

WATER TRANSPORT STUDY IN HIGH TEMPERATURE FUEL CELL STACK

Dario Bezmalinović^{1,2}, Attila Husar²,

¹Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split, Rudera Boškovića 32, 21000 Split, Croatia

²Institut de Robòtica i Informàtica Industrial, CSIC-UPC, Parc Tecnològic de Barcelona. C/ Llorens i Artigas 4-6, 08028 Barcelona, Spain

RESUMEN: *En este trabajo se presenta un análisis de los fenómenos del transporte de agua en una pila de combustible PEM 120 W_{el} de alta temperatura. Las membranas PBI de ácido fosfórico dopadas son conocidas por sus capacidades para el trabajo con gases secos, sin embargo el agua continúa siendo una cuestión importante en el mecanismo de conducción del electrolito. La presencia de agua en la membrana aumenta la conductividad de protones, mientras que a temperaturas de operación más altas en ambientes anhídricos el ácido fosfórico puede deshidratarse y en consecuencia reducir su conductividad. Por lo tanto, el entendimiento del transporte de agua en membranas PBI-H₃PO₄ es importante ya que puede explicar ciertos fenómenos dentro de la celda. Las pruebas han demostrado que el transporte de agua desde el cátodo hacia el ánodo debido a acumulación de agua crece casi linealmente con la densidad de corriente, mientras que disminuye con la estequiometría de cátodo. El transporte de agua también parece ser independiente de la temperatura de funcionamiento. Incluso, en algunos casos, inversión del flujo de agua (desde el ánodo hacia el cátodo) parece tener lugar cerca de la salida. La resistencia óhmica también se ha visto ligeramente reducida con un aumento de la densidad de corriente y estequiometrías bajas.*

ABSTRACT: *This work presents analysis of water transport phenomena in the 120 W_{el} high temperature PEM fuel cell stack. Phosphoric acid doped PBI membranes are known for their abilities to work with dry gases; however water in the electrolyte still plays an integral role in the proton conduction mechanism. The presence of water in the membrane increases proton conductivity, however at high operating temperatures in the anhydrous environment phosphoric acid can dehydrate consequently lowering its conductivity. Therefore, understanding of water transport in the PBI- H₃PO₄ membranes is important as it can explain certain phenomena inside the cell. Tests have shown that water transport from cathode to anode due to water accumulation rises almost linearly with current density while decreases with cathode stoichiometry. Water transport seems to be independent of operating temperature. Also, in some cases, reverse flow water transport (from anode to cathode) appears to take place near the outlet. Ohmic resistance was also found to decrease slightly with an increase in current density and lower stoichiometries.*

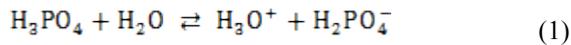
Keywords: HT-PEM, water transport, stack, PBI- H₃PO₄

1. INTRODUCTION

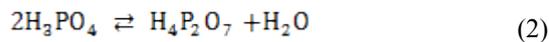
Polymer electrolyte membrane fuel cells (PEMFC) have been attracting a lot of attention in the last few decades as one of the most promising candidates for the stationary and especially vehicular applications because of their high efficiency, high power density and low emissions. However, in the last several years, the focus has been increasingly turning towards PEM fuel cells that operate above 100°C (HT-PEMFC) [1]. Advantages are numerous, most notably very high CO tolerance which enables direct coupling with fuel processing units (no need for an extra CO clean up stage). Also, humidification of the reactants is unnecessary and easy heat disposal due to high temperature gradient make overall system design very simple in comparison with PEMFC. Because of all this, high temperature fuel cells are especially

interesting in natural gas fed CHP systems where overall efficiency can be around 90%.

Goal of this study was to analyse water transport in the MEA and the effect of reactants humidification on stack's performance. One of the most often emphasised advantages of phosphoric acid doped PBI membranes, commonly encountered in HT-PEMFC, is no need for humidification of reactant gases. Unlike PFSA-type membranes proton conduction mechanism in the PBI-H₃PO₄ membranes is not water assisted, in other words proton does not migrate from anode to cathode bonded to a H₂O (vehicle mechanism) in the form hydronium ion. It is rather structure diffusion where proton migration occurs between hydrogen bonds (Grotthuss mechanism) [2]. However, water still plays vital role in conduction mechanism of PBI-H₃PO₄ membranes. Presence of water ionizes phosphoric acid and therefore increases number of charge carriers:



Furthermore, water decreases viscosity of the electrolyte rendering it more conductive and enhances cathode kinetics because solubility of oxygen in the water is much higher than in the phosphoric acid. Phosphoric acid is also known to dehydrate at temperatures higher than 120°C forming less conductive pyrophosphoric acid.



Previous process is fully reversible but the water partial pressure equilibrium rises with the temperature. So at the 150 °C it was found to be around 5 kPa while at the 170 °C around 10 kPa [3]. Although, authors in [3] claim that water produced at the cathode in the end should be enough to keep the membrane humidified, this may not always be the case. Even though it is generally accepted that the increase of the operating temperature is normally followed by the increase of the performance some authors found that the performance actually decreases when operating at temperatures above 170 °C [4]. This phenomenon is explained by phosphoric acid dehydration. At higher operating temperatures and higher reactants' stoichiometries membrane dehydration followed by the decline of performance can occur. Obviously, water back-transport due to concentration gradient plays significant role in preventing electrolyte from drying out at the anode side.

2. EXPERIMENTAL

Experimental tests were conducted on the high temperature fuel cell stack consisting of 12 cells with 50 cm² active area and rated power of 120 W_{el}. MEAs used were commercial Celtec®-P 1000 with operating temperature range 120°C-180°C. Celtec®-P membranes are polymer gels PBI-H₃PO₄ with phosphoric acid content of about 95 wt% or up to 70 phosphoric acid molecules per PBI repeat unit and can tolerate up to 3% CO [5]. Membrane thickness is approximately 50-75 μm. Each single cell's voltage was monitored while temperatures were measured with three thermocouples pinned to the cells number one, six and eleven.

Polarization curves were run from 0.1 to 1.0 Acm⁻² with the step of 0.1 Acm⁻² (ten points). Each current density value was kept for 60 s and each test was repeated three times with final reported values being averaged. Before each test stack was run for 30 minutes with given parameters at the current density of 0.2 Acm⁻² to ensure steady state was reached. Stack was fed with the dry gases in co-flow

mode at atmospheric back-pressures. On the anode pure hydrogen was used with constant stoichiometry of 1.3 in all tests, while as an oxidant synthetic air was used with three different stoichiometries (1.5, 2 and 3). The measurements were conducted for the two different operating temperatures, 140 °C and 160 °C. At both outlets, temperature and relative humidity were measured by T-RH transducers. Since both reactants were introduced dry in the stack total water transport across the membrane was equal to the water vapour flow at the anode outlet. Water vapour flows at the both outlets were simply calculated by multiplying water vapour concentration (obtained from measuring RH and T) with the dry reactants flow (calculated by mass conservation law). Water vapour flow on the anode was finally divided by the number of the cells to obtain average water transport across the membrane for the each cell. This assumption is believed to be fairly accurate due to negligible pressure differences between the cells (small overall pressure drop) and very small variations of the single cell's voltage readings which imply uniform cell to cell condition inside the stack.

3. RESULTS AND DISCUSSION

Figure 1 shows a polarization curve of the stack recorded at the temperature 160 °C with hydrogen and air stoichiometries of 1.3 and 2 respectively. Stack performance is lower than for the corresponding low temperature stack and single cell voltages show very little variability (±3%). Ohmic resistivity is around 80 mΩcm⁻² and tends to decrease with higher current densities and lower stoichiometries. However, these changes are still very small in comparison with low temperature fuel cells when working with dry gases.

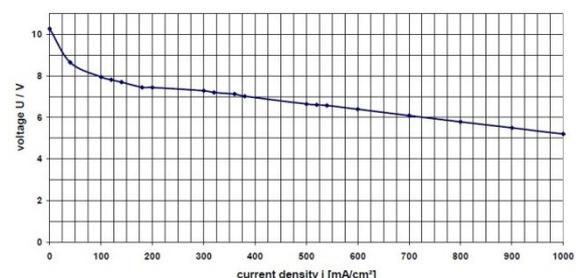


Fig. 1. Polarization curve of the stack for hydrogen and air stoichiometries of 1.3 and 2 respectively.

Figure 2 shows water transport across the membrane for various air stoichiometries at a temperature of 160 °C. As it can be seen, water transport increases almost linearly with current density while it decreases with air stoichiometry. As it was shown by Weng et al. [6] electro-osmotic drag in the phosphoric acid doped PBI membranes is practically zero and therefore the only driving force that pushes

water from one side of the membrane to another is concentration gradient. Water is generated on the cathode and builds up along the channel length increasing the gradient between concentrations across the membrane. Increasing the air stoichiometry local water vapour concentration decreases which explains lower water transport. Also, at certain conditions, it was discovered that the water concentration at the anode outlet is actually higher than on the cathode indicating that a reverse flow of water may have occurred near the end of the channel. Due to hydrogen consumption stream velocity at the anode side decreases rapidly and the local water concentration can become higher than on the cathode despite the total water vapour flow at the outlet being order of magnitude higher on the cathode.

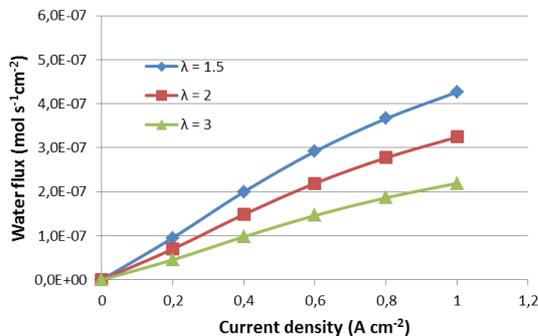


Fig. 2. Water transport across the membrane from cathode to anode for hydrogen stoichiometry of 1.3 and different air stoichiometries at the atmospheric backpressure and 160 °C.

Also, measurements have shown no detectable difference in water transport at the different operating temperatures. These obtained results are in accordance with [7] even if their water transport appears to be slightly higher. The results were also verified with the simple 1-D model assuming no pressure drop and constant current density along the channel length.

4. CONCLUSIONS

Even if the water management is not essential in HT-PEM fuel cells as in low temperature fuel cells, water still plays a role in membrane conductivity. It was found that concentration difference driven water

transport from cathode to anode is independent on operating temperature, rises almost linearly with current density and decreases with air stoichiometry. Future work will focus on the long term influence of the stack working in hydrous/anhydrous environment with respect to stack performance.

Acknowledgements

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