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Probe beam deflection study of ion exchange in self-assembled redox polyelectrolyte thin films

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Probe beam deflection during chronoamperometric oxidation–reduction of osmium complex in layer-by-layer self-assembled redox active polyelectrolyte multilayers has shown that the nature of the charge in the topmost layer determines the ion flux that balances the redox charge.

Ultrathin multilayers self-assembled layer-by-layer (LBL) by sequential adsorption of oppositely charged polyelectrolytes from dilute aqueous solutions onto solid surfaces has been employed to assemble a wide variety of different materials.[1,2]

The alternate immersion of a charged surface to polyelectrolyte solutions containing polyanion and polycation respectively leads to the formation of polyelectrolyte multilayers with surface charge reversal in every immersion step with intrinsic compensation of charge between polycation and polyanion.[1–3] In redox active multilayers the charge of the constituent polyelectrolytes can be altered by oxidation–reduction of redox centers after film build up, this may result in changes in ion or salt population within the multilayer (*extrinsic* charge compensation).[4,5]

During oxidation and reduction of redox polymer films, exchange of ions with the electrolyte occurs to maintain the electroneutrality in the film. Anion or cation ingress or release from the film or a combination of both ion fluxes is possible; however the fraction of redox charge compensated by either ion cannot be determined in electrochemical experiments alone since only the total charge exchanged with the electrolyte can be monitored.[4,5]

Radiotrace studies in poly(viologen)/poly(styrenesulfonate), (PSS), multilayers revealed the exchange of both anion and cation.[6] The study of Donnan permselectivity in layer-by-layer self-assembled redox polyelectrolyte, poly(allylamine) modified with Os(bpy)$_2$ClPyCHO (PAH–Os) and anionic poly(styrene)sulfonate (PSS) thin films has shown that the nature of the polyelectrolyte capping layer, the electrolyte pH, and ionic strength determine the apparent redox potential of the Os redox couple.[7] This has been related to Donnan exclusion by the fixed charge of the polyions in the film. For PAH–Os capped films (surface excess of positive charge) during Os(II) oxidation, the ingress of anions to balance charge has been observed under permselective conditions. For negatively charged PSS capped films, on the other hand, cation expulsion has been found for high pH (low PAH–Os excess charge) and low ionic concentration.

Ellipsometry simultaneous to oxidation (reduction) of similar films has shown a fast thickness increase (decrease) in potential step experiments due to the ingress of solvent and swelling.[8] The electrochemical quartz crystal microbalance (EQCM) has shown that under cation exclusion conditions only anions are exchanged during the redox switching of the film. For negatively charged surfaces under cation permselectivity, on the other hand, the egress of cations is masked by the ingress of solvent.[7]

In the present study a (PAH–Os)$_{15}$(PSS)$_{15}$ (negative surface) film with an ellipsometric thickness of 93 nm and (PAH–Os)$_{15}$(PSS)$_{14}$ (positive surface) film of 80 nm were oxidized chronoamperometrically. A thickness increase of 6–8 nm for a redox charge of 0.40 mC cm^{-2} and mass uptake of 0.32 μg cm^{-2} were recorded. Note that while the EQCM cannot distinguish between the mass of ions and solvent exchanged with the electrolyte, the current or electrical charge cannot distinguish the nature of the ion flux either.

The ion exchange during electrochemical oxidation of PAH–Os/PSS films can be described by:

$$\begin{aligned}&\left[PAH - Os(II)PSS.C^{+}_{1-t_-}\right]_{film} + t_- A^{-}_{so\ln} + yH_2O \rightarrow \\ &\left[PAH - Os(III)PSS.A^{-}_{t_-}\, yH_2O\right]_{film} + (1-t_-)C^{+}_{so\ln} + e^{-} \quad (1)\end{aligned} \qquad (1)$$

depending on the exchange of anion (A^{-}) or cation (C^{+}). The anion transference number is t$_{-}$.

Probe Beam Deflection technique, extensively used in electro-active (random) polymers,[9–16] measures the concentration gradient in front of the electrode by monitoring the refractive index gradient with a light beam[17] and is much less affected than EQCM by solvent exchange.[12,13,15–17]

When the ion concentration at the electrode surface changes, a refractive index gradient normal to the electrode surface is created in the electrolyte. A beam travelling parallel to the surface suffers a deviation proportional to the concentration gradient, therefore proportional to the extent and direction of ion flux. Positive beam deflection (away from the electrode) corresponds to ingress of ions in the film while negative deflection (towards the electrode) implies release of ions to the solution.

To evaluate quantitatively the ion exchange, the deflection signal is recorded while the potential is stepped from the fully reduced Os(II) to the fully oxidized Os(III) state and back (chronodeflectometry[11]). The resulting PBD signal during the oxidation step of a repetitive oxidation-reduction pulse train is depicted in Fig. 1 A and B for 15 layers of PAH–Os and 14 and 15 layers of PSS respectively.

The oxidation-reduction of redox polyelectrolyte multilayers is a discontinuous reaction and the redox charge is limited by the number of reaction sites available on the electrode surface. For a potential pulse driving a discontinuous process, such as complete oxidation or reduction of a thin redox film, the experimental deflection signal follows eqn. (2):[11]

$$\theta(x,t) = \left(\frac{l}{n}\frac{\partial n}{\partial C}\right)\frac{C_s}{\sqrt{\pi D_o t}}\,\frac{x}{2D_o t}\,\mathrm{e}^{-x^2/4D_o t} \qquad (2)$$

where C_s is the concentration of sites on the electrode surface and thus the concentrations of bound ions, D_o is the diffusion coefficient of the mobile ion species, x is the beam electrode distance, l is the beam path length, n is the bulk solution refractive index and dn/dC is the change of refractive index with the concentration of mobile ion species.

It is assumed that ion exchange of the film with the bathing solution, occurs in a pulse with a time span negligible compared to that of the PBD peak.[11,15,17]

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A relevant result in Fig. 1, is that the PBD transients strongly depend on whether the multilayer is capped by PAH–Os or PSS. The arrows indicate the time at which the potential has been stepped from 0.15 to 0.60 V. The solid lines in Figs. 1 A and B correspond to the best fit of the sum of two ion pulses (anion and proton) shifted in time. The time difference could be due to the different diffusion coefficient for the ions, inside the film,[18] or other kinetic constraints. In most media the proton flux is faster since the proton mobility is larger than that of chloride ion.[19,20] On the other hand, the proton and chloride mobilities outside the film are linked by migration in a binary electrolyte.[15] The good agreement of the fit with the experimental data suggests that the model describes well the ion exchange. A similar experimental profile and fit with same x and D_o have been observed in the reduction steps for each film.

For positively charged PAH–Os capped film $(PAH–Os)_{15}(PSS)_{14}$ (Fig. 1A) the main contribution during Os(II) oxidation is anion uptake by the film with a small release of protons ($Cs_{\mathrm{anion}}/Cs_{\mathrm{proton}}$ = 4.2). For negatively charged PSS capped films, $(PAH–Os)_{15}(PSS)_{15}$ the PBD shows a very different transient (Fig. 1B). While anion insertion remains the main ion exchange process at longer times,[7] a larger fraction ($Cs_{\mathrm{anion}}/Cs_{\mathrm{proton}}$ = 1.4) of the oxidation charge is compensated by the expulsion of protons from the film and less by uptake of anions than in Fig. 1A. Upon reduction of Os(III) sites in the film the opposite trend is observed with ingress of protons and egress of anions, with different ion concentration ratios depending on the topmost layer surface charge.

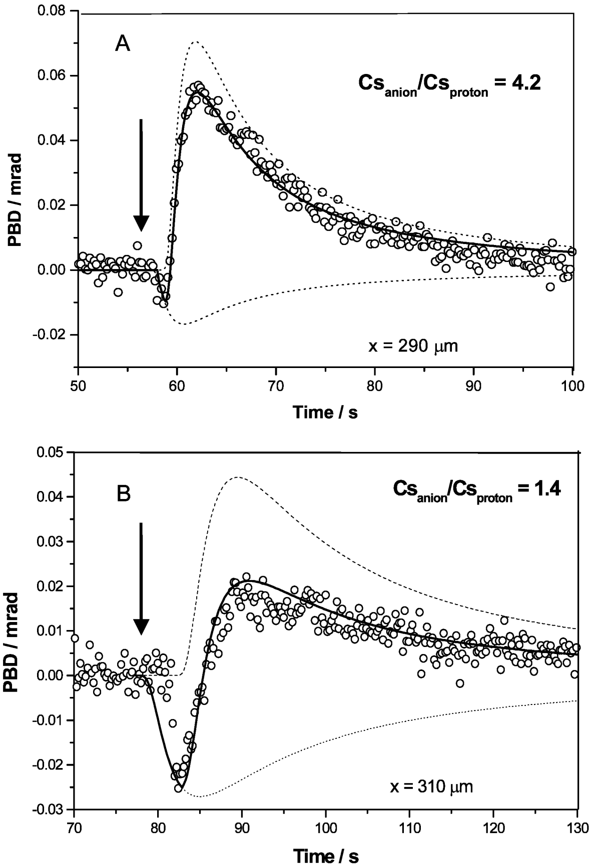

Fig. 1 Probe beam deflection (PBD) transients during the oxidation of PAH–Os(II) in 0.01 M HCl: Experimental data (o), best fit to eqn. (2) for individual anion and cation fluxes (dotted line) and total ion flux (full line). A) $(PAH–Os)_{15}(PSS)_{14}$ and B) $(PAH–Os)_{15}(PSS)_{15}$. Potential step 0.15 to 0.60 V *vs.* SCE. The individual PBD profiles (dotted lines) are fitted using the corresponding x and same D_o (for each figure) and a time delay between ion pulses.

It could be argued that a change in the relative amount of fixed anionic and cationic polymer will affect the ion exchange mechanism. However, in the present results a change of only 1 layer in 15 (a 6% variation) induces a threefold (4.2/1.4) change in the cation/anion exchange ratio measured by PBD. Thus, it is the charge of the uppermost layer and not the relative amount which is affecting the ion exchange. The study of films of different thickness is in progress.

In conclusion we have demonstrated that the potential distribution at the self-assembled polyelectrolyte multilayer (PEM) electrolyte interface determines the mechanism of ion exchange and charge compensation during the oxidation-reduction of redox active PEM's.

Electrochemically active self-assembled films are better defined than conventional polymer modified electrodes, with spatial control of the components. Thus, ion exchange can be tailored at the nanometer level by control of the layer ζ-potential.

A systematic study of kinetics and equilibrium factors for the exchange of different anions is in progress. To the best knowledge of the authors this is the first use of PBD to study the redox active organized PEM's.

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