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Electronic Supplementary Information

Crosslinked Poly(phenylene oxide)-Based Nanofiber Composite Membranes for Alkaline Fuel Cells

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1. Gravimetric and in-plane swelling of nanofiber composite membranes

To assess the dimensional stability of electrospun nanofiber composite membranes, the gravimetric and in-plane swelling of one membrane (2.0 mmol/g effective IEC, 50% PPSU reinforcement, and benzyl trimethylammonium functional groups in the hydroxide counterion form) were determined in degassed liquid water at 23°C and 80°C. Membrane swelling was calculated by equation S1 below,

$$\%Swelling = \frac{x_{wet} - x_{dry}}{x_{dry}} \qquad \text{(S1)}$$

where x is either the weight or geometric x-y (in-plane) area of the nanofiber composite membrane. Swelling results are listed in Table S1. As can be seen, the nanofiber composite membranes have very good dimensional stability, with a modest increase in x-y (areal) swelling from 34% to 41% when the water temperature was increased from 23°C to 80°C. Apparently, the hydrophobic PPSU reinforcing polymer apparently does not allow the high-IEC polyelectrolyte fibers to swell excessively, even at elevated temperatures.

Table S1. Gravimetric and in-plane (areal) swelling of a nanofiber composite membrane in liquid water. The membrane contained 50% PPSU reinforcement, the effective membrane IEC was 2.0 mmol/g, and the polyelectrolyte fibers contained benzyl trimethylammonium fixed charge groups.

Temperature (°C)	Gravimetric Swelling (%)	In-Plane Swelling (%)
23	92	34
80	114	41

2. Crosslinking Degree as a Function of Soak Time

When brominated PPO precursor fibers are crosslinked by diamine, the IEC of the final polyelectrolyte fibers decreases due to fewer bromomethyl groups being available for conversion to ion-exchange sites. As more crosslinks are added, the effective membrane IEC proportionally decreases. The crosslinking degree in the fibers is defined as the percentage of bromomethyl groups that react with a diamine end group of hexamethylenediamine. Experimentally, crosslinking degree can be determined from equation S2

$$Crosslinking\ Degree(\%) = \frac{IEC_u - IEC_c}{IEC_u} \times 100 \qquad \text{(S2)}$$

where IEC_u is the uncrosslinked fiber polyelectrolyte IEC (from NMR) and IEC_c is the crosslinked fiber polyelectrolyte IEC (from titration with a fully processes membrane). Figure S1 shows a plot of crosslinking degree as a function of soak time in a hexamethylenediamine solution. Crosslinking increases with soak time due to higher diamine crosslinker solution uptake into the fibers and more diamine/bromomethyl crosslink reactions.

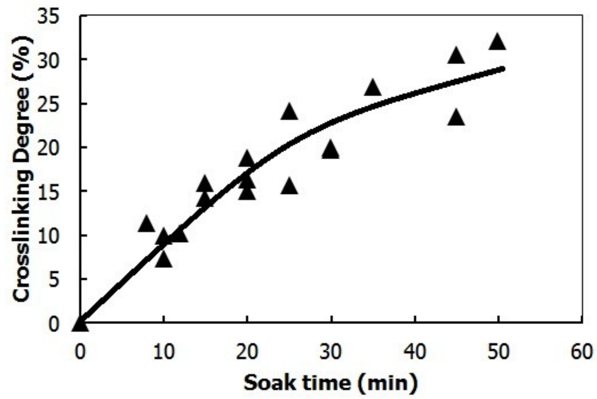

Figure S1. Crosslinking degree as a function of soak time in a 0.1 wt% hexamethylenediamine solution with a solvent of 7:3 dimethylacetamide:water.