

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):

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 Library

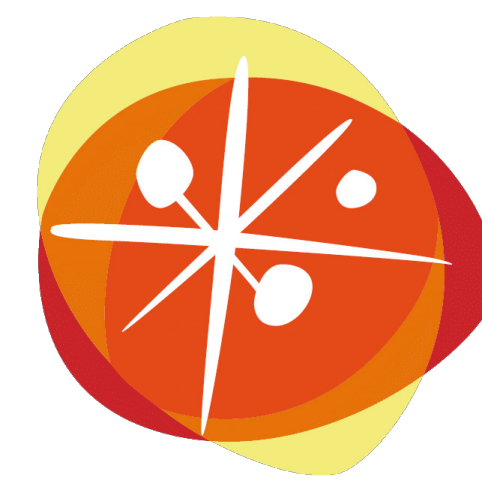
Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Polybenzimidazole membranes for zero gap alkaline electrolysis cells

Mikkel R. Kraglund, David Aili, Erik Christensen, Jens O. Jensen

Section for Proton Conductors, Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark

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

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-H₂O-KOH system is formed which display a high ionic conductivity.

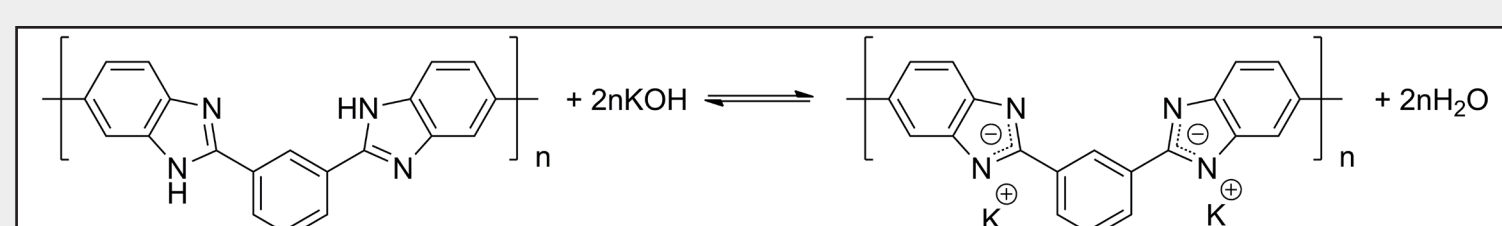


Figure 1. Deprotonation of *m*-PBI happens at high pH and the potassium form of *m*-PBI is predominant in KOH (aq) solutions of more than 15 wt% KOH.

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 $Z_{im} = 0 \Omega$. 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].

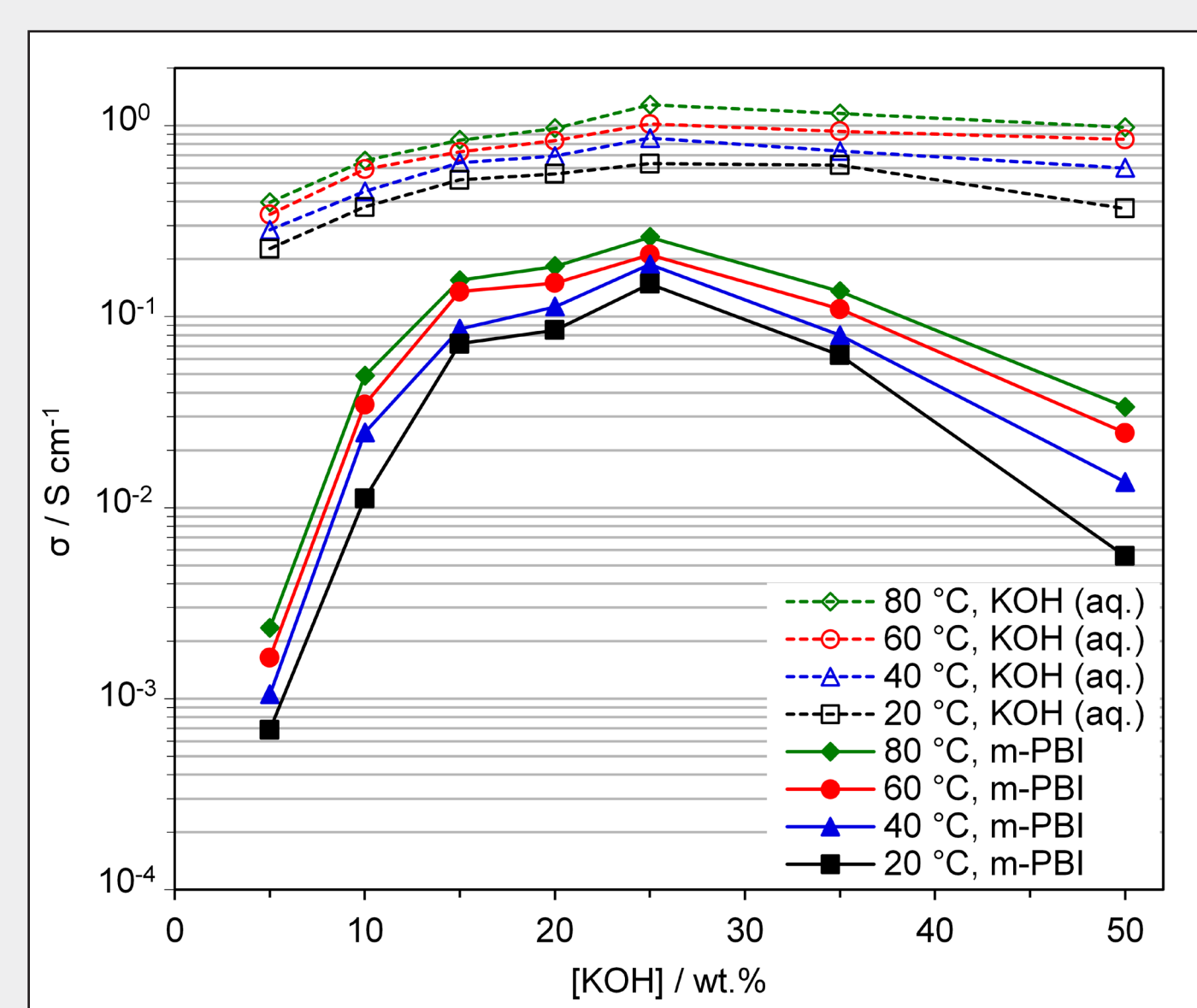


Figure 2. Measured conductivity, σ , of *m*-PBI and bulk solution at different concentrations of aqueous KOH at varying temperatures [2].

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.

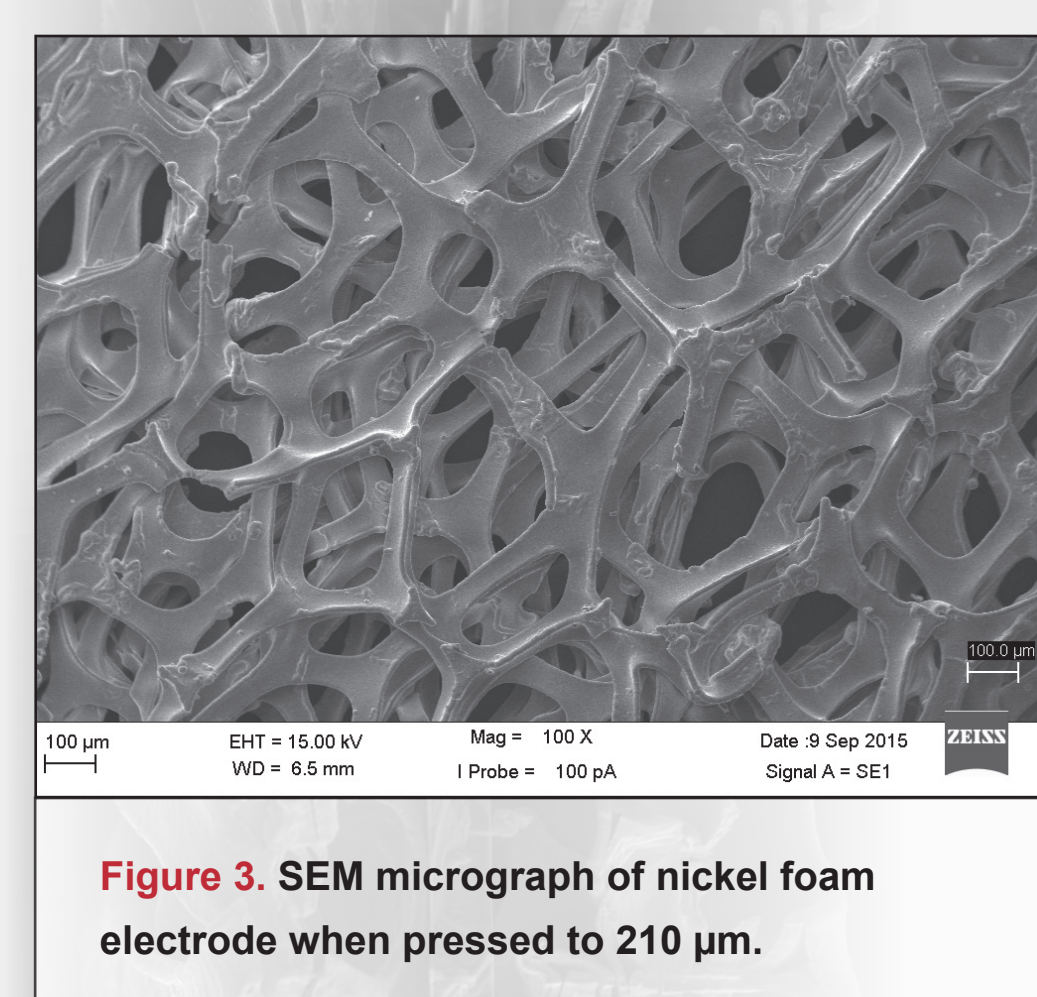


Figure 3. SEM micrograph of nickel foam electrode when pressed to 210 µm.

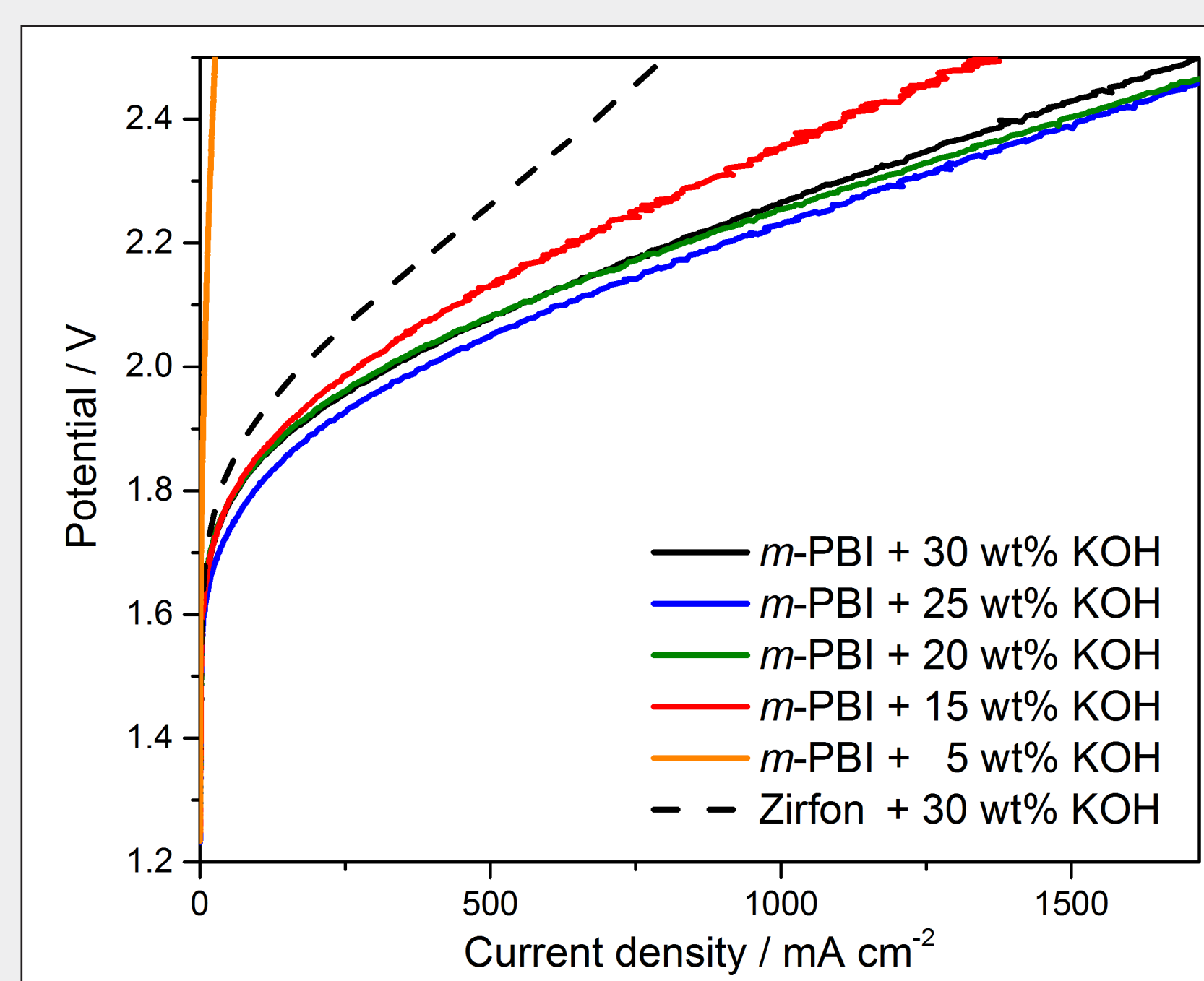
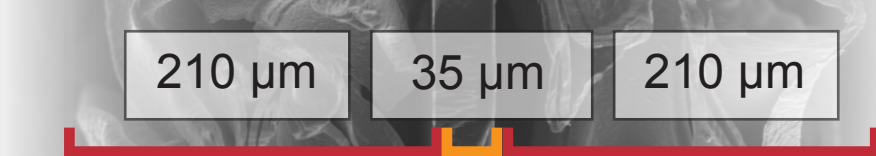


Figure 4. Cell polarization at 80 °C with *m*-PBI membranes at different KOH (aq) concentrations. Electrodes of pressed nickel foam. Membrane thickness in the range 50-60 µm. Thickness of Zirfon is about 500 µm.

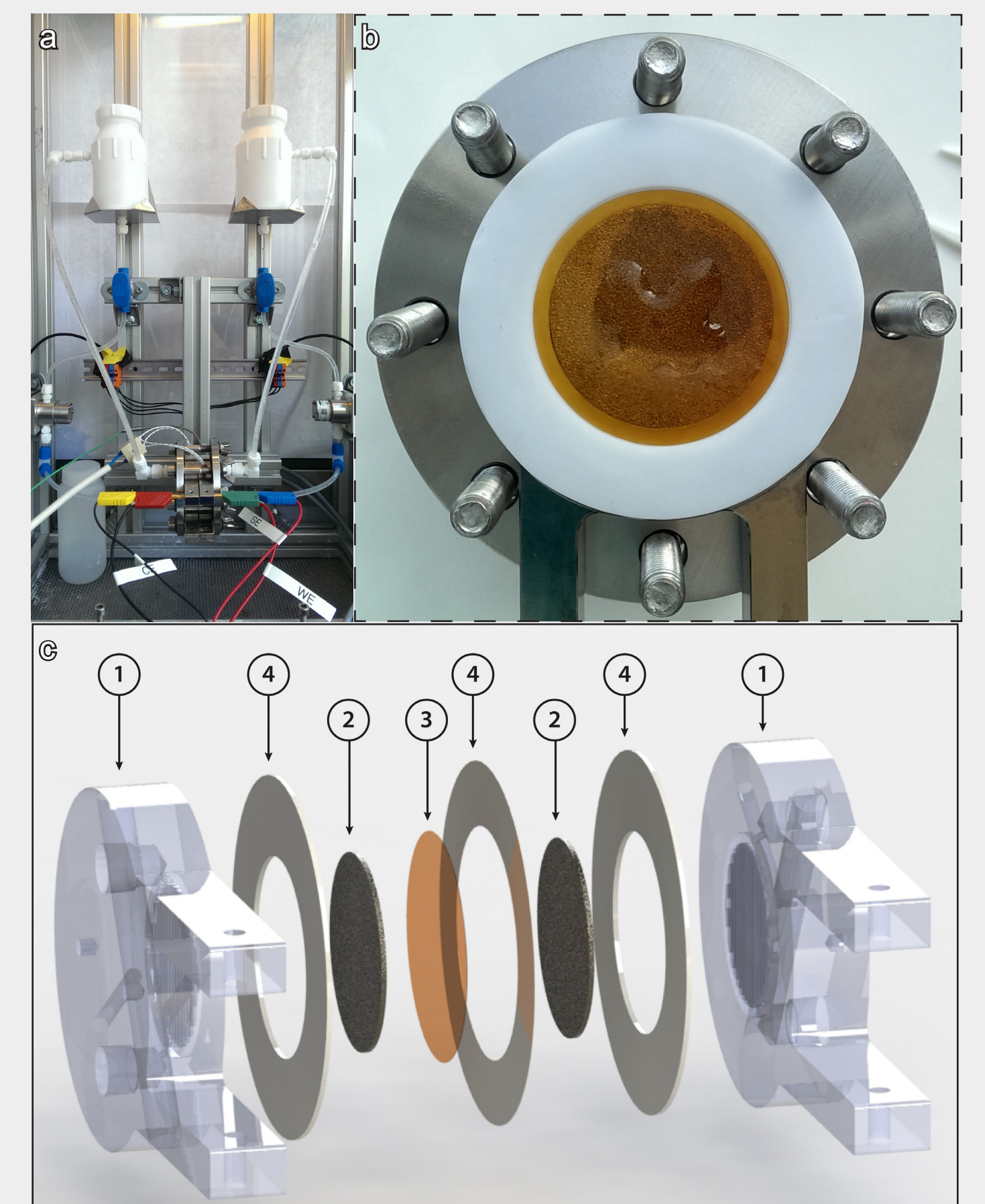


Figure 5. Cell setup. (a) System setup; tubes, fittings and containers from PFA or PTFE. Gear pumps for active electrolyte circulation. (b) Cell assembly. (c) Exploded view of the cell: 1) Linear flowfield plates (P-rich Ni coated steel), cell house Ø70 mm. 2) Nickel foam electrodes Ø38.5 mm. 3) *m*-PBI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

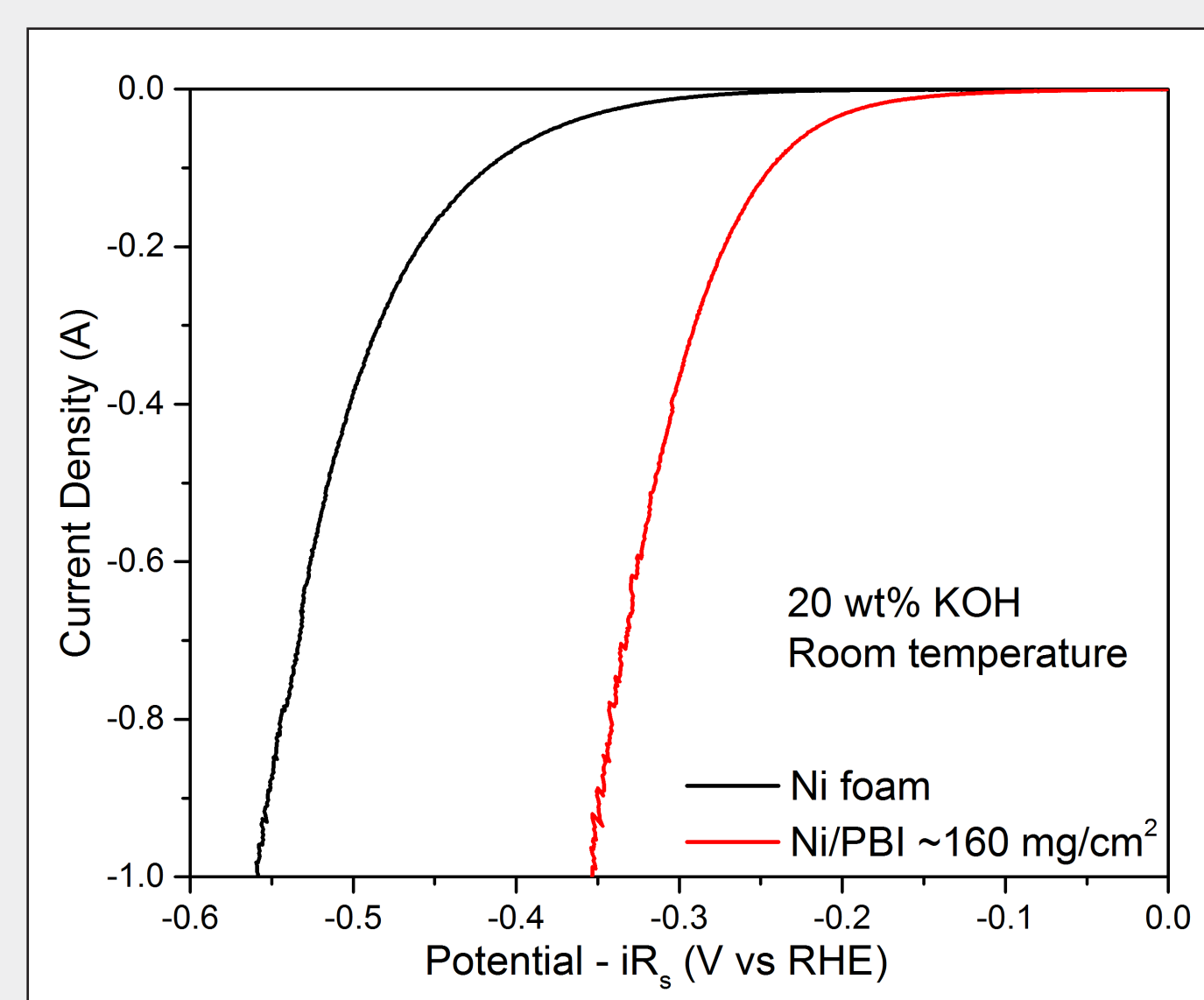


Figure 6. Hydrogen evolution polarization curves. Conditions: 20 wt% KOH and room temperature. Scan rate 2 mV/s. CE: Large nickel mesh surrounding the WE and RE RE: Reversible Hydrogen Electrode

Oxygen evolution

Increasing the active surface area of nickel does not seem to have the same effect on the OER compared to 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.

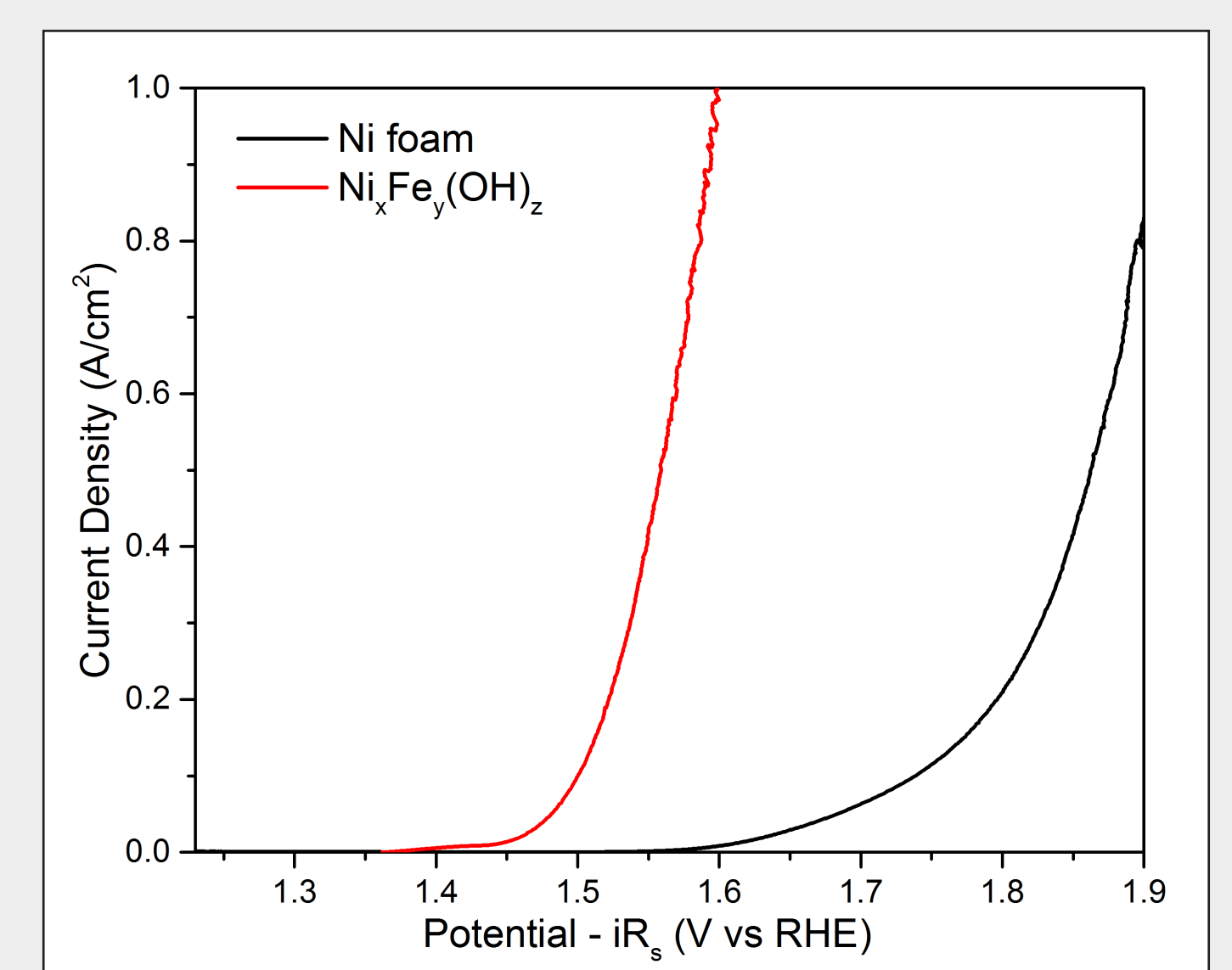


Figure 7. Oxygen evolution polarization curves. Conditions: 20 wt% KOH and room temperature. Scan rate 2 mV/s. CE: Large nickel mesh surrounding the WE and RE RE: Reversible Hydrogen Electrode

Acknowledgements

This work is funded by their internal project "Porouz" at DTU Energy

References

- [1] D. Aili et al., Understanding ternary poly(potassium benzimidazole)-based polymer electrolytes. *Polymer*, 84, 304-310 (2016).
- [2] M. Kraglund et al., Zero-gap alkaline water electrolysis using ion-solvating polymer electrolyte membranes at reduced KOH concentrations. Submitted.
- [3] S. Marini et al., Stable and inexpensive electrodes for the hydrogen evolution reaction. *Int. J. Hydrogen Energy*, 38, 11484-11495 (2013).
- [4] Z. Lu et al., Three-dimensional NiFe layered double hydroxide film for high-efficiency oxygen evolution reaction. *Chem. Commun.* 50, 6479-82 (2014).