

Gases permeability study in dual membrane fuel cell

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Gases permeability in a porous mixed (proton and oxide ion) conductive membrane, which is a component of a new high temperature dual membrane fuel cell design is investigated by specially designed testing system based on measurements of the gas flow [ml/min] and pressure P (mm H₂O) when penetrating through porous media. A strong correlation expressed in increase of the permeability with the decrease of the gases molecular weight is registered. The water vapor permeability decreases with the temperature. This is in agreement with data from the literature which show that the viscosity of gases, including water vapor, increases with the temperature. The results obtained suggest optimal porosity in respect to permeability, mechanical stability and conductivity in the range of 35 - 40%. They confirm the need of optimization concerning not only the pores fraction, but also the pores geometry and distribution, as well as the central membrane geometry and the configuration of the cell. This approach can be applied also for optimization of the electrodes porosity (pores concentration, geometry, distribution etc), especially in cases when gas mixtures (including water vapor) are used or produced.

Keywords: gases permeability, dual membrane fuel cell, porous mixed conducting ceramics, electrochemical impedance spectroscopy.

INTRODUCTION

Following the strategic objectives of Europe 2020 for 20% lower greenhouse gas emissions, 20% of energy from renewables and 20% increase of energy efficiency, hydrogen can play an essential role not only as a fuel, but also as an universal energy carrier easy to be integrated in electrical systems. Thus the commercialization of solid oxide fuel cells (SOFC) as extremely efficient device to produce electricity with no deleterious emission if fed by hydrogen is of primary importance.

Classical SOFCs have 50 years of technical history. They operate at high temperatures, use a solid oxide (ceramic) electrolyte to conduct oxide ions created at the cathode to the anode, where they react with hydrogen and produce water as by-product. In our days more than 40 companies and thousands of research groups all over the world are working intensively towards decreases of material costs and operating temperature, improvement of performance stability as well as fuel flexibility and efficiency.

In the last 20 years, due to the discovery of proton conductivity in perovskite-doped cerates

[1–3], more and more attention is drawn to the development of proton conducting fuel cells (pSOFC). They use a solid state proton conducting electrolyte, which transports hydrogen ions created at the anode to the cathode. Since the more mobile proton is transported through the electrolyte, PCFCs have the potential to operate at lower temperatures (500–800°C).

However the dilution of the reacting gases with the exhaust water (at the anode side in SOFC and at the cathode side in PCFC) combined with decrease of their catalytic activity can be regarded as a limiting factor that slows down their marketing. In order to overcome those limitations, innovative Dual Membrane Fuel Cell (DMFC) architecture was proposed [4] and proved [5–8].

The new concept combines the advantages and eliminates the disadvantages of both oxide ion and proton conducting high temperature fuel cells. The main idea is the separation of the hydrogen and oxygen from the exhaust water. It is realized by the introduction of a junction central membrane (CM) layer between a SOFC electrolyte/cathode (cathode compartment) and a PCFC anode/electrolyte (anode compartment). The CM has mixed (H⁺ and O²⁻) conductivity and porous microstructure. Thus protons produced at the anode progress toward the junction membrane where they meet the oxide ions

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that are created at the cathode and produce water, which is evacuated through the pores of the membrane. Therefore hydrogen, oxygen and exhaust water are located in three independent chambers. The innovative concept has the potential to considerably enhance the overall efficiency and reduce costs of SOFC systems thanks to fine-tuning of the catalytic properties of electrodes, pressurization of both electrode compartments, production of pure water for steam reforming and employment of less sophisticated metallic alloys for interconnects. More details for the concept and its proof are given in [5–8].

The most challenging component of the DMFC design is the composite CM. It should have high anionic and protonic conductivities in the presence of sufficient porosity and proper connectivity among the different phases (proton conductor, oxide ion conductor, open porosity for water evacuation), avoiding tortuous and/or resistive paths. Moreover, both solid phases - the proton conducting BCY15 ($\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2-\delta}$) and no oxide - ion conducting YDC15 ($\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$) should percolate towards their respective electrolyte, while porosity must percolate towards the outside of the cell for water evacuation. Thus each triple phase boundary (TPB) segment should be connected to both electrolytes. The CM needs the optimization of two processes with contradictory initial requirements: (i) water vapor formation and evacuation for which a porous structure is needed and (ii) high mixed ion conductivity, favored by higher density. Obviously a compromise between the two targets is needed, since the increase of porosity will improve the water permeability, but will also decrease the conductivity.

For optimization of the CM new research approaches were introduced and developed for deeper insight into the mechanisms and processes of mixed conductivity and water formation and release: X-ray micro-tomography 3D image analysis [9, 10]; “in situ” conductivity measurements of the CM composite matrix components; gas and water vapor permeability studies; capacitive and impedance measurements of water behavior in the CM [8, 11].

This paper aims at summarizing the results of one new and systematic study of gases (including water vapour) permeability in porous ceramic media. Although it is performed for deeper insight into the water permeation in the central membrane of the DMFC design, the applied approaches and

obtained results can be introduced in the electrodes performance optimization procedures.

EXPERIMENTAL

The mixed oxide-ion and proton conductivity of the central membrane was obtained by the application of composite based on the chemically compatible BCY15 and YDC15 electrolytes [6, 7], (YDC15 is a decomposition product of BCY15 [12]). Samples with diameter about 2 cm and thickness about 1 mm were produced by cold pressing and sintering at 1300°C. The ratio of the two ceramic phases was varied in the range from 40/ 60 to 60/40 vol %. Different porosity (25 – 60 v%) was obtained by adjustments of the type (graphite, starch, polyvinyl butyral) and quantity of the pore former.

Morphological studies performed by X-ray micro-tomography 3D image analysis [9, 10] confirmed good percolation rates and tortuosity of the three phases, indicating easy pathways for the ions through the central membrane and for the water evacuation from shaping point of view. Graphite pore former was estimated as the best one.

Since the CM consists of three phases (BCY, YDC and pores), their co-existence influences the way each of them forms and evolves during sintering (the 2 ceramic components have different sintering temperatures). Thus an essential point was to study “in situ” the conductivity behaviour of every ceramic component, i.e. in the presence of the other two phases. This target was successfully realized with the design of a new type of symmetrical CM supported half cells (diameter about 2 cm, thickness about 1 mm) Pt/YDC_{porous}BCY_{porous}/Pt which were measured by electrochemical impedance spectroscopy (EIS). The impedance measurements were carried out with Solartron 1260 FRA in temperature interval 100–750 °C, frequency range from 1 MHz down to 0,1 Hz, density five points/decade and amplitude of the AC signal 50 mV in wet (3%) hydrogen or air/oxygen, which ensured separate information for the conductivity of every component of the composite.

For the performance of the permeability studies a new testing system was specially designed. It is based on measurements of the gas flow q_{flow} [ml/min] and pressure P (mm H₂O) when penetrating through media with different porosity which determine a new characteristic parameter, named permeability resistance R_p (inversely proportional to the permeativity):

$$R_p = P/q_{\text{flow}} \quad (1)$$

The testing system ensures measurements of R_p in the range 0.01 to 600 mm.min/ml. The permeability measurements were carried out with different gases: air, H₂, O₂, N₂, Ar and humidified air. The gas flows varied from 0 to 140 ml/min. The tests with humidified air were performed in temperature range 20 – 600°C at a constant gas flow. The humidity (3% H₂O) was ensured by passing the gas flow through watered vessel at room temperature. The experiments were carried out on samples with different porosity, evaluated by mercury porosimetry. Two configurations of the gas flow set-up were used - lateral, which is similar to the CM configuration in the DMFC, where the water vapor formed in the porous membrane is evacuated through its periphery, and transversal, which represents the gas flows in the porous electrodes layers, cf. Fig. 1.

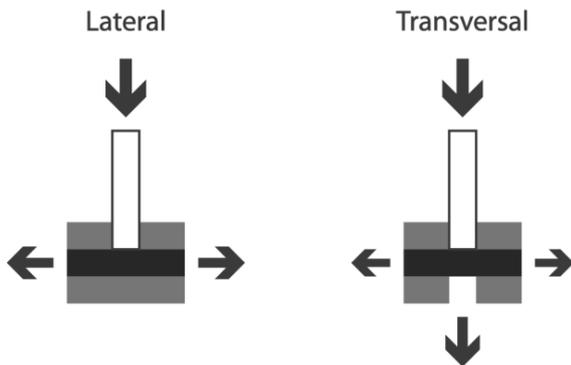


Fig. 1. Different gas flow configurations of the experimental set-up.

Similarly to the ohmic resistance, the permeability resistance can be expressed as:

$$R_p = \rho_p h s^{-n} \quad (2)$$

where “s” is the sample’s surface and “h” is its thickness.

Measurements of gases permeability were calibrated on pipes with varying diameter and length. It was found that for pipes with diameter bigger than 2 mm $n = 1$. However, for internal pipe diameter less than 2 mm the geometrical factor increases, i.e. $n > 1$. For pipes with diameter between 1 and 2 mm it is 1,13. Obviously in porous ceramic media this coefficient should be much bigger.

RESULTS

The impedance measurements of half cells with CM support of different porosity were performed in both air and wet hydrogen atmospheres and thus provided important information about the individual conductivity of each one of the two electrolytes in the real ceramic structure. Results for central membranes with different porosity are presented in Fig. 2. As it could be expected, the porosity increases the resistivity of both electrolytes. It is higher in air/oxygen, where the YDC15 contribution is represented. The influence of the porosity is more pronounced in hydrogen, where the BCY15 resistivity is exhibited.

The obtained results, however, do not give information about the water vapor transport in the CM, which is an important factor in the optimization of the cell performance. For this purpose permeability studies were performed, starting with gases permeability in the CM at room temperature.

As expected, the permeability in the CM is bigger for transversal configuration of the testing rig (Fig. 3). Logically the gas permeability decreases with the decrease of the porosity (Fig. 4). Measurements with different gases at room temperature and constant conditions (set-up configuration and porosity) registered a strong

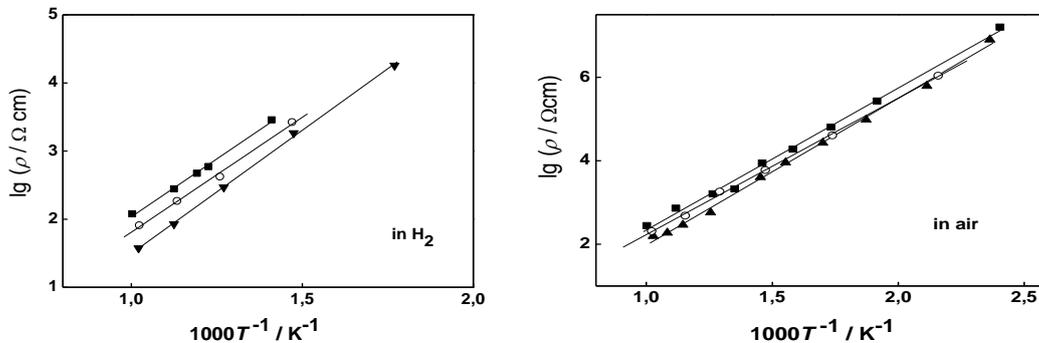


Fig. 2. Arrhenius plots for the resistivity of central membrane with different porosity and 50 v % of BCY15 and YDC15 (■ – 40% porosity; ○ – 35 % porosity; ▼ – 30% porosity).

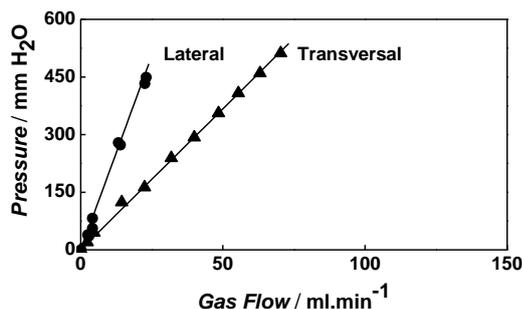


Fig. 3. Permeability measurements of H₂ in CM with 40% porosity at different measurement configurations of the experimental set-up.

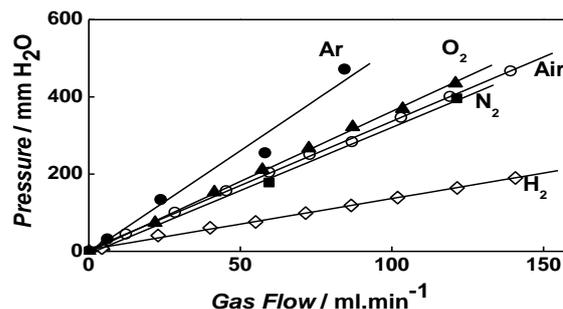


Fig. 5. Gases permeability measurements in CM with 50% porosity at room temperature (transversal configuration).

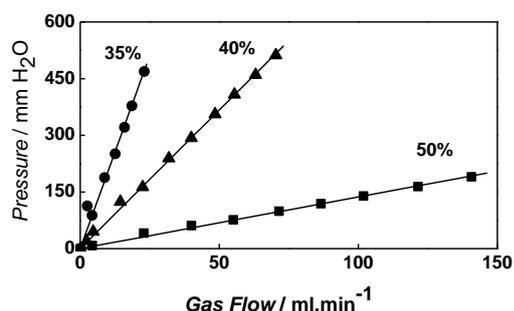


Fig. 4. Permeability measurements of H₂ in CM with different porosity at room temperature (transversal configuration).

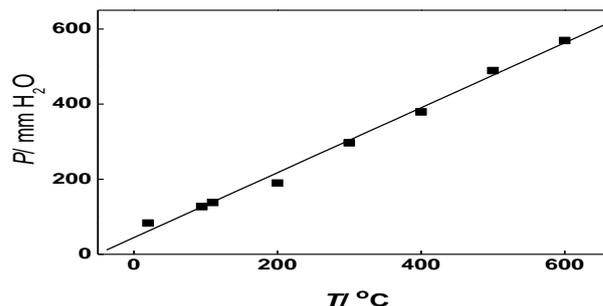


Fig. 6. Temperature dependence of wet air permeability in CM with 40% porosity at constant gas flow.

correlation expressed in increase of the permeability with the decrease of the gases molecular weight (Fig.5).

Water permeability in the CM at elevated temperatures was studied by measurements performed in wet air in the temperature range 20 – 600°C. A decrease of the permeability was registered with the increase of the temperature (Fig. 6). This result is in agreement with data from the literature which show that the viscosity of gases, including water vapor, increases with the temperature (Fig. 5) [13]. Since the available data is up to 300–400°C, the obtained results give important information that at operating temperatures the water produced in the pores of the CM has higher viscosity.

The results obtained from the conductivity and permeability studies showed that the optimal porosity of the mixed ion conducting central membranes in respect to permeability, mechanical stability and conductivity is about 35 – 40%.

CONCLUSIONS

The analysis of the permeability studies shows that the phenomenon is complicated and strongly dependent on the CM porosity, pores geometry,

tortuosity, sample configuration. The obtained results confirm the need of optimization concerning not only the pores fraction, but also the pores geometry and distribution, as well as the CM geometry and configuration in the cell, which brought to the construction of a new cell design [14]. It facilitates the water vapor evacuation from the central membrane.

Gases permeability studies can be applied also for optimization of the electrodes porosity (pores concentration, geometry, distribution etc), in solid oxide fuel cells and electrolyzers especially when gas mixtures (including water vapor) are used, or produced. Obviously the optimal porosity of the cathode and anode will differ since the two electrodes are fed with different gases.

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ИЗСЛЕДВАНЕ НА ГАЗОВАТА ПРОПУСКЛИВОСТ В ДВОЙНО МЕМБРАННА ГОРИВНА КЛЕТКА

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(Резюме)

Тествана е нова система за изследване на газовата пропускливост, в това число пропускливост и на водни пари, в пореста керамична мембрана (т. н. централна мембрана – ЦМ) със смесена йонна проводимост, която е основен компонент в иновативен дизайн на високо температурен твърдооксиден горивен елемент. Системата за изследване на газовата пропускливост се базира на измерването на газовия поток q [ml/min] и налягането P (mm H₂O). Установена е строга корелация между увеличаването на газовата пропускливост и намалението на молекулното тегло на газовете. Газовата пропускливост на водни пари намалява с увеличение на температурата. Този резултат е в синхрон с литературните данни, които показват, че вискозитета на газовете се увеличава с повишаването на температурата. Получените резултати дават възможност да се определи оптимално съотношение между газова пропускливост и пористост, механична стабилност и проводимост в диапазон 35 - 40%. Разработеният подход е особено интересен и за оптимизиране микроструктурата на пористостта на електродите - концентрация на порите, тяхната геометрия и разпространение, особено в случаите, когато се използват или произвеждат газови смеси (включително водна пара).