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Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Kraglund, M. R., Aili, D., Christensen, E., & Jensen, J. O. (2016). *Polybenzimidazole membranes for zero gap alkaline electrolysis cells*. Poster session presented at The 21st World Hydrogen Energy Conference (WHEC), Zaragoza, Spain.

DTU Energy
Department of Energy Conversion and Storage

Polybenzimidazole membranes for zero gap alkaline electrolysis cells

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Membranes of *m*-PBI doped in KOH (aq), 15-35 wt%, show high ionic conductivity in the temperature range 20-80 °C.
In electrolysis cells with nickel foam electrodes m-PBI membranes provide low internal resistance. With a 60 µm membrane at 80 °C in 20 wt% KOH, 1000 mA/cm^2 is achieved at 2.25

m-PBI

One of the distinct disadvantages of alkaline electrolysis is the use of a thick porous diaphragm as an electrolyte containing separator. Commonly investigated alternatives are often anion exchange polymer membranes or ion-solvating polymer membranes.

A promising ion-solvating polymer is poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole), *m*-PBI. When equilibrated in aqueous KOH solution the polymer deprotonizes, and at >15 wt% KOH (aq) the potassium form predominates [1], see Figure 1.

For membranes, this results in breaking of intermolecular hydrogen bonds, which decrease mechanical robustness and allows for significant swelling and electrolyte uptake. As a result, a ternary *m*-PBI-H_2O-KOH system is formed which display a high ionic conductivity.

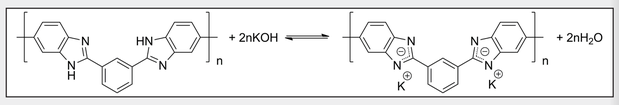

Figure 1. Deprotonization of *m*-PBI happens at high pH and the potassium form of *m*-PBI is predominant in KOH (aq) solutions of more than 15 wt% KOH.

Conductivity of the *m*-PBI membranes were measured in a tubular PTFE cell with 2 expanded nickel mesh electrodes, Figure 2. Temperature was controlled by placing the assembly in a heating cabinet. Electrochemical Impedance spectra were recorded, and the resistance taken as Z_{re} at Z_{im} = 0 Ω. Membrane conductivity, σ, was found by subtracting a blank sample measurement.

$$\sigma = \frac{t}{(R - R_{blank}) * A}$$

While the uncertainty is largest in the 15-35 wt% KOH concentration range where the conductivity peaks, there is a trend that suggests a conductivity peak near 20-25 wt%, which is lower than for bulk solution. At 25 wt% we measure 148 mS/cm at room temperature and 255 mS/cm at 80 °C.

Previous measurements have shown a peak conductivity of 130 mS/cm for 20 wt% KOH at room temperature [1].

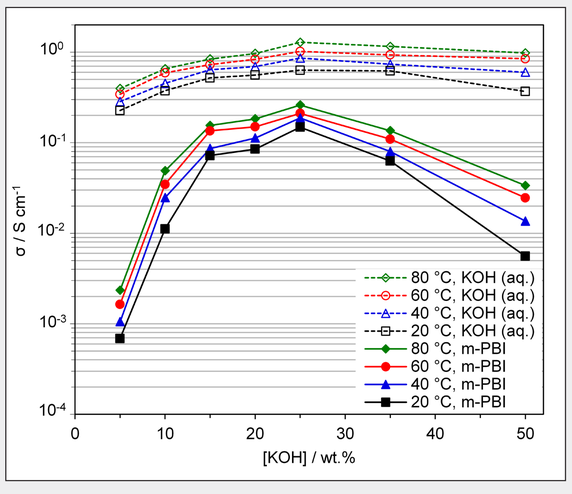

Figure 2. Measured conductivity, σ, of *m*-PBI and bulk solution at different concentrations of aqueous KOH at varying temperatures [2].

Cell polarization

For zero gap electrolysis cell measurements, *m*-PBI membranes were equilibrated in aqueous KOH at a given concentration overnight prior to cell assembly. Electrodes used were pressed (thickness ~ 210 µm) nickel foam, Figure 3.

Current-voltage-curves are presented in Figure 4. Data were recorded by scanning the potential from 1.2 to 2.5 V at 2.5 mV/s. The cells were operated at 80 °C.

The cell house and external setup is displayed in Figure 5, on the right. Aqueous KOH with concentration identical to the doping solution is circulated on both sides.

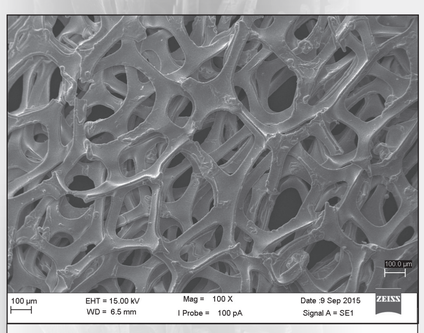

Figure 3. SEM micrograph of nickel foam electrode when pressed to 210 µm.

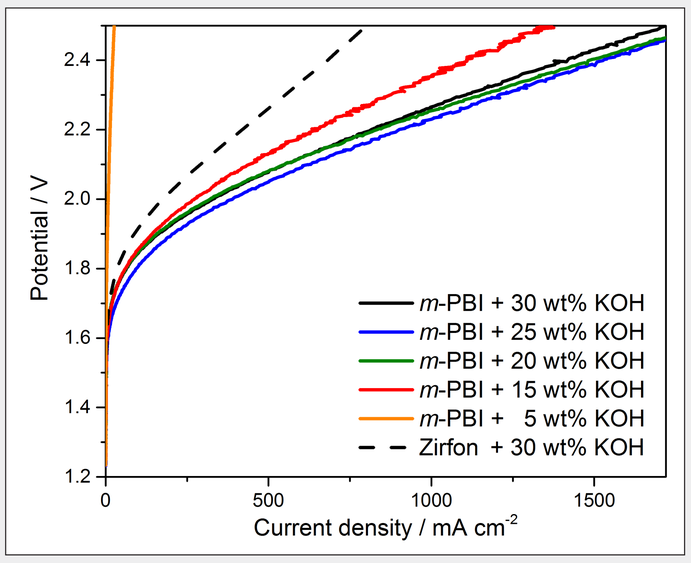

Figure 4. Cell polarization at 80 °C with *m*-PBI membranes at different KOH (aq) concentrations. Electrodes of pressed nickel foam. Membrane thickness in the range 50-60 µm. Thickness of Zirfon is about 500 µm.

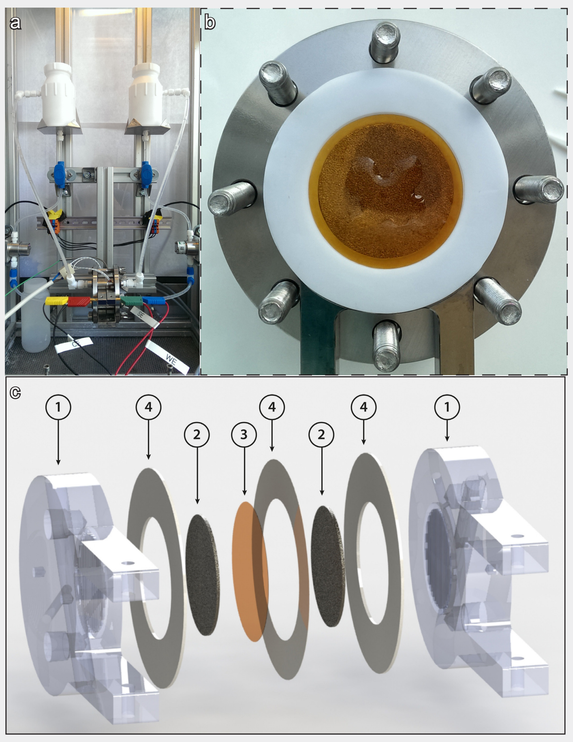

Figure 5. Cell setup. (a) System setup; tubes, fittings and containers from PFA or PTFE. Gear pumps for active electrolyte circulation.
(b) Cell assembly.
(c) Exploded view of the cell:
1) Linear flowfield plates (P-rich Ni coated steel), cell house Ø70 mm.
2) Nickel foam electrodes Ø38.5 mm.
3) *m*-PBI membrane Ø44.5 mm.
4) PTFE gaskets.

Novel electrode concepts

Hydrogen evolution

Increasing the active surface area of nickel catalysts is an efficient way to improve the hydrogen evolution activity. This is commonly done by using Raney catalysts, or by immobilizing nickel powder through the use of a binder, e.g. PTFE, or both [3].

We are using *m*-PBI polymer as a binder to make porous electrodes. The good alkaline stability and hydrophilic properties makes this an interesting binder for alkaline electrolysis in particular.

So far, we have prepared electrodes by first dissolving ~5 wt% *m*-PBI in alkaline ethanol (~5 wt% KOH in ethanol), and adding nickel powder to form a viscous mixture. The mixture was applied by a dip-coating procedure, in which nickel foam pieces was briefly submerged and otherwise left to dry in air.

A polarization curve for such an electrode is presented in Figure 6, compared to a non-coated nickel foam electrode.

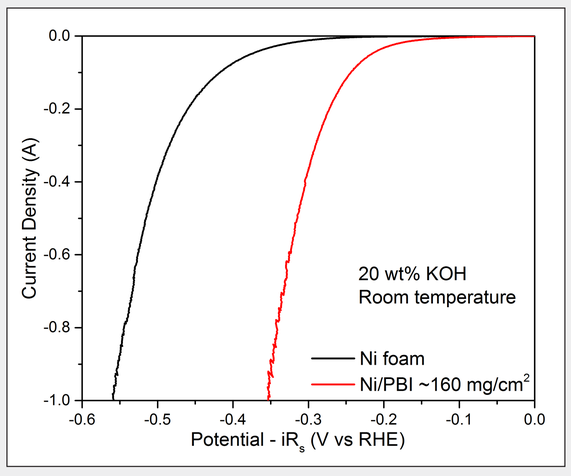

Figure 6. Hydrogen evolution polarization curves. Conditions: 20 wt% KOH and room temperature. Scan rate 2 mV/s.
CE: Large nickel mesh surrounding the WE and RE
RE: Reversible Hydrogen Electrode

Oxygen evolution

Increasing the active surface area of nickel does not seem to have the same effect on the OER compared the HER, and stability issues are more severe for OER. However, recent research have shown that Fe-doped nickel hydroxide is a very active OER catalyst [4].

Electrodes can be made in various ways, here, Figure 7, an electrode prepared by a hydro thermal process using urea, and nickel and iron nitrates is presented. This demonstrate a huge potential for overall cell improvements.

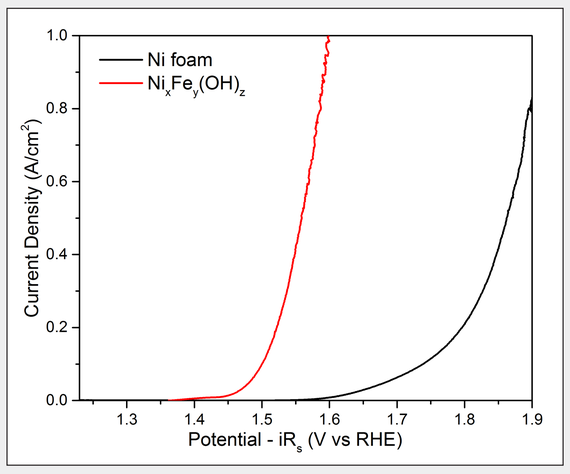

Figure 7. Oxygen evolution polarization curves. Conditions: 20 wt% KOH and room temperature. Scan rate 2 mV/s.
CE: Large nickel mesh surrounding the WE and RE
RE: Reversible Hydrogen Electrode

Acknowledgements
This work is funded by ther internal project "PorouZ" at DTU Energy

References

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World Hydrogen Energy Conference 2016
Zaragoza, 13th-16th of June, 2016
Hydrogen Production: Electrolysis / Electrolyzers
Poster code: P-103

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