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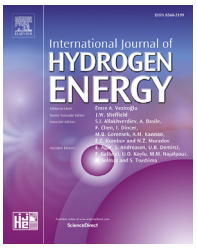

High performance cathode-unsintered solid oxide fuel cell enhanced by porous $Bi_{1.6}Er_{0.4}O_3$ (ESB) interlayer

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ABSTRACT

Dense bismuth oxides stabilized with lanthanide dopants (δ-Bi_2O_3) are always used as interlayer for thin layer GDC (gadolinia-doped ceria) or YSZ (yttria-stabilized zirconia) electrolyte solid oxide fuel cell to improve the cell performance. Dense ESB ($Bi_{1.6}Er_{0.4}O_3$) layer preparation needs special equipment or well synthesized nano-sized powders, which is not friendly for large scale and commercial application. In this paper, anode support unsintered cathode cell with porous ESB interlayer is prepared through simple screen print and its electrochemical performance is tested. No matter sintered or not, porous ESB interlayer lowers both the polarization resistance and ohmic resistance, and enhances cell performance, especially for the ohmic resistance of unsintered cells. The cell with ESB porous interlayer and SSC ($Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$)-ESB unsintered cathode achieves a peak power density of 1.329 W cm^{-2} at 700 °C, which is 1.61 times higher than that of the cell without ESB interlayer and 0.93 times higher than that of the sintered cell. However, the durability of porous ESB interlayer enhanced cells is not ideal and it should be improved in further works.

Introduction

Solid oxide fuel cell (SOFC), consisting of porous anode and cathode separated by a dense electrolyte, is an electrochemical and environmental friendly device, which efficiently converts the chemical energy of fossil and hydrocarbon fuels into electricity and heat without combustion and mechanical motion involved [1]. The operating temperature of primary thick electrolyte-supported SOFCs is near 1000 °C, which has been lowered to the intermediate-temperature range of 600–800 °C by accepting anode-supported configuration, which naturally come with the benefits in more extensive materials selection, higher materials stability, better performance durability, and lower manufacturing cost [2,3].

Yttria-stabilized zirconia (YSZ) is the most widely used electrolyte material for both commercial products and laboratory scale researches, which benefits from its high stability at a wide range of oxygen partial pressure [4]. Other electrolyte materials, such as Gadolinia-doped Ceria (GDC) and Bismuth oxides stabilized with lanthanide dopants (δ-Bi_2O_3, e.g., $Bi_{1.6}Er_{0.4}O_3$ (ESB)), have higher oxygen ion conductivity but worse stability at low oxygen partial atmosphere [5,6]. At a typical anode atmosphere, pure H_2, GDC is partially reduced and then gets certain electronic conductivity leading to a lower OCV (open circuit voltage) [7], while ESB is easily

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reduced leading to the birth of metal Bi [5,8]. Compared with YSZ, GDC has a better chemical compatibility with many perovskite cathode materials, such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). GDC was usually used as the barrier layer between YSZ electrolyte and cathode to prevent the unexpected interactions [9,10]. At most conditions, the GDC barrier layer, usually prepared by screen print, was porous, because it's expensive to prepare dense GDC thin layer on YSZ surface. What's more, it has been reported that the inter-diffusion between doped-ceria and stabilized zirconia during high temperature sintering (over 1200 °C) results in insulating phases, thus significantly increasing ohmic resistance by at least 1 order of magnitude compared to that of pure YSZ [11].

Bismuth oxide stabilized with lanthanide dopants (δ-Bi_2O_3) has been known as a promising electrolyte material with higher oxygen ions conductivity than both GDC and YSZ, but its application is limited by its weak tolerance of reduction atmosphere. So, different with GDC, dense ESB is always prepared between YSZ or GDC electrolyte and cathode constituting a bilayer electrolytes SOFC [12]. Wachsman et al. pioneered bismuth oxide/ceria bilayer electrolytes SOFCs: ceria electrolyte at the fuel side can shield the bismuth oxide from the reduction atmosphere and maintain the chemical stability; at the same time ESB will block the electrons transportation through GDC layer; moreover, total area specific resistance is decreased [13–15]. Joh et al. [16] replaced GDC with YSZ and used LSM ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$)-ESB as cathode, and a higher OCV than that of GDC electrolyte condition and a peak power density of 2.08 W cm^{-2} at 700 °C was achieved. But the establishment of such dense ESB layer requires special equipment, such as pulsed laser deposition (PLD) [12], or nano-sized ESB powers prepared by special method, such as wet chemical co-precipitation [16]. For cell with ESB interlayer, cathode was usually prepared through the strategy of compositing with Bi_2O_3 based oxygen ions conductor, such as $Er_{0.4}Bi_{1.6}O_3$ decorated $La_{0.76}Sr_{0.19}MnO_{3+\delta}$ [17], $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$-$(Er_{0.2}Bi_{0.8})_2O_3$ [18], $La_{0.76}Sr_{0.19}MnO_{3+\delta}$ decorated $Er_{0.4}Bi_{1.6}O_3$ [19], Sr doped $LaMnO_3$ (LSM)-Y & Ce co-doped Bi_2O_3 (BYC7) [20], and $(Bi_2O_3)_{0.7}(Er_2O_3)_{0.3}$-Ag [21]. These composite cathode cells achieved reasonable performance at temperature below 750 °C and partial materials also showed good durability performance.

However, bare work about the function of a porous ESB layer has been reported. It is still not clear whether a porous ESB layer has the same ability to improve electrochemical performance. Therefore, in this paper, a solid oxide fuel cell with porous ESB ($Bi_{1.6}Er_{0.4}O_3$) interlayer between the dense YSZ electrolyte and unsintered cathode was fabricated by a low cost and easy prepared screen print method. Moreover, novel SSC ($Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$)-ESB composite was used as the cathode for solid oxide fuel cell.

Experimental

ESB and SSC powers preparation

ESB powers were synthesized through a citrate process (CP). Stoichiometric amounts of $Er(NO_3)_3 \cdot 5H_2O$ (99.9%, Sinopharm) and $Bi(NO_3)_3 \cdot 5H_2O$ (99.9%, Sinopharm) were added into distilled water contained in a Pyrex container, to which ethylene glycol and citric acid were added. This solution was slowly heated to 80 °C for 2 h and white precipitates appeared, and then it was dried at 200 °C for more than 10 h to get the finally white-yellow ash, which at last was calcined in air at 700 °C for 5 h to form the fluorite structure.

SSC powders were synthesized through a similar process using corresponding metal nitrates. The difference was that no precipitate appeared in the solution at 80 °C and the final calcine temperature was 900 °C.

Cells preparation

The anode substrate of the cell was prepared by tape casting technique and the details can be found in previous reports [22,23]. A mixture of nickel oxide (NiO) powders (Type A, Inco.) and YSZ powders (TZ-8YS, Tosoh) with a mass ratio of 57:43, adding fish oil as dispersant, polyvinyl butyral as organic binders, and polyaleneglycol as plasticizer, was ball milled for 36 h to from a uniform slurry with toluene and ethanol as solvent. Then the slurry was collected to form band shape by tape casting process. After dried at room temperature for more than 24 h, the green substrate was cut into circular samples with target size. At last, the anode functional layer and electrolyte layer was screen printed on the substrate in sequence and co-sintered at 1400 °C for 4 h.

ESB slurry with a weight ratio of 60% was screen printed on the surface of YSZ electrolyte, after dried at 80 °C for 6 h, SSC-ESB composite cathode slurry with the same weight percentage was screen printed on the surface of ESB interlayer, which repeated twice. For the cell without porous ESB interlayer, SSC-ESB composite was directly screen printed on the surface of YSZ. At last, partial cells were sintered at 750 °C for 2 h to decompose the organics.

Characterizations

A Solartron 1260 frequency response analyzer and a Solartron 1287 electrochemical interface (Solartron Analytical) were employed to measure the impedance of the cell in a frequency range between 1000 kHz and 0.1 Hz with a signal amplitude of 20 mV at open circuit, as well as the current-voltage (I-V), current-power (I-P) and time-voltage curves. The X-ray curves of ESB and SSC were examined by X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V.) The cell microstructure was examined by a scanning electron microscope (SEM, Sirion 200 and Quanta 200, FEI).

Results and discussion

Citrate process has been known as a mature and widely used method to synthesize nano-sized and micron-sized powders. As shown by the X-ray spectra of ESB and SSC in Fig. 1, both powders were well fitted with previous reported results [20,24,25]. ESB and SSC mix powders with a weight ratio of 1:1 were well manual grinded for more than 2 h to form a uniform cathode slurry. Two type cells were fabricated: type A without porous ESB interlayer and type B with porous ESB interlayer. A

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