



Property optimization for strontium-rich lanthanum chromium ferrite cathodes: A demonstration of lanthanide replacement effect

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ABSTRACT

The structure, electrical conducting, thermal expansion and electrocatalytic properties of $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$) perovskites were investigated to evaluate their potential for cathodes of intermediate temperature solid oxide fuel cells (IT-SOFCs). Reducing the size of the lanthanide cations enhanced the deformation of the perovskite structures and decreased the dimension of the primitive unit cells. Meanwhile, the oxygen nonstoichiometry (δ) values at elevated temperatures slightly increased. The electrical conductivity degraded with smaller lanthanide cation sizes, while the thermal expansion coefficients (TECs) tended to decrease. These property changes were diagnosed with respect to the corresponding structural evolutions. $\text{Sm}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ was identified to be the optimal composition after an overall property assessment. This composition exhibited an average TEC ($\sim 14 \times 10^{-6} \text{ K}^{-1}$ between 40 and 1000 °C) compatible with IT-SOFC electrolytes, eligible electrical conductivity and good electrocatalytic activity. The good overall properties of $\text{Sm}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ demonstrate that this composition is a promising cathode material for IT-SOFCs.

1. Introduction

Mixed ionic-electronic conducting (MIEC) materials have found applications in diverse technical aspects, such as cathodes for intermediate temperature solid oxide fuel cells (IT-SOFCs), oxygen separation membranes, membrane reactors for syngas production and catalysts for oxidation of hydrocarbons [1–3]. SOFCs are electrochemical devices that can convert chemical energy stored in fuels into electrical power with high efficiency and nearly negligible pollution emission [4]. Cobalt-containing perovskite-type (ABO_3) complex oxides, represented by $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ [5–8], $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ [9] and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [10], have been the typical MIEC cathodes for IT-SOFCs since the late 1980 s. These cobalt-containing perovskite cathodes exhibit high electrocatalytic activity towards oxygen reduction reaction (ORR) at intermediate temperatures (600–800 °C) or even lower temperatures. Unfortunately, they suffer from extraordinarily large thermal expansion coefficients (TECs) and unsatisfactory structure stability under the practical working conditions of SOFC cathodes, unfavorable to the long-term duration of the SOFC devices with these cathodes [11–13].

It has been established that the high mixed conductivity and electrocatalytic activity of cobalt-containing perovskite cathodes are

essentially associated with the labile oxidation states of the cobalt at the B-site [6–8]. On the other hand, it has also been recognized that the B-site cobalt is the culprit for the TEC and structure stability problems of these cathodes [12,13]. The last decade has witnessed growing interest to seek for cobalt-free MIEC cathodes with improved overall properties [12–17]. Among various efforts to realize this purpose, an explicit and often-used strategy is to replace the cobalt in cobalt-containing perovskite cathodes with other transition metals with higher redox stability (e.g. copper or zinc) [13–17].

Recent work has shown that $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ ($y = 0.1\text{--}0.3$) perovskites possess promising structural stability and desired property combination [18], igniting a new inspiration for composition engineering of cobalt-free MIEC cathodes. These strontium-rich chromium ferrites can maintain structural stability over a wide range of oxygen partial pressure ($0.21\text{--}1.9 \times 10^{-19}$ atm). The heavy strontium substitution at the A-site ensures high mixed conductivity, while the chromium present at the B-site serves to stabilize the perovskite structures and prevent formation of oxygen vacancy ordering in the lattice. Additionally, more recent research has demonstrated that, interestingly, the B-site chromium is beneficial to the electrocatalytic activity of these chromium ferrites towards the ORR occurring on their surface [19]. Incorporating robust structural stability, high mixed

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conductivity and good cathodic catalytic activity, these $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ perovskites are attractive for utilization as cathodes in IT-SOFCs.

Regrettably, the large TECs ($16\text{--}19 \times 10^{-6} \text{ K}^{-1}$ between $50\text{--}900^\circ\text{C}$) of these $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ perovskites appear as an imperfection in their properties [18], dissatisfying the demand for thermodynamic compatibility with the other SOFC components (e.g. the electrolyte). From a structural viewpoint, the framework of perovskite cathodes is constituted by the BO_6 octahedrons connected via corner-sharing mode. For this reason, the structure and properties of perovskite cathodes are dominated by the B-site cations. On the other side, the A-site cations surrounding the BO_6 octahedrons are also contributive to the structure and thus the properties. It has been discovered that the TECs of cobalt-containing perovskite cathodes tended to decrease with reducing the average size of the A-site cations [7,20–22]. Our recent attempts have indicated that replacing the strontium cation in the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ perovskites with smaller calcium cation optimized the overall properties, with the derivative $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ ($y = 0.2$ and 0.3) perovskites achieving suitable TECs ($\sim 12 \times 10^{-6} \text{ K}^{-1}$ between $40\text{--}1000^\circ\text{C}$) while showing acceptable electrical conductivity and good cathodic catalytic activity [23,24]. Considering the complex A-site composition of the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ perovskites, it is expected that replacing the lanthanum cation with a smaller lanthanide cation should generate a similar effect. Verification of this expectation would strengthen the understanding on the effect of A-site dimension modulation and in turn offer an alternative strategy to tune the properties of these chromium ferrite perovskites.

$\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ has been identified as the optimal composition of the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$ series based on a trade-off between various properties [18]. In this work, we investigated the structure, electrical conducting and thermal expansion properties of $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Sm}$) perovskites in relation with the size of the lanthanide cations at the A-site. The structure-property relationship was diagnosed. The electrocatalytic properties of the $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ perovskites were also examined. Based on the outcomes of these investigations, we appraised the effect of the lanthanide replacement on the resulting property changes in view of the criteria for IT-SOFC cathodes.

2. Experimental

2.1. Synthesis and preparation procedures

$\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Sm}$) powders were synthesized by a poly-aminocarboxylate complex precursor method. The nominal compositions of these specimens are hereafter abbreviated as LSCr, PSFCr, NSFCr and SSFCr, respectively. Reagent grade ($> 99.5\%$) $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and diethylenetriaminepentaacetic acid (H_5DTPA) were used as the starting materials. The nitrates were weighed according to the nominal compositions of the specimens and dissolved into deionized water, followed by adding an appropriate amount of H_5DTPA . The mole ratio of H_5DTPA to the total metal cation content was 1.1:2.0. The resulting mixture was stirred at 90°C to form a transparent aqueous solution. The aqueous solution was heated at 100°C to produce a solid poly-aminocarboxylate complex. The solid complex precursor was pulverized and calcined at 1200°C for 2 h in air. X-ray diffraction (XRD) analysis certified that each of the calcined powders had a single-phase perovskite structure. Scanning electron microscopy (SEM) observation indicated that the particle morphology of the calcined powders was uniform and fine ($\sim 200 \text{ nm}$). These results are presented in the Supplement file (Section 1).

To investigate the electrical conducting and thermal expansion properties of the $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, the ceramic specimens of these perovskites were prepared by conventional sintering technique.

The calcined powders were compacted into rectangular bars ($30 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$) and then sintered in air at 1350°C for 4 h. This sintering temperature was determined after inspecting the dilatometric behavior of the compacted bars. The dilatometric curves of these specimens are presented in the Supplement file (Section 2).

To survey the electrocatalytic properties of the $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, three-electrode half cells with these perovskites as the working electrodes were fabricated. $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) ceramic discs were used as the electrolyte substrates. The SDC ceramic discs were prepared from the powder synthesized by a urea-combustion method and sintered in air at 1350°C for 2 h [25]. The relative density of the SDC ceramics discs exceeded 96%. The $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ electrodes were screen-printed onto the dense SDC substrates and sintered in air at 900°C for 1 h. Platinum was used as the counter and reference electrodes, respectively. The fabrication procedures, configurations and geometrical parameters of the half cells were almost the same as those described in our earlier publication [26], except for different working electrodes. The thickness of the SDC substrates was 1 mm. For each half cell, the working and reference electrodes were located on the same side of the electrolyte substrate. The areas of the working and reference electrodes were 28.3 and 7.0 mm^2 , respectively, and the distance between these two electrodes was more than five times larger than the electrolyte thickness.

2.2. Structure analyses

The microstructure of the ceramic specimens and half cells was observed using a JEOL JSM-5610LV scanning electron microscope. The observed ceramic specimens was polished and thermally etched before the SEM analysis. The crystal structure of the ceramic specimens was investigated using a Philips X'pert PRO X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation and a graphite monochromator. XRD data were recorded with a step of 0.017° and a counting time of 2 s. The recorded XRD data were analyzed using the MDI Jade 6.0 software. The values of the R factor (residual error of fit) were less than 4.8% for the results achieved from the XRD analysis.

The oxygen nonstoichiometry (δ) values of the $\text{Ln}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ perovskites were tested by thermogravimetric analysis (TGA) [18] and the iodometric titration method [19,27], respectively. The TGA test was performed in air between 30 and 900°C using a Netzsch STA 449C thermal analyzer. Weight change data were recorded as a function of temperature upon cooling at a rate of 2°C min^{-1} . The δ values at different temperatures were derived from the recorded data. For the iodometric titration test, to probe the information at elevated temperatures, the specimens to be tested were equilibrated in air at pre-set temperatures for 8 h and then quenched in liquid nitrogen.

2.3. Property investigation

The bulk density of the ceramic specimens was measured by the Archimedes method with ethanol as the medium. The relative densities of the specimens were calculated from the bulk densities and theoretical densities determined by the XRD analysis. The electrical conductivity was measured in air by the direct-current (dc) four-terminal method. The measurement was performed using a home-made setup in the temperature range from 150 to 900°C . The thermal expansion data were recorded in air using a Netzsch DIL 402C dilatometer upon heating at a rate of $10^\circ\text{C min}^{-1}$ between 40 and 1000°C . The recorded data were calibrated with an alumina bar as the standard.

The electrochemical impedance spectroscopy (EIS) of the half cells was investigated in air using a CHI 660C electrochemical workstation under open-circuit voltage (OCV) conditions. The amplitude of input testing signals was 15 mV and the frequencies ranged from 10^{-2} to 10^5 Hz . To resolve the distribution of relaxation time (DRT) for involved impedance response processes, the measured data were

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