Effect of Redox Site Concentration on the Rate of Electron Transport in a Redox Copolymer Film

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This paper describes the dependency of the rate of electron transport between Os(III/II) complex redox sites as a function of their concentration, in a redox copolymer film prepared from the monomers[1] $[Os(2,2'\text{-}bpy)_2(4\text{-}pyNHCOCH{=}CHPh)_2]^{2+}$ (I) and $[Ru(2,2'\text{-}bpy)_2(4\text{-}pyNHCOCH{=}CHPh)_2]^{2+}$ (II). The copolymer film is prepared on Pt electrodes by an established electroreductive polymerization method[2] using solution mixtures of I and II. Illustrative cyclic voltammetry of two copolymer films[3] is shown in Figure 1. The mole fraction, X_{Os}, of osmium sites observed in the film[5] is identical with the mole fraction of I in the solution monomer mixture; I and II individually electroreductively homopolymerize to form films at nearly identical rates,[2f] and angular resolved XPS detects no systematic variation of the Os/Ru ratio over the first few outer copolymer layers. These facts, documented elsewhere,[6] plus the great structural similarity of I and II, lead us to propose that the Os redox sites are randomly dispersed in a structurally isomorphous sea of copolymer Ru sites. Such an ideal, variable-composition redox copolymer has not been described heretofore.

Electrons are transported through redox polymers[7] by hopping between redox sites. The overall transport rate is measurable[8] as a diffusion constant, D_{ct}, but the detailed electron-transport rate-limiting factors remain poorly understood despite much discussion.[8,9] Central to this issue is determining how D_{ct} depends on the concentration of redox sites in the polymer. There is generally unrecognized difficulty with how to properly vary the redox site concentration yet at the same time avoid extraneous influences on D_{ct} caused by replacing the redox site with a *dissimilar diluent site*, since solvent swelling,[8d,9c] cross-linking,[9b] and other aspects of internal polymer structure[9d] can also be thereby altered. The copolymer of I and II deals with this problem by diluting the Os sites with Ru polymer sites identical in all structural and electrostatic respects but not electroactive at the same potential (Figure 1).

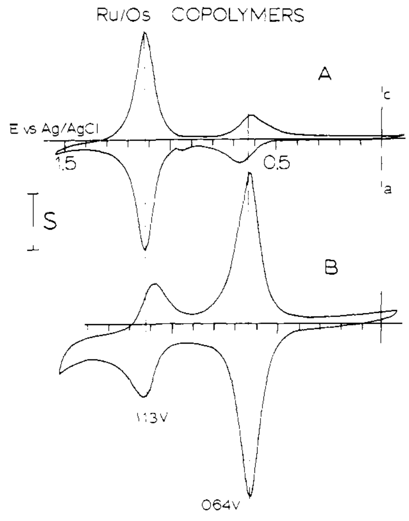

Figure 1. Steady-state cyclic voltammograms of I and II copolymer films on Pt in 0.1 M Et_4NClO_4/CH_3CN where $X_{Os} = 0.20$ (curve A) and 0.70 (curve B). Vertical lines represent $E^0{}_{surf}$ for Os(III/II) and Ru(III/II) at 0.64 and 1.13 V vs. Ag/AgCl, respectively. Note ΔE_p and diffusionlike tailing for the Os(III/II) wave in curve A and for the Ru(III/II) wave in curve B, reflecting slow charge transport at low X_{Os} and X_{Ru} (S = 250 $\mu A/cm^2$). The potential of Ag/AgCl is within 5 mV of SSCE.

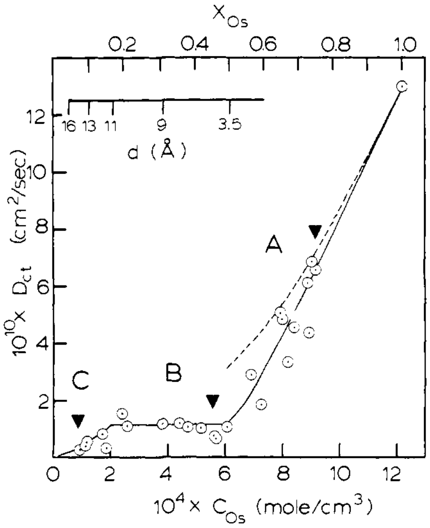

Figure 2. Dependence of charge-transport diffusion coefficient D_{ct} on X_{Os} and C_{Os} for the Os(II) → Os(III) oxidation in films of copolymer I and II. d is edge-to-edge separation of Os complex sites at various X_{Os}. Activation energies measured at the pointers (X_{Os} = 0.074, 0.45, 0.74) are 11.2, 6.4, and 3.6 kcal/mol, respectively.

Qualitatively, Figure 1 immediately shows that the rate of electron transport D_{ct} between Os sites is decreased by decreasing X_{Os}. At high X_{Os} (curve B), the Os(3+/2+) wave is symmetrically shaped with small ΔE_p, symptomatic of fast transport, whereas at low X_{Os} (curve A), the wave has a diffusionlike tail and larger ΔE_p, indicating much slower electron transport. The Ru(3+/2+) wave shows analogous behavior. D_{ct} for Os sites was measured by chronoamperometry;[8a,10] results are given in Figure 2. Three

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(1) I is bis(2,2'-bipyridyl)bis(*N*-4-pyridylcinnamamide)osmium(II) hexafluorophosphate.

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(3) The reactions are the M(3+/2+) couples of I and II at 0.64 and 0.13 V vs. Ag/AgCl, respectively. The quantities of I and II in the film are measured by the charges under slow potential scan cyclic voltammograms at scan rates where the charges (e.g., coverage, Γ_{Os}, Γ_{Ru}, mol/cm²) are independent of scan rate. Spectrophotometry[2e,4] of a closely related Ru homopolymer film confirms that such Γ values represent the total amount of redox sites present in these films. The quantity of Os sites is expressed as coverage (Γ_{Os}), mole fraction $X_{Os} = \Gamma_{Os}/(\Gamma_{Os} + \Gamma_{Ru})$, or concentration $C_{Os} = C_{Os}/d$ where d is film thickness based on 1.35 g/cm³ film density.[2a]

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regions of behavior are evident: in region A the rate of transport decreases from $X_{Os} = 1.0$ to ca. 0.50, then becomes relatively independent (region B) of X_{Os} when $X_{Os} = 0.50$–0.15, and (region C) decreases further at $X_{Os} < 0.15$. D_{ct} changes overall by ca. 10^2 times as the Os sites are isomorphically diluted from 1.2 to 0.10 M. This pattern of behavior has not been revealed in any of the prior redox site concentration studies[9b,9d] of D_{ct}.

We offer the following scheme in explanation of Figure 2:

$$Os^{2+} + [Ru^{2+},Os^{3+}] \rightarrow Ru^{2+} + [Os^{2+},Os^{3+}] \quad (1)$$

$$[Os^{2+},Os^{3+}] \xrightarrow{\tau} [Os^{3+},Os^{2+}] \quad (2)$$

$$Ru^{2+} + [Os^{3+},Os^{2+}] \rightarrow Os^{3+} + [Ru^{2+},Os^{2+}] \quad (3)$$

The symbols represent different redox site locations in the polymer, and nearest neighbors are in brackets. The scheme assumes that electron hopping (reaction 2) occurs solely between nearest neighbor Os/Os site pairs, with time constant τ. Calculation of the rate of reaction 2 by a random walk model[6,11] in which the forward, reverse, and lateral electron-jump probabilities are defined as, respectively, $P(d_n,d_{n+1})$, $P(d_n,d_{n-1})$ (both equal to $X_{Os}{}^2/2$), and $P(d_n,d_n)$ $(=1 - X_{Os}{}^2)$ is in excellent agreement with experiment (dashed line, Figure 2). This shows that the X_{Os} dependence of D_{ct} in region A can be accounted for simply by the statistical population of Os/Os site pairs.

The simple statistical calculation fails for more dilute copolymers because it assumes that the redox polymer sites are completely stationary. We propose that in region B, polymer self-diffusive motions generate additional, reactive, Os/Os nearest neighbor pairs, as in reaction 1, and also by the elastic reverse diffusion reaction (3) act to aid translocation of electron-bearing Os^{2+} sites toward the electrode. These two factors conspire to make D_{ct} relatively insensitive to X_{Os} over region B.

The polymer motions must have considerable frequency since region B begins at a X_{OS} where the Os/Os nearest neighbor population is still high, approximately equal to that of Ru/Os neighbors. Interestingly, when X_{Os} is such that there are on the average *no* Os/Os nearest neighbor pairs (complex edge-to-edge distance exceeds ca. 11–12 Å), D_{ct} begins to decrease further, starting region C. Now, reaction 1 does not just supplement reaction 2 but is required for any electron transport at all. It is reasonable to assume that elastic polymer diffusive motions away from a site's equilibrium position occur considerably more slowly as they are required to occur with larger amplitude, and so D_{ct} in region C represents a concentration-dependent self-diffusion constant for Os redox sites in the polymer.

Activation barrier studies are consistent with the above assignments of regions A–C. The thermal barrier ΔE_a decreases in the order C > B > A (11.2, 6.4, and 3.6 kcal/mol, respectively) and remains approximately constant in region A. Furthermore, the differing barriers mean that Figure 2 can take on different shapes at different temperatures as the several kinetic factors change their relative importance. These effects will be described in the full paper.[6]

Finally, reactions 1 and 3 have cautioning implications for use of redox polymers as models to study distance-of-electron-transfer phenomena, since in them we regard the sites as not "stationary". The diffusive motions would blur attempts at exponential term correlation[14] of average site–site distances with the electron-transport rate. Also, when the redox sites are not affixed to the polymer as they are here but are counterions of ion exchange polymer films,[15] site mobility clearly plays a major and perhaps dominating role.

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(10) This method involves a potential step from 0.40 to 0.90 V, plotting anodic current for Os(2+ → 3+) reaction vs. $t^{-1/2}$ and taking D_{ct} from the linear short time slope by using the equation $i = nFAD_{ct}{}^{1/2}C_{Os}/(\Pi t)^{1/2}$. D_{ct} is reproducible to ca. 8% for a given electrode film and to ca. 15% for different films having the same X_{Os}. Potential steps to 0.98 V produce identical results, showing the Ru sites remain uninvolved in electron transport. Full details are reported elsewhere.[6]

(11) In the calculation, an electron originating at distance coordinate $d_n = 0$ is allowed to undergo a 250-step random walk a total of 20000 times, each time with notation of the final d_n coordinate of the particle, thus generating a curve for frequency of occurrence vs. displacement from origin. The variance σ^2 of this gaussian curve measured in terms of d is the rms displacement for an "average" electron,[12] thus $D_{ct} = \sigma^2/2(250)\tau$. These calculations done for a series of X_{Os} generated the result in Figure 2, dashed line, where $1/\tau = 1.3 \times 10^5\ s^{-1}$ is normalized for D_{ct} at $X_{Os} = 1$ and the jump distance[13] 14.2 Å. We are not aware of analogous random walk calculations having been done.

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Generation of Superoxide in a Cobalt(II) Tetraphenylporphyrin–Thiolate–Oxygen System

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Superoxide, O_2^-, has been shown to be generated in several biochemical and chemical reactions[1,2] such as the xanthine oxidase system,[3] hydrogen peroxide–periodate system,[3] pulse radiolysis of oxygenated aqueous solution,[4] electrochemical reduction of oxygen in an organic solvent,[5] and potassium superoxide in Me_2SO.[6,7] In these studies, EPR spectroscopy has proved useful for unambiguous identification of superoxide. The first clear evidence for the presence of the superoxide was obtained by the rapid freezing technique of Bray.[3] The asymmetric free radical, O_2^-, gives an EPR signal with a $g_\perp$ at about 2.00 and a $g_\parallel$ component of low amplitude at about 2.08.

Since oxygen acitvation in heme proteins such as cytochrome *P*-450 monooxygenases and some oxidases involving electron transfer from iron plays a central role in the catalytic activities of these enzymes,[8] it is essential to construct model systems involving a one-electron reductant for oxygen using metal ion such as iron and cobalt ions. In fact, studies have been made on a number of superoxide complexes of transition metals, especially cobalt, prepared by reacting a lower valence transition-metal complex with O_2.[9–12] However, little is known about the gen-

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(7) Abbreviations: Me_2SO, dimethyl sulfoxide; EPR, electron spin resonance; TPP, *meso*-tetraphenylporphyrinato; Me_4NOH, tetramethylammonium hydroxide; TGE, thioglycolic acid ethyl ester; P-450_{cam}, cytochrome *P*-450 from *Pseudomonas Putida*.

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