UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

Anion selective membranes for alkaline water electrolysis

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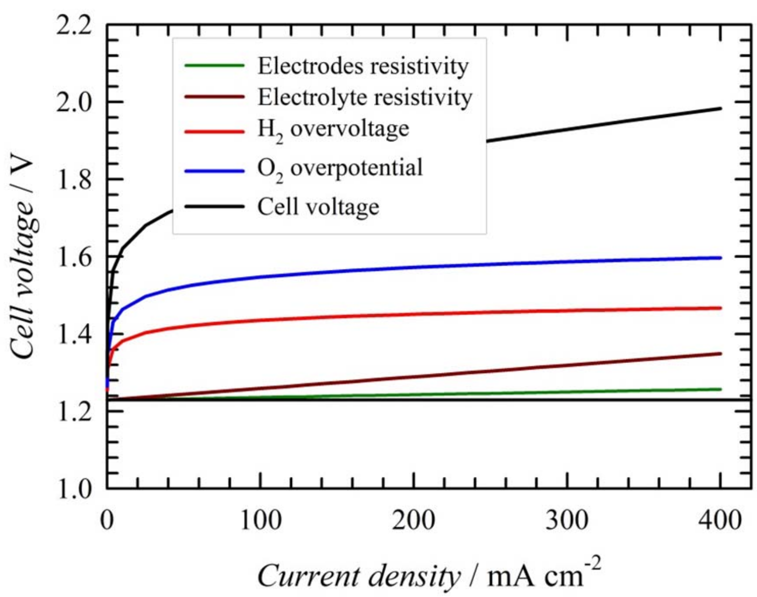
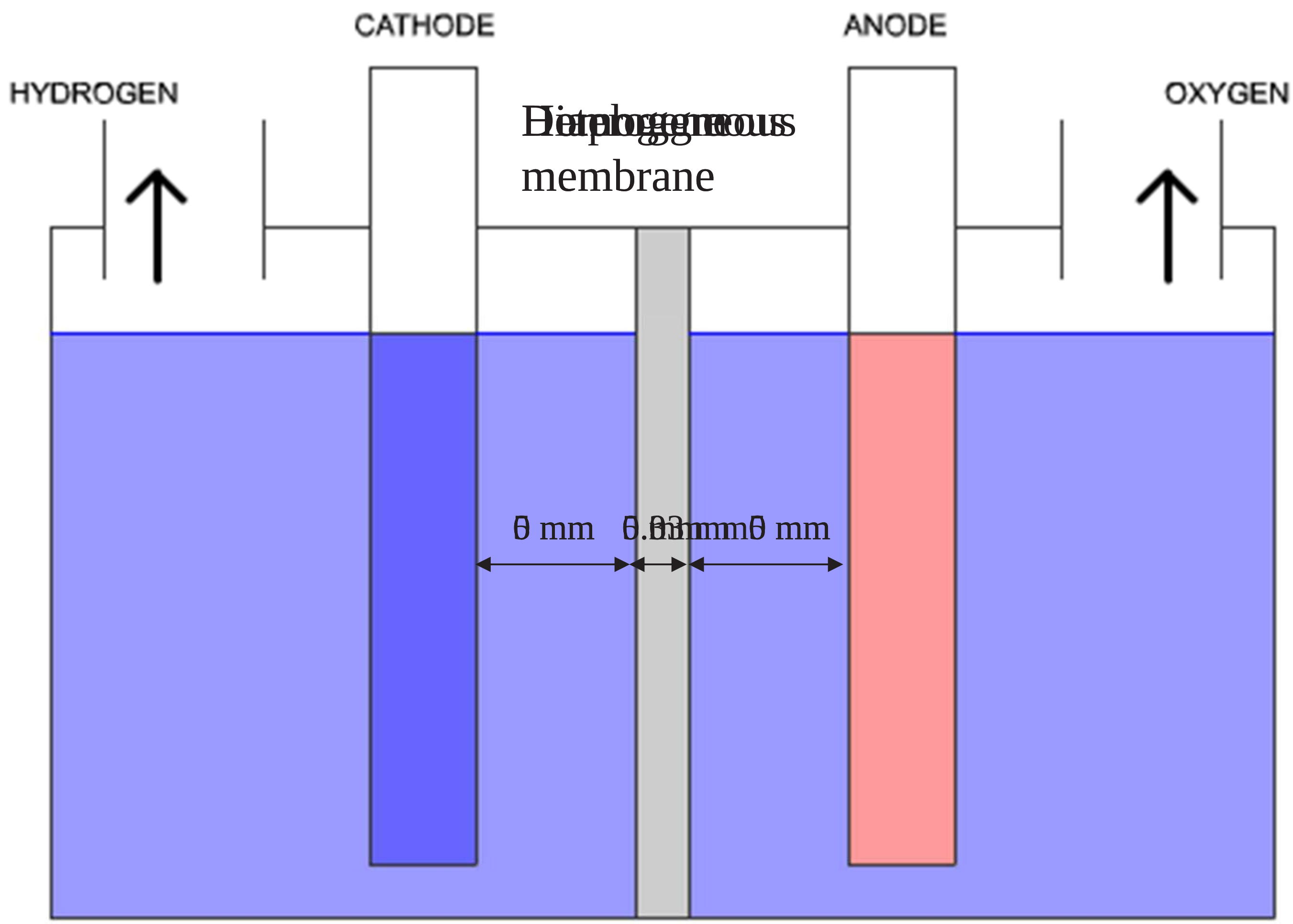
Alkaline Water Electrolysis

Alkaline water electrolysis

- Often understood as a well established process
- Complementarity vs. competition with PEM process
- Renewed interest often related to the reduced material demands
- Problem shifted from catalysis to polymer electrolyte
- Standard materials not yet established



Electrode compartments separation



$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

$4OH^- - 4e^- \rightarrow O_2 + 2H_2O$

Target of the study at UCT Prague

To develop well preforming anion-selective membrane

Targets to be met

- High OH^- conductivity
- Gas tight
- High chemical stability
- Good mechanical stability
- Availability in a form of solution
- Process ability
- …

Target of the study at UCT Prague

Characterization techniques used

Morphology

- SEM, optical microscopy

Mechanical properties

- Tensile strength, elongation to break

Chemical composition

- FT-IR, SS NMR, NMR, elemental analysis

Electrochemical properties

- Chemical stability in KOH solution
- Ion exchange capacity, ionic conductivity

Test in the water electrolysis cell

Experimental part

Mechanical properties

- Sample with the defined dimension placed into the pneumatic holder
- Stretched by 5 mm min^{-1}
- The tensile strength evaluated at the point of the failure

Ion-exchange capacity

- Evaluated by potentiometry using pH glass electrode
- Transition of OH^- from membrane to solution
- Alternative method represents UV-Vis spectrophotometry (low pK)
- Inert argon atmosphere

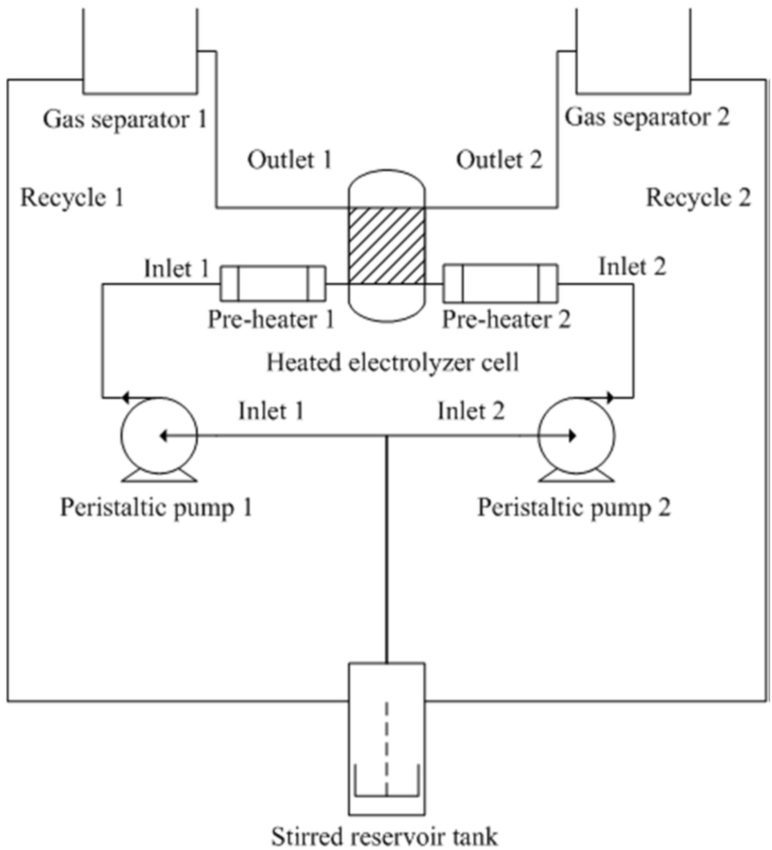
Experimental part

Ionic conductivity

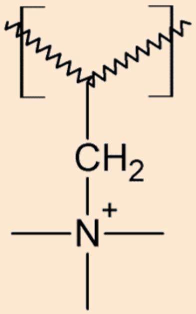
- Evaluated by electrochemical impedance spectroscopy
- Four electrode arrangement
- In(through)-plane measurement
- OH^- cycle
- 100% relative humidity
- 30 °C

Alkaline water electrolysis

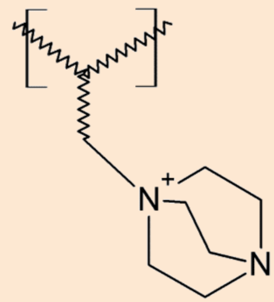
- 10 wt.% KOH solution
- 1.5 – 2.0 V cell voltage
- 5 ml min^{-1} flow rate
- 4 cm^2 geometric area



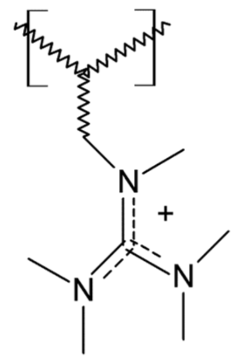
Functional groups



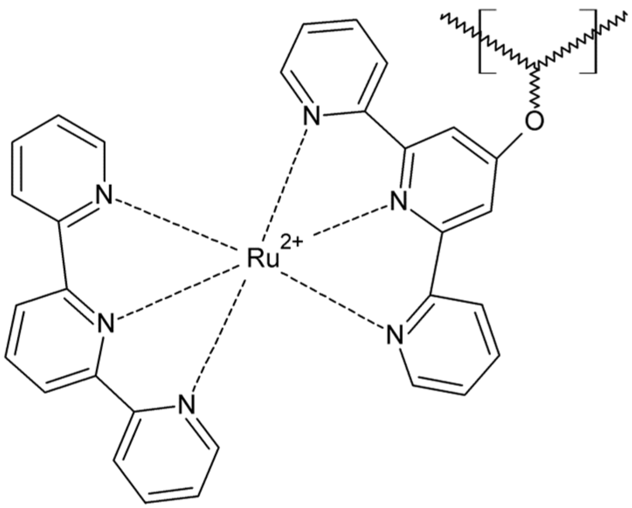
Trialkyl ammonium



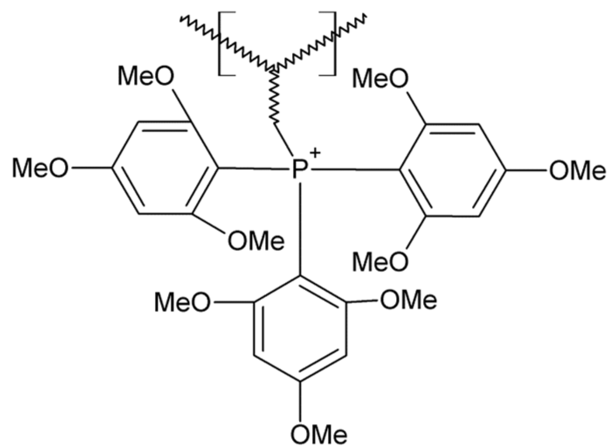
1,4-diazabicyclo[2.2.2]octane (DABCO)



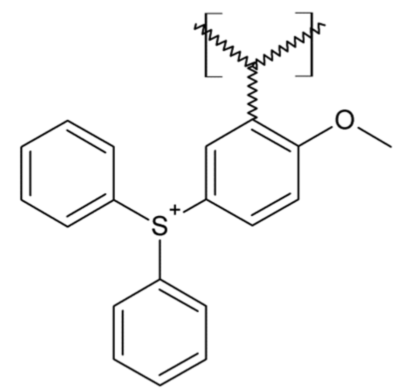
Guadinium



Metal-cation



Phosphorous ion

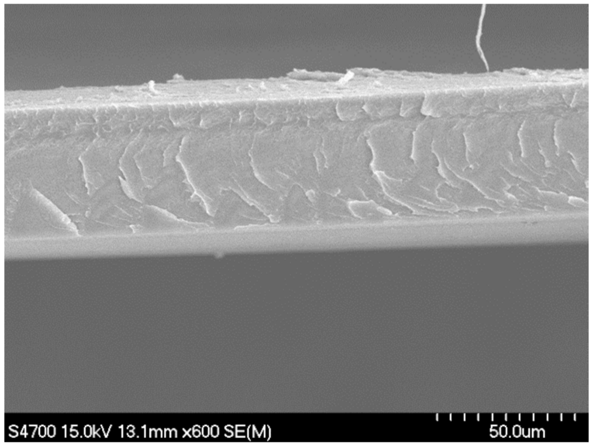


Sulphur ion

Anion selective membranes

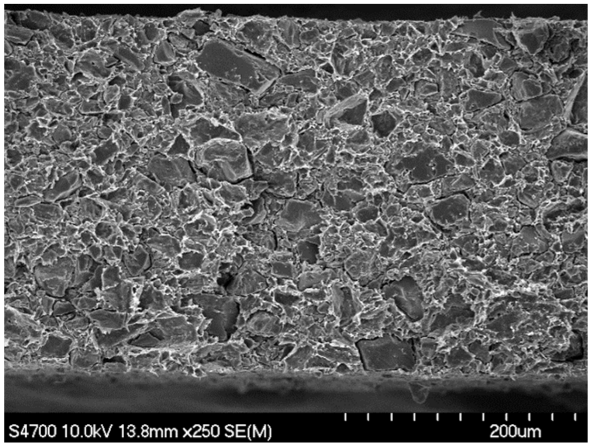
Homogeneous

- Formed by one polymer or copolymer
- Good electrochemical properties
- Lower stability
- Possibility of preparation of the liquid solution acting as catalyst layer binder



Heterogeneous

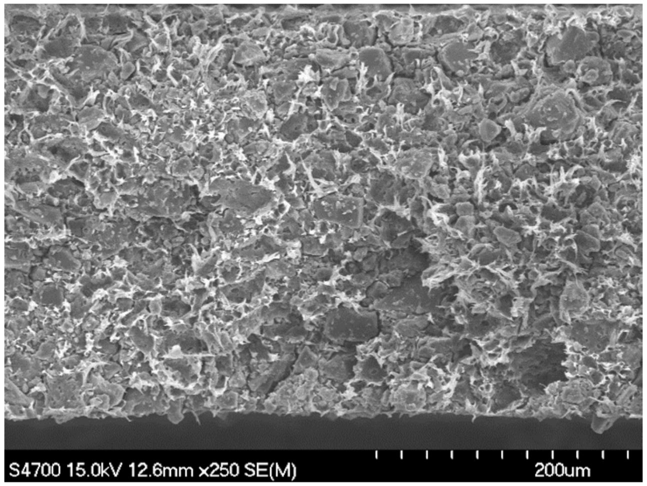
- Formed by ion exchange particles blended with polymer binder
- Worse electrochemical properties
- Better stability

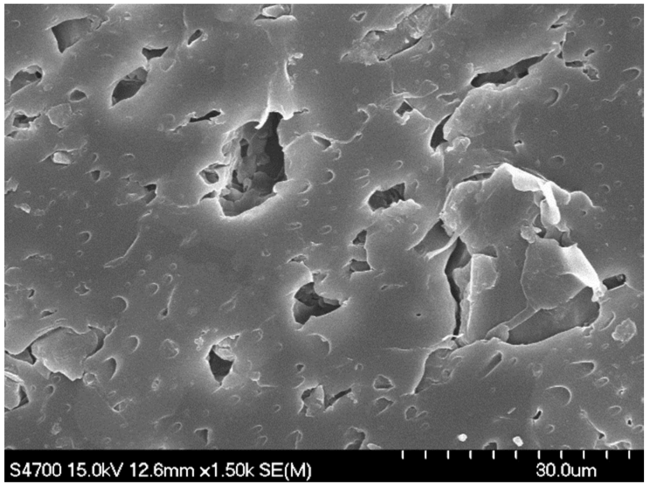


Synthesis of heterogeneous membranes

Heterogeneous

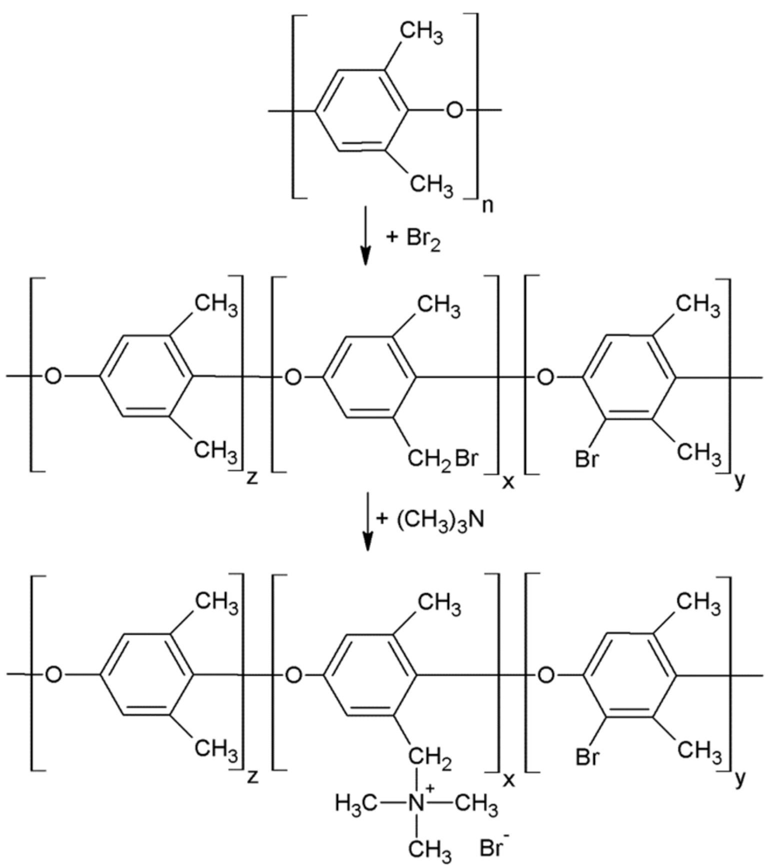
- Anionselective particles (66 wt.%) blended with low density polyethylene (LDPE) (30.6 wt.%) and water soluble component poly(ethylene glycol-*ran*- propylene glycol) (PEG-PPG) (3.4 wt.%) at 140 °C until constant torque value.
- Blend press-molded at 140 °C and 10 MPa for 3 minutes
- Cooled down to 25 °C within 4 minutes
- Typical thickness 0.30 mm



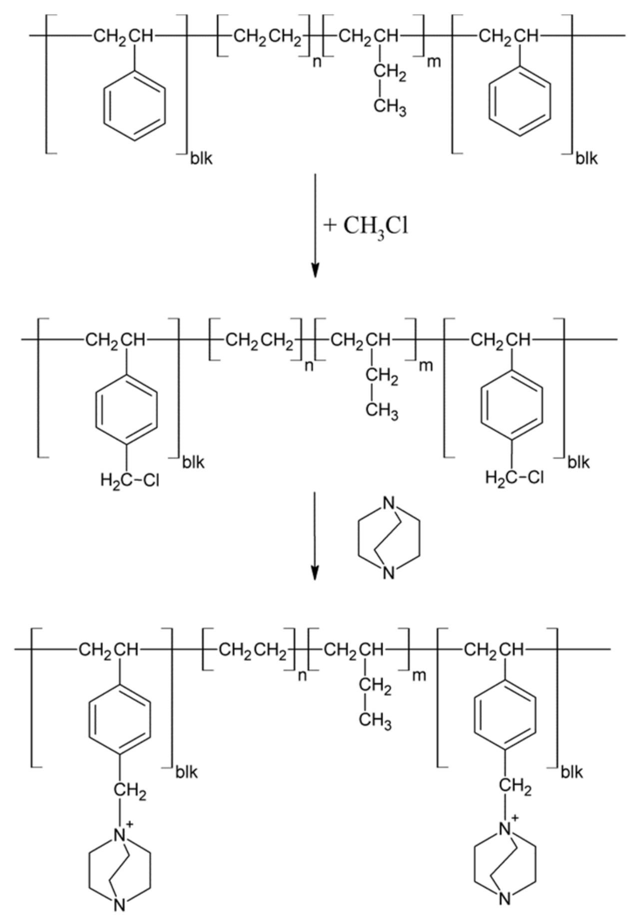


Synthesis of homogeneous membranes

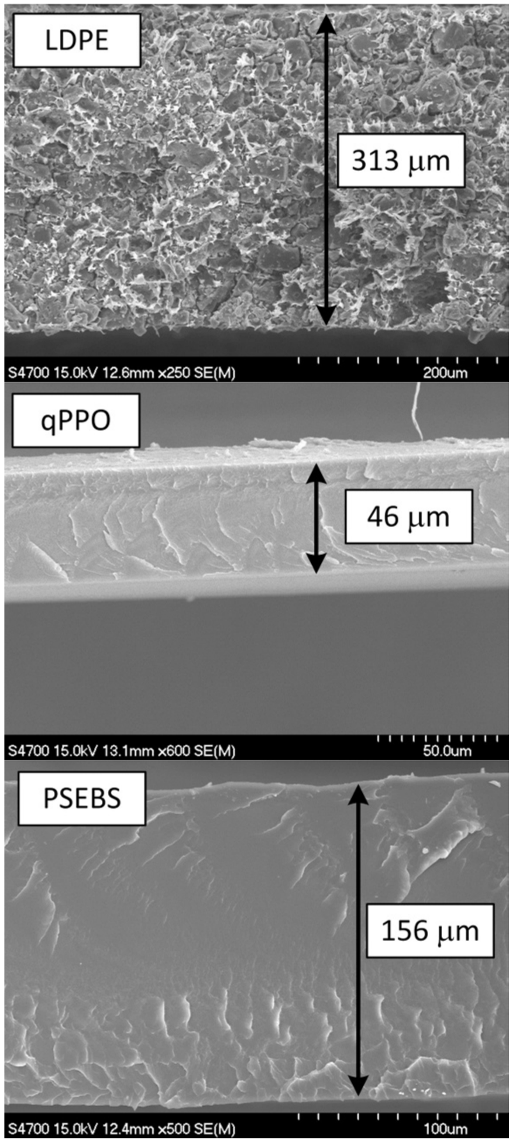
Quaternized poly(phenylene oxide) (qPPO)

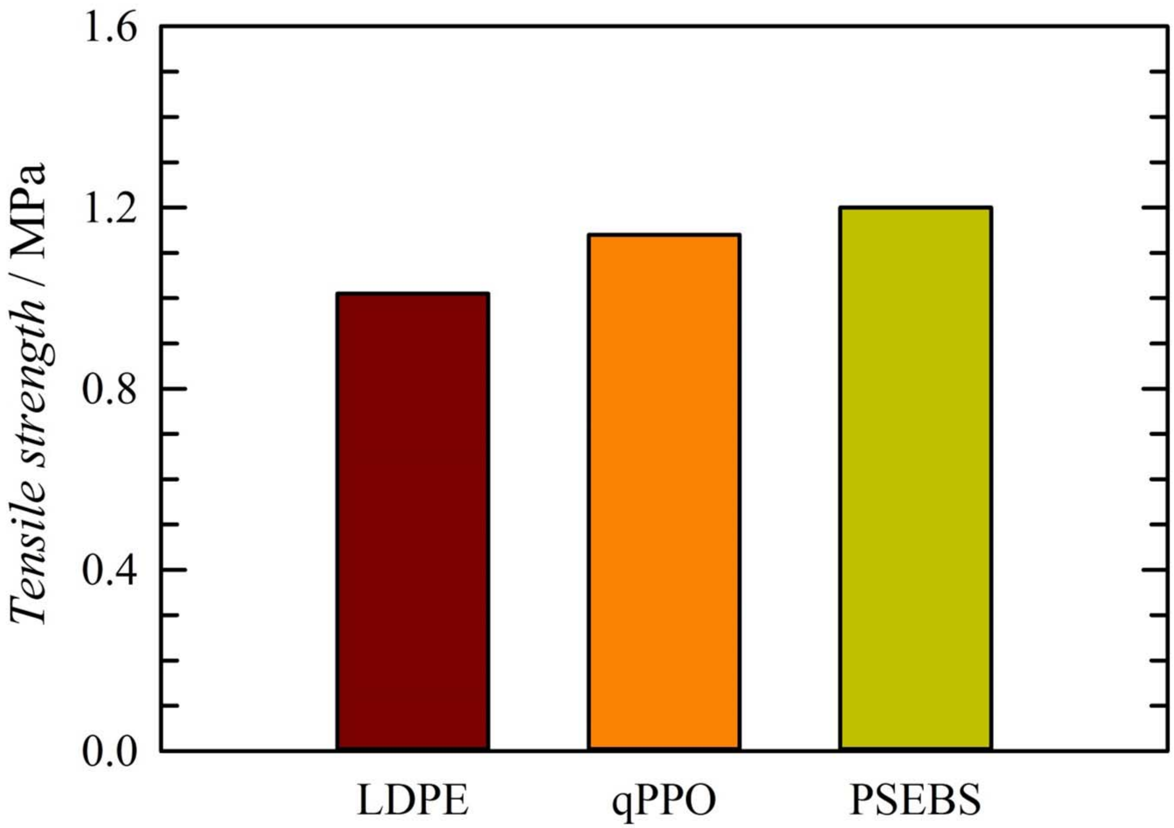


Poly(styrene-ethylene-butylene-styrene) (PSEBS)

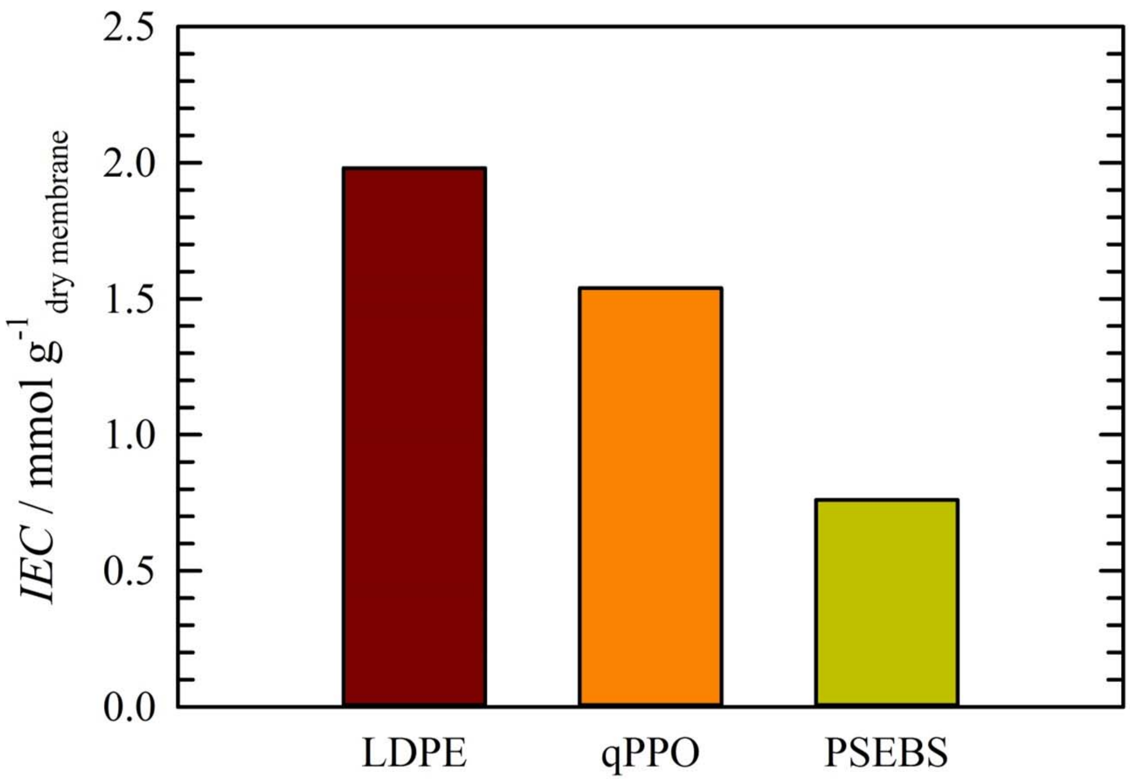


Morphology and tensile strength



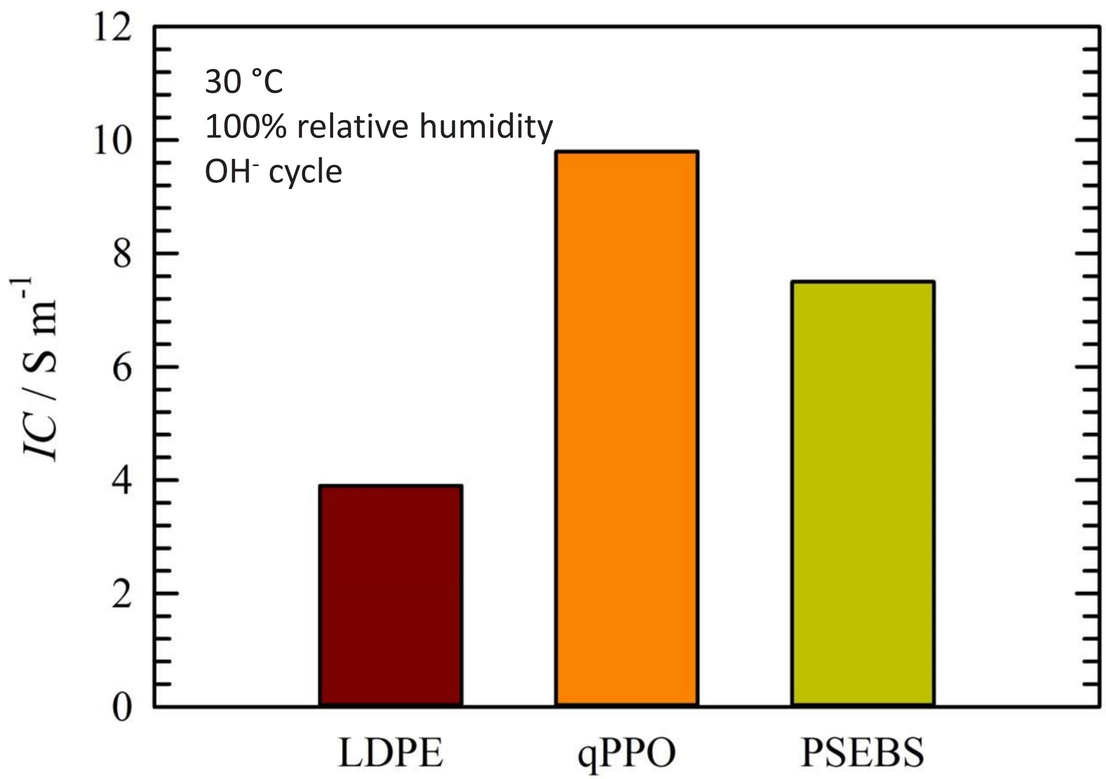


Ion exchange capacity



LDPE – heterogeneous membrane (66 wt.% anion exchange particles)
qPPO – homogeneous membrane with trimethyl ammonium (TMA) functional groups
PSEBS – homogeneous membrane with DABCO functional groups

Ionic conductivity



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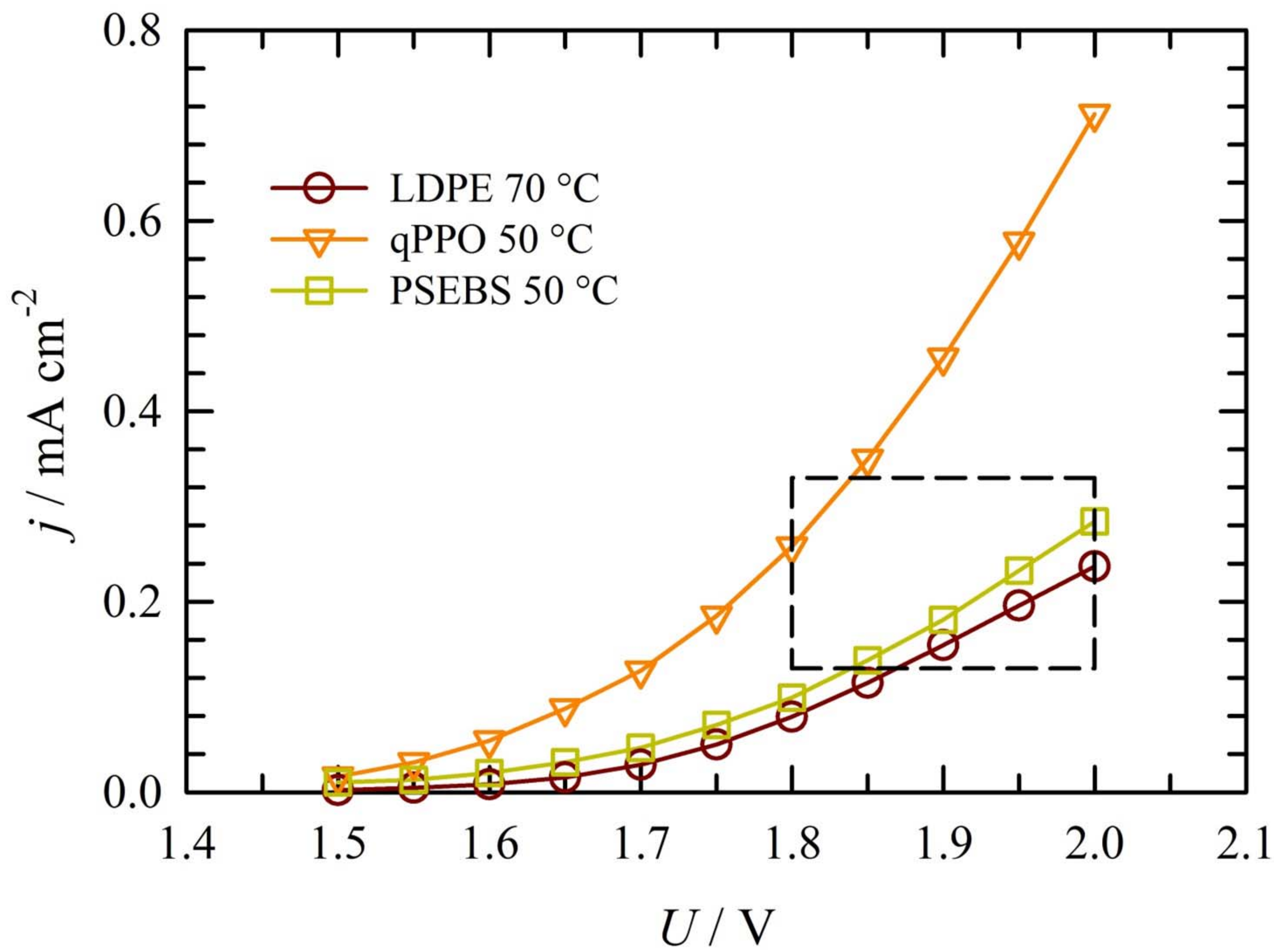
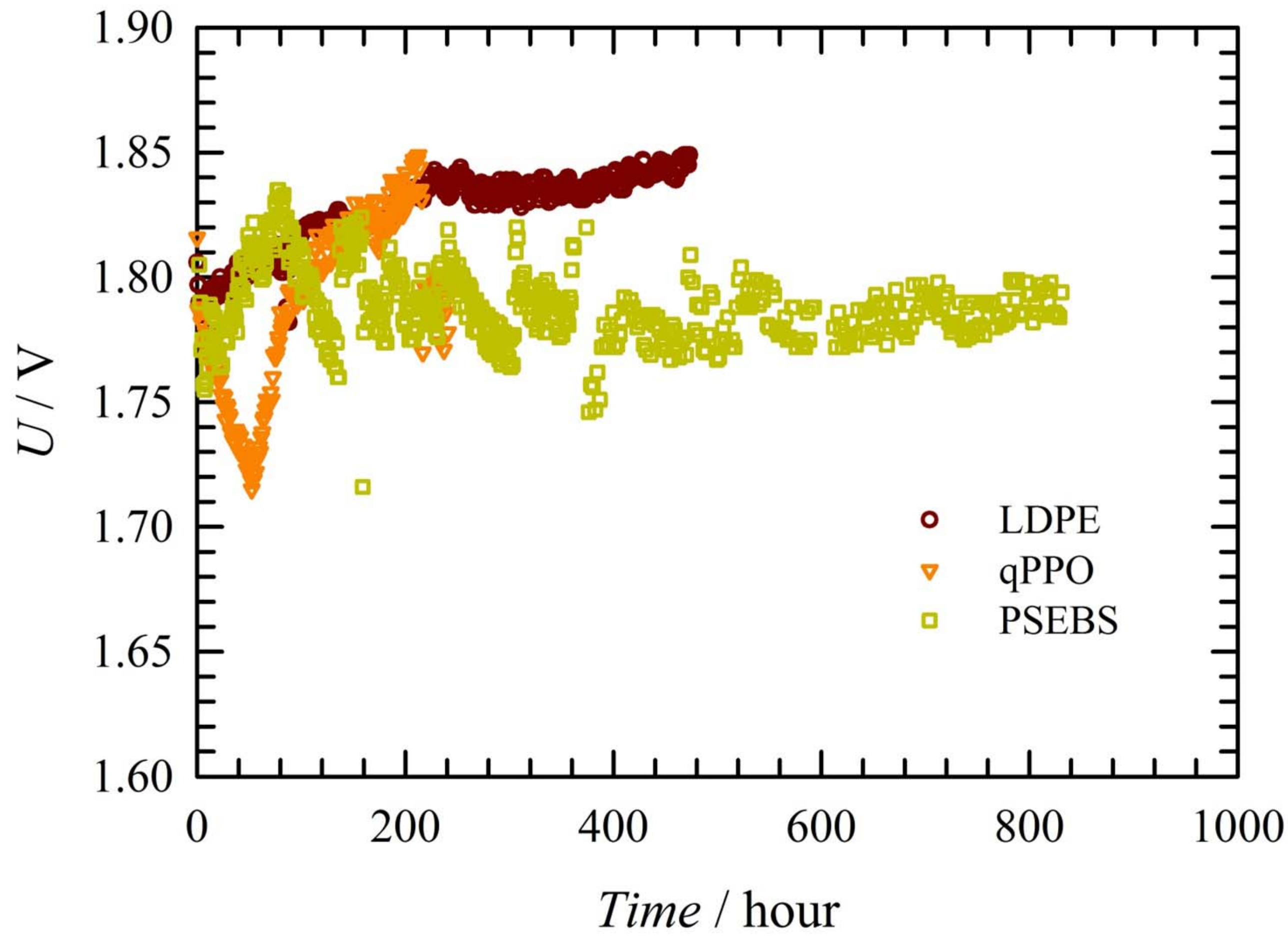
Alkaline water electrolysis



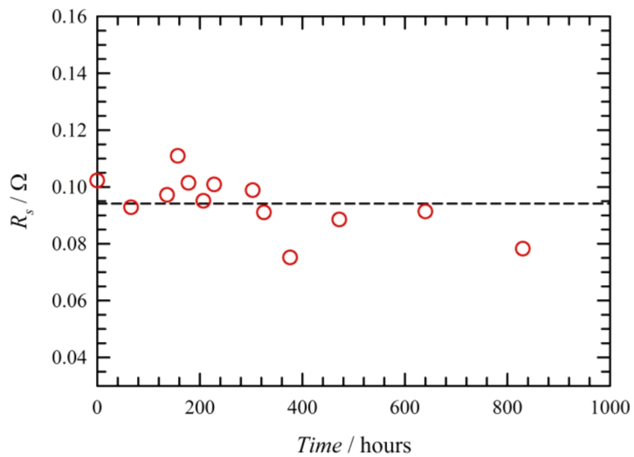
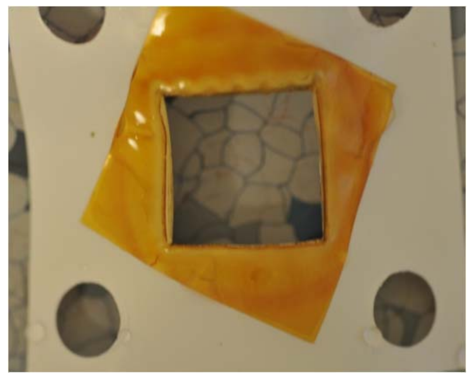
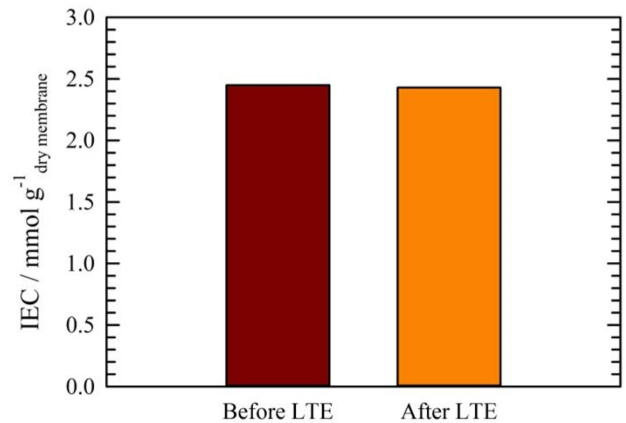
separator: showed in figure inset; anode: Ni foam; cathode: Ni foam; temperature: showed in figure inset; electrolyte: 10 wt.% KOH; area marked by dash line shows the range of operational parameters of the industrial water electrolyzers

Long-term water electrolysis



Separator: shown in the figure inset; Anode: 8 mg $NiCo_2O_4$ cm^{-2} + qPPO; Cathode: 0.3 mg Pt cm^{-2} + 5 hm.% qPPO; Temperature: 50 °C; current density: 300 mA cm^{-2}; electrolyte: 10hm.% KOH

Long-term water electrolysis

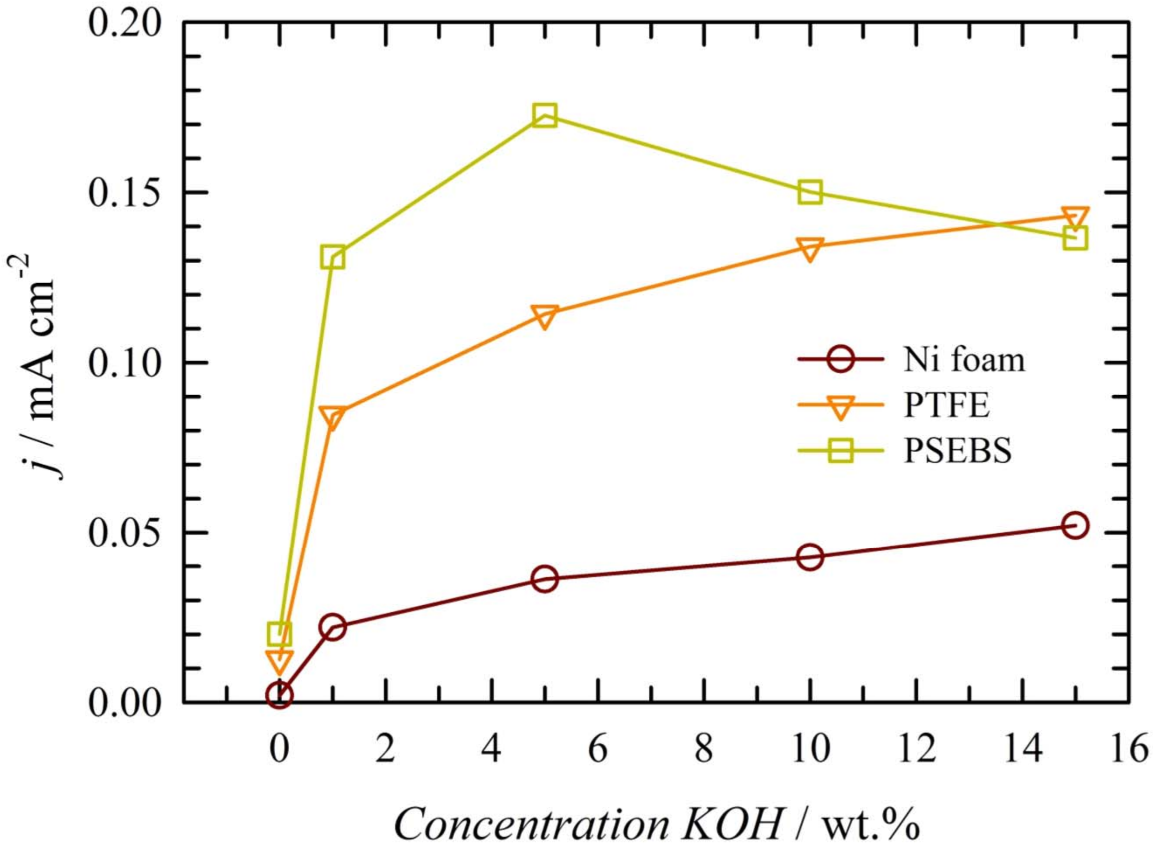
PSEBS	qPPO	LDPE
		

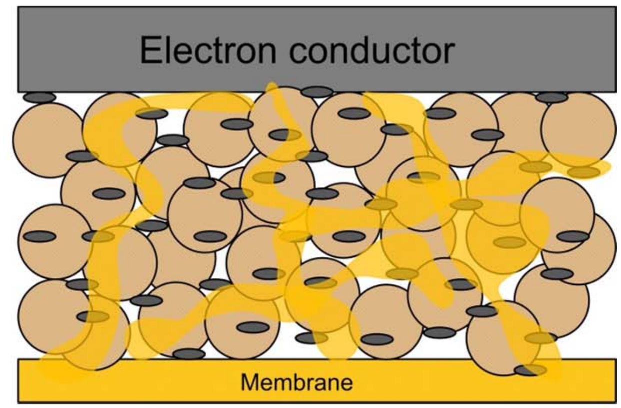
PSEBS: Average R_s: 0.094±0.003 Ω

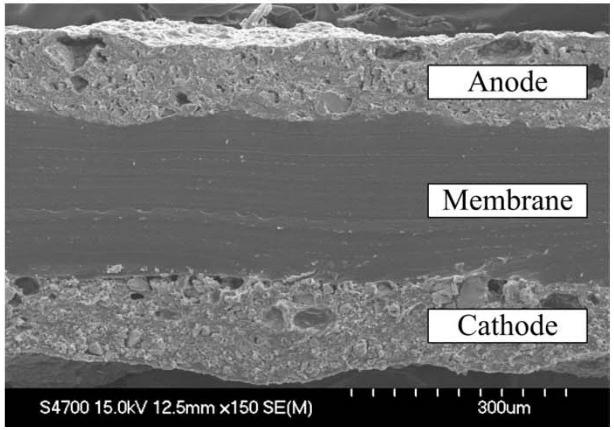
qPPO: Membrane dissolved

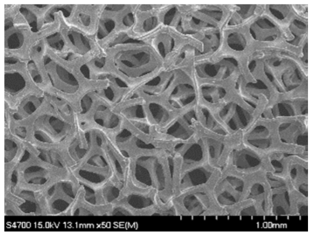
LDPE: The IEC did not changed during the long-term water electrolysis with LDPE membrane.

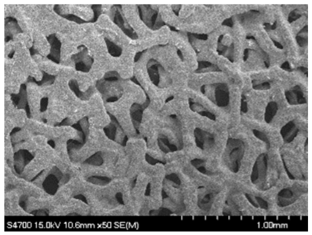
Catalyst layer polymer binder











Separator: LDPE; Anode: Ni foam, 8 mg $NiCo_2O_4$ cm^{-2} + 2.67 mg PTFE, 8 mg $NiCo_2O_4$ cm^{-2} + 2.67 mg PSEBS; Cathode: 0.3 mg Pt cm^{-2} + 0.05 mg PTFE; Temperature: 70 °C; surface area: 4 cm^2; current density achieved at 1.74 V

Conclusions

Alkaline polymer electrolytes represent an interesting and promising option

- Zero-gap arrangement possible
- Cell construction based on experience from PEM systems
- Due to differences in properties between H^+ and OH^- certain limitations remain also in the alkaline system design and operational conditions

Important aspect represents MEA construction

- Availability of suitable OH^- conducting binder opens an option of broad spectrum of catalyst utilization
- CCE option quite well established, but CCM strategy still under development
- Additional progress in alkaline polymer electrolytes synthesis needed

Key issue remains the operational temperature

- Low temperature – high ohmic losses, difficult to control
- High temperature – functional group degradation

PSEBS membrane with DABCO (but also TMA) represents a promising option

Thank you for your attention