

## Novel Electrospun and Crosslinked Fiber Composite Anion-Exchange Membranes

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### Introduction

The anion-exchange membrane fuel cell (AEMFC) continues to draw increasing attention in the electrochemistry community. AEMFCs are attractive because, unlike the more common proton-exchange membrane fuel cell, they do not require platinum as a catalyst for the rate-limiting oxygen reduction reaction. Still, AEMFC technology has been hampered by the lack of a suitable membrane with a high hydroxide ion conductivity, robust mechanical properties, and chemical stability in a high temperature alkaline environment. It is generally recognized that an AEM must possess a high ion-exchange capacity (IEC) to achieve an acceptable ion conductivity, but this leads to excessive water swelling and a weakening of the membrane's mechanical properties.

Park and Pintauro have shown that a dual-fiber electrospinning method can be used to fabricate high conductivity and mechanically durable AEMs<sup>1</sup>. Membrane conductivity, however, was limited by the IEC of the quaternary ammonium polysulfone (QAPSF) ionomer. QAPSF has a maximum theoretical IEC of 3.4 mmol/g, but it cannot surpass ~2.5 mmol/g without becoming water soluble. To create an anion-exchange membrane (AEM) with very high IEC ionomer fibers, we have electrospun fibers of the chloromethylated precursor of QAPSF (henceforth abbreviated as CMPSF). To render the fibers insoluble in water, a small number of chloromethyl groups were crosslinked. The subsequent conversion of unreacted groups to tetramethylammonium fixed charge sites created a high IEC and water insoluble composite membrane.

In this presentation, two different approaches for fabricating an electrospun crosslinked composite anion-exchange membrane will be discussed and compared. In both cases, a dual fiber electrospinning approach is utilized where polyphenylsulfone and chloromethylated polysulfone are simultaneously electrospun from separate needle spinnerets. In one scheme, crosslinking is carried out at high temperature with an aliphatic diol, while the other approach creates crosslinks at room temperature with an aliphatic diamine. The two crosslinking strategies produced a composite anion exchange membrane where fibers of crosslinked ionomer are surrounded by uncharged polyphenylsulfone.

### Experimental

Chloromethylated Udel® P-3500 LCD polysulfone (PSF, MW=83,000 g/mol) was used as the ionomer precursor while Radel® poly(phenyl sulfone) was used as the uncharged/inert polymer in a dual fiber electrospun mat (each polymer acquired from Solvay, LLC)

Before fabricating a mat with diol crosslinks, the CMPSF polymer was soaked in dimethylacetamide saturated with potassium iodide to convert some chloromethyl side chain groups to iodomethyl moieties. This step increased the side chain reactivity with hexanediol crosslinker (which was added to the electrospinning solution). Fiber mats were subsequently heated between glass plates at 100°C for 4 hr to crosslink the ionomer precursor fibers.

When crosslinking with diamine, a dual fiber mat of CMPSF and polyphenylsulfone was soaked in a 20% w/w solution of hexamethylenediamine (in DMAc/water) for 3-45 minutes to crosslink the CMPSF fibers (longer times generated more crosslinks).

After crosslinking with either diol or diamine, membranes were exposed to chloroform vapor at room temperature to soften the polyphenylsulfone and allow it to flow and fill the void space around the crosslinked CMPSF fibers. The resulting dense membranes were soaked in trimethylamine solution for 24 hours at 40°C to convert all remaining chloromethyl groups to quaternary ammonium ion-exchange sites. Films were then soaked in 1 M KOH to exchange hydroxide counter-ions for chloride ions. Finally, the films were washed with de-gassed DI water before testing.

### Results and Discussion

The IEC of the quaternized fibers without crosslinking was ~3.3 mmol/g, well above the water solubility threshold for uncrosslinked quaternary ammonium polysulfone. A series of crosslinked electrospun composite membranes were prepared using the diol and diamine crosslinking schemes, where the membranes contained 65 wt.% ionomer and 35 wt.% polyphenylsulfone. The ionomer IEC, in-plane conductivity and gravimetric water swelling of membranes crosslinked with hexanediol or hexamethylenediamine, along with an electrospun composite membrane with low IEC non-crosslinked tetramethylammonium-functionalized polysulfone are presented in Table 1.

**Table 1** – Properties of composite membranes in water at room temperature

Sample	Ionomer Fiber IEC (mmol/g)	In-plane Conductivity at 25°C (mS/cm)	Gravimetric Swelling (%)
1	2.47	40	93
2	2.80	52	108
3	3.11	65	144

Sample 1: Uncrosslinked ionomer/PPSU; 63 wt.% ionomer (from reference 1)

Sample 2: Diol-crosslinked ionomer/PPSU; 65 wt.% ionomer

Sample 3: Diamine-crosslinked ionomer/PPSU; 65 wt.% ionomer

For both crosslinked membrane samples, the hydroxide ion conductivity in water was significantly higher than that of the low IEC uncrosslinked composite membrane. As expected, membrane water swelling increased with increasing IEC of the ionomer fibers. For membrane sample 3, the hydroxide ion conductivity is near record high.

### References

1. Park, A. M.; Pintauro, P. N. *Electrochem. Solid State Lett.* **2012**, *15*, B27.

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