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Long term testing of BCZY-based protonic ceramic fuel cell PCFC: Micro-generation profile and reversible production of hydrogen and electricity

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ABSTRACT

High performing and reliable 20 cm^2 size protonic ceramic fuel cell has been elaborated by wet chemical routes (tape-casting and screen-printing) as following: Anode substrate NiO–$BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCZY81)/electrolyte BCZY81–ZnO (5 mol%)/cathode $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) – BCZY81/current collector BSCF. The cell fabrication steps were optimized to achieve power density of 165 $mW \cdot cm^{-2}$ at 600 °C for a potential E = 0.7 V. Finally, endurance test including dynamic (seasonal) power demand (micro-cogeneration profile) and reversible (electrolysis/fuel cell) cycles have been successfully performed during 3000 h. A low electrical degradation rate of $\delta V = -1.2\%/kh$ under fuel cell power cycles revealed promising reliability behaviour of such cell under flexible energy services profiles.

1. Introduction

Proton Conducting Cell (named PCC) has received significant attention in the last decade in the context of lowering the operation temperature of ceramic-based cell technologies below 700 °C. Proton conducting ceramic cell can offer also the benefit to avoid the dilution of fuel inlet by producing the water reactant at the air cathode side. This fact leads to the improvement of the overall electrical efficiency of Protonic Ceramic Fuel cell (PCFC) versus classical low temperature Solid oxide fuel cell (LT SOFC). Moreover, Proton conducting solid oxide technology could allow to be versatile in a wide range of environmental-based applications, in particular methane reforming [1] and steam electrolysis applications [2,3,4].

Among all ceramic materials studied, perovskite-based oxides keep the leadership as electrolyte or electrodes into optimized lab-scaled cell fabrication processes [5,6]. In particular, the investigation of Ba-based perovskite type oxides led to promising outcomes in terms of cell performances beyond 400 $mW \cdot cm^{-2}$ [4,7,8,9,10] and reliability for several hundred hours [7,11,12]. Even more, the stack cell research and development is now on track. Thus, the elaboration of up-scaled PCFCs by wet chemical routes recently showed pioneer electrochemical results. Power density up to 150 $mW \cdot cm^{-2}$ at 600 °C was obtained with a 20 cm^2 sized Proton Conducting Ceramic Cell using Ba-based perovskite materials without any significant degradation observed during 100 h of endurance test [13].

In the present work, $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCZY81)-based PCFC with $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ - $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BSCF-BCZY81) as composite air electrode have been investigated by studying and optimizing industrial fabrication routes: tape casting and screen-printing techniques. The electrochemical performances of single cell were evaluated at 600 °C under non-humidified hydrogen and air environment and the reliability of PCC was assessed under diverse operation conditions including dynamic load cycling demand while mimicking micro-cogeneration stationary profile and under reversible fuel cell/electrolysis cycling.

2. Experimental

Anode slurry was prepared by mixing powders ($BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCZY81) (CerPoTech A.S.)/NiO (J.T.Baker®) 40: 60 wt%), solvents (Ethanol/MEK) and a dispersing agent in a TURBULA® type T2F (WAB). After 24 h of mixing, polyvinyl butyral binder and two plasticizers were added, then the solution was mixed for 3 h. After a 1-day standing period, air was removed from the slurry using a vacuum process. The slurry was then casted on a silicon coated PET film using a ZAA 2300 automatic film applicator coater (Zehntner GmbH, Switzerland), and then dried for 12 h at room temperature, in a confined box under ventilation to help removing solvent vapors. A 10-hour pre-sintering step at 1000 °C was performed on the green samples in order to remove the organics.

Electrolyte ink was composed of ceramic BCZY81 powder (CerPoTech A.S.) mixed with 5 mol% of ZnO (Sigma-Aldrich)) in a mixture composed of 6 wt% of ethylcellulose (Sigma Aldrich) in terpineol (Alfa Aesar). Two BCZY81-ZnO layers were coated by screen-printing

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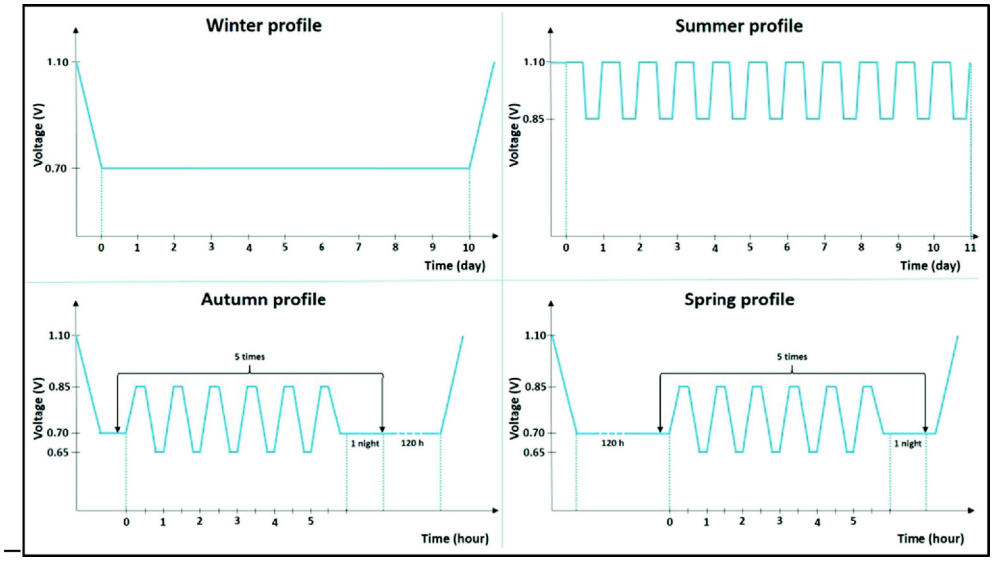

Fig. 1. Operating parameters for the micro-cogeneration profile.

onto the top of the anode substrate followed by a drying step at 60 °C before a sintering step at 1400 °C/9 h. An ironing step at 1350 °C was necessary to improve the flatness of the half-cell.

Air electrode was also coated by screen-printing. The two layers electrode was composed of a first layer of BSCF (Sigma-Aldrich)/BCZY81 (80:20 wt%) powders. The current collector upper layer was a pure composed of pure BSCF, which electronic conductivity is sufficient and chemically stable and compatible with the composite layer. Both inks were prepared as the electrolyte ink (mixture of ceramic powders with a vehicle composed of 6 wt% ethylcellulose into terpineol). After a drying step at 60 °C, the cathode was sintered at 1100 °C for 1 h.

Single cells were tested in a Fiaxell® Open Flange fuel cell test bench at 600 °C with non-humidified hydrogen as fuel and non-humidified compressed air as oxidant. During electrolysis steps, purified water was added on the air side using a neoLab® mini-pump. The current collection was performed using gold wires connected to a gold mesh at the air side and nickel wires connected to a nickel mesh at the fuel side. Electrochemical measurements (IV and IP curves) were carried out with the software CorrWare®. Electrochemical Impedance Spectroscopy measurements were obtained over the frequency range from 0.31 to 103 Hz using a Solartron FRA 1255 and the software ZPlot®. External morphologies of the cell were studied by electron microscopy in a field-emission scanning secondary electron microscope.

The micro-cogeneration cycle consists in four successive profiles corresponding to the seasonal electricity consumption (Fig. 1). Such profile has been chosen in accordance with our internal on field benchmarking experimental feedback with typical semi-commercial fuel cell-based micro-cogeneration devices. The consumption is constant and maximal during the winter (E = 0.70 V), whereas it is cyclic between no consumption and an average one in summer (E = 1.10 or 0.85 V). Both spring and autumn corresponds to cycles between full and middle consumption (E = 0.65 and 0.85 V) and a full consumption step because of the beginning and the end of winter (E = 0.70 V). During the micro-cogeneration profile, only the current density has been modified. The reversibility profile consists in successive cycles between fuel cell (E = 0.70 V) and electrolysis (E = 1.20 V) operating conditions, e.g. electricity and hydrogen production (Fig. 2). During this profile, only current density and gas conditions (water partial pressure) have been modified. Fuel cell mode was carried out at E = 0.70 V with non-

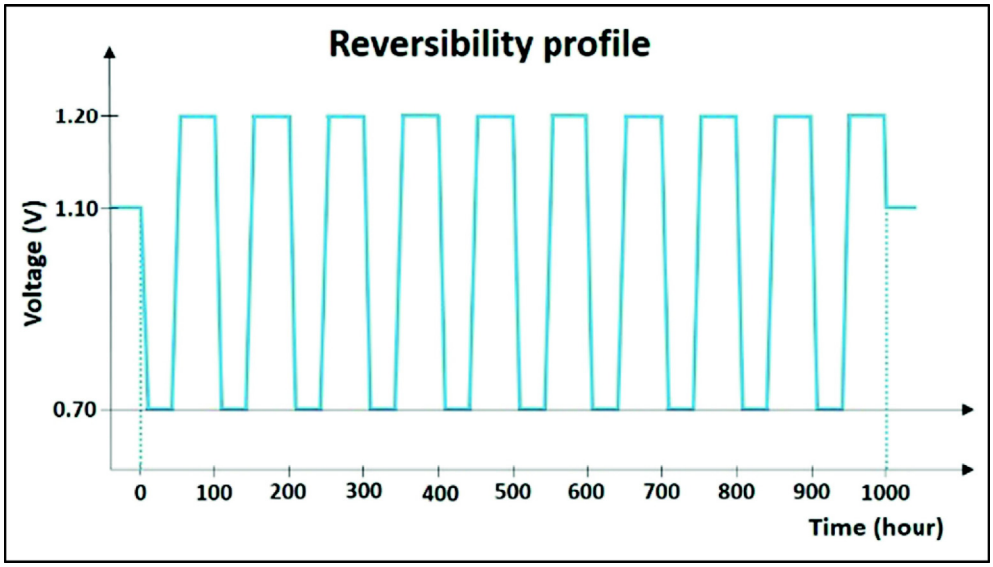

Fig. 2. Operating parameters for the reversibility profile.

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