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Effect of 'A'-site non stoichiometry in strontium doped lanthanum ferrite based solid oxide fuel cell cathodes

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ABSTRACT

Effect of A-site non-stoichiometry in strontium doped lanthanum cobalt ferrite ($La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$, $x = 0.4$; $y = 0.2$) is studied in a systematic manner with variation of 'A' site stoichiometry from 1 to 0.94. The perovskite based cathode compositions are synthesized by combustion synthesis. Powder characterizations reveal rhombohedral crystal structure with crystallite size ranging from 29 to 34 nm with minimum lattice spacing of 0.271 nm. Detailed sintering studies along with total DC electrical conductivities are evaluated in the bulk form with variation of sintering temperatures. The electrode polarizations are measured in the symmetric cell configuration by impedance spectroscopy which is found to be the lowest (0.02 $\Omega\,cm^2$ at 800 °C) for cathode having highest degree of 'A'-site deficiency. The same cathode composition exhibits a current density of 2.84 A cm^{-2} (at 0.7 V, 800 °C) in anode-supported single cell. An attempt has been made to correlate the trend of electrical behaviour with increasing 'A'-site deficiency for such cathode compositions.

1. Introduction

To increase the efficiency of the intermediate temperature solid oxide fuel cell (SOFC), the mixed ionic and electronic conductor (MIEC) materials, such as, $Ba_{1-x}Sr_xCo_{1-y}FeO_{3-\delta}$ (BSCF), Nd-doped BSCF (BSNCF) and $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ ((LSCF) have proven promising and demonstrated faster oxygen diffusion and improved surface exchange kinetics [1–9]. Among the MIEC materials as mentioned above, LSCF based cathode materials have good electrical conductivity as well as high oxygen surface exchange coefficient and also have a good oxygen self-diffusion coefficient between the temperature range of 600 °C and 800 °C. The oxygen self-diffusion coefficient of LSCF is $2.6 \times 10^{-9}\,cm^2\ s^{-1}$ at 500 °C, which is far better in performance to that of LSM having oxygen self-diffusion coefficient value of $10^{-12}\,cm^2\,s^{-1}$ at 1000 °C [10]. There are many factors concerning the duration of stability for LSCF based cathodes. One of the probable mechanisms for voltage deterioration is explained to be slow decomposition of the LSCF perovskite due to partial de-mixing of strontium [11–13]. Mai et al. [14] reported that a small A-site deficiency and high 'Sr' content in LSCF cathodes increase the cell performance using gadolinium doped ceria (CGO) interlayer [14]. The long term stability of the cell using LSCF cathode materials with off-stoichiometry in the 'A'-site have also been tested [15]. The off-stoichiometry in the 'A' site lattice of LSCF-based cathode materials leads to the formation of the stable aliovalent states of the metal ions in the 'B' site of the perovskite and hence results in higher conduction. Moreover, change of the oxygen off-stoichiometry by inducing such deficiency in the 'A' site also enhances such conduction [10]. It has also been found that 'A'-site vacancy plays an important role for the performance of the LSCF cathode but long-term cell tests lasting up to 3000 h revealed a degradation of the cell. The sintering of the cathode having off-stoichiometry in the 'A' site is also found to be prevalent through the formation of a congruent eutectic melt which results in easy process of grain to grain interlocking at low temperature [16] and hence higher grain conductivity. It has been observed that in iron-based cathodes, reactivity with YSZ electrolyte is significantly reduced. In addition, thermal expansion coefficient of the ferrite based–perovskite is relatively close to that of the electrolyte YSZ. On the other hand, LSCF-type perovskites are generally incompatible with YSZ electrolytes due to undesirable interface reactions. Therefore, a CGO diffusion barrier layer is used to prevent the formation of low conductive compounds without negatively affecting the electrochemical performance [17,18]. Besides, the composition and microstructure of cathode materials has a significant impact on the performance of SOFCs. Hence, rational design of materials composition through controlled oxygen non-stoichiometry and consequent increase in defect aspects can enhance the ionic and

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electronic conductivities as well as the catalytic properties for oxygen reduction in the cathode material.

In the present study, systematic variation of lanthanum concentration in 'A'-site oxygen non-stoichiometry in ferrite based LSCF materials (LSCF; $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$, $x = 0.4$; $y = 0.2$) has been carried out in the range of 0.54–0.6 while the concentration of dopant 'Sr' is kept constant at 0.4. Ferrite based LSCF materials have been chosen as cathode material for the application in intermediate temperature solid oxide fuel cell for the thermal compatibility with the electrolyte YSZ. Powder and bulk characterizations including the DC electrical conductivities of the cathode materials have been carried out in details and clinically correlated with the microstructures. Impedance spectroscopy is employed to investigate the electrode polarizations of the cathodes as thick film in symmetric cell configuration. Electrochemical performances of all cathode compositions are evaluated in conjunction with ceria-based interlayer in the form of Ni-YSZ anode-supported single cells and the performances are correlated with the off-stoichiometry of the 'A' site of the synthesized perovskites.

2. Experimental

The compositions of the cathodes as investigated under this study are given in Table 1. All the four compositions (LS-1, LS-2, LS-3 and LS-4) were prepared by the combustion synthesis technique as reported earlier using starting materials lanthanum (III) nitrate hexahydrate (99%, Sisco Res. Lab. Ltd., India), strontium (II) nitrate (99%, s.d.fine, India), iron (III) nitrate nonahydrate (98%, Merck) and cobalt (II) nitrate hexahydrate (99.5%, E. Merck, Germany) and L-alanine as a fuel (99%, SRL, India) [19]. In all the four combustion synthesis, the ratio of metal nitrate and fuel were maintained 1:1 to prevent the undesired hydrolysis of the respective precursor salts. The as-synthesized powders were calcined at 800 °C for 4 h in air. The Co-CGO was prepared using combustion synthesized technique and already reported by our group [20]. For the evaluation of thermal analysis of the cathode materials the viscous precursor gels of all the samples were collected. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out from room temperature to 800 °C in air at a heating rate of 5 °C/min using Simultaneous Thermal Analyzer (STA 449C, Netzsch, Germany). Phase purity of the samples was checked by recording X-ray data in the 2θ range 10°–80° using X'Pert Pro software (PANalytical, Philips, Holland). For structural characterization, Rietveld refinement of the powder diffraction profiles and quantitative phase analysis of LS samples calcined at 800 °C were carried out using X'Celerator operating at 40 kV and 30 mA using CuK_α radiation with step size 0.05° (2θ) and step time 75 sec from 15° to 90° for all the samples. The BET surface areas of the powder calcined at three different temperatures were carried out using Quantachrome Instruments (version 9.0). The morphology of both the powder was characterized using transmission electron microscopy (TEM, Tecnai G^2 30ST) with evaluation of lattice spacing by high resolution TEM (HRTEM). For the densification studies, powders calcined at 800 °C were pressed uniaxially and then sintered in the temperature range of 1050 °C–1150 °C in air in an interval of 50 °C. Field emission scanning electron microscopy (FESEM, Gemini Supra 35 Zeiss) was used to examine the microstructure of the fractured surface of the sintered samples. The thermal expansion coefficients (CTE) of all the sintered samples of different compositions under the present investigation were measured by a dilatometer (NETZSCH, DIL402) up to 900 °C with a constant heating rate of 10 °C/min. The electrical conductivity of the sintered samples (1050 °C–1150 °C) was evaluated in the temperature range 500 °C–800 °C in air by 4-probe technique using a Power Source (Agilent E3631A) and a Multimeter (Keithley 2002). Electrochemical impedance of symmetric cells having screen printed LSCF cathode on both the sides $Co_{0.01}Ce_{0.79}Gd_{0.20}O_{2-\delta}$ (Co-CGO) electrolyte in the configuration, LSCF / Co-CGO /LSCF, were carried out in the form of circular disc of diameter of ~10 mm with the full range swipe of the AC frequency of 10^{-1} Hz ≤ f ≤ 10^6 Hz. While the sintering temperature of bulk Co-CGO was kept at 1100 °C, the thick films of the composite cathode were fired at 900 °C [21]. For electrochemical performance evaluation of the cathodes of varied composition, thick film paste prepared using such powders were screen printed onto anode-supported planar half-cell of configuration, NiO-YSZ/YSZ. The half-cell was fabricated by tape casting method which is also reported our group previously [22]. Single cells in the form of coupon cells (16 mm diameter, 1.5 mm thick with active cathode area of ~0.3 cm^2) of configuration Ni-YSZ/YSZ/CoCGO/LSCF were fabricated after heat treatment of screen printed LSCF-based cathodes at 950 °C. Co-CGO was used as an interlayer in between the electrolyte and cathode to reduce the unwanted reaction and thermal compatibility. The electrochemical measurements of such single cells were carried out in the temperature range 700 °C–800 °C using an in-house electrochemical measurement setup. Moist H_2 (~3% H_2O) was used as a fuel on the anode side and oxygen was fed on the cathode side. During the measurement, the flow rates for both the fuel gas and O_2 were maintained at 100 SCCM. The best performing cathode was also tested with air for comparison with the results of oxygen and the flow rates for the same is maintained at 500 SCCM.

3. Results and discussion

The 'A'-site deficient LSCF-based cathode plays a major role in improving the performance of SOFC by the increase of the electronic conductivity and catalytic behavior. However, the deficiency in 'A' site has a limitation with respect to the substitution of Sr^{2+} in the trivalent site (La^{3+}) of perovskite having formula $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$. It has been reported that at $x > 0.4$ makes the perovskite structure metastable and the 'A' site deficiencies greater than 5% results a negative effect on measured performance [23]. Keeping the view of the above, the 'Sr' content in the LSCF compositions has been kept constant at 0.4 whereas, the 'A' site deficit has been made upto 6% with respect to 'La' site as shown in Table 1.

Table 1
Compositions of the LSCF powders and relative densification and CTE values of the sintered bulk samples.

Sample ID	Composition	Relative densification (%) at the following sintering temperatures			Coefficient of thermal expansion (CTE) of sintered (1150 °C) bulk cathodes in the temperature range 30–900 °C × 10^6 (K^{-1})
		1050 (°C)	1100 (°C)	1150 (°C)	
LS-1	$La_{0.54}Sr_{0.40}Co_{0.20}Fe_{0.80}O_{3-\delta}$	80.1	90.6	94.5	16.88
LS-2	$La_{0.56}Sr_{0.40}Co_{0.20}Fe_{0.80}O_{3-\delta}$	80.2	87.2	94.1	15.46
LS-3	$La_{0.58}Sr_{0.40}Co_{0.20}Fe_{0.80}O_{3-\delta}$	79.7	86.4	89.5	15.72
LS-4	$La_{0.60}Sr_{0.40}Co_{0.20}Fe_{0.80}O_{3-\delta}$	76.2	84.8	88.3	15.76