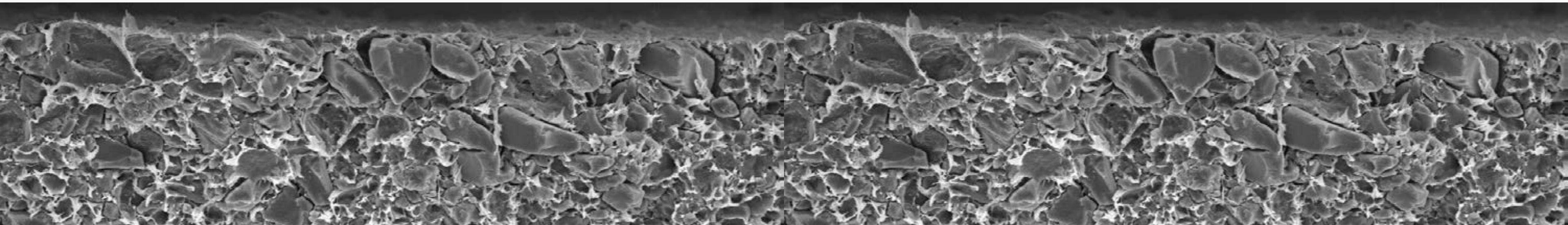
Properties of novel anion selective material with DABCO functional groups for alkaline water electrolysis

Jaromír Hnát, Jan Žitka, Martin Ďurovič, Martin Paidar, Karel Bouzek

Department of Inorganic Technology
Institute of Chemical Technology Prague

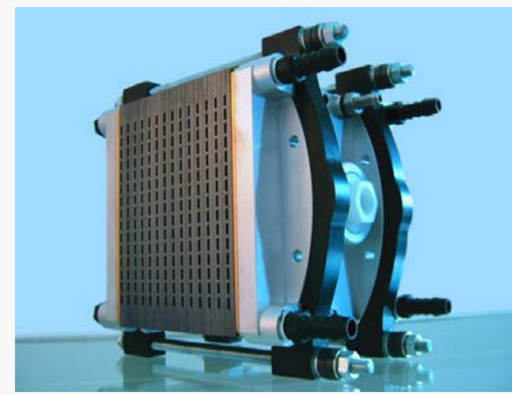
Department of Macromolecular Chemistry
Academy of Sciences of the Czech Republic



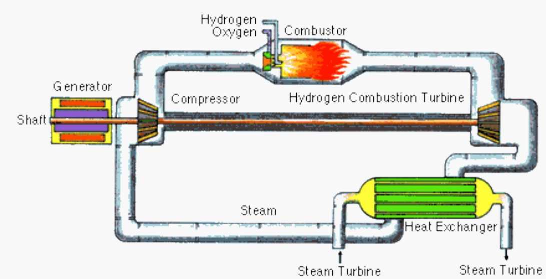
Hydrogen and hydrogen economy

Hydrogen as energy vector

- Produced from renewable sources
- Energy storage – alternative to batteries
- Water as side product

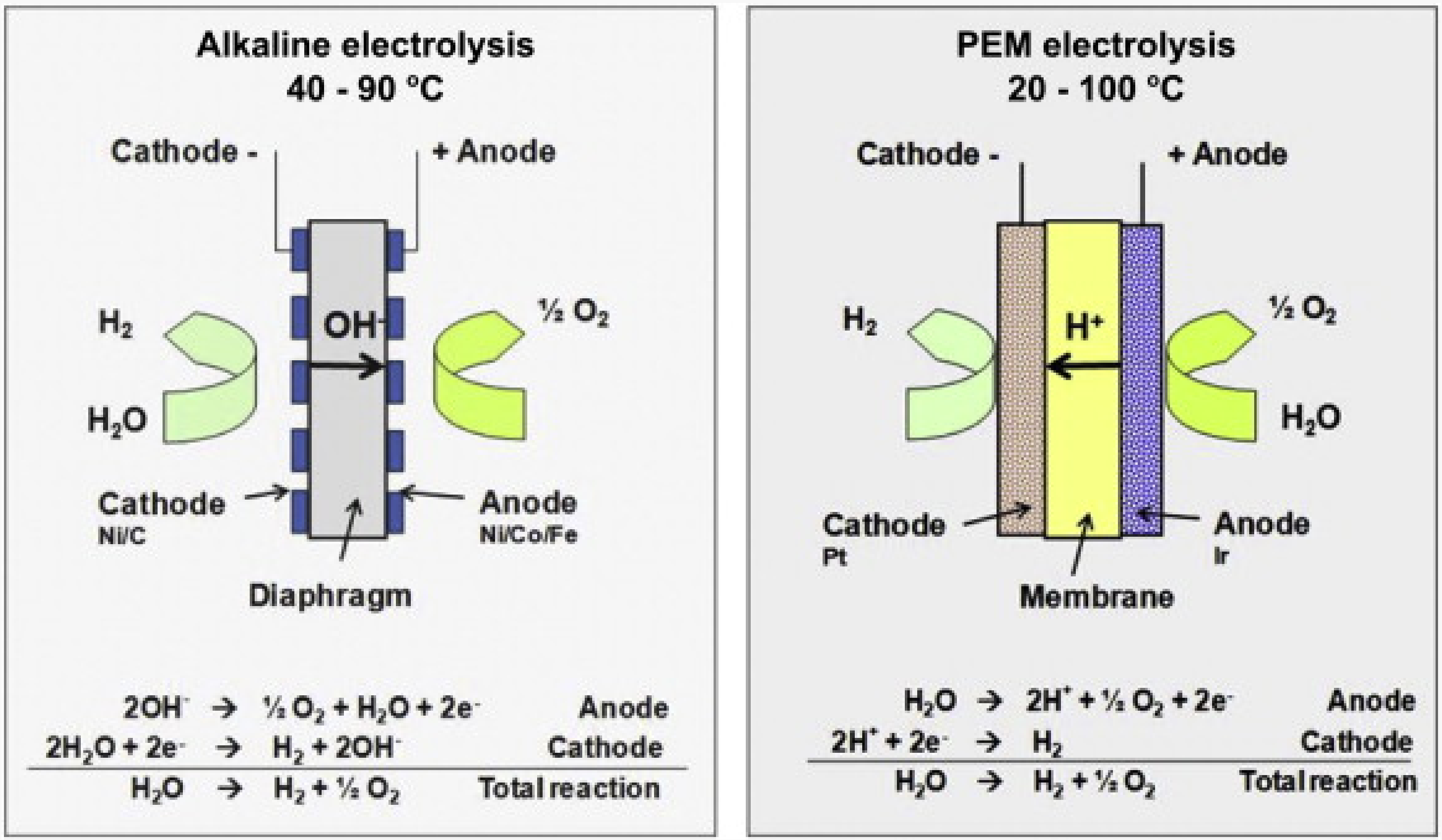


$$2H_2O \leftrightarrow 2H_2 + O_2$$



Renewable sources → Water electrolysis → Electricity production

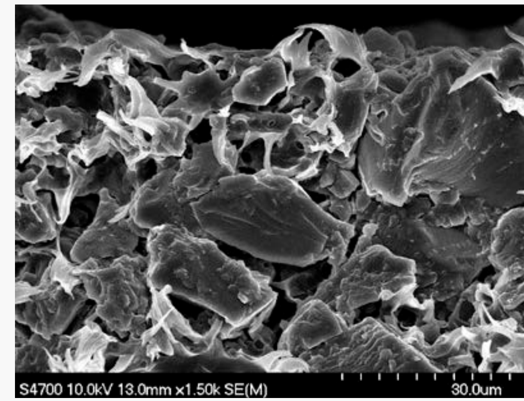
Alkaline vs. Proton Exchange Membrane water electrolysis



Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. International Journal of Hydrogen Energy. 2013;38:4901-34
http://origin-ars.els-cdn.com/content/image/1-s2.0-S0360319913002607-gr2.jpg

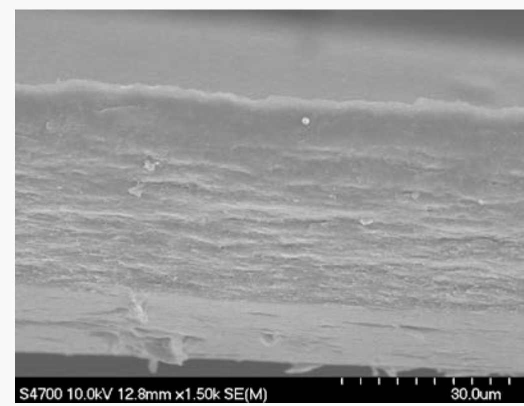
Anion selective membranes

Heterogeneous membranes



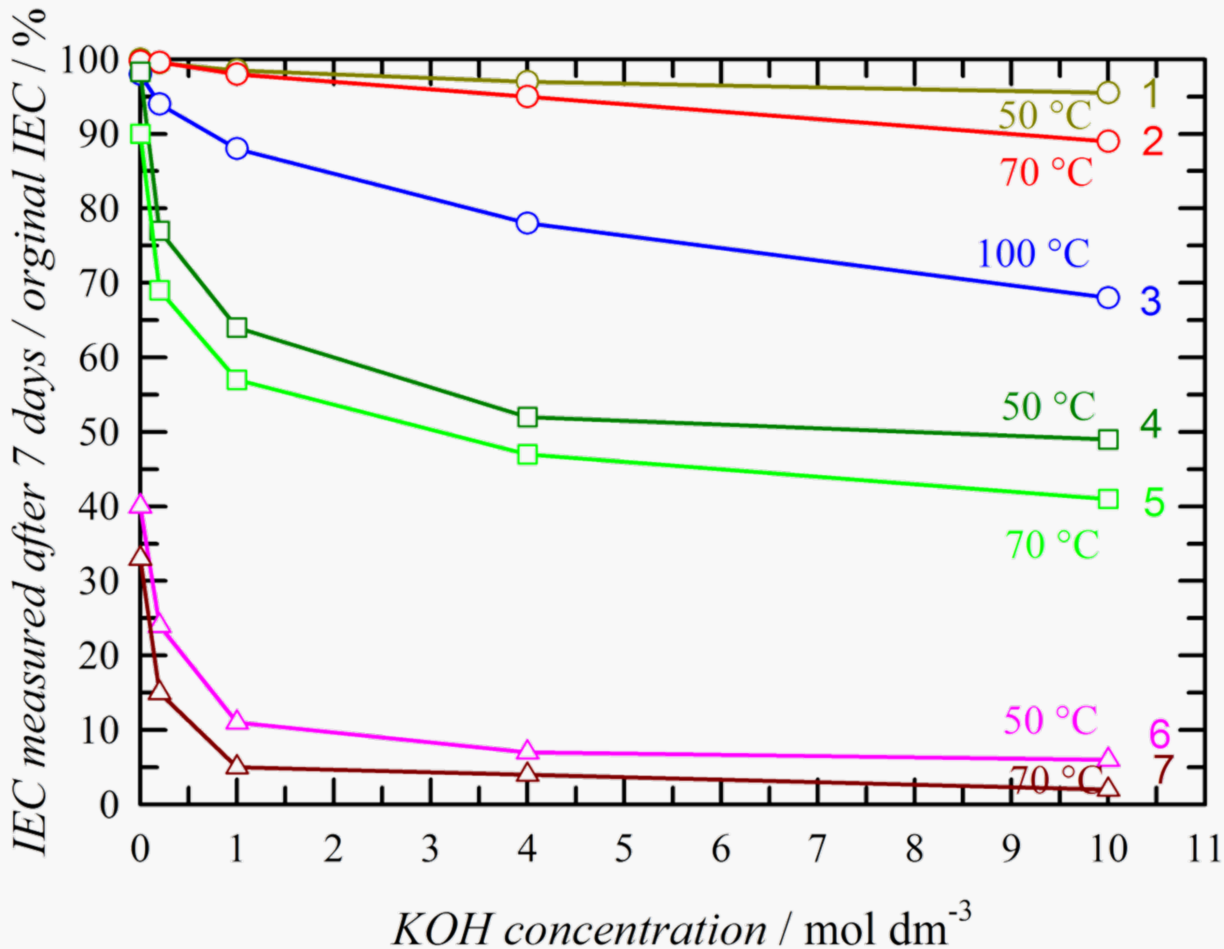
- Consist of the inert and functional phase
- Properties given by ratio of the phases
- Good stability
- Easy way of preparation
- Low cost

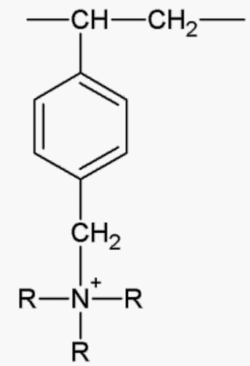
Homogeneous membranes

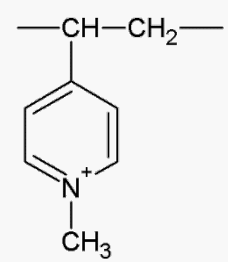


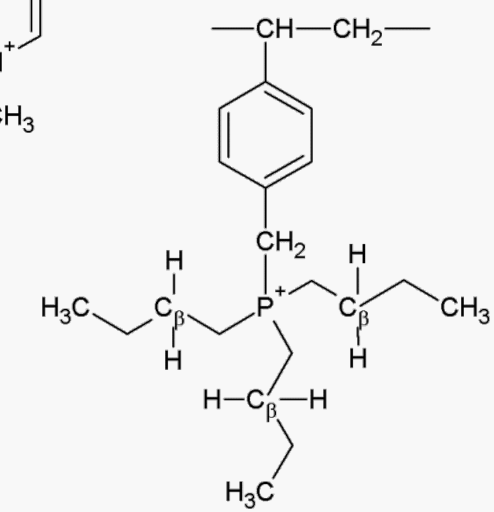
- Consist of one polymer/copolymer
- Properties given by degree of the functionalization
- Questionable stability
- Multistep synthesis

Stability of functional groups



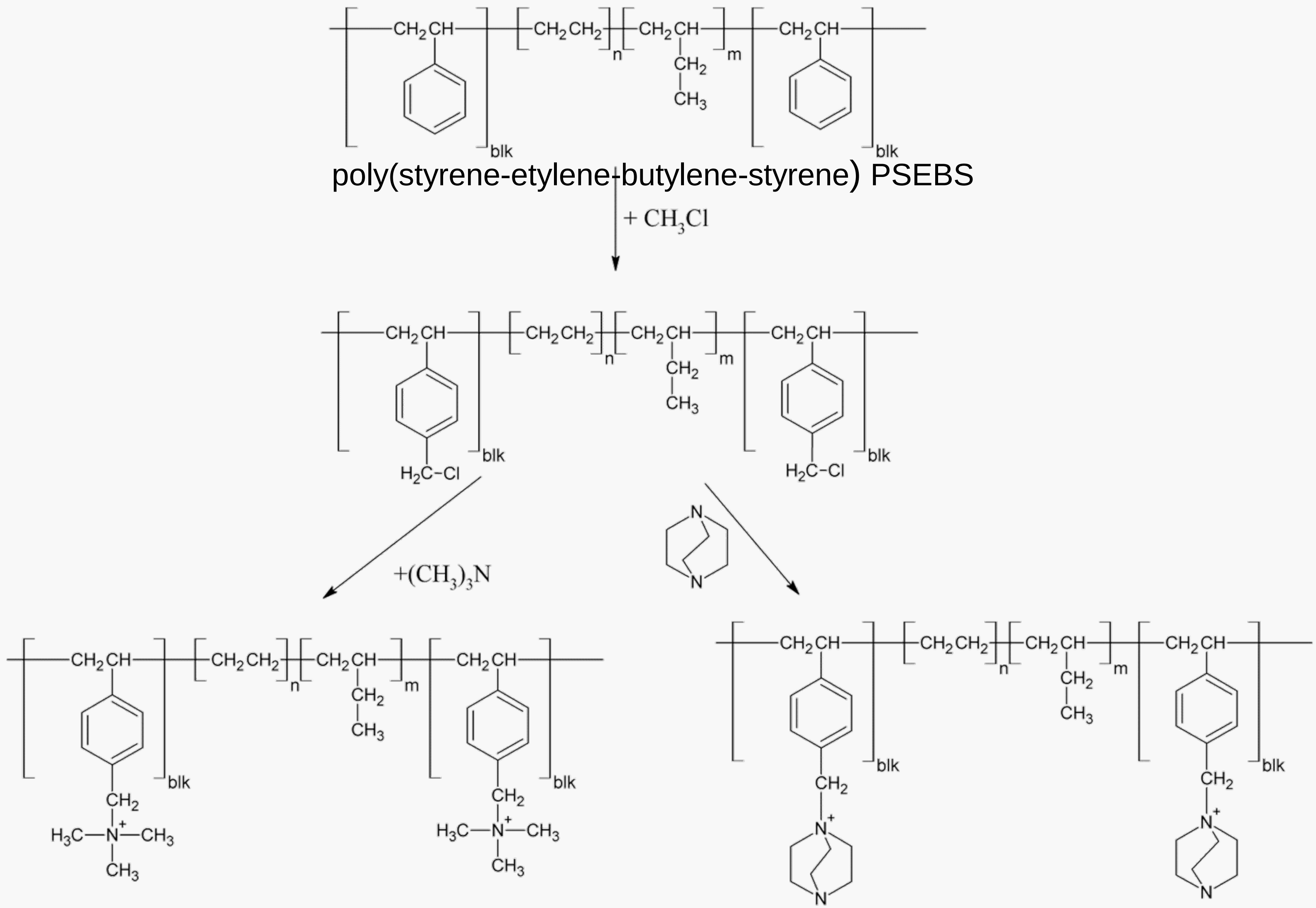






1 – 3: Functional group trimethylbenzylamonium
4 – 5: Functional group methylpiridinium
6 – 7: Functional group trimethylbenzylfosfonium

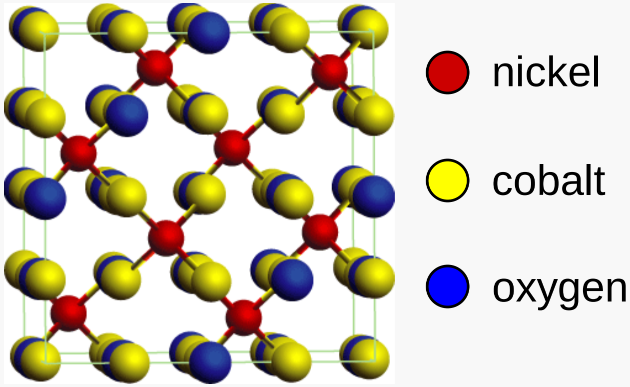
Experimental part – polymer synthesis



Experimental part – catalysts synthesis

Anode catalyst

- $NiCo_2O_4$
- Sufficient catalytic activity
- High corrosion resistance
- Low cost
- Prepared by coprecipitation of stoichiometric amounts of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$



Cathode catalyst

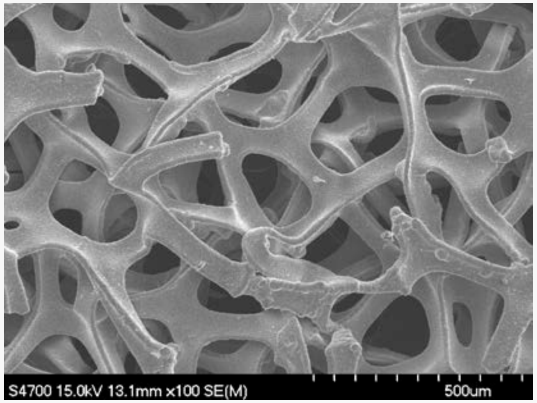
- $Fe_{60}Co_{20}Si_{10}B_{10}$
- Prepared by metal spinning
- Produced as ribbons
- Milled for 2 hours

Experimental part – electrode preparation

Anode

- Composition of the catalytic layer:

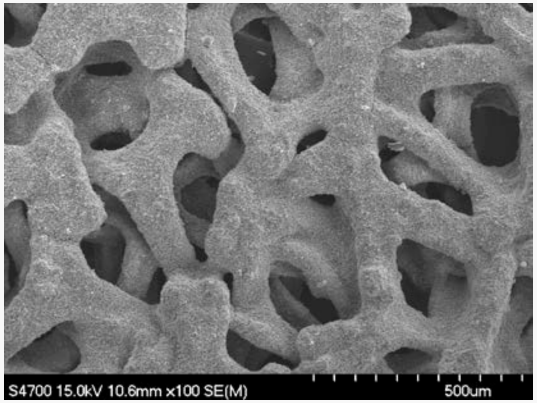
  5 mg $NiCo_2O_4$ cm^{-2} + 0.56 mg PSEBS cm^{-2}
- Ni Foam used as support
- Prepared by spraying on hot electrode



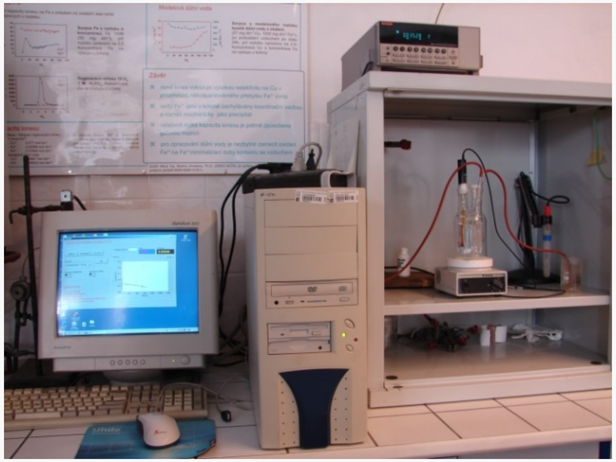
Cathode

- Composition of the catalytic layer:

  3.3 mg $NiCo_2O_4$ cm^{-2} + 0.37 mg PSEBS cm^{-2}
- Ni Foam used as support
- Prepared by sedimentation in ethylene glycol



Experimental part – methods

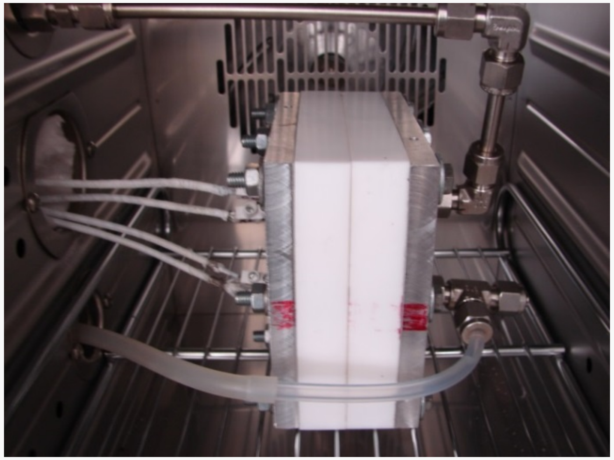


Ion Exchange Capacity

- Evaluated by potentiometry using pH glass electrode
- Digital electrometr Keithly
- pH Ross electrode
- Argon inert atmosphere
- Evaluated from OH^- ions change

Ionic Conductivity

- 4-electrode arrangement
- Measured in OH^- form
- Perturbation signal amplitude: 5 mV
- Frequency range: 65 kHz – 100 Hz
- 0 V vs. OCP
- Deionized water environment



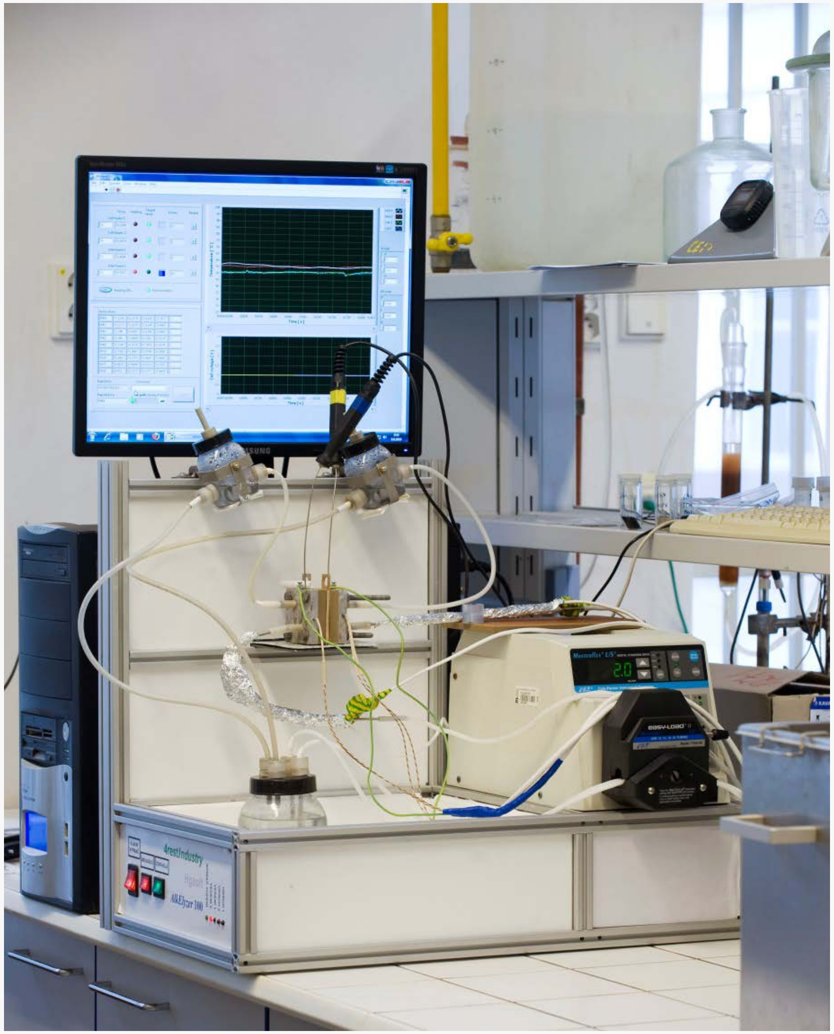
Experimental part – methods

Alkaline water electrolysis

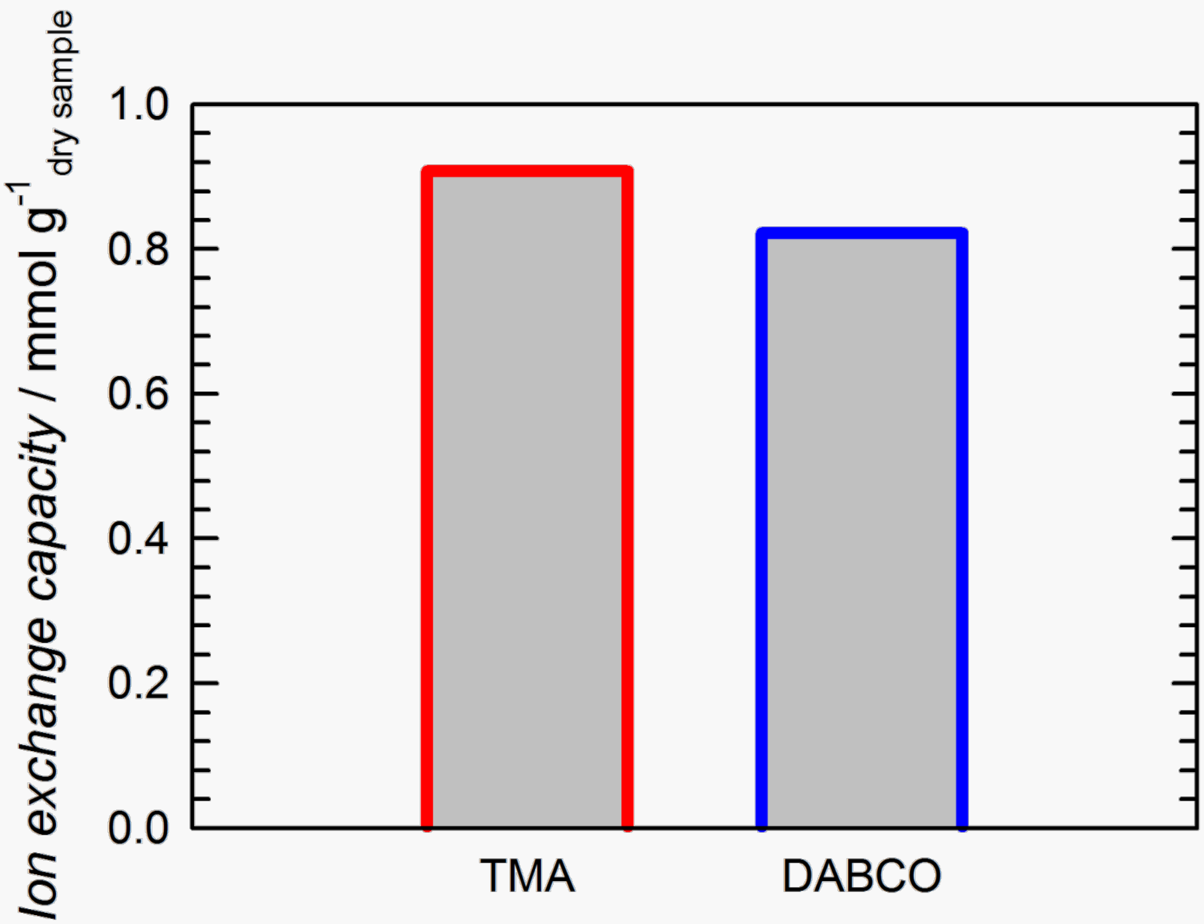
- 2-electrodes arrangement
- KOH solutions
- Flow rate: 5 ml min^{-1}
- Polymer electrolyte:
  anion selective membrane

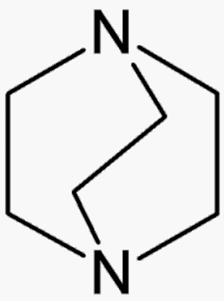
Electrochemical impedance spectroscopy

- Measured in 2 electrode arrangement
- Max. amplitude: 20 mV
- Cell voltage: 1.74 V
- Freequency range: 20kHz – 1 Hz

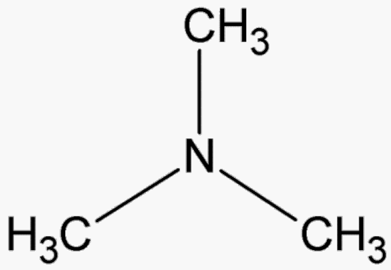


Ion exchange capacity



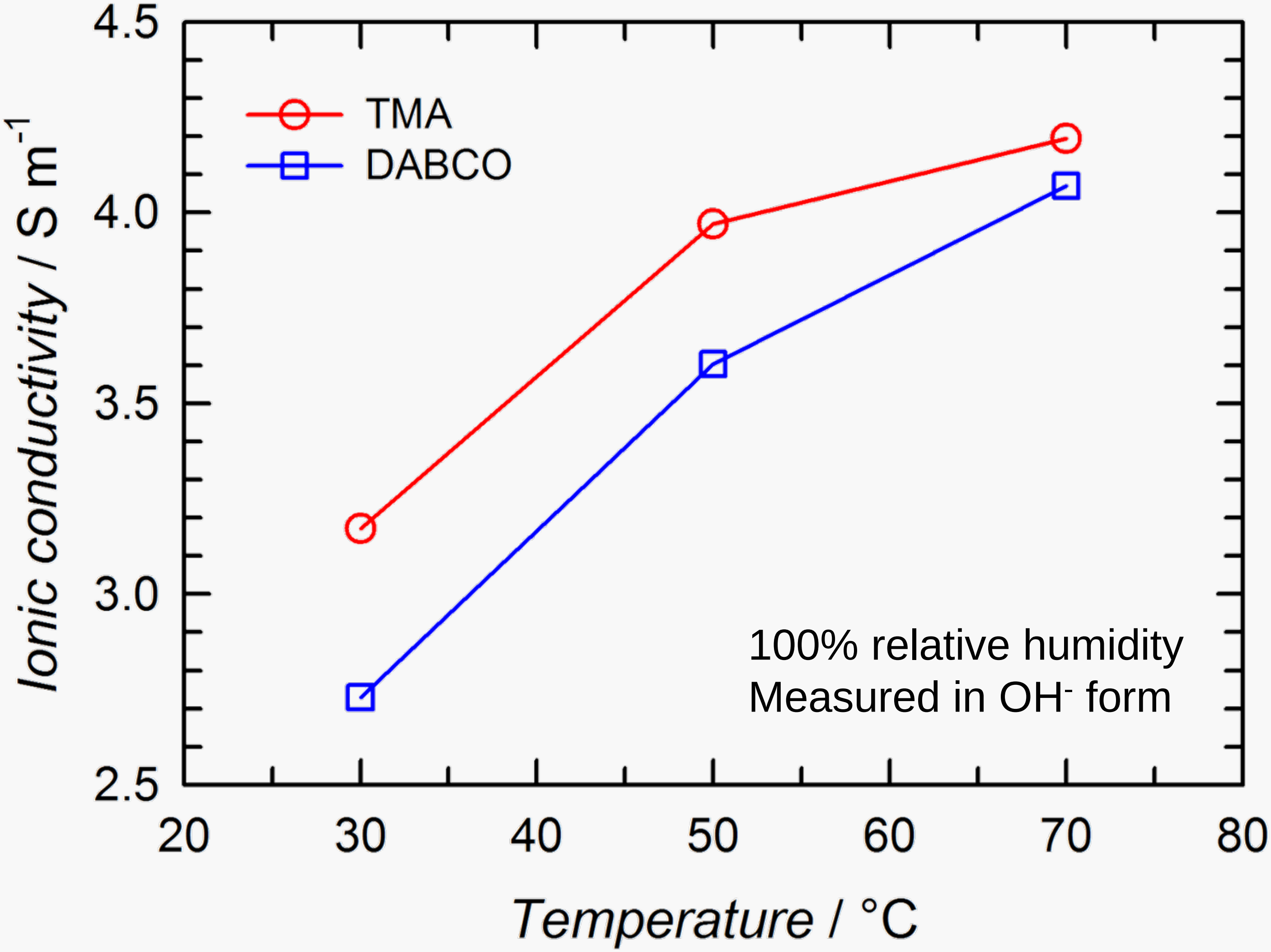


1,4-diazabicyclo[2.2.2]octane (DABCO)

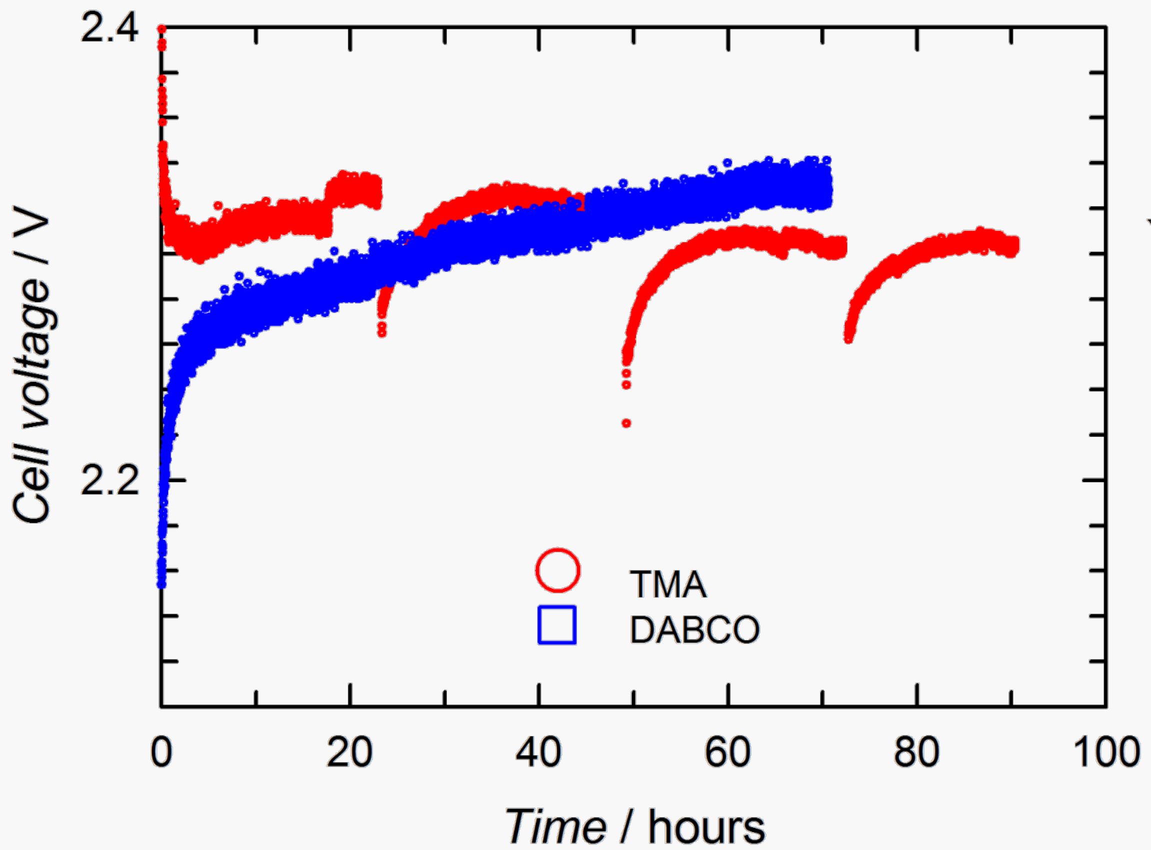


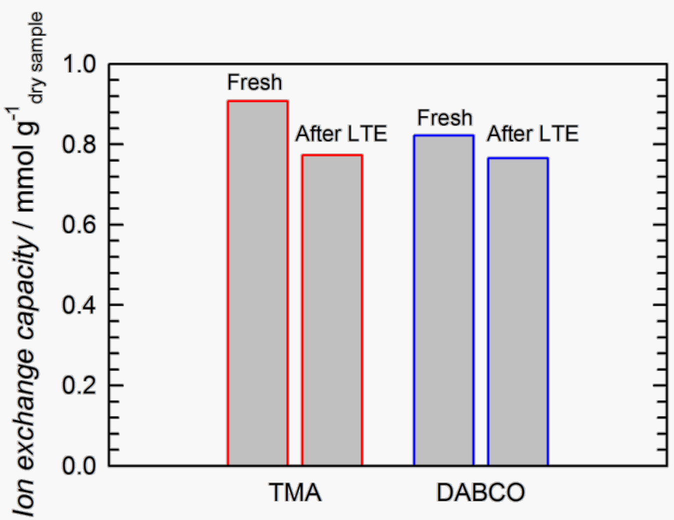
Trimethylamine (TMA)

Ionic conductivity



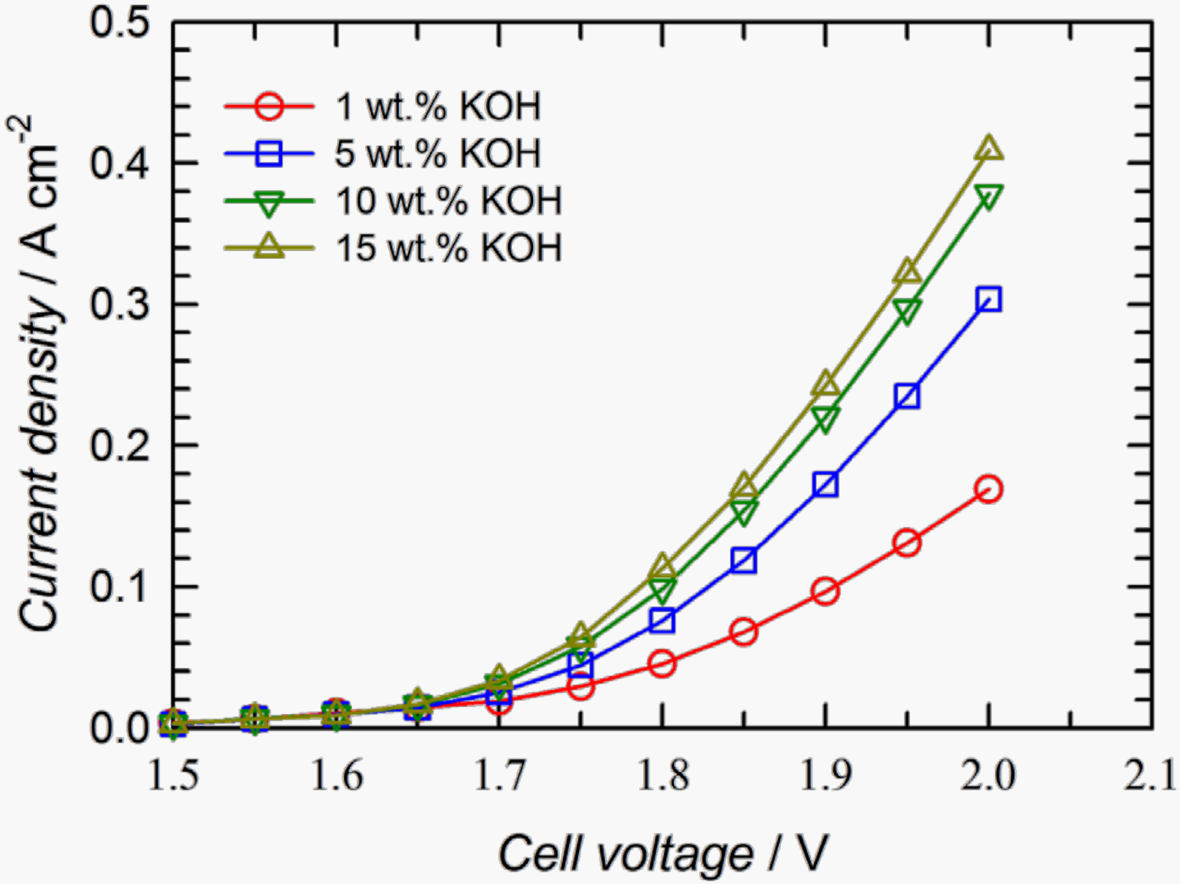
Stability under the conditions of alkaline water electrolysis





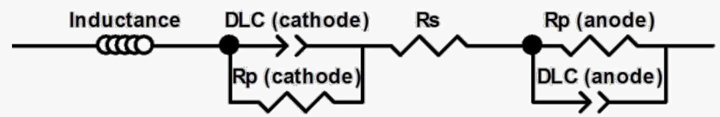
Separator: PSEBS membrane with corresponding functional groups indicated in the figure; electrolyte: 10 wt.% KOH; Temperature: 50 °C; anode: bare Ni foam; cathode: bare Ni foam; current density: 0.3 A cm^{-2}.

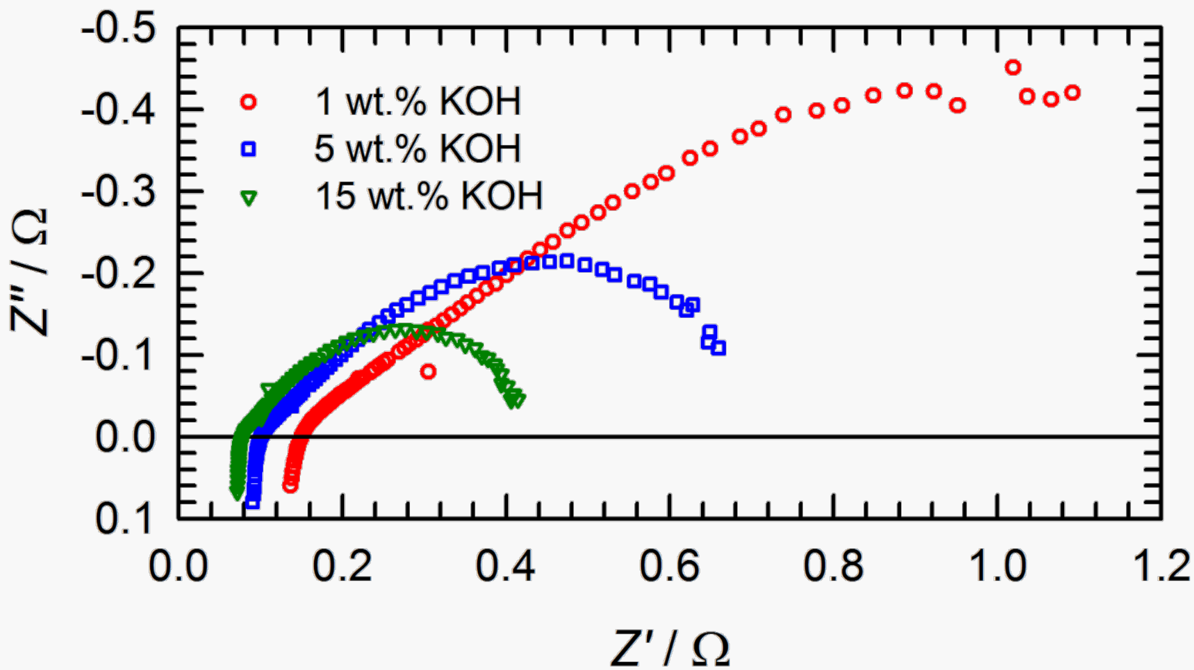
Alkaline water electrolysis – Electrochemical impedance spectroscopy

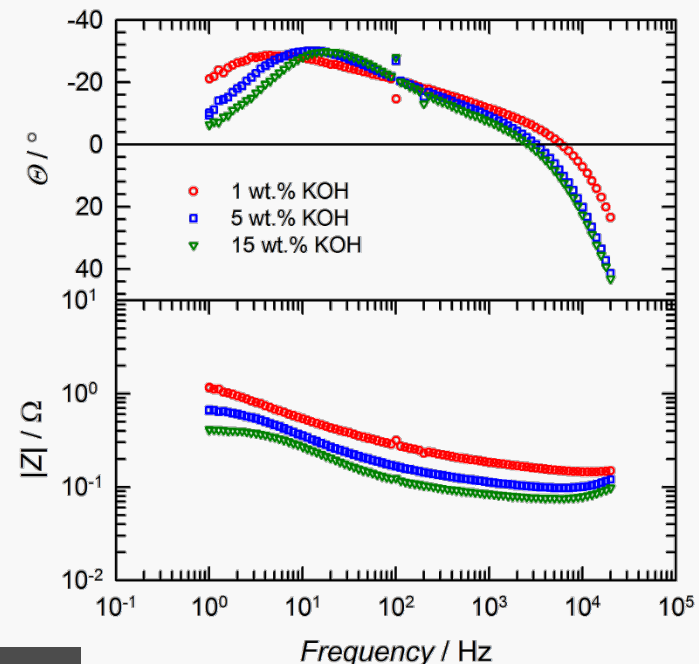


Separator: PSEBS membrane with DABCO functional groups; electrolyte: indicated in the figure; temperature: 50 °C; anode: 5 mg $NiCo_2O_4$ cm^{-2} + 0.56 mg PSEBS cm^{-2}; cathode: 3.3 mg $Fe_{60}Co_{20}Si_{10}B_{10}$ cm^{-2} + 0.37 mg PSEBS cm^{-2}.

Alkaline water electrolysis – Electrochemical impedance spectroscopy

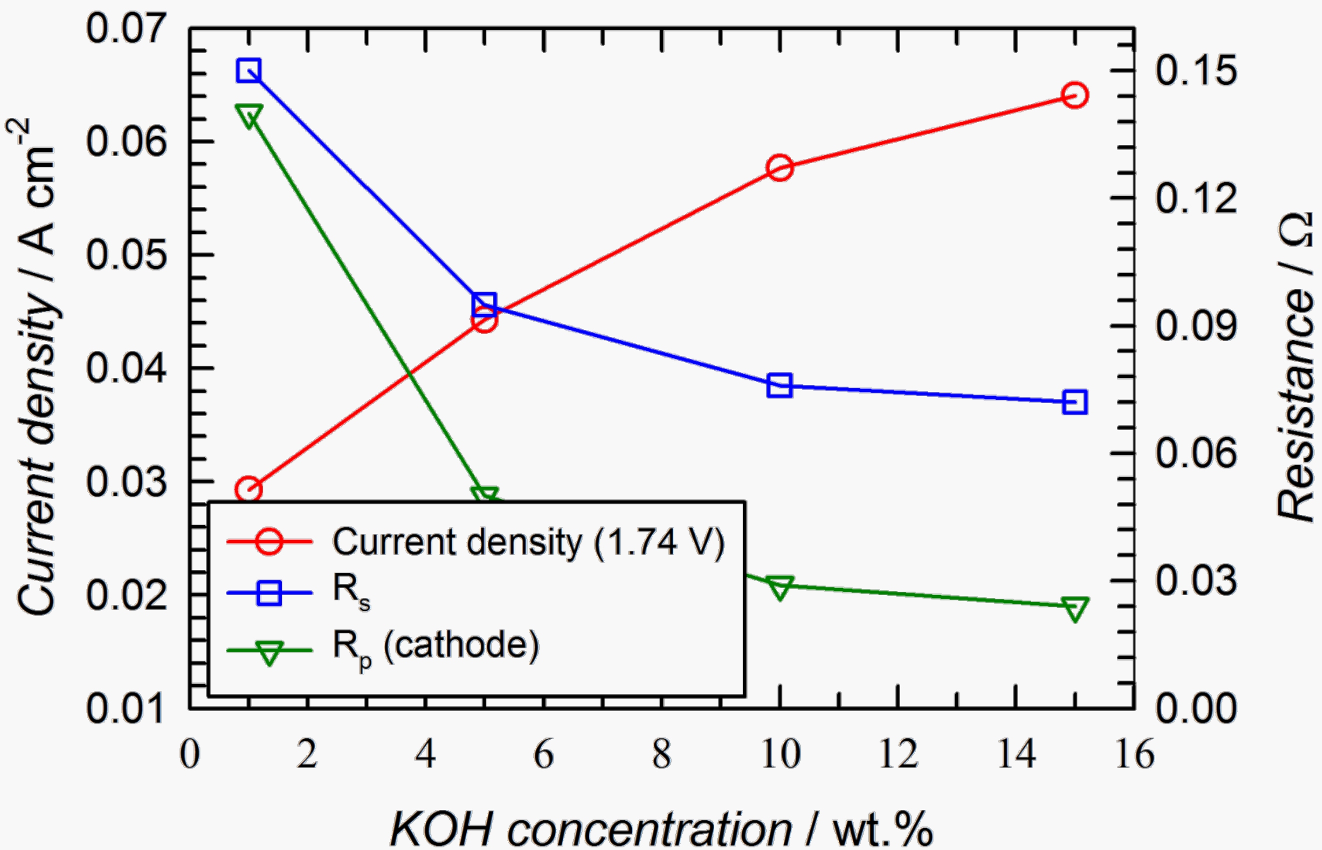






KOH concentration [wt. %]	R_s [Ω]	R_p cathode [Ω]	R_p anode [Ω]
1	0.150	0.140	1.09
5	0.095	0.050	0.58
10	0.076	0.029	N/A
15	0.072	0.024	0.35

Alkaline water electrolysis – Electrochemical impedance spectroscopy



Separator: PSEBS membrane with DABCO functional groups; electrolyte: indicated in the figure; temperature: 50 °C; anode: 5 mg $NiCo_2O_4$ cm^{-2} + 0.56 mg PSEBS cm^{-2}; cathode: 3.3 mg $Fe_{60}Co_{20}Si_{10}B_{10}$ cm^{-2} + 0.37 mg PSEBS cm^{-2}; cell voltage: 1.74 V

Conclusions

Replacement of trimethylamine functional group by less aggressive DABCO is possible.

Anion exchange material based on PSEBS proven ability replace partially function of liquid electrolyte.

Utilization of anion exchange material based on PSEBS allows reduction of liquid electrolyte concentration

Next step is to find optimal composition of catalytic layers for both electrodes. Evaluate long term stability (thousands of hours)