Interfacial stability of iron doped lanthanum strontium chromite and scandia stabilized zirconia in oxidizing and reducing atmosphere

Sapna Gupta^a, Jonathan Lane^b, Jamie Wilson^b, Pawel Plonczak^b and Prabhakar Singh^{a,*}

^a Center for Clean Energy Engineering, Department of Materials Science and Engineering, University of Connecticut, 44 Weaver Road, Storrs, CT 06269

^b Praxair Inc., Tonawanda, NY

Abstract:

This study reports the interfacial stability of doped $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ (LSCF) and 10Sc1CeSZ system in oxidizing and reducing atmosphere for the application of oxygen transport membrane (OTM) device. Role of oxygen partial pressure (PO_2) on the interfacial stability of LSCF with 10Sc1CeSZ is studied under OTM fabrication conditions (1400°C , $\text{PO}_2 \sim 0.21 - 10^{-10}$ atm). Interfacial stability corresponding to the interaction between LSCF and 10Sc1CeSZ decreases with decrease in PO_2 . Interfacial study of LSCF with 10Sc1CeSZ shows absence and presence of strontium zirconate (SrZrO_3) at the interface in oxidizing ($\text{PO}_2 \sim 0.21$ atm) and reducing atmosphere ($\text{PO}_2 \sim 10^{-10}$ atm) at 1400°C respectively. Mechanism for the formation of SrZrO_3 is reported.

* Corresponding author. Tel.: +1 860 486 8379; fax: +1 860 486 8378.

Email address: singh@engr.uconn.edu (P. Singh)

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1. Introduction

Dense ceramic materials with high mixed ionic-electronic conductivity (MIEC) have shown promising potential for economic, clean and efficient oxygen separation from air [1-2]. Applications range from small-scale oxygen pumps which can be utilized in medical industries to large scale oxygen production system for coal gasification/combustion in power plants [3-7]. MIEC materials also finds application in chemical processing which includes the partial oxidation of hydrocarbons [1-2,8]. For example, oxygen transport membrane prepared with MIEC materials can be used to convert natural gas to value-added chemicals such as syngas which can be further processed for hydrogen production and liquid fuels [2,9-10].

An overview of MIEC materials for use in oxygen separation devices like OTMs and technology development was recently published [2]. Lanthanum chromite doped at A-site with strontium and B-site with iron (La Sr)(Cr, Fe)_{3-δ} is currently being investigated for use in membranes and fuel side electrodes for use in oxygen transport membrane (OTM) devices [2,11-12]. It is reported that Fe-doping improves electrode performance in solid state electrochemical devices (e.g. SOFC) [13-14]. Lower polarization resistance is obtained for iron doped La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-δ} (LSCF55) than Mn-doped La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM55) [13]. Furthermore, ionic conductivity of (La Sr)(Cr, Fe)_{3-δ} is found to be higher than acceptor-doped lanthanum chromites and (La Sr)(Cr, Mn)_{3-δ} (LSCM) [15-16]. However, the authors have noted that most of the literature exists on LSCF55 [11,13,17]. An oxygen permeation flux and oxygen ionic conductivity of $2.5 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $\sim 0.01 \text{ S/cm}$ were found at 950 °C under air/CO gradient [11]. On the other hand, it is reported that LSCF55 is not stable and partially decomposes into metallic iron along with some other unknown phases when exposed to pure H₂ atmosphere at 950°C (30 h) [17]. Fang et al. [17] have calculated the decomposition oxygen

partial pressure of LSCF55 as 6.3×10^{-28} atm. Addition of a fluorite phase is required to achieve the higher ionic conduction and oxygen flux performance required for oxygen separation devices such as OTMs [2]. For instance, single phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ perovskite exhibited an oxygen flux of $\sim 2.5 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ while flux of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}/\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$ composite exhibited a higher oxygen flux of $\text{JO}_2 \sim 2.6 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ under an air/CO gradient at 950°C [18-19].

Interfacial stability of (La Sr)(Cr, Fe)_{3-δ} based materials with fluorite phase is not reported in literature under fabrication conditions (1400°C, $0.21 - 10^{-10}$ atm) required for oxygen separation devices like OTMs. Due to the reported lower stability of higher Fe-containing LSCF perovskites, this study examines $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ and 10Sc1CeSZ system with higher Cr: Fe ratio and lower Fe doping level. It is important to understand the interaction between LSCF perovskite and 10Sc1CeSZ fluorite under OTM processing which have not been reported upon in the literature [2]. This study, therefore, focuses on the interfacial stability of LSCF with 10Sc1CeSZ in oxidizing and reducing atmosphere under OTM fabrication conditions.

2. Experimental Procedure

2.1. $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ and 10Sc1CeSZ synthesis

Pellets of 10Sc1CeSZ fluorite were made and then calcined at 1100°C for 2h. $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF) powder was received from Praxair Inc. LSCF composition ink was prepared using Fuel Cell Materials ink vehicle. The LSCF ink was then screen printed onto the 10Sc1CeSZ disk shaped pellet and dried at 125°C for 2h. The LSCF/10Sc1CeSZ system was then processed at 1400°C for 10h in oxidizing (air) and reducing (Ar-3% H_2 -3% H_2O) atmosphere.

2.2. Characterization

Microstructural changes, elemental analysis and third phase formation of the processed samples were analyzed using scanning electron microscope (SEM) (FEI - ESEM Quanta 250, Hillsboro, OH) with energy dispersive spectroscopy (EDS). Elemental compositional analysis was further conducted using energy dispersive spectroscopy (EDS) attached to the transmission electron microscopy (TEM). Focused Ion Beam (FEI Strata 400S DUALBEAM FIB) was used for the sample preparation of LSCF73/10Sc1CeSZ for the TEM elemental analysis.

3. Results and Discussion

3.1. Interfacial stability

Single phase LSCF was screen-printed on a 10Sc1CeSZ disk and processed in oxidizing (air, $PO_2 \sim 0.21$ atm) and reducing atmosphere ($Ar-3\%H_2-3\%H_2O$, $PO_2 \sim 10^{-10}$ atm) at $1400^\circ C$. Fig. 1 shows the SEM micrographs of LSCF screen printed on 10Sc1CeSZ disk and sintered in air (Fig. 1a) and $Ar-3\%H_2-3\%H_2O$ (Fig. 1b). No third phase formation is identified in the bulk or LSCF/10Sc1CeSZ interface when processed in oxidizing atmosphere. However, a uniform and dense layer with a thickness of $\sim 1.7\mu m$ is found at the interface between LSCF and 10Sc1CeSZ indicating to an interaction between LSCF and 10Sc1CeSZ in a reducing atmosphere. SEM-EDS spot analysis indicates that the interfacial layer is enriched in Sr and Zr in the ratio of approximately 1:1 indicating the formation of $SrZrO_3$. Elemental mapping (Fig. 2) and line profile (Fig. 3) showed Sr and Zr enrichment at the interface of LSCF and 10Sc1CeSZ in $Ar-3\%H_2-3\%H_2O$ atmosphere, but not in air. A line profile of LSCF/10Sc1CeSZ system shows two zones (LSCF and 10Sc1CeSZ) when exposed to air as shown in Fig. 3a. However, three zones (LSCF, $SrZrO_3$ and 10Sc1CeSZ) are identified in samples processed in a reducing gas

atmosphere (Fig. 3b). Interaction of LSCF and 10Sc1CeSZ results in to the intermediate zone of SrZrO₃ phase as shown in Fig. 3b.

The electrical conductivity of SrZrO₃ phase is $\sim 10^{-3}$ and 10^{-6} S cm⁻¹ at 1000°C in air and reducing atmosphere (10^{-16} atm) respectively [20]. This is significantly lower than the conductivity of 10ScSZ which is 0.3 S cm⁻¹ at 1000°C [21]. Due to the formation of the insulating phase at the LSCF and 10Sc1CeSZ interface, fast degradation and lower performance is expected for oxygen separation devices incorporating LSCF/10Sc1CeSZ system. The third phase would act as a barrier to the ion conduction and greatly increase the overall cell resistance, causing low performance and durability. The thermal expansion coefficient of SrZrO₃ (2.6×10^{-5} K⁻¹) is lower than 10ScSZ (10.3×10^{-6} K⁻¹) [22]. This can generate stress and small cracks over time leading to failure.

3.2. Reaction mechanism for SrZrO₃ formation in reducing atmosphere:

The interaction between the perovskite and fluorite resulting in the formation of La₂Zr₂O₇ and/or SrZrO₃ is well documented in the literature for lanthanum strontium manganite (LSM)/YSZ system [23-24]. The reported mechanism suggests that interaction between perovskite and fluorite phases proceeds by the unidirectional diffusion of manganese into YSZ.

At lower PO₂, the solubility of Mn with lower valence state and larger ionic radii is higher than Mn with higher valence state [25-26]. After Mn diffuses from the B-site into YSZ, LSM perovskite gets enriched on the A-site resulting into La/Sr interaction with Zr at the interface of LSM/8YSZ and the formation of La₂Zr₂O₇ and/or SrZrO₃ [23-24]. Similar results have been reported for the case of LSCM/8YSZ and LSCM/10ScSZ [27]. Strontium zirconate formation is identified at the interface of LSCM and 8YSZ/10ScSZ at lower PO₂ due to the Mn⁴⁺→Mn³⁺→Mn²⁺ reduction and higher solubility of reduced Mn with larger radii.

An identical mechanism for SrZrO₃ formation is proposed for LSCF/10Sc1CeSZ composite systems where presence and migration of iron in LSCF is considered to play a significant role in the formation of SrZrO₃ in reducing atmosphere. Iron tends to reduce its valence state from Fe⁴⁺→Fe³⁺ (Eq. (1)) and Fe³⁺→Fe²⁺ (Eq. (2)) in reducing atmospheres and the charge is balanced by oxygen vacancies as shown below:

where Fe_{Fe}[×] refers to Fe³⁺ on Fe³⁺ sites, Fe_{Fe}[•] refers to Fe⁴⁺ on Fe³⁺ sites, Fe_{Fe}' refers to Fe²⁺ on Fe³⁺ sites, and V_O^{••} refers to oxygen vacancy with two positive charges.

Ionic radii variation occur with change in the valence state of Fe [2, 27]. Based on the LSM/8YSZ, LSCM/8YSZ and LSCM/10ScSZ literature report on diffusion and higher solubility of Mn (transition metal) into fluorite phase with lower oxidation state [25-27], it is hypothesized that Fe (transition metal) diffusion into 10Sc1CeSZ is higher in reducing atmosphere with lower PO₂ on comparison with oxidizing atmosphere with higher PO₂. This is attributed to higher solubility of Fe into the zirconate with lower oxidation state and larger ionic radii when compared to Fe with higher oxidation state. The chemical diffusion coefficient of Fe in 8YSZ is ~10⁻¹¹ cm²/sec at 1000°C [28]. To confirm the Fe diffusion into the 10Sc1CeSZ phase in reducing atmosphere, TEM-EDS spot analysis was conducted on the focused ion beam cross-sectioned LSCF/10Sc1CeSZ system after exposure to reducing atmosphere at 1400°C. 5-7 at. % of Fe is identified in 10Sc1CeSZ corresponding to Fe diffusion from the perovskite phase to fluorite phase in reducing atmosphere. Likewise for the LSM/8YSZ and LSCM/8YSZ system, Fe

diffuses into 10Sc1CeSZ and the perovskite lattice is then enriched on the A-site and therefore, Sr from the A-site reacts with Zr in 10Sc1CeSZ resulting in the formation of SrZrO₃ (SZO). Fig. 4 shows a schematic of mechanistic steps for SrZrO₃ formation in reducing atmosphere. Step 1 shows an initial stage of LSCF/10Sc1CeSZ system heating to reaction temperature. Diffusion assisted changes occur in step 2. Fe reduction occurs ($\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) and therefore, Fe diffuses from the LSCF lattice into 10Sc1CeSZ due to the higher solubility of reduced Fe into the fluorite phase. In step 3, LSCF perovskite lattice is A-site enriched after the Fe-diffusion. Subsequently, in step 4, Sr from the A-site reacts with Zr to form SrZrO₃ at the interface of LSCF/10Sc1CeSZ.

4. Conclusion

Interfacial stability of (La_{0.8}Sr_{0.2})_{0.95}Cr_{0.7}Fe_{0.3}O₃ (LSCF)/10Sc1CeSZ system has been studied under OTM processing (1400°C and PO₂ ~ 0.21 – 10⁻¹⁰ atm) conditions. SrZrO₃ formation is identified in the samples processed at lower PO₂. When processed in oxidizing atmosphere, interface layer formation of SrZrO₃ is not observed in the LSCF/10Sc1CeSZ system. TEM elemental analysis exhibits 5-7 at. % of Fe in the 10Sc1CeSZ phase attributed to Fe diffusion from perovskite (LSCF) to fluorite (10Sc1CeSZ) lattice. Mechanism for the formation of SrZrO₃ is proposed for iron doped lanthanum strontium chromite and scandia stabilized zirconia system in reducing atmosphere.

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Figure Captions

Fig. 1. SEM micrograph of LSCF screen printed on 10Sc1CeSZ and processed in: (a) air and (b) Ar-3% H₂-3% H₂O.

Fig. 2. SEM-EDS elemental mappings of LSCF screen printed on 10Sc1CeSZ and processed in air and Ar-3% H₂-3% H₂O: (a, c) secondary electron image and (b, d) elemental mapping.

Fig. 2. SEM-EDS elemental line profiles of LSCF screen printed on 10Sc1CeSZ and processed in: (a) air and (b) Ar-3% H₂-3% H₂O.

Fig. 4. Schematic of reaction steps for the formation of SrZrO₃ in reducing atmosphere.

Figure 1

Figure 2

Figure 3

Figure 4