

Investigation of aliovalent transition metal doped $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{X}_{0.2}\text{O}_{3-\delta}$ ($\text{X} = \text{Ti}, \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni}$) as electrode materials for symmetric solid oxide fuel cells

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Abstract

The crystal phase, chemical stability, thermal expansion behavior, oxygen non-stoichiometry, electrical conductivity, and electro-catalytic activity of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{X}_{0.2}\text{O}_{3-\delta}$ ($\text{X} = \text{Ti}, \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni}$) electrode materials have been investigated. All the compositions are chemically stable with a single-phase perovskite structure in both reducing and oxidizing atmospheres at high temperature. The linear thermal expansion coefficients of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{X}_{0.2}\text{O}_{3-\delta}$ are approximately $10 \times 10^{-6} \text{ K}^{-1}$. The total electrical conductivity of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{X}_{0.2}\text{O}_{3-\delta}$ increases in the order of $\text{X} = \text{Ti} < \text{Ni} < \text{Fe} < \text{Co} < \text{Mn}$, which is correlated to the porosity, valence orbital ionization potential, and oxygen non-stoichiometry upon the reduction process. The overall reaction process of the hydrogen oxidation for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{X}_{0.2}\text{O}_{3-\delta}$ anodes is limited by the charge transfer process that requires higher activation energy. In a similar trend observed in electrical conductivity, $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ exhibits the lowest polarization resistance value of $0.12 \Omega \text{ cm}^2$ at 800°C . Finally, the symmetric single cell with $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ as both the cathode and anode shows a maximum powder density of 220 mW cm^{-2} at 800°C .

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1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that can oxidize chemical fuel to directly produce electricity. Because of the fuel flexibility, high efficiency, and low emission, SOFCs are regarded as one of the most attractive solutions for future environmental-friendly power generation [1–3]. The state-of-the-art electrode material for SOFCs is Ni-yttria stabilized zirconia (YSZ) cermet and (La,Sr)MnO₃-based perovskite for the anode and cathode, respectively. Although a low cost Ni-based cermet anode exhibits excellent electro-catalytic activity for H₂ oxidation and good compatibility with a YSZ electrolyte, it suffers severe limitations such as abnormal grain growth due to Ni sintering, carbon deposition

under hydrocarbon fuel leading to deactivation of the anode and consequent cell performance loss. Moreover, sulphur even at concentration levels of parts per million (ppm) is readily adsorbed on the Ni surface and thus blocks active sites for the oxidation of fuel, resulting in considerably increased anodic polarization resistance [3]. In this regard, several approaches have been proposed to address these drawbacks and find suitable alternative materials [3].

Symmetric SOFCs have great advantages over conventional SOFCs. The reduced number of cell components could facilitate the assembly of a fuel cell in a single thermal treatment and minimize thermal and chemical compatibility requirements. However, the requirements of electrode materials for symmetric SOFCs are rather stringent because they should simultaneously satisfy all conditions applicable to both anodes and cathodes: (i) high catalytic activity for reduction of oxygen and oxidation of fuel; (ii) chemical stability under both

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reducing and oxidizing atmospheres; (iii) compatible linear thermal expansion with other fuel cell components; and (iv) high enough electronic and oxygen ionic conductivity in both reducing and oxidizing atmospheres. It is a challenging task to investigate materials that meet all requirements simultaneously [4–7]. The electrochemical performances of symmetric SOFCs are somewhat lower than traditional SOFCs due to the extreme difficulty in finding a perfect material that fulfils all requirements [8–13].

Numerous interests have focused on perovskite-based materials (ABO_3) because of their stability over a wide range of oxygen partial pressures (pO_2). [14,15]. Moreover, the perovskite structure can incorporate aliovalent cations with multiple oxidation states that facilitate electro-catalytic processes and provide mechanisms for electronic conductivity [14,16,17]. In general, perovskite oxides satisfy most of the requirements for the symmetric electrode. Among the various perovskite-based electro-ceramics, doped $LaBO_3$ ($B=Cr, Mn, Co$) shows exceptionally good redox-stability and high electrical conductivity in both reducing and oxidized atmospheres [18–20]. For example, Ca-doped $LaCrO_3$ exhibits a high electrical conductivity of 35.1 and 1.12 S cm^{-1} in air and a reducing atmosphere, respectively, and shows significantly high electrochemical performance for oxidation of hydrogen [21,22].

Metcalf et al. also reported that the complete oxidation of methane by $La_{0.8}Ca_{0.2}CrO_{3-\delta}$ occurs in the intermediate temperature range [23]. Moreover, the thermal expansion coefficient (α_L) of doped $LaCrO_3$ is also compatible with the state-of-the-art electrolyte materials under the cell operating condition. Nevertheless, the catalytic activity of the doped lanthanum chromite-based anode is still very low compared to Ni/YSZ cermet. Therefore, it is useful to modify the (La,Ca) $CrO_{3-\delta}$ system by suitable substitution or doping at the B-site to increase the electrical conductivity and the electro-catalytic activity. This information would be needed to study the effect of doping on the thermal stability, chemical stability, redox stability, electrochemical activity and electrical transport behavior of the transition metal doped (La,Ca) $CrO_{3-\delta}$ system. Very little research has been reported on this kind of perovskite. A systematic investigation of aliovalent-doped lanthanum calcium chromate materials as a symmetric electrode (anode and cathode) material for SOFCs is scarcely available in literature. With this perspective, we present the characterization of $La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ ($X=Ti, Mn, Fe, Co,$ and Ni) as an electrode material for symmetric SOFCs and the effect of aliovalent ion doping on the electrical transport, catalytic activity, and electrochemical performance.

2. Experimental

2.1. Powder synthesis

$La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ ($X=Ti, Mn, Fe, Co,$ and Ni) powders were synthesized by a modified sol–gel combustion method using sucrose and pectin as a fuel and catalyst for combustion, respectively. The raw materials used for the synthesis are La

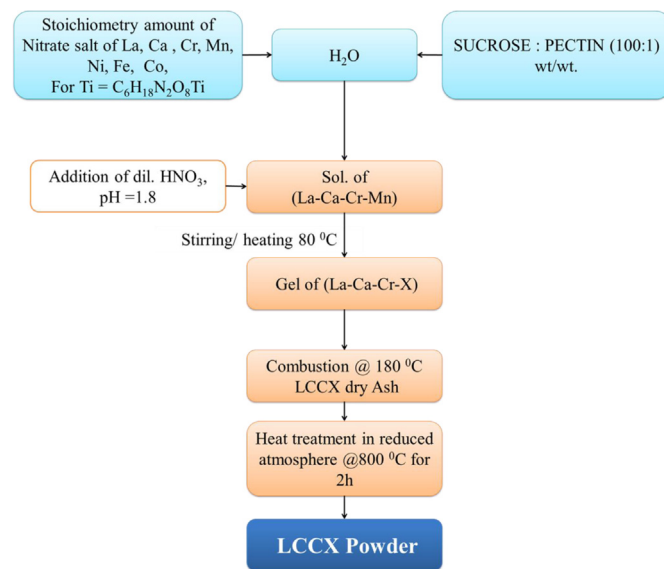


Fig. 1. Flow chart for the synthesis of $La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ ($X=Ti, Mn, Fe, Co,$ and Ni) powders using a modified sol–gel combustion technique.

(NO_3) $_3 \cdot 5H_2O$ (Aldrich, 99.9% metal basis), $Ca(NO_3)_2 \cdot 4H_2O$ (Merck, ACS), $Cr(NO_3)_3$ (Alfa Aesar, 99.0%), $Mn(NO_3)_2 \cdot 4H_2O$ (Alfa Aesar, 98%), $(CH_3CH(O-)NH_4)_2 Ti(OH)_2$ (50%w/w aq. soln, Alfa Aesar), $Fe(NO_3)_3 \cdot 9H_2O$ (Alfa Aesar, 98%, ACS), $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, 98%), $CO(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, 98%, ACS), sucrose (Alfa Aesar, 99%), and pectin (Aldrich). The flowchart for the modified sol–gel combustion method is described in Fig. 1. The synthesized $La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ compositions are named LCCT, LCCM, LCCF, LCCC and LCCN for $X=Ti, Mn, Fe, Co,$ and Ni, respectively.

2.2. Materials characterization

Phase analysis of the as-synthesized $La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ ($X=Ti, Mn, Fe, Co,$ and Ni) powders was performed by X-ray diffraction (XRD) using $Cu-K\alpha$ radiation. The morphology and microstructure were observed by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX, SN-3000 Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed by AXIS-NOVA (Kratos Inc.) using $Al K\alpha$ (1486.6 eV) monochromatic X-ray sources at 120 W. Thermo-gravimetric analysis (TGA) was performed to evaluate the oxygen non-stoichiometry in the $La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ ($X=Ti, Mn, Fe, Co,$ and Ni) compositions. The $La_{0.7}Ca_{0.3}Cr_{0.8}X_{0.2}O_{3-\delta}$ ($X=Ti, Mn, Fe, Co,$ and Ni) powders were first placed in a clean alumina crucible and reduced at 800 °C for 6 h under flowing H_2 at a rate of $100 \text{ cm}^3 \text{ min}^{-1}$. Then, the reduced powders were analyzed by TGA (TA Q600, TA instruments, USA) under constant air flow in the temperature range of 30–1000 °C at a heating rate of $2 \text{ }^\circ\text{C min}^{-1}$. The change of weight during the oxidation process was then analyzed. The linear thermal expansion coefficients (TECs) of the sintered samples were measured by thermo-mechanical analysis (TMA) using a thermo-mechanical analyzer (TA Q400, TA instruments, USA) from room temperature

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