

Supplementary Material

Enhancement of Heavy Ion Track-Etching in Polyimide Membranes with Organic Solvents

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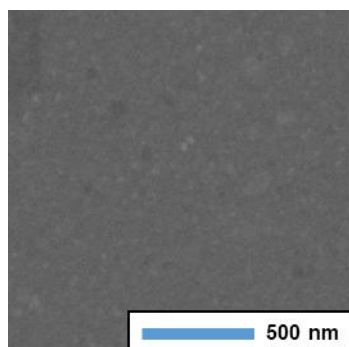


Figure S 1 SEM image of a PI membrane (10^7 pores cm^{-2}) soaked in ACN solvent at 50°C for 60 min.

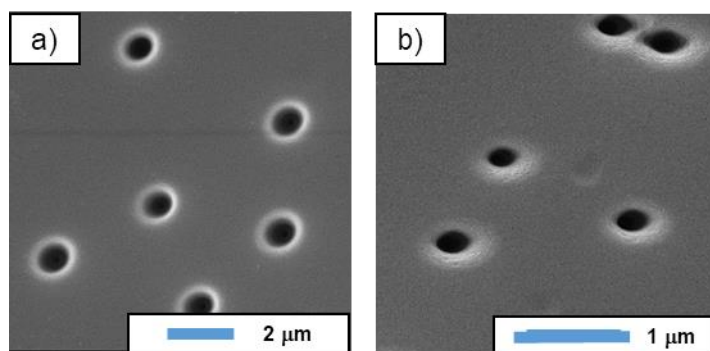


Figure S 2 Pore shape in dependence of the sample position during etching process. SEM images of PI membranes (10^7 pores cm^{-2}) after 45 min symmetrical etching with etchant mixture composed of NaOCl/*i*-PrOH (9:1), in a) etch bath, where the sample is immersed in the etchant or b) sample fixed in between the two chambers of the etching cells.

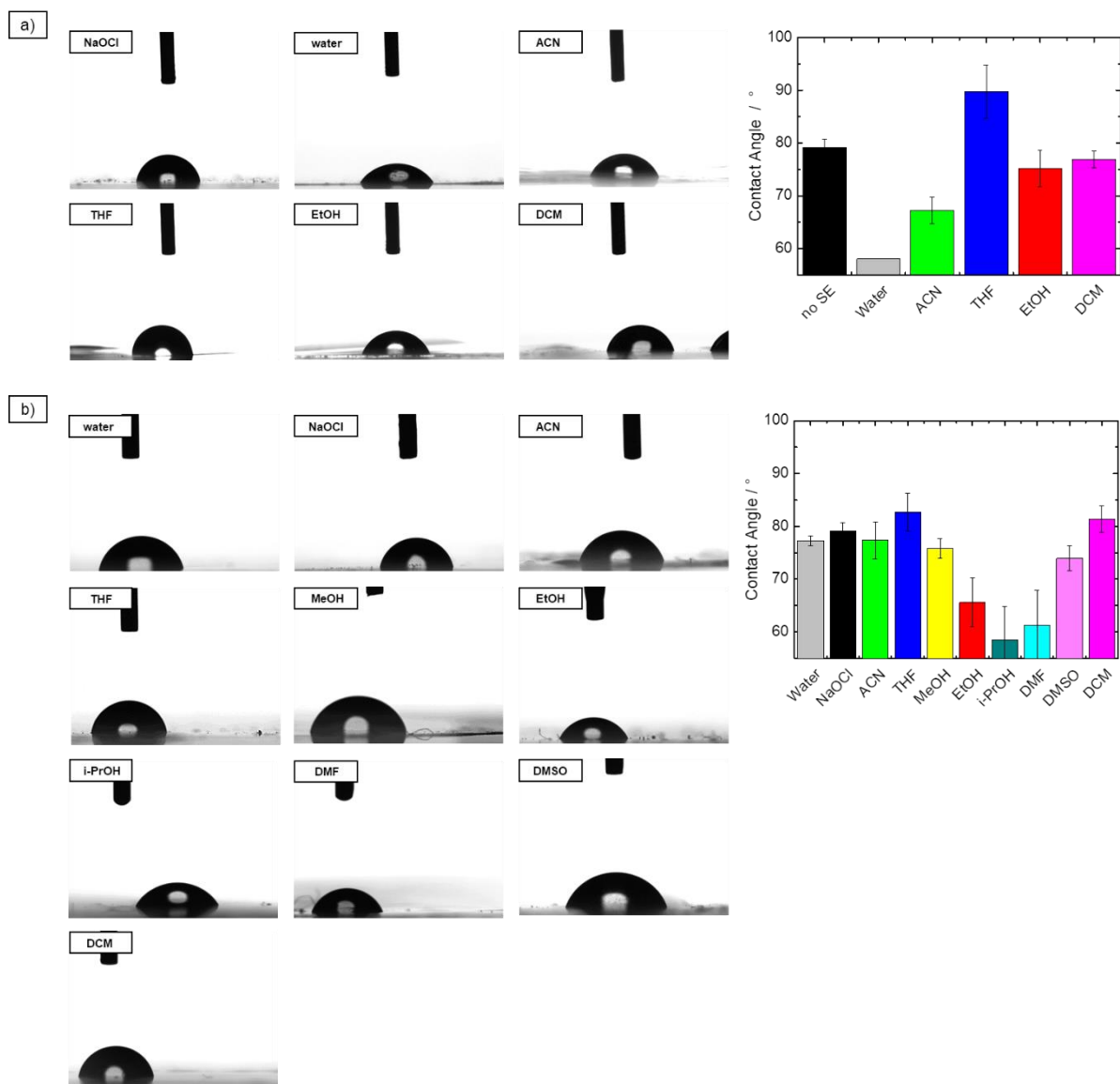


Figure S 3 Images and averaged contact angles of 3 μL droplets of a) the NaOCl solution placed on solvent-treated PI membranes obtained by soaking membranes for 90 min in water, ACN, THF, EtOH or DCM at 23°C, and b) of water, NaOCl solution and etchant mixtures containing a 9:1 mixture of NaOCl and organic solvents placed on PI membranes without any pretreatment. The contact angles are counted on the left side of the droplets.

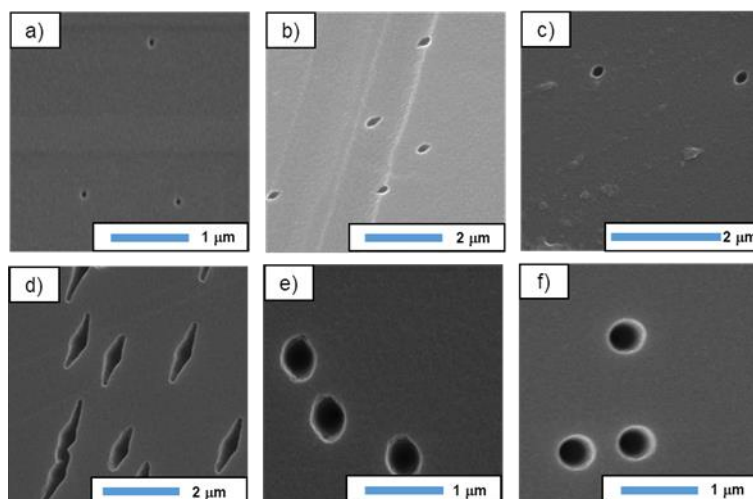


Figure S 4 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with NaOCl for a) 20 min, b) 25 min, c) 30 min, d) 35 min, e) 40 min and f) 45 min.

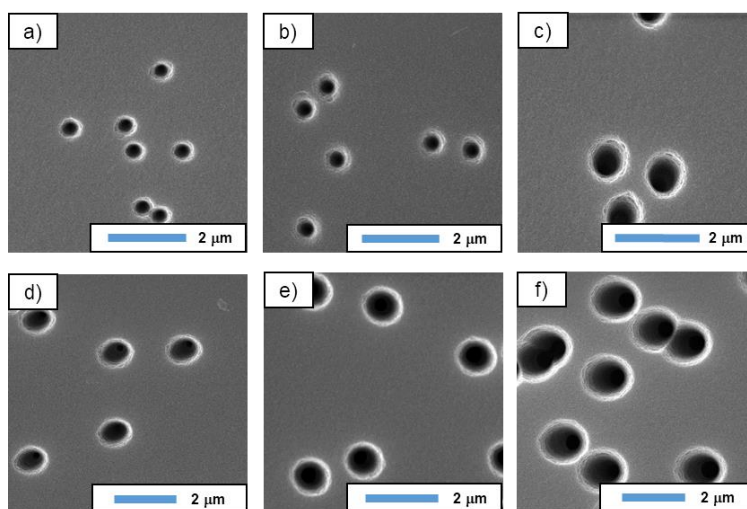


Figure S 5 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with a 9:1 mixture of NaOCl/ACN for a) 20 min, b) 25 min, c) 30 min, d) 35 min, e) 40 min and f) 45 min.

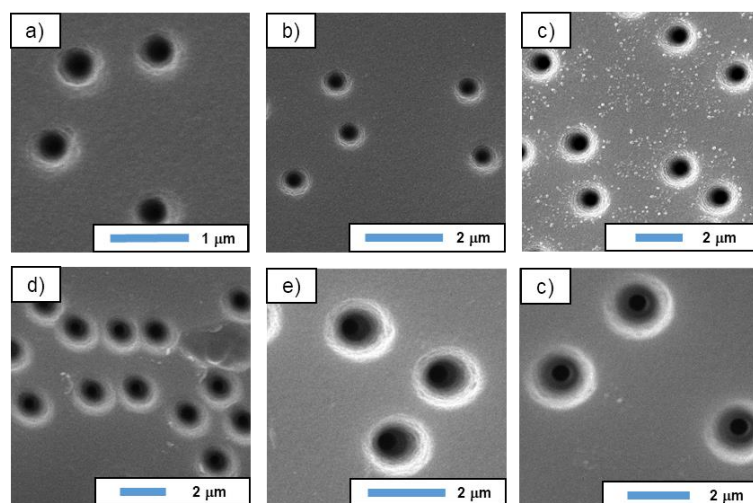


Figure S 6 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with a 9:1 mixture of NaOCl/THF for a) 20 min, b) 25 min, c) 30 min, d) 35 min, e) 40 min and f) 45 min.

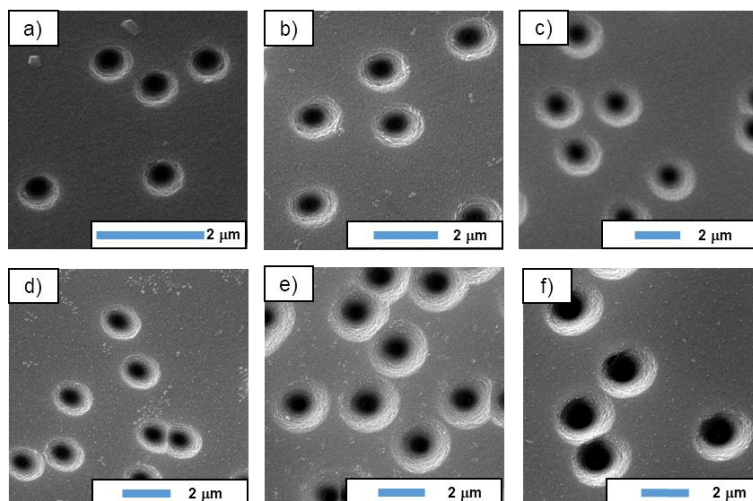


Figure S 7 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with a 9:1 mixture of NaOCl/EtOH for a) 20 min, b) 25 min, c) 30 min, d) 35 min, e) 40 min and f) 45 min.

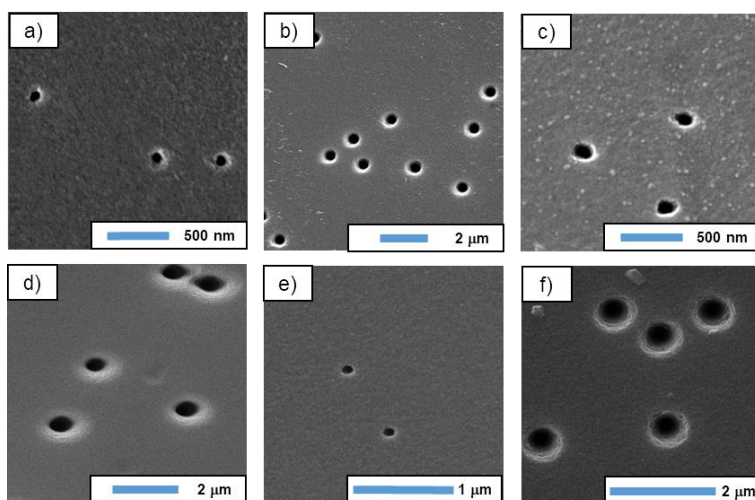


Figure S 8 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with a 9:1 mixture of NaOCl/solvent for 45 min a) DMF, b) DMSO, c) MeOH, d) i-PrOH, e), EA, and f) DCM.

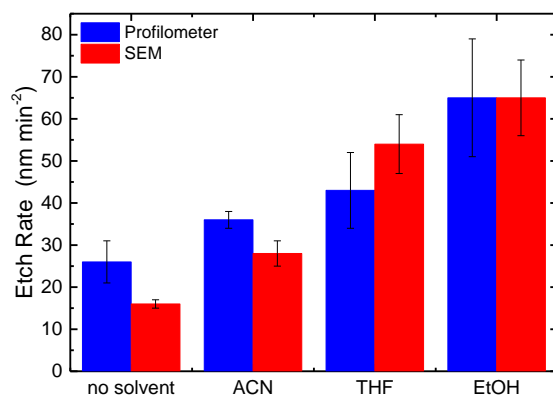


Figure S 9 Comparison of etch rates of NaOCl and etchant mixtures of NaOCl/solvents (9:1) obtained from the SEM imaging (ϵ_{xy}) and profilometer analysis (ϵ_z).

Table S 1 Pore diameter D of PI membranes (10^7 pores cm^{-2}) etched symmetrically for 45 min at 50°C . The etchant mixture is prepared by adding different vol% of organic solvents in NaOCl solution

vol%	ACN D [μm]	THF D [μm]	EtOH D [μm]
5	0.58 ± 0.03	0.28 ± 0.01	0.76 ± 0.02
10	1.22 ± 0.04	1.70 ± 0.06	2.32 ± 0.13
20	2.00 ± 0.04	2.05 ± 0.09	-
30	1.49 ± 0.07	2.67 ± 0.16	-
40	1.37 ± 0.06	1.14 ± 0.05	-

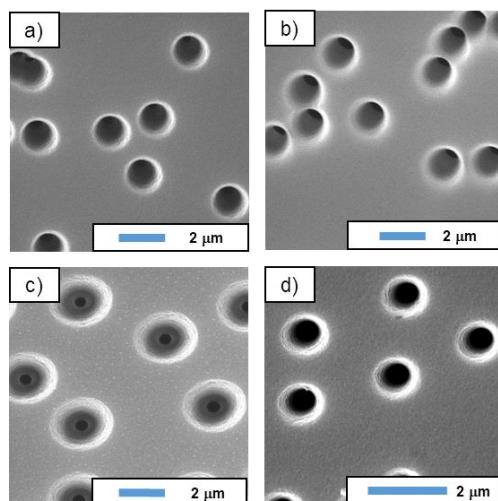


Figure S 10 Symmetrical etching of PI membranes (10^7 pores cm^{-2}) with mixtures of 12% NaOCl solution and organic solvents at 50°C in dependence of the organic solvent compound. SEM images after 45 min etching with 30% and 40% of ACN a) + b) and THF c) + d).

Table S 2 Pore diameter D of PI membranes (10^7 pores cm^{-2}) etched symmetrically with 12% NaOCl solution and 9:1 mixtures of NaOCl/solvents for 45 min at different temperatures.

Temperature / $^\circ\text{C}$	NaOCl D [μm]	ACN D [μm]	THF D [μm]	EtOH D [μm]	DCM D [μm]
23	-	0.036 ± 0.002	-	-	-
35	0.060 ± 0.001	0.32 ± 0.04	0.45 ± 0.03	0.47 ± 0.04	0.14 ± 0.01
50	0.43 ± 0.02	1.22 ± 0.04	1.70 ± 0.06	2.32 ± 0.13	0.81 ± 0.04

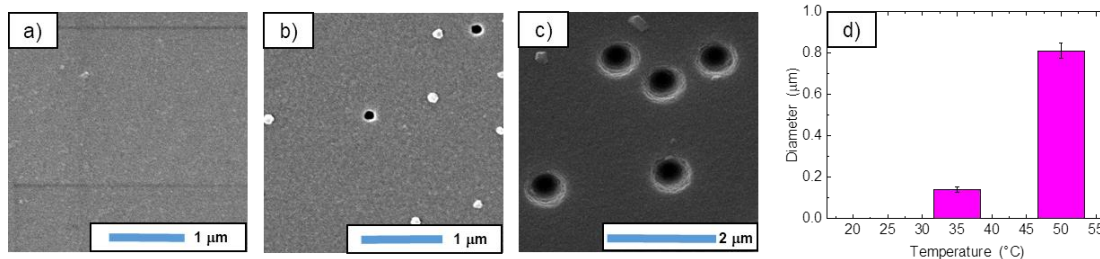


Figure S 11 Symmetrical etching of PI membranes (10^7 pores cm^{-2}) with a 9:1 mixture of NaOCl/DCM in dependence of the etching temperature. SEM images after 45 min etching at a) 23°C , b) 35°C and c) 50°C , and d) the effect of the etching temperature on the pore diameter.

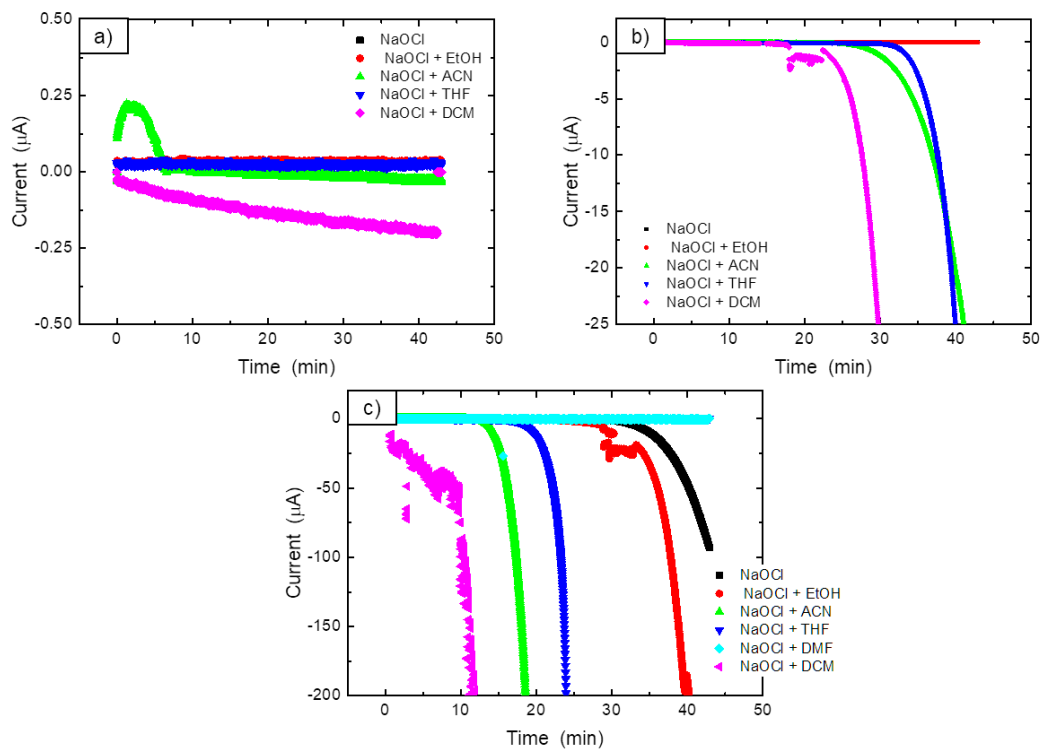


Figure S 12 Etching curves monitored during symmetrical etching process at a) 23°C, b) 35 °C and c) 50°C with 12% NaOCl solution and 9:1 mixtures of NaOCl/solvents showing the breakthrough current related to the etch rates ϵ_t .

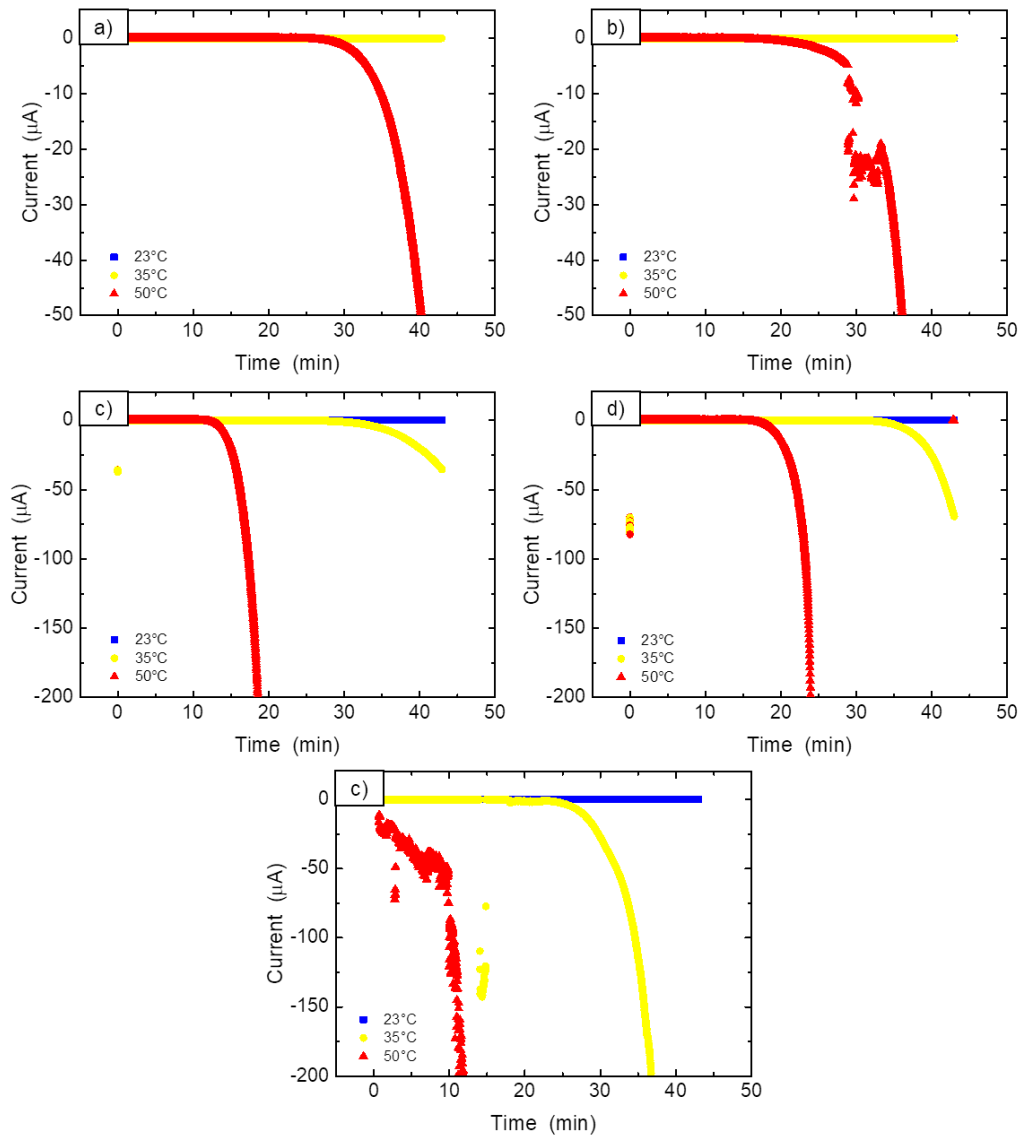


Figure S 13 Etching curves monitored during symmetrical etching process at 23°C, 35 °C and 50°C with a) 12% NaOCl solution and 9:1 mixtures of NaOCl/solvents b) EtOH, c) ACN, d) THF and e) DCM showing the breakthrough current related to the etch rates ϵ_r .

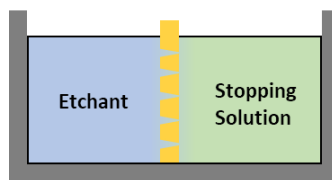


Figure S 14 Illustration of the experimental set-up for nanopore fabrication in PI membranes (10^7 pores cm^{-2}) using asymmetrical ion track-etching technique. The etchant (12% NaOCl) and the stopping solution (1 M KI) are a mixture of 100-x vol% of 12% NaOCl solution or 1 M KI and x vol% of an organic solvent.

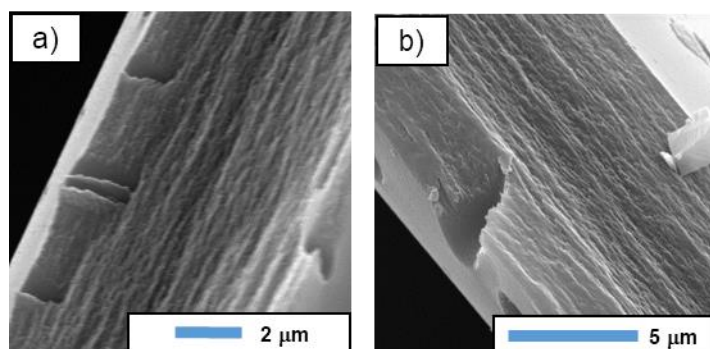


Figure S 15 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with a) NaOCl solution and b) a 9:1 mixture of NaOCl/EtOH for 45 min at 50°C.

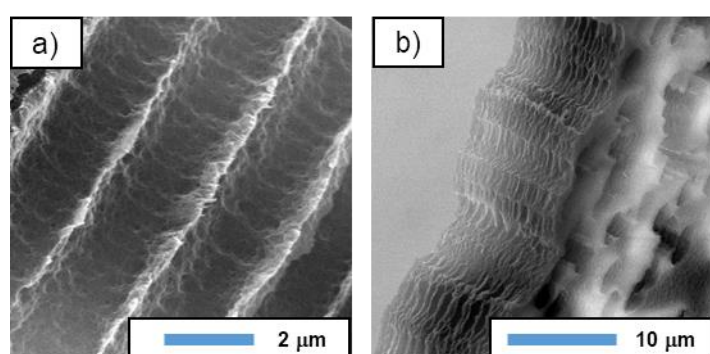


Figure S 16 SEM images of PI membranes (10^7 pores cm^{-2}) etched symmetrically with NaOCl solution for 45 min at 50°C after solvent treatment with a) DMF and b) THF.

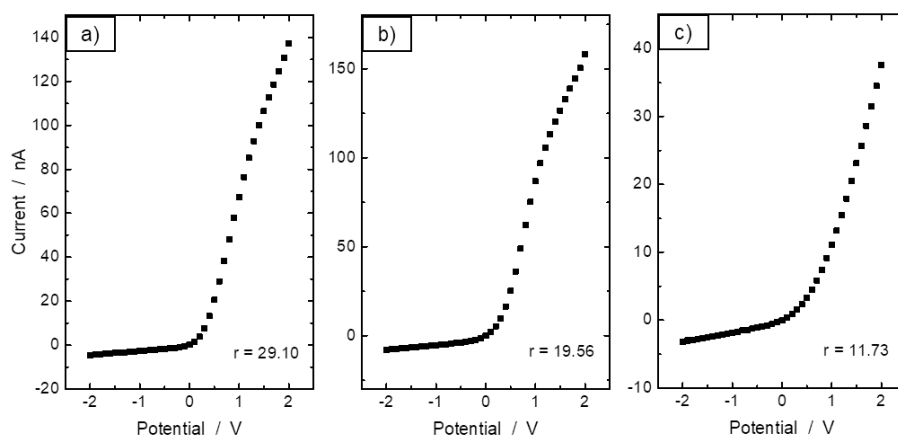


Figure S 17 PI single-nanopore membranes prepared by using NaOCl etching solution after 1 h pretreatment at 50°C with a) DMF and b) THF, and c) by using a 9:1 etchant mixture of NaOCl/THF. The electrolyte solution used for the *I-V* measurements is 0.1 M KCl.