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Sandia National Laboratories

Polyelectrolyte Modification of Nanoporous Membranes for Selective Ion Transport in Electrodialysis

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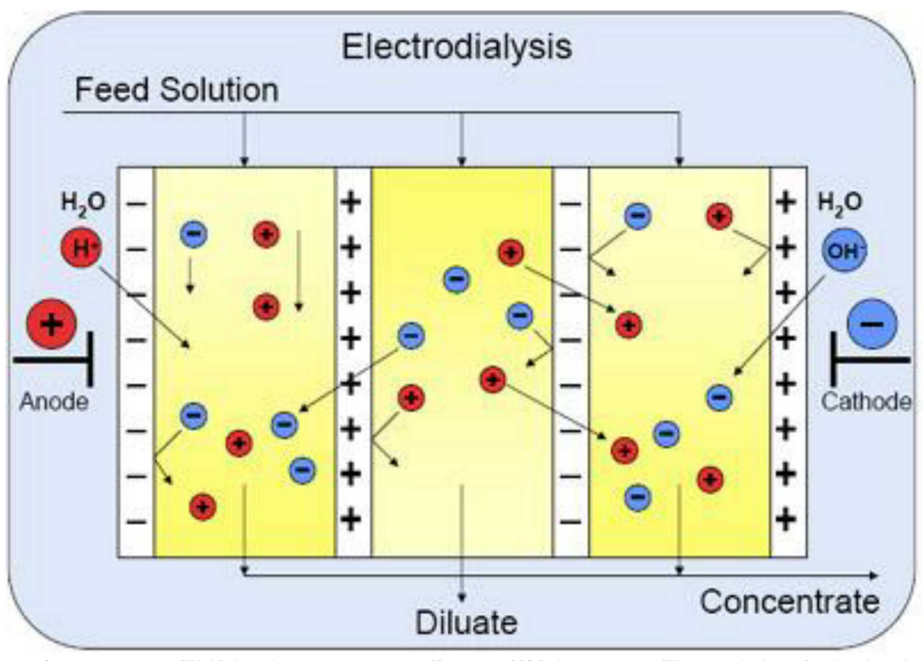
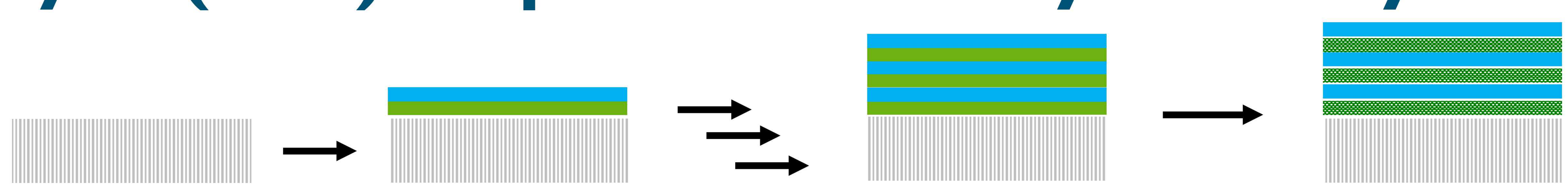
- ***Electrodialysis is an industrial-scale technique used to purify water where a DC electric field drives dissolved ions across ion-selective membranes to create a purified water stream.***
- ***Key factors include: ionic conductivity, ionic selectivity and materials cost of the ion-selective membranes.***
- ***Layer-by-Layer (LbL) deposition of polyelectrolytes onto nanoporous polymer supports creates thin, ionically conductive and ionically selective membranes and is demonstrated as an inexpensive, scalable method that can be used to bring associated electrodialysis costs down.***
- ***Addition of small functional molecule amino acids to the dip coat solutions is shown to increase ionic selectivity while maintaining low Area Specific Resistance (ASR).***



www.fumatech.com/EN/Membrane-processes/Process%2Bdescription/Electrodialysis/index.html

Layer-by-Layer (LbL) Deposition of Polyelectrolytes

Ion-tracked polycarbonate (PC) membrane with 50 nm pores



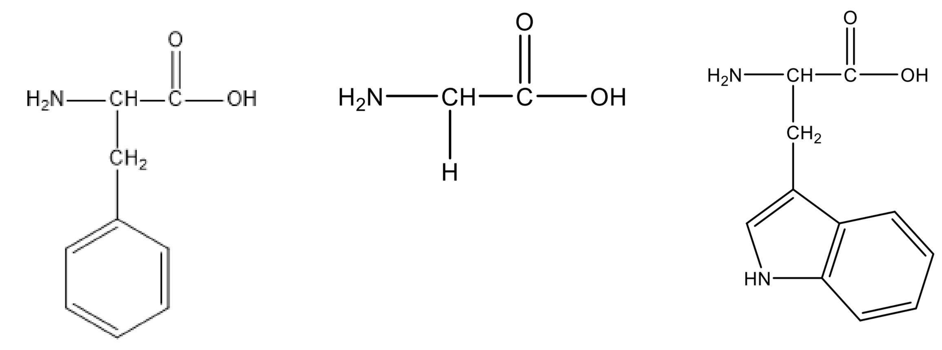
Poly(Acrylic Acid) (PAA)
Polyethyleneimine (PEI)

Dip coat PEI then PAA *1 bilayer (BL)*

Additional LbL Assembly

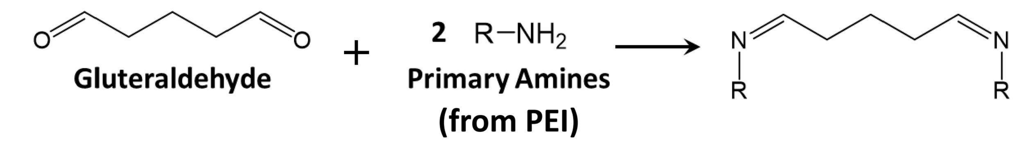
Crosslink films with Glutaraldehyde (GA)

Small Molecule Additives



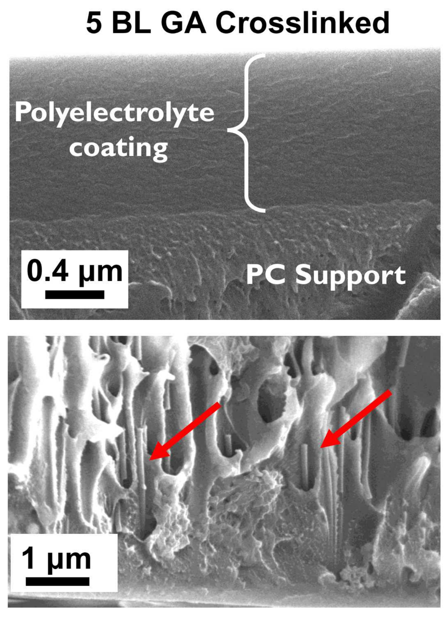
Phenylalanine | Glycine | Tryptophan

Glutaraldehyde (GA) Crosslinking

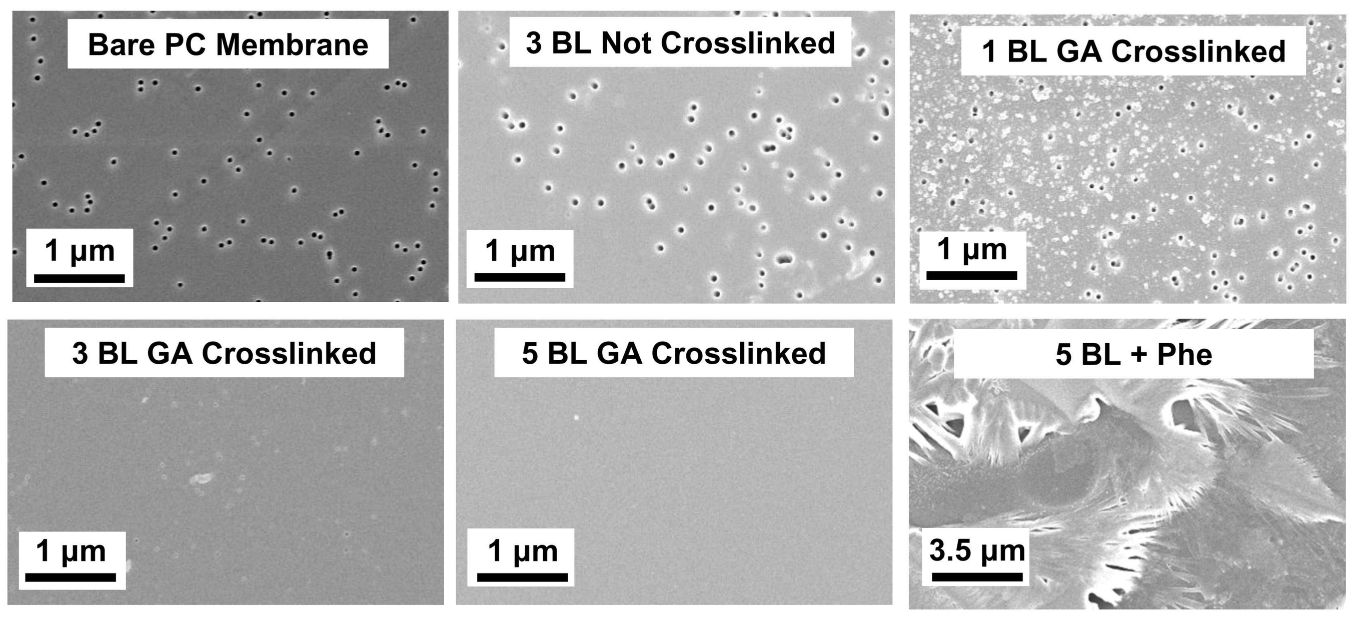


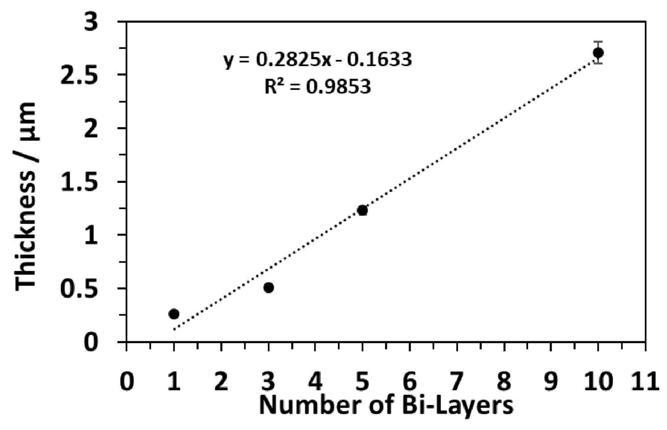
Surface Morphology and Cross Sections

5 BL GA Crosslinked



SEM micrographs reveal poor coverage on films either not crosslinked or 1 BL thick. Uniform film morphology on crosslinked 3 and 5 BLs.



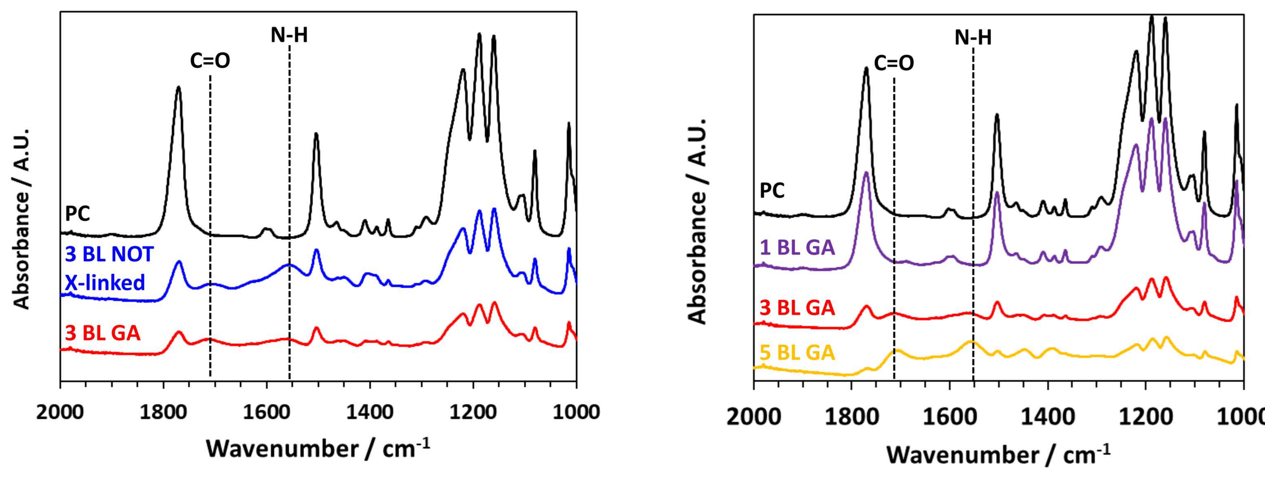


Cross sectional SEM images used to measure polyelectrolyte thicknesses. Thickness increases with number of applied bilayers.

Polyelectrolyte pore filling observed inside nanopores.

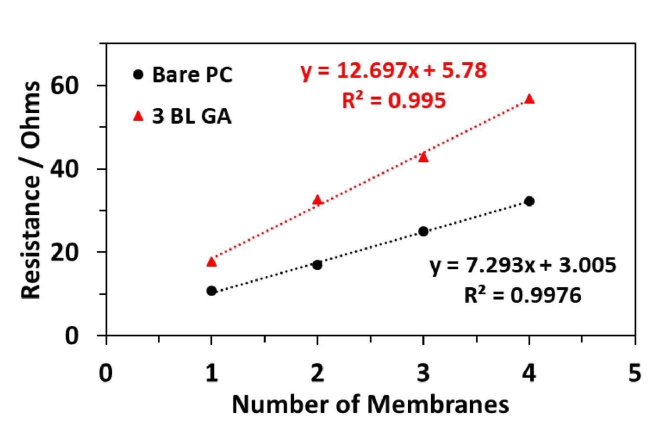
Interesting "dendritic" features observed on PE+Phe samples.

Infrared Spectroscopy

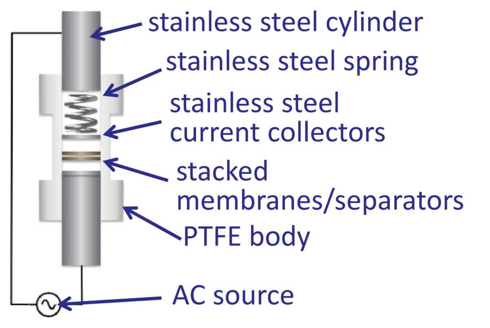


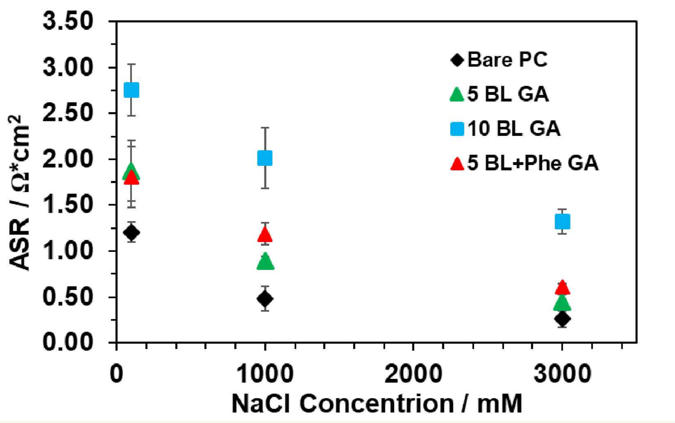
Presence of PEI and PAA confirmed by C=O stretch in PAA at 1700 cm^{-1} and N-H bend of PEI at 1560 cm^{-1}. As expected, GA decreases N-H intensity vs. not crosslinked. PC peaks near 1760 and 1200 cm^{-1} suppressed with additional BLs.

Membrane Ionic Resistance



1-4 membranes were stacked in a Swagelok style cell and resistance measured in different ionic strength NaCl solutions.





Polyelectrolyte increased Area Specific Resistance (ASR) compared to bare PC.

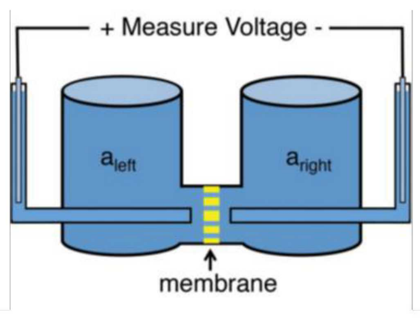
Thicker polyelectrolyte further increases the ASR.

ASR shows little change with amino acid additives.

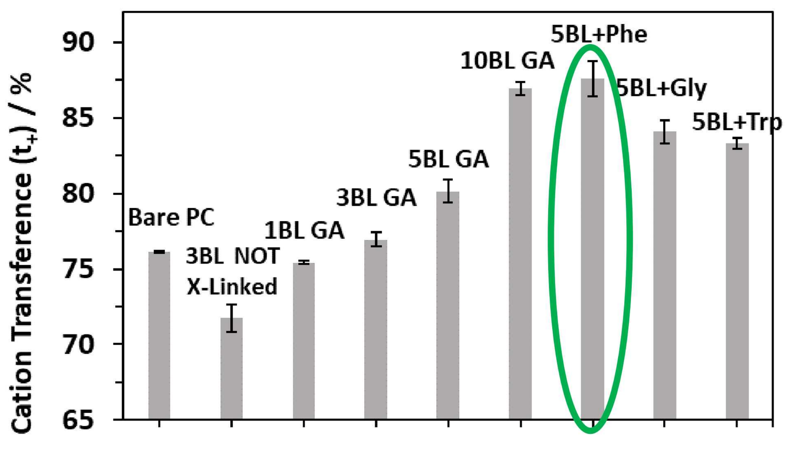
ASR for polyelectrolyte modified films are on par or lower than commercial ion exchange membranes (~1-2 Ω*cm² in 1 M NaCl).

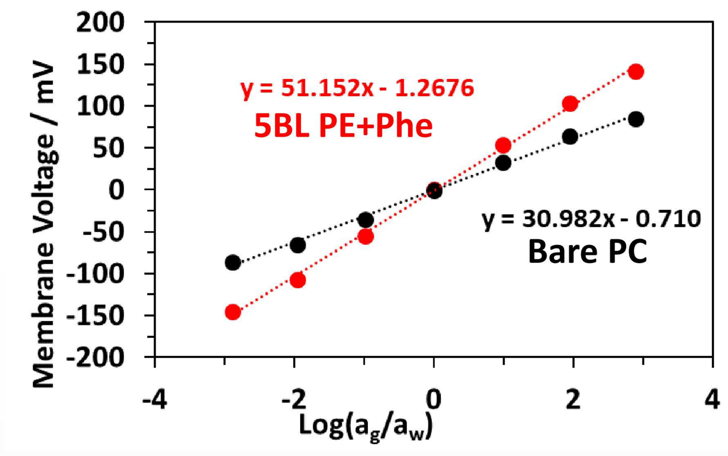
Ionic Selectivity

Cation transport number (t_+) calculated by measuring the potential difference when the membrane separates different NaCl concentrations. Higher slope indicates higher cation selectivity.



$$V_m = 0.059 \cdot (t_+ - t_-) \cdot \log \frac{a_{right}}{a_{left}}$$





Increasing number of BL results in increasingly cation-selective transport.

Addition of amino acid additives significantly increases the selectivity without increasing thickness.

Continued improvements of polyelectrolytes offer a simple, inexpensive method for tailored ionic transport in electrodialysis membranes.

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