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Fabrication of novel electrolyte-layer free fuel cell with semi-ionic conductor ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$- $Sm_{0.2}Ce_{0.8}O_{1.9}$) and Schottky barrier

Muhammad Afzal [a], Mohsin Saleemi [b, d], Baoyuan Wang [a, c], Chen Xia [a], Wei Zhang [c], Yunjuan He [a], Jeevan Jayasuriya [a], Bin Zhu [a, c, *]

[a] Department of Energy Technology, KTH Royal Institute of Technology, 10044 Stockholm, Sweden
[b] Department of Materials and Nano Physics, KTH Royal Institute of Technology, 16440 Stockholm, Sweden
[c] Hubei Collaborative Innovation Center for Advanced Materials, Faculty of Physics and Electronic Science, Hubei University, Wuhan, Hubei 430062, PR China
[d] Department of Materials and Environmental Chemistry, Stockholm University, 10691 Stockholm, Sweden

HIGHLIGHTS

- Novel EFFC based on perovskite Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC).
- Electrical conductivity of as prepared BSCF measured above 300 S/cm in air at 550 °C.
- Device performance reached above 600 mW/cm^2.
- Schottky junction explored by HOR mechanism to overcome short circuiting problem.
- Anodic activity supported by coating of NCAL on Ni-foam.

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ABSTRACT

Perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is synthesized via a chemical co-precipitation technique for a low temperature solid oxide fuel cell (LTSOFC) (300–600 °C) and electrolyte-layer free fuel cell (EFFC) in a comprehensive study. The EFFC with a homogeneous mixture of samarium doped ceria (SDC): BSCF (60%:40% by weight) which is rather similar to the cathode (SDC: BSCF in 50%:50% by weight) used for a three layer SOFC demonstrates peak power densities up to 655 mW/cm^2, while a three layer (anode/electrolyte/cathode) SOFC has reached only 425 mW/cm^2 at 550 °C. Chemical phase, crystal structure and morphology of the as-prepared sample are characterized by X-ray diffraction and field emission scanning electron microscopy coupled with energy dispersive spectroscopy. The electrochemical performances of 3-layer SOFC and EFFC are studied by electrochemical impedance spectroscopy (EIS). As-prepared BSCF has exhibited a maximum conductivity above 300 S/cm at 550 °C. High performance of the EFFC device corresponds to a balanced combination between ionic and electronic (holes) conduction characteristic. The Schottky barrier prevents the EFFC from the electronic short circuiting problem which also enhances power output. The results provide a new way to produce highly effective cathode materials for LTSOFC and semiconductor designs for EFFC functions using a semiconducting-ionic material.

1. Introduction

Fuel cells directly convert chemical energy of the fuel into electrical energy with high efficiency and minimal fossil emissions. Solid oxide fuel cell (SOFC) is represented as a fuel flexible, reliable and efficient among the several fuel cell types [1–3], with long term stability and capacity to adapt the existing fuel infrastructure [4]. Conventionally, SOFCs consisting of three functional components operate at high temperatures (HT) (800–1000 °C). They provide several advantages e.g., high power and less chance of short

* Corresponding author. Department of Energy Technology, KTH Royal Institute of Technology, 10044 Stockholm, Sweden.
E-mail addresses: zhubin@hubu.edu.cn, binzhu@kth.se (B. Zhu).

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circuiting especially when high quality heat is required. However, there are many challenges for these systems e.g., long start-up time, material degradation at such a high temperature, thermal stress factor, and high cost of the required cell components [5]. Therefore, current SOFC research is focused towards the development of lower temperature (LT) (500–600 °C) SOFCs, which in some cases is also known as intermediate temperature SOFC (IT-SOFC) [6]. Generally, HT-SOFCs operate between 800 and 1000 °C, IT-SOFCs function in the range of 600–800 °C and LT-SOFCs work below 600 °C. In general, low operating temperatures of the LT-SOFC bring new challenges on the catalyst and conductivity of the materials desired for high FC power outputs [7].

Commonly used cathode materials are perovskite oxides with ABO_3 structure formula [8,9]; these materials have demonstrated a good mixed ionic and electronic conductivity at low temperatures (<600 °C). Some of the known compositions of perovskite oxides tested (for cathodes) are $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) [10,11], $Ba_{1-X}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (BSCF) [12–14], $Sm_{1-x}Sr_xCoO_3$ (SSC) [15], $Ba_{1-x}Pr_xCo_{1-y}Fe_yO_{3-\delta}$ [16] etc. BSCF has been proposed as a good cathode material in IT- and LT-SOFCs because it exhibits good mixed electronic and ionic conductivity, oxygen transport and catalytic activity at the desired operating temperatures. In addition, the perovskite structure allows the doping by different metals bearing the possibility to optimize the material compositions with composite structure [17].

In the latest developments, a revolutionary fuel cell technology, electrolyte-layer free fuel cell (EFFC) has been invented [18–21]. These EFFCs are based on single layer/component material consisting of semiconductor and ionic materials which can integrate fuel cell anode, electrolyte and cathode functions altogether and are available in literature with working principle and mechanism [22–29].

In this work, we explore a new combination of electrode and electrolyte based on a new principle of a Schottky barrier [30] to construct the fuel cell. Additionally, conventional 3-layer SOFCs and the EFFCs based on the Schottky type using perovskite $Ba_{1-X}Sr_{x-}Co_{1-y}Fe_yO_3$ (BSCF) material have been investigated for a comprehensive way with promising device performance. The prepared BSCF material has revealed its potential use in both low temperature ceria-based electrolyte SOFCs and EFFCs. The combinations of the ionic conductor samarium doped ceria, $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) and synthesized BSCF as cathode in 3-layer FC while as semiconductor material for EFFC have proven new opportunities to use in low temperature SOFC technologies.

2. Experimental

2.1. Material preparation

Perovskite BSCF, an electrode material, is synthesized by the chemical co-precipitation method. All chemicals and reagents with high purity are purchased from Sigma-Aldrich. Desired stoichiometric ratios (0.5:0.5 M) of Barium Nitrate, $Ba(NO_3)_2.H_2O$ and Strontium Nitrate, $Sr(NO_3)_2.H_2O$, which are corresponding to 139.67 g and 114.82 g respectively, are weighed and mixed into Deionized (DI) water to prepare solution A which is kept at 70 °C for 1 h under constant stirring. In parallel, solution B is also prepared by mixing Cobalt Nitrate hexa-hydrate, $Co(NO_3)_2.6H_2O$ and Iron Nitrate nona-hydrate, $Fe(NO_3)_3.9H_2O$ in a separate beaker in a molar ratio of 0.8:0.2 which are equivalent to 232.83 g and 80.80 g respectively. This mixture is also stirred at 70 °C for half an hour till a homogeneous solution is obtained. Solution B is then added dropwise into solution A under constant vigorous stirring at elevated temperature. The resulting solution is kept under further stirring for 30 min until uniform mixing has been completed. The mixture of solution A & B is used as metal ion precursor. For the co-precipitation reaction, 0.047 mol of oxalic acid (precipitating agent) dehydrated solution is prepared and added dropwise into the precursor's solution. Ammonium hydroxide, NH_4OH and hydrochloric acid (HCl) are used to adjust the pH between 2 and 4 to get the homogenous precipitation formation; this solution is mixed again at a constant stirring for 2 h at 70 °C. The final solution is stirred until the clear precipitates of the BSCF material are observed in the beaker. Precipitates are filtered and washed in distilled water three times and collected on the filter paper. The resultant precipitates are dried overnight (12 h) in a furnace at 120 °C. The dried precipitates are ground and sintered at 1000 °C for 5 h to acquire the perovskite phase of the as-prepared material. A detailed scheme for the preparation of perovskite BSCF is presented in flow chart in Fig. 1.

The sintered material is ground thoroughly to obtain BSCF powder for further assessment. The as-prepared BSCF and commercial SDC are mixed in a 50:50 wt ratio under a solid state reaction method and ground, then heat-treated at 700 °C for 2 h to get the nanocomposite cathode material for SOFC. A similar procedure is performed for the EFFC material.

2.2. Characterization of the powder material

The powder X-ray diffraction (XRD) pattern of the locally prepared BSCF sample is recorded on a Bruker AXS D8 advanced X-ray diffractometer (Germany, Bruker Corporation), operated with Cu Kα (λ = 1.54060 Å) as the source. The microstructure and morphologies are analyzed through a JSM7100F field emission scanning electron microscope (FESEM, Japan) working at 15 kV, equipped with an energy dispersive X-ray spectrometer (EDS) analyzer (EDX-720, Oxford). The electrical conductivity of the as-prepared material is measured by a DC 4 Probe Technique (KD2531 digital micro-ohm meter), AC impedance analysis is conducted by using an EIS instrument (CHI660B electrochemical work station) and for fuel cell I-V data an automatic measurement system (ITECH8511) is used. Specimens for conductivity measurement are compacted by a uniaxial powder pressing machine to get pellets of a typical size (active area 0.64 cm^2 and 2 mm thickness). The pellet used for conductivity measurement is fabricated using 200 MPa of pressure with a specific amount of pure BSCF and then heated at 650 °C for 1 h. Finally, silver paste is coated on both sides of the pellet as a current collector for electrical conductivity measurements.

2.3. Fuel cell (FC) fabrication

The commercial $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$ (NCAL), a nickel-cobalt-based oxide material, is purchased from Tianjin Bamo Sci.&Tech. Joint Stock Ltd, China and used as an anode material in a mixture with SDC in a 60:40 wt ratio to prepare the anode layer. The BSCF as the cathode material is mixed with SDC in a 50:50 wt ratio to prepare the cathode layer. The SDC as the electrolyte layer is sandwiched between the anode and cathode layers to form a three layer fuel cell in a configuration of NCAL + SDC/SDC/SDC + BSCF. The FC assembly containing nickel foam coated by NCAL as a current collector and catalytic agent attached on the anode side is pressed under 200 MPa and silver pasted on cathode side is coated as a current collector. The pelletized cell is 13 mm in diameter and 0.8–1.0 mm in thickness consisting of a 0.2 mm SDC electrolyte layer, 0.4–0.5 mm anode layer, and 0.2–0.3 mm cathode layer. The EFFC device with a 60SDC-40BSCF homogeneous mixture is fabricated under the same parameters with thickness of 0.8–1.0 mm. Nickel foam coated by NCAL is used on both sides as a current collector and for enhanced electrode catalytic activity. Fig. 2 depicts schematic diagrams for two types of the fuel cell devices.