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Phase evolution and electrochemical performance of iron doped lanthanum strontium chromite in oxidizing and reducing atmosphere

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Abstract:

Effect of oxygen partial pressure (PO_2) on the processing and phase evolution in $(La_{0.8}Sr_{0.2})_{0.95}Cr_{0.7}Fe_{0.3}O_3$ (LSCF) is investigated under high temperature electrochemical device fabrication conditions at 1400°C and oxygen partial pressure (PO_2) varying from 0.21 – 10^{-10} atm. Formation of Fe enriched phase is identified in the samples exposed to reducing atmosphere and the amount of the phase increases with decrease in PO_2 . LSCF dissociates and forms FeO_x when exposed to Ar-3% H_2 -3% H_2O at 1400°C. LSCF decomposition and the formation of FeO_x is in agreement with the thermodynamic simulation results obtained using ThermoCalc with the La-Sr-Cr-Fe-O thermodynamic database. Electrochemical impedance spectroscopy measurement on the symmetrical cell of configuration LSCF-YSZ / YSZ / LSCF-YSZ shows high polarization resistance in oxidizing atmosphere when compared to reducing atmosphere under operating conditions ($T \sim 950$ °C and $PO_2 \sim 0.21 \cdot 10^{-16}$ atm). No degradation and microstructural changes are identified in the samples exposed to air for 80 h. Surface of LSCF phase is significantly modified in Ar-3% H_2 -3% H_2O atmosphere after electrochemical testing for 80 h. Higher stability and electrochemical performance of LSCF is obtained in air when compared with Ar-3% H_2 -

3%H₂O. Unlike oxidizing atmosphere, post characterization TEM results show thin SrZrO₃ layer formation at the LSCF/8YSZ interface in reducing atmosphere.

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1. Introduction

Solid oxide fuel cells, solid oxide electrolysis cells (SOFC and SOEC) and oxygen transport membrane (OTM) are a few high temperature electrochemical devices and advanced technologies that are currently being investigated for clean energy conversion and utilization of fossil fuels/hydrocarbons with CO₂ capture and no/negligible emissions [1-30]. Efficient and clean energy conversion, oxy-combustion of fossil fuels/hydrocarbon allows minimization in greenhouse gas emissions resulting in global climate change [14-28]. OTM is also useful for syngas production which can be further processed via water gas shift reaction to generate hydrogen as a fuel [1,29]. Using Fisher-Tropsch process, the syngas can also be utilized to generate liquid fuel for transportation.

SOFC/SOEC/OTM consists of three electrochemically active layers i.e. air electrode layer, electrolyte/membrane and fuel electrode layer. Oxygen exchange between the membrane surface and gas phase involves several steps: adsorption and dissociation of oxygen molecules at the air electrode, oxygen transport through oxygen vacancies across the membrane, and desorption and association of oxygen ions at the fuel electrode [21,31-32]. For long term stability of the system, it is important that the component materials are stable under fabrication and operation conditions. Air electrode layer should be stable in oxidizing atmosphere and the fuel electrode in reducing atmosphere at the operating temperature [1,16]. It is a challenge to find stable materials that can provide a combination of structural and chemical stability under processing conditions as well as stable performance during electrochemical operation at high temperatures [2-3, 33-40]. This is mentioned in detail in the review paper [1].

LSM/YSZ is the state of the art electrode material for the solid state high temperature electrochemical systems such as SOFC (cathode) and SOEC (anode) [7-9]. However, LSM/YSZ is not stable under the long term operating conditions and degrades with time. Electrode delamination after testing, migration of cations and lanthanum/strontium zirconate insulating interface layer formation at the interface of LSM and YSZ are a few challenges in using LSM/YSZ as air electrode [7-9]. On the other side, Ni-YSZ is the state of the art material for SOFC (anode) and SOEC (cathode) because of its high mixed (electronic and ionic) conductivity and electro-catalytic activity. The electrode, however, remains prone to degradation due to redox exposure, carbon deposition, agglomeration of Ni particles and sulfur poisoning [6,16].

To overcome the above mentioned challenges, lanthanum chromite based perovskites are being investigated as candidate electrode materials (air electrode and fuel electrode) for these high temperature electrochemical systems due to structural and chemical stability at high temperatures in both oxidizing and reducing atmospheres [1,15-27,41-42]. Lanthanum chromites are commonly doped at A-site with alkaline earth metal and at B-site with transition metal to enhance their sinterability, electrical conductivity and electrochemical performance [15-27,43-46]. However, the type and level of dopants tend to deteriorate the structural and thermo-chemical stability of lanthanum chromite based materials specifically at lower PO_2 ($\leq 10^{-10}$ atm.) [47-49]. To overcome this barrier, the materials are further doped at B-site with transition metals to maintain the stability and further improve the electrochemical properties [16, 50-54].

(La Sr)(Cr, Fe)_{3-δ} (LSCF) is currently being investigated as mixed ionic electronic conductor (MIEC) electrode for air/fuel side applications [1,15-16,22,24-27,53,55-56]. Acceptor-substituted LaCrO_{3-δ} with Fe-doping has been reported to enhance electrode performance in SOFC and other electrochemical devices [57, 58]. For instance, Fe-containing La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-δ} (LSCF55) showed lower polarization resistance when compared to La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) [57]. Ionic conductivity of (La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-δ} is reported to be higher than acceptor-doped lanthanum chromite's and (La Sr)(Cr, Mn)_{3-δ} (LSCM) [52,59]. However, most of the literature exists on LSCF55 with 50 mol% Fe [55,57,60-61]. He et al. [55] have examined stability and oxygen transport property of LSCF55. The authors also reported that LSCF55 gets partially decomposed into metallic iron and some unknown phases when exposed to pure H₂ gas atmosphere for 30h at 950 °C. Based on thermodynamic calculations [60], decomposition oxygen partial pressure of LSCF55 was reported to be 6.3×10^{-28} atm. According to the literature search, it is identified that LSCF55 is not very stable under reducing atmosphere. The literature search also shows lack of information pertaining to the electrochemical performance and interaction of perovskite (LSCF) and fluorite (8YSZ) phases under both oxidizing and reducing gas atmospheres.

Due to the reported lower stability of higher Fe-containing LSCF perovskites and limited information on the structural stability of LSCF, this study is focused on investigating LSCF perovskites/composites with lower concentration of Fe (30 mol%) in oxidizing and reducing gas atmospheres. This paper, for the first time, assesses the processing behavior, phase evolution and structural-chemical-thermochemical stability of LSCF73 under simulated processing and fabrication condition (1400 °C, $\sim 0.21 \cdot 10^{-10}$ atm.). This study also shows the first attempt to use

the computational thermodynamics and simulation for the selected LSCF system using ThermoCalc with the La-Sr-Cr-Fe-O thermodynamic database. Electrochemical performance is investigated under simulated cathodic and anodic operating (~ 950 °C, $\sim 0.21 - 10^{-18}$ atm.) conditions.

2. Experimental Procedure

2.1. $(La_{0.8}Sr_{0.2})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ synthesis

LSCF73 powder was obtained from Praxair Inc. and then uniaxially pressed into pellets. The pellets were bisque fired at 1100 °C (2 h) in air. Sintering of the pellets were carried out at 1400 °C in three different gas atmospheres i.e. air (0.21 atm.), N₂ ($\sim 10^{-5}$ atm.) and Ar-3% H₂-3% H₂O ($\sim 10^{-10}$ atm.). Pellets were cooled in the same gas atmosphere for maintenance of the oxygen partial pressure while cooling.

2.2. Characterization

Archimedes principle was utilized for density measurement of all LSCF73 sintered samples. The microstructural and elemental analysis was performed using scanning electron microscope (FEI - ESEM Quanta 250, Hillsboro, OR) with energy dispersive spectroscopy (EDS).

Crystal structure and compound formation in LSCF73 were identified using X-ray diffraction (BRUKER-D8 ADVANCE, Bruker AXS Inc. Madison, WI) technique with scan step of 0.02° using CuK α radiation ($\lambda = 1.5406$ Å).

2.3. Symmetric cell fabrication

A mixture of LSCF73 with 8YSZ was prepared in the weight ratio of 50:50 for electrochemical testing. LSCF73/8YSZ ink was prepared using Fuel ink vehicle (Fuel Cell Materials). Symmetrical cells were then prepared by screen printing LSCF73/8YSZ on both sides of $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ (YSZ) electrolytes (200 μm thick Fuel Cell Materials) as working and counter electrodes (thickness: ~ 20 μm , diameter: 10 mm). The electrode layers on both sides were dried and subsequently, sintered at 1200 $^{\circ}\text{C}$ (heating rate of 3 $^{\circ}\text{C}/\text{min}$) for 2 h in air. Lower sintering temperature (1200 $^{\circ}\text{C}$) was chosen for the cell fabrication to obtain porous electrode layer. Platinum screen current collector (Alfa Aesar, 50 mesh) and wires (Alfa Aesar, 0.25 mm) were then attached to each electrode. The electrochemical active area of the cell electrode was 0.8 cm^2 .

2.4. Electrochemical testing

Symmetrical cells were heated to 950 $^{\circ}\text{C}$ (3 $^{\circ}\text{C}/\text{min}$) and tested in two atmospheres i.e. oxidizing (air) and reducing ($\text{Ar}-3\%\text{H}_2-3\%\text{H}_2\text{O}$). The electrochemical measurement was performed using potentiostat under constant bias of 0.5 V for 80 h. Every two hour interval, the electrochemical impedance was measured in the frequency range of 100 mHz - 200 kHz using a sinusoidal voltage of 10 mV. The measurement was repeated on different cells to ensure repeatability under similar experimental conditions.

Post-test characterization, using SEM-EDS, was conducted on the symmetrical cells after completion of testing. To understand the interfacial interaction between the electrode layer and electrolyte, the electrode layer is removed from the electrolyte (8YSZ) surface. The interfacial

section was observed using SEM. Transmission electron microscopy (TEM) was used to further understand the interfacial reaction and compound formation. After removal of the electrode, focused ion beam (FIB) instrument and technique was used to prepare the cross-sectional TEM sample of the cells tested in reducing atmosphere. TEM-EDS was used for the elemental analysis of the tested cells.

3. Computational Thermodynamics

The CALculation of PHase Diagram (CALPHAD) approach was adopted for the thermodynamic calculations [62-68]. The customized thermodynamic database for La-Sr-Cr-Fe-O system was adopted in the current investigations to simulate the phase equilibria of LSCF perovskite at different oxygen partial pressure. The data base includes the Gibbs energy of all the phases of interest in the current work, including the perovskite, ionic liquid, spinel, corundum, and other phases inside the La-Sr-Cr-Fe-O system. For instance the perovskite was modeled with the three-sublattice model:

this results in the Gibbs energy definition as:

$$G_m = \sum_{i,j,k} y_i y_j y_k {}^\circ G_{i:j:k}^{Perov} + RT \cdot (\sum y_i \ln y_i + \sum y_j \ln y_j + 3 \sum y_k \ln y_k) + {}^E G_m^{Perov} \quad (1)$$

where y_i represents the A-site cations site fraction, y_j is the B-site cations site fraction, y_k represents the site fraction of species in the oxygen site, ${}^\circ G_m^{Perov}$ is the Gibbs energy of perovskite endmembers and ${}^E G_m^{Perov}$ is the excess Gibbs energy of the solid solution perovskite phase. The basis for the current simulation is 1 mol of atoms occupying the A-site, 1 mol of atoms on the B-site and 3 mol of atoms on the oxygen site, for a total of 5 mol of atoms for

LSCF73. However, the total moles can be different than 5 due to the existence of A-site, B-site, and oxygen site deficiencies.

4. Results and Discussion:

4.1. Crystal structure

The crystal structure and phase evolution in LSCF73 in air, N₂ and Ar-3%H₂-3%H₂O atmosphere is shown in Fig. 1. LSCF73 samples sintered in air at 1400 °C shows rhombohedral structure. The peak splitting corresponding to rhombohedral structure, however, disappears in lower PO₂ sintered samples (N₂ and Ar-3%H₂-3%H₂O). This attributes to a phase transformation from rhombohedral (JCPDS 75-9872) in oxidizing atmosphere to higher symmetry cubic phase (JCPDS 074-1961) in reducing atmosphere [42]. No secondary phases are identified for the samples sintered in air at 1400 °C. However, the XRD patterns corresponding to N₂ and Ar-3%H₂-3%H₂O sintered samples show new peaks (indicated by asterisk) when compared to those sintered in air. The new peaks correspond to secondary phase (FeO_x) formation. This provides us with an important information that LSCF73 is not stable under processing conditions of N₂/Ar-3%H₂-3%H₂O at 1400 °C and decomposes to form FeO_x if processed under reducing gas atmosphere. Therefore, oxidizing atmosphere (air) is considered as an appropriate condition to be utilized for fabrication of LSCF based electrodes for high temperature electrochemical devices.

Fig. 1. XRD pattern of LSCF73 sintered at 1400 °C in air, N₂ and Ar-3% H₂-3% H₂O.

4.2. Sintering behavior and microstructural analysis

Relative density of LSCF73 sintered at 1400 °C for 10 h in air, N₂ and Ar-3% H₂-3% H₂O is 65.6% (± 1.5), 74.9% (± 2.1) and 96.3% (± 2.6) respectively.. The density increases with decrease in PO₂. The highest density is achieved in reducing gas atmosphere (Ar-3% H₂-3% H₂O).

Fig. 2 shows surface morphologies and elemental distribution in LSCF73 samples sintered in air, N₂ and Ar-3% H₂-3% H₂O atmosphere at 1400 °C. Microstructural and elemental analysis of air sintered samples does not show any compound formation as shown in Fig. 2a. However, in N₂ atmosphere, a significant difference in the microstructure of LSCF73 sample is noticed when compared to that of air. Smaller grain size structure is obtained at lower oxygen partial pressure ($\leq 10^{-6}$ atm) at 1400 °C as shown in Fig 2b.

With further decrease in processing oxygen partial pressure PO_2 ($\sim 10^{-10}$ atm), a secondary phase formation of FeO_x is identified in the LSCF73 samples, in agreement with the XRD results. This indicates decomposition of LSCF perovskite into FeO_x in reducing gas atmosphere. Formation of a FeO_x second phase surface layer is observed as shown in Figs. 2c, 3a and c. SEM-EDS analysis shows that the phase is predominantly Fe and O-rich (Fig. 3c). Small and large size grain structure is observed indicating inhomogeneity in the microstructure (Fig. 3b). In addition, SEM-EDS semi-quantitative analysis show composition variation with respect to differing grain size structure as shown in Fig. 3b. SEM-EDS elemental mapping profile is also performed to further analyze the elemental distribution. Fig. 4 shows the distribution of each element in the LSCF73 microstructure. From the analysis, it is evident that La (red), Sr (green), Cr (yellow) and oxygen (cyan) are present in the region 1. However, minimal Fe (magenta) is observed in region 1. In region 2, only Fe and O are present corresponding to the FeO_x surface layer formation. This supports the SEM-EDS semi-quantitative elemental analysis and XRD results.

Fig. 2. SEM micrographs of sintered LSCF73: (a) air, (b) N_2 and (c) $Ar-3\%H_2-3\%H_2O$ at 1400 °C (10 h).

Fig. 3. SEM micrographs and elemental analysis of LSCF73 in reducing gas atmosphere (Ar-3%H₂-3%H₂O).

Fig. 4. SEM elemental distribution mapping of LSCF73 in reducing gas atmosphere (Ar-3%H₂-3%H₂O).

Evolution of phase containing transition metals (Ni, Co and Ru) in the perovskites have been reported in the literature [69]. For example, Ni evolution occurred from the A (Sr/Ca) and B site doped lanthanum chromite in reducing gas atmosphere. Similarly, Ru phase evolution have been identified in the Sr and Mn/Ru co-doped LaCrO_3 based anode at lower PO_2 [69]. A and B-site compositions and stoichiometry plays a significant role in producing a range of phase composition and surface distribution [1, 69]. Similar to FeO_x evolution in LSCF, MnO_x phase evolution is observed in Sr and Mn doped lanthanum chromite when exposed to reducing gas atmosphere [16, 23].

Fe containing lanthanum chromite based materials tend to reduce to Fe metal and LaCrO_3 phase when exposed to reducing atmosphere [70]. For instance, at 850 °C, the Fe substituted lanthanum chromite would decompose to Fe metal and LaCrO_3 at $\text{PO}_2 \sim 10^{-23}$ atm [70]. In addition, LSCF55 partially decomposed into metallic iron and unidentified phases when exposed to pure H_2 gas atmosphere for 30 h at 950 °C [62]. Our results indicate formation of FeO_x secondary phase due to exposure to less reducing atmosphere ($\text{PO}_2 \sim 10^{-10}$ atm). To further understand the microstructure evolution and phase stability of LSCF73 with varying PO_2 at high temperature, we conducted thermodynamic simulation using the ThermoCalc software with the CALPHAD approach. The thermodynamic simulation technique and the results obtained are explained in detail in the next section.

4.3. Predictions from computational thermodynamics

Thermodynamic phase stability of 1 mole per formula LSCF73 at 1400 °C with different oxygen partial pressures were simulated as shown in Fig. 5(a). It is observed that the LSCF73 perovskite coexists with very limited amount of corundum phase ($(\text{Fe,Cr})_2\text{O}_3$) in air. With the

drop of oxygen partial pressure, the LSCF73 perovskite coexists with very limited spinel phase (FeCr_2O_4) LSCF73 starts to decompose and form ionic liquid when PO_2 is less than 10^{-5} atm. Significant amount of ionic liquid (~ 0.7 mole) forms at $\text{PO}_2 \sim 10^{-10}$ atm. The existence of ionic liquid in reducing condition matches very well with the possible liquid formation observed in Fig. 3 and 4.

The increase in the densification rate for the sintered samples under N_2 ($\sim 10^{-5}$ atm) and $\text{Ar}-3\%\text{H}_2-3\%\text{H}_2\text{O}$ ($\sim 10^{-10}$ atm) is linked with the formation of the liquid phase with decrease in PO_2 in Fig. 5(a). While the liquid phase is just forming under 10^{-5} atm, the densification increases for less than 10% for LSCF being sintered under N_2 . When the concentration of the liquid phase is greatly increased at 10^{-10} atm, the densification suddenly rises by more than 30%, compared to the sintered LSCF under air, and 20%, compared to the sintered LSCF under N_2 . The liquid phase changes the sintering behavior of the samples and enhances the densification rate possibly through increased diffusion or filling of empty spaces among grains. The thermodynamic simulation of the phase stability of LSCF73 at $\text{PO}_2 = 10^{-10}$ atm at different temperatures is shown in Fig. 5(b). It shows the stability of the ionic liquid quickly drops with the decrease of temperature. It is worth noting that the prediction in Fig. 5 is purely based on thermodynamic consideration and the kinetics effect is neglected. The composition of LSCF, including the dopant concentration in A site and B site and the A site deficiency also greatly affect the stability of ionic liquid.

The ionic liquid in the La-Sr-Cr-Fe-O thermodynamic database was modeled to consider ions including La^{2+} , Sr^{2+} , Cr^{2+} , Cr^{3+} , Fe^{2+} , Fe^{3+} , and O^{2-} . For example, the thermodynamic simulation shows that the ionic liquid formed from LSCF73 at 1400°C and $\text{PO}_2 = 10^{-10}$ atm has the

composition of $(\text{La}^{2+}_{0.134}\text{Sr}^{2+}_{0.337}\text{Fe}^{2+}_{0.493}\text{Fe}^{3+}_{0.035})_p(\text{O}^{2-})_q$, where p and q in the first and the second sub-lattice is not fixed to keep the charge neutrality in ionic liquid. It is observed that the ionic liquid is Sr and Fe rich and has negligible Cr concentration. The formation of liquid causes significant compositional changes of the remaining LSCF perovskite with La and Cr enrichment in perovskite.

During the cooling process, the ionic liquid may not reach thermodynamic equilibria with the perovskite. The solidification simulation of the ionic liquid at $\text{PO}_2 = 10^{-10}$ atm shows that the liquid will form perovskite with spinel (Fe_3O_4) and corundum (Fe_2O_3) at lower temperatures, which is again in good agreement with the SEM-EDS and XRD analysis in Fig. 4 and 1.

Fig. 5. (a) Thermodynamic prediction of the phase stabilities of 1 mole per formula LSCF73 at 1400°C with different oxygen partial pressure; (b) Thermodynamic prediction of 1 mole per formula LSCF73 at $\text{PO}_2 = 10^{-10}$ atm at different temperature.

4.4. Electrochemical measurements and post-test observations

Fig. 6a (I) and b (I) shows impedance spectra of the symmetrical cell of configuration LSCF-YSZ / YSZ / LSCF-YSZ at 950 °C in oxidizing (air) and reducing (Ar-3% H_2 -3% H_2O) atmospheres under a constant voltage of 0.5 V. High frequency intercept corresponds to ohmic resistance and the semicircle diameter is attributed to non-ohmic contributions [71]. Two semicircles are observed in reducing atmosphere and correspond to the steps of ion transfer at high frequency and charge transfer at the interface at low frequency [72]. Unlike reducing atmosphere, the two semicircles are merged in oxidizing atmosphere [73]. Comparison plot of non-ohmic resistance changes is shown in Fig. 6 (II). Under oxidizing atmosphere, the symmetrical cells show a small increment in the polarization resistance as the time changes from 0 to 80 h as shown in Fig. 6 (II). In reducing atmosphere, on the other hand, polarization resistance increases significantly with increase in time as indicated in the Fig. 6 (II). The polarization resistance for the tested cell increased from $\sim 3.8 \text{ } \Omega \cdot \text{cm}^2$ (0 h) to $\sim 6.6 \text{ } \Omega \cdot \text{cm}^2$ (80 h) when exposed to Ar-3% H_2 -3% H_2O at 950 °C. Similar study have been conducted for manganese doped lanthanum chromite (LSCM) under above operating conditions in oxidizing and reducing atmosphere. In the case of LSCM, it is found that the polarization resistance for the tested symmetrical cells increased from $\sim 12.0 \text{ } \Omega \cdot \text{cm}^2$ at 0 h to $\sim 24.9 \text{ } \Omega \cdot \text{cm}^2$ at 80 h in reducing. When compared to LSCM, the electrochemical performance of LSCF is found to be higher with ~ 4 times lower polarization resistance. Similarly, higher performance of LSCF is also achieved in oxidizing atmosphere. This demonstrates that the Fe-doped LSCF/YSZ is a better candidate for the above mentioned application than Mn-doped LSCM/YSZ.

Fig. 6 (I). Nyquist plots of impedance spectra obtained from symmetrical cell (LSCF-YSZ / YSZ / LSCF-YSZ) tested at 950 °C with 0.5 V from 0 to 80 h: a) in air, and b) in Ar-3% H_2 -3% H_2O .

Fig. 6 (II). Comparison plot of non-ohmic resistance changes with time for the cell (LSCF-YSZ / YSZ / LSCF-YSZ) tested at 0.5 V in air and Ar-3%H₂-3%H₂O.

Examination of pre and post tested LSCF-YSZ / YSZ / LSCF-YSZ symmetrical cells shows that the electrode layer adheres well to the 8YSZ substrate even after testing for 80 h in oxidizing and reducing gas atmosphere. Microstructural analysis of the cell tested in air shows no modification in the bulk/surface of LSCF/8YSZ as well as show stable interface between LSCF and 8YSZ as shown in Fig. 7. In the case of LSM/YSZ, degradation due to electrode delamination after electrochemical testing, cation migration and lanthanum/strontium zirconate insulating interface layer formation is reported in the literature in oxidizing atmosphere [7-9]. Unlike LSM/YSZ, Fe-doped LSCF/YSZ does not show the above challenges in oxidizing atmosphere indicating a better promising candidate.

In reducing atmosphere, on the other hand, the cell showed a significant modification in the microstructure of LSCF/8YSZ (Fig. 7d (I)) and interface with 8YSZ. The behavior is attributed to the increase in the polarization resistance of the cell in Ar-3% H_2 -3% H_2O atmosphere than air.

Fig. 7 (I). SEM micrographs of the symmetrical cell of LSCF-YSZ / YSZ / LSCF-YSZ (anode surface): a) LSCF73/8YSZ and 8YSZ interface, b) as-sintered in air, c) tested in air, and d) tested in Ar-3% H_2 -3% H_2O .

Fig. 7 (II). SEM micrographs of the electrode/electrolyte interface of the 80 h tested symmetrical cells: a) in air, b) in Ar-3% H_2 -3% H_2O and c) magnified image in Ar-3% H_2 -3% H_2O .

Electrolyte surface after the removal of the electrode is shown in Fig. 7 (II) for the cells tested in oxidizing and reducing atmospheres. It is observed that the interface between the electrode and electrolyte layer remains unchanged (Fig. 7a (II)) when exposed to air atmosphere for 80 h under the bias of 0.5 V. However, in the reducing atmosphere, electrode/electrolyte interface experiences significant structural and chemical changes. Surface

morphology of the electrolyte (8YSZ) is modified at the interface as shown in Fig. 7b (II). Magnified image (Fig. 7c (II)) shows more clearly the interfacial reaction zone at the point of contact of electrode/electrolyte.

TEM elemental distribution mapping of LSCF/8YSZ interface is shown in Fig. 8. It shows the formation of a thin (~10 nm) Sr and Zr enriched layer at the LSCF/8YSZ interface. Using TEM-EDS, it is identified that the layer consists of Sr and Zr in the ratio of 1:1 which suggests the formation of SrZrO₃. Similar interfacial SrZrO₃ compound formation has been reported for LSCM/LSM and YSZ reactions [1, 7-9, 16, 74]. Mn diffusion from perovskite to fluorite phase occurs in reducing gas atmosphere due to the change in the valence of Fe with corresponding variation in ionic radii. Valence of Fe changes from Fe⁴⁺→Fe³⁺→Fe²⁺ in reducing atmosphere as shown below:

where $\text{M}_{\text{M}}^{\times}$ (M = Fe) indicates M³⁺ on M³⁺ sites, $\text{M}_{\text{M}}^{\cdot}$ indicates M⁴⁺ on M³⁺ sites, $\text{M}_{\text{M}}^{\prime}$ indicates M²⁺ on M³⁺ sites, and $\text{V}_{\text{O}}^{\cdot\cdot}$ correspond to oxygen vacancy along with two positive charges.

Ionic radii variation occurs due to the change in the valence state of transition metals (e.g Fe, Mn) [1,16]. Literature also indicates that the solubility of manganese in 8YSZ is higher in reducing atmosphere in comparison with the oxidizing atmosphere. This is due to the higher solubility of lower valence Mn with larger ionic radii in comparison with higher valence Mn [75-77]. Similar changes and phenomenon occurs in the case of iron. Chemical diffusion coefficient of Fe in 8YSZ is 10⁻¹¹ cm²/sec at 1000°C. Fe from LSCF diffuses into 8YSZ

making LSCF enriched in A-site with subsequent reaction with Zr at the interface to form SrZrO_3 .

With the TEM spot elemental analysis, ~7 at % of Fe is found in 8YSZ supporting the hypothesis. It is known that SrZrO_3 is an insulating phase [1,78] and therefore possibly responsible for the higher polarization resistance of the LSCF/8YSZ cell in reducing atmosphere.

Fig. 8. TEM elemental distribution mapping of LSCF and 8YSZ interface after testing and removable of electrode layer in reducing atmosphere ($\text{Ar-3\%H}_2\text{-3\%H}_2\text{O}$).

5. Conclusion

Stability of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ (LSCF73) is examined in three different gas atmospheres (air, N_2 , $\text{Ar-3\%H}_2\text{-3\%H}_2\text{O}$) with varying PO_2 at 1400 °C. Density of LSCF73

increases with decrease in PO_2 . The stability of LSCF73, however, decreases with decrease in PO_2 . For the first time, phase evolution and FeO_x formation in LSCF73 sintered in $\text{Ar-3\%H}_2\text{-3\%H}_2\text{O}$, is identified and reported. In addition, the current work presents the first attempt to use the computational thermodynamics to predict the thermodynamic stabilities of LSCF. Analysis shows that LSCF73 decomposes and form ionic liquid phase at high temperature in reducing atmosphere in agreement with our experimental findings. Higher electrochemical performance of symmetrical cells of configuration LSCF-YSZ / YSZ / LSCF-YSZ is obtained in oxidizing atmosphere when compared to those obtained in reducing atmosphere at 950 °C for 80 h. Lower polarization resistance is achieved in case of Fe-doped LSCF73 when compared to Mn-doped LSCM73. Electrode layer adheres well with the substrate after testing. Microstructural analysis of the post-tested cells shows no morphological and chemical changes in the cells tested in air. Surface modification of 8YSZ phase and SrZrO_3 compound formation is found at the interface of LSCF/8YSZ in reducing atmosphere resulting in the higher polarization resistance of the cell tested in reducing atmosphere.

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