Processing and electrochemical performance of manganese-doped lanthanum-strontium chromite in oxidizing and reducing atmospheres

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Abstract:

This study reports the role of oxygen partial pressure (PO_2) on the microstructural changes and compound formation during the exposure of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.7}Mn_{0.3}O_3$ (LSCM73) to 1400°C to emulate oxygen transport membrane device fabrication. Results of electrochemical testing of LSCM73+8YSZ//8YSZ//LSCM73+8YSZ symmetrical cells, is also reported at 950°C with time for 80h in oxidizing (air) and reducing atmospheres (Ar-3% H_2 -3% H_2O). Our results from elevated temperature exposure studies show a decrease in the density during exposure to reducing atmospheres due to the absence of liquid phase assisted sintering and inability to form $SrCrO_4$. Formation of rhombohedral structure and $MnCr_2O_4$ spinel phase is evident in air whereas Mn_3O_4 phase formation occurs along with lattice transformation to cubic structure at lower PO_2 . Our experimental results are in agreement with LSCM73 phase diagram constructed using Thermo-Calc. Stable electrochemical performance is obtained in air and in reducing atmosphere, non-ohmic resistance increases with time which is attributed to Sr-segregation on LSCM73 surface and interaction between LSCM/8YSZ. No delamination of the electrode layer is observed in both oxidizing and reducing atmosphere.

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1. Introduction

The world energy council projects primary energy demand to increase dramatically in the future as population grows and developing nations elevate their living standards. Finding an effective and timely solution to the emerging global climate change and related environmental issues are universally recognized as the major challenge of this decade. High temperature ($\geq 650^{\circ}\text{C}$) solid-state electrochemical devices such as oxygen transport membrane (OTM) enables clean and efficient utilization of fossil fuels via oxy-combustion [1-2]. The technology can be adapted globally to enhance energy efficiency, reduce carbon foot print and extend the fuel reserve for future [1-4]. OTM system is also advantageous for tonnage oxygen production and syngas production which can be further processed for hydrogen production via water gas shift reaction [3]. The syngas can also be converted into liquid fuels for transportation via Fischer-Tropsch process [5].

Fig. 1 shows a schematic of oxygen transport membrane. The system consist of three layers i.e. air electrode (surface exchange layer), oxygen transport membrane and fuel electrode (intermediate layer) [6]. Oxygen molecules from air dissociate into oxygen ions at the air electrode, migrate through the membrane, and recombine with the electron to form oxygen molecule on the fuel side [7]. The driving force for the selective oxygen transport is the existence of oxygen partial pressure gradient. Air and fuel electrodes are used to enhance surface exchange kinetics and improve the oxygen flux performance of OTM system [7]. Wide spread implementation of the aforesaid, however, remains critically limited by the current unfavorable economics, unproven reliability and lack of longevity.

Chemical/structural/redox stability and high ionic as well as electronic conductivity have been identified as one of the key requirements for oxygen transport membrane and fuel

electrode [8-9]. Ni-YSZ is conventionally used as the fuel electrode for SOFC due to its excellent electro-catalytic activity, electronic and ionic conductivity and thermal expansion match with the electrolyte. However, carbon deposition, volume change during redox cycling and susceptibility to sulphur poisoning are the limitations of Ni-YSZ [10]. To overcome the limitations of Ni-YSZ, mixed ionic and electronic conducting perovskites with/without fluorite phase are being considered as an alternative SOFC anode and membrane/fuel electrode for OTM device [11-12]. This paper focuses on materials development for oxygen transport membrane (OTM) system. However, the results can also be utilized for the development of SOFC fuel electrode.

Lanthanum chromite based perovskites have been studied extensively as an oxygen transport membrane and fuel electrode [13-26]. This is due to its high chemical and structural stability at high temperatures in oxidizing as well as reducing atmospheres. Lanthanum chromite is commonly doped with alkaline earth metal at A-site and transition metal at B-site for improving its electrical conductivity, electrochemical performance, thermal expansion coefficient and densification. The dopants, on the other hand, have also been found to deteriorate the structural and thermo-chemical stability of these materials specifically in reducing atmosphere ($\leq 10^{-10}$ atm). A review article is recently published on the effect of A and B-site dopants on the structure-thermal-electrical-mechanical properties of lanthanum chromite based materials for oxygen transport membrane by Gupta et al. [16].

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3$ (LSCMx) is being investigated for fuel side electrode and oxygen transport membrane (OTM) as it provides the combination of high electrochemical activity, high electrical conductivity and good thermal expansion match with 8YSZ [16-19, 25-30]. LSCMx is also identified as promising fuel electrode for direct utilization of hydrocarbon

fuels [27]. The electrode polarization resistance for $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM55) is $0.2 \Omega \text{ cm}^2$ at 900°C in $97\%\text{H}_2$ - $3\%\text{H}_2\text{O}$, comparable to Ni/YSZ cermets [30]. The conductivity of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is 38 S cm^{-1} at 900°C and remains same for PO_2 values above 10^{-10} atm [29-30]. However, further lowering of PO_2 to $\sim 10^{-21}$ atm, the conductivity decreases to 1.5 S cm^{-1} [29-30]. The thermal expansion coefficient (TEC) of LSCM55 is $9.3 \times 10^{-6} \text{ K}^{-1}$ in air in the temperature range of 64 - 956°C . The TEC is comparable to 8YSZ ($10.3 \times 10^{-6} \text{ K}^{-1}$), a most commonly used oxygen ion conducting fluorite phase [31].

For lanthanum chromite based materials, density increases with decreasing oxygen partial pressure [32-33]. Because, the vapor pressure of CrO_3 significantly decreases in reducing atmospheres. Subsequently, Cr_2O_3 deposition at the inter-particle necks is inhibited resulting in higher densification [32-33]. The sintering behavior of A-site doped lanthanum chromite based materials is well known in the literature [16].

As mentioned above, these materials are further doped at B-site to improve the structural-thermal-electrical properties as required for OTM system. However, the sintering behavior of simultaneously A-site and B-site doped LaCrO_3 is not investigated in the literature. In this study, we report the sintering and electrochemical behavior of manganese-doped lanthanum-strontium chromite, which is one of the most promising candidates for oxygen transport membrane and fuel electrode. However, LSCMx with higher Mn-doping level destabilizes in reducing atmosphere. For example, $(\text{La,Sr})_2\text{MnO}_4$ and MnO secondary phases have been detected for LSCM55 when exposed to 900°C and 10^{-20} atm [34]. Formation of Mn-Cr-O spinel (MnCr_2O_4) has also been indicated in LSCM55 [35]. In reducing atmosphere, the spinel phase reduces to MnO [35-36]. The results exhibit that LSCMx with high Mn doping level (LSCM55) is not stable in reducing atmosphere [16, 35-36]. Furthermore, it is identified

in the recently published review article that B-site (e.g. Mn) doping level is good to be restricted (≤ 30 mol.%) from stability point of view [16]. However, in the reported literature, LSCMx is not investigated with higher Cr: Mn ratio or lower Mn doping level under OTM processing and operating conditions. Therefore, a composition with lower concentration of Mn i.e. $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$ (LSCM73) is chosen for this study. A-site deficient composition is chosen for this study to avoid the Sr-segregation which is likely to occur in lanthanum strontium manganite/chromite based materials [16,37]. Furthermore, A-site deficiency is found to be beneficial to avoid the interaction of lanthanum strontium manganite/chromite based materials with stabilized zirconia fluorite phase to form insulating phase such as $\text{La}_2\text{Zr}_2\text{O}_7$ and SrZrO_3 [16,38]. Sintering behavior and microstructure analysis of LSCM73 is examined under simulating OTM fabrication conditions ($\sim 1400^\circ\text{C}$ and $\text{PO}_2 \sim 0.21 \cdot 10^{-10}$ atm). On the other hand, electrochemical impedance measurement is performed at lower temperature under simulating anodic OTM operation conditions ($\sim 950^\circ\text{C}$ and $\sim 10^{-17}$ atm).

2. Experimental Procedure

2.1 $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$ synthesis

LSCM73 powder was obtained from Praxair Inc. The particle size distribution of the powder was $D_{50} = 1.34\mu\text{m}$. The powder was uniaxially pressed into cylindrical pellets. Subsequently, LSCM73 powder was also mixed with 0.5% SrCrO_4 to understand the effect of SrCrO_4 on densification and validate our results and hypothesis. The pellets were bisque fired at 1100°C for 4h and then, sintered in air, N_2 ($\sim 10^{-5}$ atm) and Ar-3% H_2 -3% H_2O ($\sim 10^{-10}$ atm) atmosphere at 1400°C with 10h dwell time. Samples were cooled in the flowing gas environment to ensure the maintenance of the oxygen pressure during cooling.

2.2 Characterization

Density of all the samples was measured using Archimedes principle. The microstructural analysis was conducted using scanning electron microscope (FEI - ESEM Quanta 250, Hillsboro, OH). Energy dispersive spectroscopy (EDS) attached to the SEM was used for elemental compositional analysis.

X-ray diffraction (BRUKER-D8 ADVANCE, Bruker AXS Inc. Madison, WI) technique was used to determine the crystal structure of LSCM73 and secondary compounds, if any, sintered in different gas atmospheres. The scan step was 0.02° using CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.4 Symmetric cell fabrication

LSCM73 is predominantly electronic conductor, and therefore mixed with 8YSZ for ionic conduction in 50:50 weight ratios for the fabrication of symmetrical cell and testing. LSCM73+8YSZ paste was prepared using ink vehicle (Fuel Cell Materials). LSCM73+8YSZ working and counter electrodes (thickness: $\sim 20 \mu\text{m}$, diameter: 10 mm) were screen-printed on both sides of $200 \mu\text{m}$ thick $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ (YSZ) electrolyte (Fuel Cell Materials). After drying at room temperature, the electrodes were sintered at 1200°C (heating rate of $3^\circ\text{C}/\text{min}$) for 2 h in air. Lower sintering temperature (1200°C) was chosen for fabrication of the cell to obtain porous electrode layer as well as to avoid secondary phase's formation that were observed at 1400°C . No secondary phases are identified in the as-sintered symmetrical cells. Platinum screen current collector (Alfa Aesar, 50 mesh) and platinum wires (Alfa Aesar, 0.25 mm) were attached to each electrode using platinum paste (Electro-Science Laboratories Inc.). The platinum paste was cured in air at 900°C for 1 h ($3^\circ\text{C}/\text{min}$). The electrochemical active area of the cell electrode

was calculated to be 0.8 cm^2 . As-assembled symmetric cells of configuration LSCM73+8YSZ //8YSZ//LSCM73+8YSZ were installed in a tubular alumina reaction chamber placed in the constant temperature zone of a furnace. The leads from a multi-channel potentiostat (VMP2, Bio-Logic) were attached to the assembled symmetric cell.

2.5 Electrochemical testing

The symmetrical cells were heated to 950°C ($3^\circ\text{C}/\text{min}$) in flowing air and Ar-3% H_2 -3% H_2O with flow rate maintained at 300sccm. 3% water vapor was introduced in the Ar-3% H_2 gas stream through a water bubbler at room temperature. Using the potentiostat, a pre-determined constant bias of 0.5V was applied for 80 h. The impedance was measured (at four hour intervals) in the frequency range from 100 mHz to 200 kHz using a 10 mV alternating current. To ensure reproducibility, experiments were repeated several times at the imposed voltage condition. Post-test characterization of the symmetrical cells was performed using SEM-EDS (FEI - ESEM Quanta 250).

3. Results and Discussion:

3.1 Crystal structure

Fig. 2 shows the XRD pattern of LSCM73 bisque-fired at 1100°C in air and sintered at 1400°C in air, N_2 , and Ar-3% H_2 -3% H_2O atmosphere. Extra peaks corresponding to the SrCrO_4 (JCPDS 073-1082) are identified in the bisque-fired sample in agreement with $\text{SrO-Cr}_2\text{O}_3\text{-La}_2\text{O}_3$ phase diagram [39]. The width of the peaks appears to increase likely due to the diminution of the perovskite grain size with decreasing in the PO_2 as is indicated in the next section 3.2. The crystal structure for LSCM73 is rhombohedral (JCPDS 75-9872). However,

the peaks splitting corresponding to the rhombohedral phase decreases with decrease in PO_2 . And, it almost disappears in case of the samples sintered in Ar-3% H_2 -3% H_2O attributing to less distortion of the lattice and higher symmetry phase formation. The possible higher symmetry phase is cubic (JCPDS 074-1961) after rhombohedral [36]. This is consistent with the co-existence of cubic and rhombohedral phase for LSCM73 when sintered in N_2 . But, in Ar-3% H_2 -3% H_2O , predominantly cubic phase is identified corresponding to disappearance of the peaks splitting and phase transformation to the higher symmetry phase. In future, a detailed study will be investigated for in-depth understanding of the phase transformation as a function of PO_2 .

In case of air and N_2 atmosphere, new peaks are identified as Mn-Cr-O spinel phase (marked by blue five pointed star) i.e. $MnCr_2O_4$ (JCPDS 075-1614) as shown in Fig. 2. The peaks disappearance corresponding to $MnCr_2O_4$ is observed for the samples sintered in Ar-3% H_2 -3% H_2O atmosphere. However, presence of new peaks (marked by green four pointed star) is observed for the samples sintered in lower oxygen partial pressure (N_2 and Ar-3% H_2 -3% H_2O). The peaks are identified as Mn_3O_4 (JCPDS 086-2337) in reducing gas atmospheres [36,40]. Co-existence of $MnCr_2O_4$ and Mn_3O_4 is observed for the samples sintered in N_2 ($\sim 10^{-5}$ atm) atmosphere. However, in Ar-3% H_2 -3% H_2O atmosphere, only Mn_3O_4 peaks are identified.

3.2 Sintering behavior and microstructural analysis

Fig. 3 shows the density of LSCM73 as a function of oxygen partial pressure (PO_2) sintered at 1400°C for 10h. The density of bisque fired sample is ~48% which increases to ~68% for air sintered sample. However, it decreases to ~56% with decrease in PO_2 for the sample sintered in Ar-3% H_2 -3% H_2O . Also, the average grain size decreases from 3.0 μm (air)

to 1.2 μm (N_2) to 0.6 μm ($\text{Ar-3\%H}_2\text{-3\%H}_2\text{O}$) with decrease in PO_2 . Fig. 4 shows the polished surface SEM microstructures of the samples sintered in air, N_2 ($\sim 10^{-5}$ atm) and $\text{Ar-3\%H}_2\text{-3\%H}_2\text{O}$ ($\sim 10^{-10}$ atm) gas atmosphere. In oxidizing atmosphere (air), secondary phases have been observed predominantly at grain boundaries as marked in Fig. 4a. Elemental analysis reveals that the secondary phases mainly consist of Mn and Cr with small amount of La and Sr as shown in Table 1. Fig. 5 shows the elemental mapping of air sintered sample with enriched Mn and Cr phases. These phases are MnCr_2O_4 spinel as confirmed from XRD. The spinel formation decreases with decrease in PO_2 . However, a new Mn-rich phase is observed in the samples sintered in reducing atmosphere, and it increases with decreasing oxygen partial pressure as shown in Fig 4b and 4c. This is also observed in the elemental mapping (Fig. 6) of LSCM73 sintered in $\text{Ar-3\%H}_2\text{-3\%H}_2\text{O}$. Table 2 shows the SEM-EDS elemental analysis of Mn-rich phase and bulk. The phase is identified as Mn_3O_4 using XRD in Fig 2.

It is known that densification of Sr-doped LaCrO_3 is assisted by liquid phase (SrCrO_4) sintering [41]. The reaction (1) is favored at an oxygen partial pressure of 0.21 atm.

Gibb's free energy formation for SrCrO_4 are -158 and -50 kJ mol^{-1} at $\text{PO}_2 \sim 0.21$ and 10^{-5} atm (900°C) respectively. With decreasing oxygen partial pressure, the Gibb's free energy for the formation of SrCrO_4 increases, and becomes positive at 900°C for the partial pressures less than $10^{-7.2}$ atm. For example, the free energy for SrCrO_4 formation is $+75 \text{ kJ mol}^{-1}$ at $\sim 10^{-10}$ atm 900°C [42]. In addition, according to $\text{SrO-Cr}_2\text{O}_3\text{-La}_2\text{O}_3$ system, SrCrO_4 phase is unstable at low oxygen partial pressure ($\sim 10^{-9}$ atm) at 1600°C [39].

In case of A-site doped $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$, SrCrO_4 phase exolution occurs at $\sim 800^\circ\text{C}$ and melts at 1256°C [43]. The SrCrO_4 liquid phase re-dissolves into the perovskite at high

temperature and assists densification. Similarly, in case of A and B-site doped LSCM73, the SrCrO_4 , which is present in the bisque fired sample liquefies and re-dissolves into the lattice at high temperature resulting in higher densification. Higher grain growth is also achieved for the samples sintered in air due to the liquid phase assisted sintering. However, the grain growth and density decrease on lowering PO_2 . Lower densification with decreasing oxygen partial pressure is associated with decreasing SrCrO_4 and subsequent liquid phase sintering. To validate our hypothesis, 0.5% of SrCrO_4 is added to LSCM73 and sintered in air under same conditions. The results show higher densification for LSCM73+0.5% SrCrO_4 when compared to LSCM73 sintered sample as shown in Fig. 3. The SEM micrograph of the sintered LSCM73+0.5% SrCrO_4 sample is shown in Fig. 4d. Highest density (~73%) is achieved for LSCM73 when mixed with 0.5% SrCrO_4 and sintered in air. This corresponds to the higher amount of liquid phase formation [44].

On the other hand, chromium evaporation is likely to occur for lanthanum chromite based materials in the form of CrO_3 and it condenses as Cr_2O_3 (Eq. 2) at the grain boundaries (irregular contacts) due to the surface energetics [13].

Manganese is soluble in Cr_2O_3 up to a limit of 1.6% of the cation sites at 1000°C [45]. Manganese tends to diffuse and react with Cr_2O_3 to form MnCr_2O_4 (Eq. 3), preferentially at the grain boundaries of LSCM73 as shown in Fig. 4a and d. Thermodynamically, the spinel phase formation is favorable at 1400°C with the Gibbs free energy of formation for MnCr_2O_4 to be -40.1kJ/mol [46].

The formation of spinel phase is also in agreement with Mn-Cr-O phase diagram [36]. According to the phase diagram, the cubic spinel phase forms at 1400°C in air. With decrease in PO_2 , the Cr-evaporation and condensation with the formation of Cr_2O_3 decreases. Subsequently, the formation of $MnCr_2O_4$ also decreases with decrease in oxygen partial pressure. This is in agreement with our observation in the SEM micrographs of LSCM73 in air (Fig. 4a), N_2 (Fig. 5b) and Ar-3% H_2 -3% H_2O (Fig. 4c). On the other hand, Mn_3O_4 phase is observed in the samples sintered in N_2 ($\sim 10^{-5}$ atm) and Ar-3% H_2 -3% H_2O ($\sim 10^{-10}$ atm) gas atmosphere. However, the formation of Mn_3O_4 increases with decrease in PO_2 . In the literature, it is given that $MnCr_2O_4$ dissociates into MnO in reducing gas atmosphere [35-36]. However, no experimental or theoretical evidence is provided. Furthermore, if the spinel phase dissociates into MnO and Cr_2O_3 in reducing atmosphere, the appearance of Cr_2O_3 should be detected like MnO using XRD or SEM. The presence of Cr_2O_3 is not identified in the literature as well as in our study. The formation of $MnCr_2O_4$ is dependent on Cr_2O_3 (Eq. 3). According to our study, in reducing atmosphere, we propose that Mn diffuses into the condensed Cr_2O_3 until it is consumed to form $MnCr_2O_4$. Afterwards, Mn diffuses at the outer surface and exits in the lattice as MnO. During cooling, the temperature and PO_2 decreases to the region where MnO is not stable and it forms Mn_3O_4 in agreement with our XRD results [40].

The exolution of MnO phase in LSCM73 in reducing gas atmosphere can also be explained based on the oxygen exchange defect reactions. It is known that Mn can exist in three valence states i.e. $Mn^{2+}/Mn^{3+}/Mn^{4+}$ in LSCM [34]. Due to the existence of disproportionate Mn valence state, oxygen vacancies exist in the lattice of LSCM73 for the charge compensation. At lower PO_2 , the transition of $Mn^{4+} \rightarrow Mn^{3+}$ and $Mn^{3+} \rightarrow Mn^{2+}$ results in higher amount of oxygen

vacancies formation for charge neutrality. The oxygen exchange between LSCM73 and gas phase can be represented as shown below [34]:

where $Mn_{Mn}^{\times}$ refers to Mn^{3+} on Mn^{3+} sites, $Mn_{Mn}^{\cdot}$ refers to Mn^{4+} on Mn^{3+} sites, Mn'_{Mn} refers to Mn^{2+} on Mn^{3+} sites, and $V_O^{\bullet\bullet}$ refers to oxygen vacancy with two positive charges.

We postulate that LSCM73 perovskite lattice structure destabilizes due to the existence of higher amount of oxygen vacancies and Mn^{2+} (0.830 Å) with higher ionic radii than Mn^{3+} (0.645 Å). Therefore, in reducing atmosphere, Mn^{2+} does not retain in the $A^{3+}B^{3+}O_3^{2-}$ perovskite lattice of LSCM73 and exolve as MnO. Oishi et al. [34] have reported similar exolution of MnO from LSCM55 lattice when exposed to $PO_2 \sim 10^{-20}$ atm at 900°C.

Mechanism and the sintering behavior of LSCM73 in air, N_2 and Ar-3% H_2 -3% H_2O gas atmosphere are shown in Fig. 7. In step 1, the starting material is same for the three cases i.e. bisque fired (at 1100°C) LSCM73 with the existence of $SrCrO_4$ (indicated by yellow color). In step 2, the $SrCrO_4$ melts (indicated by yellow color) at ~1256°C in case of air and N_2 atmosphere. However, due to the positive Gibbs free energy of formation in reducing atmosphere, $SrCrO_4$ is unstable for the samples sintered in Ar-3% H_2 -3% H_2O ($\sim 10^{-10}$ atm). It is hypothesized that the $SrCrO_4$ would dissociate into SrO and Cr_2O_3 and dissolve back into the lattice when heating up to the sintering temperature. During Step 3, the evaporated CrO_3 condenses and deposits in the form of Cr_2O_3 (indicated by green color), preferentially at the grain boundaries due to higher surface energy. And, Mn diffuses at the outer surface and reacts with Cr_2O_3 to form $MnCr_2O_4$ spinel (indicated by red color). However, as explained above, the CrO_3 evaporation and condensation as Cr_2O_3 decreases (step 3) in reducing atmosphere. Therefore, the

availability of Cr_2O_3 to react with Mn to form MnCr_2O_4 decreases with decrease in PO_2 .

Consequently, Mn diffuses at the outer surface and exists as Mn_3O_4 in the lattice. As a result, both MnCr_2O_4 and Mn_3O_4 exist for the sample sintered in N_2 atmosphere as shown in the step 4. In Ar-3% H_2 -3% H_2O atmosphere with least PO_2 ($\sim 10^{-10}$ atm) among the three cases, there is no MnCr_2O_4 formation due to the absence of Cr_2O_3 (step 3) and therefore, Mn comes out as Mn_3O_4 (indicated by orange color) in step 4.

3.3 Thermodynamic calculations:

To support our experimental results and hypothesis on the sintering behavior of LSCM73, we performed thermodynamic calculations using the CALculation of PHase Diagram (CALPHAD). The CALPHAD approach was pioneered by Kaufman [47] to model complex phase equilibria in multicomponent systems. Its theoretical basis is thermodynamic description of individual phases. The thermodynamic database was developed using Thermo-Calc [48]. Thermo-Calc is a program developed by KTH Royal Institute of Technology in the 1970s. For over 40 years, Thermo-Calc has been at the forefront of scientific software and databases for calculations involving computational thermodynamics [47,49].

The customized thermodynamic database for La-Sr-Cr-Mn-O-H-S system was adopted in the current investigations, which is able to simulate the phase equilibria of perovskite at various gas conditions including the gas species like H_2O , O_2 , SO_2 , H_2S , etc. It is a combined database with the La-Sr-Cr-Mn-O database [46,50-51] and SSUB database [52]. It has the Gibbs energy description of all the phases we are interested in the current work, including the perovskite and spinel phases. It is expanded by adding Cr on the basis of the La-Sr-Mn-O thermodynamic database, which was initially developed to consider the Cr poisoning effect to LSM.

In the current work, the phase stabilities of LSCM73 were examined at different oxygen partial pressures at 1400°C in comparison with the experimental observations. According to our thermodynamic calculations and Fig. 8, LSCM73 will form spinel in air, with the decrease of the oxygen partial pressure, phases like MnO and SrO will form. The theoretical predictions are in agreement with our experimental results at 1400°C. Spinel phase co-exists with perovskite phase in air (0.21 atm). However, at lower PO_2 ($\sim 10^{-5}$ atm), three phase co-exists as shown in our experimental observations i.e. perovskite, spinel and MnO. With further decrease in PO_2 , only MnO phase co-exists with perovskite as shown in Fig. 8 which is also in agreement with our experimental results. As mentioned in the previous section, during cooling, it is to be noted that the temperature and PO_2 reduces to the region where MnO is not stable and it forms Mn_3O_4 [40]. This is in agreement with our XRD results.

3.4 Electrochemical measurements and post-test observations

Fig. 9a and b shows electrochemical performance of the symmetrical cell (LSCM73+8YSZ//8YSZ//LSCM73+8YSZ) at 950°C and 0.5 V in air and Ar-3% H_2 -3% H_2O respectively. Ohmic resistance is represented by high frequency intercept, while the semicircle diameter represents sum of the non-ohmic contributions [53]. In case of reducing atmosphere (Ar-3% H_2 -3% H_2O), two semicircles are observed corresponding to the charge (ion) transfer at the electrolyte/electrode interface and electrochemical kinetics involved with electrode material (e.g. adsorption and/or diffusion processes to/from the interface) [54-55]. However, the two electrode arcs merged in oxidizing atmosphere (air) [41]. Fig. 10 shows comparison plot of ohmic and non-ohmic resistances as a function of time for the cell tested at 0.5 V in air and Ar-3% H_2 -3% H_2O . In case of oxidizing atmosphere, ohmic and non-ohmic resistances increase with

time, but there is no significant variation observed especially after 20h as shown in Fig 9a and 10. This corresponds to higher stability of LSCM73 in oxidizing atmosphere. On the other hand, in reducing atmosphere, the ohmic resistance almost stabilizes with increase in time as shown in Fig. 10. However, non-ohmic resistance continuously increases with time. The non-ohmic resistance for the tested cell is $\sim 12.0 \Omega \cdot \text{cm}^2$ (0h) and increases to $\sim 24.9 \Omega \cdot \text{cm}^2$ (80h) in Ar-3% H_2 -3% H_2O at 950°C when bias of 0.5V is applied. Resistance of the tested cell increases when exposed to reducing gas atmosphere as shown in Fig. 10.

Symmetrical cells (LSCM73+8YSZ//8YSZ//LSCM73+8YSZ) before and after testing are analyzed. No changes are identified with the naked eye. In addition, no delamination of the porous electrode layers is observed after manual removal of Pt mesh along with Pt wires. Bulk electrode and electrode/electrolyte interfaces are examined for microstructural changes and reaction products formation. Fig. 11a shows the interface of LSCM73+8YSZ (anode) and 8YSZ (electrolyte). There is no interface layer or compound formation observed at the interface in air. Furthermore, when compared to as-sintered cell (Fig. 11b), no changes are identified in the microstructure of the tested cell in air (Fig. 11c). However, in Ar-3% H_2 -3% H_2O , surface morphology of LSCM73 phase is significantly modified as shown in Fig. 11d. Nano-size particles segregation is observed on the anode surface of the tested cell as shown in Fig. 11d. Surface compositional analysis is performed using SEM-EDS at ~ 20 different points. It is observed that the average Sr: La ratio is higher for the symmetrical cell tested in Ar-3% H_2 -3% H_2O (Sr: La $\sim 0.65 \pm 0.05$) when compared to those tested air (Sr: La $\sim 0.44 \pm 0.05$) which matches with as-sintered cell (Sr: La $\sim 0.43 \pm 0.04$). This corresponds to the Sr-segregation in case of the cell tested in reducing atmosphere. Sr enrichment on lanthanum strontium manganite surface is reported earlier after heat treatment (1000°C) in nitrogen atmosphere (humid) at low

partial pressure of oxygen [56]. Hu et al. [50] have observed similar surface morphological changes attributing to Sr-segregation in $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM) after electrochemical cell testing in air (with 50% water vapor) at 850°C for 100h. Consequently, the resistance of the LSM based symmetrical cells increased [57]. Similarly, it is postulated that the SrO segregation on LSCM73 surface results in the increase of resistance with time when tested in Ar-3% H_2 -3% H_2O . Figure 12a and b shows electrode-electrolyte interface after removal of LSCM73 layer from the cells tested in air and Ar-3% H_2 -3% H_2O respectively. Ridges and lip formations along with the reaction zone (indicated by yellow circles) are observed at the contact of LSCM/8YSZ and attributes to an interaction between electrode and electrolyte in Ar-3% H_2 -3% H_2O unlike air. Similar interactions are reported between LSM/8YSZ by Keane [58] and Li et al. [59] resulting into an increase in the polarization resistance under the applied bias. However, less interaction is identified in this study for LSCM-8YSZ system when compared to LSM-8YSZ.

4. Conclusion

$(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Mn}_{0.3}\text{O}_3$ (LSCM73) experiences enhanced densification in air during sintering at 1400°C when compared to reducing atmosphere. Spinel phase formation (MnCr_2O_4) has been observed when sintered in air (0.21 atm) and N_2 ($\sim 10^{-5}$ atm) whereas Mn_3O_4 phase formation is observed at lower oxygen partial pressure ($\sim 10^{-5}$ and $\sim 10^{-10}$ atm). Thermodynamic calculations as well as construction of phase diagram, developed using Thermo-Calc software, supports experimental observations. The crystal structure of the sintered LSCM73 shows rhombohedral lattice structure in air and its transformation to cubic in reducing atmosphere. Stable and superior performance of the symmetric cell of configuration

LSCM73+8YSZ//8YSZ//LSCM73+8YSZ, during electrochemical testing at 950°C, is attributed to surface and interface stability and lack of Sr segregation in oxidizing atmospheres when compared to exposure to reducing atmospheres.

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Figure Captions

Fig. 1. Schematic of oxygen transport membrane.

Fig. 2. XRD pattern of LSCM73 bisque-fired (1100°C) in air and sintered (1400°C) in air, N₂ and Ar-3%H₂-3%H₂O.

Fig. 3. Relative density of sintered LSCM73 in air (0.21 atm), N₂ (10⁻⁵ atm) and Ar-3%H₂-3%H₂O (10⁻¹⁰ atm).

Fig. 4. Polished surface SEM micrographs of sintered LSCM73 in a) air, b) N₂, c) Ar-3%H₂-3%H₂O, and d) air (with 0.5% SrCrO₄).

Fig. 5. Elemental mapping of polished surface SEM micrographs of sintered LSCM73 in air.

Fig. 6. Elemental mapping of polished surface SEM micrographs of sintered LSCM73 in Ar-3%H₂-3%H₂O atmosphere.

Fig. 7. Schematic of sintering steps for LSCM73 sintered in air, N₂ and Ar-3%H₂-3%H₂O.

Fig. 8. Relationship between the phase stabilities of LSCM73 at 1400°C and oxygen partial pressure.

Fig. 9. Nyquist plots of impedance spectra obtained from the symmetrical cell of configuration LSCM73+8YSZ//8YSZ//LSCM73+8YSZ tested at 950°C with 0.5 V from 0 to 80 h: a) in air, and b) in Ar-3%H₂-3%H₂O. For clarity, only five spectra are shown.

Fig. 10. Comparison plots of resistance (ohmic and non-ohmic) changes with time (80h) for the symmetrical cell of configuration LSCM73+8YSZ//8YSZ//LSCM73+8YSZ tested at 0.5 V in air and Ar-3%H₂-3%H₂O.

Fig. 11. SEM micrographs of the symmetrical cell of configuration

LSCM73+8YSZ//8YSZ//LSCM73+8YSZ (anode surface): a) LSCM73+8YSZ and 8YSZ interface b) as-sintered in air, c) tested in air, and d) tested in Ar-3%H₂-3%H₂O.

Fig. 12. SEM micrograph of the anode-side electrolyte interface after testing and removing LSCM73 layer: a) air and b) Ar-3%H₂-3%H₂O.

Figure 1

OXYGEN TRANSPORT MEMBRANE

Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9a

Figure 9b

Figure 10

Figure 11a

Figure 11b

Figure 11c

Figure 11d

Figure 12

Tables

Table 1. SEM-EDS elemental analysis of LSCM73 sintered in air.

Element	La (at. %)	Sr (at. %)	Cr (at. %)	Mn (at. %)
Area 1 (Mn-Cr-spinel)	8.1±1.0	2.7±4.3	51.6±1.1	37.6±4.6
Area 2 (Bulk)	37.8±0.1	16.4±0.4	31.7±0.2	13.7±0.3

Table 2. SEM-EDS elemental analysis of LSCM73 sintered in Ar-3%H₂-3%H₂O.

Element	La (at. %)	Sr (at. %)	Cr (at. %)	Mn (at. %)
Area 1 (Mn-oxide)	10.2±3.0	5.6±4.3	11.4±2.3	70.8±3.9
Area 2 (Bulk)	35.4±0.9	16.4±2.2	32.9±0.4	15.3±0.3