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Elaboration of intermediate size planar proton conducting solid oxide cell by wet chemical routes: A way to industrialization

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ABSTRACT

Despite significant progress in terms of electrical performances and reliability, Protonic Ceramic Cell (PCC) technology faces too many technical hurdles concerning the validation of suitable processes for making large sized cells. Thus, the wet chemical techniques have been evaluated to the preparation of complete protonic ceramic cells from laboratory to industrial scales. According to results, the combination of tape-casting/screen-printing techniques is suitable for the elaboration of larger size planar hydrogen electrode supported PCC up to 50 cm^2. Using BSCF-based air electrodes, electrochemical performances of a 20 cm^2-size BaCeZrY-PCC based cell have been reached to 0.15 W/cm^2 at 600 °C and stable during few tens of hours without electrical degradation.

1. Introduction

The high energy conversion efficiency and the low impact to the environment are part of great advantages of Solid Oxide Fuel Cells (SOFCs), which are promising devices for electricity generation. They convert directly the chemical energy from the fuel to electricity. However, most of technical issues of SOFCs remain the high operating temperatures (>700 °C), leading to accelerated ageing of materials. Since Iwahara' works in the eighties [1–3], the last decades supported the pertinence to use proton conducting ceramic cell as the new generation of ceramic-based cell technology in the operation temperature domain below 700 °C. Now, although widely investigated for a variety of applications such as electrolyte in fuel cell [4–7] and steam electrolysis [8–10], as reactor in ammonia synthesis [11–13] or as hydrogen separator [14–16], proton conducting solid oxide development remains confined to the laboratory level. Indeed, shy investigations of efficient upscaling routes have been led until now [17] and this aspect appears fundamental to approach the industrial interest.

Recently, our group evaluated the feasibility of large size planar PCC made by co-pressing method and demonstrated the technical limit of such process [18].

Here is proposed the assessment of wet chemical routes for the up-scaling step of planar hydrogen electrode-supported configuration. Microstructure and electrical performances of such cells are then investigated.

2. Experimental

Commercial powders were supplied by Marion Technologies® and Cerpotech AS. It has been selected $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (labelled BCZY8) as electrolyte with the addition of 1.2 weight percentage (wt.%) of ZnO as sintering aid, the corresponding NiO-electrolyte cermet (60:40 wt.%) as hydrogen electrode and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (named BSCF) as air electrode. The particle sizes of the as-prepared compounds are summarized in the Table 1.

The hydrogen electrode-supported cell was prepared by humid methods. The anode slurry was prepared by mixing in a Turbula® type T2F (WAB) the $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ powder in mixed solvent (MEK/ethanol) with the addition of a dispersing agent for 24 h. The binder and plasticizers were added and further milled for 3 h before a standing period of 48 h. Then, the slurry was de-aired for 15 min before casting.

The raw hydrogen electrode NiO–BCZY8 (60:40 wt.%) slurry was coated onto a polyethylene film by tape casting, and then dried for one day at room temperature. After a 10 h pre-sintering step at 1000 °C of a green tape piece in order to remove out organic reactants, BCZY8-5 mol% ZnO ink is then coated as electrolyte by screen printing. The crude half-cell was then co-fired at 1400 °C during 9 h. An ironing step at 1350 °C is necessary to free the physical curvatures encountered during the sintering step.

Finally, the air electrode is made by screen printing, composed of a first thin porous layer of BSCF/BCZY8 (80:20 wt.%) and a second layer of BSCF alone, both dispersed in 6 wt.% ethylcellulose into Terpineol mixture. After drying at 100 °C between each step, the complete assembly was fired at 1150 °C for 2 h in ambient air.

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Table 1
Particle size measurements provided by the suppliers.

Type of materials	Crystallite size (μm)
$BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$	0.4
$NiO–BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$	1–1.5
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	0.4

The cell morphologies are evidenced by electron microscopy in a field-emission scanning electron microscope.

Single cells were tested in a Fiaxell® Open Flange test stand at 600 °C under non-humidified hydrogen as fuel and non-humidified compressed air as oxidant. Electrical contacts to the cell were made using gold wires welded to a gold mesh at the air side and nickel wires melded to a nickel mesh at the hydrogen side. AC impedance spectroscopy was obtained over the frequency range from 0.31 to 10^3 Hz under open-circuit conditions and under polarization using a Solartron FRA 1255.

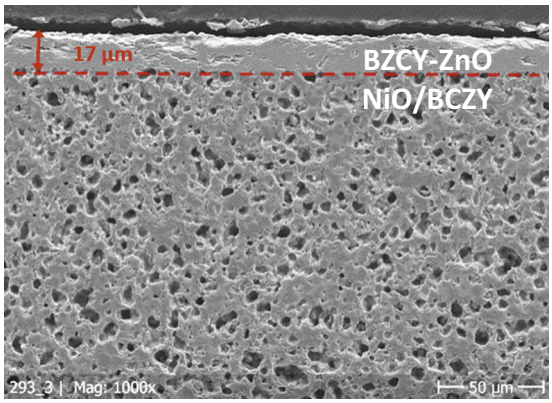

Fig. 2. Scanning microscopy cross-section of a 20 cm^2 size NiO–BCZY8/BCZY8–ZnO half-cell.

3. Results and discussion

The up-scaling of NiO–BCZY8/BCZY8-5 mol% ZnO/BSCF–BCZY8/BSCF cell fabrication consisted in increasing the size of samples from lab to industrial scale while using easy and affordable techniques. Thus, by using the wet chemical routes, a 4.5 * 4.5 cm^2 size cell has been prepared. Fig. 1 illustrates that there is no real effect of dimension for the macro-structure, the planarity and the crack-free assembly of the sample.

Microscopic observations of the half-cell show a fully densified electrolyte (more than 95% estimated by software analysis ImageJ®) with a thickness reaching nearly 17 μm which is well stuck on a homogeneous and porous anode (Fig. 2).

Electrochemical performances of typical 4.5 * 4.5 cm^2 size BCZY8–ZnO based-PCC have been assessed. Fig. 3a presents the I–V and I–P curves of such sample. High and stable Open Circuit Voltage value (~1.09 V at 600 °C) reveals a gas-tight electrolyte and chemical stability of the system under test conditions.

I–V curves are nearly linear and it can be deduced that the voltage drop of the cell is mainly coming from ohmic resistance falling across the electrolyte. A power density of around 0.14 W/cm^2 at 0.75 V is obtained at 600 °C. The total ASR of the cell (ASR_{cell}) was calculated from the slope of the I–V curve and is reported in the Table 2. The deduced conductivity of the electrolyte reaches around 0.3 mS/cm one order of magnitude lower than those raised in the literature with ex-situ measurements of pellet [19]. Such variation of values can be justified by several aspects related to set-up differences (nature of atmospheres, cell and material configurations, nature of electrodes, electrical contact troubles, etc.) but so can the non-optimized activation step of the tested cell which can induce additional contact resistances.

Impedance measurements were performed in order to study the electrochemical behaviour of the different layers. Fig. 3b shows typical Nyquist plots of the impedance data on such BCZY8–ZnO-based cell at 600 °C. The high-frequency intercept corresponds to the ohmic resistance of the single cell (ASR_{Ω}), whereas the low-frequency intercept gives the total resistance of the cell ($ASR_{cell} = ASR_{\Omega} + ASR_{Pol}$). As shown in Table 1, ASR_{cell} values obtained under dc conditions are in good agreement with EIS measurements.

In order to study the stability of as-fabricated fuel cell, endurance tests were conducted on 20 cm^2 size PCC cells. The evolution of the voltage has been recorded regarding time at 600 °C under constant current conditions (corresponding to an initial voltage of 0.8 V) (Fig. 4). A power

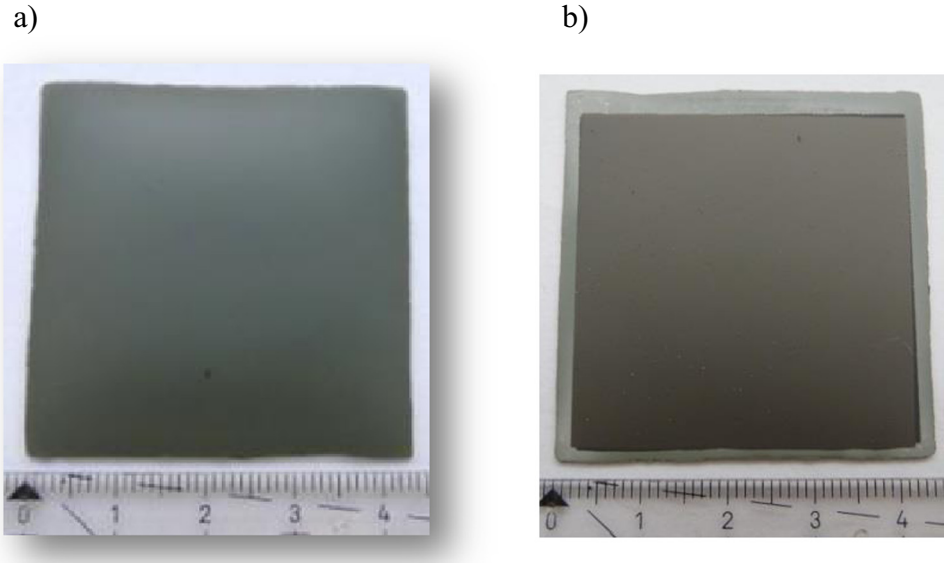

Fig. 1. a) Picture of an intermediate 4.5 * 4.5 cm^2 size NiO–BCZY8/BCZY8–ZnO half-cell co-sintered and b) the same PCC after printed BSCF–BCZY8–BSCF air electrode.

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