Electronic Supplementary Material (ESI) for Energy & Environmental Science.


**Experimental**

**Fabrication of multilayer nanomembrane.** Multilayers were built on an inverted copper substrate with a surface area of 2cm$^2$ using a Nanostrata robot. The substrate was spun and immersed in a dilute polymer solution of a positively charged polyelectrolyte such as PAH, PDAD or PPy for 5 minutes. Three 30 second rinses followed after which the substrate was dried with nitrogen for 30 seconds. Next the substrate is immersed (for 5 minutes) into a dilute solution of a negatively charged polyelectrolyte such as PEDOT:PSS or Nafion. Three 30 second rinses were followed by 30 second nitrogen drying time segments. All polymer solutions contain 0.1M $LiNO_3$ and are below 10mM in polymer concentration. Rinse solutions also contain 0.1M $LiNO_3$. The PEDOT:PSS polymer solution was prepared by diluting 0.1ml of 1% stock PEDOT:PSS solution to 100 ml. The PPy solution preparation consisted of two steps. First, 0.1ml of the 5% stock solution from Sigma was diluted to 100 ml and maintained at a pH of 1.7. Second, 6 ml of this solution was diluted to 100 ml and maintained at a pH of 1.7. In the case of the PPy containing nanomembrane, the oppositely charged polymer solution and all the rinses were also maintained at pH=1.7. All polymers and salts were purchased from Sigma Aldrich. After assembly, the nanomembrane coated substrate was inserted in a pH=10 solution (prepared with sodium hydroxide) for 5 hours, rinsed well then dried under vacuum in an oven at a temperature of 70 ˚C for 2 hours. The thickness of the PAH containing nanomembranes change from ~60 nm after fabrication to ~90nm after exposure to pH 10. A layer by layer buildup performed by hand, where the thickness of the nanomembrane on a polished silicon wafer substrate is measured after each layer with a Gaertner ellipsometer is plotted in figure S1.

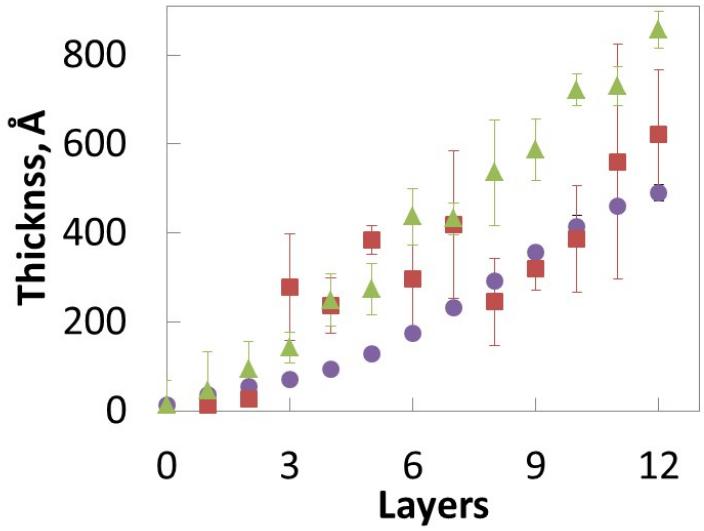


Figure S1. Layer by layer adsorption of multilayer nanomembranes composed of PPy/PEDOT:PSS (purple circles), PDAD/PEDOT:PSS (garnet squares) and PDAD/Nafion (green triangles). All multilayers were built on polished silicon wafers from dilute polymer solutions as described above. The thickness of each (nitrogen gas) dried layer was measured with a Gaertner ellipsometer.

**Electrochemical testing.** The dry, nanomembrane coated copper electrode was inserted into an EL-Cell as the working/reference electrode. One Celgard separator was placed on top of the copper electrode, followed by 150 µl electrolyte. The electrolyte consisted of a 1M LiTFSI solution in a 50:50 DOL:DME solvent also containing 0.2M $LiNO_3$ and 50mM $CsNO_3$. A pretreated lithium metal foil was placed on top of the wet separator. Pretreatment consisted of exposure of the lithium metal to a concentrated solution of lithium polysulfides for 2 hours. After pretreatment, the lithium metal foil was rinsed with THF, dried and inserted in the test cell containing the nanomembrane coated copper electrode. Galvanostatic lithium deposition/dissolution was precluded by 10 cyclic voltammograms between 0.1V and 2.0V vs. Li designed to form a stable SEI on the nanomembrane. 0.5 mAh lithium per $cm^2$ was then deposited. Dissolution was carried out to 2V vs. lithium. All electrochemical measurements were performed using a Bio-Logic VMP3 tester.

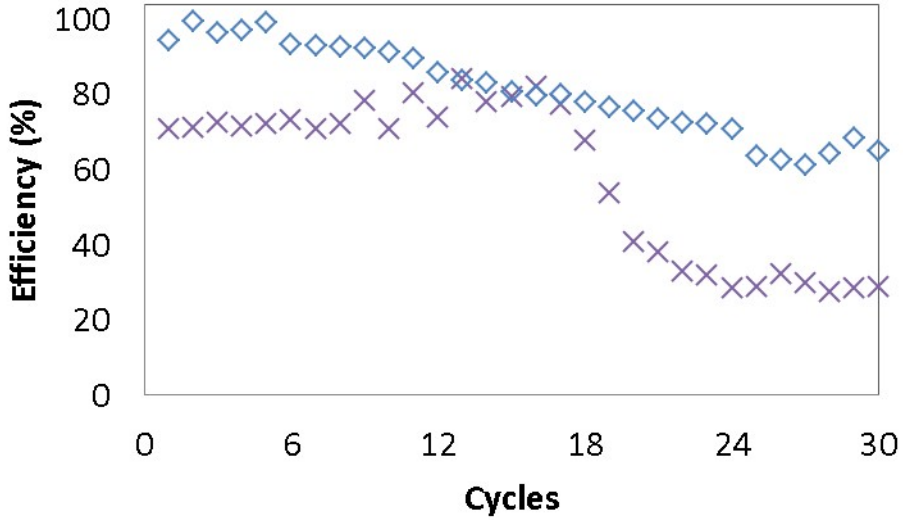


Figure S2. Comparison of cycling performances of untreated copper current collector (diamond, ◊) to copper current collectors coated by nanomembranes composed of $(PEDOT:PSS/PDAD)_{14}$ (square, X).

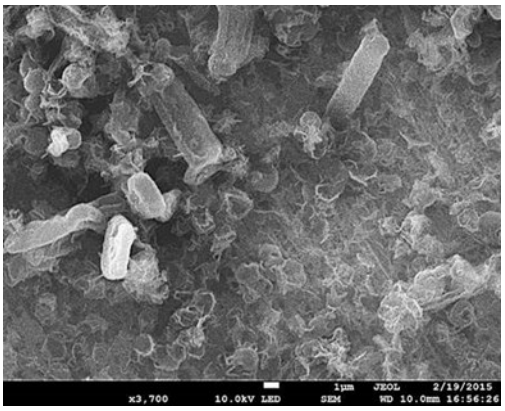

Figure S3. SEM image of lithium deposits on untreated copper current collector. Dendrites are visible.