

Electrochemical Performances of a Reversible High Temperature Fuel Cell Based on a Mixed Anionic-Protonic Conductor

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This paper deals with the fabrication and study of a high temperature solid electrolyte supporting electrochemical cell operating as SOFC and SOEC. The cell is based on the idea of a dual membrane electrolyte, which has the advantage to separate the cell in three different chambers: hydrogen side, oxygen side and dual membrane (D.M.), where water production-SOFC or splitting-SOEC takes place. The tape casted supporting electrolyte is constituted by a dense/porous/dense tri-layer, made of BaCe_{0.85}Y_{0.15}O_{3-δ} (BCY), which is a mixed ionic conductor. The electrolyte sandwich was formed by in-situ sintering of stacked green tapes with or without pore former. The process optimization (slurry formulation, lamination and thermal treatments) led to flat, crack-free, 580 μm thick BCY discs with a well-controlled microstructure. Platinum electrodes were deposited on both sides of the sandwich-structured electrolyte. The cell was then electrochemically studied under different operating conditions of temperature, overpotentials and gas feeding, either in SOFC and SOEC mode.

From the presented results it can be highlighted that despite the dense electrolyte layers were kept thick and the electrodes were made of platinum, the electrochemical study of the cell show: i) a promising power density, ii) an interesting reversibility SOFC/SOEC, iii) a proved splitting of the water contained in the porous central membrane when the cell operates as an electrolyser (SOEC). Degradation of the cell performance is also focused.

1. Introduction

Improving energy efficiency is a priority as well as diversification in energy production and supporting measures for Renewable Energy Sources (RES).

Fuel cells state-of-the-art could be indeed very promising for the low carbon economy planned for 2050, especially if carbon free hydrogen produced through renewable, nuclear or CCS methods will be widely available. Regarding this last point, SOFCs may produce a very flexible power output, in terms of high-grade waste heat that can be used in big production power plants as well as in domestic production, allowing the modulation of the ratio heat/electricity between wide ranges independently from sizes. High temperatures working conditions results in very high efficiencies even when they operate in reverse polarisation, as solid oxide electrolyzers (SOEC). This capability to work in reverse mode, besides their strong ability to work inside a distributed power generation, makes them suitable to be integrated in Hydrogen Production Units with renewable energies in both autonomous and grid-connected systems.

As regards the reduction of the investment costs, which is one of the "key-point" for fuel cells energy market penetration, it is noteworthy the advancements made on the use of proton-conducting ceramics such as Barium cerate-based oxides, instead of the oxide-conducting electrolytes (gadolinia-doped ceria and yttria-stabilized zirconia). These ceramics exhibit protonic conductivity at intermediate temperatures, in the order of 500-650 °C, and advantageously both in SOFC and SOEC mode hydrogen is not water

vapour diluted in the fuel electrode. Stability of this type of ceramics is still an open issue, however, the opportunity to work at lower temperatures reduces drawbacks related to mismatches among materials, sealing between cells and materials selection (interconnects) in stack systems, as well as problems related to long-term chemical stability and compatibility between the layers components.

Functional-graded or sandwiched ceramic multilayers are well-known structures used to effectively modulate the mechanical, thermal and electrical properties along the thickness of the final device. This study deals with the preparation of a cell which allows the separation of the main gas streams (hydrogen, oxygen and water) thanks to a particular cell design, in which the electrolyte includes a volume dedicated to the production/feeding of water through a dense-porous-dense electrolyte architecture. In particular, it will be shown the possibility to produce the sandwiched structure, based on $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3.5}$ (BCY), by tape casting.

In this work the sandwich structure was formed by in-situ sintering layer-stacked green tapes with or without this pore former. Doing so, a dense/porous/dense BCY sandwich with a controlled microstructure was obtained and electrochemically characterized. Using only one ceramic component (BCY) for all the layers, taking advantage of its mixed conductivity, helped to reduce the problems related to mismatches during the thermal processes.

The final aim of this work is to analyse the behaviour of the electrochemical cell, both in SOFC and in SOEC mode, having such supporting dual membrane coated with simple Pt electrodes, in different operation conditions, which can occur in a flexible system. The effective role, played by the dual membrane in the fuel cell and electrolyser mode of the cell is the central point of this research.

2. Experimental

2.1 Preparation of the cell

BCY powders ($\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3.5}$) with $d_{50} = 0.25 \mu\text{m}$ were supplied by Marion Technology (France) while Rice Starch (RS, Fluka, Germany), with average particle size of $5\text{--}6 \mu\text{m}$ was used as sacrificial pore-forming agent. The amount of pore former was fixed at 30 vol.% respects to the BCY powders.

The slurries were prepared by adding to the starting ceramic powders the desired amounts of solvent (azeotropic mixture of ethyl alcohol and methyl ethyl ketone, Sigma–Aldrich), deflocculant (glycerine trioleate (GTO), Fluka), binder (Butvar B98, Monsanto Co., St Louis, MO, USA) and plasticizer (Santicizer 160 Monsanto Co., St Louis, MO, USA). The ball-milled suspension was deaerated under vacuum and cast on a moving Mylar carrier ($v=6 \text{ mm/s}$) obtaining, after solvent evaporation, green tapes with the desired thickness. The green tapes with or without pore former (T-BCY+RS and T-BCY respectively) were punched in discs of 40 mm diameter.

A uniaxial warm press was used to laminate the different green tapes. One T-BCY+RS disc was sandwiched between two T-BCY layers, stacked between polished parallel steel plates and heated for 15 min at different temperatures. During the thermal treatment a constant loading was maintained. The BCY multilayers were finally debinded and sintered at different temperatures. The microstructure of the as-sintered samples was investigated by Scanning Electron Microscopy (SEM, Leica Cambridge Stereoscan 360). Samples for electrochemical characterization were electroded, screen printing a Pt layer on both sides.

2.2 Electrochemical characterisation

The cells were placed in a rig inside an alumina shoe sliding over an alumina supporting tube inserted in a tubular furnace. Measurements were carried out between 600 and 800 °C, at different polarisations and varying oxygen partial pressures. The temperature was checked by a thermocouple placed close to the cell (1 cm). The cell was connected to the electrochemical instruments through platinum wires, which were shielded to reduce noise. EIS and potentiodynamic measurements were conducted for electrochemical investigations using an AUTOLAB (PGSTAT302N) over a 0.1 Hz to 100 kHz frequency range, with 20 mV A.C. signal amplitude, at equilibrium potential and under polarisation conditions. Linearity of the impedance response was checked before fixing the signal amplitude. The cell was left at the highest temperature for 24h before starting the measurements.

Inductance correction of the cell rig and wires was performed to the electrochemical data. After the electrochemical investigation, the cells were analysed by Scanning Electron Microscopy (SEM), to check electrode thickness uniformity and other relevant morphological features.

3. Results and discussion

The tape-cast slurry formulations were optimized to obtain 400 μm thick BCY green tapes (T-BCY) for the dense layers, and 80 μm thick T-BCY+RS for the porous membrane. The effect of the lamination temperature was evaluated.

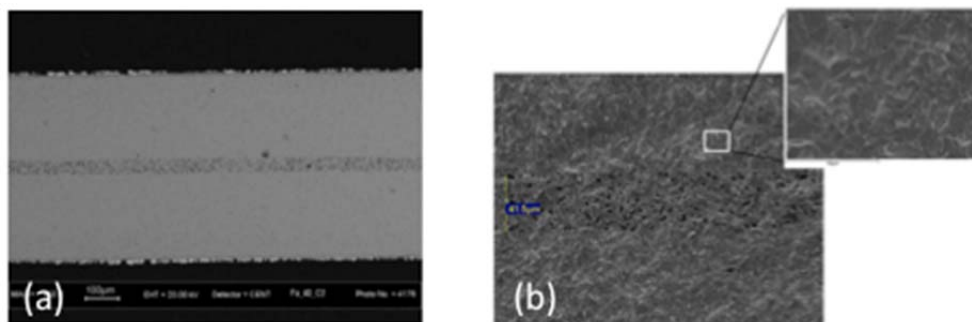


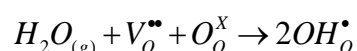
Figure 1: SEM micrographs (a) and enlargement (b) of the multilayer fracture surface of sample S40. The white layers visible in (a) are the Pt electrodes.

A thermo-compression at a temperature lower than 60°C leads to poor adhesion among the layers. Only the combination of 60°C with a pressure of 7.3 MPa allowed to produce green multilayers with good interlayer adhesion without squeezing defects. Both single tapes and multilayers were debinded using a slow thermal cycle to avoid any cracks or deformations due to the organic elimination.

In order to assess the best sintering conditions needed to make dense the two external layers and at the same time to preserve a porous central membrane, the single tapes of each composition were sintered at temperature between 1300 and 1400°C for 4 hours. To obtain highly dense BCY, the multilayers had to be sintered at the highest temperature (1400°C for 4h). Flat, crack-free, 570 μm thick dense/porous/dense BCY multilayers were obtained at those sintering conditions. The SEM micrograph of the fracture surface (Figure 1(a) and 1(b)) shows how a 40- μm thick porous layer is perfectly sandwiched between two properly dense layers. Moreover it is worth to observe the perfect adhesion of the three laminated layers. To evaluate the porosity amount of the DM porous central membrane, a multilayer constituted of ten T-BCY+RS discs was thermally treated at the same conditions and characterized by mercury intrusion technique. The open porosity of the DM measured with this method results as high as 16 vol%. A similar procedure was used to form samples with 80- μm porous DM thick.

The cell was fed with hydrogen (humidified 3 vol. %) and air and some preliminary impedance measurements were performed. Since the temperature was firstly risen to 900°C in order to sinter the platinum electrodes on site (with the electrical contacts in position), impedances were recorded at high temperature first. From an initial value of the polarization resistance of the system of about 2,2 ohm cm^2 , in few hours the impedance decreased to 0,8 ohm cm^2 . This activation process (Figure 2) of the cell has been observed in all the tested samples. Besides to this phenomenon also the high frequency part of the plot showed a shift to lower values, likely due to the progressive water uptake in the BCY electrolyte from the humidified hydrogen.

The mechanism of proton conductivity in perovskite oxides has indeed been demonstrated by Iwahara and co-workers and detailed by Kreuer, to be due to free proton migration. Proton defects are formed by the dissolution of hydrogen from the water molecules contained in the gas atmosphere and behave the charge carriers. The mechanism can be written according the Kroger-Vink notation:



where $V_O^{\bullet\bullet}$ is the oxygen vacancy, O_O^X the oxide ion at normal lattice site and OH_O^{\bullet} is the hydroxide ion.

The i-V curves of the cells show an interesting behaviour if compared with literature, in fact a power density of 16, 53 and 123 mW cm^{-2} at 600, 700 and 800°C is obtained respectively for S40 (Figure 3). The linear trend of the i-V curve at 800 °C highlights that ohmic constrain controls the overall process. This is in agreement with the fact that even if electrodes nature is very basic the thickness of the tri layers electrolyte constitutes the main obstacle for the current flux. At 700 and strongly at 600 °C, the curves behaviour of S40 is influenced by the poor electrode performances.

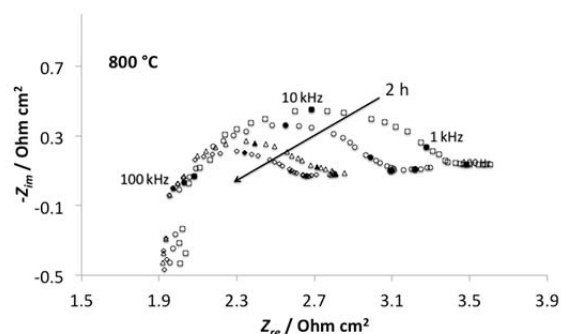


Figure 2: impedance spectra at 800 °C before and after activation of the cell. $CM = 80 \mu m$ (S80).

Considering that it is expected that water is formed in the central membrane, the processes take place spontaneously till the potential difference of the cell approach zero volts, while they are forced when the cell potential is externally pushed to negative values. This means that the consumption of hydrogen at the anode and oxygen at the cathode is forced by current to produce more water than that naturally obtainable. This test has been carried out with the aim to verify the evacuation of the water from the porous and space limited central membrane. If water diffusion from this volume became the controlling process a deviation from linearity of the i - V curve has to be observed. The results show that also in the “forced” regime (reversed polarisation) diffusion phenomena are not controlling the overall process. Only in the final part of the curve (Figure 4 (a)) the fluctuation of the current for a fixed potential highlights a partial flooding of the dual membrane by water vapour.

Because one of the advantage of this cell concept is to separate the three main involved processes, i.e. anodic reaction, cathodic reaction and water formation, in three separated cell compartments, it gains great interests the reversibility from SOFC to SOEC. With this characteristic, potentially, in SOEC mode the water is provided in the porous central membrane, where is split in hydrogen and oxygen ions transported by the forced electric field respectively at the cathode to produce hydrogen and to the anode to produce oxygen. To verify that this process takes place, the filling of the porous DM by water has been obtained through a potentiostatic polarisation at 0.2 V of cell potential difference (i.e. high current density in fuel cell mode), by feeding hydrogen and air at the respective electrodes. This “pre-conditioning” has been continued for 15 minutes. After this, the OCV was checked (around 1 volt depending on T) to ensure no leakages or cracks of the cell and the gases where changed feeding only nitrogen at both side of the cell. The washing of the fuel and air in the respective compartments by nitrogen, progressively shifts the OCV to zero volts. In this conditions the water, trapped into the dual membrane during the pre-conditioning, presumably constitutes the reservoir for the formation of hydrogen and oxygen, if enough electrical energy is supplied in SOEC mode and the cell concept works. The electromotive force was then raised by reverse potentiodynamic polarisations.

The results obtained under nitrogen fluxes with and without preconditioning of the central membrane are displayed in Figure 4 (b), which shows i - V curves with the cell operating in SOEC mode, at different starting conditions.

Curve a) shows the current measured in the cell in absence of water trapped in the C.M. The current registered has to be ascribed to the presence of oxygen and humidity in the gas lines due to their diffusion trough the nylon walls of the gas tubes (riksan) or trough the cell sealing. In this case oxygen is reduced in the cathodic side of the cell, transported to the other side under migration thanks to the mixed conduction of BCY and oxidised at oxygen with a measurable current. When the same polarisation is performed after the DM conditioning (curve b and c) the current observed is significantly increased, for instance at 1,5 volts curve a) displays a value of 52 mAcm^{-2} and curves b) and c) about 65 mAcm^{-2} . This increase of the current is a clear demonstration that water in the dual membrane is split. Oxygen reduction and oxidation maintain their regime but are accompanied by the mechanism shown in Figure 5 c).

To find support to this interpretation, some amperometric measurements were performed in SOEC mode, with and without “pre-conditioning” of the DM. The current, extracted at different temperatures, was plotted versus time and the results (sample S40) are shown in Figure 6 (a), (b). Dry or wet N_2 was fed at both the electrodes and the current was measured at a the cell potential difference of 1.5 V. Figure 6 (a) shows the current measured at 600 °C by feeding dry nitrogen, after pre-conditioning of the DM (dotted line), or when no saturation had been carried out (dry DM, continuous line).

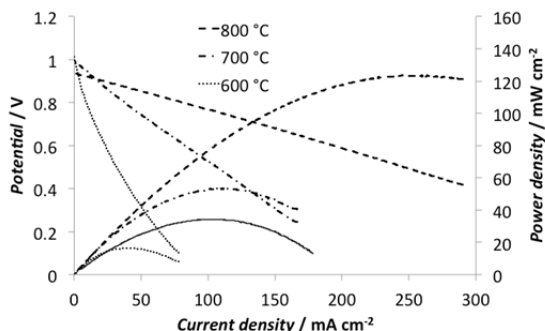


Figure 3: *i*-*V* curves at 600, 700 and 800 °C obtained from sample S40.

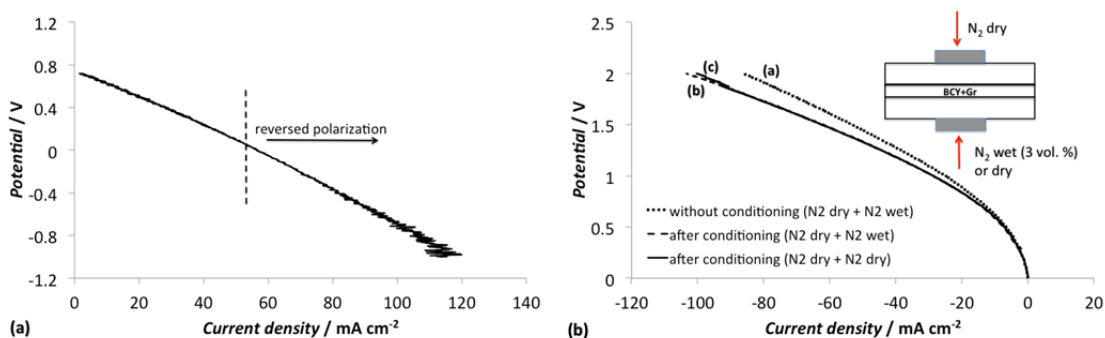


Figure 4: (a) potential vs current extracted in SOFC mode (up to 0 V) and in reversed polarisation (0 to -1 V). (b) Polarisation curves of under nitrogen flux, without (a) pre-conditioning of the CM, and after (b), (c) pre-conditioning of the CM. Sample: S80.

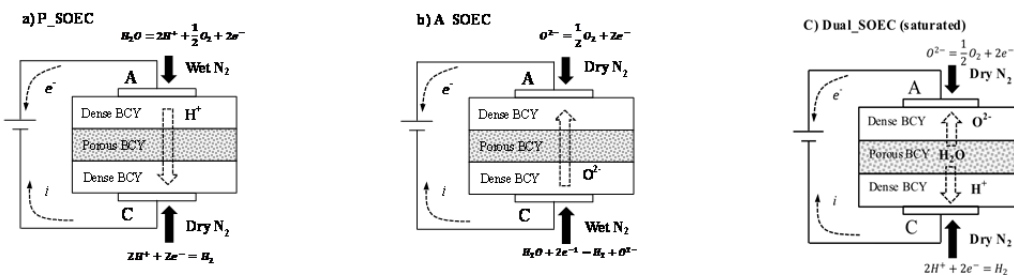


Figure 5: schematic representation of the cell mechanisms, a) and b) in absence of CM pre-conditioning, c) after CM pre-conditioning.

In these gas conditions the only reactive species was the water inside the DM; if the water splitting would take place (see Figure 5 (c)), it was expected that the current measured at the beginning with the wet DM would be higher than the case of the dry DM. And actually this is highlighted in the picture (Figure 6 (a)). When the water inside the DM was widely consumed, the two systems became similar and the currents trends started to converge, presumably due to the water splitting of water molecules coming inside the DM from the atmosphere surrounding the cell. When humidified nitrogen (3 vol. %) was fed (Figure 6 (b)), the cell could operate also like a protonic (water at the oxygen electrode) or/and an anionic (water at the hydrogen electrode) electrolyzer (see Fig. 5 (a) and (b), respectively). At the beginning of the measurement, the two currents showed the same values, since the current flow was likely due by the water splitting and in both cases the DM was wet.

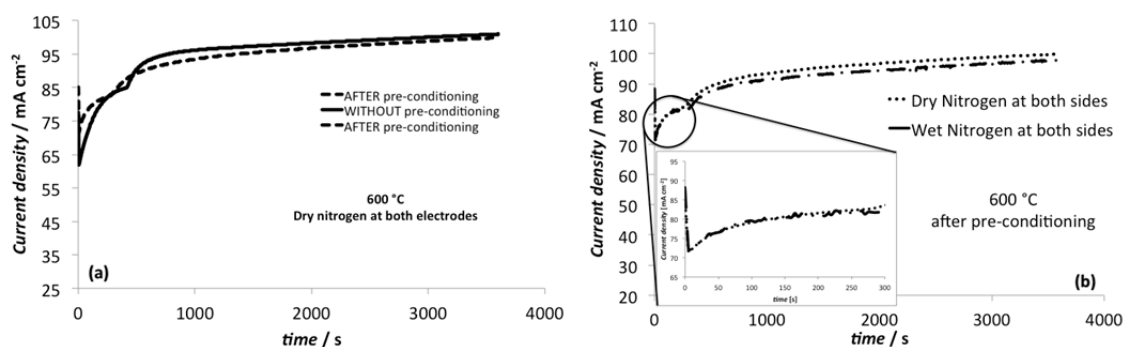


Figure 6. Current measured versus time at 600 °C in SOEC mode. Operating conditions: (a) dry N₂ fed at both the electrodes, wet DM (dotted curve) and dry DM (continuous curve); (b) dry DM, dry N₂ (dotted curve) and wet (H₂O, 3 vol.%) nitrogen (point-line curve). Working point: potential difference at the cell: 1.5 V.

When water accumulated in the DM was consumed, other H₂O molecules adsorbed into the DM continued to be split, but in the case wet nitrogen feeding, other protons and oxygen ions migrated inside the dense layers because of the water reduction (at the oxygen electrode) and/or oxidation (at the hydrogen electrode), so that a recombination of water occurred at the interphases electrolyte/DM, causing a decreasing in current output (Figure 6 (b)). After such type of electrochemical investigation the cells begin to experience degradation in performances. An observation of the cell post-mortem cross section showed extensive compositional defects. It was observed in some tested samples, whose results are not here presented, the presence of cracks inside the two dense layers, close to the dual membrane side, which originally in cells belonging to the same fabrication batch were instead limited in amount. These defects are likely to be ascribed to mechanical stresses induced during the water formation in the electrolyte layers, when the cell operated as SOFC at high current density.

4. Conclusions

The aim of this study was to explore the behaviour of a new solid oxide cell concept, able to separate water produced-SOFC or consumed-SOEC from the hydrogen and oxygen fluxes. Using only one ceramic component (BCY), taking advantages from its double conductivity, resulted in simplifying fabrication issues. The obtained results suggested that through a system geometry optimisation promising results in terms of power and reversibility could be achieved.

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