Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Fuel cell evaluation of anion exchange membranes based on PPO with different cation placement

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Experimental setup and spiral flow field

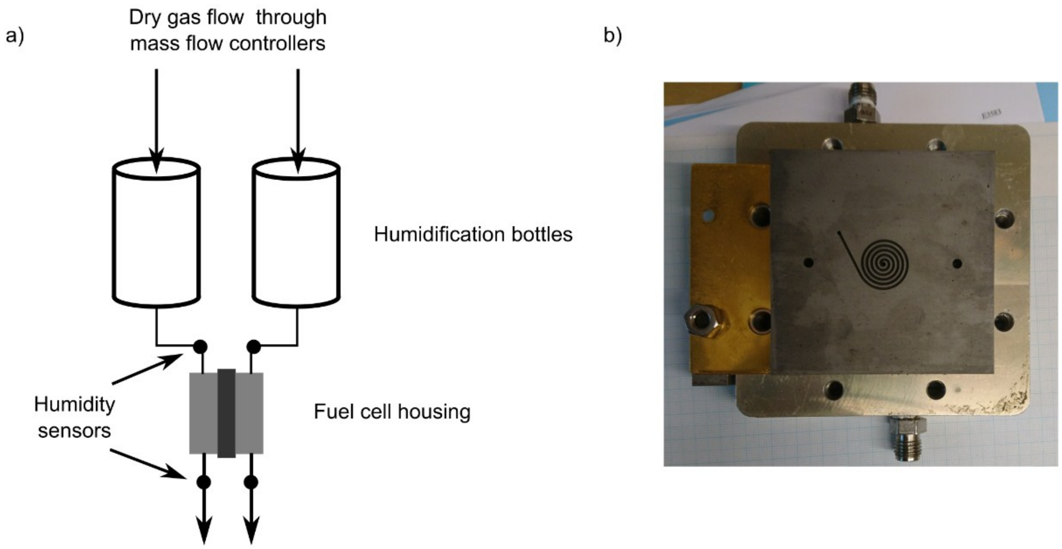

Figure S1 – a) Schematic of experimental setup, b) image of spiral flow field fuel cell.

Polarization curve for different membrane thicknesses

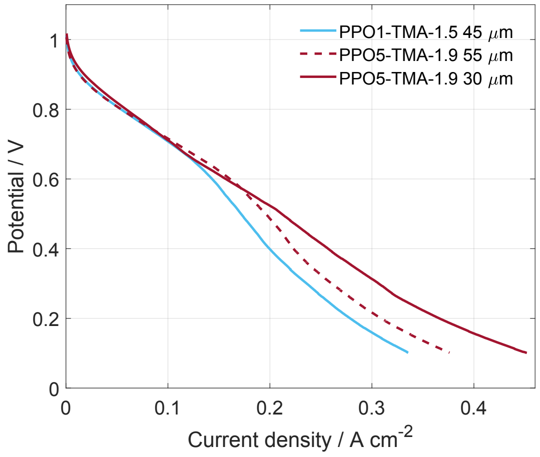

Figure S2 – Comparison of I-V curves two PPO5-TMA-1.9 membranes and on PPO1-TMA-1.5 with different thickness. At 90 % RH, 50 ℃, and O_2/H_2 *flows of 130* $ml_n min^{-1}$ *with 1* $mV\ s^{-1}$ *scan rate from OCV to 0.1 V.*

In order to ensure that the best performing membrane was not only due to its lower thickness, 30 um, a cell with a 55 um PPO5-TMA-1.9 membrane was also studied. The cells show similar performance down to 0.6 V even without IR-correction. However, it should be noted that due to humidification issues the 55um membrane is not measured exactly at 90% RH, but closer to 95 %.

Additional raw data from the water flux measurements

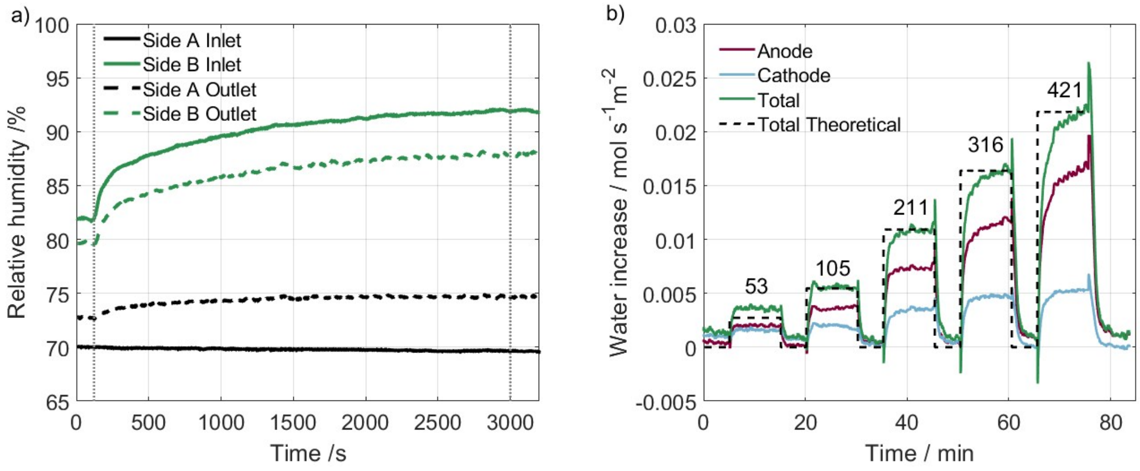

Figure S3– Shows the sensor response for both a diffusion driven water flux measurement a) and one under applied load b) at gas flows of 130 130 $ml_n min^{-1}$*.*

In Fig. S3 a) the raw data diffusion driven water flux is shown. At the start of the measurement one humidifier is set to 70 % RH and the other to 82 %. After 100 s the set point of one of the humidifiers is changed to 90 % RH. As can be seen it takes approximately 3000 s (50 min) before the system reaches a new steady state. A mass balance on both sides shows that the loss of water on one side is the same as the increase on the other, indicating that there are no leaks in the system. In Fig. S3 b) the raw data current driven water flux is shown. Here the anode sensor, the cathode sensor, the total of the two and the theoretical amount of water produced calculated using Faraday's law of electrolysis are plotted. This shows that all of the water produced at the applied load leaves the cell, however, at slightly higher currents there is a time delay before sensor response.

Stability data

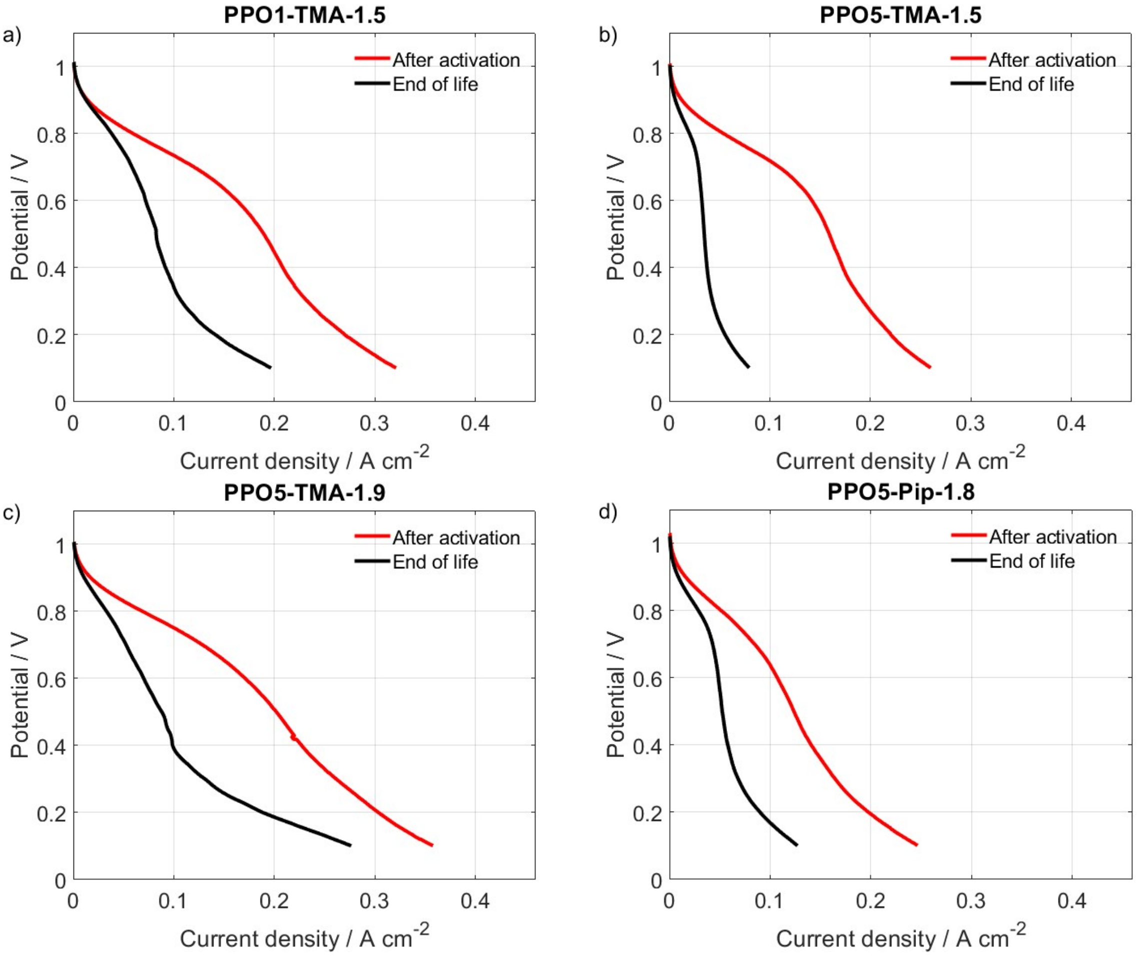

Figure S4 – I-V curves without IR-correction comparing beginning and end of life for the four different types of membranes. a) PPO1-TMA-1.5, b) PPO5-TMA-1.5, c) PPO5-TMA-1.9 and d) PPO5-Pip-1.8. Measured at 50 ℃, and O_2/H_2 flows of 130 ml$_n$min^{-1} with 1 mV s^{-1} scan rate from OCV to 0.1V

In Fig. S4 the I-V curves for cells at beginning and end of test are shown. There is a large drop in performance for all the membranes. To check if this was due to degradation of the polymers, they were analysed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy using a Bruker DR X400 spectrometer at 400.13 MHz and polymer solutions in DMSO-d_6 (δ=2.50 ppm). In-between the fuel cell tests and characterization, the MEAs were stored in 1 M KBr to avoid any degradation outside of the fuel cell. Prior to the characterization the gas diffusion electrodes were gently peeled off and the samples were thoroughly washed with deionized water during at least 48 h, replacing the water at least 5 times. The samples were then dried under vacuum at 50 °C during 24 h before dissolution in DMSO-d_6 and NMR analysis. The resulting NMR spectra, presented in Fig. S5, show no detectable changes in the polymer structure before (red) and after (black) fuel cell tests.

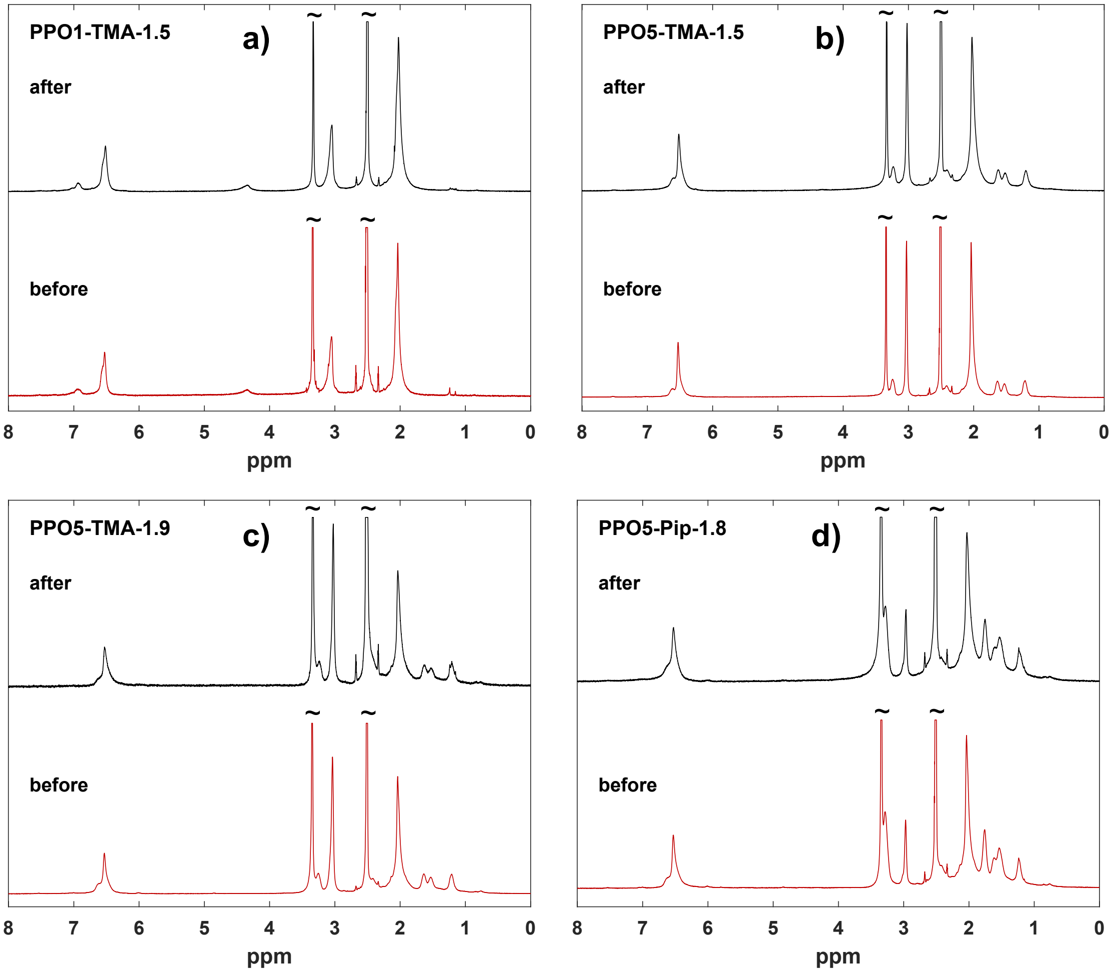

Figure S5. ^{1}H NMR spectra of a) PPO1-TMA-1.5, b) PPO5-TMA-1.5, c) PPO5-TMA-1.9 and d) PPO5-Pip-1.8 in DMSO-d_6 solutions. Before (red) and after (black) fuel cell tests at 50 °C and 90% RH for up to 20 h.

Additional impedance measurements

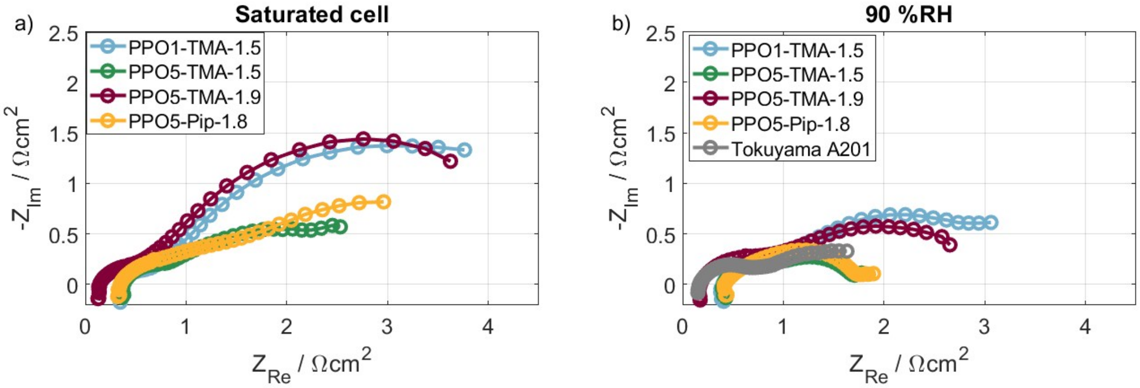

Figure S6 - EIS data at 200 mA and a) saturated or b) 90% RH, represented as Nyquist plots. Performed at 50 ℃ and O_2/H_2 *gas flows of 130* $ml_n min^{-1}$*, the amplitude used was 1 mA for all currents below 100 mA and 10 mA for the higher currents, the frequency was scanned from 100 KHz to 200 mHz, using 8 steps per decade.*

At 200 mA the potential and the slope of the polarization curve vary significantly depending on the membrane studied, so here the impedance, see Fig. S6 a) and b), for the studied cells corresponds to different regions in the I-V curves. This can explain why, under saturated conditions, the total impedance seems higher for the two best performing membranes PPO1-TMA-1.5 and PPO5-TMA-1.9. At 200 mA, they reach a slope change in the I-V curve. This change in slope is not seen as clearly when the humidity is decreased, resulting in the lower LFR for 90% RH compared to saturated conditions. The impedance for PPO5-TMA-1.5 and PPO5-Pip-1.8 at 200 mA instead describes a different region of the curve, where their polarization curve again changes to a lower slope at very low potentials, this improvement is described by the low LFR seen most clearly in the impedance at 90% RH. Further, for 200 mA the two semicircles seen at 16 mA become more difficult to distinguish.