Polybenzimidazole membranes for zero gap alkaline electrolysis cells

Kraglund, Mikkel Rykær; Aili, David; Christensen, Erik; Jensen, Jens Oluf

Publication date:
2016

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

Link back to DTU Orbit

Citation (APA):
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/cm² is achieved at 2.25 V.

### m-PBI

One of the distinct disadvantages of alkaline electrolysis is the use of a large volume of an electrolyte containing separator. Commonly investigated alternatives are often anion exchange polymer membranes or on-solvolating polymer membranes. A promising ion-exchange polymer is poly(2,2’-(m-phenylene) 5,5’-bithiazole), 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 decreases mechanical robustness and allows for significant swelling and electrolyte uptake. As a result, a ternary m-PBI-H₂O-KOH system is formed which displays a high ionic conductivity.

![SEM micrograph of nickel foam electrode when pressed to 210 µm.](image)

**Figure 1.** Depolarization of m-PBI happens at high pH and the presence of water promotes protonation in KOH (aq) solutions of more than 15 wt% KOH.

Conductivity of the m-PBI membranes were measured in a laboratory 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 $Z_{eq}$ at $ω = 0$ Hz. Membrane conductivity was found by subtracting a blank sample measurement.

$\sigma = \left( V_{app} / \Delta I \right) / t$

While the uncertainty is large in the 15-25 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].

![Graph showing measured conductivity vs. wt% KOH at different temperatures.](image)

**Figure 3.** Measured conductivity, $\sigma$, of m-PBI and bulk solution at different concentrations of aqueous KOH at varying temperatures [3].

### 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), and adding nickel powder to form a viscous mixture. The mixture was applied by a dip-coating procedure, in which nickel foam piece 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.

![Graph showing POTential vs. CURRENT DENSITY for different electrodes.](image)

**Figure 5.** Cell polarization at 80 °C with m-PBI membranes at different KOH (aq) concentrations. Membrane thickness in the range 50-60 µm. Thickness of Zifron is about 500 µm.

### Oxygen evolution

Increasing the active surface area of nickel does not seem to have the same effect on the OER compared to the HER, and stability issues are more severe for OER. However, recent research have shown that Fe-doped nickel hydroxide in 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 anise, and nickel and iron nitrate is presented. This demonstrate a huge potential for overall cell improvements.

![Graph showing Oxygen evolution polarization curves.](image)

**Figure 7.** Oxygen evolution polarization curves. Conditions: 20 wt% KOH and room temperature. Scan rate 2 mV/s. C1: Large nickel mesh surrounding the WE and RE. C2: Scale Hydrogen Electrode. C3: Standard Hydrogen Electrode.

### References


**World Hydrogen Energy Conference 2016**
Zaragoza, 10-14 June, 2016
Hydrogen Production: Electrolysis / Electrolyzers
Poster code: P-103

Contact Info:
Mikkel Rykær Kraglund
mir@dtu.dk
+45 43252385

DTU Energy
Kemitorvet 207
DK-2800 Kgs. Lyngby
Denmark