



Short communication

Cobalt-free layered perovskite $\text{GdBaFe}_2\text{O}_{5+x}$ as a novel cathode for intermediate temperature solid oxide fuel cells

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ABSTRACT

A cobalt-free layered perovskite oxide, $\text{GdBaFe}_2\text{O}_{5+x}$ (GBF), was investigated as a novel cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs). Area-specific resistance (ASR) of GBF was measured by impedance spectroscopy in a symmetrical cell. The observed ASR was as low as $0.15 \Omega \text{ cm}^2$ at 700°C and $0.39 \Omega \text{ cm}^2$ at 650°C , respectively. A laboratory sized $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC)-based tri-layer cell of NiO-SDC/SDC/GBF was tested under intermediate temperature conditions of $550\text{--}700^\circ\text{C}$ with humidified H_2 ($\sim 3\% \text{ H}_2\text{O}$) as a fuel and the static ambient air as an oxidant. A maximal power density of 861 mW cm^{-2} was achieved at 700°C . The electrode polarization resistance was as low as 0.57, 0.22, 0.13 and $0.08 \Omega \text{ cm}^2$ at 550, 600, 650 and 700°C , respectively. The experimental results indicate that the layered perovskite GBF is a promising cathode candidate for IT-SOFCs.

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1. Introduction

Since high operating temperature ($800\text{--}1000^\circ\text{C}$) conditions induce very complex material degradation problems, there is an increasing interest in developing intermediate temperature ($500\text{--}800^\circ\text{C}$) solid oxide fuel cells (IT-SOFCs). Nevertheless, reducing operating temperature generally leads to the increases of electrolyte ohmic resistance and electrode polarization losses, and consequently poor SOFC performance [1,2]. For example, widely utilized cathode material $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ (LSM) shows very good performance around 800°C , but has poor ionic conductivity and increased cathode overpotential in reduced temperature conditions [3]. Many cobalt-containing perovskite-type mixed ionic–electronic conductors (MIEC), such as $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) [4], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) [5] and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) [6], have been extensively studied as possible cathodes due to the fact that cobalt is beneficial to the activation of oxygen molecules reduction. These cobalt-based cathodes, however, often suffer from problems like poor chemical stability in CO_2 , high thermal expansion coefficients (TECs), ease of evaporation, as well as high cost of cobalt element [7,8]. Clearly, it is significant to develop cobalt-free cathodes with sufficient catalytic activity at reduced temperatures for IT-SOFCs. Several cobalt-free oxides with simple perovskite structure, such as $\text{La}_x\text{Sr}_{1-x}\text{FeO}_{3-\delta}$ (LSF) [9], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSZF) [7], etc., have been reported as IT-SOFC cathodes.

Recently, layered perovskites have attracted much attention because their A-sites are ordered. The ordering A-sites are recognized to be able to greatly enhance the diffusivity of oxygen-ion in the bulk of the material by orders of magnitude [10–13], and consequently improve cathode performance. In this paper, we present the development of a novel cobalt-free material $\text{GdBaFe}_2\text{O}_{5+x}$ (GBF) with a layered perovskite structure. The GBF was investigated as a cathode on SDC electrolyte for IT-SOFC. The electrochemical performance was characterized by complex impedance technique.

2. Experimental

2.1. Sample preparation and X-ray diffraction measurement

$\text{GdBaFe}_2\text{O}_{5+x}$ (GBF) powder was synthesized using modified Pechini process, where citrate and ethylene diamine tetraacetic acid (EDTA) were employed as parallel complexing agents. Gd_2O_3 was first dissolved in nitric acid under heating; the calculated amount of $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in EDTA– NH_3 aqueous solution under heating and stirring conditions. An appropriate amount of citric acid was then added in the solution. After converted into viscous gel under heating and stirring conditions, the solution was ignited to flame and result in ash. The resulting ash-like material was afterwards calcined in air at 1000°C for 10 h. Fine GBF powders were then mixed thoroughly with a Heraeus binder (V006) to obtain the cathode slurry. Powders of SDC electrolyte were synthesized by glycine-nitrate process (GNP).

The phase identification of prepared cathode powders was studied with X-ray powder diffraction by Cu– $\text{K}\alpha$ radiation

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(D/Max-gA, Japan). A scan rate of 5° min^{-1} was used in the range of $20^\circ < 2\theta < 80^\circ$.

2.2. Electrochemical characterization

2.2.1. ASR measurement of symmetrical cells

The SDC powder was dry-pressed into pellets at 250 MPa and sintered in air at 1400°C for 5 h to obtain dense pellets with thickness of 0.77 mm and diameter of 12.1 mm. The as-prepared cathode slurry was painted on both sides of electrolyte pellet with active area of 1.15 cm^2 to form a symmetrical cell (GBF/SDC/GBF). The cell was sintered at 1000°C in air for 3 h. Platinum (Pt) was used as the current collector on either of the electrodes. The polarization resistance of electrode materials was measured using AC impedance spectroscopy with as-prepared symmetrical cells. The electrochemical impedance spectra (EIS) were obtained using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 potentiostat. The sweeping frequency range of EIS measurement was from 0.01 Hz to 5 MHz. The area-specific resistance (ASR) was obtained from EIS result. The ASR result was employed to describe the combinational resistances resulting from gas–electrode interface, bulk electrode, as well as electrode–electrolyte interface.

2.2.2. Fuel cell fabrication and tests

The anode-supported SDC bi-layer ($\Phi = 15 \text{ mm}$) was prepared using a dry-pressing method. NiO+SDC+starch mixture (60:40:20 wt%) was pre-pressed at 200 MPa as an anode substrate. Then loose SDC powder synthesized above was uniformly distributed onto the anode substrate, co-pressed at 250 MPa and co-sintered subsequently at 1400°C for 5 h to densify the SDC membrane. The cathode slurry was then painted on SDC electrolyte film, and sintered at 1000°C for 3 h in air to form single cells of NiO-SDC/SDC/GBF.

The cells were tested from 550 to 700°C with humidified hydrogen ($\sim 3\% \text{ H}_2\text{O}$) as a fuel and the static air as an oxidant. The flow rate of fuel was about 30 ml min^{-1} controlled by mass flow meter. The voltage–current curves were recorded by Scribner 890ZV at a 30 mV s^{-1} scan rate.

Impedance spectra were measured over the frequency range from 0.01 to 10^5 Hz under open-circuit conditions. A scanning electron microscope (SEM) was used to observe the microstructure of the post-test cells.

3. Results and discussion

As shown in Fig. 1, the as-prepared powder of GBF exhibits a pure layered perovskite phase with orthorhombic lattice geometry of space group (*Pmmm*) [14]. The diffraction peaks are identical with $\text{GdBaCo}_2\text{O}_{5+\delta}$ reported in the literature by Taranc3n et al. [15]. The replace of Fe at B site did not affect the formation of layered perovskite phase.

Fig. 2 shows the SEM image of tri-layer cell Ni-SDC/SDC/GBF after electrochemical testing. It can be seen that the SDC membrane is completely dense and the thickness is about $20 \mu\text{m}$. The electrolyte layer adheres to both porous anode substrate and cathode layer fairly well, and no cracks or pores can be observed from the cross-section view.

To evaluate the properties of GBF as cathode material, ASR values of a symmetrical cell GBF/SDC/GBF were measured using impedance spectroscopy in operating temperature range between 500 and 700°C . The corresponding cathode ASR (Fig. 3a) was determined from raw impedance plots as shown in Fig. 3b, where the high-frequency offset is induced by electrolyte resistance and the radius of the arc is attributed to the cathode resistance [5]. The

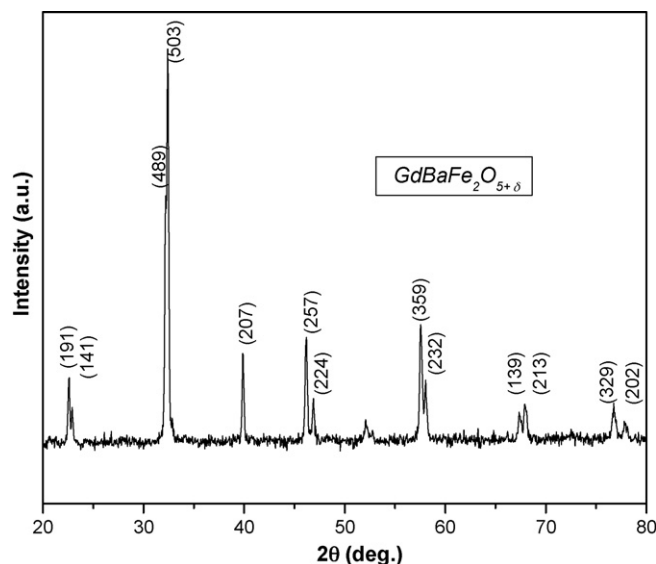


Fig. 1. XRD pattern for the layered $\text{GdBaFe}_2\text{O}_{5+\delta}$ (GBF) perovskite powders.

ASR was about $0.15 \Omega \text{ cm}^2$ at 700°C and $0.39 \Omega \text{ cm}^2$ at 650°C , respectively. Compared with reported cobalt-free cathodes, e.g. $\text{LaBaCuFeO}_{5+\delta}$ ($0.21 \Omega \text{ cm}^2$ at 700°C) [16], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($0.22 \Omega \text{ cm}^2$ at 700°C) [7], the ASR of GBF is much lower. This comparison implies that the layered perovskite GBF cathode has higher activity for oxygen reduction. Furthermore, the ASR of GBF is also comparable to other cobalt-containing cathodes. For example, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, a widely used cathode, the ASR was about $0.44 \Omega \text{ cm}^2$ at 690°C on $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (GDC) electrolyte [4].

The E_a value of GBF is 142 kJ mol^{-1} , comparable to other E_a values reported in the literature [17], e.g. $E_a = 164 \text{ kJ mol}^{-1}$ for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $E_a = 183 \text{ kJ mol}^{-1}$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$, and $E_a = 202 \text{ kJ mol}^{-1}$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, respectively. It is obvious that GBF exhibits promising high activity for oxygen reduction and mobility. This observation is consistent with that reported by Taskin et al. [13], in which the oxygen diffusion in layered perovskites becomes very fast at relatively low temperature conditions, e.g. exceeding $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 600°C for $\text{GdBaCo}_2\text{O}_{5+\delta}$.

The *I*–*V* curve and *I*–*P* curve of the as-prepared cell with GBF as cathode, as shown in Fig. 4a, were obtained in operating temperature range of 550 – 700°C , in which humidified H_2 ($\sim 3\% \text{ H}_2\text{O}$) is utilized as a fuel and static ambient air as the oxidant. The open-circuit voltage (OCV) is lower than 1.0 V, and increases with the decrease of the operating temperature. The decrease of the cell OCV

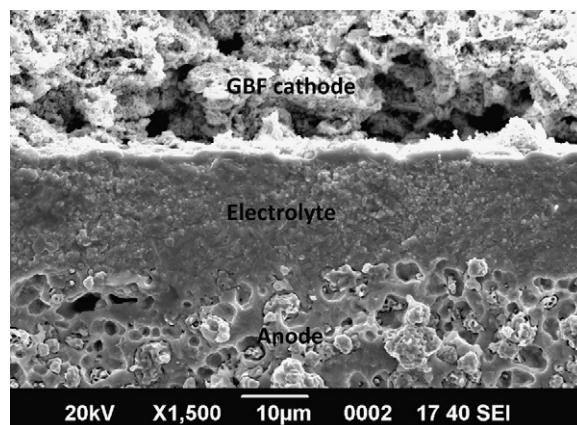


Fig. 2. The cross-section of tri-layer cell after electrochemical testing.

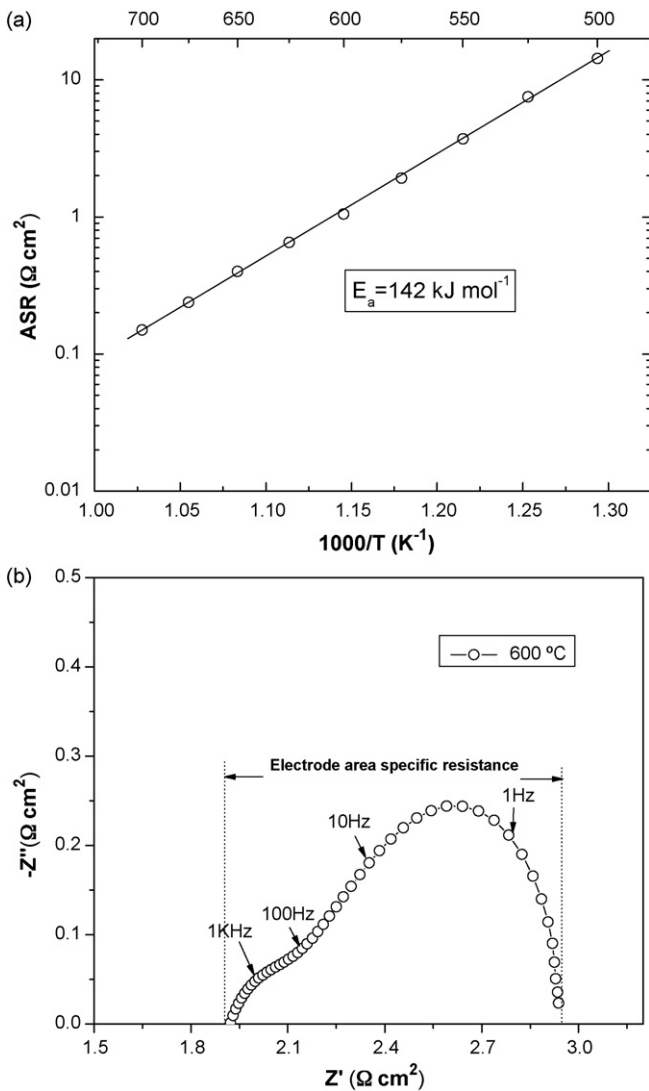


Fig. 3. (a) Area-specific resistance as a function of temperature for a symmetric GBF/SDC/GBF cell and (b) a typical impedance spectra obtained at 600 °C.

is induced by the fact that the doped ceria is not a pure oxide ion conductor [18]; the reduction of Ce^{4+} to Ce^{3+} in the SDC electrolyte film causes an internal current. Peak power densities of the cell were 861, 644, 471 and 218 mW cm^{-2} at 700, 650, 600 and 550 °C, respectively. The cell performance is encouraging and suggests that GBF is a promising cobalt-free cathode material for IT-SOFCs.

The electrochemical impedance spectra of cells under open-circuit condition are presented in Fig. 4b. There are two flattening arcs in each of impedance spectra, indicating that at least two electrode processes are involved. The high-frequency arc could be attributed to polarization during charge transfer process. The low frequency arc might be attributed to mass transport losses [19]. Increase operating temperature leads to significant reduction of electrode polarization resistance (R_p), typically from 0.57 $\Omega \text{ cm}^2$ at 550 °C to 0.08 $\Omega \text{ cm}^2$ at 700 °C, respectively. It is generally recognized that the overall cell polarization loss is dominated by cathode polarization loss [20]. The low R_p values indicated that GBF exhibited high electrochemical activity for the reduction of molecular oxygen in practical fuel cell system.

The performance observed from experimental results of cell Ni-SDC/SDC/GBF can be understood using the microstructure characteristic of layered perovskite cathode GBF. It is well known that the ionic conductivity is dependent on both the chemical diffu-

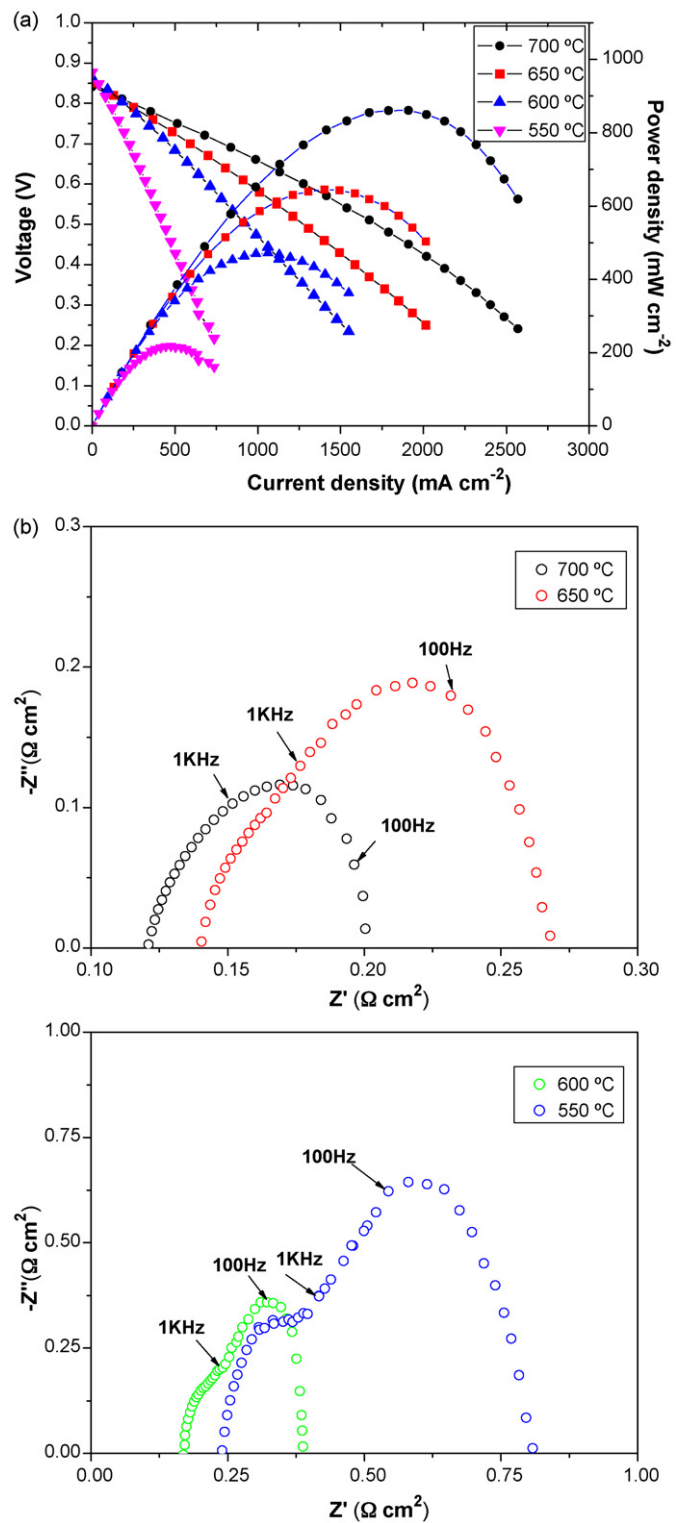


Fig. 4. (a) Performance of the as-prepared cell with hydrogen at different temperatures and (b) impedance spectra of the cell Ni-SDC/SDC/GBF under open-circuit conditions from 550 to 700 °C.

sion coefficient D and the surface exchange coefficient K . Due to the ordering A-sites in layered perovskite oxide, the rate of the oxygen up-taking is much faster than that in simple ABO_3 -type perovskite. Similarly it is also much easier to release oxygen from layered oxides. Taskin et al. has established that the ordering of the A-site sub-lattice in layered structure significantly enhances the oxygen relaxation rate since oxygen atoms can be partially or even

completely removed from the Gd^{3+} planes, generating numerous oxygen vacancies in the crystal lattice [13].

4. Conclusions

A cobalt-free GBF cathode with layered perovskite exhibited unusually high activity for oxygen reduction and mobility. In the symmetrical cell system, the ASR of $0.23 \Omega \text{ cm}^2$ was achieved at 650°C for cathode polarization. The low activation energy (E_a) of GBF indicated its excellent catalytic activity for oxygen reduction. Anode-supported single cells with SDC electrolyte and GBF cathode were fabricated and evaluated. The maximum output density reached 861 mW cm^{-2} at 700°C . The low interfacial polarization resistance is as low as 0.57, 0.22, 0.13 and $0.08 \Omega \text{ cm}^2$ at 550, 600, 650 and 700°C , respectively. The experimental results indicated that layered perovskite GBF is a promising cobalt-free cathode material for IT-SOFCs.

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