Limit of Slow Diffusion to Electrodes: Molecule-Scale Diffusion Paths in a Redox Melt

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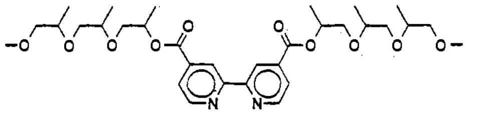
This report describes the time dependency for electrolysis of diffusing reactants that at $t = 0$ already contact or are within a few molecular diameters of the electrode surface. The path length L of a diffusing reactant during an electrolysis of duration t is[1a] $L = (2Dt)^{1/2}$. Short reactant path lengths have occurred in investigations of nanoscopic electrodes[2] and ultrashort electrolysis times at microelectrodes,[3] but experiments in which the diffusion of molecules to electrodes is confined to distances comparable to their own dimensions, "molecule-scale diffusion", have not been reported. Rates of molecule-scale near-surface transport should probe effects of interfacial structural organization (relative to bulk) and potential distribution, and the relation of near-surface transport to electrode kinetics.

We have approached this subject by seeking extremely slow diffusion (small D) and report here molecule-scale diffusion based on the bulky metal complex $[\mathrm{Co(bpy(pppm)_2)_3}]^{2+}$, $\mathbf{I}^{2+}$, in its clear yellow, room temperature molten salt, $\mathbf{I}^{2+}\ (\mathrm{ClO_4^-})_2$.

bpy(pppm)$_2$ =



The metal–metal spacing[4] of the *ca.* 0.6 M Co(II) sites in this extremely viscous material is *ca.* 18 Å.

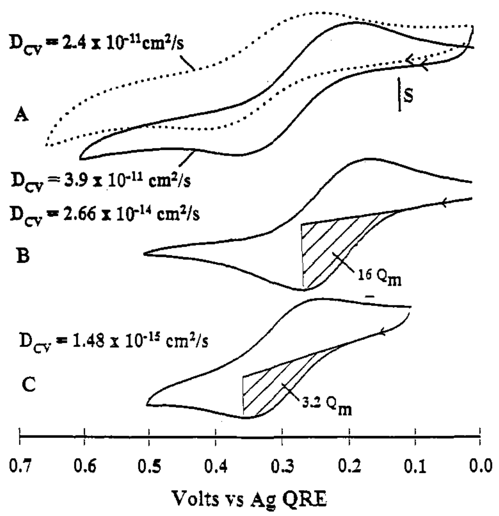


Figure I. (A) $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$ dissolved in 2000 MW poly(propylene oxide), solid line, 19 mM $\mathbf{I}^{2+}$, LiClO$_4$ electrolyte at 16:1 (ether oxygen):Li, v = 0.500 mV/s, S = 100 pA; dashed line, 7.4 mM $\mathbf{I}^{2+}$, Mg(ClO$_4$)$_2$/LiClO$_4$ electrolyte at 16:1 O:M (M = 4:1 Li:Mg), v = 0.250 mV/s, S = 20 pA; (B) undiluted $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$, no added electrolyte, v = 0.500 mV/s, S = 2 pA, Q_M = charge to oxidize one monolayer of $\mathbf{I}^{2+}(\mathrm{ClO_4})_2$ (see text); (C) undiluted $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$, LiClO$_4$ electrolyte at 16:1 O:Li, v = 0.500 mV/s, S = 15 pA; working electrode (A, C) Pt microband $A = 1.6 \times 10^{-4}$ cm^2, (B) Pt microdisk $A = 4.9 \times 10^{-6}$ cm^2. Diffusion coefficients calculated from Randles–Sevcik equation.[1b]

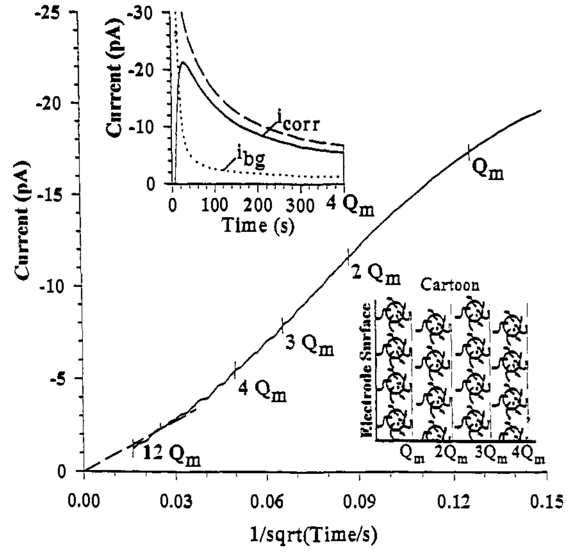


Figure 2. Current–time response to 400 s (experiment continued to 4000 s, not shown) in upper left inset (background transient i_{bg} collected in a "double layer" potential region), plotted according to Cottrell equation,[1c] for Co(II/III) oxidation by a 0-V to 0.6-V potential step at Pt microband ($A = 1.6 \times 10^{-4}$ cm^2) in undiluted $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$, LiClO$_4$ electrolyte at 16:1 O:Li, marks on Cottrell plot are for multiples of the charge Q_M; $4Q_M$ corresponds, for example, to reaction of the first four monolayers as illustrated in the cartoon.

Figure 1 shows voltammetry[5] for the Co$^{2+/3+}$ oxidation of $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$, (A) dissolved in linear poly(propylene oxide) (PPO) containing LiClO$_4$ or LiClO$_4$/Mg(ClO$_4$)$_2$ electrolyte, and as an undiluted $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$ melt with (B) no added electrolyte or (C) dissolved LiClO$_4$. The diffusion coefficients[1b] of $\mathbf{I}^{2+}$ in these media become progressively smaller. Of the two electrolytes in linear PPO, $\mathbf{I}^{2+}$ (Figure 1A) diffuses more slowly with the strongly ether-coordinating Mg^{2+}. However, in an undiluted state (Figure 1B), $\mathbf{I}^{2+}$ self-diffuses much more slowly,[6] especially when LiClO$_4$ is added (Figure 1C). While the reason(s) for the extremely slow $\mathbf{I}^{2+}$ self-diffusivity are not yet understood—possibly arising through self-entanglement and ionic self-association—the self-diffusivities of $\mathbf{I}^{2+}$ in its melt are interestingly small. Considering the charge Q_M (6.44×10^{-6} C/cm^2) to oxidize a monolayer (6.6×10^{-11} mol/cm^2) of $\mathbf{I}^{2+}$, the equivalent of only three monolayers in the $\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$ melt have become oxidized at the voltammetric peak in Figure 1C.

A potential step current–time response for $\mathbf{I}^{2+}$ oxidation in the LiClO$_4$/$\mathbf{I}^{2+}(\mathrm{ClO_4^-})_2$ mixture is shown in Figure 2, inset. According to Figure 1C and the Nernst equation, the 0.6-V final potential should drive the surface concentration of the Co(II) form of $\mathbf{I}^{2+}$ to 0. The background current-corrected transient indicates that interfacial potential control is attained at electrolysis

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(1) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 129. (b) D calculated from i_{peak} assuming linear diffusion (ref 1a, p 218). Ionic migration may depress D by *ca.* 3-fold in Figure 1B, there being no added electrolyte. (c) Cottrell equation, $i = nFAD^{1/2}C/(\pi t)^{1/2}$, ref 1a, p 143.

(2) Seibold, J. D.; Scott, E. R.; White, H. S. *J. Electroanal. Chem.* **1989**, *264*, 281.

(3) Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. *J. Phys. Chem.* **1988**, *92*, 5992.

(4) Calculated from $2[3/(4\pi CN_A)]^{1/3}$ where C is concentration (mol/cm^3).

(5) (a) Thin films of $\mathbf{I}^{2+}(\mathrm{ClO_4})_2$ (100 μm) were cast from solvent onto upward-facing electrodes to ensure uniform contact and were dried in vacuum for 18 h. Use of small potential sweep rates (BAS 100B potentiostat) and microelectrodes (12.5-μm-radius Pt disks[4b] or 2.3-μm-wide, 7-mm-long Pt microbands with flanking Ag reference bands 2 μm away[4c]) minimizes uncompensated resistance distortions. Results were reproducible in multiple experiments and when repeated over intervals of several days. (b) Wooster, T. T.; Longmire, M. L.; Zhang, H.; Watanabe, M.; Murray, R. W. *Anal. Chem.* **1992**, *64*, 1132. (c) Porat, Z., unpublished results, University of North Carolina, 1993.

(6) (a) $\mathbf{I}^{2+}$ self-diffuses 10-fold more slowly than does the Co complex of the ethylene oxide trimer analog[6b] of pppm. (b) Velazquez, C. S.; Hutchison, J. E.; Murray, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 7896.

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times > 40 s. Analyzing the current–time response as for a diffusion-controlled electrode reaction,[1c] a *i vs* $t^{-1/2}$ plot (Figure 2) curves upward at short times, but approaches the expected linearity at longer times. The diffusion coefficient of I^{2+} obtained from the slope[1c] at the shortest time is $D = 1.3 \times 10^{-15}$ cm^2/s; that (– – –) at the longest is 8.4×10^{-16} cm^2/s.

The Figure 2 *i vs* $t^{-1/2}$ plot is remarkable in several respects. Firstly, the charge under the current–time response shows that although the electrolysis was continued for 4000 s, the equivalent of only 12 monolayers ($12Q_M$) of I^{2+} became oxidized. Secondly, although only a partial current–time transient for oxidation of the very first monolayer (that nearest the electrode at $t = 0$) could be measured, the complete current–time transient during which the second and successive monolayers[7] of oxidative charge for diffusing I^{2+} are passed could be measured (see Q_M multiples and illustrative cartoon in Figure 2). Passage of the first, second, third, etc. monolayers of charge for I^{2+} oxidation of course does not occur in discretely sequential steps, because the relatively huge *lateral* dimension of the microband electrode will ensure a stochastic distribution in the reaction times of the overall near-surface I^{2+} population. Thus, even on monolayer distance scales, models of diffusion as a statistically averaged random walk retain physical significance.

It is instructive nonetheless to parameterize[1a,8] D as $k_{hop}\delta^2$ where k_{hop} and δ are hopping rate (s^{-1}) and length. Taking $\delta = 18$ Å, we calculate $k_{hop} = 0.04$ s^{-1} over the earliest electrolysis times usable in Figure 2. The current–time response in Figure 2 can alternatively be analyzed [ln(*i*) *vs t* plot] as a first-order decay of a reactive thin film,[9] in which the rate constant for consumption of the monolayer of I^{2+} initially adjacent to the electrode (k_{et}) is formally that of the electrochemical reaction itself. Such a plot for currents at $t = 60$–120 s gives $k_{et} = 0.006$ s^{-1}, a value close to the above k_{hop} rate.

That electrochemical reaction rates are controlled by either the rate of reactants diffusing to the electrode or their rate of electron transfer at the electrode, but not both, has been an important concept[1a] in the analysis of electrochemical experiments. The similarity of k_{et} and k_{hop} values in the above comparison emphasizes that these two processes must lose distinctiveness and converge when, as in the present case, the diffusion step can be measured for reactants already lying, at time zero, within 1 or 2 molecular diameters from the electrode surface. The similarity of k_{et} and k_{hop} values further indicates that the rate of oxidative electron transfer for I^{2+} is controlled by nuclear motions that have rates similar to those of center-of-mass transport (i.e., D) of the near-surface I^{2+} complexes. Whether these rates can be influenced by the size of the potential employed in the experiment is not yet known.

The third remarkable aspect of Figure 2 is that the apparent diffusion constants (or $k_{hop}\delta^2$ values) are larger for the I^{2+} complexes nearest the electrode. This aspect of the molecule-scale diffusion results has not yet been interpreted and will require further study. Its origin(s) may include (a) violation of electroneutrality within a "diffusion layer" whose depth is comparable to that of the electrical double layer,[10] (b) interfacial structure or dynamics differing intrinsically from that of the bulk, (c) a minor degree of interfacial homogeneous electron hopping[11] between I^{2+} and I^{3+}, and (d) the changing composition of the interfacial region [i.e., 0.6 M $I^{2+}(ClO_4^-)_2$ changes to 0.6 M $I^{3+}(ClO_4^-)_3$].

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(7) The molecule-scale resolution of the electrolysis is actually better than shown since microscopic Pt surface roughness (*ca.* 1.5×) is neglected in estimating the Q_M value.

(8) Druger, S. D.; Nitzan, A.; Ratner, M. A. *J. Chem. Phys.* **1983**, *79*, 3133.

(9) Chidsey, C. E. D. *Science* **1991**, *251*, 919.

(10) (a) Smith, C. P.; White, H. S. *Anal. Chem.* **1993**, *65*, 3343. (b) The double layer may also be nonclassical since ClO_4^- and I^{2+} probably have differing distances of closest approach to the electrode.

(11) (a) k_{ex} for $[Co(bpy)_3]^{2+/3+}$ in CH_3CN is 2 M^{-1} s^{-1}. Homogeneous self-exchange would contribute[6b] noticeably to diffusion if k_{ex} for I^{2+}/I^{3+} were ≥ 0.4 M^{-1} s^{-1}. On the basis of the observed 10^3-fold depression[6b] of the homogeneous k_{ex} for Co(II/I) in the undiluted trimer analog of I^{2+} and the 13-fold depression of the heterogeneous rate for $[Co(bpy)_3]^{2+/3+}$ in network PEO[11b] (relative to CH_3CN solvent), it is unlikely, however, that the I^{2+}/I^{3+} k_{ex} is large enough to affect D. (b) Wooster, T. T.; Longmire, M. L.; Watanabe, M.; Murray, R. W. *J. Phys. Chem.* **1991**, *95*, 5315.