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Microwave effect on barium strontium ferrate and co-fired fuel cells

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ABSTRACT

The microwave effect on barium strontium ferrate (BSF) was determined, and core-shell BSF-xCe cathode was co-fired with ceria-based electrolyte in a focused microwave cavity. The solubility of cerium (Ce) in BSF was up to $x = 10$ mol%. The grain size of the microwave-sintered BSF was smaller. The conductivity of BSF-20Ce cathode with the lower transition temperature was significantly higher than that obtained by conventional sintering. The ohmic (R_{ohm}) and electrode polarization (R_p) resistances of the fuel cells were significantly reduced. The open-circuit voltage and peak power density of the microwave co-fired fuel cells increased with the Ce coatings. The high ionic conductivity at high operation temperature was due to the generation of more oxygen vacancies without clustering, caused by the effective absorption of microwave by the low valence iron oxide. Thus, the enhanced diffusion of Ce and the reduced R_p and R_{ohm} by the microwave energy improved the performance of fuel cells.

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Introduction

$ABO_{3-\delta}$ perovskite structures contain cations of alkaline earth metals ($A = Sr, Ba$) and transition metals ($B = Mn, Fe, Co$ and Ni), which possess mixed ion and electron conducting (MIEC) properties. They are excellent cathode materials for intermediate temperature solid oxide fuel cells (ITSOFC) at temperatures below 800 °C [1–4]. The crystal structure and the A or B-site cations in such perovskites play an important role in determining the MIEC properties [5,6]. Mn and Fe substitutions provide reasonable binding to the oxygen in the lattice [7,8].

The perovskite cathode materials that are mostly studied include $(La, Sr)MnO_3$ (LSM); $(La, Sr)(Co, Fe)O_3$ (LSCF); and $(Ba, Sr)(Co, Fe)O_3$ (BSCF). The LSM material achieves good matching with YSZ or ceria-based electrolyte in high-temperature SOFC (HTSOFC) [9,10]. However, the electron-conductivity of LSM decreases when the fuel cell is operated at a low temperature. LSCF and BSCF possess MIEC properties with longer triple phase boundaries (TPBs) than electron-conductive LSM. Therefore, the electrocatalytic activity of oxygen in LSCF and BSCF is better than that in LSM. Hence, the two former materials are considered to be candidate materials for the cathode in ITSOFC. Nevertheless, the coefficient of thermal

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expansion (CTE) for both LSCF and BSCF is about $20 \times 10^{-6} \text{ K}^{-1}$, which is considerably larger than that of the ceria-based electrolyte ($\sim 12.5 \times 10^{-6} \text{ K}^{-1}$). This thermal matching issue causes problems in co-firing with the electrolyte and in the operation temperature of the fuel cell. Additionally, Co-based cathodes also possess many disadvantages, such as high cost, high evaporation due to the reduction of Co, and the transition of Co^{3+} (with octahedral coordination) from a low-spin state to a high-spin state [11–13].

Ferrite-based materials that are cobalt-free are good candidates as the cathode material, because iron is inexpensive and shows almost zero toxicity. Studies have been conducted on iron-substituted materials such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ (BSFC) [14], $\text{Sr}_x\text{Ba}_{1-x}\text{FeO}_{3-y}$ [15], $\text{SrFe}_{0.95}\text{Mo}_{0.05}\text{O}_{3-\delta}$ [16], and $\text{Sr}_{1-x}\text{Ce}_x\text{FeO}_{3-x}$ [17]. Although the material $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (BSF) has the highest electrical conductivity among ferrites [18,19], this perovskite oxide still exhibits a high CTE [20]. It makes co-firing with zirconia and ceria-based electrolytes difficult.

Iron-containing $\text{ABO}_{3-\delta}$ perovskites exhibit high oxide-ion conductivities because of their lower B–O bonding energies and the facile transitions of charge carriers between the various coordination polyhedra. They are unstable at low O_2 partial pressures and high temperatures, and are also sensitive to the moisture present in the air [5]. Cerium (Ce) doping can improve the stability of the lattice by forming a cubic structure [17,21]. The Ce in BSF provides lattice stability, better cathode-electrolyte adhesion, and enhanced cell performance by increasing the TPBs in SOFC.

Most SOFC co-firings consume considerable amounts of time and energy when conventional heating processes are used. Microwave heating provides a cost effective way to fabricate uniform cathodes and SOFCs without involving long periods of time, and these resultant products possess many high performance characteristics. Several researchers have used microwave energy for the rapid sintering of single materials and for the co-firing of fuel cells [22–27]. It has been shown that with the use of microwave sintering, the sintering temperature and activation energies of the composite cathodes are lowered, and lower grain size and open pore electrodes that adhere well to the electrolyte are obtained. Nevertheless, it has been suggested that the cell performance can be improved if a commercial microwave oven with precise electromagnetic field control is used in the sintering process [23,28].

Microwave sintering produces inverse thermal gradients in the sample from the inside to the outside due to the faster kinetics associated with the ponderomotive force and non-thermal effect compared to conventional sintering. The ability to absorb power is dependent on the dielectric and/or magnetic losses within the material upon microwave irradiation [29], and on the microwave susceptor as well as the processing cavity design. Iron oxides can exhibit significant dielectric and/or magnetic losses under microwave fields [30]. However, it has not yet been investigated how the BSF containing iron oxide absorbs microwave radiation and enhances Ce diffusion into the lattice.

In this work, we employed BSF coated with CeO_2 (BSF-xCe) as the cathode and $(\text{La}_{0.75}\text{Sr}_{0.2}\text{Ba}_{0.05})_{0.175}\text{Ce}_{0.825}\text{O}_{1.891}$ (LSBC) as the electrolyte [31] for ITSOFCs. The BSF-xCe formed a core-shell structure. The microwave effect on BSF-xCe and Ce

diffusion were investigated. Further, the performance and various properties of BSF-xCe cathodes and (BSF-xCe)||LSBC half cells fabricated by microwave sintering (MW) were studied.

Material and methods

Fabrication of the LSBC and the BSF powders

Cathode powders of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ (BSF) and electrolyte powders of $(\text{La}_{0.75}\text{Sr}_{0.2}\text{Ba}_{0.05})_{0.175}\text{Ce}_{0.825}\text{O}_{1.891}$ (LSBC) were prepared by the solid-state reaction method. The starting materials were SrCO_3 (Alfa, 98%), BaCO_3 (SHOWA, 99%), Fe_2O_3 (SHOWA, 98%), La_2O_3 (STREM Chemistry, 99%), and CeO_2 (ACROS, 99.9%). They were mixed in a polyethylene bottle containing a milling solvent and an yttrium-stabilized zirconia milling medium. Both BSF and LSBC were directly mixed in a designed molar ratio by ball milling for 24 h with ethanol (for BSF) and de-ionized water (for LSBC). The LSBC and BSF slurries were dried at 80°C in an oven. Both the powder mixtures were calcined at 1000°C for 4 h in an air furnace.

Fabrication of the BSF-xCe core-shell

The compound $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in an ethanol solvent. This mixture was then added to the calcined BSF powders at molar ratios of 5, 10, 15, and 20%. The ethanol-to-water volume ratio in each reaction mixture was then adjusted to 9:1. These semi-organic solutions were stirred for 6 h and dried at 80°C . The dried powders were subsequently ground and calcined at 800°C for 4 h. The resulting CeO_2 -coated BSF powders, which are referred to as core-shell BSF-xCe ($x = 5, 10, 15$ and $20 \text{ mol}\%$), were milled using motor and pestle. All the BSF-xCe ($x = 0, 5, 10, 15$ and $20 \text{ mol}\%$) powders were mixed with ethyl cellulose and terpineol by milling and blending to make BSF-xCe core-shell pastes, and then dried. The dried powders were then passed through a 60-mesh screen. The granulated BSF-xCe powders were pressed in a die press with a disk size of 10 mm diameter and 1 mm thickness. The BSF-xCe disks were then sintered at $300\text{--}650^\circ\text{C}$ for 5–10 min in a focused microwave cavity. The microwave generator used in this work had a 2.45 GHz magnetron head. The applied microwave power and the corresponding temperature profiles of the susceptor, with and without the samples, were recorded during the microwave processes.

Fabrication of a half-cell with the BSF-xCe core-shell cathode

The LSBC powder was mixed with the binder PB72, and then it was ground and dried. The dried powders were passed through a 60-mesh screen. The granulated powders were then pressed in a die with a disk size of 15 mm diameter and 1 mm thickness. The as-pressed LSBC disks were sintered at 1500°C for 6 h in an electrical furnace. The sintered disks were then polished and cleaned sequentially with D.I. water, acetone, and ethanol using an ultrasonic cleaner. The calcined and ground BSF-xCe ($x = 0, 5, 10, 15$ and $20 \text{ mol}\%$) powders were mixed with methanol, ethyl cellulose, and terpineol to form cathode pastes. Each cathode paste was then printed onto the

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