Electrochemistry of Polymer Films not Immersed in Solution: Electron Transfer on an Ion Budget

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Electrochemistry of Polymer Films not Immersed in Solution: Electron Transfer on an Ion Budget

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Electrochemistry, osmium, polymer film, ionic conductor
This laboratory recently described steady state electron conductance through sub-micron films of electroactive polymeric transition metal complexes sandwiched between two electrodes. Complexes like [Os(bpy)$_2$(vpy)$_2$](ClO$_4$)$_2$ were electropolymerized onto polished Pt overlaid with a porous film of evaporated Au, which was contacted through a polymer electrolyte solution containing reference and auxiliary electrodes. Paper, we show that electroactivity with large limiting currents can be obtained only a test solution, bathed in an electrolyte vapor, or dry N$_2$ gas.

The essential features of the previous sandwich voltammetry are summarized in Figs. 1A and 1B. Fig. 1A is a voltammogram where only E$_{Fe}$ is controlled (Ag/AgCl, Saturated KCl), and shown was Os(III/II), Os(II/I), and Os(I/0) (formal) couples. In Fig. 1B, where E$_{Fe}$ and E$_{Au}$ are controlled (Ag/AgCl, Saturated KCl), E$_{Au}$ at 0V and E$_{Fe}$ being varied, steady state current-potential curve appears when E$_{Fe}$ passes each redox state. In the wave at positive E$_{Fe}$, for instance, a limiting current (111/111) means that all of the polymer next to the electrode in Os(III) and all of that next to the Ag electrode in Os(II) is in the Os(III/II) state in the film as in Fig. 1B inset. This limiting current is by the rate of electron hopping between Os(III) and Os(II) sites and is proportional to the concentration of Os(III)/Os(II) couple and inversely proportional to film thickness d.

Fig. 1C shows a Pt/poly-[Os(bpy)$_2$(vpy)$_2$](ClO$_4$)$_2$/Au sandwich with two electrodes cell bathed in acetonitrile vapor (sat'd, 25°C). We
flows until the potential \( \Delta E \) applied between the Pt and Au electrodes exceeds ca. 1.9V. Then, a reproducible, steady state voltammogram appears with an \( E_a = 2.02 \pm 0.01 \)V (for 7 electrodes) which equals the difference between the formal potentials +0.73 and -1.32V of the Os(III/II) and Os(II/I) couples appearing in Figs. 1A and 1B.

We ascribe the electrical behavior in Fig. 1C to the production of Os(III) and Os(I) sites at Pt and Au electrodes, respectively. Without a bathing electrolyte solution, charge conservation requires that for each Os(II) site oxidized to Os(III) at the Pt electrode, another must be reduced to Os(I) (releasing a CI04^- counterion) at the Au electrode. This can be called an ion budget, to emphasize the coupling of the redox chemistry of the film to its fixed but evidently quite mobile pool of electroinactive CI04^- counterions.

The limiting current \( i_{\text{III/I}} \) in Fig. 1C can be related to that of the Os(III/II) wave \( i_{\text{III/II}} \) in Fig. 1B with simple electron diffusion and charge conservation statements to give:

\[
 i_{\text{III/II}} = i_{\text{III/II}} \left[ \frac{\eta_{\text{III/II}}}{\eta_{\text{III/II}}} \right] \tag{1}
\]

If the electron diffusion coefficients \( D_{\text{III/II}} \) and \( D_{\text{III/II}} \) for the Os(III/II) and Os(II/I) couples in Fig. 1C are assumed to be the same as those in acetonitrile liquid-bathed polymer in Fig. 1B, this equation predicts that \( i_{\text{III/I}} / i_{\text{III/II}} = 2.66 \), which is fairly close to the ratio observed in Fig. 1C and analogous experiments, 2.15±0.4 (avg. of 7 electrodes). Eq. 1 seems to give a good first order account of the vapor-bathed experiment. The same theory predicts that concentration profiles of Os(III), Os(II), and Os(1) sites in the film when the \( i_{\text{III/I}} \) is flowing are as in Fig. 1C inset. The diagram contains the elements that Os(III) and Os(I) sites react quantitatively in the interior of the film Os(II) sites, whose position of maximum concentration is determined jointly by the ion budget and the relative values of \( D_{\text{III/II}} \) and \( D_{\text{III/II}} \). It occurs at \( \frac{\partial}{\partial t} \left[ \frac{\eta_{\text{III/II}}}{\eta_{\text{III/II}}} \right] \left[ \frac{i_{\text{III/I}}}{i_{\text{III/II}}} \right] \).

As discussed previously for redox conductivity, Eq. 1 rests on an electrochemical driving force in the form of a concentration gradient of Os redox sites and not transfilm current. The electron conduction in Fig. 1C in respect differs from that discussed previously for dry mixed solvents. Also, we believe \( i_{\text{III/I}} \) and the electron diffusion coefficients in eq. 1 reflect electron rather than ionic mobilities in the polymer so \( i_{\text{III/I}} \) is additionally different from currents in polymer electrolyte with ion-blocking electrodes. The Fig. 1C experiment does find analogues to the polymer electrodes containing solutions of redox species as described by Host and coworkers.10

Voltammetry of the same Pt/poly-(Os(bpy))2(C104^-)/Au model dry H2 gas shows (Fig. 1D) a recognizable wave even though solvent has been deliberately added. The "dry" voltammogram does show significant differences from Fig. 1C. First, there is hysteresis between currents recorded when \( \Delta E \) is increasing vs. decreasing; this effect is less pronounced for slowly scanned \( \Delta E \). Apparently, CI04^- counterions are mobile in the absence of acetonitrile vapor, and on the time scale of scan do not move rapidly enough first toward and then away from the Pt side of the film (upon its oxidation and reduction, respectively) to a true steady-state current and concentration profiles of Os sites. At \( i_{\text{III/I}} \) plateaus, the CI04^- mobility should again become less significant.
relation to the electron diffusion rate. Secondly, $E_0$ for both increasing and decreasing $\Delta E$ scans, 2.47$\pm$0.14 and 2.13$\pm$0.05V (avg for 8 electrodes), respectively, are both larger than that (2.02V) for the vapor-bathed film of Fig. 1C. This suggests that one or both of the "dry" Os(III/II) and Os(III/III) formal potentials differs significantly from those of the vapor-solvated couples. Thirdly, limiting currents $i_{111/1}$ in dry $H_2$ (Fig. 1D) are 2.5$\pm$0.6 (avg of 7 electrodes) times larger than those in acetonitrile vapor (Fig. 1C). According to Eq. 1, this might occur either through an increase in $D_{e(s/1)}$ or a decrease in $D_{e(111/1)}$ All three effects have interesting connotations but further experiments must elucidate their origin(s).

Low temperature voltammetry of a Pt/poly-[Os(bpy)$_2$(vpy)$_2$][ClO$_4$]$_2$/Au sandwich electrode in acetonitrile vapor (Fig. 1E) is similar to room temperature results (Fig. 1C) except for a slight hysteresis indicating lowered ClO$_4^-$ mobility and a depressed $i_{111/1}$ limiting current showing that electron hopping is an activated process in the vapor-bathed film.

The significance of the experiments in Figs. 1C-E is that voltammetry that can be understood (at least to a first order) with a simple electron diffusion model, is observable in the absence of an electrolyte solution. This opens a variety of possibilities for probing how electron transfer events depend on their environment. An obvious requirement of the experiment is that electroactive material be a good ionic conductor. However two redox couples are not strictly required since one can, for instance, start with an Os(III/II) mixed valent film.

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REFERENCES

2. bpy = 2,2'-bipyridine; vpy = 4-vinylpyridine.
4. Similar results are obtained in pure acetonitrile liquid, but because of ionic impurity the limiting currents were less reproducible upon successive potential scans.
5. Electroneutrality will not rigorously apply at the interfaces between phases at equilibrium or at steady-state.$^6$ However, space charges will on lead to minor deviations from the predictions made here. These deviations will be examined thoroughly in a future report.$^7$
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11. While the films have not been analysed, the procedure for making the Au
electrode contact of the sandwich (see Figure legend) leads us to expect that
after Au deposition the polymer contains little residual acetonitrile solvent.
Figure 1. Voltammetry of Pt/poly-[4(4-xylylpyridine)2][ClO4]2/Au sandwich electrode in various media; $i=31.25 A/m^2$, $T_0 = 2.95 \times 10^{-3} \text{mol/m}^2$ (ca. 400 nm film). All voltammograms at 25°C obtained with the same electrode with a scan rate of 50mV/s except as noted. The electrode was thoroughly rinsed with CH3CN after electropolimerisation, dried, and subjected to 10^-7 torr vacuum and moderate heating during Au evaporation. It was stored in a dessicator and then, in the order of the experiments, exposed to H2 gas (Curve D), CH3CN vapor (Curve C), and electrolyte solution (Curves A and B).

Curve A) $i_{p_1}$ vs $E_{p_1}$ in 0.1M Et4NClO4/CH3CN; Curve B) $i_{p_2}$ vs $E_{p_2}$ with $E_{p_2}$ vs SSCE in 0.1M Et4NClO4/CH3CN; Curve C) $i$ vs $E$ between Pt and Au electrodes in dry H2 saturated with acetonitrile vapor; Curve D) $i$ vs $E$ in dry H2 gas; scan rate=2mV/s; Curve E) $i$ vs $E$ in dry H2 saturated with CH3CN vapor at -34°C using a different sandwich electrode.