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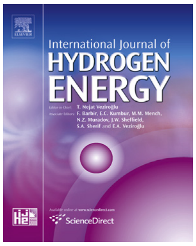

# High performance anode-supported proton ceramic fuel cell elaborated by wet powder spraying

*Gilles Taillades**, *Paul Pers*, *Visot Mao*, *Mélanie Taillades*

*ICGM UMR 5253, Aggregates, Interfaces and Materials for Energy, Université de Montpellier, Place Eugène Bataillon, 34095 Montpellier cedex 5, France*

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A B S T R A C T

Wet Powder Spraying (WPS) is a well-known method of deposition recently used for elaboration of dense electrolytes or porous electrodes thin films in solid oxide fuel cells. In this work, WPS has been used to deposit the electrolyte and cathode materials of a proton conducting ceramic fuel cell (PCFC) operating at intermediate temperature. A cell with a dense 4 μm thick $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) electrolyte, a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ – BZCYYb (BSCF-BZCYYb) composite cathode and a porous Ni-electrolyte cermet was developed and characterized. The electrolyte and the cathode materials were successfully deposited by WPS on an anode support of 40 mm in diameter. High open-circuit voltages (OCV > 1 V) were observed with this cell, and maximum power densities of 418, 532 and 634 mW $cm^{-2}$ were obtained at 600, 650 and 700 °C respectively. The results demonstrated that WPS is an attractive technique, suitable for up-scaling planar anode supported PCFC.

## Introduction

Solid Oxide Fuel Cells (SOFCs) based on an oxygen ion conducting electrolyte remain very attractive with respect to their high-energy efficiency, modularity and excellent fuel flexibility. Due to the high activation energy for oxygen ion conduction, SOFCs normally operate at temperatures above 750 °C, this high operating temperature accelerates corrosion, limits the long-term durability and increases the cost of materials. Consequently, significant efforts have been made to lower the operation temperature of SOFC and Proton Ceramic Fuel Cells (PCFCs) have attracted great interest in the last few years for fuel cell operation in the 400–600 °C temperature range [1,2]. However, the performance of PCFCs is lower than that of SOFCs and research has focused on the development of advanced electrolyte materials as a strategy to increase PCFC performance.

The most investigated high temperature proton conducting electrolytes currently are perovskites ($ABO_3$) where the tetravalent element (B) is partially substituted by a trivalent element which generates protonic defects on reaction with water vapour. The main challenge for these materials is to achieve high proton conductivity while preserving chemical stability in the fuel cell environment. Yttrium doped barium cerates (BCY) are considered as having highest proton conductivity (~$10^{-2}$ S $cm^{-1}$ at 600 °C) but they suffer from poor chemical stability under acidic ($CO_2$) and/or wet atmospheres [3] while yttrium doped barium zirconate (BZY) shows good chemical stability but its proton conductivity (~$10^{-3}$ S $cm^{-1}$ at 600 °C) is an order of magnitude lower than that of BCY because of high grain boundary resistance [4]. In order to increase stability of BCY compounds, solid solutions of BCY and BZY (BCZY) have been widely investigated [5], as well as core–shell arrangements [6], and shown to exhibit both sufficient

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* *Corresponding author*. Tel.: +33 467 144620; fax: +33 467 143304.
E-mail address: gilles.taillades@umontpellier.fr (G. Taillades).

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conductivity and stability. In 2009, Yang et al. [7] have reported high ionic conductivity for $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) and chemical and thermal stabilities in $H_2O$ and $CO_2$ containing atmospheres [8]. Indeed, at temperatures below 750 °C, BZCYYb shows higher conductivity ($5.10^{-2}$ S $cm^{-1}$ at 600 °C [9]) than either the known oxygen ion (yttria stabilized zirconia, YSZ or gadolinium doped ceria, GDC) or proton conducting ceramics. Consequently, BCZYYb seems to be potentially a very promising material for PCFC application.

In all cases, a thin electrolyte film is needed to reduce the resistance losses and to yield improved cell performance at reduced operating temperatures. For this purpose, a number of coating techniques such as Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD), Electrochemical Vapour Deposition (EVD) [10] have been developed, however these methods are either costly or complicated. Wet chemical routes, like casting or screen printing are efficient and economical but the large shrinkage due to the removal of organic additives may reduce the quality of large area thin films. Wet Powder Spraying (WPS) is 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 and has been recently used for SOFC applications. YSZ-8 [11], samarium doped ceria [12], scandia stabilized zirconia [13] or BCZY [14] dense thin films have been successfully deposited on a pre-sintered anode disc by wet powder spraying and co-firing. Moreover, wet powder spraying has been used as a processing technique to form porous gas electrodes [15] and for protective layers [16].

The primary objective of this work was to fabricate a large anode supported single cell with a high power density using $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte, ceramic composite anode ($NiO\text{-}BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$) and cathode ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}0_{3-\delta}\text{-}BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$). Both the electrolyte and the cathode were deposited by Wet Powder Spraying.

## Experimental

### Preparation of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}0_{3-\delta}$

$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}0_{3-\delta}$ (BSCF) were prepared by the flash combustion glycine-nitrate process [17]. Aqueous solutions containing appropriate molar ratios of metal nitrates and glycine were heated on a hot plate at 150 °C. Upon complete evaporation of the water, the dried mixture was placed into an oven at 600 °C to start the combustion reaction which occurred within 2–3 min. The powders obtained were annealed at 600 °C for 10 h and calcined at 900 °C for 10 h for BCZYYb and at 1100 °C for 10 h for BSCF to obtain powders of high crystallinity. A small amount (2 wt.%) of ZnO was added to the BCZYYb powder elaborated by combustion to increase its sinterability.

A NiO-BCZYYb (60:40 wt.%) composite powder was elaborated for the anode by co-combustion of BCZYYb nitrate precursors and $Ni(NO_3)_2$. For the cathode, a physical mixture of BSCF-BCZYYb (70:30 wt%) was produced by mixing the BSCF and BCZYYb prepared by flash combustion.

### Cell fabrication

The anode substrate was prepared by a dry-pressing method. NiO-BCZYYb elaborated by co-combustion was pressed uniaxially in a stainless steel 40 mm die under 200 MPa for 10 min. The resulting green pellets were pre-sintered at 1100 °C for 6 h which increases their mechanical strength and adapts their shrinkage to that of the electrolyte.

BCZYYb-ZnO was dispersed in isopropanol under ultrasonic vibration to form a stable suspension with 10 wt.% of BCZYYb. No further additives such as binders, plasticizers, or dispersants were used. The suspension was sprayed onto the pre-sintered anode substrate held at 250°C with the help of a hot plate using a Spray Coater ND-SP from Nadetech Innovations. Air was used as the carrier gas at a working pressure of 1.3 atm. The spraying nozzle was aligned vertically to the anode substrate and at a distance of 6 cm above it. The spray process was carried out with a suspension flow rate of 100 ml $h^{-1}$ and a nozzle velocity of 500 mm $min^{-1}$.

Subsequently, the anode/electrolyte half-cell was co-sintered at 1300 °C for 5 h in ambient air to densify the electrolyte film. The complete single cell was fabricated by spraying the BSCF-BCZYYb cathode suspension (8 wt.% in isopropanol) on to the sintered half-cell. The final anode/electrolyte/cathode cell was fired at 1050 °C for 2 h.

### Characterization

X-ray diffraction (XRD) was carried out on all materials synthesized by flash combustion using a Seifert diffractometer with $CuK_\alpha$ radiation. XRD patterns were recorded over an angular range of $2\theta = 10\text{–}90°$ with a step size of 0.03°. The microstructure of the single cells was observed by Scanning Electron Microscopy (SEM, FEI Quanta 200). Impedance spectra (from 0.1 Hz to 100 kHz with an AC voltage amplitude of 10 mV) and current–voltage curves were obtained using a potentiostat/galvanostat (Biologic SP150). An open flange setup from Fiaxell was used, with a Ni foam and Au grid mesh as current collectors at the anode and cathode surfaces respectively. The response of the cells using humidified hydrogen (≈3% $H_2O$) and air was investigated in the temperature range 600–700 °C.

## Results and discussion

### X-ray diffraction phase analysis

X-Ray diffraction patterns of BCZYYb, BSCF and NiO-BCZYYb after calcination in air are shown in Fig. 1. BCZYYb (Fig. 1a) shows an orthorhombic perovskite structure similar to that of the less complex $BaCe_{1-x}Zr_xO_3$ materials. As $Y^{3+}$ (0.900 Å) and $Yb^{3+}$ (0.868 Å) have similar ionic radii to that of $Ce^{4+}$ (0.870 Å), a solid solution is expected to form by doping Y and Yb into B sites. Thus, the crystal structure of BCZYYb is orthorhombic with a = 8.7477 (3) Å, b = 6.2866 (2) Å and c = 6.1988 (2) Å in agreement with the data reported by Liu et al. [8]. Fig. 1b shows

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