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Optimization of SOFC anode/electrolyte assembly based on $BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07)/Ni-BIT07 using an interfacial anodic layer

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HIGHLIGHTS

- Anode active layers.
- Tape casting and co-sintering.
- Electrochemical performance and durability of SOFC.

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ABSTRACT

$BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07) is a potential electrolyte material for Solid Oxide Fuel Cells (SOFCs) due to its high ionic conductivity and its compatibility with commonly used cathode materials. By using tape casting and co-sintering shaping methods symmetrical cells BIT07-Ni/BIT07/BIT07-Ni have been prepared. In order to improve the interface between BIT07-Ni and BIT07, a thin anode functional active layer (AAL) deposited between the BIT07-Ni and BIT07 is used. The effect of this layer on the electrochemical performance of the symmetrical cells as well as the influence of an additional Ni current collecting layer deposited on the anode side are discussed in this study. It is shown that the presence of the AAL decreases the area specific resistance (ASR) of the anode/assembly by a factor of about two, and that the presence of the Ni layer slows down the ageing of the assembly.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are of great interest as energy conversion devices due to their high energy efficiency and environmentally friendly behaviour [1]. Nowadays, cells operate at 800–750 °C or even higher and a decrease to less than 700 °C is expected in order to increase the life-time of the cell. In this intermediate temperature range, anode supported cells are considered with an electrolyte layer as thin as possible to limit the ohmic loss, and exhibiting a specific ionic conductivity level around 10^{-2} S cm^{-1}. According to this criterion, $BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07) is regarded as a potential electrolyte material [2].

Using tape casting [3,4], it is possible to prepare anode/electrolyte assemblies based on BIT07-Ni/BIT07. The anode is a cermet (ceramic–metal), i.e. a composite made of BIT07, which will provide the ionic conductivity, and of nickel, which will provide both the electronic conductivity and catalytic properties towards the hydrogen oxidation [5–10]. During its shaping step the raw anode tape is composed of BIT07 and NiO and the co-firing of the anode/electrolyte assembly is carried out in air. The cermet is obtained after the sintering step by reducing the NiO to Ni at the working temperature of the cell under reducing atmosphere.

In a previous paper [11], the anode microstructure has been optimized (porosity, phase distribution and particle size), and complete cells have been also realized. The best power densities obtained at 700 °C and 0.7 V was 336 mW cm^{-2}. In this case, the total ASR of the cell is roughly of 0.65 Ω cm^2, in which 0.38 Ω cm^2 comes from the electrodes polarization and the rest (0.27 Ω cm^2) from the current collector and electrolyte. The main part of the polarization resistance (approximately the two thirds), comes from the anode. Improvements must therefore be done in order to decrease the resistance due to the anode part. The anode must fulfil three main requirements (i) oxygen anionic conductivity, (ii) electronic conductivity and (iii) catalytic activity toward fuel oxidation. In the anode, the electrochemical reaction can only

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occur at the triple phase boundary (TPB) that is the interface between the electrolyte, the electron-conducting metal phase and the gas phase. According to published works, it seems that the region in which the TPB exists extends no more than 20 μm–10 μm from the electrolyte into the electrode [12–16], and that a special attention must be brought to the electrolyte/anode interface [17,18]. In order to extend this region, some authors [3,13,14,19,20] have proposed to add intermediate layers between electrolyte and anode layers. Taking into account the previous results obtained with Ni/BIT07 cermets prepared with BIT07 and NiO in weight ratios comprised in the 30:70–50:50 range, with addition of 2.5–15 wt.% of pore-forming agent [21,22], anode/electrolyte symmetrical cells were realized by inserting an intermediary layer between the anode and the electrolyte. The anode cermet has been realized with BIT07 and NiO in a 50:50 wt. ratio, and 5 wt.% carbon black (CB) as pore-forming agent and the intermediary layer is based on BIT07 and NiO in a 45:55 wt. ratio, and 2.5 wt.% CB.

In order to further improve the anode performance, the addition of a Ni current collecting layer between the anode and the current collector has been also tested.

2. Materials and methods

2.1. Powders

BIT07 powder was synthesized by solid-state reaction as detailed in Ref. [2]: its constituents, high purity barium carbonate (Alfa Aesar), indium oxide (Alfa Aesar) and titanium dioxide (Merck), in stoichiometric ratio, were mixed in mortar and pestle using ethanol. The mixture was first heated at 1200 °C for 24 h, then ground and compacted into pellets and sintered at 1350 °C for 24 h, and finally ground and passed through mesh 100. To obtain a grain size of about one micron or less, the powder was ball-milled in 45 ml silicon nitride pot with 15 silicon nitride balls in ethanol at 500 rpm using FRITSCH P7 planetary micro mill. Nickel oxide powder, with a grain size ranged between 0.5 and 1 μm, was provided by Pharmacie Centrale de France. Carbon Black super P, the pore-forming agent, was provided by Timcal.

2.2. Preparation of symmetrical anode/electrolyte/anode assemblies

2.2.1. Slurry preparation

The anode, the AAL and the electrolyte were prepared by tape casting. First, the electrolyte (E) slurry is prepared by mixing the ball milled BIT07 powder, a dispersant (oleic acid) and an azeotropic mixture of solvents (ethanol and 2-butanon) in 45 ml silicon nitride pot with 12 silicon nitride balls at 240 rpm for 1 h. Binders (Polyvinyl Butyral PVB-90 and PVB-98) and plasticizers (Polyethylene glycol PEG-400 and dibutyl phthalate) are subsequently added to the former preparation and ball-milled for 24 h at 180 rpm [5].

Then, the anode (A) slurry is prepared by mixing NiO powder with the previous electrolyte slurry in the BIT07:NiO weight ratio of 50:50. CB was added (5 wt.% of the powder amount) to obtain porous anode material. The AAL slurry is prepared by mixing NiO and BIT07 in the weight ratio of 55:45, and adding CB in 2.5 wt.%.

2.2.2. A/E/A symmetrical cells

The anode/electrolyte (BIT07-NiO/BIT07) assembly is realized in two steps. First an electrolyte tape with a thickness of 100 μm is cast on Mylar and dried in air for one night [23], then on its surface, an anode tape with a thickness of 800 μm is deposited and dried in air for one night. This method, named co-tape casting, allows us to obtain a bilayer anode/electrolyte noted AE [24]. Then, this bilayer is cut into two pieces and the two parts are joined so the electrolyte is face to face: AE/EA. The cohesion at the electrolyte–electrolyte interface is obtained by co-pressing the assembly. The green tape is cut in discs of 9 mm in diameter.

Finally the following thermal treatment is applied to remove slowly the organic species and to sinter the half-cell:

$$\mathrm{RT} \xrightarrow{50\,\mathrm{K\,h^{-1}}} 600\,^{\circ}\mathrm{C}\,(4\,\mathrm{h}) \xrightarrow{100\,\mathrm{K\,h^{-1}}} 1300\,^{\circ}\mathrm{C}\,(9\,\mathrm{h}) \xrightarrow{100\,\mathrm{K\,h^{-1}}} \mathrm{RT}$$

After sintering, an “anode” supported symmetrical cell is obtained with 100–110 μm thick anode and 20–30 μm thin electrolyte, as schematized on Fig. 1a. The surface is comprised between 0.28 and 0.45 cm^2.

2.2.3. A/AAL/E/AAL/A symmetrical cells

As described in previous section, an electrolyte tape with a thickness of 100 μm is cast on Mylar and dried in air for one night. Second, the AAL tape with a thickness of 150 μm is deposited on the surface of the electrolyte tape and dried in air for one night. Finally an anode tape (800 μm) is deposited onto the previous tapes, and dried in air for one night. This multilayer is cut into two pieces and the two parts are joined so the two electrolyte tapes are face to face and sintered as explained in Section 2.2.2.

2.2.4. TAAL/E/TAAL symmetrical cells

Other symmetrical cells have been prepared, in which the anode consists in a thick anode active layer, they are noted TAAL/E/TAAL. In this case the anode slurry corresponds to the composition of the anodic active layer AAL (NiO and BIT07 in the weight ratio of 55:45 and 2.5 wt.% of CB). The electrolyte and anode tapes are cast with respective thicknesses of 100 μm and 800 μm.

Schematic representation of A/E/A, TAAL/E/TAAL and A/AAL/E/AAL/A are given on Fig. 1a, b and c respectively.

2.2.5. 2A/E/2A and 2A/AAL/E/AAL/2A symmetrical cells

In order to separate the influence of the addition of the anodic anode layer and the influence of an increase of the anode thickness, symmetrical assemblies, in which two successive tapes of anode slurry of 800 μm are cast onto the electrode tape cast at 100 μm. The corresponding symmetrical assembly is noted 2A/E/2A and its realization is schematized on Fig. 1d. In the same manner, assemblies are realized by casting successively onto the electrolyte tape an AAL tape, cast a 100 and 150 μm, respectively, and two successive anode layers of 800 μm. The corresponding symmetrical assembly is noted 2A/AAL/E/AAL/2A and its realization is schematized on Fig. 1e.

2.2.6. Addition of a nickel collecting layer

In some cases and in order to check the validity of these measurements, and also to avoid false interpretations due to current

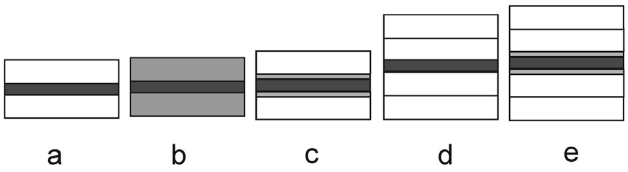

Fig. 1. Schematic representation of the different assemblies A/E/A (a), TAAL/E/TAAL (b), A/AAL/E/AAL/A (c), 2A/E/2A (d), and 2A/AAL/E/AAL/2A (e). The white, grey and black layers correspond to the anode, active anodic and electrolyte layers, respectively.