

Electrolysis test of different composite membranes at elevated temperatures

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Outline

A promising way to produce hydrogen from a sustainable energy source is water electrolysis. However a major part of the hydrogen production cost is the energy consumption. Therefore, there is a large potential in improving the efficiency of the electrolysis in order to make hydrogen produced this way cheaper.

A strategic way to reach this goal is to increase the operating temperature of the Proton Exchange Membrane (PEM) electrolyser. The energy efficiency may then be significantly improved because of the decreased thermodynamic energy requirement, enhanced electrode kinetics, and the possible integration of heat recovery.

To achieve this strategic target, it is critical to develop and improve fundamental materials such as anodic catalysts, membranes, gas diffusion layers, bipolar plates, and other construction materials. The final target of the project, a 1 kW prototype PEM steam electrolyser will be designed, constructed and tested for demonstration.

Problem

As mentioned in the outline one of the key materials that should be improved to operate at elevated temperature is the membrane. Phosphoric acid doped polybenzimidazole (PBI) membranes have been tested for electrolysis at elevated temperatures where they showed quite good performance, but their durability were too poor. Perfluorinated sulfonic acid (PFSA) membranes like Nafion® have been demonstrated to function with high performance and durability at temperatures below 100 °C. As a consequence of the poor durability of the PBI membranes, the focus on PFSA membranes was intensified. The problem with PFSA membranes at elevated temperatures and ambient pressures is that the ionic conductivity is highly dependent on the water content of the membrane. To improve the conductivity and the physical properties of the membranes a composite system composed of a PFSA membrane (Nafion®), phosphoric acid (H_3PO_4)^[1] and zirconium phosphate ($Zr(HPO_4)_2 \cdot nH_2O$, ZrP)^[2] was prepared. These composite membrane systems were tested in different variations. For example different membranes thickness and with or without ZrP.

Furthermore different kinds of gas diffusion layers (GDLs) were tested to see the importance to the overall performance.

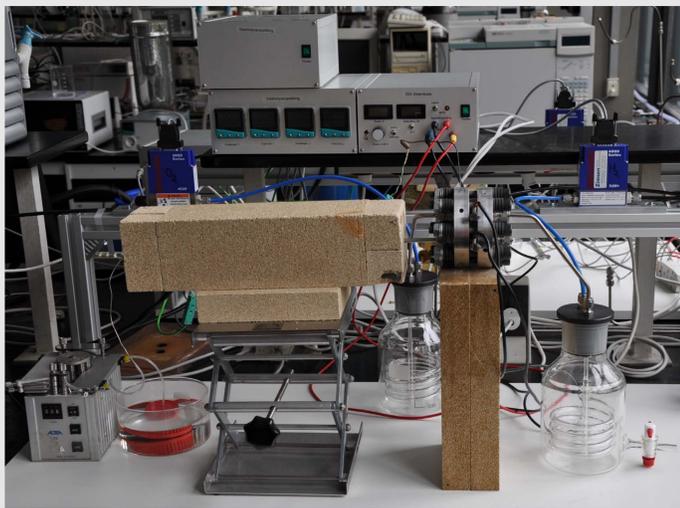
Experimental

The electrolysis tests were done on an in-house build test equipment consisting of: Galvanostat, data collection device, temperature controller, peristaltic pump, evaporator, condensation units and mass flow meters.

Tests were performed at 130 °C with an over-stoichiometric steam flow (15 mL/h liquid water) on a 10 cm² single cell at ambient pressure.

Both the anode and cathode was sprayed directly to the respective GDLs. The cathode was a 0.7 mg/cm² 40 wt% Pt/C electrode on wet-proofed carbon cloth. The anode was an approx. 4 mg/cm² IrO₂ electrode on tantalum covered stainless steel felt.

All the polarisation data was collected under steady state conditions. The composite membranes were treated over night at 150 °C in 85 wt% H_3PO_4 or in a ZrP saturated 85 wt% H_3PO_4 solution.



Electrolysis test results

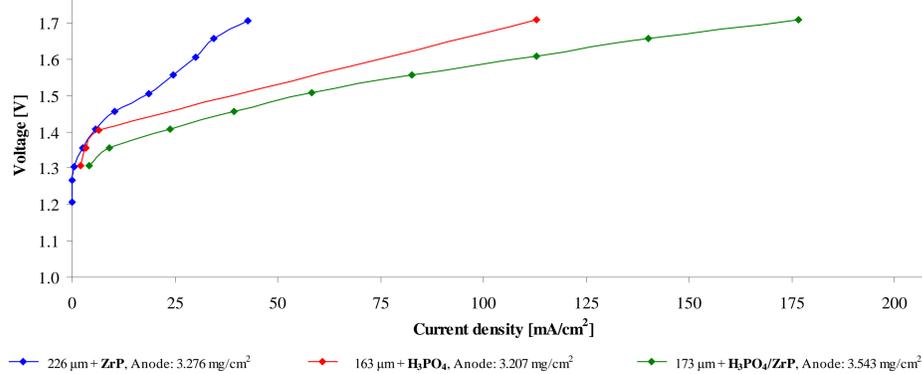


Figure 1: Comparison of different Nafion® 115 composite MEAs. Tested at 130 °C and ambient pressure.

As seen in figure 1, there is a clear trend, the overall performance improves greatly by going from a composite membrane only consisting of Nafion® and ZrP, to one consisting of Nafion® and H_3PO_4 . Furthermore there is an improvement when the composite membrane consist of Nafion®, H_3PO_4 and ZrP.

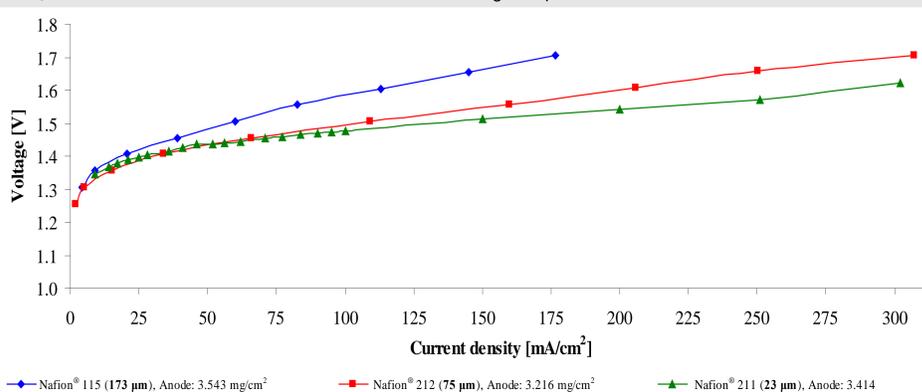


Figure 2: Comparison of different Nafion® thicknesses in a composite system with H_3PO_4 and ZrP. Tested at 130 °C and ambient pressure.

From figure 2 it is clear that the performance of a composite membrane system is very dependent on the thickness of the membrane in question. There is a clear improvement when going from a thick Nafion® 115 membrane to thinner Nafion® 212 and 211 membranes. The thinnest membrane Nafion® 211 shows the best performance, but the handling is very difficult due to the very thin thickness (~25 µm).

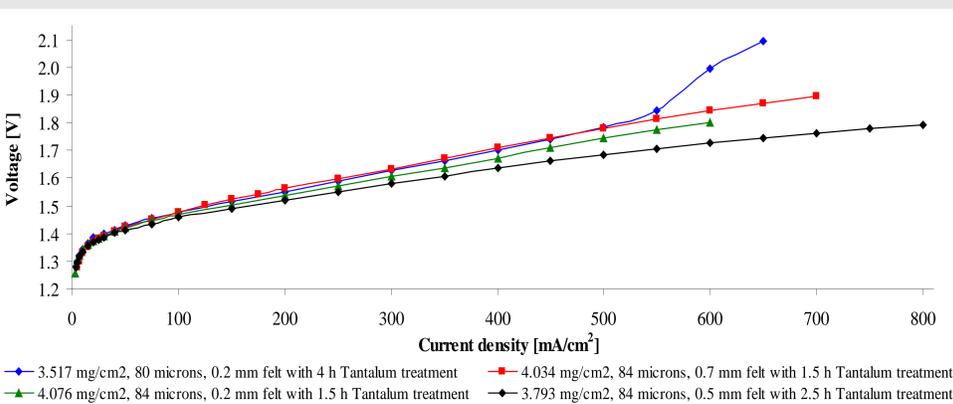


Figure 3: Comparison of different GDLs with H_3PO_4 doped PBI-MEAs. Tested at 130 °C and ambient pressure.

In figure 3 it can be seen that it is possible to treat the GDL with too much tantalum, so the porosity is partly lost. The GDL which had been treated with 4 hours of tantalum (the blue curve) exhibit clear transport problems (sudden increase in voltage) at higher current densities. Apparently from the polarisation curves in figure 3, a GDL with a thickness of 0.5 mm treated 2.5 h with tantalum (black curve) should be the best choice. But the differences seen are more likely to be due to differences in contact resistance between the membrane and GDL, than actual differences between the GDLs.

Conclusion

The composite system consisting of Nafion® 212, H_3PO_4 and ZrP shows the best combination between performance and handleability, but it is clear that the performance needs to be improved greatly to reach the same current densities as for H_3PO_4 /PBI systems. Further tests of the GDLs is necessary to find the optimum for the electrolysis setup, but it was found that the GDLs should be treated with rather thin tantalum layers (short exposure times), in order to keep its initial high porosity that is crucial to avoid transport problems at high current density.

References

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WELTEMP project partners

Technical University of Denmark (Project coordinator)
Institute of Chemical Technology Prague
The Norwegian University of Science and Technology
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