SUPPORTING INFORMATION

Water and Ion Transport through the Glass Transition in Polyelectrolyte Complexes

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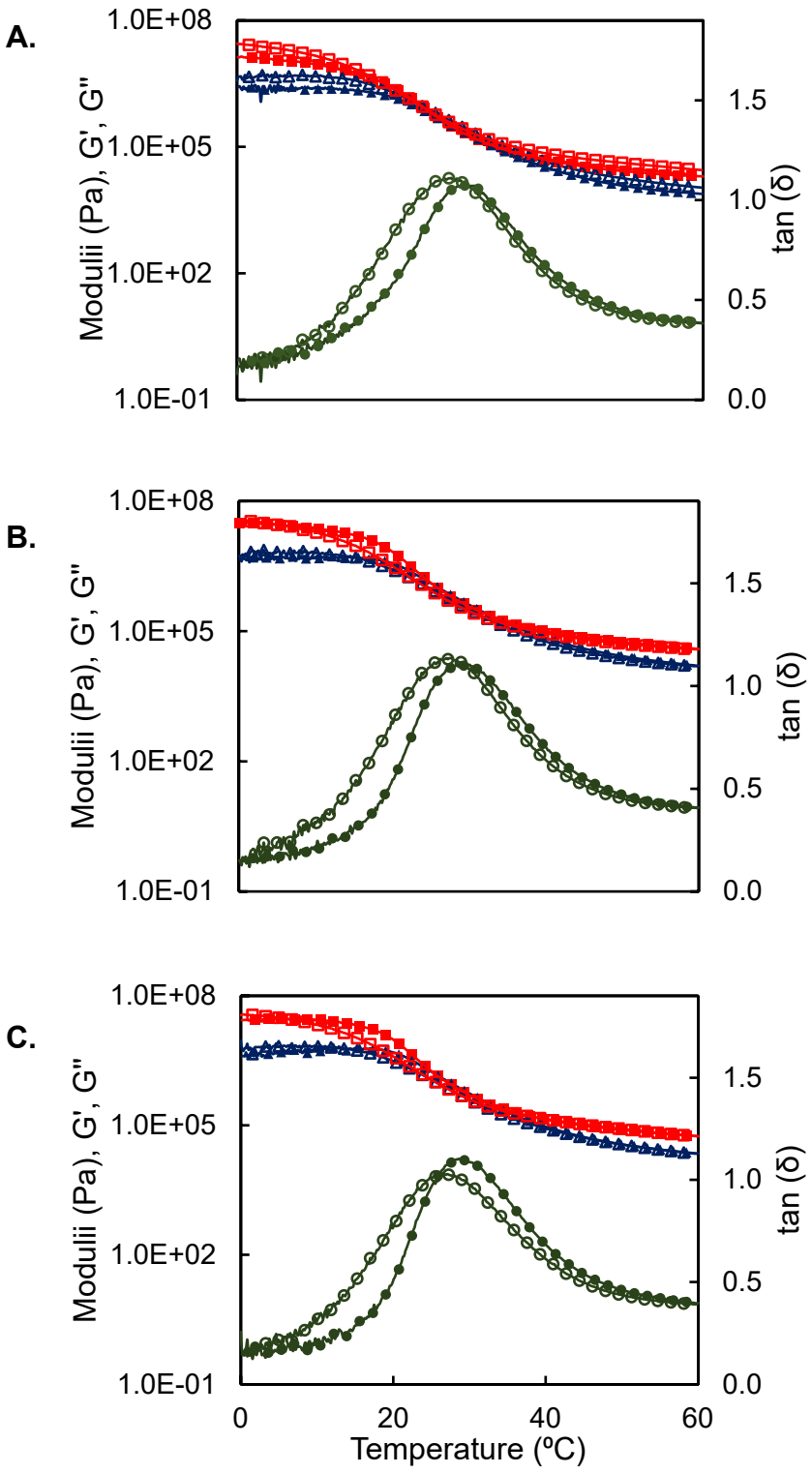

Figure S1. Storage modulus G′ (squares), loss modulus G″ (triangles), and tan δ (circles) at 0.1 Hz, measured at increasing (filled symbols) and decreasing (open symbols) temperature for PDADMA/PSS PEC soaked in **A)** 0.3 M NaCl **B)** 1 mM ferricyanide in 0.3 M NaCl **C)** 0.3 M NaCl.

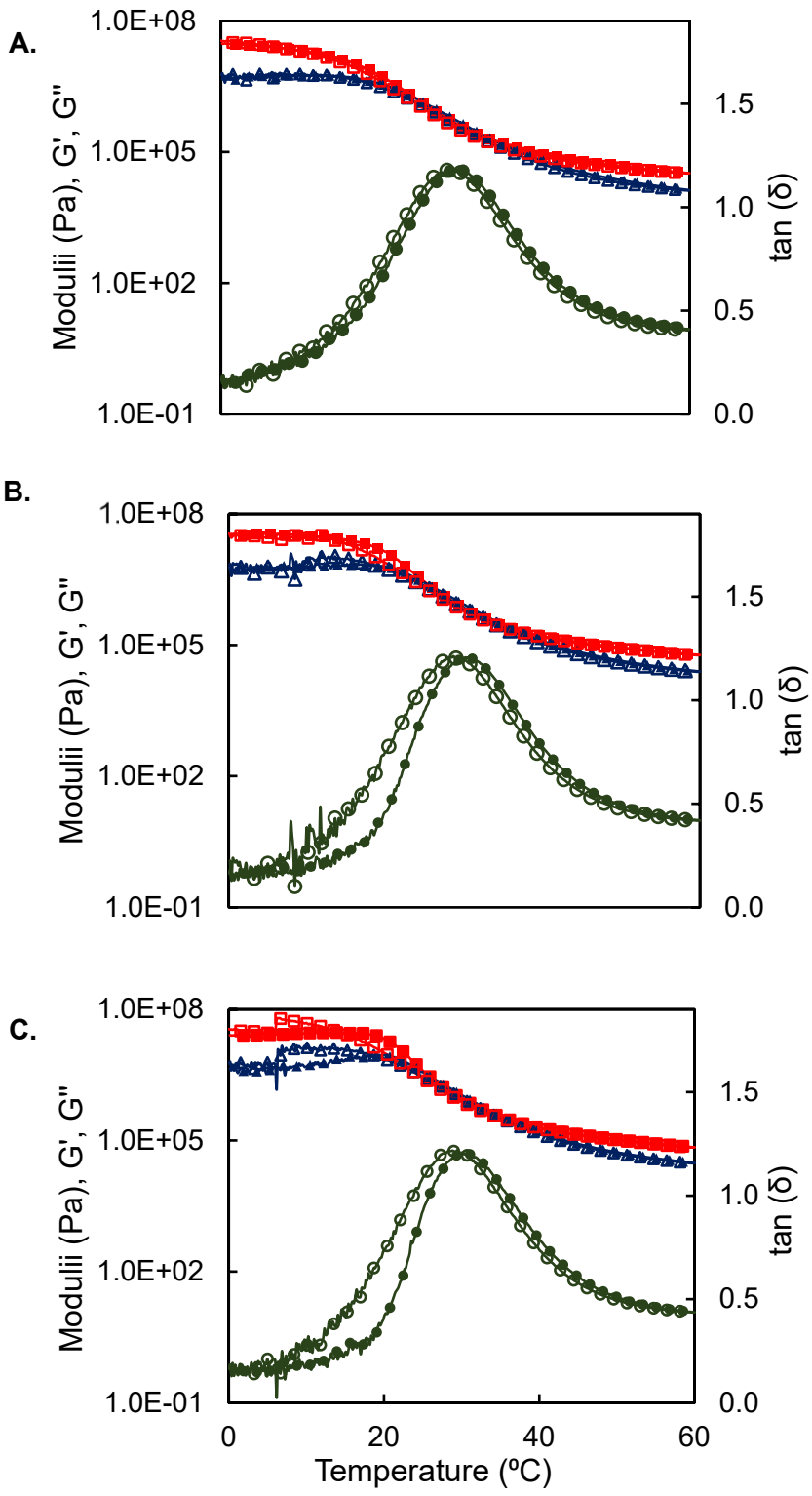

Figure S2. Storage modulus G′ (squares), loss modulus G″ (triangles), and tan δ (circles) at 0.1 Hz, measured at increasing (filled symbols) and decreasing (open symbols) temperature for PDADMA/PSS PEC soaked in **A)** 0.3 M NaCl **B)** 1 mM ruthenium hexamine in 0.3 M NaCl **C)** 0.3 M NaCl.

Table S1. The effect of 1 mM probe ion concentration on the glass transition of PEC in 0.3 M NaCl. Before addition of probe to 0.3 M NaCl, with the probe present, and in 0.3 M NaCl only after the experiments

Probe Ion	**T_g ± 0.5 °C**		
	Before	*With*	*After*
Ferricyanide	28.4	27.9	27.6
Ruthenium Hexamine	29.7	29.2	29.7

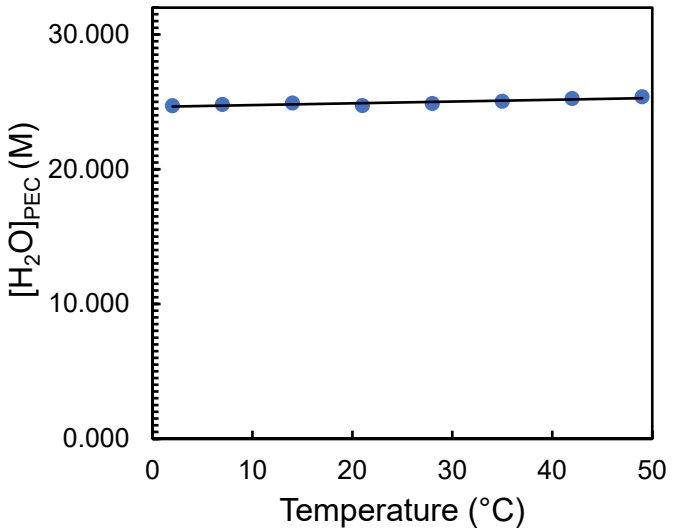

Figure S3. Concentration (mol L^{-1}) of H_2O inside PDADMA/PSS PEC doped in 0.5 M NaCl vs temperature.

^{1}H NMR

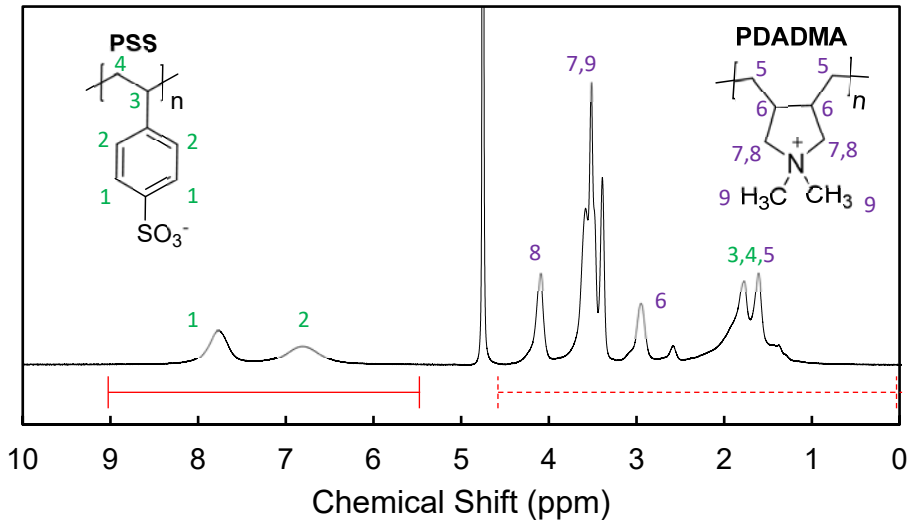

Figure S4. Solution ^{1}H NMR of 100 mg mL^{-1} PEC dissolved in 2.5 M KBr in D_2O recorded on a Bruker Avance III 600 MHz NMR spectrometer with 512 scans at room temperature. The solid bar represents the integration between 5.5 and 9 ppm for the aromatic hydrogens, and dashed bar represents the integration between 0 and 4.6 ppm for the aliphatic hydrogens. The stoichiometry of PSS:PDADMA was found to be 1.028 using Equation S1.

$$\frac{PSS}{PDADMA} = \frac{4A_{aromatic}}{A_{aliphatic} - \frac{3}{4}A_{aromatic}} = \frac{4 \times 1.00}{4.64 - \frac{3}{4} \times 1.00} = 1.028 \qquad [S1]$$

where $A_{aromatic}$ and $A_{aliphatic}$ are the respective NMR areas for aromatic and aliphatic protons.

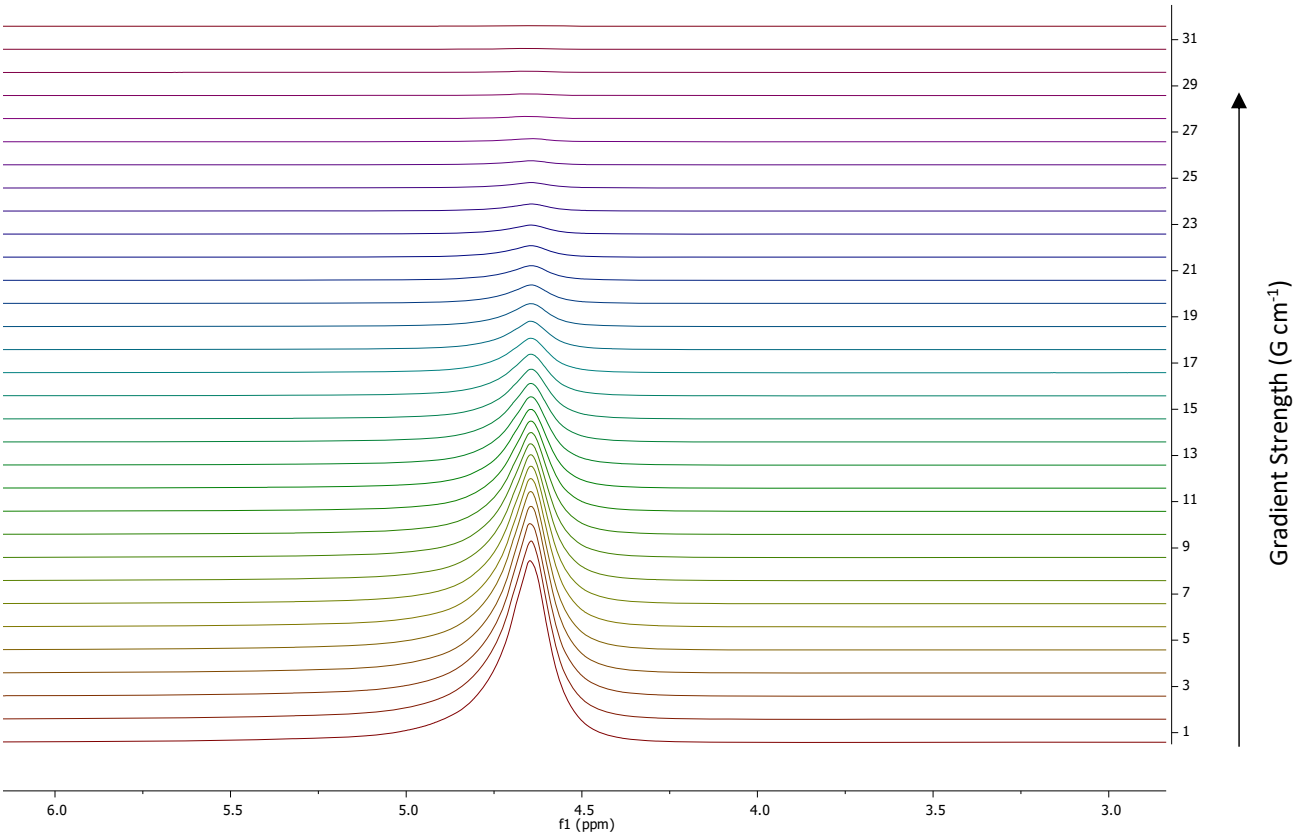

Figure S5. A stacked plot of ^{1}H NMR of water inside PDADMA/PSS PEC in 0.3 M NaCl. Peak area with increasing gradient strength recorded on a 700 MHz Bruker Avance III NMR spectrometer at 30 °C.

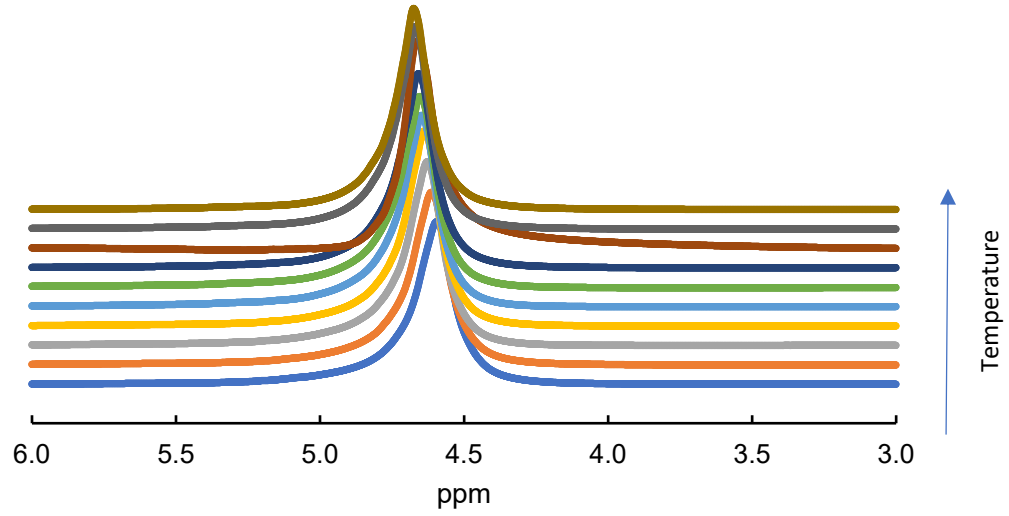

Figure S6. A stacked plot of ^{1}H NMR of water inside PDADMA/PSS PEC in 0.3 M NaCl at varying temperatures. Temperatures from 10 to 55 °C (bottom to top) with 5 °C intervals.

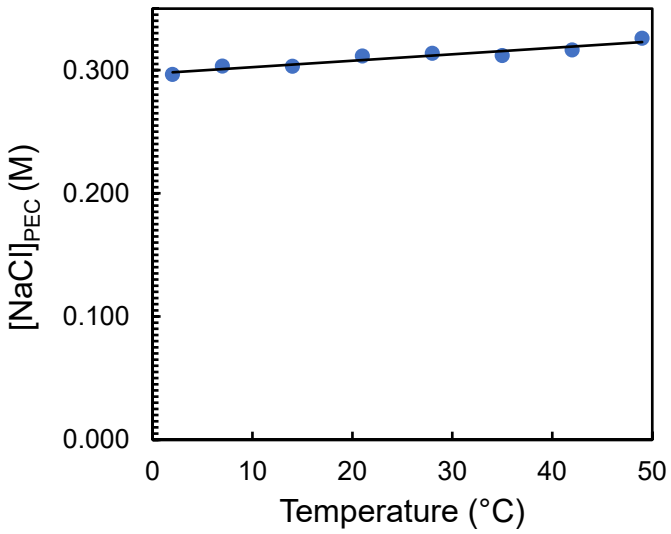

Figure S7. Concentration of NaCl (mol L^{-1}) in a PDADMA/PSS PEC doped in 0.5 M NaCl vs temperature.

Estimate of the Size of a Rearranging Ion-Compensated Region

The hopping of a single-charged ion A^- from one site Pol_a^+ to another Pol_b^+ can be represented by an exchange as follows:

$$Pol_a^+A^- + Pol_b^+Pol^- \rightarrow Pol_a^+Pol^- + Pol_b^+A^-$$

The size of a Pol^+Pol^- pair, hydrated by 10 molecules of H_2O, is estimated by

$$Pol^+Pol^- \cdot 10H_2O\ per\ cm^3 = \frac{density\ PEC}{molar\ mass\ Pol^+Pol^- \cdot 10H_2O} N_A$$

Where N_A is Avogadro's number. Assuming the density of the hydrated PEC is 1.1 g cm^{-3},

$$Pol^+Pol^- \cdot 10H_2O\ per\ cm^3 = 1.35 \times\ 10^{21}$$

Which means the volume of each pair is about 0.74 nm^3. Since there are 1.5 pairs involved in the hopping, the rearranging volume is about 1.1 nm^3

Similarly, with a triple-charged ion such as ferricyanide

$$3Pol_a^+Fe(CN)_6^{3-} + 3Pol^-Pol_b^+ \rightarrow 3Pol_b^+Fe(CN)_6^{3-} + 3Pol^-Pol_a^+$$

there are 4.5 pairs involved for a volume of about 3.4 nm^3

Cyclic Voltammetry Details

All solutions were purged for 10 min with Ar and then blanketed with Ar to exclude O_2. Cyclic voltammograms (CVs) of ferricyanide solutions in 0.3 M NaCl were performed by sweeping the potential at a scan rate of 10 mV s^{-1} in the range +300 to -250 mV vs. SCE at 1000 rpm, whereas CVs of ruthenium hexamine solutions in 0.3 M NaCl were performed by sweeping the potential at 10 mV s^{-1} in the range of +100 to -450 mV vs SCE while the working electrode was rotated at 1000 rpm. Background CVs were recorded under the same conditions in 0.3 M NaCl only. The temperature was cycled up and down (from 1 to 50 °C) to thermally anneal the multilayer and then ramped up from 10 to 66 °C at 4 °C intervals for ferricyanide solutions and from 1 to 50 °C at 5 °C intervals for ruthenium hexamine solutions. The scans were reproducible, and the results shown in the Figures correspond to the second heating scan.

To establish a fully stoichiometric PEMU, excess PDADMA trapped within the multilayer must be eliminated from the film post assembly. This was done by soaking the nonstoichiometric film in concentrated NaCl to plasticize the PEMU to ensure intermixing of polyelectrolytes, rearranging and homogenizing the film and then immersing in PSS solution to compensate the excess PDADMA.[1] This cycle was repeated until a stoichiometric film was obtained. As the composition approached 1:1 Pol^+:Pol^- stoichiometry the steady state limiting current decreased for each cycle then remained constant (Figure S8A). Ion transport stabilized after the second NaCl treatment cycle, indicating an ion-free bilayer and therefore only one cycling step was necessary to obtain a stoichiometric film.

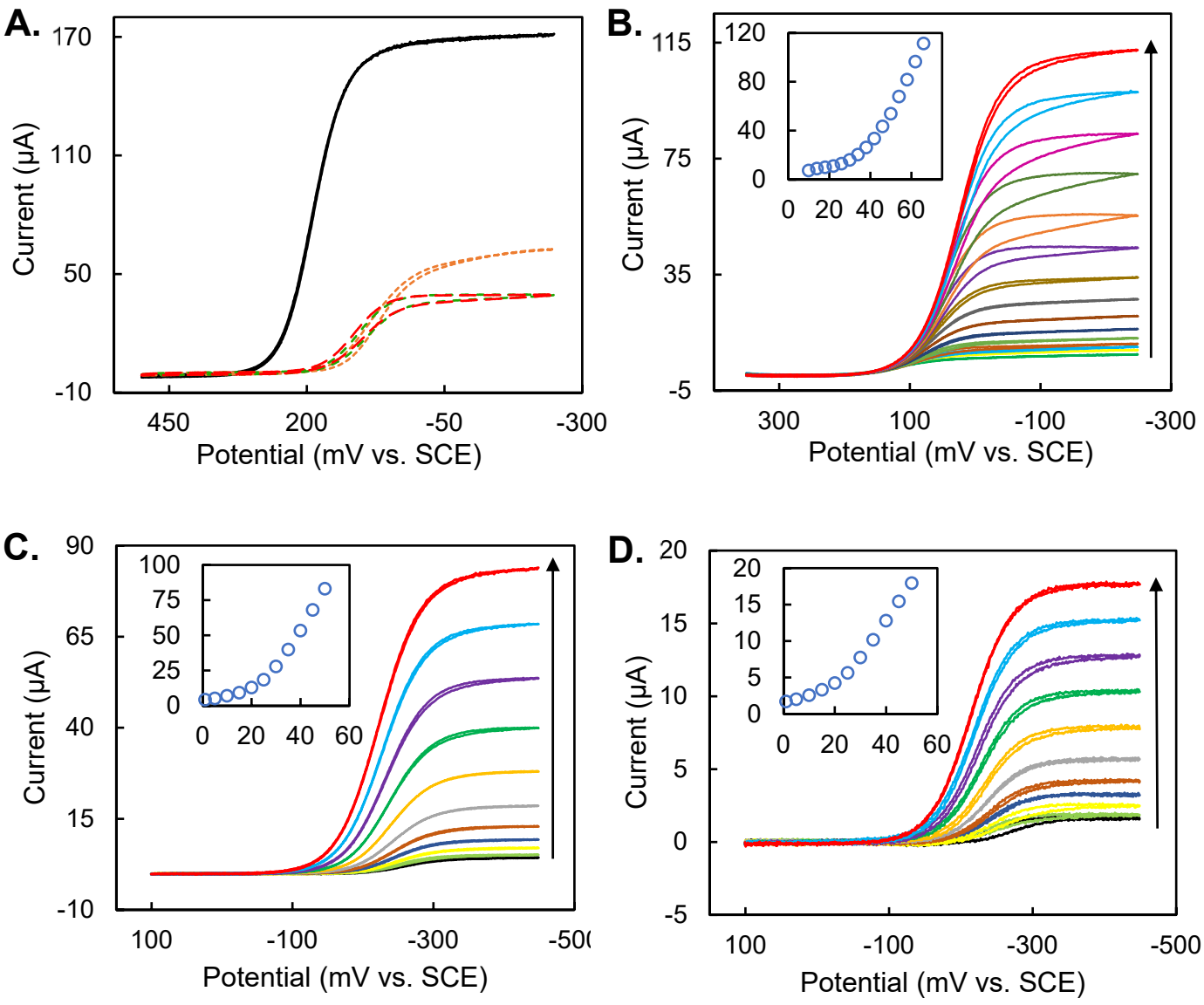

Figure S8. Cyclic voltammograms (10 mV/s sweep rate, rotation rate 1000 rpm) at a Pt RDE coated with $(PDADMA/PSS)_{10}$. **A)** 1 mM ferricyanide in 0.6 M NaCl. The bare electrode **(black solid curve)** was coated with $(PDADMA/PSS)_{10}$ built from 0.3 M NaCl **(orange square dot curve)** and then treated with 1.5 M NaCl for 5 min and 10 mM PSS in 0.3 M NaCl for 5 min at room temperature to obtain stoichiometric films **(green-dashed, and red long dashed curves)**. **B)** Cyclic voltammograms of the film from **A** in 2 mM ferricyanide in 0.3 M NaCl at temperatures from 10 to 66 °C (bottom to top) with 4 °C intervals; **C)** 1 mM ruthenium hexamine in 0.3 M NaCl at temperatures from 1 to 50 °C (bottom to top) with 5 °C intervals; **D)** 0.2 mM ruthenium hexamine in 0.3 M NaCl at temperatures from 1 to 50 °C (bottom to top) with 5 °C intervals. All insets show the plot of the limiting current (μA) at each temperature (°C); positive currents indicate reductions.

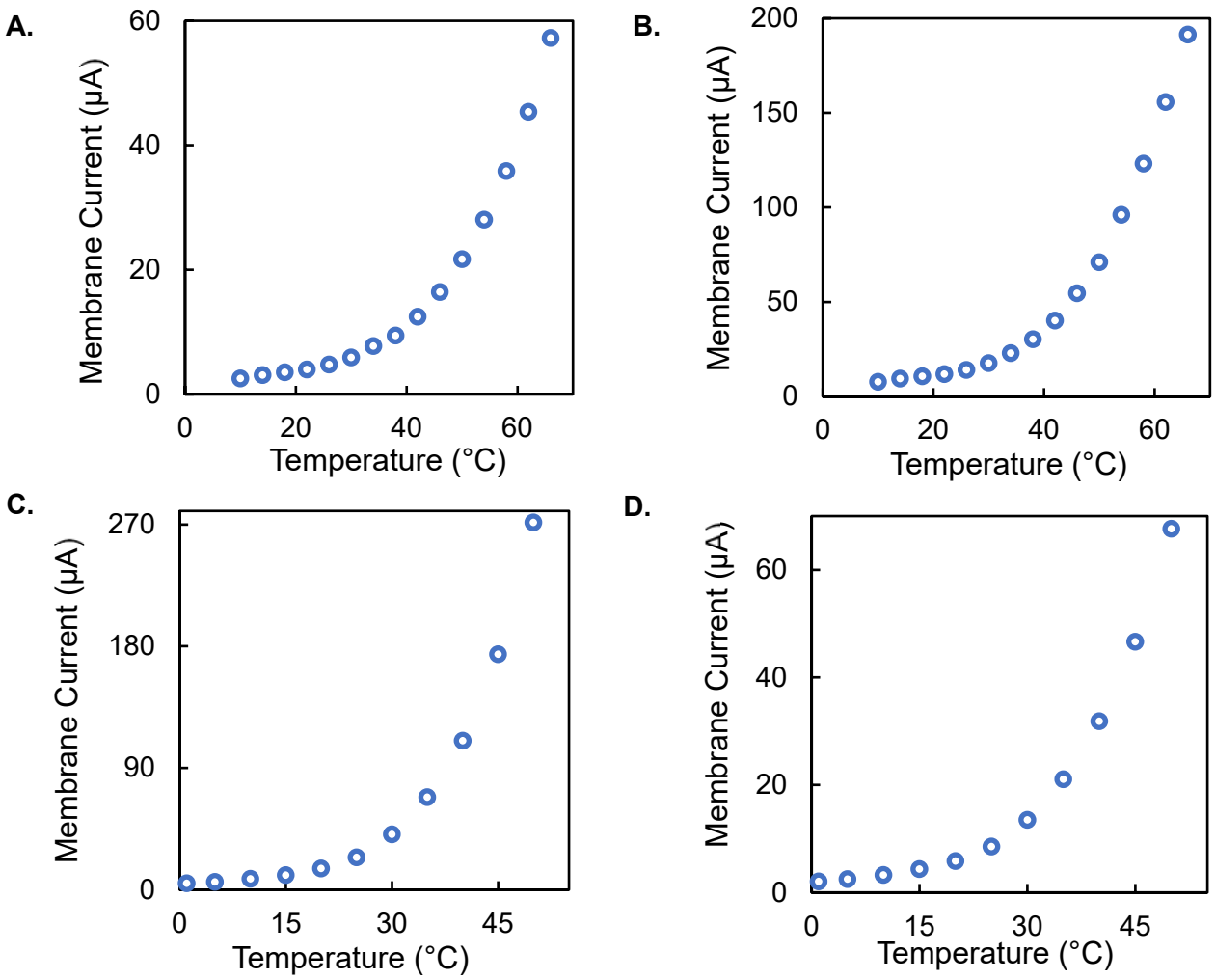

Figure S9. Membrane current vs temperature for a 79 nm $(PDADMA/PSS)_{10}$ film using **A)** 1 mM ferricyanide; **B)** 2 mM ferricyanide; **C)** 1 mM ruthenium hexamine; **D)** 0.2 mM ruthenium hexamine, each in 0.3 M NaCl. Equation 4 was used to obtain the membrane current values by substituting the limiting currents shown in insets of Figure S8 and the Levich current of the bare electrode at each temperature. Errors are less than ±5% the size of the points.

Redox Ion Concentrations versus Temperature

Twelve compact transparent PDADMA/PSS samples, 2 cm diameter and 0.1 cm thick, were thermally annealed in 0.3 M NaCl then doped in 1 mM ferricyanide solution in 0.3 M NaCl at room temperature in the dark for 14 days. Pairs of these samples were then incubated for 7 days in 1 mM ferricyanide solution in 0.3 M NaCl at temperatures ranging from 10 to 50 °C with 8 °C intervals. The samples were then dab dried and dissolved in 2.5 M KBr. UV-Vis measurements were carried out to measure the absorbance spectrum (λ_{max} = 420 nm, see Figure S10) and the concentration of ferricyanide was determined using a calibration curve.

To determine the equilibration time of ruthenium hexamine inside the PEC, kinetic measurements were done on a PDADMA/PSS disc, 2 cm in diameter and 0.1 cm thick. The

sample was annealed in 0.3 M NaCl then doped in 1.0 mM ruthenium hexamine solution in 0.3 M NaCl for a week. Using a PANalytical Epsilon 3 X-ray fluorometer the counts per seconds (cps) for the $K_{\alpha 1,2}$ line of Ru were monitored using PANalytical Epsilon 3 software. A standard addition method was used to determine the concentration of ruthenium hexamine inside the PEC. 20 μL aliquots of 10 mM ruthenium hexamine were added to a PDADMA/PSS disc doped at room temperature for 6 days in 1 mM ruthenium hexamine in 0.3 M NaCl. The counts for the $K_{\alpha 1,2}$ fluorescence line of Ru were recorded after each addition and the concentration was calculated using the resulting calibration curve.

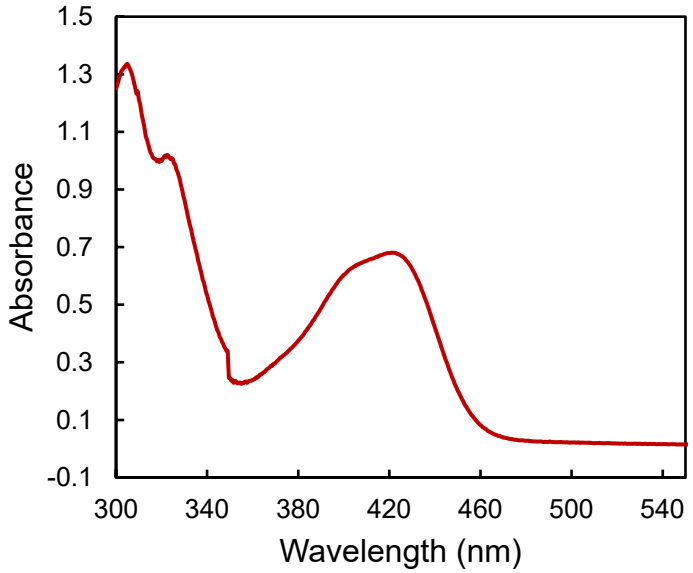

Figure S10. UV-Vis absorption spectrum of PDADMA/PSS sample (2 cm long, 1 cm wide and 0.1 mm thick) doped with 1 mM ferricyanide in 0.3 M NaCl for a week at 20 ºC.

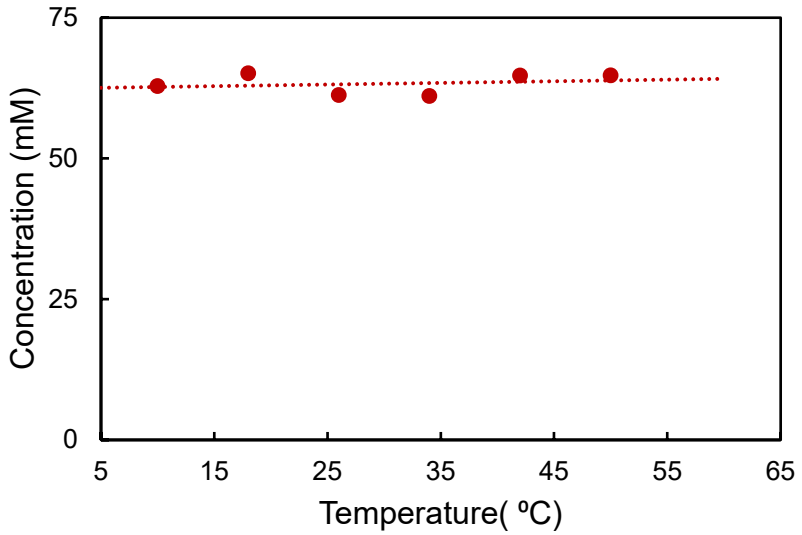

Figure S11. Concentration of ferricyanide in PDADMA/PSS PEC samples at varying temperatures. The samples were in contact with 1 mM ferricyanide in 0.3 M NaCl.

Calculation of the Flux of Water and Ions

The magnitude of the one-dimensional flux of species i, J_i (mol cm^{-2} s^{-1}), inside a film of thickness d (cm) is given by

$$J_i = \frac{D_i\, C_i}{d}$$

Where D_i (cm^2 s^{-1}) and C_i (mol cm^{-3}) are the diffusion coefficient and concentration of i respectively.

Therefore, J_w at 30 °C, for example, in a 78.7 nm film would be

$$J_w = \frac{-3.70 \times 10^{-6}\ \text{cm}^2\text{s}^{-1} \times 0.0244\ \text{mol cm}^{-3}}{78.7 \times 10^{-7}\ cm} = 0.0115\ \text{mol cm}^{-2}\ \text{s}^{-1}$$

The values of D_w at each temperature are found in Figure 2C whereas the value of the concentration of water inside PEC, C_w is a constant 0.0244 mol cm^{-3} over the temperature range studied

Similarly, J_s at 30 °C in the same film would be

$$J_s = \frac{-5.56 \times 10^{-7}\ \text{cm}^2\text{s}^{-1} \times 0.00018\ \text{mol cm}^{-3}}{78.7 \times 10^{-7}\ cm} = 0.0000127\ \text{mol cm}^{-2}\ \text{s}^{-1}$$

The values of D_s at each temperature are found in Figure 3B whereas the concentration of salt inside the PEC, C_s, is a constant 0.00018 mol cm^{-3} over the temperature range studied.

References

1. Fares, H. M.; Ghoussoub, Y. E.; Surmaitis, R. L.; Schlenoff, J. B., Toward Ion-Free Polyelectrolyte Multilayers: Cyclic Salt Annealing. *Langmuir* **2015**, *31*, 5787-5795.