing at 709.4 eV/723.5 eV and 710.8 eV/724.6 eV, whereas for pristine LaFe<sub>2</sub>O<sub>4</sub>, the Fe<sup>3+</sup> and Fe<sup>2+</sup> are accredited at 709.8212 eV/723.7 eV and 711.52 eV/724.9 eV,<sup>43</sup> signifying a binding energy down shift of  $0.4 \pm 0.05$  eV related to sample after testing. The LaFe<sub>2</sub>O<sub>4</sub> sample after testing exhibits more mixed valence states of Fe than that of pristine LaFe<sub>2</sub>O<sub>4</sub>, which help to create more oxygen vacancies while maintaining the overall charge-neutrality by La oxidation state. The O 1s spectra of the material also influence a lot on protonic and ionic conductivity of a material. The O 1s spectrum of LaFe<sub>2</sub>O<sub>4</sub> contains lattice oxygen (lattice  $O^{2-}$ ), surface active oxygen ( $O^{1-}$ ) and chemically adsorbed water, which are located at 528.8, 532.1, and 533.0 eV, respectively. The O 1s spectra of LaFe<sub>2</sub>O<sub>4</sub> sample after electrochemical performance test shows relatively high ratio of surface active oxygen to lattice oxygen that could be an indicator for the assessment of adsorption capability of LaFe<sub>2</sub>O<sub>4</sub>. The LaFe<sub>2</sub>O<sub>4</sub> after test shows high surface exposure of hydroxide species that assist the proton transport.44,45 The high concentration of surface-active oxygen species on the LaFe<sub>2</sub>O<sub>4</sub> after fuel cell measurements as compared to pristine LaFe<sub>2</sub>O<sub>4</sub> could be associated with extra oxygen vacancies produced by proton insertion and also detected by Raman spectroscopy. They are described to play an important role in the proton conduction. Further experimental studies about the effects of selfdoping on improved ORR, proton transport and performance of  $LaFe_2O_4$  are explored in the following parts.

# 3.4. Theoretical calculations

To deeper understand LaFe<sub>2</sub>O<sub>4</sub> towards ORR and ion diffusion properties, DFT calculation method was employed. Fig. 6(a) displays the computed structure of LaFe<sub>2</sub>O<sub>4</sub>. To realize the self-doping strategy the oxidation states of Fe<sup>2+/3+</sup> atoms into LaFe<sub>2</sub>O<sub>4</sub> were controlled by TS-method. Fig. 6(b) shows spin up and spin down PDOS of each individual orbital, such as d-orbital, s-orbital, p-orbital and total density contributed by La, Fe and O elements in LaFe<sub>2</sub>O<sub>4</sub> structure. The PDOS of LaFe<sub>2</sub>O<sub>4</sub> strongly follows the orbital coupling and PDOS is more populated across the Fermi level. The p-band



**Fig. 6.** (a) The optimized structure of LaFe<sub>2</sub>O<sub>4</sub>; (b) Calculated partial electron density of states (PDOS) for the different orbital of each species; (c) Energy band structure of LaFe<sub>2</sub>O<sub>4</sub>; (d) Electron density difference under different species of LaFe<sub>2</sub>O<sub>4</sub>; Possible migration path of oxygen ions/protons (e) and their relative migration energies (f).

center of LaFe<sub>2</sub>O<sub>4</sub> lies at 1.42 e, which is much closer to Fermi level as compared to many other states-of-the-art cathodes.<sup>46,47</sup> The d and p band centers of LaFe<sub>2</sub>O<sub>4</sub> lie in the same range and could be the reason for much population of DOS by all-neighboring atoms at Fermi level. The high DOS along the Fermi level would increase the electron-transfer efficiency and adsorb proton and oxygen species  $O^{2-}_{ads}$ . Thereby more likely, it could be the main reason of the faster ORR kinetics and charge transfer in LaFe<sub>2</sub>O<sub>4</sub> cathode.

Therefore, we have experienced good local reduction process of  $\mbox{Fe}^{3+/2+}$  into  $\mbox{LaFe}_2\mbox{O}_4$  by proton inserted from electrolyte layer and water formation at cathode layer provides more strength to enhance ORR electrocatalytic activity. The DFT findings are very similar to EIs, XPS and TGA results. The low proton transfer in LaFe<sub>2</sub>O<sub>4</sub> could be due to internal strengths of LaFe<sub>2</sub>O<sub>4</sub> structure from the hydro-oxo-bonds along with intra-atomic exchange energy as a vacancy driving force. The doublet d-orbital of La and Fe could experience repulsion force with oxygen lone pairs to weaken these bonds. The exclusive Fe–O–Fe bonds into LaFe<sub>2</sub>O<sub>4</sub> structure provide high electronic movement along percolation paths and excess  $\ddot{V_0}$  due to self-dopants. In these contexts, the  $3d_{eg}$  Fe orbitals may overlap with the  $2p_{\sigma}$  orbitals of  $O^{2-}$  to form  $\sigma$  bonds, and the  $3d_{t2g}$  orbital of Fe ions may overlap with the  $2p_{\pi}$  of  $O^{2-}$  ions to form  $\pi$  bonds, e.g.,  $e_g - p_\sigma - e_g$  and  $t_{2g} - p_\pi - t_{2g}$  bonds. That is why LaFe<sub>2</sub>O<sub>4</sub> shows good ORR activity with fast charge and mass transfer charges and it could only be due to the synergistic effects of self-doping, which can decrease the energy barrier for  $H^+/O^{2-}$  intake.<sup>48,49</sup>

# 4. Conclusions

We developed a spinel-structured LaFe<sub>2</sub>O<sub>4</sub> ferrite through a simple and effective approach for use as cathode in PCFC. The prepared LaFe<sub>2</sub>O<sub>4</sub> exhibits high ORR electrocatalytic activity and stability with BZCY proton conducting electrolyte. It is found that multiple self-developed effects in LaFe<sub>2</sub>O<sub>4</sub> structure explain the high electrochemical performance, e.g., 806 mW/cm<sup>2</sup> at 500 °C. The reduction in oxidation state of Fe by proton insertion leads to self-doping and being highly deficient into LaFe<sub>2</sub>O<sub>4</sub> structure. Both spectroscopy and DFT analysis reveal that self-doping in LaFe<sub>2</sub>O<sub>4</sub> demonstrates high ORR catalytic activity and could be suitable candidate for developing synergistic catalysts for oxygen reduction reaction with fast electron and ion transfer kinetics.

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# Appendix A. Supplementary data

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