

Electrochemical testing of an innovative dual membrane fuel cell design in reversible mode

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Solid oxide fuel Cells (SOFC) are intrinsically reversible which makes them attractive for the development of reversible devices (rSOC). The main hurdles that have to be overcome are the higher degradation in electrolyzer (EL) mode and the slow and difficult switching from mode to mode. This work aims at the development and experimental validation of a concept for rSOC based on a new dual membrane fuel cell (dmFC) design which can overcome the existing problems of the classical SOFC. The kernel of the system is additional chamber - central membrane (CM) for water formation/evacuation in FC mode and injection in EL mode. Its optimization in respect of microstructure and geometry in laboratory conditions is carried out on button cells. The electrochemical performance is evaluated based on volt-ampere characteristics (VACs) combined with impedance measurements in different working points. The influence of a catalyst in the water chamber is also examined. The VACs which give integral picture of the cell performance are in excellent agreement with the impedance studies which ensure deeper and quantitative information about the processes, including information about the rate limiting step. The results from the optimization of the water chamber show that the combination of design and material brings to important principle advantages in respect to the classical rSOC – better performance in electrolyzer mode combined with instantaneous switching.

Key words: Reversible solid oxide cells, dual membrane fuel cell, BCY15, impedance measurements

INTRODUCTION

The ambitious European targets for CO₂ emission reduction require accelerated transition to clean and efficient energy system, since two thirds of the greenhouse emissions result from energy production and use. The problem solving approach is to increase the energy efficiency and integration of renewables in the energy mix, based on new technological solutions. Hydrogen is determined as the energy vector of the future, since it is a universal clean energy carrier which can be produced by water electrolysis with renewable energy, and then transformed by fuel cells into electricity and heat for transport and stationary applications. Solid Oxide Cells (SOC) are intrinsically reversible. They can be operated in electrolysis mode (EL) to produce hydrogen from steam, or in fuel cell (FC) mode to produce electricity. Using two separate devices - an electrolyser and a fuel cell means both will be used part time, which increases the investment costs. However, they can achieve higher efficiency and flexibility using the same device. The present State of the Art shows that in electrolyzer mode the degradation is much higher - about 2-5% after 1000h

of operation for the H₂O electrolysis reaction, which is behind the commercialization threshold [1]. In this respect special measures are taken for improvement of the electrodes performance and stability. This will reflect also in the reversible operation of solid oxide cell (rSOC) devices. Although the construction of SOELs and SOFCs looks similar, there is no optimized application of reversible high temperature electrochemical device due to their asymmetry which causes big differences in the operating conditions. For instance the high current density associated with a large amount of water in the fuel electrode for SOELs compared to SOFCs strongly increases the polarization resistance, the constraints on interconnects and the overall degradation rate [1]. Durability, performance and efficiency of rSOC are also affected by accelerated degradation and delamination at the electrodes due to the presence of water, slow and difficult switching from mode to mode, high humidity of the produced H₂, and difficulties in cell pressurization [2-6]. Studies point out the negative effect of water vapor on interconnect durability both in a reducing and oxidizing environment (related to Cr diffusion/evaporation), which renders the presence

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of a coating to protect interconnects mandatory [7, 8]. Thus the ability of rSOC to perform real dynamic cycling between power storage and power generation modes (SOEL to SOFC and back) while keeping an acceptable degradation combined with fast switching between the two modes and lower costs, is still an important target.

Recently a new design of SOFC with a separate chamber for the water production and evacuation named “dual membrane fuel cell” (dmFC) was introduced [9]. It was proved in the FP 7 FET project IDEAL Cell [10-12]. The new architecture eliminates the problems coming from the water formation and evacuation from the electrodes [11, 12]. The assembly combines the cathode compartment (cathode/electrolyte) of a SOFC and the anode compartment (anode/electrolyte) of pSOFC sandwiching a porous central membrane (CM) layer with mixed proton and oxide ion conductivity, where the water is produced and evacuated. This leads to numerous advantages (no dilution of fuel or oxidant, lower electrodes overpotential, easy pressurization). Since water is the major source of SOFC and SOEL failure, the long term viability of this concept should be significantly enhanced.

The separation of the water in a special compartment which eliminates its damaging presence at the electrodes in both modes, combined with the reduced operating temperature from 800-950°C to 600-800°C, are strong logical arguments in favor of the idea for development of advanced reversible electrochemical device based on the dmFC design. Additionally a mixed ionic conductivity in the proton conducting electrolyte (BCY15) was registered and preliminary experiments were performed on the so called “monolithic design” which strongly simplifies the technology since only one type of electrolyte with mixed ionic conductivity is used [13-15]. It was also supposed that the registered new phenomenon – formation of highly polarizable nanometer film of “organized” water at the surface of the BCY15 pores should facilitate the water formation/splitting [16].

The central membrane is the new component which ensures the advantages of the dmFC. On the one hand it should have high mixed ionic conductivity, which is favored by a dense microstructure. On the other hand it plays a role of a chemical reactor where water is formed and evacuated or injected, which requires porous microstructure. For the optimization of the CM a new design of an experimental symmetrical half-cell with CM support and Pt electrodes was investigated applying a combination of several experimental

techniques: (i) impedance spectroscopy for collection of information about the mixed conductivity by measurements of samples with different porosity in different atmospheres and temperatures; (ii) SEM for microstructural characterization; (iii) gases permeability measurements applying especially developed simple and fast procedure and equipment [16, 17].

The systematic studies of the central membrane of monolithic dual membrane fuel cell showed that 25-35% porosity could ensure an optimal microstructure in respect to conductivity, gas permeability and mechanical stability [17].

The next optimization parameter is the thickness of the CM. It has to guarantee smaller resistance combined with sufficient periphery for evacuation/injection of water. Since the CM works as chemical reactor, the density of the reaction triple phase boundaries in its volume should be sufficient.

This work aims at optimization of the CM in respect to its thickness by electrochemical testing of the electrolytes-central membrane assembly (ECMA) in full cell configuration. Since the reaction in the CM involves the most active particles – protons and oxide ions, the question which arises is about the need of a catalyst. Its answer is also in the scope of the study.

EXPERIMENTAL

The electrolytes-central membrane assembly BCY15_{dense}/BCY15_{porous}/ BCY15_{dense} was prepared by the standard ceramic technology following a procedure of three- step cold pressing: the three layers were pressed one after the other with pressure 1.72 kN/cm² for several seconds, followed by a final pressing at 5.16 kN/cm² for 5 minutes. The second layer which forms the Central Membrane has graphite pore former which ensures the optimal porosity [18]. In half of the cells a catalyst - Pt particles (Aldrich) with grains size 0.14 – 0.45 μm in quantity 1 wt. % in respect to the CM weight was also added. The samples were sintered at 1300°C for 5 hours. The final dimensions of ECMA were: diameter 21 mm and thickness 1, 2 mm. For the fabrication of cells with different thickness of the CM the total quantity of the raw material was kept constant, while the BCY15 weight ratio for the two dense electrolytes and that for the CM was varied. Samples with CM between 200 and 500 μm were fabricated. The exact thickness was determined by SEM (Fig. 1). Since the kernel of the monolithic dmFC design is the ECMA, Pt electrodes (with active surface 0.28 cm²) were used which eliminates eventual influence of the electrodes composition and deposition technology on the electrolytes behavior [18].

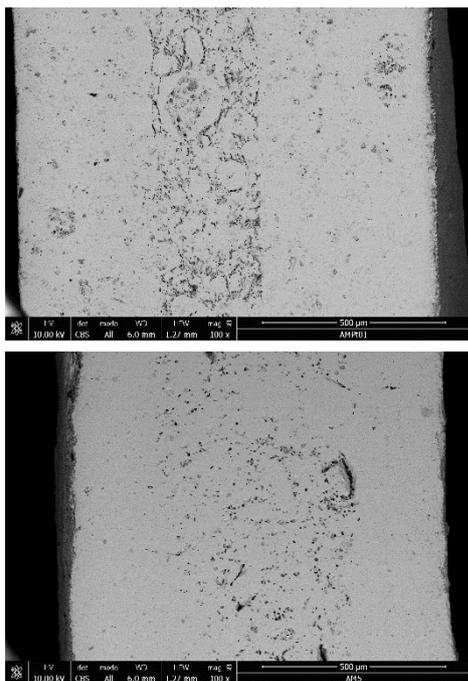


Fig. 1. SEM images of ECMA with different thickness of the Central Membrane: about 250 μm (upper position); about 500 μm (lower position)

The electrochemical testing included measurements of the volt-ampere characteristics (VACs) combined with impedance in different working points, performed on IVIUM - CompactStat e10030 in frequency range 1 MHz – 0,01 Hz with density 5 points/ decade in the temperature interval 600°C - 850°C. The working gas atmospheres were: air (61,85 ml.min⁻¹) or oxygen (133 ml.min⁻¹) and hydrogen (54,32 ml.min⁻¹).

A comparative analysis was performed on samples with different thickness of the CM and presence or absence of Pt catalyst. More details about the measured samples are given in Table 1.

RESULTS AND DISCUSSIONS

The linear shape of the volt-ampere curves for all samples measured at different temperatures in both FC and EL mode can be attributed to domination of the transport losses (Fig. 2). Since non-optimized cells with similar thickness show influence of the activation losses [19], the bigger cell thickness cannot be the only reason for the observed linear dependence. This result suggests for good catalytic activity of the water formation/splitting reaction, which is confirmed by the impedance

measurements (Fig. 2c) that show small charge transfer resistance.

Table 1. Samples tested in FC/EL mode

<u>Sample</u>	<u>CM [μm]</u>	<u>Pt</u>
<u>Sample 1</u>	<u>250</u>	<u>Yes</u>
<u>Sample 2</u>	<u>250</u>	<u>No</u>
<u>Sample 3</u>	<u>500</u>	<u>Yes</u>
<u>Sample 4</u>	<u>500</u>	<u>No</u>

It is well known that proton conductivity is higher than the oxide ion one and above 700°C it exhibits significant decrease [20, 21]. The measured VACs show performance improvement in both FC and EL mode with the increase of the temperature (Fig. 2). As it has been experimentally confirmed [15, 17] at operating temperatures (about 700°C) BCY15 has similar proton and oxide ion conductivity which is one of its advantages. Since in the dmFC both types of conductivity are used, the decrease in proton conductivity is compensated by the increase of the oxide ion one, which enhances the range of working temperatures. For operation in reverse mode the upper temperature limit is also important.

The comparison of the volt-ampere curves for cells with CM thickness 250 and 500 μm in the presence of Pt catalyst registers better electrochemical performance of the cell with the thinner CM in both FC and EL mode (Fig. 3). For the samples without catalyst the influence of the thickness is not so essential (Fig. 4). As it was already marked the thicker membrane ensures better evacuation/injection of the water, while the thinner one improves ECMA conductivity.

Obviously in samples without Pt the transport losses of water cannot be compensated by the decrease of the resistance in the thinner membrane. It is possible that the presence of catalyst outside the reaction zone of the CM facilitates the transport. This hypothesis is confirmed by the impedance measurements which register the water transport in the low frequency range [11, 15]. As it can be seen in Fig. 4c, regardless the differences in the impedance behavior in the high frequency range, the samples with different thickness of the CM have similar total resistance. Those observations bring to a new direction of optimization concerning the cell architecture. One approach is the “Zebra” design [22].

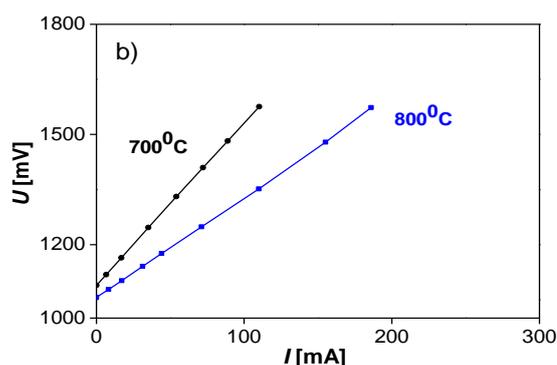
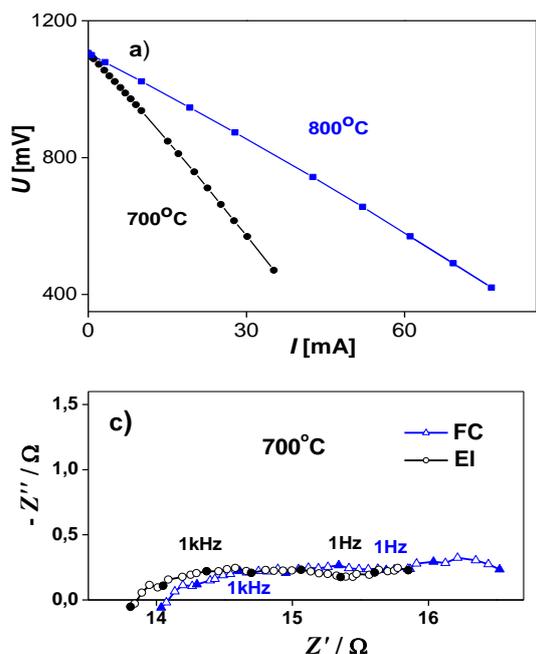


Fig. 2. Electrochemical testing of Sample 1 at different temperatures: a) Volt-ampere characteristics in fuel cell mode; b) Volt-ampere characteristics in electrolyzer mode; c) impedance diagrams in FC and EL mode at OCV

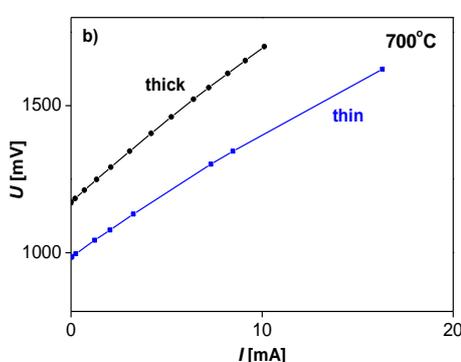
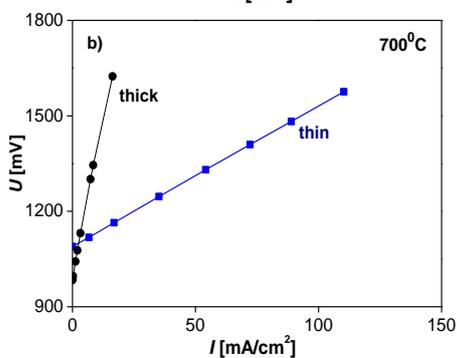
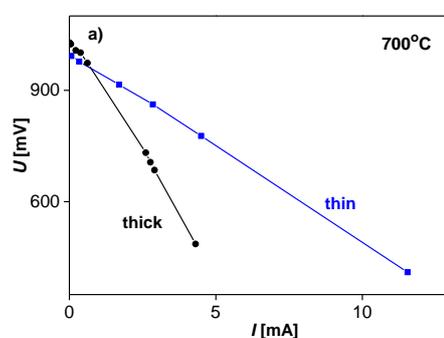
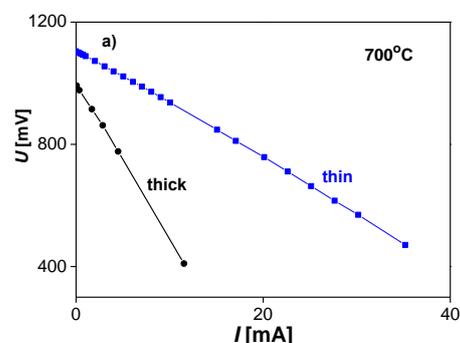
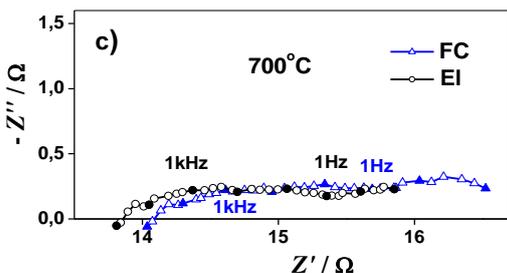


Fig. 3 Electrochemical testing of Samples 1 and 3 (with Pt in the CM): a) Volt-ampere characteristics in FC mode; b) Volt-ampere characteristics in EL mode.

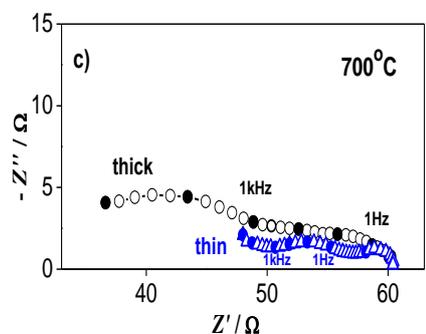


Fig. 4. Electrochemical testing of Samples 2 and 4 (with Pt in the CM): a) Volt-ampere characteristics in FC mode; b) Volt-ampere characteristics in EL mode; c) impedance diagrams in FC mode at OCV.

For optimization of the dmFC reversible monolithic design it is important to study the effect of the catalyst. As already mentioned, in FC mode the central membrane serves as a chemical reactor where the most active particles - protons and oxide ions meet. In EL mode the application of BCY15 which has the natural property to split water also facilitates the process. The first experiments showed good performance without catalyst. For experimental proof of the preliminary hypothesis

that the catalyst might not strongly influence the operation of the reverse cell, a comparison between the electrochemical behavior of ECMA with and without catalyst was done. Both VACs and impedance analysis confirmed the positive influence of the catalyst in FC and EL mode (Fig. 5). The effect is more pronounced for the cells with thin CM probably due to activation outside the reaction zone of the CM.

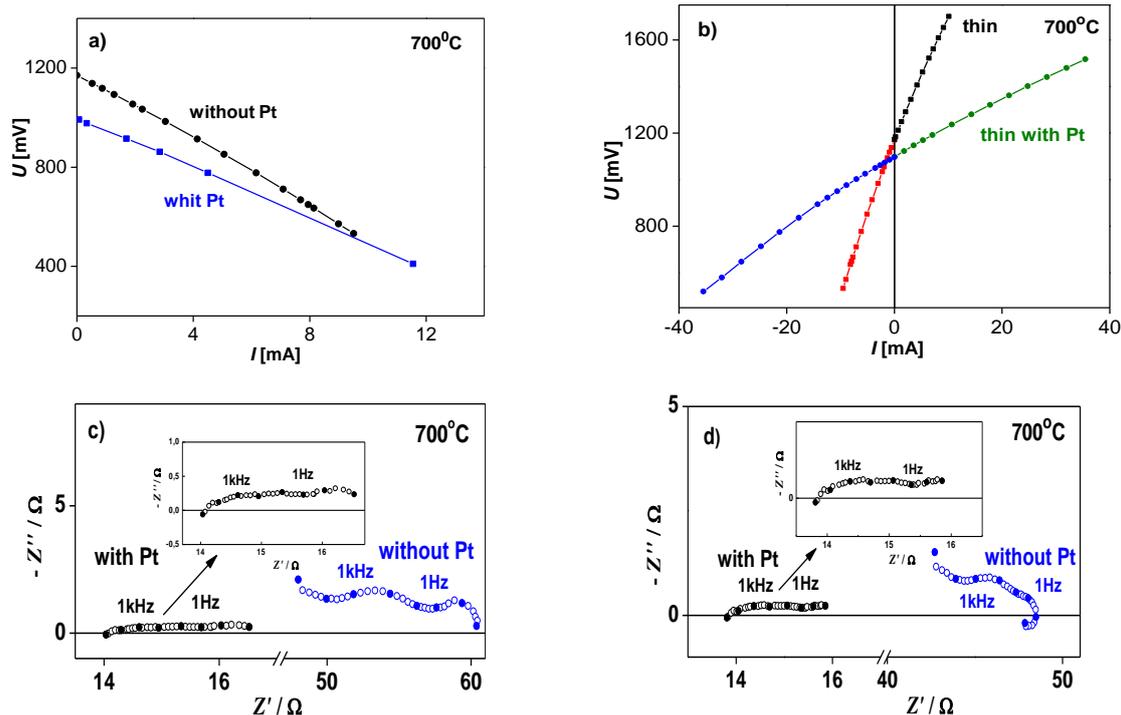


Fig. 5. Electrochemical testing of samples with and without Pt in the CM: a) Volt-ampere characteristics of Samples 3 and 4 (thick CM) in FC mode; b) Volt-ampere characteristics of Samples 1 and 2 (thin CM) in both FC and EL mode; c) Impedance diagrams of Samples 1 and 2 (thin CM) in FC mode at OCV; d) Impedance diagrams of Samples 1 and 2 (thin CM) in EL mode at OCV.

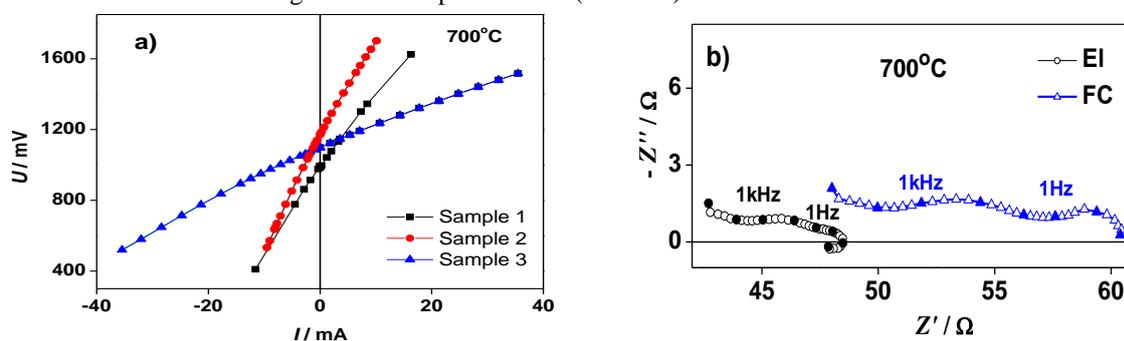


Fig. 6. Electrochemical testing of Samples 1 - 4 in reverse mode: a) Volt-ampere characteristics of Samples 1, 2 and 3 in FC and EL mode; b) Impedance diagrams of Sample 4

The main goal of this study is to analyze the operation of the monolithic dmFC in reverse mode, for which a comparison of the electrochemical behavior of Samples 1-4 was performed in both FC

and EL mode. The Volt-ampere characteristics confirm better performance for all cells in electrolyzer mode (Fig. 6). This result is interesting and important, since the main disadvantage of the

classical rSOC is the worst performance in EL mode. In addition the selection of BCY15 which splits water also influences positively the operation in EL mode. This result illustrates the big potential of the dmFC concept in rSOC which is one of the directions for increased efficiency of RES introduction in the energy mix.

An important parameter for reversibility is the switching time. In the dmFC the reversibility was found to be in practice instantaneous due to the presence of water in the common “water chamber”, adsorbed on the defect surface of the CM pores [16]. Thus the combination of design and material makes the dmFC concept very promising for reversibility.

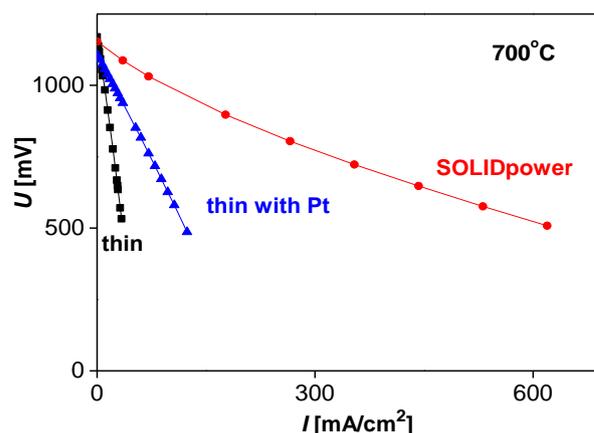


Fig. 7. Comparison of VACs in FC mode

Table 2. Maximum power of the Samples in Fuel Cell

Sample	P_{max} [mW/cm ²]/Air				P_{max} [mW/cm ²]/O ₂			
	600°C	700°C	800°C	850°C	700°C	800°C	850°C	
1	35.3	60.2		123	80	132.4	159.4	
2	5.5	18	28.5			32.3		
3	8.32	16.7						
4	5.6	18.3						
SOLID power	113	315	584					

CONCLUSIONS

The electrochemical studies of reversibility applying the innovative concept of the “monolithic” dual membrane fuel cell which has a separate “water chamber” show that the combination of design and material brings to important principle advantages in respect to the classical rSOC – better performance in electrolyzer mode combined with instantaneous switching. The VACs which give integral picture of the cell performance are in excellent agreement with the impedance studies which ensure deeper and quantitative information about the processes, including information about the rate limiting step. This work can be accepted as giving “green light” for further development of the dmFC concept combining fundamental and technological improvements.

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REFERENCES

1. <http://www.fch.europa.eu/page/call-2018> (p. 69).
2. H. Uchida, P. Puengjinda, K. Miyano, K. Shimura, H. Nishino, K. Kakinuma, M. E. Brito, M. Watanabe, *ECS Transactions*, **68**, 3307 (2015).
3. O.A. Marina, L. R. Pederson, M. C. Williams, G. W. Coffey, K. D. Meinhardt, C. D. Nguyen, E. C. Thomsen, *J. Electrochem. Soc.*, **154**, B452 (2007).
4. N. Q. Minh, M. C. Williams, *ECS Transactions*, **68**, 3301 (2015).
5. T. Ishihara, A. Inoishi, H. Kim, S. Ida, *ECS Transactions*, **68**, 3279 (2015).
6. S. Presto, A. Barbucci, M.P. Carpanese, M. Viviani, R. Marazza, *J. Appl. Electrochem.*, **39**, 2257 (2009).
7. Y. Zhang, K. Chen, C. Xia, S. P. Jiang, M. Ni, *Int. J. Hydrogen Energy*, **37**, 13914 (2012).
8. V. N. Nguyen, Q. Fang, U. Packbier, L. Blum, *Int. J. of Hydrogen Energy*, **38**, 4281 (2013).
9. A. Thorel, Patent N°0550696000 (2005).
10. www.ideal-cell.eu.
11. D. Vladikova, Z. Stoynov, G. Raikova, A. Thorel, A. Chesnaud, J. Abreu, M. Viviani, A. Barbucci, S. Presto, P. Carpanese, *Electrochimica Acta*, **56**, 7955 (2011).
12. A. Thorel, J. Abreu, S. Ansar, A. Barbucci, T. Brylewski, A. Chesnaud, Z. Ilhan, P. Piccardo, J. Prazuch, S. Presto, K. Przybylski, D. Soysal, Z. Stoynov, M. Viviani, D. Vladikova, *J. Electrochem. Soc.*, **160**, F360 (2013).
13. A. Thorel, Z. Stoynov, D. Vladikova, A. Chesnaud, M. Viviani, S. Presto, Fuel Cell With Monolithic Electrolytes Membrane Assembly, US Patent № 20120156573, 21.06.2012.
14. M. Viviani, S. Presto, A. Barbucci, M. P. Carpanese, R. Amendola, A. S. Thorel, A. Chesnaud, J. Abreu, R. Costa, Z. Ilhan, S-A. Ansar, D. E. Vladikova, Z. B. Stoynov, *MRS Proceedings*, 1330 (2011).
15. D. Vladikova, Z. Stoynov, A. Chesnaud, A. Thorel, M. Vivianu, A. Barbucci, G. Raikova, P. Carpanese, M. Krapchanska, E. Mladenova, *Int. J. Hydrogen Energy*, **39**, 21561 (2014).
16. Z. Stoynov, D. Vladikova, E. Mladenova, *J. Solid State Electrochem.*, **17**, 555 (2013).

17. D. Vladikova, Z. Stoynov, B. Burdin, G. Raikova, M. Krapchanska, A. Thorel, A. Chesnaud, *Machines, Technologies, Materials*, **4**, 190 (2017).
18. M. Viviani, G. Canu, M. Carpanese, A. Barbucci, A. Sanson, E. Mercadelli, C. Nicoletta, D. Vladikova, Z. Stoynov, A. Chesnaud, A. Thorel, Z. Ilhan, S. Ansar, *Fuel Cells 2012 Science & Technology – A Grove Fuel Cell Event*, Energy Procedia, **28**, 182 (2012).
19. D. Vladikova, Z. Stoynov, G. Raikova, A. Thorel, A. Chesnaud, J. Abreu, M. Viviani, A. Barbucci, Z. Ilhan, P. Carpanese, S. Presto, *Proc. 15th European Fuel Cell Forum Lucerne: Switzerland*; Ch. 18/B1205, 29 (2011).
20. S. C. Singhal, K. Kendall, *Solid Oxide Fuel Cells: Fundamentals, Design and Applications*, Elsevier (2003).
21. K. C. Liang, A. S. Nowick in: T.A. Ramanarayanan (Ed.), *Ionic and Mixed Conducting Ceramics III*, The Electrochemical Society Proceedings Series, Pennington, NJ **28**, 97 (1997).
22. Z. Stoynov, D. Vladikova, A. Thorel, A. Chesnaud, M. Viviani, A. Barbucci, Patent N ES2554456T3 (2011).

ЕЛЕКТРОХИМИЧНО ТЕСТВАНЕ НА ИНОВАТИВЕН ДИЗАЙН НА ДВОЙНОМЕМБРАННА ГОРИВНА КЛЕТКА В ОБРАТИМ РЕЖИМ

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(Резюме)

Твърдооксидните горивни клетки (SOFC) са вътрешно обратими, което ги прави привлекателни за разработването на обратими твърдооксидни клетки (rSOC). Основните препятствия които трябва да бъдат преодоленни, са повишената деградация в режим на електролизатор (EL) и забавеното и затруднено превключване между двата режима. Настоящата работа има за цел разработване и експериментално потвърждение на концепцията за rSOC въз основа на новия дизайн на двойно мембранна горивна клетка (dmFC), който преодолява проблемите на класическите SOFC. В центъра на разработката е въвеждането на допълнителна камера, т.н. централна мембрана (CM), в която в режим на FC се формира и евакуира вода, а в режим на EL тя се впръсква отвън. Оптимизацията на CM в лабораторни условия по отношение на микроструктурата и геометрията е проведена на клетки тип „копче“. Електрохимичното им поведение е оценено въз основа на волт-амперни характеристики (VAC), в комбинация с измервания на импеданса в различни работни точки. Изследвано е и влиянието на катализатора във водната камера. Волт-амперните характеристики, които дават цялостна картина на поведението на клетките, са в съответствие с импедансните изследвания, което осигурява по-задълбочена количествена информация за процесите, в т.ч. и за скорост-определящия стадий. Резултатите от оптимизацията на CM показват, че комбинацията от дизайн и материал осигурява важни основни предимства спрямо класическия rSOC - по-добро поведение в режим на електролиза, комбинирано с много бързо превключване на режимите.

Ключови думи: обратима твърдооксидна горивна клетка, двойно мембранна горивна клетка, VCY15, импедансни измервания