

# Electronic control over detachment of a self-doped water-soluble conjugated polyelectrolyte

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# Supporting information

## 1. EQCM-D introduction

EQCM is a powerful tool to study small changes in mass depending on the applied voltage and has been extensively used to investigate both electropolymerisation<sup>1,2</sup> and redox cycling<sup>3-5</sup> of conducting polymer films. In EQCM measurements, the change in areal mass density  $\Delta m$  is related to the charge density  $Q$  passed in or out from the film. The equivalent or molar mass of polymer deposited upon the transfer of one electron ( $n = 1$ ) can be calculated using the following formula:

$$M_{eq} = \frac{F\Delta m}{Q} \quad (1)$$

where  $\Delta m$  is the mass change,  $Q$  is the charge consumed by the sample,  $M_{eq}$  is the equivalent or molar mass per electron, and  $F$  is the Faraday constant. The total charge applied to the electrode and film, during deposition, oxidation or reduction, is commonly used as an estimate for  $Q$ . However, accurate subtraction of background and side reaction currents is sometimes difficult. Thus, the calculated  $M_{eq}$  value might then be either smaller or larger than the actual molar mass. Several possible reasons have been identified for the uncertainties in measuring  $M_{eq}$ ; (i) slow diffusion of solvent molecules, (ii) triple ions taking part in the process, (iii) viscoelastic properties of the film.<sup>6,7</sup>

In the case of a viscoelastic film, the measured dynamic mass that is sensed during periodic oscillation will depend on the density, elastic modulus and on the viscosity of the film.<sup>8</sup> The mass can thus be either larger or smaller than the static mass, resulting in errors when determining  $M_{eq}$ . However, in EQCM-D measurements the frequency response reflects the viscoelastic properties, thickness and density of any mass coupled to the quartz crystal that will appear as a change in frequency ( $f$ ) and dissipation ( $D$ ) at various overtones.<sup>9</sup> The EQCM-D senses the mass of the deposited film as well as trapping of water and co-ions. With appropriate modeling of the  $f$  and  $D$  data the thickness and viscosity for the adsorbed or deposited layer can be estimated. Two different models are used depending on the  $\Delta D$  value: if  $\Delta D$  is around zero, the Sauerbrey relation is valid, and if  $\Delta D > 0$ , the Voigt model is used.

## 2. Additional experimental details

**Detachment experiments:** For PVPA and PAA the solution concentrations were calculated for monomer units. For  $\text{Na}_2\text{SO}_4$ , the reported concentrations are given for sodium ions. For NaDBS, higher concentrations than 0.25 M could not be prepared due to limitation to dissolve this salt in water. The beaker was gently shaken at regular intervals to facilitate the actual detachment process. The detachment time was defined as the time needed to detach the entire polymer film from the underlying substrate. In the experiments with temperature-controlled 0.1 M NaCl, an ordinary hot plate was used or the electrolyte was cooled in a freezer. When evaluating the effect of pH, 1 M HCl or 1 M NaOH was added to 0.1 M NaCl until the desired pH (measured with a MetroOhm pH-meter) was reached. In the  $\text{CaCl}_2$  experiments, bar-coated PEDOT-S:H was incubated in 0.1 M  $\text{CaCl}_2$  for period of times ranging from one to seven days. After this exposure, the films were transferred to a 0.1 M NaCl solution and then the detachment experiment was triggered. Alternatively, films were detached (with no prior incubation) in an electrolyte containing both  $\text{CaCl}_2$  and NaCl. The amount of  $\text{CaCl}_2$  was between zero and 20 volume-% in a total volume of 20 ml.

**EQCM-D:** All electrochemical QCM-D measurements were performed using a Q-Sense AB (QEM 401) electrochemistry module connected to a Q-Sense (E4) chamber. The electrochemistry module was connected to a peristaltic pump (Ismatec Reglo Digital M2-2/12 (Q-Sense)) to guarantee a well-controlled flow of sample solutions and an Autolab PGSTAT 10 was used as the potentiostat setup. All substrate electrodes (AT-cut quartz crystals,  $f_0 = 5$  MHz and gold coated), fittings for electrochemistry (including cables and reference electrode) were purchased from Q-Sense AB.

Prior to use, the AT-cut quartz crystals were cleaned by immersion in SC1 (Milli-Q water: $\text{H}_2\text{O}_2$ : $\text{NH}_3$  mixed at a 5:1:1 volume relation) solution and heated to 80 C° for five minutes and then extensively rinsed with Milli-Q water. The EQCM-D experiments were performed as follows: The flow rate was set to 100  $\mu\text{L}/\text{min}$  during the entire measurement. The sensor surface was first probed in air and then removed. Then, the surface was spin coated (1500 rpm) with a solution of PEDOT-S:H (20 mg/ml). The coated sensor was then dried in an oven (65 C°) for 45 minutes and reinserted into the EQCM-D cell. After obtaining a stable baseline in air for the films, they were then compared against the electrode baseline of the unloaded substrate. The dry masses were then calculated from the difference of the baselines, using the Sauerbrey relationship:

$$\Delta m = - \frac{C \Delta f}{n} \quad (2)$$

where  $C$  is the mass sensitivity constant ( $17.7 \text{ ng/cm}^2$ )  $\Delta f$  is the shift in frequency and  $n$  (1, 3,...) is the overtone number.

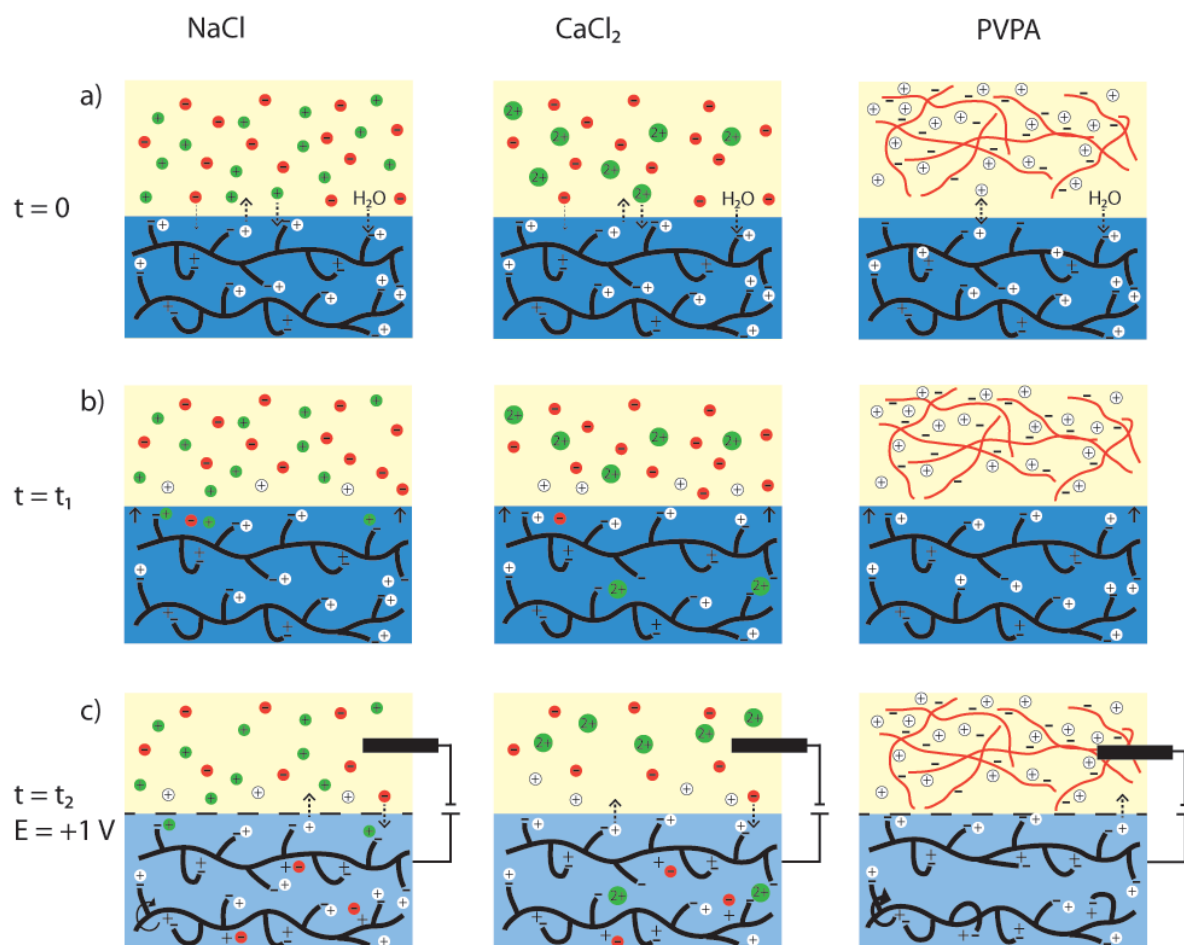
The EQCM-D cell was filled with an electrolyte solution and a stable baseline frequency was reached. Then, the pumping was stopped and the potentiostatic polarization of the substrate electrode was initiated. The significant dissipation parameter shifts of the PEDOT-S:H layer in response to the potentiostatic field. This reveals that the polymer layers exhibit a considerable change of the viscoelastic properties. The Sauerbrey relationship, which couples the change in mass to a rigid sensor (i.e., elastic), was used together with the Voight model to determine the properties of the PEDOT-S film. The Q-tools software package v.3.0.10.286 (Biolin Sci, AB) was used to apply the Voigt model in order to determine the mass ( $\text{ng/cm}^2$ ) changes to the adhered PEDOT-S:H layer of the sensor surface, using specific input parameters that provides the best data fit for the layer density ( $1100 \text{ kg/m}^3$ ), fluid density ( $1000 \text{ kg/m}^3$ ), layer viscosity ( $1^{-5} \leq 1^{-2} \text{ kg/ms}$ ), layer shear modulus ( $1^3 \leq 1^7 \text{ Pa}$ ), and mass ( $1^3 \leq 1^6 \text{ ng/cm}^2$ ). The first, third and fifth overtones were used for all modeling calculations.

**AFM:** Due to the inherit roughness of the PEDOT:PSS foil, PEDOT-S:H (20 mg/ml) was instead spin coated (2500 rpm) on acetone-cleaned ITO-glass samples. The substrates were dried in  $80^\circ\text{C}$  for 15 min. Four different samples of PEDOT-S:H on ITO-glass were analysed with AFM; the first was a pristine PEDOT-S:H film. The second and third samples were incubated in 0.1 M NaCl for 5 and 90 seconds respectively. The fourth sample was oxidized in 0.1 M NaCl using a potential of 0.9 V (vs. Ag/AgCl) for 90 seconds. For this sample, care was taken to stop the oxidation process before the film actually started to detach. The films were dipped into water to remove residual salt. Samples two, three and four were all dried ( $80^\circ\text{C}$  for 15 min) prior to analysis with AFM (Veeco Dimension 3100). Tapping mode AFM was carried out in air at room temperature using scan sizes of  $1 \text{ }\mu\text{m}$  and  $10 \text{ }\mu\text{m}$  and scan rates of 1 Hz or 0.75 Hz. Surface roughness ( $R_a$ ) was calculated using the NanoScope software.

**Patterning and inkjet printing:** PEDOT:PSS foil (Agfa-Gevaert Orgacon F-350) was patterned using standard lithography techniques. Electrodes with a line width of  $50 \text{ }\mu\text{m}$  and spacing of  $10 \text{ }\mu\text{m}$  were manufactured. The PEDOT:PSS foils were washed in acetone and water and then precoated with poly(methyl methacrylate), PMMA, prior to spin coating the

photoresist (Shipley-1818). Both the PMMA and the photoresist layer were spin coated at 2000 rpm and cured at 110°C for 15 minutes in a convection oven. After developing the photoresist in Microposit MF-319 reactive ion etching with O<sub>2</sub> and CF<sub>4</sub> plasma was used to pattern the PEDOT:PSS foil. The patterned PEDOT:PSS electrode substrates were coated with PEDOT-S:H (5 mg/ml) using an inkjet printer (Dimatix 2831). Prior to printing, the ink was degassed and filtered using a 0.45 µm filter and then loaded into the 10pl cartridge. The electrodes of PEDOT:PSS were coated with PEDOT-S:H by printing an areal rectangle covering all electrodes. All printing was performed at room temperature with a drop spacing of 40 µm. The substrates were dried at 110°C for 5 min. To define the electrolyte area, SU-8 was paint-brushed to allow only the area coated with PEDOT-S:H to be exposed to electrolyte.

### 3. Figures



**Figure S1.** Ion movements between PEDOT-S:H (blue) and electrolyte (yellow) for three different electrolytes; NaCl (left), CaCl<sub>2</sub> (middle) and PVPA (right). a) the partly oxidized polymer film is first submerged ( $t=0$ ) in electrolyte. The positive charges are counteracted through self-doping and additional negative charges are counteracted by protons (white circles). In NaCl and CaCl<sub>2</sub> cation exchange will occur between protons and cations (green circles) from the electrolyte. Anions (red circles) will also diffuse into the polymer film but to a much lesser extent. b) After some time ( $t=t_1$ ) the polymer film has swelled due to inflow of water and ions. Ion exchange has occurred in NaCl and CaCl<sub>2</sub>, and calcium ions have cross-linked the polymer chains. c) When PEDOT-S:H is oxidized ( $t=t_2$ ), anions will enter the film submerged in NaCl and CaCl<sub>2</sub>. In PVPA, and also in NaCl, the polymer chains will rearrange to facilitate more self-doping, as indicated by the curved arrow. Finally the film will detach, indicated by the dashed line in the electrolyte-interface.

#### 4. References

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