Development of anode supported PCFC button cells by wet chemical routes

Editorial

The 1st of December 2011 marked the start of the METPROCELL project: **Innovative fabrication routes and materials for METal and anode supported PROton conducting fuel CELLs.** It is a collaborative project funded by the Fuel Cell and Hydrogen Joint Undertaking (FCH JU) where 8 partners work together to develop a new generation of intermediate temperature fuel cells based on the Proton Conducting Fuel Cell technology.

This report summarizes the activities performed in the frame of METPROCELL in relation to the development of anode supported PCFC button cells by wet chemical routes.

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Content

1. Introduction

This report summarizes the work performed in the frame of the METPROCELL Project, in relation to the development of anode supported PC button fuel cells by wet chemical routes. The implemented electrode/electrolyte compositions as well as the related processing routes have been optimized in a previous stage of the project. Corresponding results have been published elsewhere ["Development of improved electrode and electrolyte materials for PCFCs", also available under: http://www.metprocell.eu].

Two strategies have been followed for the manufacture of small substrates for the anode-supported configuration: pressing and tape-casting. Cells based on pressed anode have been elaborated by CNRS-ICGM, while those fabricated by tape casting have been produced by EIFER. Both BCZY and $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ as electrolyte and BSCF as cathode material have been used. The deposition of electrolytes and cathode materials has been performed by wet powder spraying or by screen printing. **Table 1** summarizes the elaborated button cell configurations.

Table 1: Configuration of developed button scale cells.

Ref.	Cathode layer	Electrolyte	Anode support	Cell Geometry
C1	BSCF-BCZY WPS	BCZY-ZnO WPS	BCZY-NiO Pressing	Φ:30 mm
C2	BSCF/BSCF-BCZY WPS	BCZY-ZnO WPS	BCZY-NiO Pressing	Φ:30 mm
C3	BSCF/BSCF-BCZYYb WPS	BCZYYb-ZnO WPS	BCZYYb-NiO Pressing	Φ:30 mm
C4	BSCF/BSCF-BCZY Screen-printing	BCZY-ZnO Screen-printing	BCZY-NiO Tape-casting	4 x 4 cm^2

2. Cells Elaborated on Pressed Anodes by WPS

Wet Powder Spraying (WPS), can be considered as an attractive and alternative processing route for the facile fabrication of dense thin film electrolytes. This non-contact technique is applicable to planar surfaces or tubes with high deposition rates. Recently, YSZ, SDC or BCZY dense thin films have been successfully deposited on pre-sintered anode disc by wet powder spraying and co-firing. Moreover, WPS has been successfully used as a processing technique for forming porous gas electrodes and for protective layers.

In the work presented hereafter, NiO-BCZY(Yb) anode substrates were prepared by a dry-pressing method. In subsequent steps, both electrolyte (BCZY(Yb)) and composite cathode

layers have been deposited by WPS. Half-cells (anode/electrolyte) were co-sintered at 1200 or 1450 °C for 5 h in ambient air to obtain dense electrolyte films. The final anode/electrolyte/cathode cells were co-fired at 1050 °C for 2 h. The effective cathode area of the cell was 2 cm^2. The final sintered cells had a diameter between 2.6 and 3 cm. **Figure 1** shows the microstructure of the developed cells.

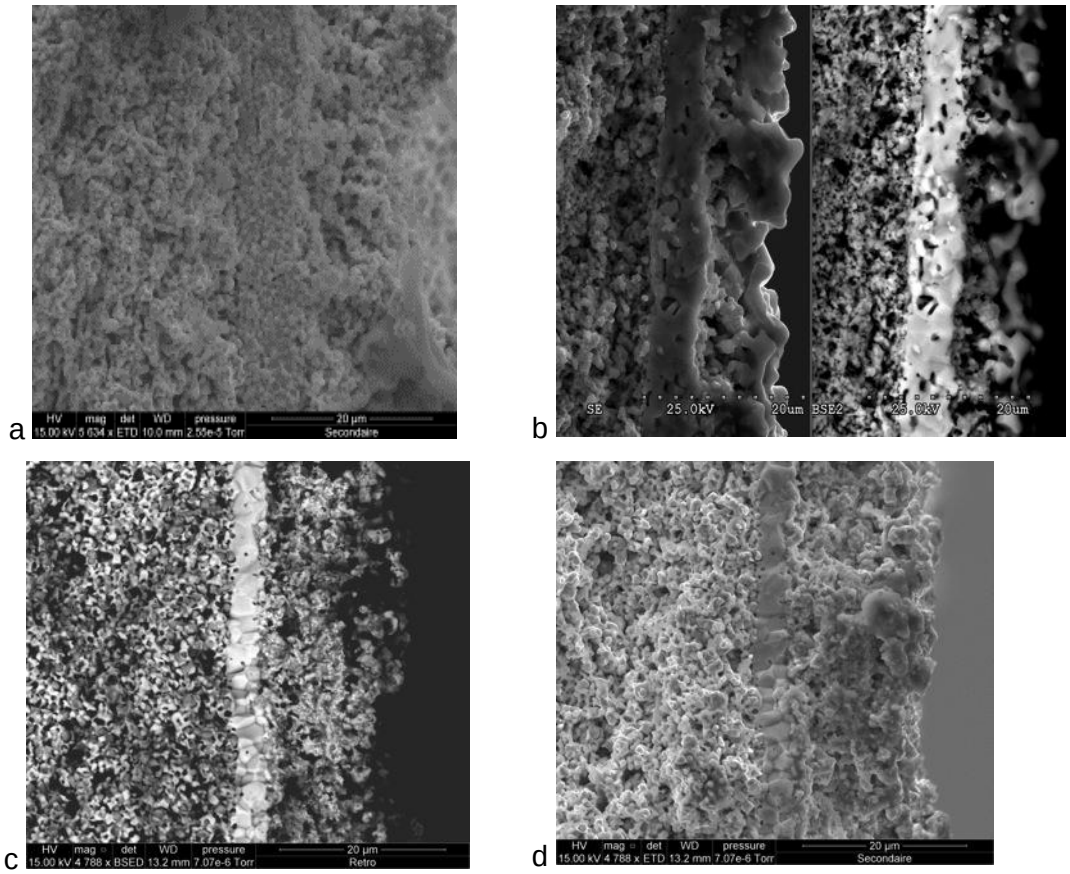


Figure 1: Microstructure of cell 1 (a), cell 2(b) and cell 3 (c and d) (see **Table 1**).

As shown in **Figure 1a**, related to cell 1, the thicknesses of the electrolyte and the cathode layers are 8 and 30 µm, respectively (after sintering). The SEM micrograph indicates that the NiO-BCZY anode and the BSCF-BCZY cathode have enough porosity for gas diffusion. The BCZY electrolyte layer is dense. There is a good adhesion between the electrolyte and the anode substrate and between cathode and the electrolyte layer.

The cross section view of cell 2 with the structure Ni-BCZY / BCZY / BSCF –BCZY / BSCF is shown in **Figure 1b**. In this case, the BCZY and the cathode films are thinner. The electrolyte is about 6 and the cathode about 9 µm thick. The bi-layered cathode adheres very well to the electrolyte.

The **Figures 1c** and **1d** show the cross-sectional SEM micrographs of the cell 3. As it can be observed, the sintering at 1300 °C allows achieving planar and crack free cell with a good adherence of the $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-d}$ (BCZYYb) electrolyte (4 µm thick) on the cermet and of the composite cathode on the electrolyte. The thickness of the bi-layered cathode layer is around 10 µm with a high porosity. BZCYYb was reported to have high ionic conductivity and sufficient chemical and thermal stabilities in H_2O and CO_2 containing atmospheres. The structure Ni-BCZYYb / BCZYYb / BSCF – BCZYb /BSCF with a thin bi-layered cathode and an efficient electrolyte seems to be very promising in terms of performances.

3. Cells Elaborated by Tape Casting and Screen Printing

Tape-casting and screen-printing are processes which are already commonly used in the industry for the manufacture of various metal-, ceramic- or other material-based products. These shaping methods could be easily automatized to produce large quantities of cells with a wide range of size (thickness, area). This section describes the manufacturing process and the morphological characterization of the configuration C4 from the **Table 1**.

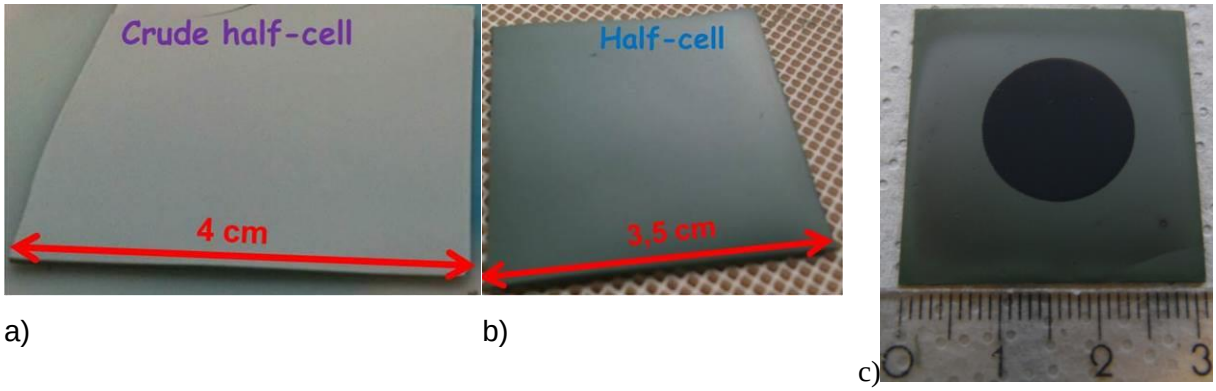
The anode substrate has been elaborated by a tape-casting process. Tape casted anodes are pre-sintered at an intermediate temperature (around 1000°C) in order to evacuate the organic compounds and to give a mechanical strength to the support (see **Figure 2**).

Figure 2: Tape casted and dried.

The electrolyte layer is then deposited by screen-printing onto the pre-sintered substrate. Subsequently, the crude half-cell are dried at 100°C and co-sintered at 1400°C for 10 hours (see **Figure 3**). Complete lab-scale half-cells (3.5 x 3.5 cm²) have been produced with good reproducibility. Finally, the cathode is deposited by screen-printing onto the half-cell. The wet cathode layer is firstly dried at 100°C during several hours, then co-fired at 1000°C for one hour.

The microstructure of half-cells has been observed by Scanning Electron Microscopy. **Figure 4** shows a cross-section of a complete PCFC cell elaborated by tape-casting and screen-printing. It reveals a crack-free dense and thin layer of BCZY electrolyte (nearly 12 µm thin), on which are well stuck both air and hydrogen porous electrode. The three networks of the anode (nickel, electrolyte and pores) are very homogeneous, meaning a great percolation of

each one. The morphological characteristics of such cells fit with the criteria required for the manufacture of fuel cells.



a) b) c)

Figure 3: a) Crude half-cell after the screen-printing of the electrolyte; b) Complete half-cell after the co-sintering step and c) Complete lab-scale cell.

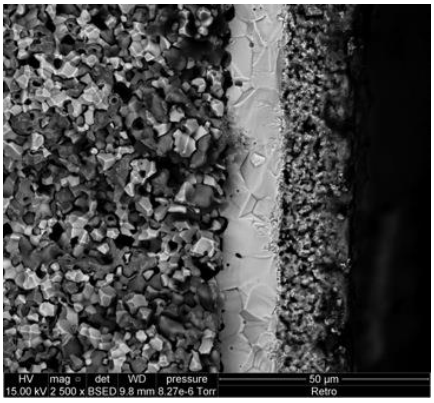


Figure 4: SEM observation of the cross-section of a lab-scale half-cell.

4. Conclusions

Two different processes have been investigated for the elaboration of la-scale cells:

- The first process consists in the deposition of the electrolyte layer by WPS on anode substrate elaborated by pressing. The cathode layer is deposited by spraying the composite cathode suspension on the sintered half-cell.
- The second process is composed of a tape-casting step to manufacture the anode substrate, followed by two screen-printing steps for the coating of the electrolyte and the air electrode.

The microstructures presented in this report are very promising and reach the objectives of the METPROCELL project. Moreover, the combinations of pressing / spraying or tape-casting / screen-printing techniques are suitable for the elaboration of larger size PCFC.

Results related to the in-situ electrochemical characterization of these cells have been published elsewhere ["Electrochemical characterization of the developed Proton Conducting Fuel Cells (PCFCs) at lab scale", also available under: http://www.metprocell.eu].

Project details

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Project cost: 3.4 million euro

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