



Nickel and titanium doubly doped lanthanum strontium chromite for high temperature electrochemical devices



Sapna Gupta ^{a, b}, Prabhakar Singh ^{b, c, *}

^a Intel Corporation, Hillsboro, OR 97124, USA

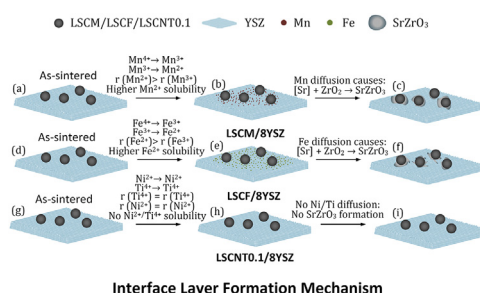
^b Materials Science and Engineering and Center for Clean Energy Engineering, University of Connecticut, Storrs, CT 06268, USA

^c Fraunhofer Center for Energy Innovation, University of Connecticut, Storrs, CT 06268, USA

HIGHLIGHTS

- Highest electrical conductivity observed for Ni and Ti co-doped LSCNT0.1.
- LSCNT0.1 stability maintained in oxidizing and reducing atmospheres.
- Highest electrochemical performance obtained for co-doped LSCNT0.1.
- SrZrO₃ interface layer formation identified in case of LSCF and LSCM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 October 2015

Received in revised form

29 November 2015

Accepted 30 November 2015

Available online 30 December 2015

Keywords:

Oxygen transport membrane

Solid-oxide fuel cell

Lanthanum chromite based materials

Electrical conductivity

Thermal expansion

Electrochemical performance

ABSTRACT

Lanthanum chromite based materials are promising candidate for use as electrochemical components in high temperature electrochemical devices. In this study, nickel and titanium doubly doped lanthanum strontium chromites are developed and the effects of nickel and titanium co-doping of the chromite perovskite $La_{0.85}Sr_{0.15}Cr_{1-2y}Ni_yTi_yO_{3-\delta}$ ($0.05 \leq y \leq 0.3$) on the electrical conductivity, chemical stability, microstructure, density, thermal expansion and electrochemical performance are measured. Density and the electrical conductivity increases with nickel concentration whereas Sr-segregation on the surface of $La_{0.85}Sr_{0.15}Cr_{1-2y}Ni_yTi_yO_{3-\delta}$ has been observed for $y \geq 0.2$ and is associated with reduction in the electrical conductivity. For $y = 0.1$, $La_{0.85}Sr_{0.15}Cr_{1-2y}Ni_yTi_yO_{3-\delta}$ shows the highest electrical conductivity in air and reducing atmosphere ($PO_2 \sim 10^{-24}$ atm). The conductivity of $La_{0.85}Sr_{0.15}Cr_{1-2y}Ni_yTi_yO_{3-\delta}$ ($y = 0.1$) in reducing atmosphere (3.58 S cm^{-1} at 950°C) also remains higher than the most widely investigated compositions such as $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (2.81 S cm^{-1}) and $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ (1.41 S cm^{-1}). Smaller deviation in the oxygen stoichiometry is similarly observed for $La_{0.85}Sr_{0.15}Cr_{0.8}Ni_{0.1}Ti_{0.1}O_{3-\delta}$ ($\delta = 0.011$) when compared to $La_{0.75}Sr_{0.25}CrO_{3-\delta}$ ($\delta = 0.091$), $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ ($\delta = 0.175$) and $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ ($\delta = 0.148$) at 1000°C and $\sim 10^{-24}$ atm. Highest electrochemical performance and structural/interfacial stability is obtained for new composition $La_{0.85}Sr_{0.15}Cr_{0.8}Ni_{0.1}Ti_{0.1}O_{3-\delta}$ (LSCNT0.1) when mixed with 8YSZ in both oxidizing and reducing atmosphere.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

High temperature ($\geq 650^\circ\text{C}$) solid-state electrochemical

* Corresponding author. University of Connecticut, Storrs, CT 06268, USA.

E-mail address: singh@engr.uconn.edu (P. Singh).

systems such as oxygen transport membrane (OTM), solid-oxide fuel cells (SOFC) and solid oxide electrolysis cells (SOEC) are a select few technologies for power generation and clean combustion which can be adapted in near term to enhance the chemical to electrical energy conversion efficiency, reduce carbon foot print and extend the fuel reserve for future energy security and environmental sustainability [1,2]. Although progress in the OTM, SOFC and SOEC technologies along with technical challenges have been reported [1–5], development of stable materials along with performance improvement remains topic of research interest [6–8].

Chemical/structural/redox stability and high electrical conductivity/performance have been identified as key requirements for OTM, SOEC and SOFC electrode/interconnect [1–3]. To improve the surface exchange kinetics and performance of oxygen transport membrane, porous air (cathode) and fuel (anode) electrodes are also utilized in the OTM system [9]. Perovskites and/or perovskite-fluorite composites are currently being developed for OTM system [8–16]. However, thermal-chemical-structural stability, high thermal expansion coefficient, lower conductivity and electrochemical performance are few challenges with the current existing materials, specifically in reducing atmosphere [8–16]. For instance, lanthanum cobaltite ($\text{LaCoO}_{3-\delta}$) obtain high thermal expansion coefficient ($20 \times 10^{-6} \text{ K}^{-1}$) and decomposes into La_2CoO_4 and CoO at 1000°C and oxygen partial pressure of $<10^{-7}$ atm [8]. Similarly, lanthanum ferrite ($\text{LaFeO}_{3-\delta}$) provides high thermal expansion coefficient ($23.8 \times 10^{-6} \text{ K}^{-1}$) for $T > 600^\circ\text{C}$ and decomposes into La_2O_3 and Fe metal at 1000°C and in reducing atmosphere ($<10^{-17}$ atm) [8].

LSM-YSZ is the state of the art material for SOFC cathode and SOEC anode [17–20]. However, LSM-YSZ tends to degrade with time under SOFC/SOEC operating conditions. Furthermore, delamination of the LSM based electrodes has been identified after testing [17–19]. Cation migration, interfacial reaction and porosity formation at the interface of LSM and 8YSZ phase are some of the major challenges with the current state of the art material [17,18]. Insulating interfacial reaction compounds such as lanthanum and/or strontium zirconate formation results in lower cell performance [17–19]. On the other hand, Ni-YSZ is conventionally used as the SOFC anode and SOEC cathode due to its high electro-catalytic activity, electronic and ionic conductivity. However, carbon deposition, stability, Ni-particles agglomeration, volume change during redox cycling and susceptibility to sulfur poisoning are the limitations of Ni-YSZ [6,7].

To overcome the limitations of the above mentioned materials namely $\text{LaCoO}_{3-\delta}$, $\text{LaFeO}_{3-\delta}$, LSM-YSZ and Ni-YSZ and others, lanthanum chromite-based perovskites have been considered as a promising candidate for OTM/SOFC/SOEC electrode [21,22], interconnect [23] and oxygen transport membrane [5,8]. Lanthanum chromite based materials have also been proposed for use as electrode materials in magnetohydrodynamic (MHD) power generators, oxygen sensors and heating element in high temperature furnaces [24,25]. The potential of lanthanum chromite based materials for the application of high temperature electrochemical devices is also demonstrated in detail in the recently published review article by Gupta et al [8]. This is mainly due to its high thermo-chemical stability at high temperature ($>1000^\circ\text{C}$) in a wide range of oxygen partial pressure ($0.21\text{--}10^{-22}$ atm) [26]. For instance, $(\text{La,Sr})(\text{Cr,Mn})\text{O}_{3-\delta}$ (LSCM) and $(\text{La,Sr})(\text{Cr,Fe})\text{O}_{3-\delta}$ (LSCF) have been extensively investigated for OTM and air/fuel side electrode as it provides the combination of high electrochemical activity, good chemical compatibility with adjacent materials and structural stability [7,27–33]. However, the properties (conductivity, thermal expansion coefficient and stability) of these materials degrade specifically in reducing atmosphere. This is considered to be due to change in the valence state or disproportional existence of

transition metal ($M = \text{Mn/Fe}$) into $M^{2+}/M^{3+}/M^{4+}$ at B-site, and charge compensation via oxygen vacancy formation. These materials also destabilize in reducing atmosphere. For example, $(\text{La,Sr})_2\text{MnO}_4$ and MnO secondary phases in $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ and $(\text{La,Sr})_2\text{FeO}_4$ in $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ have been detected at 900°C and $\sim 10^{-20}$ atm [34].

This study focuses on the development of new improved lanthanum chromite based material that can be utilized for various applications ranging from oxygen transport membrane system (as electrolyte and/or electrode) for oxy-combustion or syngas production to solid-oxide fuel/electrolysis cells (as interconnect and/or electrode) for clean and efficient power generation. Based on literature review [8], among the transition metal dopants, Ti enhances the stability of lanthanum chromite based materials due to smaller change in its valence state and/or deviation from oxygen stoichiometry in reducing atmosphere [34–36]. Ni doping increases the electrical conductivity because of increase in Cr^{4+} ions to maintain charge neutrality [37,38]. It also increases the density of lanthanum chromite, a requirement for OTM and SOFC interconnect application [38,39]. The importance of Ni and Ti co-doping at the B-site of lanthanum strontium chromite is also listed in our recently published review article [8]. To exploit the advantages of Ni and Ti doping, we have developed Ni and Ti doubly doped lanthanum strontium chromite and investigated the role of simultaneous Ni and Ti doping on the electrical, structural, thermal and electrochemical properties of $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{1-2y}\text{Ni}_y\text{Ti}_y\text{O}_{3-\delta}$ ($y = 0.05, 0.1, 0.2$ and 0.3) in oxidizing and reducing atmosphere. The results are compared with the most investigated lanthanum chromite based compositions i.e. LSCM and LSCF. To the author's knowledge, for the first time, interfacial reaction compound layer is identified for Mn and Fe doped lanthanum strontium chromites (when in contact with 8YSZ) in contrast with the new composition (LSCNT0.1) using transmission electron microscopy.

2. Experimental

2.1. Material synthesis

$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ (LSCT0.1), $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.05}\text{Ti}_{0.05}\text{O}_{3-\delta}$ (LSCNT0.05), $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.8}\text{Ni}_{0.1}\text{Ti}_{0.1}\text{O}_{3-\delta}$ (LSCNT0.1), $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.6}\text{Ni}_{0.2}\text{Ti}_{0.2}\text{O}_{3-\delta}$ (LSCNT0.2), and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.4}\text{Ni}_{0.3}\text{Ti}_{0.3}\text{O}_{3-\delta}$ (LSCNT0.3) were synthesized by solid state reaction technique using lanthanum oxide (La_2O_3 , 99.95%, Alfa Aesar, USA), chromium oxide (Cr_2O_3 , 99.9%, Sigma-Aldrich, USA), strontium oxide (SrO , 99.5%, Alfa Aesar, USA), titanium oxide (TiO_2 , 99.99%, Sigma-Aldrich, USA) and/or nickel oxide (NiO , 99.99%, Sigma-Aldrich, USA) powders. La_2O_3 , Cr_2O_3 , SrO , TiO_2 and/or NiO powders were mixed using wet-ball milling in ethanol for 48 h followed by drying in air. The mixed powders were uniaxially pressed into cylindrical pellets. The pellets were sintered at 1450°C for 24 h with a heating and cooling rate of $3^\circ\text{C}/\text{min}$.

2.2. Characterization

X-ray diffraction (BRUKER-D8 ADVANCE, Bruker AXS Inc. Madison, WI) technique was used to confirm the formation of single compound and to determine the crystal structure of $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{1-2y}\text{Ni}_y\text{Ti}_y\text{O}_{3-\delta}$ (LSCNTy) ($0.05 \leq y \leq 0.3$). The scan step was 0.02° using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

Density of all the sintered samples LSCT0.1 and LSCNTy ($0.05 \leq y \leq 0.3$) were 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

Download English Version:

<https://daneshyari.com/en/article/1292349>

Download Persian Version:

<https://daneshyari.com/article/1292349>

[Daneshyari.com](https://daneshyari.com)