Supporting Information

Membrane architecture with ion-conducting channels through swift heavy ion induced graft copolymerization

*Véronique Sproll,[a,b] Michael Handl,[c] Renate Hiesgen,[c] K. Andreas Friedrich,[d] Thomas J. Schmidt,[a,e] Lorenz Gubler,[a,]**

[a] Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland;

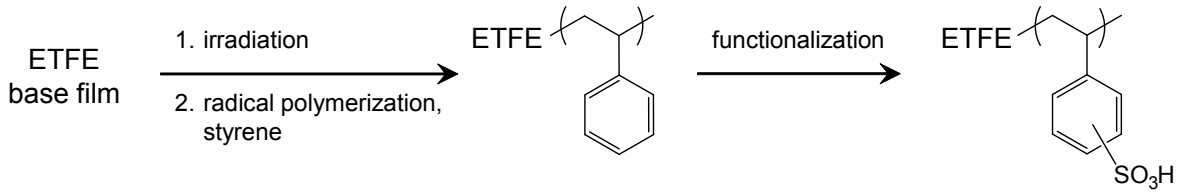
[b] Present address: Oxyphen AG, Giessereistrasse 1, 8620 Wetzikon, Switzerland;

[c] University of Applied Sciences Esslingen, Kanalstrasse 33, Esslingen 73728, Germany;

[d] German Aerospace Center, Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, Stuttgart 70569, Germany;

[e] Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland

* Corresponding author: lorenz.gubler@psi.ch



Scheme 1: Reaction scheme for the synthesis of ETFE-*g*-PSSA membranes. In the irradiation step electron or swift heavy ion (SHI, Kr^{16+}) irradiation was used . For the grafting procedure the reaction mixture consisted of 20% (v/v) styrene monomer, 70% (v/v) *iso*-propanol and 10% (v/v) ultra-pure water. The reaction temperature was 55 °C. The functionalization was performed with 2% (v/v) chlorosulfonic acid in dichloromethane solvent at room temperature (5.5h) followed by a 18h hydrolysis step at 80 °C in ultra-pure water.

EC-AFM measurements. *Sample Preparation:* For surface measurements the membranes were taped onto the AFM steel sample disc with conductive carbon adhesive tape, which was previously impregnated with nano-scaled (< 50 nm) Pt-particles (Sigma Aldrich). For measuring cross-sections, the membranes were embedded with Teroson 6700 2-component Polyurethane glue (Henkel). After curing for 24 h at room temperature, the samples were cut by microtome into slices of 150-200 µm and fixed on a sample disk similarly to the surface measurements. To ensure sufficient humidification, all cross-section samples were equilibrated at 80% relative humidity for at least 1 h prior to the measurement. Figure S14 shows a schematic sketch of the setup.

AFM-Measurements: AFM-measurements were performed by a Multimode 8 atomic force microscope (Bruker) with a closed loop scanner (nPoint) in PeakForce TUNA™ mode. The current evaluated in tapping mode was averaged with a lock-in amplifier. The contact current is averaged over the tip-sample contact time whereas the TUNA current is averaged over the whole tapping period. Platinum coated OMCL-AC240TM AFM-probes (Olympus) were used. Experiments were performed in an environmental chamber with humidified air on both sides of the cell (Figure S14). A water reservoir was used to ensure constant humidification of the membrane and enable stable measurements. The atmosphere was set to a relative humidity of 45 ± 3 %. Measurements without a water reservoir but with a higher humidification of the air atmosphere in the AFM chamber (75 ± 5 % r.h.) were performed to obtain higher resolution and measure the membrane in a less swollen condition. A bias voltage between 1.5 and 2.3 V was applied between the AFM tip and the counter electrode

(gas diffusion layer). The exact values for each measurement are noted in the results part. This current drives electrochemical reactions on both sides of the membrane. At the anode water reacts at the Pt catalyst layer to form oxygen and protons. These protons are transported through the hydrophilic channels of the membrane and recombine with the oxygen from the air atmosphere at the Pt coated tip of the AFM probe (cathode side) to form water. Therefore, current is only measured when the conductive AFM-tip is in contact with such a hydrophilic channel or a cluster thereof. Images were taken with a resolution of 1024x1024 pixels and a scan rate of 0.25 Hz.

The data of Figures 6, S15 and S16 were obtained from measurements with attached water-reservoir while the data for Figures 7, 8, S17 and S18 were obtained without attached water-reservoir.

As previously mentioned elsewhere[1]:

SEM / EDX analysis. To analyze the through-plane distribution of the grafted polystyrene on the micrometer scale, sulfonated copolymer films were swollen in water for 2 h, subsequently frozen in liquid nitrogen and fractured to obtain a sharp cross-section area without considerable smearing. Scanning electron microscopy (SEM) images were taken with an FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) and energy dispersive X-ray (EDX) analysis was performed using a compatible accessory (EDAX TSL, AMETEK) and analyzed with EDAX TEAM™ software (version V4.3). The standard gun-to-sample distance was 8.5 mm with a magnification of 1600 and an acceleration voltage of 10 kV, an aperture of 60 µm was used. The images were taken in the secondary electrons mode. For sulfur distribution profiles perpendicular to the plane of the membrane, ImageJ software (National Institutes of Health)[2] was used.

Ex-situ characterization. The ion exchange capacity (IEC), proton conductivity, water uptake and hydration number were determined in fully swollen state at ambient conditions. The IEC is defined as

$$IEC = \frac{n\,(\mathrm{H}^+)}{m_{\mathrm{dry}}} \tag{S1}$$

where $n(H^+)$ is the molar number of acid protons and m_{dry} is the dry weight of the membrane. After a proton/potassium exchange (stirring in 1 M KCl for 12 h at room temperature) the free protons were titrated with a 0.05 m KOH solution by means of a SM Titrino 702 instrument (Metrohm, Herisau, Switzerland). The theoretical IEC can be calculated using the following equation, assuming that all styrene units carry one sulfonic acid group:

$$IEC_{\mathrm{th}} = \frac{GL}{M_{\mathrm{S}} + M_{\mathrm{SSA}} \cdot GL} \quad \text{(S2)}$$

where M_S and M_{SSA} denote the molar masses of styrene (104 g/mol) and styrene sulfonic acid (184 g/mol), respectively. The water uptake (Q) of the membrane, representing the ability to absorb water, is determined by gravimetric means using the following equation:

$$Q = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \quad \text{(S3)}$$

The through-plane conductivity at different relative humidity values (r.h.) was measured with a 740 Membrane Test System from Scribner Associates Inc. (North Carolina, USA) at a temperature of 80°C, using gas diffusion electrodes from E-TEK DivisionSM (ELAT HT-140E-W).[3]

In-Situ Characterization. Fuel cell tests were performed with membranes of a graft level of ~25%. Nafion® (NR-212) was measured as reference. To form a membrane electrode assembly (MEA), membranes were laminated with gas diffusion electrodes from Johnson Matthey Fuel Cells (type ELE 0263-0983, loading: 0.4 mg Pt/cm^2) in a hot-press at defined temperature, load, and duration (110°C/2.5 MPa/180 s).[4] Subsequently, the MEAs were assembled into a single cell with a graphite flow field and an active area of 15.8 cm^2. Further details regarding the cell design can be found elsewhere.[5] The MEAs were operated in a single cell mode at 80 °C and 2.5 bar_a backpressure on both sides with hydrogen and oxygen fed at a flow rate of 600 mL min^{-1}. After 12 h conditioning at constant current density (0.5 A cm^{-2}) and 100% relative humidity, the first polarization curve was measured. Cell voltage and high frequency resistance (HFR, at 1 kHz, AC milliohm meter model 3566, Tsuruga, Japan) were continuously monitored over the entire length of the test protocol. The

cell was conditioned at 70% r.h. for 2 h (gas flow rate: 2'000 mL min^{-1}, 0.1 A cm^{-2}) before the next polarization curve was taken; the same applies to the measurements at 50% r.h..

Electrochemical hydrogen permeation measurements based on the single cell configuration were conducted to assess the mechanical integrity and gas permeability of the membranes. After the described protocol (cf. above) hydrogen crossover through the membrane was measured by an electrochemical method[6, 7] under fully humidified conditions at 80°C and 2.5 bar_a backpressure on both sides. Fully humidified gasses (H_2 and N_2, flowrate 600 mL min^{-1}) were fed to the anode and cathode, respectively. After 2 h the hydrogen permeation was evaluated as a diffusion-limited hydrogen oxidation current density in the range of 200-800 mV.

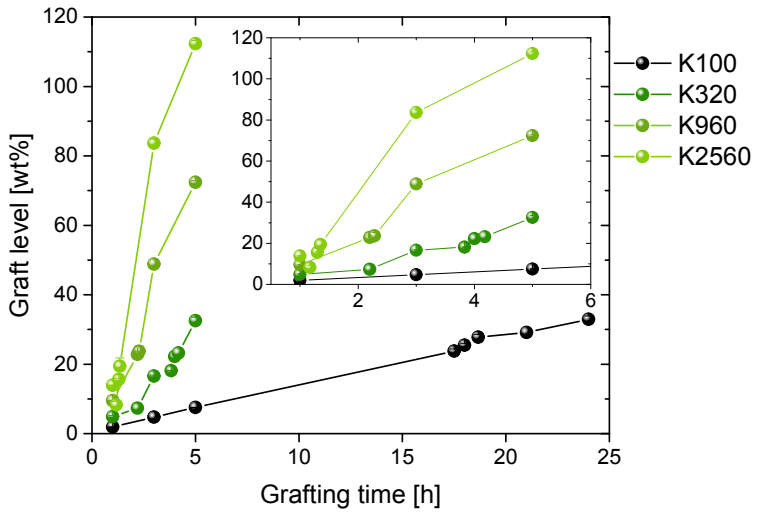


Figure S1: Kinetics of the grafting of ETFE with styrene after irradiation with different ion densities. Conditions cf. Scheme 1.

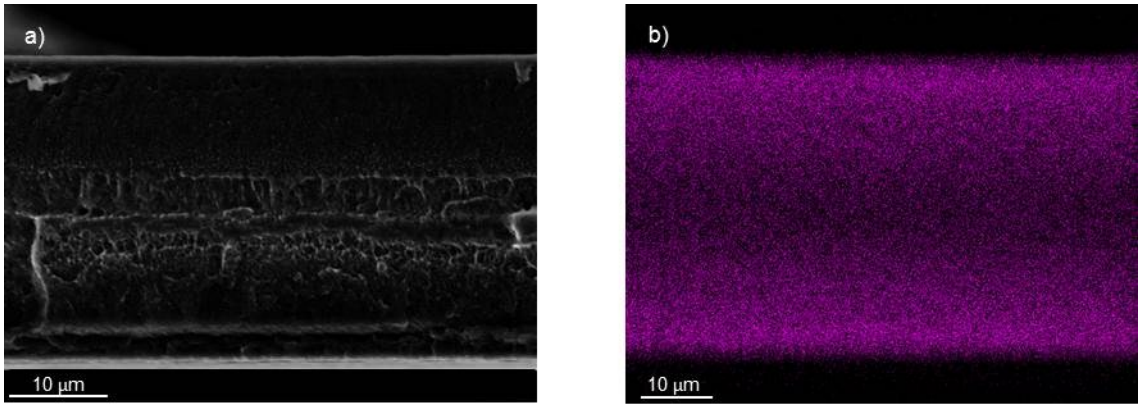


Figure S2: a) Scanning electron micrograph of the cross-section of a standard electron irradiated membrane (Std. e-, ~25% GL and b) EDX sulfur mapping thereof.

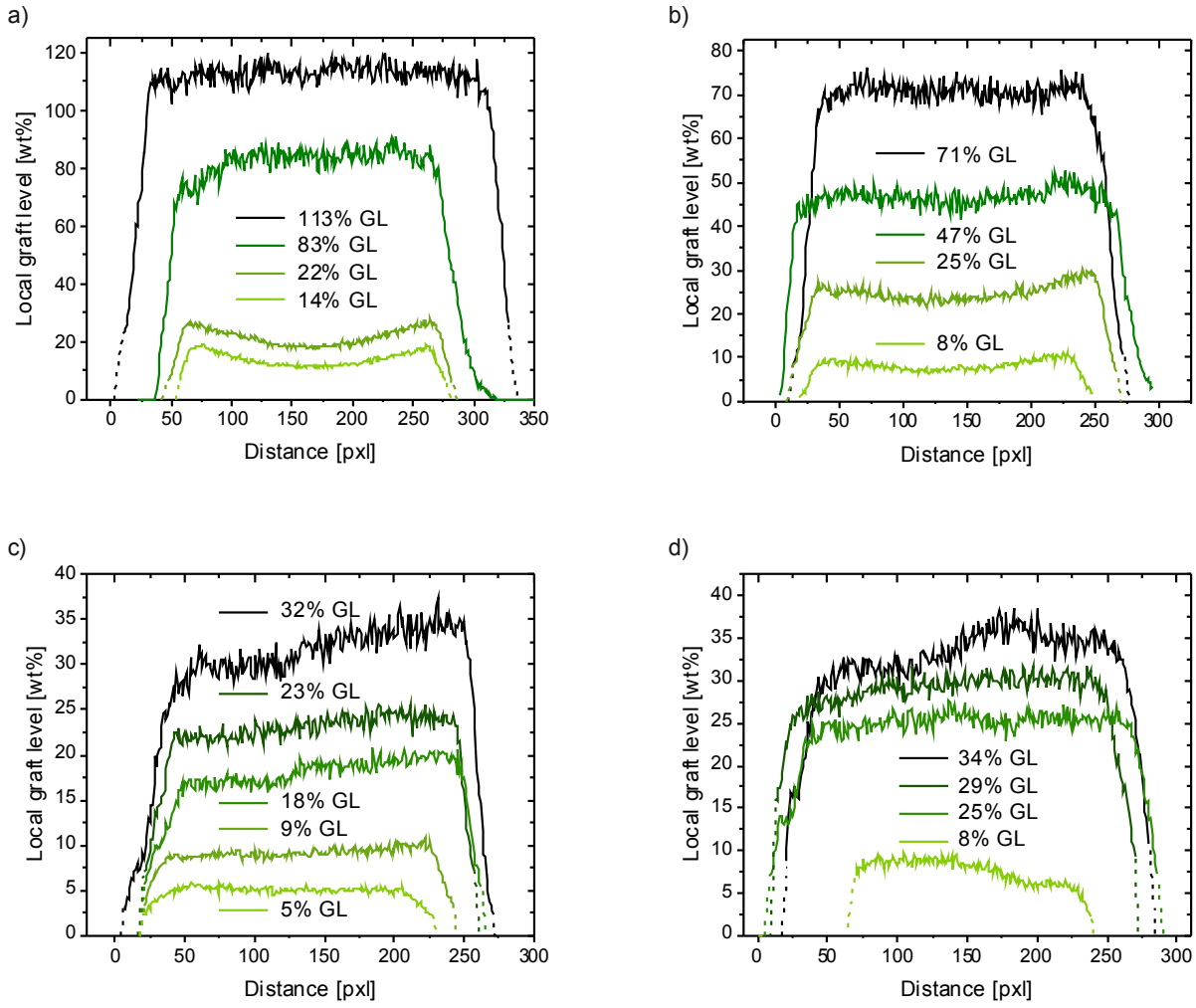


Figure S3: Graft distribution profiles obtained from EDX sulfur mappings for SHI membranes irradiated with different ion densities a) K2560, b) K960, c) K320, d) K100 and different graft levels (as indicated in the legend).

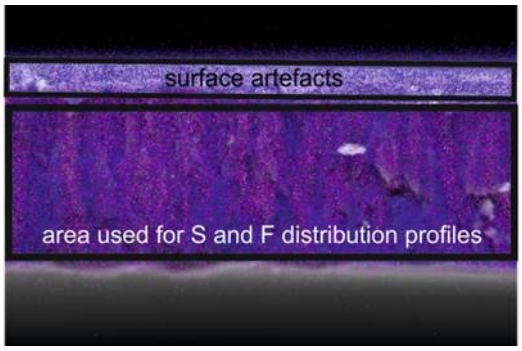


Figure S4: Sketch illustrating the area that was used for the analysis of the sulfur (magenta) and fluorine (blue) distribution profiles along the direction of the plane of the membrane.

For cross-sectional analysis the position of the EDX detector is optimized for the cross-section of the sample. This corresponds to a highly unsuitable position to measure accurately the EDX signal originating from the surface at the same time. In this position the detector measures a higher intensity of fluorine than sulfur. As no mixed colors are formed in the overlaid images of two elemental mappings (cf. main text) the surface area is displayed as fluorine dominated. However, these are artefacts and cannot be taken as real fluorine to sulfur ratio. For this we performed dedicated surface measurements (cf. Figure 5 and Figures S10-S13).

7.5% graft level:

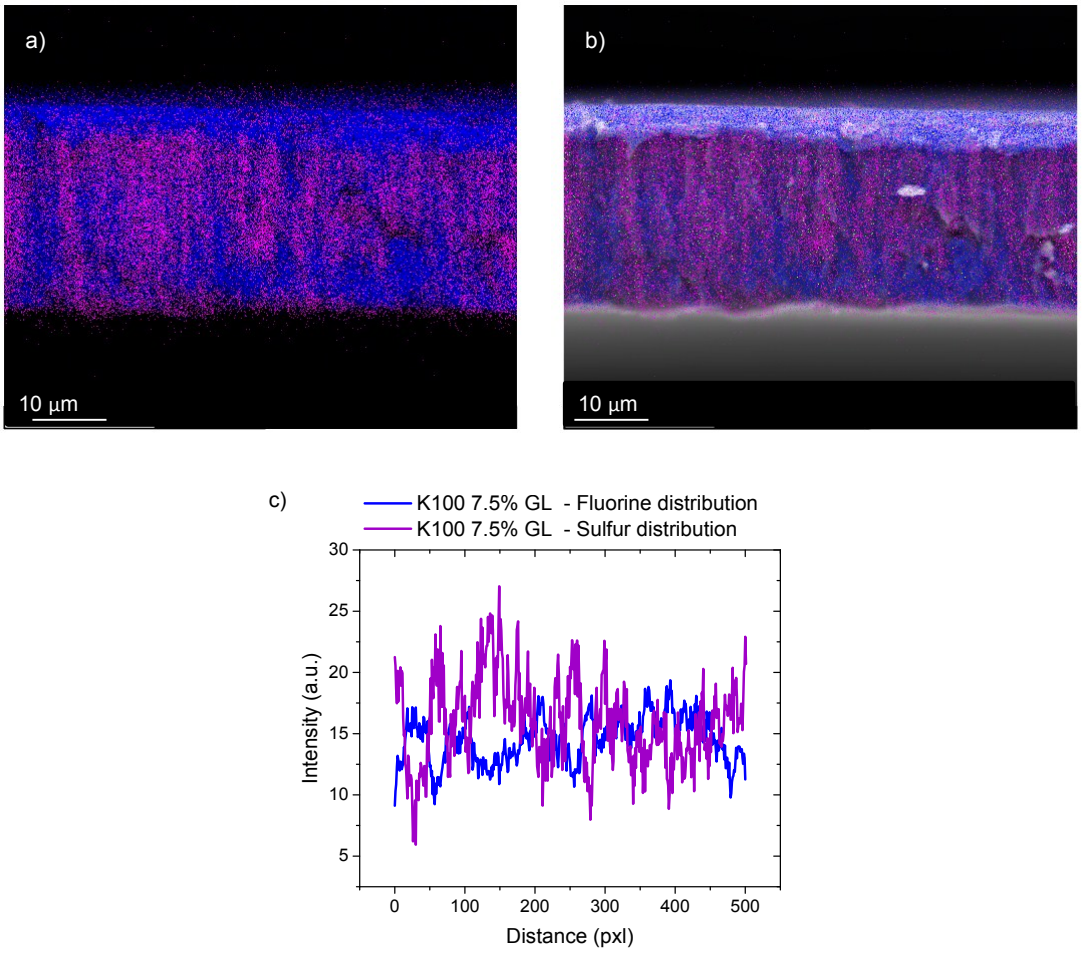


Figure S5: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (7.5% GL). b) Sulfur (magenta) and fluorine (blue) EDX mappings overlaid on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

25% graft level

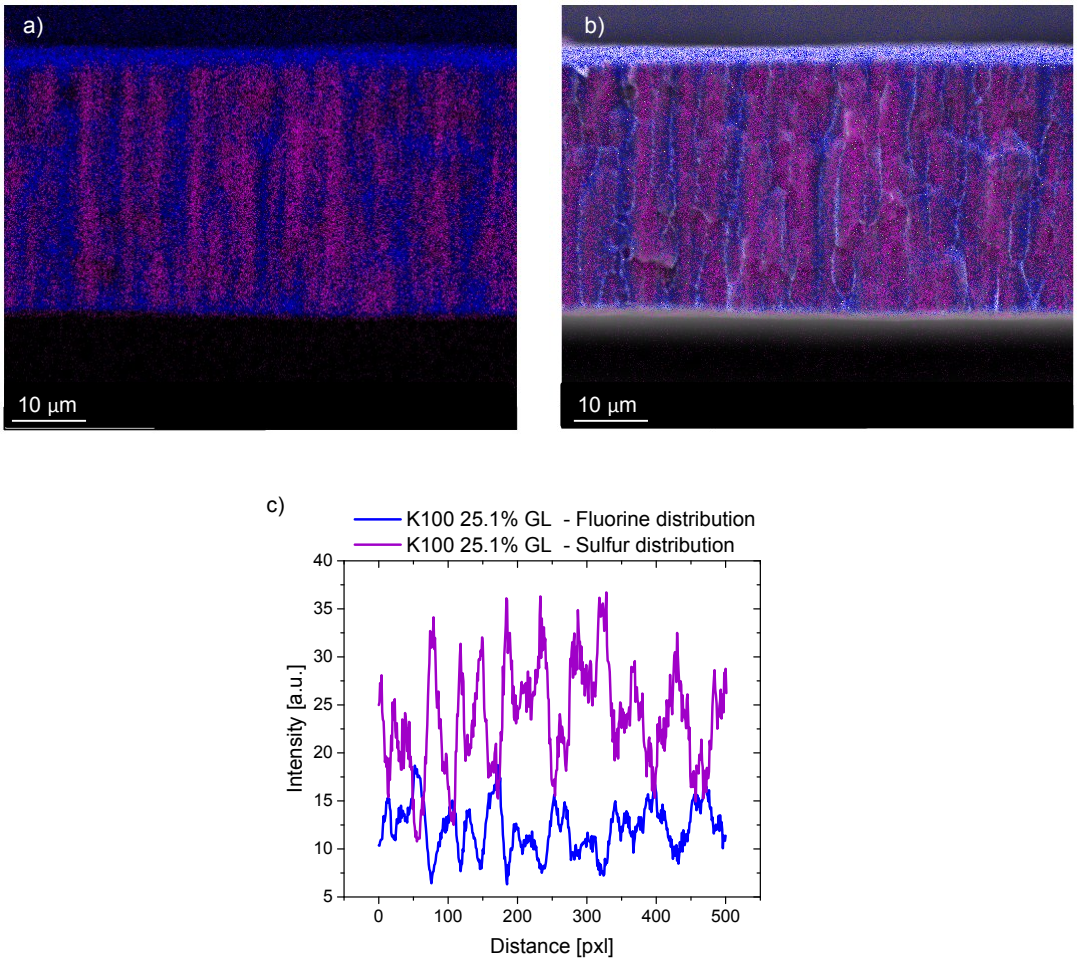


Figure S6: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (25% GL). b) Sulfur (magenta) and fluorine (blue) EDX mappings overlaid on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

29% graft level

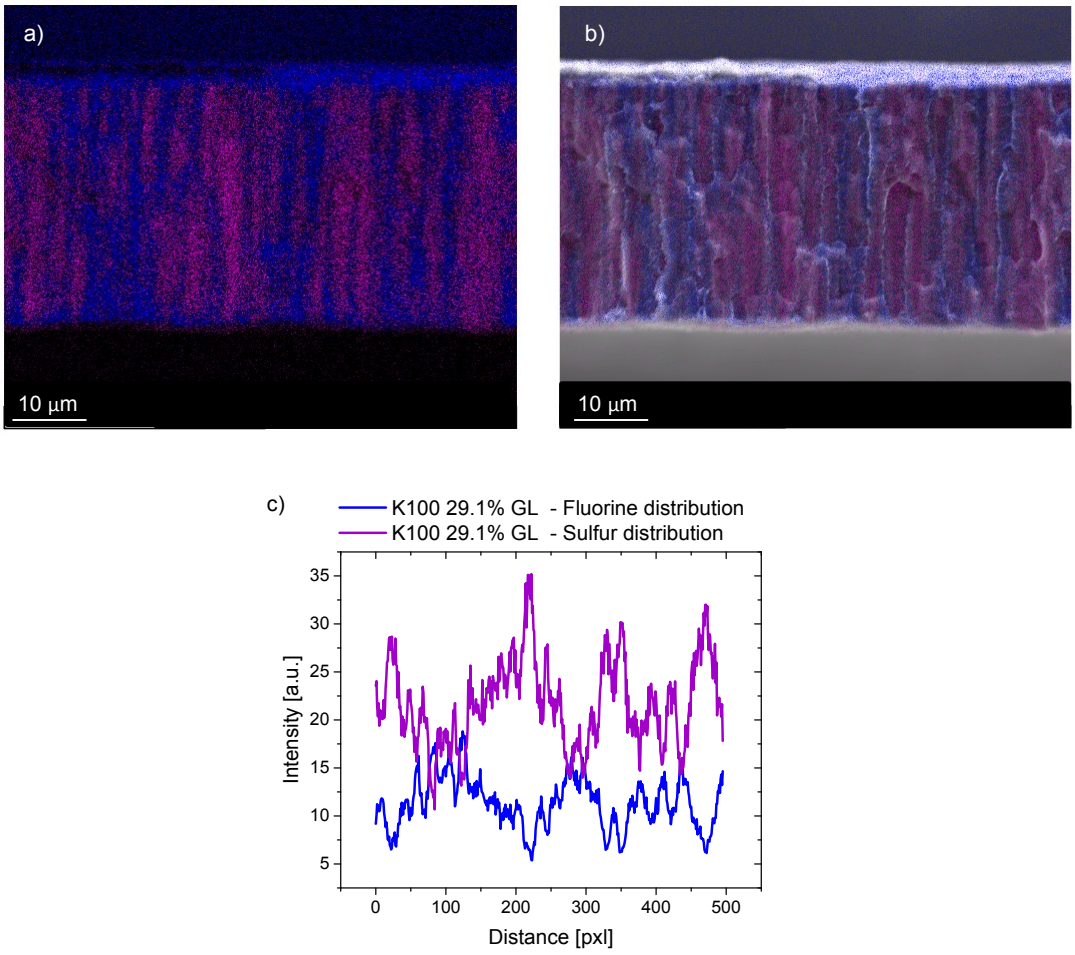


Figure S7: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (29% GL). b) Sulfur (magenta) and fluorine (blue) EDX mappings overlaid on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

34% graft level

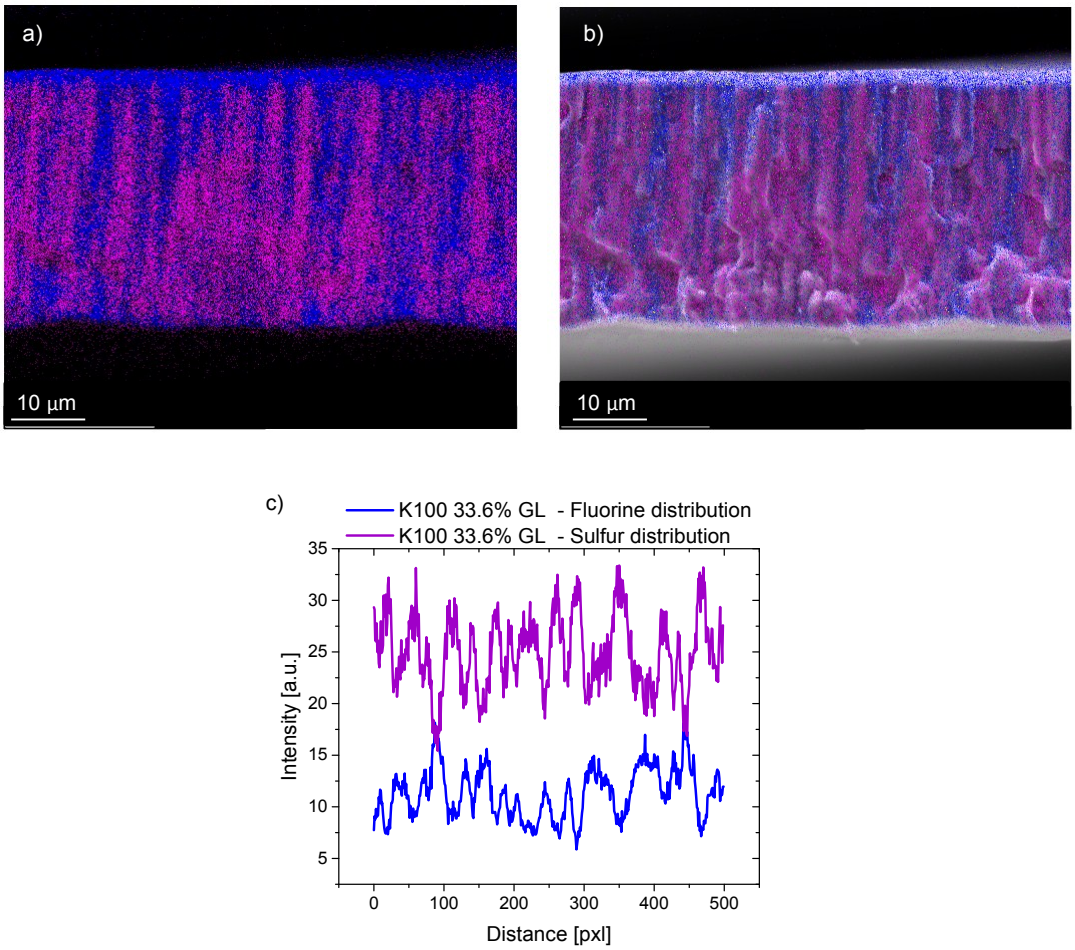


Figure S8: a) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings of a K100 membrane (34% GL). b) Sulfur (magenta) and fluorine (blue) EDX mappings overlaid on a SE image of the membrane. c) Sulfur and fluorine distribution profiles measured along the direction of the plane of the membrane.

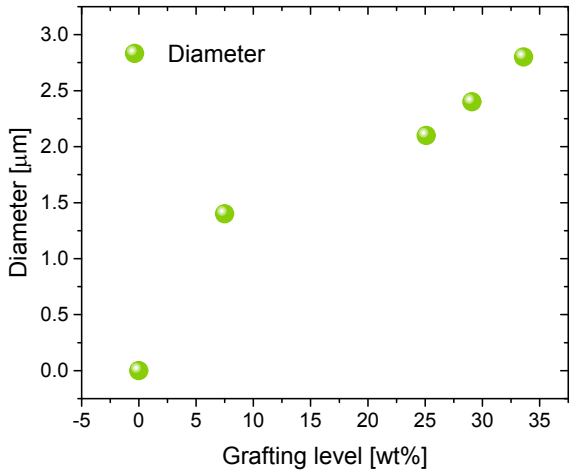


Figure S9: Correlation of the estimated diameter of the initial track with the graft level for K100 membranes.

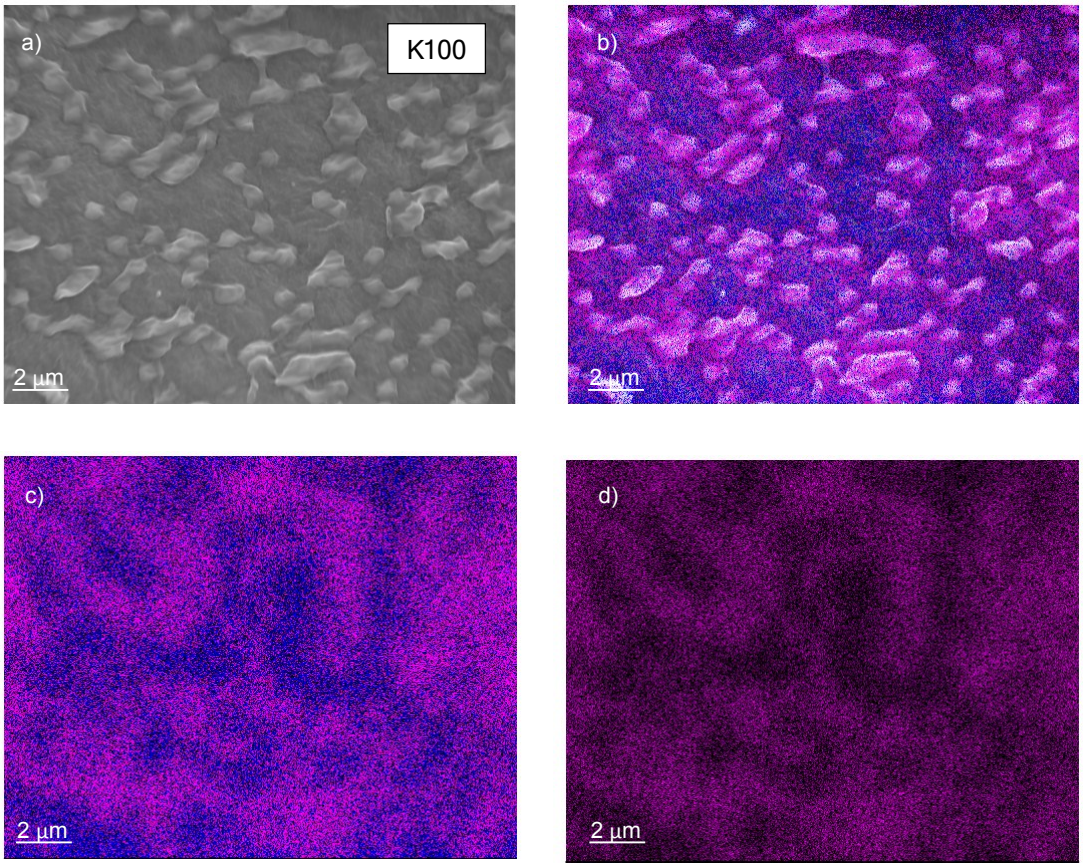


Figure S10: a) Scanning electron micrograph of a K100 membrane (25% GL). b) Sulfur (magenta) and fluorine (blue) EDX mappings overlaid on the SE image of the membrane. c) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings. d) EDX sulfur mapping.

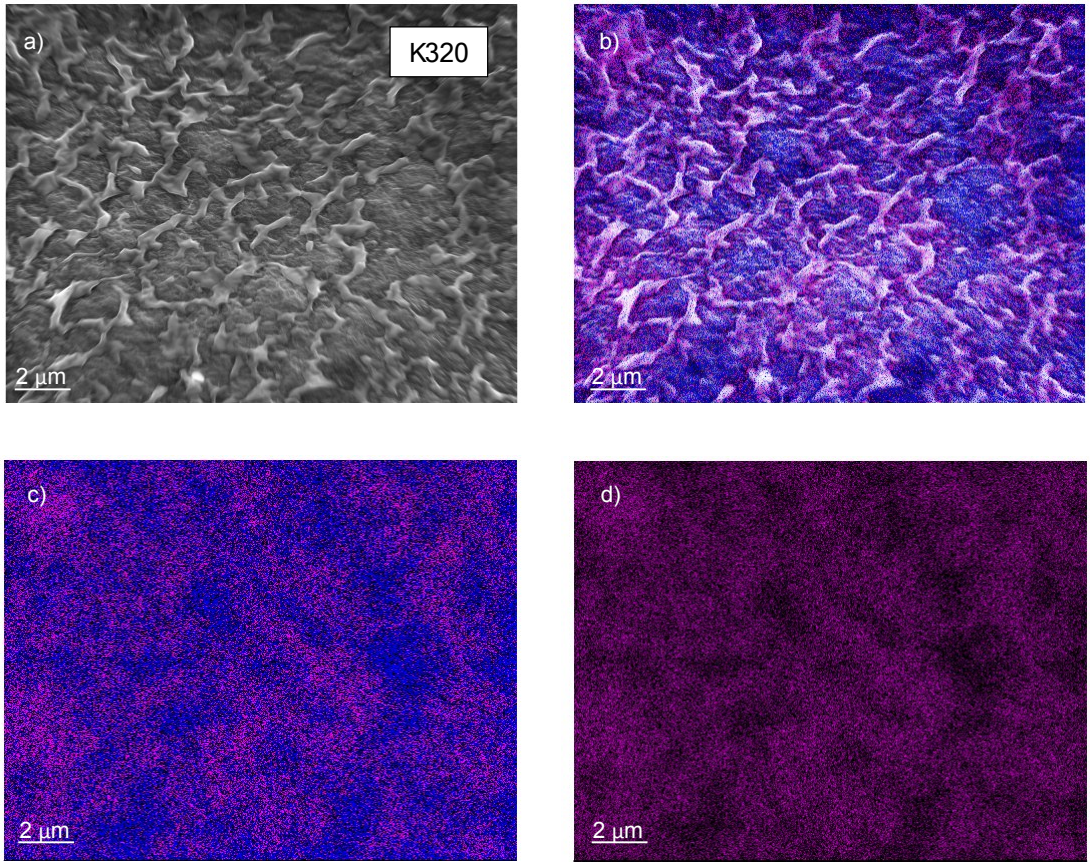


Figure S11: a) Scanning electron micrograph of a K320 membrane (25% GL). b) Sulfur (magenta) and fluorine (blue) EDX mappings overlaid on the SE image of the membrane. c) Overlaid sulfur (magenta) and fluorine (blue) EDX mappings. d) EDX sulfur mapping.

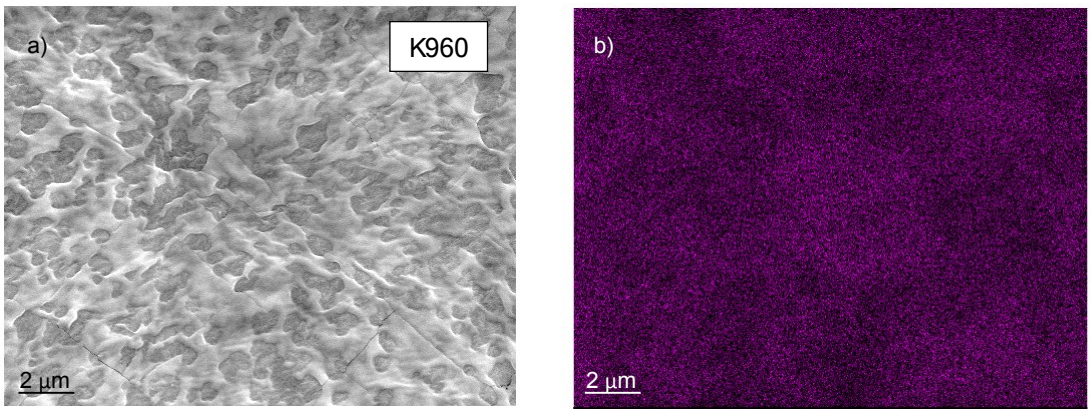


Figure S12: a) Scanning electron micrograph of a K960 membrane (25% GL). b) EDX sulfur mapping of the membrane.

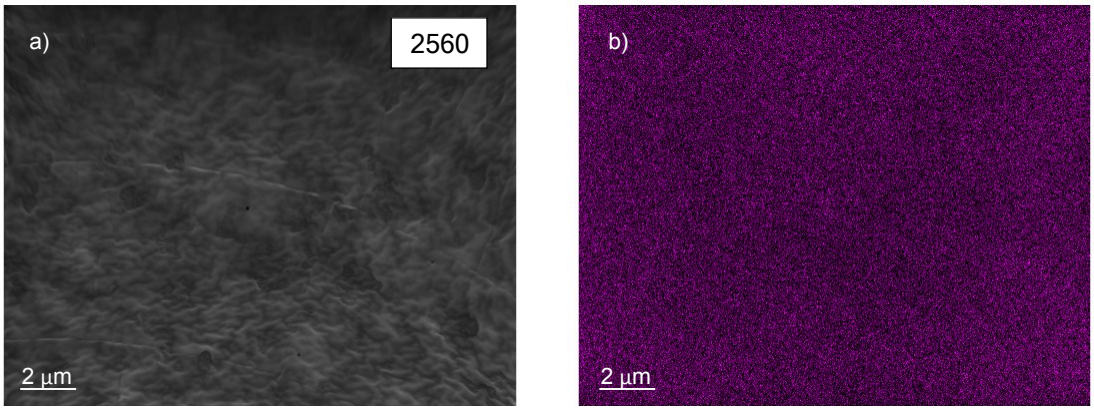


Figure S13: a) Scanning electron micrograph of a K2560 membrane (25% GL). b) EDX sulfur mapping of the membrane.

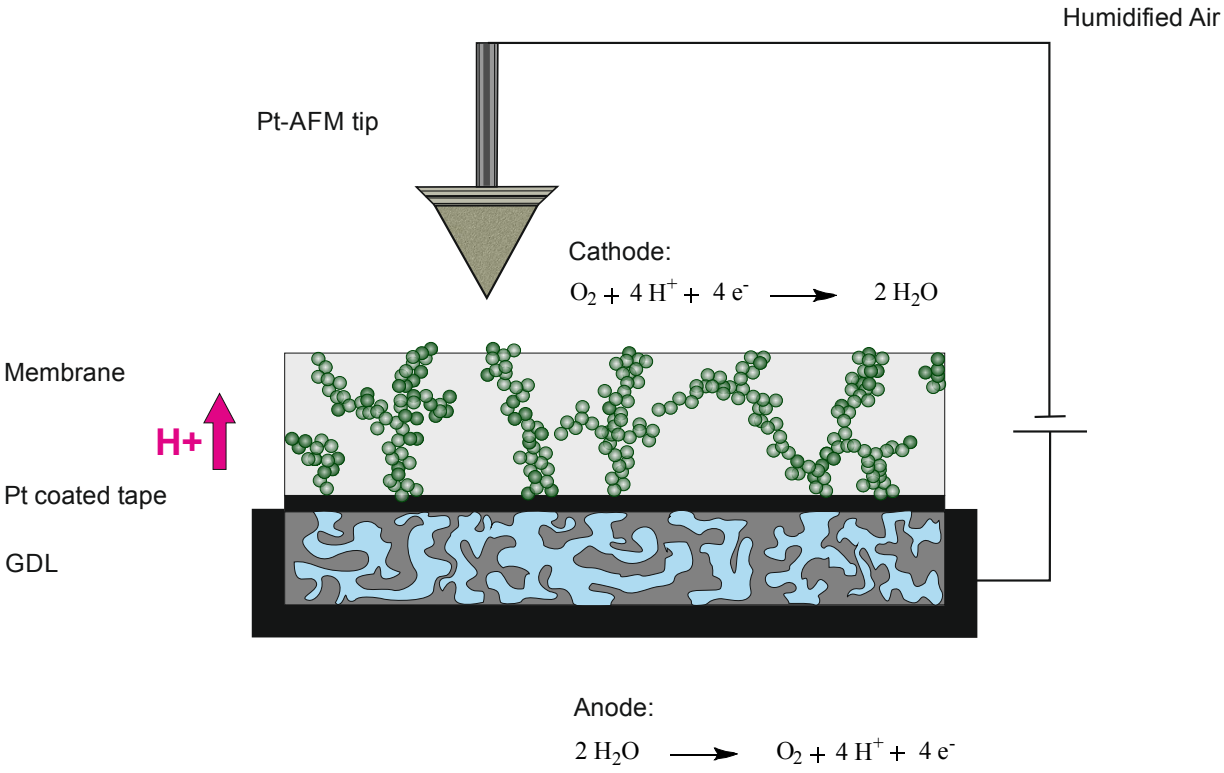


Figure S14: Schematic of the experimental setup used for EC-AFM measurements when no water reservoir was used. For the measurements with a water reservoir this was placed below the gas diffusion layer (GDL).

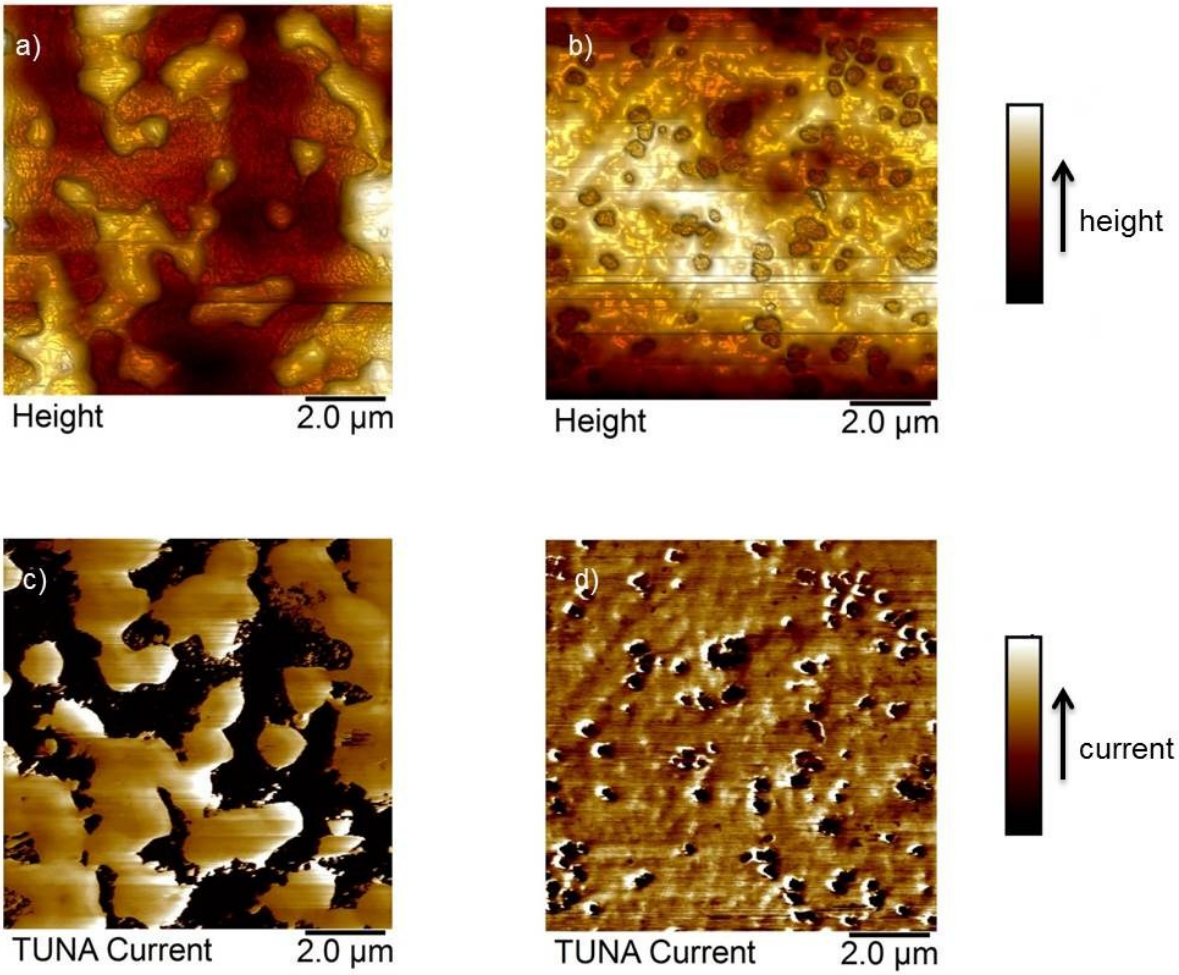


Figure S15: EC-AFM measurements (setup including water reservoir) of K100 and K2560 membranes (~25% GL). a) and b) display the topography of K100 and K2560, respectively, with elevated areas marked in brighter colors. c) and d) show the corresponding local current measurements (TUNA). The brighter areas correspond to detected current whereas the dark regions show no measured conductivity under this condition.

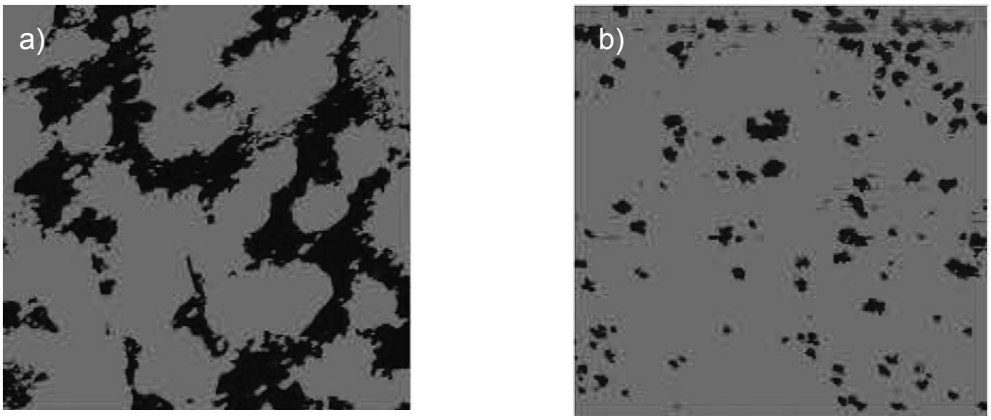
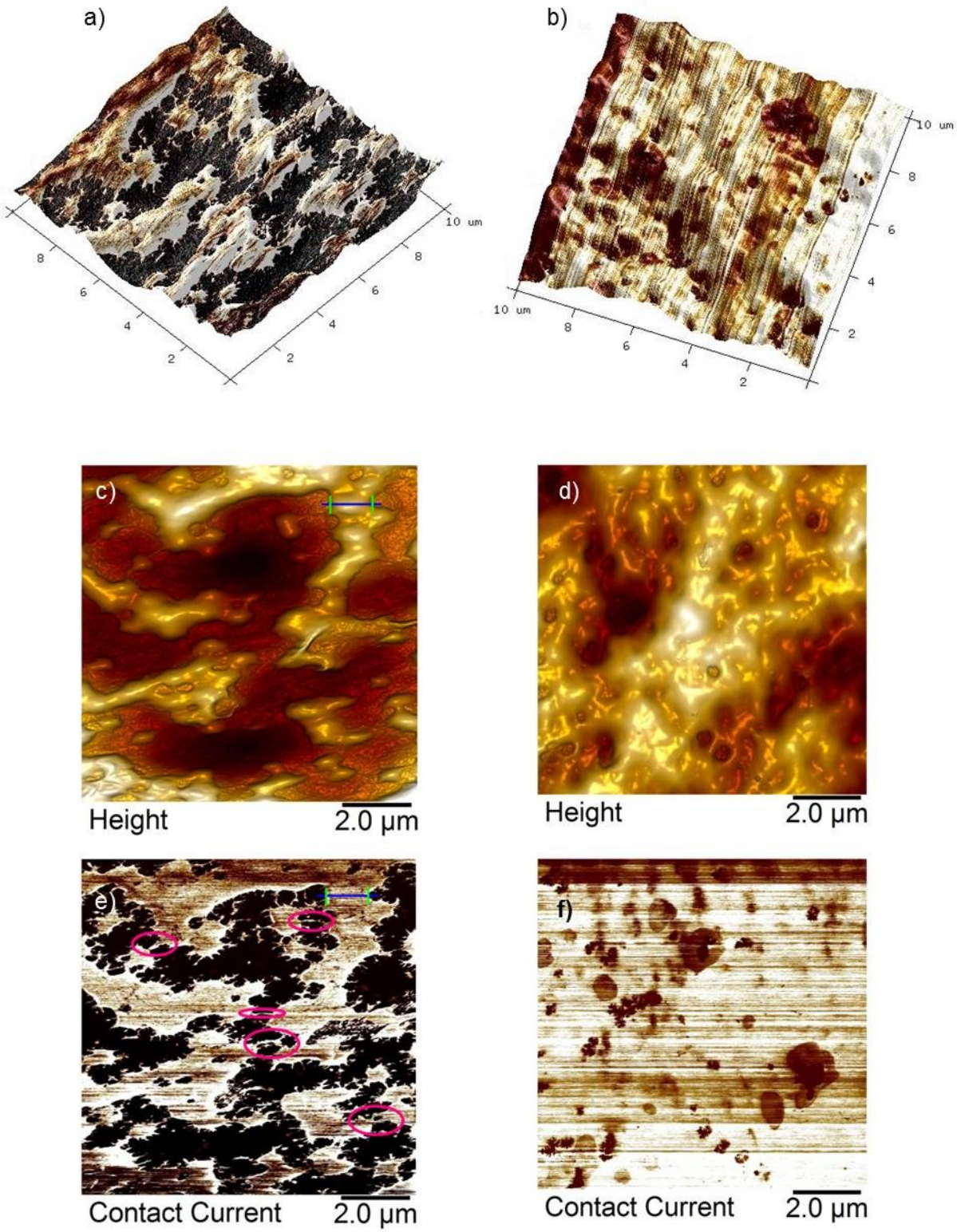


Figure S16: Conductive area fractions for a) K100, 70%, and b) K2560, 90%, membranes with a grafting level of ~25%. TUNA current was used for the evaluation and the measurement setup was equipped with a water reservoir. Grey areas correspond to conductive fractions.



(Figure S17a-f)

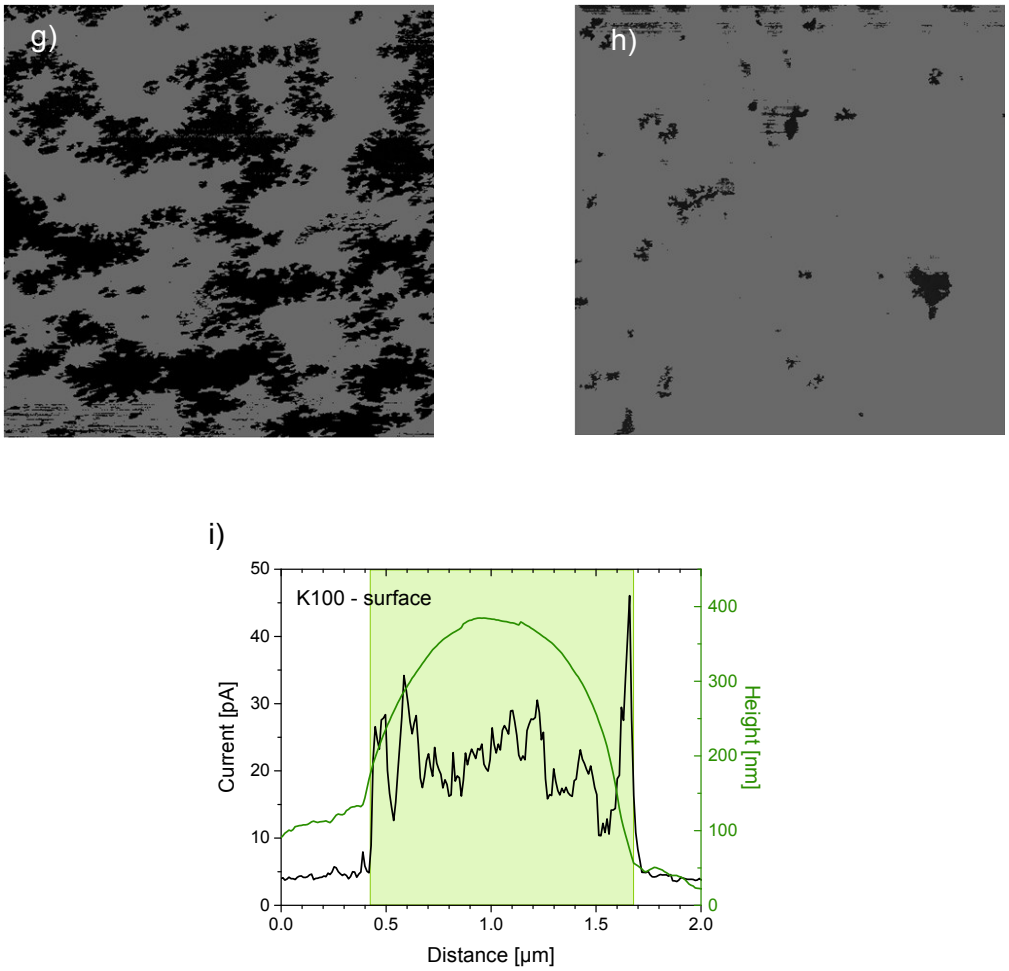


Figure S17: EC-AFM measurements (setup without water reservoir) of K100 and K2560 membranes (~25% GL). a) and b) show a current mapping overlaid over a 3D-image recorded simultaneously of the surface topography of K100 and K2560, respectively. c) and d) display the topography of K100 and K2560, respectively, with elevated areas marked in brighter colors. e) and f) show the corresponding local current measurements (contact current). The brighter areas (in a, b, e and f) correspond to detected current whereas the dark regions show no measured conductivity under this condition. Figure e) highlights furthermore the narrow bridges between the locally separated conducting elevations (magenta ellipses). g) and h) represent the conductive area fractions for K100 (g, 56 ± 4 %) and K2560 (h, 95 ± 2%) membranes. Grey areas correspond to conductive fractions. Figure i) shows the overlaid height and current line profiles corresponding to the blue line in figure e), the green boundaries mark the onset of the protrusion.

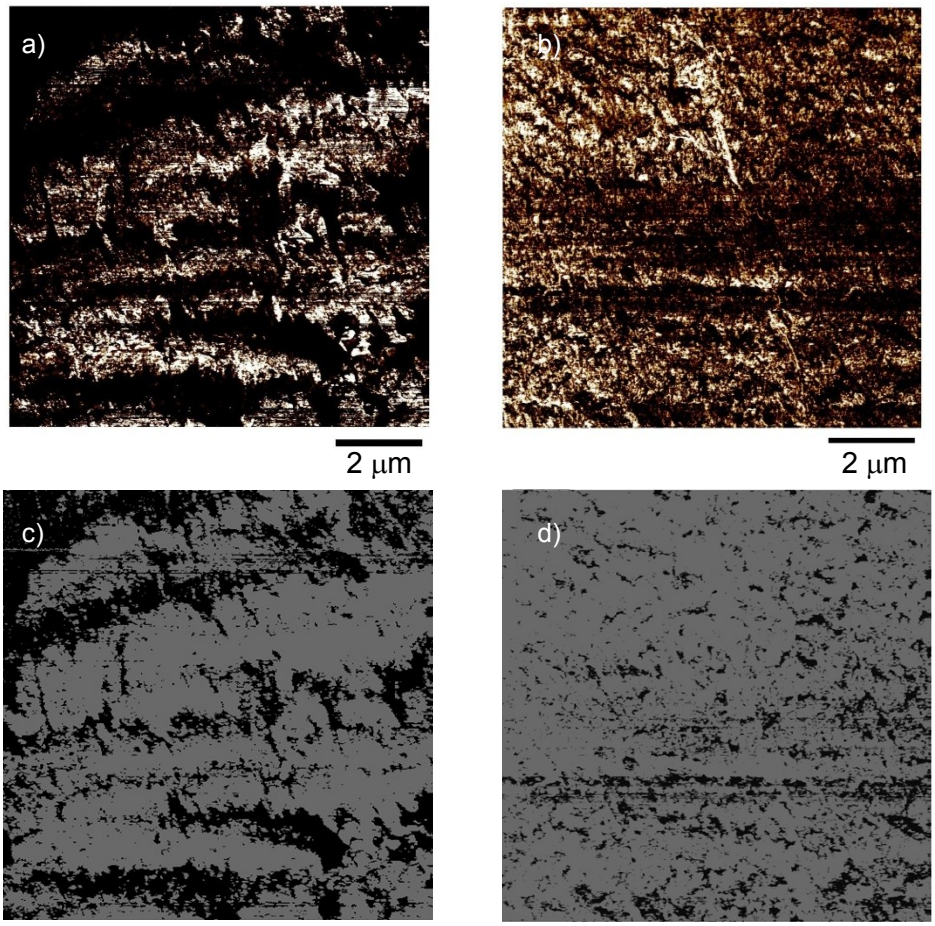


Figure S18: Contact current measurements of membrane cross-sections for K100 (a, c) and K2560 (b, d) membranes at 25% GL. Panels c and d show the conductive area fractions for the respective membranes within an area of 10 μm x 10 μm (K100: 44 ± 6 %; K2560: 81 ± 9 %).

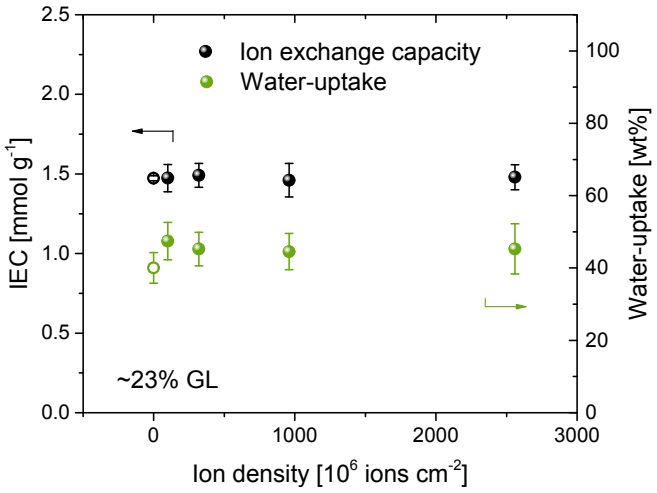


Figure S19: Experimentally determined ion exchange capacity and water-uptake for SHI membranes synthesized after irradiation with different fluences and the standard electron irradiated membrane ($0 \cdot 10^6$ ion cm^{-2}). All membranes had a graft level of ~23%.

The degree of sulfonation was determined from the experimentally measured IEC and the theoretical IEC (Equation S2) and ranges between 93 and 96% with no correlation regarding applied ion density or kind of radiation used (electron or SHI). Std.e-: ~94%; K100: ~96%; K320: ~95%; K960: ~93%; K2560: ~95%.

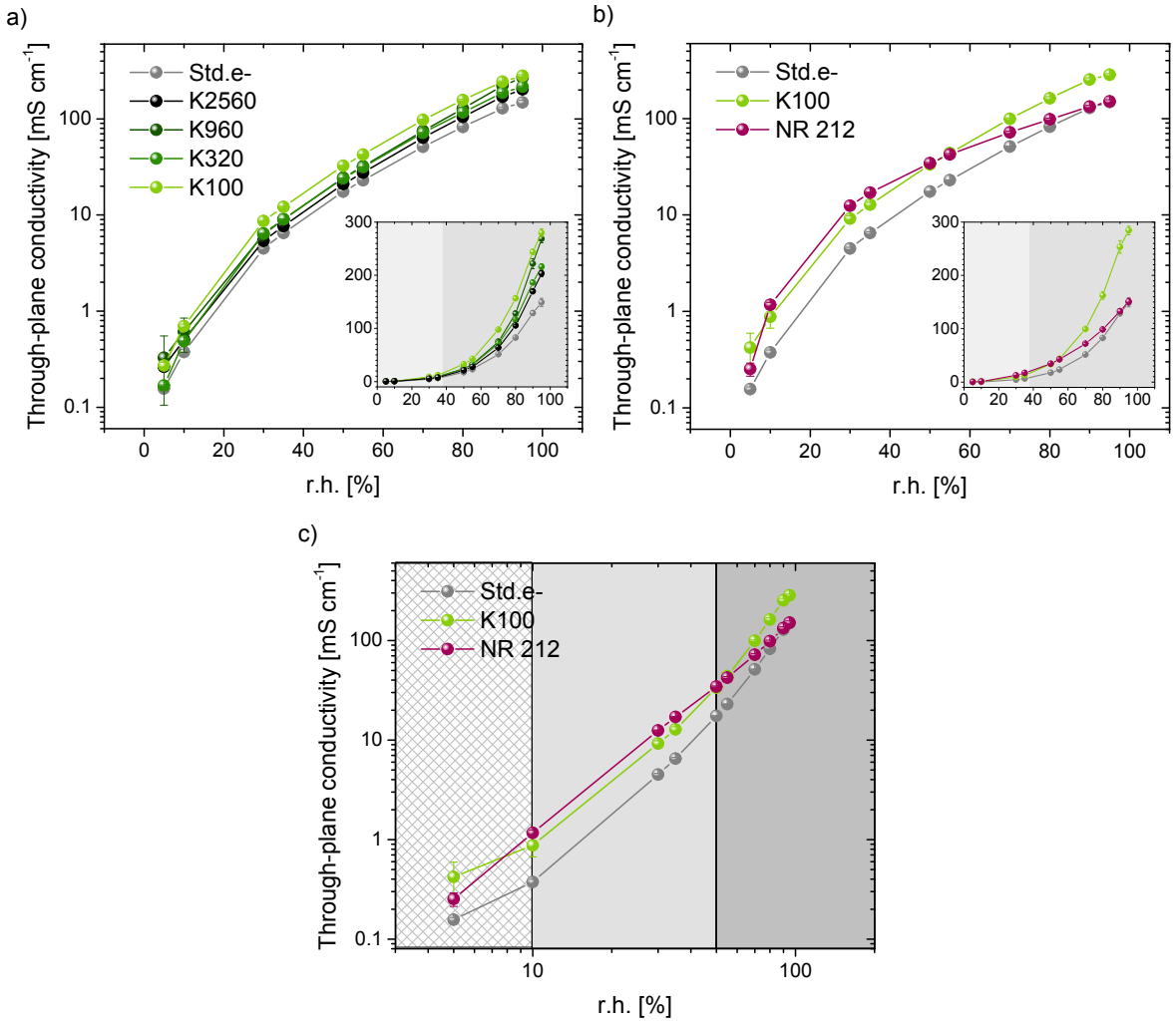


Figure S20: a) Through-plane conductivity measurements at 80°C and different relative humidity values plotted in a logarithmic scale. The inset is plotted linearly. b) Conductivity increase of SHI irradiated membranes compared to the standard electron irradiated system (Std.e-) and Nafion. c) Date plotted in a double logarithmic scale. All measured radiation grafted membranes have a graft level of ~25%.

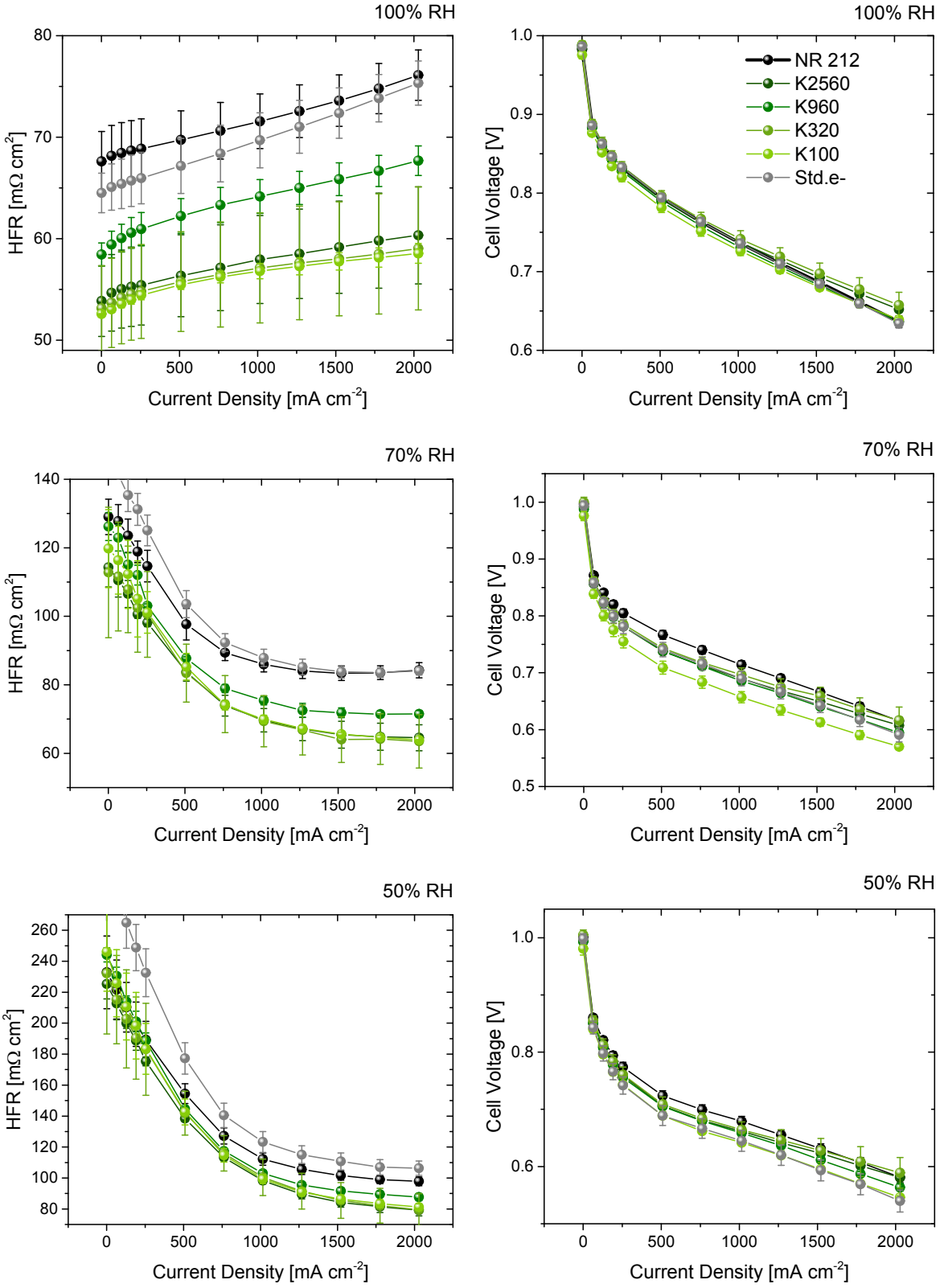


Figure S21: Polarization curves of SHI membranes (K100, K320, K960 and K2560) and Std.e- with a graft level of 25% and Nafion NR-212 at different relative humidity values (80°C; 2.5 bar_a backpressure on both sides, H_2/O_2; flow rates on both sides for 100% r.h.: 600 mL min^{-1} and for 70% and 50% r.h.: 2'000 mL min^{-1}).

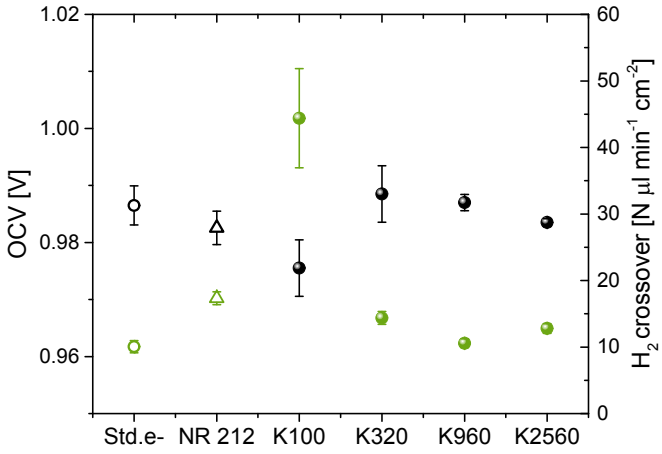


Figure S22: Electrochemically determined hydrogen permeation values (right axis, green symbols) and open circuit voltage (left axis, black symbols) for SHI membranes synthesized after irradiation with different fluences, the standard electron irradiated membrane and Nafion (NR 212).

References in Supporting Information:

1 V. Sproll, G. Nagy, U. Gasser, J.P. Embs, M. Obiols-Rabasa, T.J. Schmidt, L. Gubler, S. Balog, Radiation Grafted Ion-Conducting Membranes: The Influence of Variations in Base Film Nanostructure, *Macromolecules*, 2016**, 49**, 4253-4264.

2 W.W. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997 - 2014.

3 K.R. Cooper, Progress Toward Accurate Through-Plane Ion Transport Resistance Measurement of Thin Solid Electrolytes, *J. Electrochem. Soc*,. 2010**, 157**, B1731-B1739.

4 L. Gubler, H. Ben youcef, S. Alkan-Gürsel, A. Wokaun, G.G. Scherer, Cross-Linker Effect in ETFE-Based Radiation-Grafted Proton-Conducting Membranes, *J. Electrochem. Soc.*, 2008**, 155**, B921 - B928.

5 N. Linse, G.G. Scherer, A. Wokaun, L. Gubler, Quantitative analysis of carbon corrosion during fuel cell start-up and shut-down by anode purging, *J. Power Sources*, 2012**, 219**, 240-248.

6 M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Gas crossover and membrane degradation in polymer electrolyte fuel cells, *Electrochim. Acta*, 2006**, 51**, 5746-5753.

7 S.S. Kocha, S.; J. Deliang Yang, J.S. Yi, Characterization of gas crossover and its implications in PEM fuel cells, *AIChE Journal*, 2006**, 52**, 1916-1925.