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Polyelectrolytes for Selective Ion Transport in Nanoporous Electrodialysis Membranes

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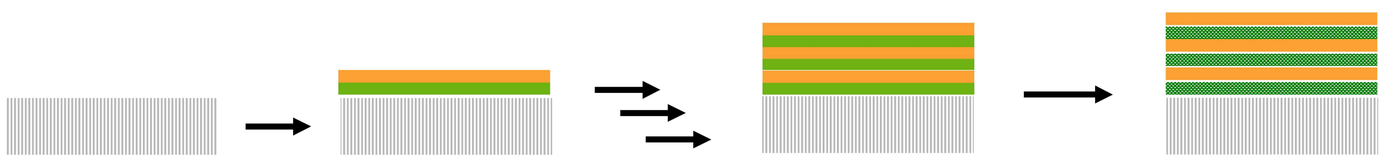
Electrodialysis is an industrial-scale technique used to purify water. Here the application of a DC electric field drives dissolved ions across ion-selective membranes to decrease the salt concentration and create a purified water stream. Due to the costs for operating such a facility, only a fraction of water purification plants are based on electrodialysis techniques, with the majority employing reverse osmosis. Key factors influencing the cost of electrodialysis include the ionic conductivity and materials cost of the ion-selective membranes. Here we leverage layer by layer (LbL) deposition of polyelectrolytes of poly(ethyleneimine) and poly(acrylic acid) onto nanoporous polymer supports to create thin, ionically conductive and ionically selective membranes for inexpensive water purification.

Layer by Layer (LbL) Deposition of Polyelectrolytes

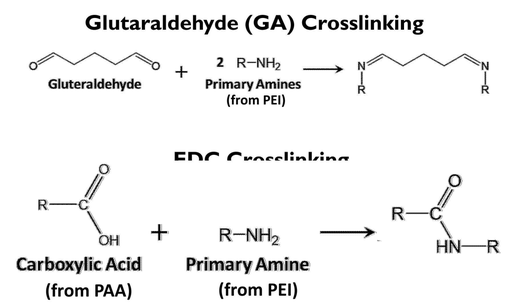
Poly(Acrylic Acid) (PAA)
Polyethyleneimine (PEI)
Ion-tracked polycarbonate (PC) membrane with 50 nm pores.



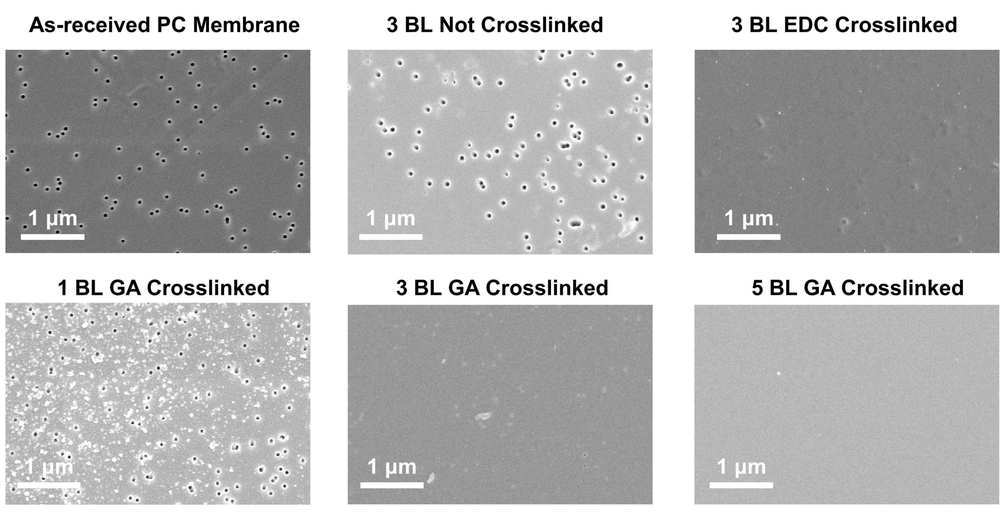
Dip coat PEI then PAA
1 bilayer (BL)

Additional LbL Assembly

Crosslink films with EDC or GA

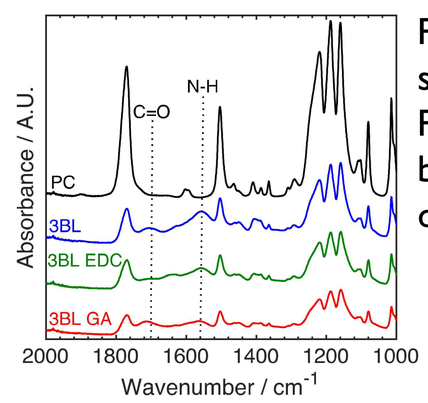


Surface Morphology



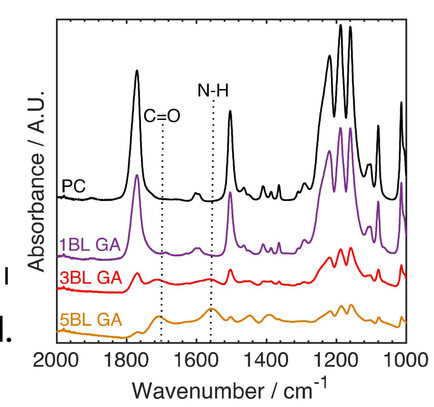
SEM micrographs reveal poor coverage on films either not crosslinked or 1 BL thick.

Infrared Spectroscopy

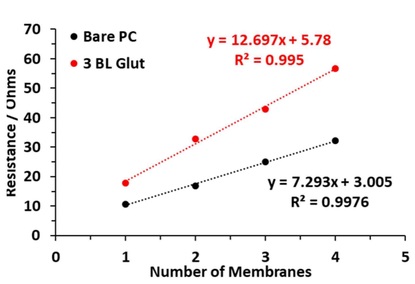


Presence of PEI and PAA confirmed by C=O stretch in PAA at 1700 cm^{-1} and N-H bend of PEI at 1560 cm^{-1}. As expected, EDC decreases both C=O and N-H intensity, while GA decreases N-H intensity vs. not crosslinked

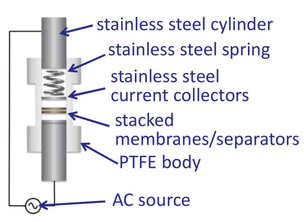
PC peaks near 1760 and 1200 cm^{-1} suppressed as more BLs added.

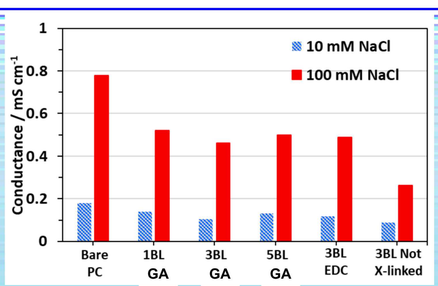


Ionic Conductivity



1-4 membranes were stacked in a Swagelok style cell and conductivity measured in 10 and 100 mM NaCl (aq).

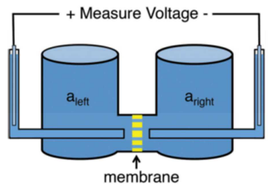




Adding polyelectrolyte decreases conductivity, though crosslinking with GA or EDC mitigates much of this initial loss. Conductances for 10 µm thick films are on par with commercial ion exchange membranes (>1 $S \cdot cm^{-2}$).

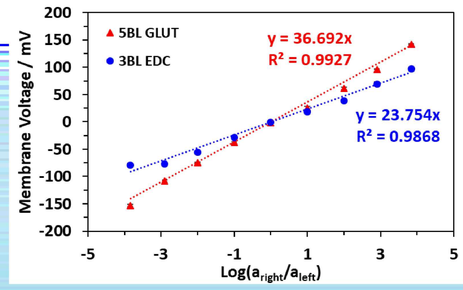
Ionic Selectivity

Calculate the cation transport number (t_+) by measuring the potential difference when the membrane separates different NaCl concentrations.



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

	Slope / mV	t_+ / %
Bare PC	28.93	74.5
1BL GA	27.39	73.2
3BL GA	30.06	75.5
5BL GA	36.69	81.1
3BL EDC	23.75	70.1
3BL Not X-linked	24.16	70.4



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

Polyelectrolytes offer a simple, inexpensive method with which to tailor ionic transport in electrodialysis membranes.

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