

Reversibility in monolithic dual membrane fuel cell

D. Vladikova^{1,*}, Z. Stoynov¹, A. Chesnaud², A. Thorel², M. Viviani³, A. Barbucci⁴, Ch. Nicoletta⁵, A. Bertei⁵, G. Raikova¹, P. Carpanese⁴, M. Krapchanska¹

¹ Institute of Electrochemistry and Energy Systems - Bulgarian Academy of Sciences, Sofia, Bulgaria

² Centre des Matériaux, Mines-ParisTech, Evry Cedex, France

³ Institute for Energetics and Interphases (IENI-CNR), National Research Council, Genova, Italy

⁴ Department of Chemical and Process Engineering (DICHeP), University of Genova, Genova, Italy

⁵ Department of Chemical Engineering, Università di Pisa, 2 Largo Lucio Lazzarino, 56126 Pisa, Italy

Received February 19, 2014; Accepted April 12, 2014

A promising direction in the development of solid oxide fuel cells (SOFC) is the reversible approach in which the device operates as a fuel cell and as an electrolyzer. A serious problem is the asymmetry of the system when operating in the two modes. A definitive breakthrough is the separation of the water production/consumption from the two electrodes. For fuel cell mode this idea has been realized in the innovative concept of the dual membrane fuel cell (dmFC). The cell consists of three independent chambers for hydrogen, oxygen and water. This work presents the reversibility studies of the dmFC. The first results are very promising. They show good reversibility without application of a special catalyst for enhancement of the water splitting.

Keywords: dual membrane fuel cell, fuel cell/electrolyzer, mechanistic model, reversible mode

INTRODUCTION

Fuel Cells and Hydrogen are part of the portfolio of technologies with expected contributions in the development of a sustainable and secure energy supply system in the medium and in the long-term strategic plans. The integration of a large share of renewable sources in the electricity production mix is one of the most crucial issues of the transformation into a low-carbon energy system. The development of efficient and cost competitive solutions for storing this renewable electricity in large quantities and for longer terms is one of the main priorities of the global energy policy. Hydrogen, as an energy carrier, is expected to play a key role in linking energy storage and power generation, in both transportation and stationary systems.

A promising direction in the development of high temperature fuel cells is the reversible approach in which the device operates as a solid oxide fuel cell (SOFC) and as an electrolyzer (SOEL), i.e. as an energy conversion/storage device. This mode of operation is very attractive for coupling with RES which usually require energy storage to meet specific power demands. However, still limited efforts are registered in reversibility studies [1,2].

SOEL and SOFC concepts are similar regarding materials and geometries. However, even if the systems are very close and can be operated in the same range of temperatures, optimum operation parameters may differ significantly, in particular in terms of current density, which is much higher in SOEL regime. In spite of the fact that the same global chemical reaction is used ($2H_2 + O_2 \leftrightarrow 2H_2O$), existing high temperature fuel cell systems and electrolyzers based on both SOFC and proton conducting pSOFC are strongly asymmetrical systems, with the production/consumption of water at the anode or cathode, respectively. This may cause implications concerning materials, microstructure, design, ageing, which introduces some constraints in the development of reversible systems.

A definitive breakthrough in the design would be the separation of the water production/consumption from the two electrodes where hydrogen and oxygen are generated and evacuated, without increase of the cell ohmic losses. This idea has been realized for the fuel cell mode in the innovative concept of the so called dual membrane fuel cell (dmFC), recently developed and proved [3-5]. The kernel of the new design is the introduction of a porous mixed ion conducting junction (central membrane CM) between the anode part of a pSOFC where protons are produced and the cathode part of a SOFC which produces oxide

* To whom all correspondence should be sent:

E-mail: d.vladikova@bas.bg

ions. The two types of ions meet in the CM, where water is produced and evacuated (Fig. 1). Thus the cell consists of three independent chambers for hydrogen, oxygen and water which could be separately optimized.

At electrolyzer operating conditions the steam should enter in the central membrane and split into protons and oxide ions. The two types of ions will propagate towards their respective electrode/electrolyte interfaces driven by potential/concentration gradients, where they will be transformed in the corresponding gases and evacuated through the porous electrodes structure.

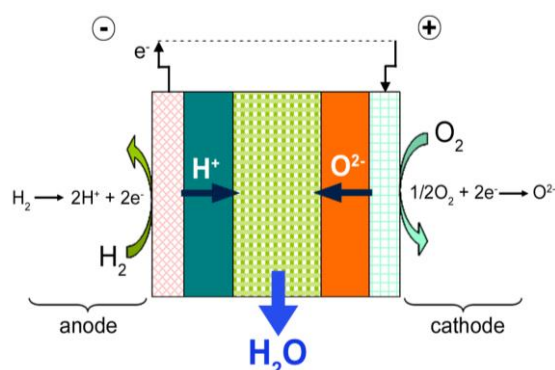


Fig. 1. Representation of the Dual membrane Fuel cell concept

The dmFC was proved [3,4] with cells in which the mixed conductivity of the CM was ensured by a composite of the two applied electrolytes: $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2.925}$ (BCY15) and $\text{Ce}_{0.8}\text{Y}_{0.15}\text{O}_{1.925}$ (YDC15). However, the application of composite structure decreases the effective triple phase boundary (BCY/YDC/pore) length and increases the ionic transport pathway tortuosity which causes enhancement of the CM internal resistance. Additional difficulties arise from the difference in the sinterability and thermal expansion of the two materials. The best solution towards optimization of the dmFC should be the replacement of the composite with a mixed ion conducting single ceramic phase.

BCY15 is well known in the literature as a good proton conductor [6,7]. Our conductivity measurements registered high proton and oxide ion conductivity at fuel cell operating temperatures. This result opens a pathway for the development of a new generation of dmFC in which YDC15 in the composite CM is replaced by BCY15. A total replacement of YDC with BCY, i.e. a “monolithic” design would strongly simplify the technology and the construction [8].

At electrolyzer mode the advantage of water splitting in the proton conducting material, which has natural properties to dissociate absorbed water,

is combined with absence of contact between the steam and the electrodes, and thus with no influence on their catalytic activity and thermo-mechanical stability, which is critical for the system durability. This work is focused on the development and first reversibility studies of the monolithic dual membrane fuel cell design. BCY15 pellets tested in water (temperature range 20-600°C) by differential thermal analysis and thermogravimetry combined with mass spectroscopy showed good chemical stability [9], which proved the applicability of this material for the performed investigations.

EXPERIMENTAL

The innovative part of the dmFC is the central membrane which has to combine high ionic (oxide ion and protonic) conductivity in the presence of sufficient porosity. The conductivity studies of the monolithic (porous BCY15) CM were successfully realized with the design of symmetrical CM supported half-cell Pt/BCY15porous/Pt. Fine powders ($d_{50} = 0.2 \mu\text{m}$) of $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2.925}$ (BCY15), prepared by the oxalate precipitation route, and delivered by Marion Technologies, were used. Previously estimated optimal porosity of about 30 v%, was ensured by applying graphite (TIMCAL, Switzerland) as pore former [10]. CM pellets with diameter ~ 2 cm and thickness ~ 2 mm were cold pressed and sintered at 1300°C for 5 hours. Platinum (Metalor) electrodes were painted and sintered in air following a procedure recommended by the producer. Since the studies concern the electrolytes part of the cell, including the CM, the application of Pt electrodes eliminates eventual influence of the electrodes composition and deposition technology on the electrolytes behaviour [11,12].

The electrolytes-central membrane assembly (ECMA) BCY15dense/BCY15porous/BCY15dense (ECMA) of monolithic button cells with diameter about 22 mm and thickness 1 to 2 mm was prepared by single stage cold pressing and sintering at 1300 °C for 5 hours (Fig. 2) and by platinum electrodes deposition.

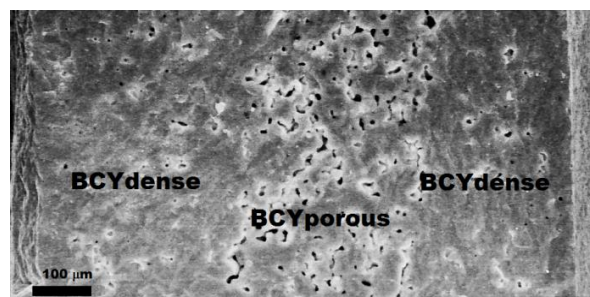


Fig. 2. SEM image of electrolytes-central membrane assembly (thickness 1,1mm)

The impedance measurements were performed on Solartron 1260 FRA in the temperature interval 100 – 800°C and frequency range from 10 MHz down to 0.01 Hz with a density of 5 points/decade and different modes and amplitudes of the AC signal. For registration and evaluation of the mixed ion conductivity, the half cell measurements were carried out at OCV in air (30 NmL/min) and in wet (3% H₂O) hydrogen (30 NmL/min). In order to acquire as much information as possible a wide frequency range was applied – from 10 MHz down to 10 mHz. During temperature scanning, the samples impedance changes from hundreds of megaohms down to milliohms. For data quality improvement different modes of operation were used [4]. At lower temperatures where the resistance of the sample is high the measurements were performed in potentiostatic regime with AC signal 20 – 200 mV, obeying the requirement for linearity. At high temperatures, where the sample's impedance is low, optimal galvanostatic mode was used. The impedance of the monolithic cells was measured in galvanostatic mode.

The low impedance at high operating temperatures increases the influence of the cell rig parasitic inductance and resistance and decreases the accuracy of the electrolyte resistance evaluation. For more precise analysis a procedure for parasitic inductance and resistance correction based on a previously developed algorithm [13,14] was applied.

RESULTS AND DISCUSSION

BaCe_{0.85}Y_{0.15}O_{2.925} is a good proton conductor [6,7]. Under humidified hydrogen atmosphere protonic defects are formed by dissociative absorption of water in the presence of oxygen

vacancies. Water vapor dissociates into a hydroxide ion which fills an oxide-ion vacancy, and a proton that forms a covalent bond with lattice oxygen, i.e. two proton defects are created stoichiometrically [14]. However, the presence of oxide-ion vacancies could be regarded as a precondition for oxide ion conductivity. Since mixed protonic and oxide ion conductivity is a phenomenon out of the scope of the classical SOFC and pSOFC applications the available information is an exception, rather than a rule [15,16]. For BaCe_{1-x}Y_xO₃, predominant protonic conductivity up to 700°C for x = 0.10 (BCY10) is reported, while for x = 0.25 (BCY25) mixed conductivity is found above 550°C [17]. For the development of the monolithic approach it was challenging to test the conductivity of BCY15 in hydrogen and in air. Impedance measurements on symmetrical half cells with dense and porous BCY15 (Fig. 3) confirmed high proton and oxide ion conductivity at operating temperatures. This result was a starting point for the development of the so called “monolithic concept”.

The replacement of the porous composite CM with a single phase of BCY15 should be *a priori* more efficient because it substitutes the triple phase boundary points with two-phase (ceramic/pore) boundary, decreases the pathway tortuosity and thus the cell ohmic resistance. Since solid-solid interfaces between different phases are expected to be the most resistive, their minimization by employing only one ionic conductor would be more effective. The 3-layered monolithic assembly - proton conducting electrolyte/mixed conducting porous CM/oxygen conducting electrolyte built from a single material with mixed conductivity should work as an oxide ion conductor in the

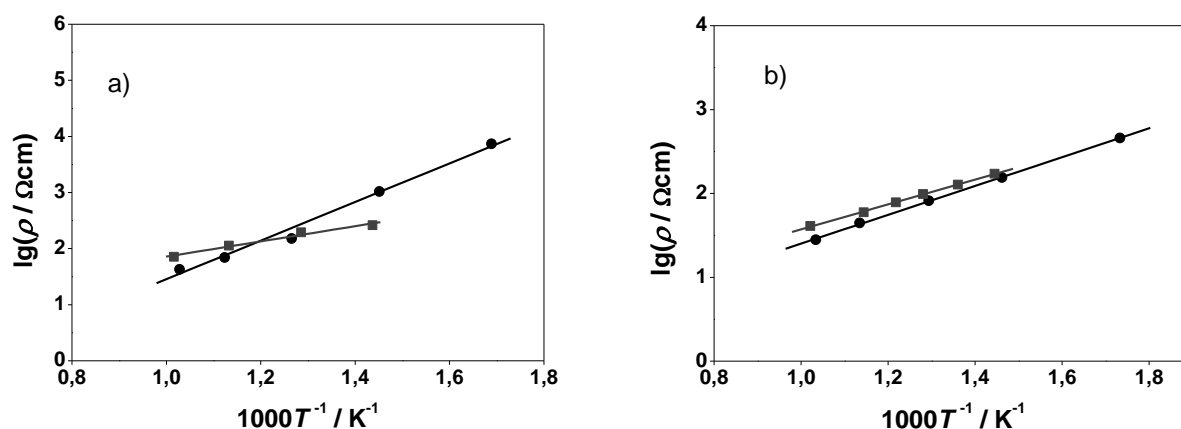


Fig. 3. Arrhenius plots of: a) dense BCY15; b) porous BCY15 measured in dry air (●) and wet hydrogen (■)

oxygen space, as a proton conductor in the hydrogen area and as a mixed conductor in the CM [8]. Experimental results obtained on the monolithic design are shown in Figure 4, which presents the current density/voltage and current density/power curves for cell with ECMA thickness of 1.1 mm (electrolyte I ~ 500 μm, CM ~ 200 μm; electrolyte II ~ 400 μm). The results are very promising - at 750°C power density of 86 mW/cm² is registered.

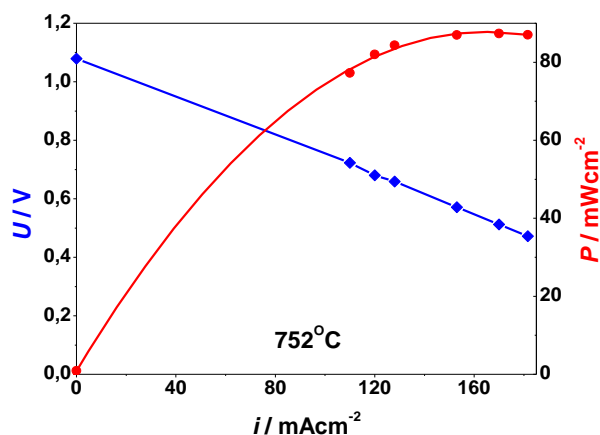


Fig. 4. Current density/voltage(■) and current density/power (●) curves of monolithic cell with thickness 1.1 mm (■) at gas flow 90% wet hydrogen and 90% oxygen

A separation of the ECMA resistance and the polarization resistance was performed based on the impedance measurements. If we accept that the polarization resistance is independent of ECMA thickness, a recalculation of the total cell resistance and the maximum power density can be done for thinner layers (Fig. 5). The results are very encouraging – the values exceed the best experimental results reported in the literature for pSOFC studies [18-20].

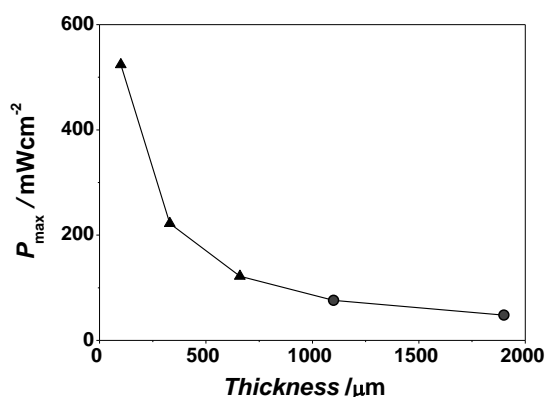


Fig. 5. Calculated values (▲) of the monolithic cell maximum power density (P_{max}) for thinner configurations based on the measured data (●)

Since BCY15 has the natural property to split water (Eqn.1), it was supposed that the monolithic design would have a good performance as an electrolyzer. Water behavior studies in porous BCY15 membrane performed by complex permittivity measurements registered gigantic enhancement of the real component of the capacitance [21]. This phenomenon was connected with the formation of a semi-liquid dipole layer. The configuration of electrochemically active volumetric layer at the pores' surface in the CM would additionally improve the performance of the monolithic dmFC in electrolyzer mode [21]. For confirmation of this hypothesis, a specialized experiment was performed in which the cell was forced to behave periodically as a fuel cell and as an electrolyzer changing the operation mode. Under cathodic current the cell works as a fuel cell, filling the pores of the central membrane with the produced water. Under anodic current, the water from the pores splits to protons and oxide ions, propagating through the hydrogen and oxygen compartments, respectively.

The obtained results of operation in reversible mode are presented in Figure 6. They show good reversibility without application of a special catalyst or water vapour pressure for enhancement of the water splitting. The electrolyser mode of operation is characterized with lower overvoltage and thus with lower internal resistance. The performed experiment confirms the applicability of the monolithic dmFC design for operation in reverse mode.

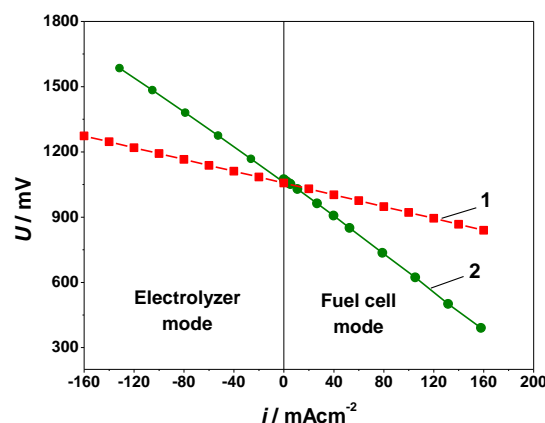
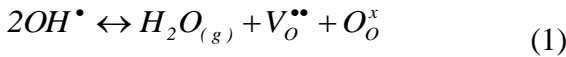


Fig. 6. Current density/voltage curves of monolithic dual membrane cell (● - measured) and central membrane (■ - calculated) in electrolyzer and in fuel cell operation mode at 700°C

The proof of the monolithic concept and its operation in reverse mode opens a new direction towards improvement of the performance. It is obvious that thinner cells should be produced.

However, in addition to the decrease of the electrolytes thickness, the CM should be optimized in respect to thickness and microstructure. For acceleration of the optimization towards operation in reverse mode, a mechanistic model of transport and reaction is under development. The first step concerns the CM. Since the CM is a porous layer of a mixed proton and oxide ion conductor, the model takes into account the following species, identified in Kröger-Vink notation: oxygen in the lattice (O_O^x), oxygen vacancies ($V_O^{\bullet\bullet}$), protonic defects (OH^\bullet) in the solid phase, gaseous water (H_2O) within the pores. The global reaction between these species is as follows [22]:



Eq. (1) represents a chemical reaction involving charged and uncharged species. Since no kinetic information about this reaction is available, an elementary kinetics is assumed:

$$r_w = \frac{k_d}{K} c_{OH}^2 - k_d p_w c_O c_{VO} \quad (2)$$

where r_w is the reaction rate, c_{oh} , c_o and c_{vo} are the concentrations per unit of perovskite cell of protonic defects, oxygen in the lattice and vacancies, p_w is the partial pressure of water in gas phase, k_d is the kinetic constant and K the equilibrium constant. It should be marked, that the simplified kinetic expression does not include the more complicated process of water adsorption/desorption and intermediate reaction steps, which were experimentally observed [21].

Assuming those simplifications, by imposing the electroneutrality of BCY and considering the total balance of oxygen sites, the concentration of vacancies and oxygen in the lattice can be expressed as a function of the concentration of protonic defects as $c_{VO} = (S - c_{OH})/2$ and $c_O = 3 - (S + c_{OH})/2$, where S is the dopant level [22] and c_{OH} is constrained between 0 and S .

Considering the reaction in Eq. (1), the balance equations on molar basis for protonic defects and vacancies along the thickness x of the CM result as follows:

$$\frac{dN_{OH}}{dx} = -2r_w a \quad \text{with} \quad N_{OH} = -D_{OH} f^{eff} \delta \frac{dc_{OH}}{dx} - \frac{F}{RT} D_{OH} f^{eff} \delta c_{OH} \frac{dV}{dx} \quad (3)$$

$$\frac{dN_{VO}}{dx} = r_w a \quad \text{with} \quad N_{VO} = -D_{VO} f^{eff} \delta \frac{dc_{VO}}{dx} - \frac{2F}{RT} D_{VO} f^{eff} \delta c_{VO} \frac{dV}{dx} \quad (4)$$

where the molar fluxes (i.e., N_{OH} and N_{VO}) account for diffusion and migration of the species [23]. The self-diffusivities, D_{OH} and D_{VO} , and the density of perovskite cells per unit volume δ are specific material properties and are taken from [24]. The morphological parameters, such as the effective conductivity factor f^{eff} and the specific surface area per unit volume a , are estimated from specific modeling studies on the basis of the particle size and porosity of the CM [25, 26].

The model is solved for the 2 dependent variables, the protonic defect concentration c_{OH} and the electric potential V , imposing, as boundary conditions, $N_{OH} = i/F$ and $N_{VO} = 0$ at the interface with the anodic electrolyte, $N_{OH} = 0$ and $V = 0$ at the interface with the cathodic electrolyte. The current density i is therefore imposed as a boundary condition: a positive current for fuel cell operation mode, a negative current for electrolysis operation mode. The solution of the model provides the value of the voltage at the anodic electrolyte interface, which is equal to the CM global overpotential.

Figure 6 shows the polarization curve of CM simulated for the operating conditions and CM geometry and microstructure of monolithic cell with thickness 1.1 mm. The polarization curve is less steep than the curve of the measured cell, since it includes in addition to the CM, the losses of electrodes and electrolytes. Although simplified in respect to water behavior in the CM, the first modeling results confirm the reversibility of the monolithic design and can be used for further development of the model, which should include the phenomena experimentally observed in this system.

CONCLUSIONS

The good performance of the monolithic design opens a new niche for the development of dual membrane-based configurations. The first reversibility results show that operation in both fuel cell and electrolyzer mode is a very promising direction for further work. Optimization of the CM geometry towards increase of water vapour evacuation/supply surface is necessary.

Acknowledgements: The research leading to these results has received funding from the European community's seventh framework programme (fp7/2007-2013) under grant agreement no 213389. powders were fabricated and supplied by Marion Technologies (MT).

The authors acknowledge also "Science and Business" BG051PO001/3.3-05-001 for the financial support that made possible the publication of this paper.

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ОБРАТИМОСТ В ДВОЙНО МЕМБРАННА ГОРИВНА КЛЕТКА

Д. Владикова^{1,*}, З. Стойнов¹, А. Чесно², А. Торел², М. Вивиани³, А. Барбучи⁴, К. Николела⁵, А. Бертей⁵,
Г. Райкова¹, П. Карпанезе⁴, М. Кръпчанска¹

¹ *Институт по електрохимия и енергийни системи "Акад. Е. Бudevски" – БАН, ул. „Акад. Г. Бончев“, бл. 10, 1113, София, България*

² *Център по материалознание, Миньо – Тех Париж, ВР 87, 91003, Еври, Франция*

³ *Институт по енергетика и интерфейс, Национален съвет за научни изследвания, Генуа, Италия*

⁴ *Катедра по инженерна химия, Университет на Генуа, Генуа, Италия*

⁵ *Катедра по инженерна химия, Университет на Пиза, бул. „Лучо Лазарино“ №2, 56126 Пиза, Италия*

Получена на 19 февруари 2014 г.; приета на 12 април 2014 г.

(Резюме)

Една от перспективните посоки в по-нататъшното развитие на горивните клетки е тяхната работа в обратими режим, при който устройството работи като горивна клетка и като електролизьор. Един от сериозните проблеми е асиметрията на системата при работа в двата режима. Стъпка напред е възможността за получаване или разлагане на водата извън електродите. В режим на горивна клетка тази идея бе реализирана в иновативната концепция за двойно мембранна горивна клетка (ДМГК), която се състои от три независими камери за водород, кислород и вода. Настоящата работа представя изследвания на обратимостта в ДМГК. Първите резултати са много обещаващи. Те показват добра обратимост без прилагане на специален катализатор за разлагането на водата.