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Nonstoichiometric $(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ electrolytes and $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$ – $(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ composite electrolytes for solid oxide fuel cells

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ABSTRACT

A-site nonstoichiometric electrolytes $(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ (LSGM, $x = 0.97, 1.00, 1.03$), and their composites $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$ (NDC)–LSGM, were synthesized and investigated. The nonstoichiometry efficiently enhanced the total conductivity of LSGM electrolyte, and the A-site deficient composition showed the highest total conductivity above 550 °C ($\sigma_{t,\text{LSGM}(x=0.97)} = 0.880 \text{ S m}^{-1} > \sigma_{t,\text{LSGM}(x=1.03)} = 0.808 \text{ S m}^{-1} > \sigma_{t,\text{LSGM}(x=1.00)} = 0.582 \text{ S m}^{-1}$ at 600 °C). The cubic fluorite and perovskite structures were adopted by all the composites. The LSGM additive significantly promoted the grain growth of the composite electrolyte. The grain boundary conductivities of the composite electrolytes were more or less 5–10 times higher than that of NDC electrolyte at 500 °C. The optimum A-site nonstoichiometry was found to be $x = 0.97$ in composite electrolytes. This study provides a possible route to design high performance single phase or composite electrolytes for SOFCs.

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1. Introduction

The strontium- and magnesium-doped lanthanum gallate (LSGM) is a promising electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs) because its high ionic conductivity and negligible electronic conductivity under wide O_2 pressure range [1–6]. The general chemical formula for ideal ABO_3 perovskite oxide contains an equal number of

the larger A-site and smaller B-site cations, i.e., $n_A/n_B = 1$. In practice, the LaGaO_3 perovskite can be prepared from unequal molar equivalents of A- and B-site cations. It has been well established that the variations in the n_A/n_B ratio of LaGaO_3 can affect the defect balance and structural parameters of the host lattice, the crystal structure defects are closely related to chemical stability and electrical property [7–10]. For instance, Zhao et al. [8] reported an increased appearance of Mg-rich

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second phase with increasing Mg-excess level, and the ionic conductivity of Mg-excess-doped LSGM becomes significantly higher than that of stoichiometric LSGM owing to the re-dissolution of the Mg-rich second phase. The oxide ionic conductivity of the electrolyte is mainly attributed to various structural defects, e.g., the introduction of additional oxygen vacancies into the lattice significantly increases the oxygen ionic conductivity [9]. Ahamd-Khanlou et al. [10] also reported that the Ga substoichiometry produced more oxygen vacancies while the oxygen vacancy concentration was reduced by hyper-stoichiometry. Therefore, the possibility of enhancing the ionic conductivity of LSGM has been explored by designing nonstoichiometry. However, the effect of A-site cationic nonstoichiometry on the ionic conductivity of LSGM has not been thoroughly investigated.

Doped ceria is a well established electrolyte material due to its high ionic conductivity and good compatibility with electrode materials for the fabrication of IT-SOFC [11–13]. However, the application of di- or trivalent cation-doped ceria has been limited because the narrow electrolytic domain resulting from the partial reduction of Ce^{4+} to Ce^{3+} . The electronic conduction causes a loss of open circuit voltage (OCV) leading to a drop of power output of the cell [14,15]. One approach to enhance the ionic conductivity has been reported by designing functional composite materials based on doped ceria and different salts (usually carbonates) [16–18]. These materials exhibit significant enhanced ionic conductivity of $0.01\text{--}1\text{ S cm}^{-1}$ in the intermediate/low temperature region [19]. The high concentration of oxygen ions/defects on the doped ceria particle surface and their interactions with two-phase constituents leads to the ionically conductive pathways for proton and oxygen ions in composite materials [20]. Until now, the doped ceria-carbonate composite has been widely investigated as electrolyte. However, the mechanism of electronic conductivity in doped ceria composite electrolyte is very complicated. On the other hand, LSGM has a negligible electronic conductivity over a broad range of oxygen partial pressures and can act as a blocking agent against the leakage current [21–23]. The composite electrolyte consisting of doped ceria and LSGM has been rarely reported [24,25], and the effect of A-site nonstoichiometry of LSGM on the performance of its composite electrolytes has not been studied as well. In this study, we investigated the effect of A-site nonstoichiometry on the structures and electrical properties of the LSGM electrolytes and the NDC–LSGM composite electrolytes in details.

2. Experiment

2.1. Sample preparation

The compositions $(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ (LSGM, $x = 0.97, 1.00, 1.03$) were synthesized via a modified sol–gel method. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Ga (99.999%) were dissolved in distilled water or nitric acid to form solutions and mixed them together. Then the solid citric monohydrate and polyethylene glycol were added into the mixture under stirring at $30\text{ }^\circ\text{C}$, the molar ratio of the metal ions to citric acid was 1:1.5. The transparent solution was vaporized overnight at $70\text{--}80\text{ }^\circ\text{C}$. The

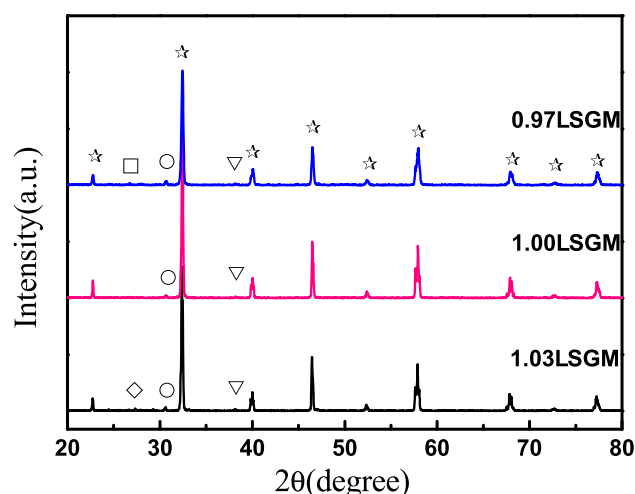


Fig. 1 – XRD patterns of sintered LSGM ($x = 0.97, 1.00, 1.03$) pellets (☆ LSGM, ◇ $\text{LaSrGa}_3\text{O}_7$, ○ MgGa_2O_4 , □ and ▽ secondary phases).

precursors were calcined at $1000\text{ }^\circ\text{C}$ for 10 h in a muffle furnace.

The preparation of $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{2-\delta}$ (NDC) precursor powder followed the same route as that of LSGM powder. $\text{Ce}(\text{N}-\text{O}_3)_3 \cdot 6\text{H}_2\text{O}$ and Nd_2O_3 ($\geq 99.9\%$) were used as the starting materials. The composite powders of $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{2-\delta}-(\text{La}_{0.95}\text{Sr}_{0.05})_x\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ ($x = 0.97, 1.00, 1.03$) were prepared with a NDC to LSGM weight ratio of 90:10 by mixing the pre-calcined LSGM powder and NDC sol. The precursor powders were calcined at $550\text{ }^\circ\text{C}$ for 10 h. Finally all the pre-calcined powders were ground in an agate mortar and then uniaxially pressed into pellets at 10 MPa. The pellets were placed on platinum foils and sintered at $1400\text{ }^\circ\text{C}$ for 10 h. In this paper, LSGM ($x = 0.97, 1.00, 1.03$) and NDC–LSGM ($x = 0.97, 1.00, 1.03$) compositions were referred to as 0.97LSGM, 1.00LSGM, 1.03LSGM, 0.97NL, 1.00NL and 1.03NL, respectively.

2.2. Characterization

The X-ray diffraction (XRD) patterns of sintered samples were recorded on a Rigaku D/MAX-2000/PC X-ray diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15406\text{ nm}$, 40 kV and 50 mA). The lattice parameters of the samples were estimated using Jade program. The microstructure was revealed by field emission scanning electron microscopy (FE-SEM, SUPPA 40, ZEISS, Germany) equipped with an energy-dispersive X-ray spectrometer (EDS, EDAX-Falcon, USA).

The ionic conductivity of the sintered pellets was measured by AC impedance spectroscopy using an impedance analyzer (PARSTAT 2273). Both sides of the pellets were coated with silver paste and fired at $700\text{ }^\circ\text{C}$ for 30 min to ensure a good bonding. The measurements were conducted in air in the temperature range from 300 to $800\text{ }^\circ\text{C}$ and in the frequency range from 0.1 Hz to 1 MHz with $50\text{ }^\circ\text{C}$ increments. Curve fitting and resistance calculation were done by ZSimpWin software, using the expression of $\sigma = L/RS$, where L and S represent the sample thickness and electrode area of the

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