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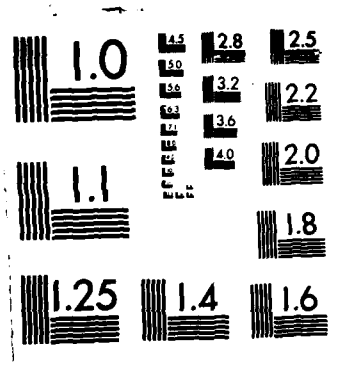

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Electrochemistry of Polymer Films not Immersed in Solution: Electron Transfer on an Ion Budget

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ELECTROCHEMISTRY OF POLYMER FILMS NOT IMMERSED IN SOLUTION:

ELECTRON TRANSFER ON AN ION BUDGET

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ABSTRACT

Films of poly-$[Os(bpy)_2(vpy)_2](ClO_4)_2$ sandwiched between two metallic electrodes can support electron hopping, concentration gradient-driven electron conduction in acetonitrile vapor and in dry N_2 gas, when the potential difference ΔE between the electrodes is made such as to generate a mixture of Os(III), Os(II), and Os(I) states. The latter requirement is dictated by the fixed pool (ion budget) of ClO_4^- counterions in the film. It is significant that ClO_4^- ions can move relatively freely in the dry film, that the apparent Os(III/II) and Os(II/I) formal potentials are different for the vapor and dry N_2 environments, and that currents through dry polymer films are larger than in vapor-exposed films.

This laboratory recently described[1] steady state electron conduc through sub-micron films of electroactive polymeric transition meta complexes sandwiched between two electrodes. Complexes like $[Os(bpy)_2(vpy)_2](ClO_4)_2$ were electropolymerized[2,3] onto polished Pt overlaid with a porous film of evaporated Au, which was contacted b electrolyte solution containing reference and auxiliary electrodes. paper, we show that voltammograms with large limiting currents can obtained for similarly prepared[1] Pt/poly-$[Os(bpy)_2(vpy)_2](ClO_4)_2$/Au sandwiches in the absence of an electrolyte solution, bathed only i acetonitrile vapor, or dry N_2 gas.

The essential features of the previous[1] sandwich voltammetry i electrolyte solution are summarized in Figs. 1A and 1B. Fig. 1A is voltammogram where only E_{Pt} is controlled (vs. SSCE), and shows wav Os(III/II), Os(II/I), and Os(I/0) (formal) couples. In Fig. 1B, wh E_{Pt} and E_{Au} are controlled (vs. SSCE), E_{Au} at 0V and E_{Pt} being vari steady state current-potential wave appears when E_{Pt} passes each re film electroactivity. In the wave at positive E_{Pt}, for instance, a limiting current ($i_{III/II}$) means that all of the polymer next to th electrode is Os(III) and all that next to the Au electrode is Os(II linear concentration gradients of Os(III) and Os(II) states in the of the film as in Fig. 1B inset. This $i_{III/II}$ limiting current is by the rate of electron hopping between Os(III) and Os(II) sites i and is proportional to the electron diffusion coefficient $D_{e(III/I}$ Os(III/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 w two electrode cell bathed in acetonitrile vapor (sat'd, 25°C). Th

flows until the potential ΔE applied between the Pt and Au electrodes exceeds ca. 1.9V. Then, a reproducible, steady state voltammogram appears with an $E_{\frac{1}{2}}$ = 2.02±0.01V (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 ClO_4^- counterion) at the Au electrode. This can be called an ion budget, to emphasis the coupling of the redox chemistry of the film to its fixed but evidently quite mobile pool of electroinactive ClO_4^- counterions.

The limiting current $i_{III/I}$ in Fig. 1C can be related to that of the Os(III/II) wave ($i_{III/II}$) in Fig. 1B with simple electron diffusion and charge conservation statements to give[7]

$$i_{III/I}/i_{III/II} = 1 + [D_{e(II/I)}/D_{e(III/II)}]^{\frac{1}{2}} \qquad (1)$$

If the electron diffusion coefficients $D_{e(III/II)}$ and $D_{e(II/I)}$ 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 $i_{III/I}i_{III/II}$ = 2.68, which is fairly close to the ratio observed in Fig. 1C and analogous experiments, 2.1±0.4 (avg. of 7 electrodes). Eq. 1 seems thus 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(I) sites in the film when the $i_{III/I}$ is flowing are as in Fig. 1C inset. The diagram contains the elements th Os(III) and Os(I) sites react quantitatively in the interior of the fi form Os(II) sites, whose position of maximum concentration is determin jointly by the ion budget and the relative values of $D_{e(III/II)}$ and D and occurs at $[D_{e(III/II)}]^{\frac{1}{2}}$ d/ $\{[D_{e(III/II)}]^{\frac{1}{2}} + [D_{e(II/I)}]^{\frac{1}{2}}\}$.

As discussed previously for redox conductivity, Eq. 1 rests on el conduction driven by concentration gradients of Os redox sites and not trans-film potential gradients. The electron conduction in Fig. 1C in respect differs from that discussed previously for dry mixed valent fi Also, we believe $i_{III/I}$ and the electron diffusion coefficients in eq. principally reflect electron rather than ionic mobilities in the polym so $i_{III/I}$ is additionally different from currents in polymer electroly with ion-blocking electrodes. The Fig. 1C experiment does find analog thin layer electrodes containing solutions of redox species as describ Bard and coworkers[10].

Voltammetry of the same Pt/poly-$[Os(bpy)_2(vpy)_2](ClO_4)_2$/Au sandwi dry N_2 gas shows (Fig. 1D) a recognizable wave even though solvent has been deliberately[11] added. The "dry" voltammogram does show significa differences from Fig. 1C. First, there is hysteresis between currents recorded when ΔE is increasing vs. decreasing; this effect is less pronounced for slowly scanned ΔE. Apparently, ClO_4^- 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 Os side of the film (upon its oxidation and reduction, respectively) to s true steady state currents and concentration profiles of Os sites. At $i_{III/I}$ plateau, the ClO_4^- mobility should again become less significa

relation to the electron diffusion rate. Secondly, $E_{\frac{1}{2}}$ for both increasing and decreasing /\E scans, 2.47±0.1V and 2.14±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/I) formal potentials differs significantly from those of the vapor-solvated couples. Thirdly, limiting currents $i_{III/I}$ in dry N_2 (Fig. 1D) are 2.5±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 $D_{e(II/I)}$ or a decrease in $D_{e(III/II)}$. 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 $i_{III/I}$ 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[7].

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2. bpy = 2,2'-bipyridine; vpy = 4-vinylpyridine.

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4. Similar results are obtained in pure acetonitrile liquid, but because an ionic impurity the limiting currents were less reproducible upon successive potential scans.

5. Electroneutrality will not rigorously apply at the interphases 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.

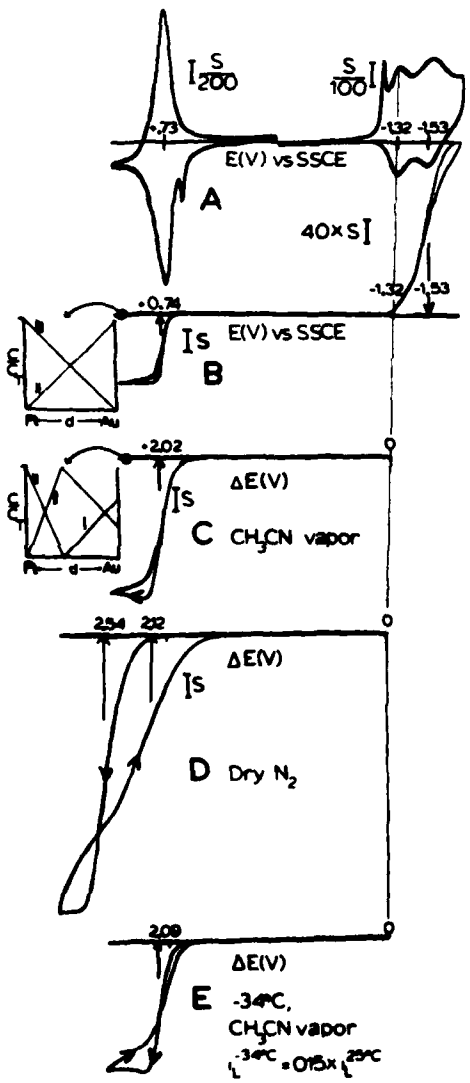
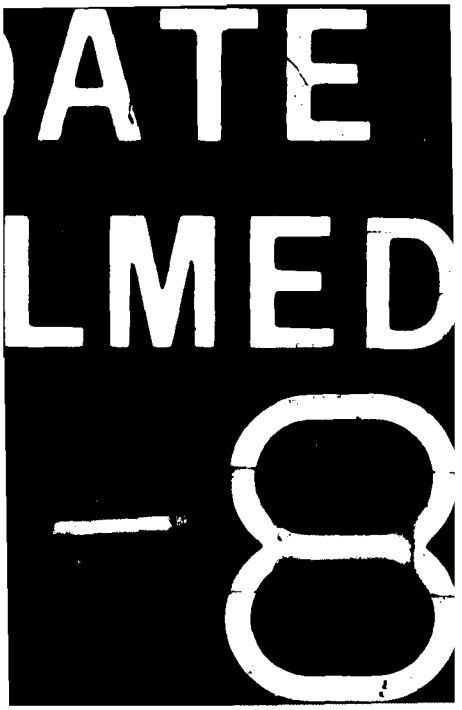


Figure 1. Voltammetry of Pt/poly-$[Os(bpy)_2(vpy)_2](ClO_4)_2$/Au sandwich electrode in various media; S=31.2mA/cm^2, Γ_{Os} = 2.95 x 10^{-8}mol/cm^2 (ca. 400 nm film). All voltammograms at 25°C obtained with the same electrode with a scan rate of 50mV/s except as noted. The electrode was thoroughly rinsed with CH_3CN after electropolymerisation, 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 N_2 gas (Curve D), CH_3CN vapor (Curve C), and electrolyte solution (Curves A and B). Curve A) i_{Pt} vs E_{Pt} in 0.1M Et_4NClO_4/CH_3CN; Curve B) i_{Pt} vs E_{Pt} with E_{Au}=0V vs SSCE in 0.1M Et_4NClO_4/CH_3CN; Curve C) i vs ΔE between Pt and Au electrodes in dry N_2 saturated with acetonitrile vapor; Curve D) i vs ΔE in dry N_2 gas; scan rate=2mV/s; Curve E) i vs ΔE in dry N_2 saturated with CH_3CN vapor at -34°C using a different sandwich electrode.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