Stability of acrylic acid grafted microporous polymeric membranes in alkaline electrolyte

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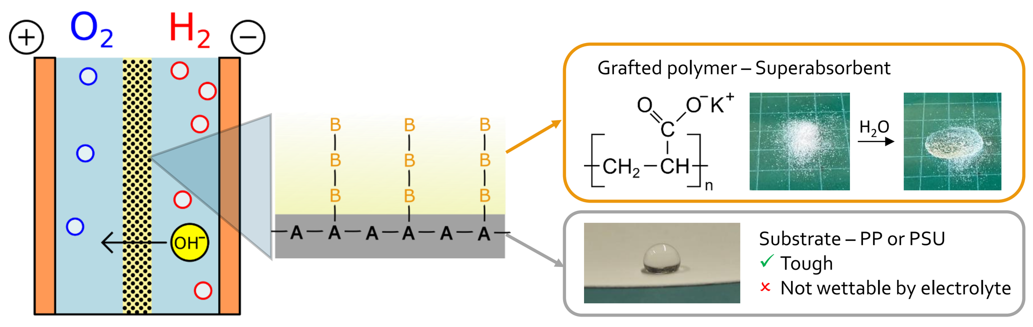
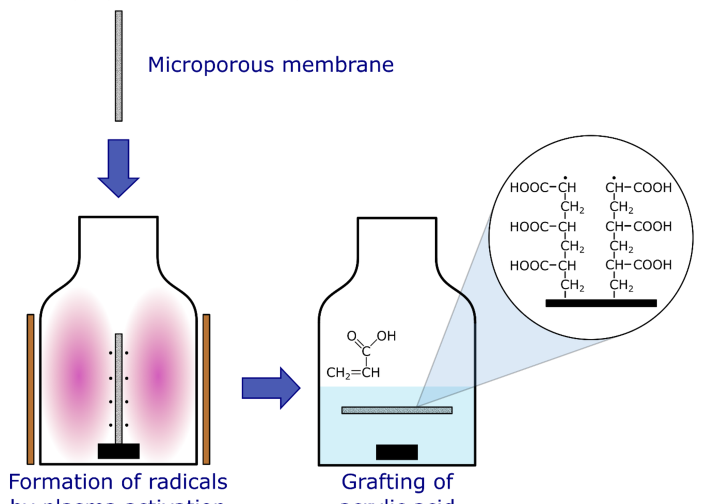
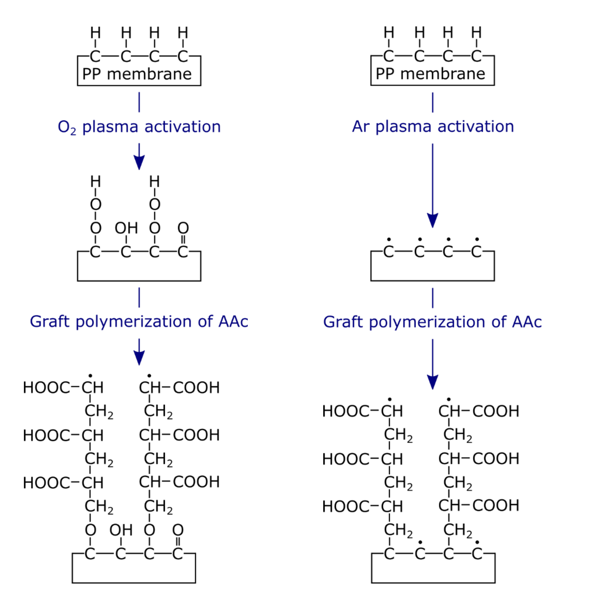
Membrane modification

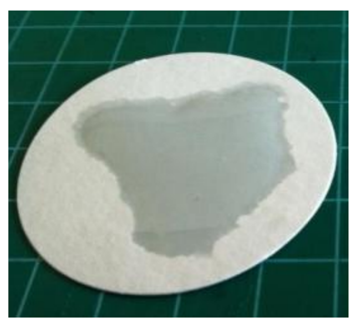


Membrane	Material	Thickness	Pore size	Porosity
PP-A [1]	PP	315 µm	1 µm	40 %
Celgard 2400 [1]	PP	25 µm	–	39 %
Tuffryn [2]	PSU	125 µm	0.45 µm	81 %
PP (Present)	PP	150 µm	1.2 µm	21 %

Porous polymeric membranes were activated in a low-pressure plasma in Ar or O_2 to generate radicals on membrane surface, including surfaces of pores. The radicals were used to initiate graft polymerization of acrylic acid (AAc) in a solution.

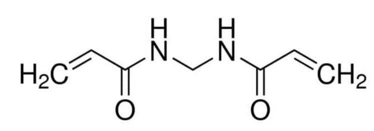




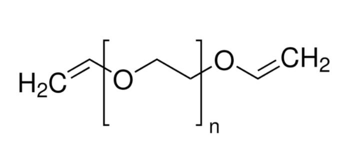


Crosslinkers

To promote crosslinking of the grafted polymer, methylene bisacrylamide (MBA) or poly(ethylene glycol) divinyl ether (PEGDE) was added as a crosslinking agent into the AAc solution.



MBA molecule



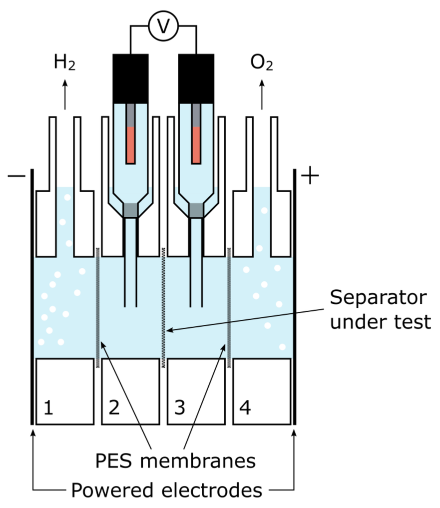
PEGDE molecule

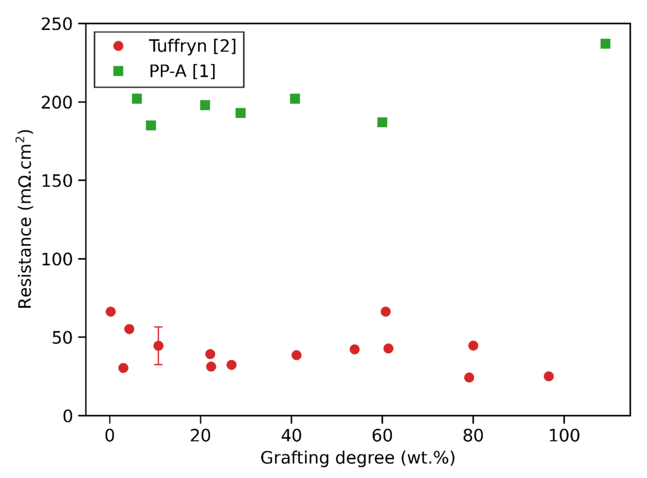
Ionic resistance

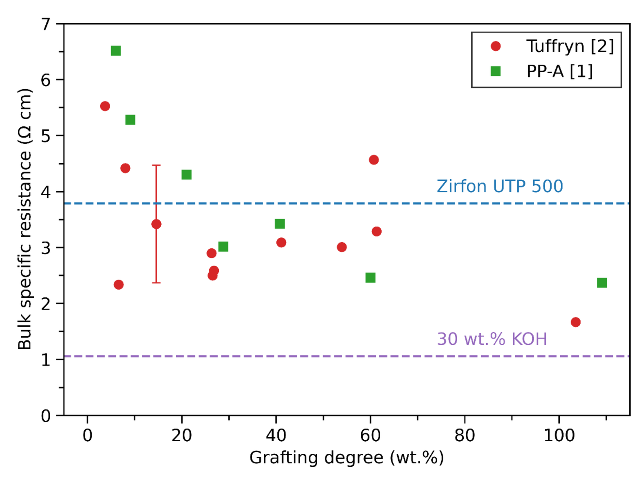
Ionic resistance of membranes was measured using a four-contact cell. Electrical current was supplied by a pair of planar Ni electrodes, while a pair of Hg/HgO probes served as sensing electrodes. The cell was immersed in a thermostat bath maintained at 50 °C.

$$R_{Sep} = \frac{U - U_0}{I_S} + \frac{1}{\sigma_E}(d_{Sep} - \Delta d_T)$$

- U – voltage between probes with inserted separator
- U_0 – voltage between probes without inserted separator
- I_S – current density
- σ_E – conductivity of electrolyte
- d_{Sep} – thickness of separator
- d_T – distance between probes terminals
- Δd_T – variation of d_T in cell with and without separator





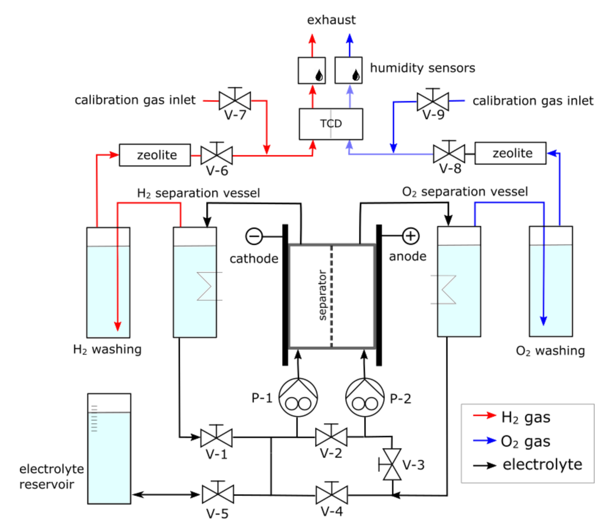


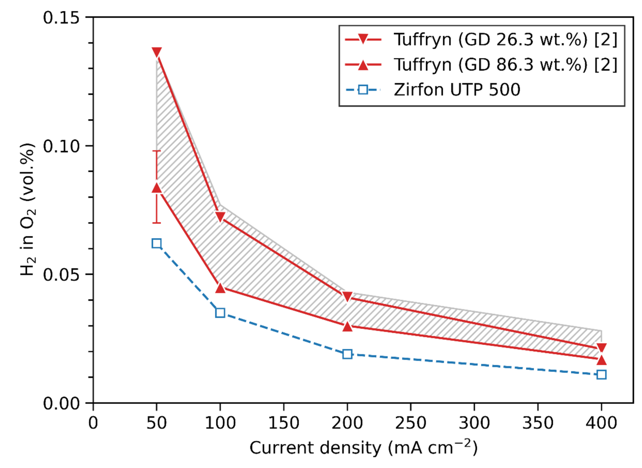
Hydrogen permeability

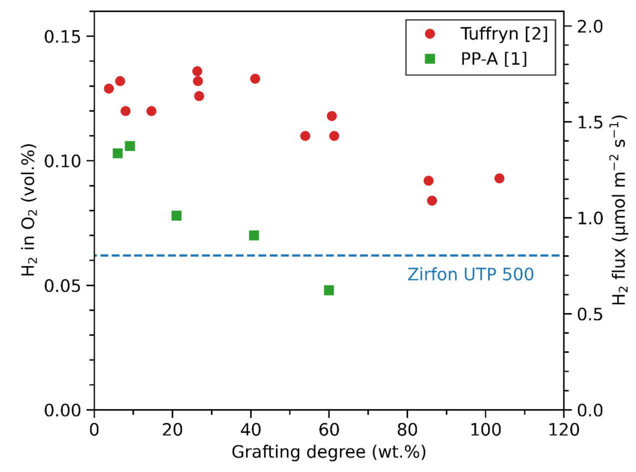
Volumetric fraction of hydrogen in the produced oxygen X_{H_2} was determined by means of an in house made thermal conductivity detector. The measurement was conducted using separated electrolyte loops, therefore all anodic hydrogen is due to H_2 flux through separator.

$$j_{H2} = \frac{I_S}{4F\left(\frac{1}{X_{H2}} - 1\right)}$$

- j_{H_2} – H_2 flux
- I_S – electrical current density
- F – Faraday constant
- X_{H_2} – volumetric fraction of H_2 in O_2

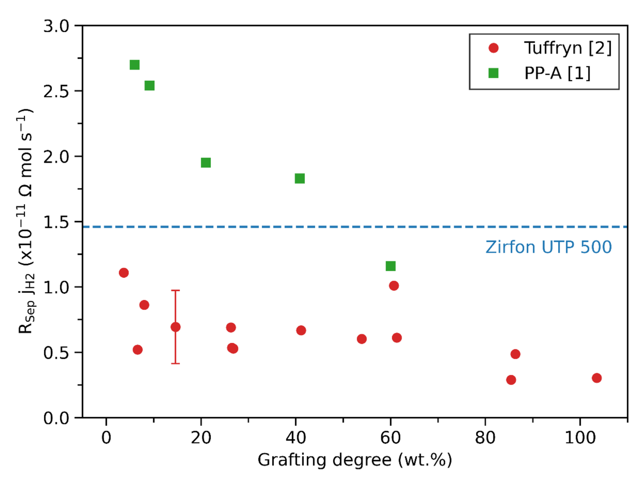






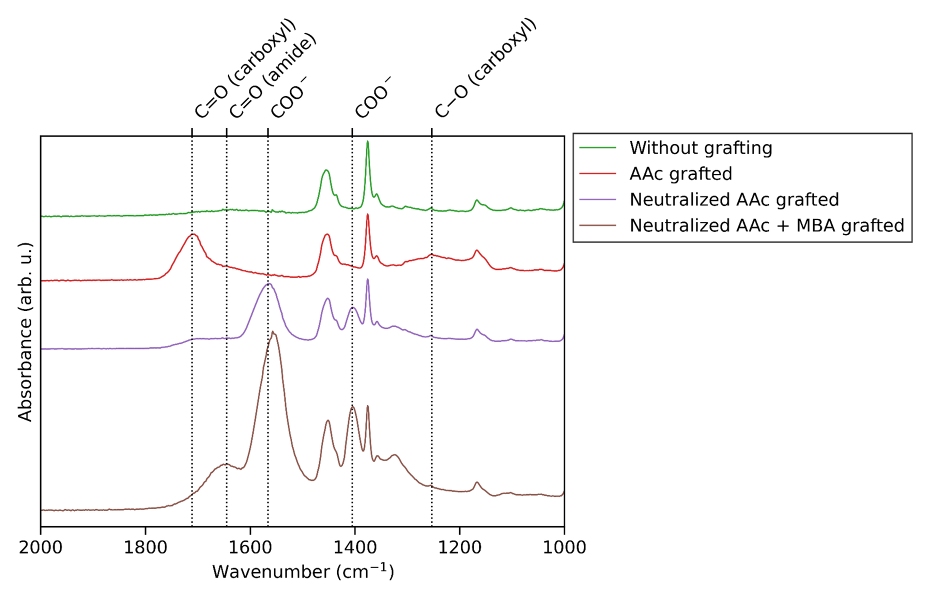
Product $R_{sep} j_{H2}$

The product of ionic resistance and hydrogen flux $R_{sep}\, j_{H_2}$ is (in theory) independent on membrane thickness and is therefore a suitable parameter to compare performance of separators of various thickness.



- Low $R_{sep}\, j_{H_2}$ is pursued
- AAc-grafted membranes can surpass performance of Zirfon UTP 500 in terms of $R_{sep}\, j_{H_2}$ under identical conditions

ATR FTIR spectroscopy



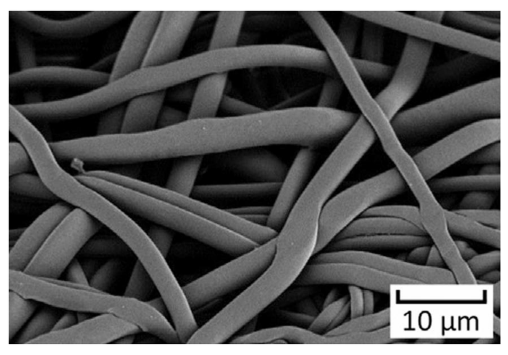
- Changes in chemical composition identified by ATR FTIR spectroscopy confirmed the presence of grafted poly(acrylic acid) polymer as well as MBA crosslinking agent

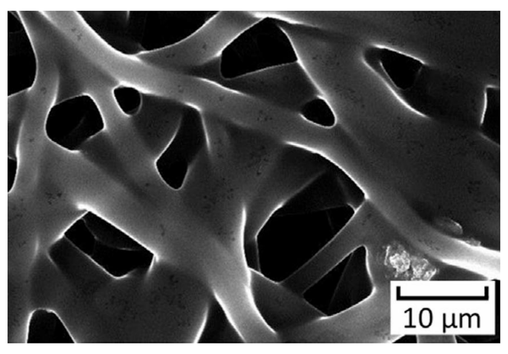
Scanning electron microscopy

- Grafting was achieved in the whole cross-section of membranes

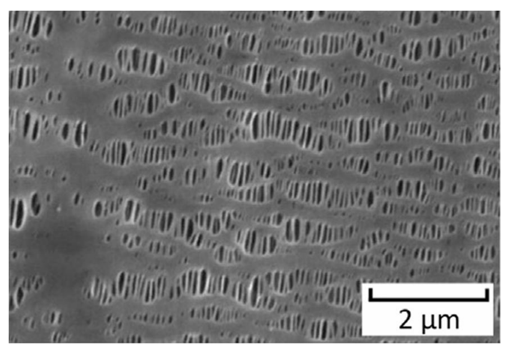
Before grafting | After grafting

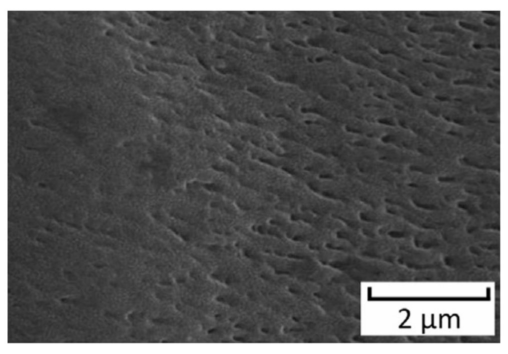
PP-A [1]



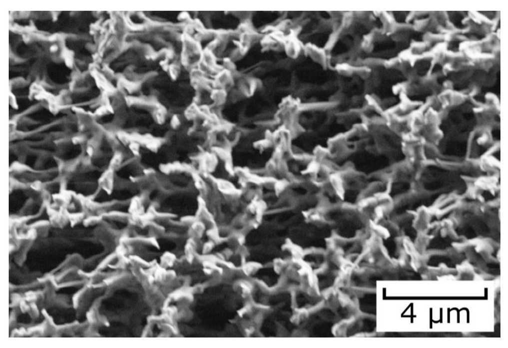


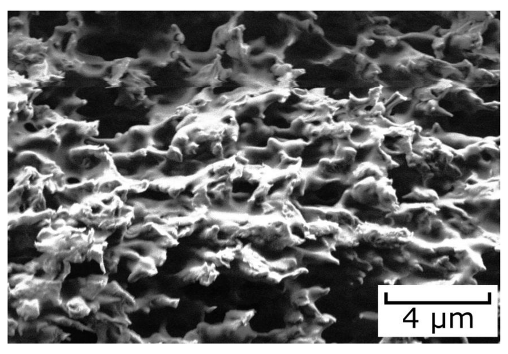
Celgard 2400 [1]



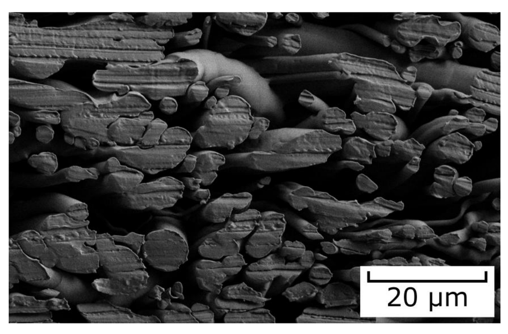


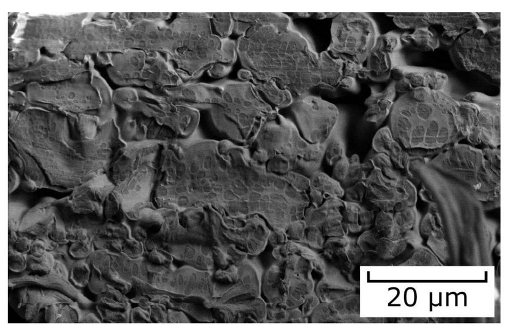
Tuffryn [2]





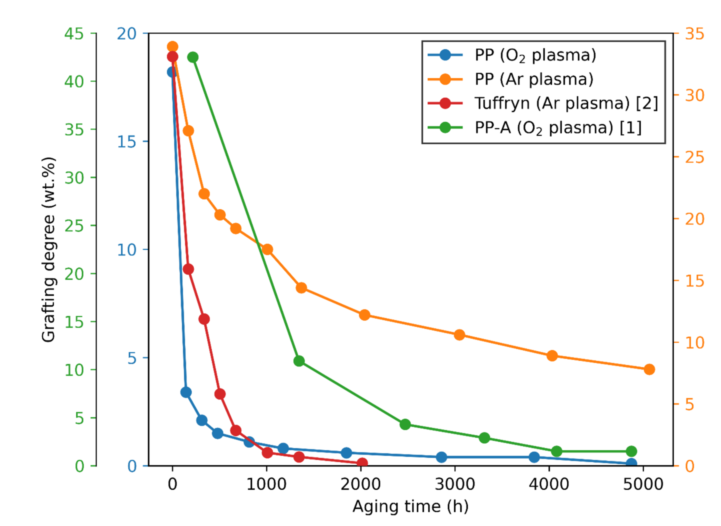
PP (Present)



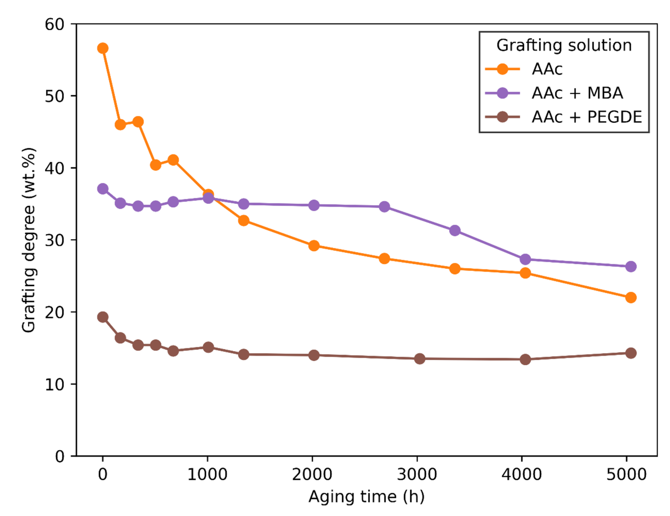


Aging tests

Long-term aging tests were performed in 30 wt.% KOH electrolyte at 60°C.



Crosslinkers



- PP membranes activated in Ar plasma before grafting exhibit the best stability
- The main drawback of AAc-grafted membranes was their weak stability in alkaline electrolyte
- Further improvement of membrane stability was achieved by addition of crosslinking agents into the AAc solution
- The present membranes exhibit considerably better stability in respect to those studied previously [1,2] and retain high grafting degree and high wettability even after 5000 hours in 30 wt.% KOH and 60 °C

References

[1] Staňo Ľ, Stano M, Ďurina P. Separators for alkaline water electrolysis prepared by plasma-initiated grafting of acrylic acid on microporous polypropylene membranes. International Journal of Hydrogen Energy 2020;45:80–93.

[2] Kuťka M, Staňo Ľ, Kováčik D, Satrapinskyy L, Stano M. Ionic conductivity and hydrogen permeability of microporous polysulfone membranes grafted by acrylic acid. International Journal of Hydrogen Energy 2024;84:224–34.