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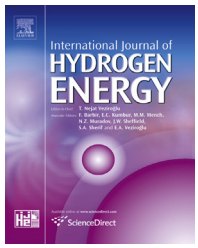

Processing and electrochemical performance of manganese-doped lanthanum-strontium chromite in oxidizing and reducing atmospheres

Sapna Gupta [a], *Yu Zhong* [b], *Manoj Mahapatra* [a], *Prabhakar Singh* [a,*]

[a] *Materials Science and Engineering, University of Connecticut, Storrs, CT 06268, USA*
[b] *Mechanical and Materials Engineering, Florida International University, Miami, FL 33174, USA*

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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 80 h 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.

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 (≥650 °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

* *Corresponding author*. 44 Weaver Road, Storrs Mansfield, CT 06269-5233, USA. Tel.: +1 860 486 8379; fax: +1 860 486 8378.
E-mail address: singh@engr.uconn.edu (P. Singh).
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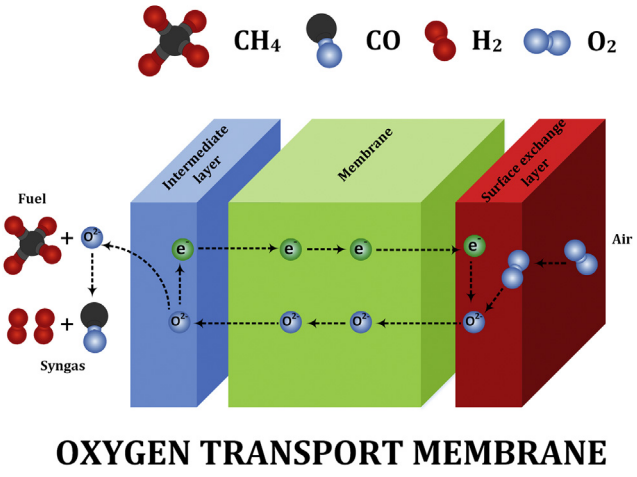

Fig. 1 – Schematic of oxygen transport membrane.

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 sulfur 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].

$La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO_3$ (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 $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM55) is 0.2 Ω cm^2 at 900 °C in 97% H_2–3%H_2O, comparable to Ni/YSZ cermets [30]. The conductivity of $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ 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 ~10^{-21} atm, the conductivity decreases to 1.5 S cm^{-1} [29,30]. The thermal expansion coefficient (TEC) of LSCM55 is 9.3 × 10^{-6} K^{-1} in air in the temperature range of 64–956 °C. The TEC is comparable to 8YSZ (10.3 × 10^{-6} 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, $(La,Sr)_2MnO_4$ 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. $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.7}Mn_{0.3}O_{3-\delta}$ (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 $La_2Zr_2O_7$ and $SrZrO_3$ [16,38]. Sintering behavior and microstructure analysis of LSCM73 is examined under simulating OTM fabrication conditions (~1400 °C and PO_2 ~ 0.21-10^{-10} atm). On the other hand,