# Supporting Information

# Ion Diffusion Coefficients Through Polyelectrolyte Multilayers: Temperature and Charge Dependence

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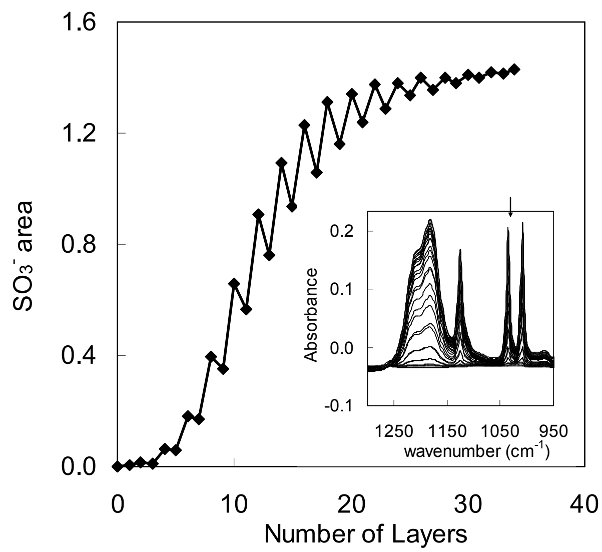


**Figure S1.** Sulfonate peak area at 1035 $cm^{-1}$ *vs.* number of layers of the buildup of $(PDADMA/PSS)_{17}$ at 1 M NaCl on the ATR germanium crystal with 1 M NaCl background. The inset is the spectrum of the sulfonate peaks during the layer by layer buildup.

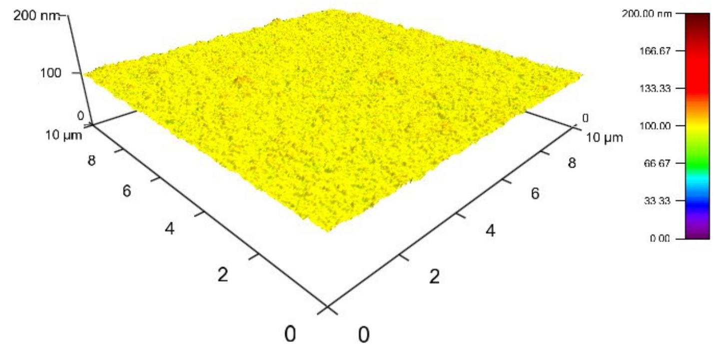


**Figure S2.** AFM image (10 x 10 µm) of a $(PDADMA/PSS)_{10}$ multilayer built at 1.0 M NaCl. The film was annealed in 1.0 M NaCl for 20 hours prior to imaging. The image clearly shows the uniformity of the surface. The roughness was measured to be less than 5 nm.

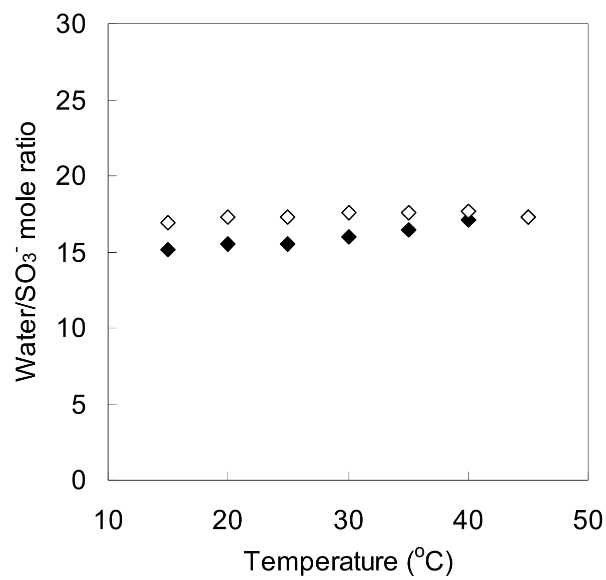


**Figure S3.** Water/$SO_3^-$ mole ratio for a $(PDADMA/PSS)_{17}$ PEMU coated on a germanium crystal at 1 M NaCl. The peak areas were taken from Figure 1 in the main article and calibrated with a standard solution of 0.2 M PSS (passed over a dry Ge crystal at different temperatures with air background).

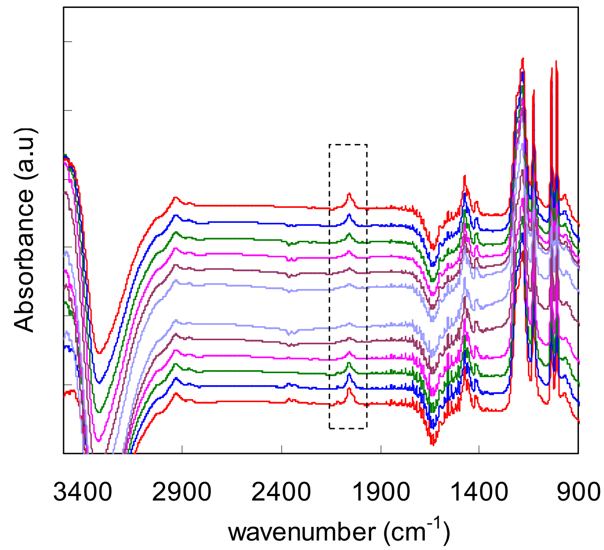


**Figure S4.** ATR-FTIR Spectra of the doping of $(PDADMA/PSS)_{17}$ built in at 1 M NaCl coated on a Ge ATR. Electrolyte was 2mM ferricyanide in 0.6 M NaCl; ferricyanide solution was allowed to equilibrate for 5 minutes. PEMU was rinsed with 1.0 M NaCl between each temperature stop to remove the ferricyanide from the film. The dashed box marks the ferricyanide peaks at each temperature. 1.0 M NaCl was taken as a background. The lower set of curves corresponds to the spectra collected while increasing temperature from 15 to 40 $^{o}$C with 5 $^{o}$C intervals, and the upper set of curves corresponds to the ones with decreasing temperature from 40 to 15 $^{o}$C.

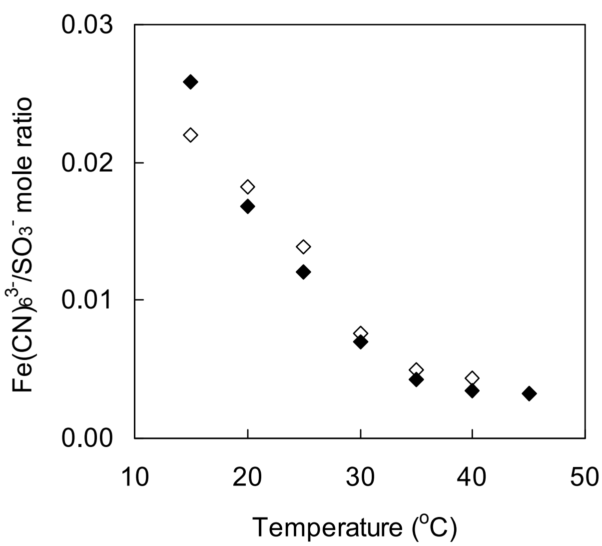


**Figure S5.** Ferricyanide/$SO_3^-$ mole ratio at different temperature from the spectra in Figure S3. Electrolyte was 2 mM ferricyanide in 0.6 M NaCl injected on a coated Germanium crystal with $(PDADMA/PSS)_{17}$ (calibrated using a mixture of 0.2 M PSS and 0.02 M ferricyanide standards on a bare crystal).

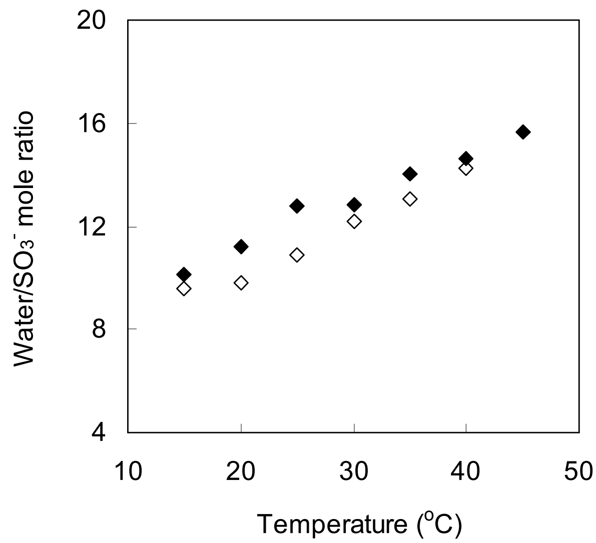


**Figure S6.** Water/$SO_3^-$ mole ratio at different temperatures when 2 mM ferricyanide in 0.6 M NaCl is injected on a coated Ge crystal with $(PDADMA/PSS)_{17}$. The corresponding spectra were taken with dry Ge crystal background.

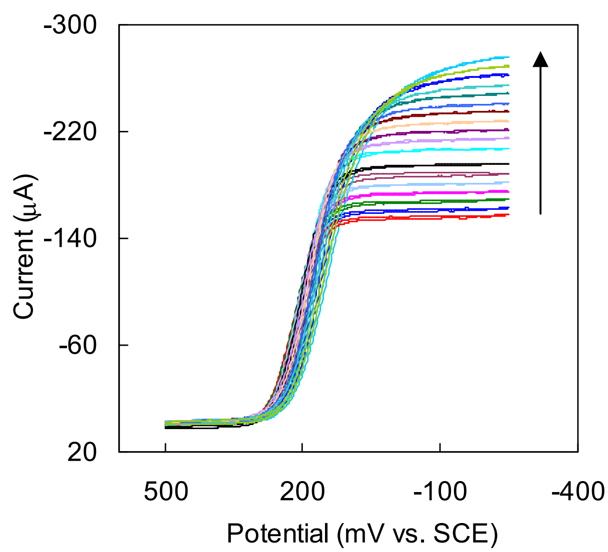


**Figure S7.** Linear scan voltammograms on a bare rotating disk electrode for 2 mM ferricyanide in 0.6 M NaCl at different temperatures (direction of the arrow from 14 to 50 $^{o}C$ with 2 $^{o}C$ intervals), 20 mV/s sweep rate, rotation rate 1000 rpm. Electrode area 0.1963 $cm^2$.

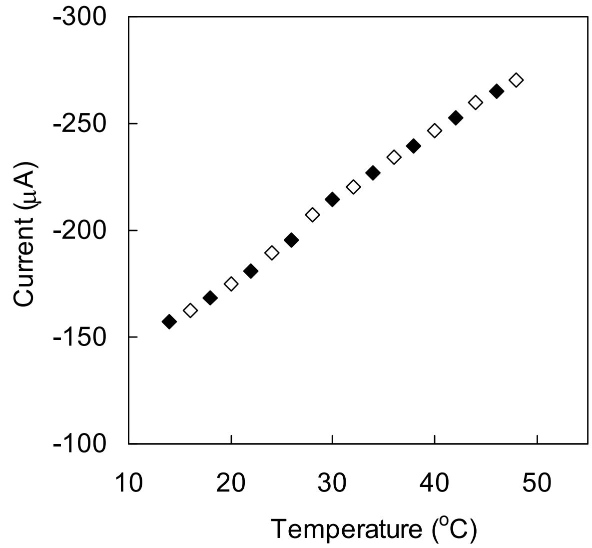


**Figure S8.** Limiting current *vs.* temperature on the bare rotating disk electrode from the CVs in Figure S7.

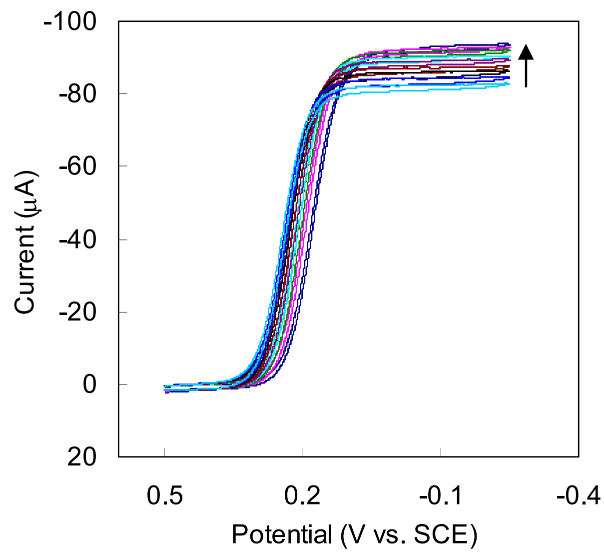


**Figure S9.** Linear scan voltammograms on a bare rotating disk electrode of 1 mM ferricyanide at different salt concentrations (direction of the arrow from 0.2 to 2.0 M NaCl), 20 mV/s sweep rate, and 1000 RPM rotation rate. Electrode area 0.1963 $cm^2$

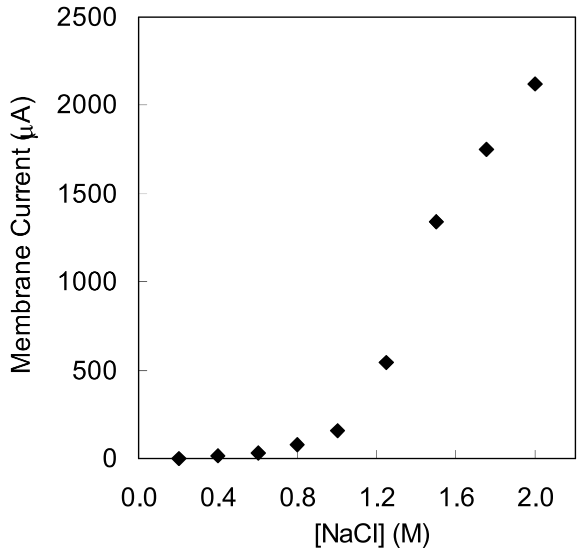


**Figure S10.** Membrane current *vs*. salt concentration for 1 mM ferricyanide at a rotating disk electrode. The electrode was coated with 20 layers PDADMA/PSS in 1 M NaCl, then annealed in 1.0 M NaCl for 18 hours; 20 mV/s sweep rate, rotation rate 1000 rpm. Electrode area 0.1963 $cm^2$

**Table S1.** Measured half-wave potentials, $E_{1/2}$ and formal potentials, $E^{o'}$ *vs*. NaCl concentration on a bare rotating disk electrode. $E_{1/2}$ was measured for 1 mM ferricyanide, and $E^{o'}$ for an equimolar mixture of ferri and ferrocyanide 1 mM each. Potentials were measured against a KCl-saturated calomel reference electrode. Rotation rate 1000 rpm, 20 mV/s sweep rate, electrode area 0.1963 $cm^2$

| [NaCl] (M) | $E_{1/2}$ (mV) | $E^{o'}$ (mV) |
|---|---|---|
| 0.20 | 181 | 182 |
| 0.40 | 195 | 195 |
| 0.60 | 206 | 203 |
| 0.80 | 214 | 210 |
| 1.00 | 220 | 217 |
| 1.25 | 226 | 223 |
| 1.50 | 234 | 230 |
| 1.75 | 239 | 235 |
| 2.00 | 244 | 240 |