Electronic Supplementary Information for:

The entropy of water in swelling PGA/PAH polyelectrolyte multilayers

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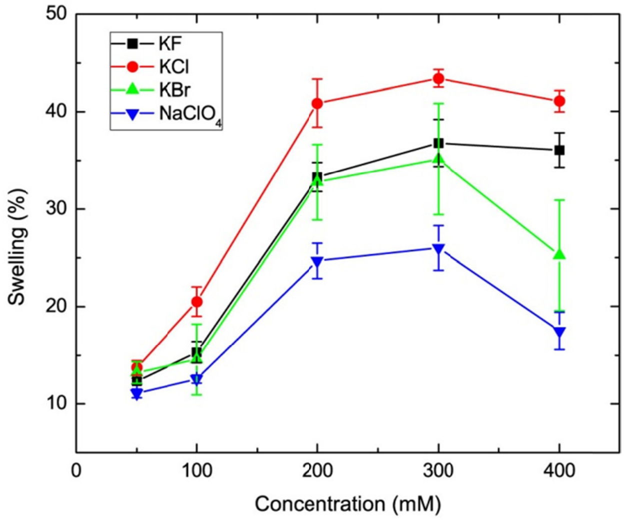

Figure S1. Influence of ionic strength and anion species on electrochemical multilayer swelling. The swelling of the multilayer increases for all measured anions, up to a concentration of 300 mM. For a higher ionic strength the swelling decreases. The degree of swelling at a given molarity is highly dependent on which anion species is present in the buffer solution.

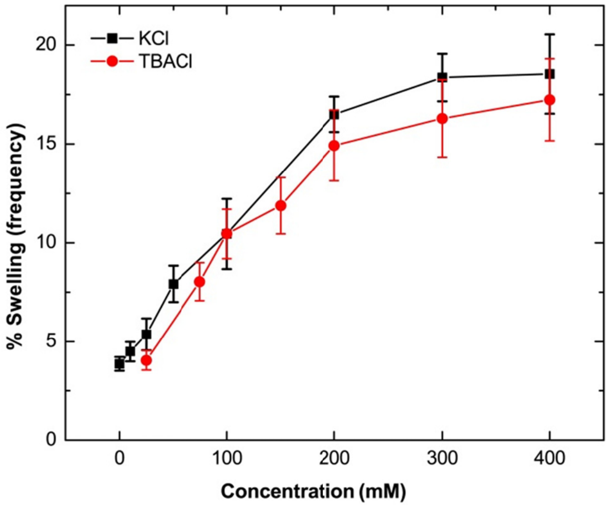

Figure S2. Influence of the ionic strength on electrochemical multilayer swelling for the cations potassium (K) and tetrabutylammonium (TBA). Although the two cations differ by a factor of 6.4 in molecular mass, the measured swelling amplitudes are identical for the tested concentration range. This demonstrates that no cations are exchanged. Note: in order to compare the concentration series for TBACl to published data for KCl[S1], the multilayers were constructed under slightly different experimental conditions. This resulted in significantly thicker multilayers for the same number of bilayer depositions (approx. 25% thicker). For thicker multilayers, the relative swelling of the multilayer (in percent) is reduced for the same experimental conditions. Therefore, the swelling magnitudes for KCl presented here cannot be compared to the corresponding ones in Figure S1.

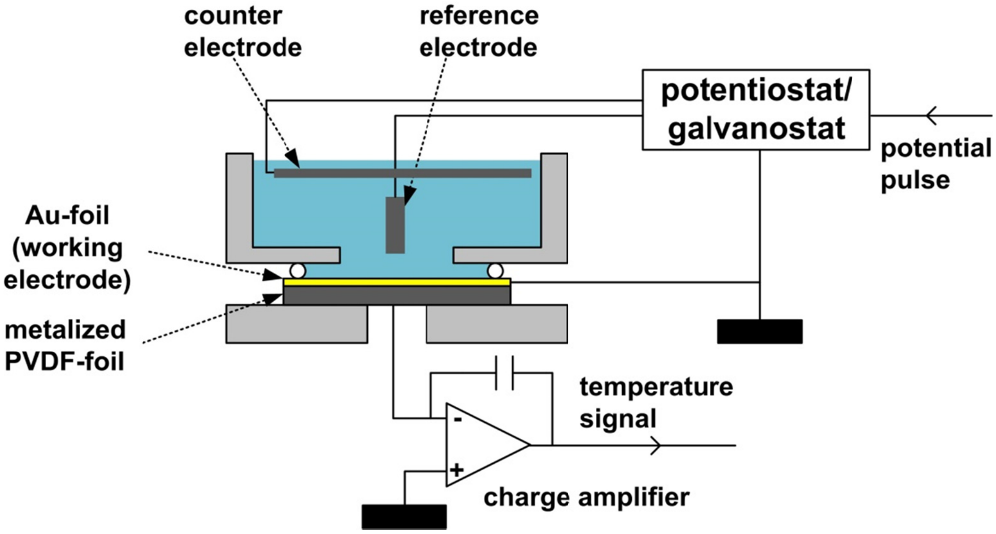

Figure S3. Simplified schematic of the home-built cell used for the electrochemical microcalorimetry measurements (not drawn to scale; see also references [S2] and [S3]). The cell represents a conventional three-electrode setup with platinum counter and reference electrodes. The working electrode is a thin gold foil, on which the polyelectrolyte multilayers are adsorbed. The gold foil is mounted directly onto a freestanding metalized polyvinyliden fluoride (PVDF) foil. Thermal contact is established by removing the air in between the gold working electrode and the PVDF foil. A temperature change (e.g. due to an electrochemical reaction) induces an accumulation of charge in the pyroelectric PVDF foil. This charge is collected on the metal coating on the backside of the PVDF foil and is amplified by a charge amplifier.

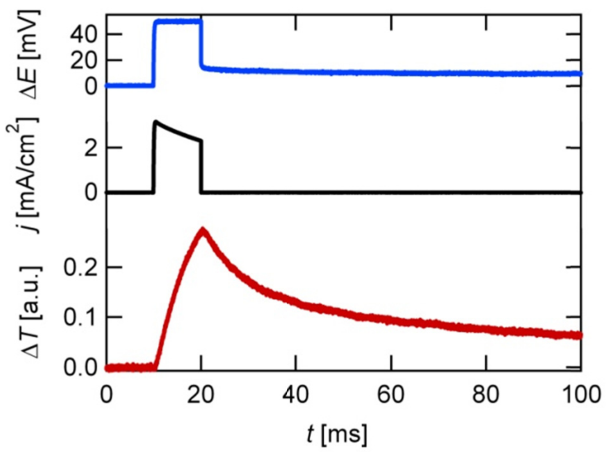

Figure S4. Potential, current and calorimetrically measured temperature transients upon a 10 ms potential pulse of 50 mV amplitude. The heat for each pulse was determined by calibrating the temperature signal with a ferrocyanide solution as described below.

Experimental Section

Materials

All chemicals were used as received unless otherwise specified. The following polymers were used: Polyethyleneimine (branched) (PEI, Sigma Aldrich 408727, MW = 25 000); Poly(L-glutamic acid) (PGA, Sigma Aldrich 408727, MW = 15 000 – 50 000); Poly(allylamine hydrochloride) (PAH, Sigma Aldrich 283 215, MW = 70 000). Buffers were prepared with ultrapure water (Milli-Q gradient A 10 system, Millipore Corporation or Sartorius Arium 611UV). All buffers contained 10 mM 4-(2-hydroxyethyl)piperazine-1-ethane-sulfonic acid (HEPES, Fluka Chemie GmbH, Switzerland). Salts were purchased from Sigma Aldrich (Buchs, Switzerland): potassium chloride (KCl), potassium bromide (KBr), tetrabutylammonium chloride (TBACl), sodium chloride (NaCl), potassium fluoride (KF) and potassium hexacyanoferrate(II) trihydrate (ferrocyanide, $[Fe(CN)_6]^{4-}$).

Film preparation

As described previously, the films were built up by alternate adsorption of positively and negatively charged polymers onto a gold surface (so-called "dip and rinse" method).[S1] PEI was used as an initial layer followed by five alternating depositions of PGA and PAH, always separated by a rinsing step. The temperature during the assembly was 25 °C for the EC-QCM experiments and room temperature for the electrochemical microcalorimetry measurements. All polymers were used at a concentration of 1 mg/ml in a buffer of pH 7.4, which contained 100 mM KCl. Adsorption steps were 5 minutes, and rinsing steps were 2 minutes. For all our experiments we used PEMs consisting of 5 bilayers of PGA/PAH. These films consist of nanometer-sized, densely packed droplets that cover the entire substrate surface.[S1] The multilayers have a molar density of approximately 92 nmol/cm^2, (calculated from QCM-D data using the Sauerbrey equation and assuming a multilayer hydration of 29%[S4]). The multilayer thickness is typically around 100 nm.[S1] For the final adsorption of $[Fe(CN)_6]^{4-}$ we exposed the multilayers to a solution containing 10 mM $[Fe(CN)_6]^{4-}$ and 100 mM KCl. for 10 minutes. This led to the incorporation of about 10^{15} ferrocyanide molecules per square centimeter of the film as determined from the oxidation and reduction charge of the electro-active layer by cyclic voltammetry. All electrochemical measurements were performed in 10 mM HEPES buffer, containing the salt under study with the respective concentration.

Electrochemical quartz crystal microbalance with dissipation monitoring (EC-QCM-D)

The buildup and the EC-QCM-D studies of PGA/PAH films were performed as described previously.[S1] Briefly, QCX 301 gold crystals (Q-Sense AB, Gothenburg, Sweden) were cleaned by immersion in a 2 % (w/w) SDS solution (>30 min), followed by rinsing with ultrapure water, drying under a stream of nitrogen and cleaning with UV/ozone for 30 min. A volume of 0.5 mL of temperature-equilibrated polyelectrolyte or buffer solution was injected into the QCM-D cells (QE 401 instrument with standard modules; Q-sense AB, Gothenburg, Sweden). The PEM buildup was monitored by continuously recording the sets of resonance frequencies and dissipation factors (3rd, 5th, 7th 9th and 11th overtones).

For the electrochemical measurements, gold crystals with the adsorbed PEM film were quickly transferred to the QEM 401 module assuring that the PEM did not dry. The QEM 401 cell represents a conventional three-electrode setup with a platinum counter electrode and an Ag/AgCl (3 M KCl) reference electrode (Micro Dri-Ref reference electrode, World Precision Instruments, Sarasota, FL, USA). The working electrode of the module is the gold surface of the QCX 301 crystal that is also used for the QCM-D measurements. Cyclic voltammetry (CV) measurements were performed using an IPS Jaissle PGU10V-1A-IMP-S potentiostat/galvanostat (Jaissle Elektronik GmbH, Germany). To measure the swelling/contraction of the PEM film, three potential scans from 0 mV to 600 mV were performed at a scan rate of 50 mV/s. The resulting QCM-D changes in resonance frequency were recorded simultaneously.

Only the values obtained from the last scanning cycle were analyzed. A typical EC-QCM-D experiment is shown in Figure 1A in the article. It shows the normalized 3rd overtone of the measured resonance frequency ($\Delta f_3/3$). The percentage of swelling was determined as described previously.[S1] Briefly, we divided the frequency change caused by electrochemical swelling by the overall change in frequency from the multilayer build-up. After one swelling/contraction measurement in our standard buffer (100 mM KCl, pH 7.4), the buffer was exchanged to one having a different counter ion species and/or molarity. A swelling/contraction measurement was then performed. Between two buffer rinses with different ionic strengths, we always measured with the standard ionic concentration (100 mM). If the swelling ratio, measured for the standard concentration, was comparable before and after measuring using a different ion concentration, we assumed fully reversible multilayer swelling. Further measurements were then performed on this PEM film. If the swelling ratio for the standard concentration was significantly reduced after a concentration variation, a new PGA/PAH multilayer was prepared for subsequent measurements. The data presented in the article show the mean values and standard deviations of 3 independently performed measurements. Our PGA/PAH multilayers are rigid thin films.[S1, 5] This can be seen from the QCM-D signal for multilayer construction and electrochemical swelling. In both cases the normalized overtones of the QCM-D resonance frequency ($\Delta f_n/n$) showed no significant dispersion and the ratio of the QCM-D dissipation values (ΔD_n) to the corresponding normalized frequencies ($\Delta D_n/-(\Delta f_n/n)$) was typically below 2 x 10^{-7} Hz.[S6] Therefore, the Sauerbrey equation can be used to analyze the QCM-D data and to calculate Δm, the mass uptake of the PEM during the electrochemical swelling.[S7, 8]

$$\Delta m = C/n \cdot \Delta f \qquad (1)$$

with C denoting the sensitivity of the crystal ($C = 18\,\mathrm{ng} \cdot \mathrm{Hz}^{-1} \cdot \mathrm{cm}^{-2}$), n the number of the analyzed overtone and Δf the change in resonance frequency.

We determined the total number of ferrocyanide ions in the multilayer (N_{FC}) from the charge (Q) required for the oxidation wave in the redox rection:

$$N_{FC} = Q/F \qquad (2)$$

with F denoting the Faraday constant. (The background charging current was subtracted before the analysis).

We calculated the number of water molecules exchanged during the multilayer swelling by combining the electrochemical and QCM-D data, as described in literature.[S1, 8] Ferrocyanide-containing PGA/PAH multilayers act as permselective films, which allow only the exchange of anions and water.[S1] Electroneutrality of the multilayer requires the uptake of one counter anion for every oxidized ferrocyanide ion in the multilayer. The mass of these ions (m_{anion}) is:

$$m_{anion} = N_{FC} \cdot M_{anion} = Q/F \cdot M_{anion} \qquad (3)$$

with M_{anion} denoting their molar mass.

Subtraction of m_{anion} from Δm yields m_{H_2O}, the mass of water molecules that are exchanged during swelling. We obtained the number of exchanged water molecules (N_{H_2O}):

$$N_{H_2O} = \frac{\Delta m - m_{anion}}{M_{H_2O}} = 1/M_{H_2O} \cdot (C/n \cdot \Delta f - Q/F \cdot M_{anion}) \qquad (4)$$

with M_{H_2O} denoting the molar mass of water.

The percentage of multilayer swelling was determined as described previously.[S1] Briefly, we divided the frequency and dissipation change caused by electrochemical swelling by the overall change in frequency or dissipation that was observed from the multilayer build-up. After one swelling/contraction measurement in our standard buffer (100 mM KCl, pH 7.4), the buffer was exchanged to one having a different counter ion species and/or molarity. A swelling/contraction measurement was then performed. A typical EC-QCM-D experiment is shown in figure 1A. The swelling/contraction was consistently observed for all measured harmonics. Only the 3rd harmonic is shown to avoid graphs with too many superposed curves. Between two buffer rinses with different ionic strengths, we always measured with the standard buffer. If the swelling ratio, measured in the standard buffer, was comparable before and after measuring in another buffer, with one different parameter, we assumed that changing this parameter did not have an irreversible influence on the multilayer structure. Further measurements are then performed on this PEM film. If the swelling ratio in the standard buffer was significantly reduced after a parameter variation, a new PGA/PAH multilayer was used for the next measurement.

Electrochemical microcalorimetry

The electrochemical microcalorimetry measurements were performed using a home-built instrument (see Figure S3 for a simplified schematic of the cell). Details about the experimental setup and data analysis have been published previously[S2, 3, 9]. Briefly, our measurement cell represents a three electrode setup with a polycrystalline gold working electrode (50 µm thick foil; 99.999%; Wieland Dental, Germany) a platinum wire as reference electrode, and a platinum ring as counter electrode. The gold foil is mounted on top of a 9 µm thick, gold-coated, pyroelectric polyvinyliden fluoride foil (PVDF; Goodfellow, UK), which serves as temperature sensor. During a typical electrochemical microcalorimetry measurement (see Figure S4), a short, 10 ms potential pulse is applied, which triggers the electrochemical reaction (in our case the oxidation/reduction of the ferrocyanide in the PGA/PAH multilayer). The duration of the applied pulse is slow enough for temperature equilibration within the electrode sensor assembly but fast enough to avoid loss of heat into the electrolyte. Therefore, the heat generated by the electrochemical reaction can be determined from the recorded temperature signal (see Figure S4). The setup allows studying heat effects upon surface electrochemical reactions with electrochemical conversion down to about 10^{12} electrons per cm^2. This ensures that for the calorimetric measurements only a small fraction (<1% to several percent) of the iron complexes react during the measurement, leaving the system close to thermal equilibrium. Prior to each series of measurements, the temperature sensor was calibrated by measuring the reversible heat of the electron transfer reaction in 100 mM $[\mathrm{Fe(CN)_6}]^{4-}$/100 mM $[\mathrm{Fe(CN)_6}]^{3-}$ and comparing the values with literature.[S3, 10]

The measured heat consists of reversibly and irreversibly exchanged heat. While the irreversibly exchanged heat is proportional to the applied potential pulse amplitudes, the reversibly exchanged heat remains constant. This behavior allows determining the reversibly exchanged heat by extrapolating the heat of the reaction for different potential pulse amplitudes to the limit of zero.

Before the microcalorimetry measurements, the gold foil was cleaned in hot Piranha solution (H_2SO_4/H_2O_2) and thermally annealed in a butane flame. Prior to the calorimetric experiments, we recorded cyclic voltammograms to determine the apparent redox potential ($E_{1/2}$) of the ferrocyanide ions in the multilayer. An electrochemical microcalorimetry measurement consists of a series 10 ms potential pulses around $E_{1/2}$ in both polarization directions. Typically, the applied potential pulse amplitudes were between ±25 mV and ±300 mV. To determine the heat of the electrochemical reaction, the temperature of the electrode sensor assembly was measured immediately before and at the end of the potential pulse. The reversible heat and thereby the entropy of the electrochemical reaction were extracted from heat *vs.* potential pulse amplitude plots at the limit of zero potential (see Figure 2A in the article). The data presented in Figure 2B and 3 shows the average of typically 2-5 independent experiments with freshly formed and doped PEM. The error bars reflect the standard deviation of these measurements together with the goodness of the extrapolation of the normalized heat data. The absolute error of the entropy, stemming from uncertainties of the calibration, is estimated to about 5 J/(mol K).

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