Electrospun Tri-Layer Proton-Exchange Membranes for H_2/Air Fuel Cells

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Abstract
Dual nanofiber electrospinning was used to fabricate a series of tri-layer fuel cell membranes with high proton conductivity and low in-plane water swelling, using 825 EW perfluorosulfonic acid (PFSA) ionomer from 3M Company and poly(amide imide) (PAI) from Solvay S.A. The relative flow rates of the PFSA and PAI solutions, supplied from separate spinnerets (needles) during electrospinning, were adjusted to create three-layer mixed-fiber mats with different PFSA/PAI weight ratios. After electrospinning, the fiber mats were transformed into dense membranes by heating and compaction, where each layer consisted of a PFSA ionomer matrix with an embedded network of reinforcing PAI fibers. The surface layers of all membranes contained 95 wt.% PFSA and 5 wt.% PAI. The center layer, depleted in PFSA, contained either 75 wt.%, 60 wt.%, or 40 wt.% 825 EW PFSA, with a uniform or gradient PFSA/PAI composition. The thickness of the center layer (uniform or gradient composition) was adjusted so that the effective/average composition of the entire membrane was 80 wt.% PFSA and 20 wt.% PAI. Representative membrane composition/property data are listed in Table 1.

Table 1: Summary of Electrospun and Solution Cast Membrane Properties

	Membrane	Dry Thickness (μm)	In-Plane Conductivity in H_2O at 25°C (S/cm)	Sheet Resistance* (Ω-cm^2)	In-plane swelling in H_2O at 25°C (%)
1	825 EW PFSA Solution Cast Film	30	0.115	0.026	28
2	80 wt.% 825 EW PFSA Single Layer (homogeneous PFSA/PAI distribution throughout the entire film)	20	0.091	0.022	11
3	80 wt.% 825 EW PFSA Tri-Layer (uniform composition center layer)	20	0.087	0.023	6
4	80 wt.% 825 EW PFSA Tri-Layer (gradient composition center layer)	17	0.089	0.019	5
5	Nafion 211	25	0.091	0.027	16

* Sheet resistance is defined as the membrane thickness divided by in-plane conductivity.

As seen in Table 1 (row 2 vs. row 1), the use of single-layer dual fiber electrospinning allowed for the fabrication of a composite membrane with 80% of the neat ionomer's proton conductivity with only 40% of its in-plane swelling. With a tri-layer membrane structure (row 3) an additional reduction in swelling with a negligible loss in proton conductivity is possible. The best membrane had a tri-layer structure with a PFSA/PAI gradient morphology middle layer (row 4); this film had a sheet resistance that was 30% less than a commercial Nafion 211 membrane (row 5) with a 3-fold decrease in in-plane water swelling. Although the gradient membrane was thin (only 17 μm), it was very strong, with a stress at break of 20 MPa (versus 22 MPa for commercial Nafion).