

## ON THE MODELLING OF CHARGE TRANSPORT IN MODIFIED ELECTRODES

M V SANGARANARAYANAN

Central Electrochemical Research Institute, Karaikudi-623006, INDIA

## INTRODUCTION

The theoretical analysis of charge transport through modified electrodes containing immobilised redox centres is fascinating on account of several competing processes occurring simultaneously at the interface(s) and also because the starting equations are governed by the scene of action (electrode/film interface or film/solution interface) in which the mechanism of the process viz. physical diffusion vs extended electron transfer plays a significant role. Amidst such a scenario, it becomes imperative to analyse prototype systems that offer wide variations in their characteristics (such as thickness/loading, pH effects, supporting electrolyte, etc.) without causing substantial perturbation in the polymer matrix, so that the dynamic effects can be entangled from structural considerations [1,2]. Among the systems fulfilling this criteria, mention may be made of ferrocene polymers, iridium, osmium, and ruthenium complexes.

Whatever be the potential use envisaged for chemically modified electrodes (electrocatalysis/redox polymer batteries/biosensors etc.), the crucial role played by charge transport\* in toto cannot be underestimated.

Our emphasis in the present report is on a critical appraisal of the 'electron diffusion coefficient' ( $D_{et}$ ) since the latter has been presumed to be a measure of the facility with which electron transport occurs. We also discuss in passing, the formulation of the diffusion migration equation and the subtleties associated with it.

## ELECTRON TRANSPORT BY HOPPING MECHANISM

Since electron transport occurs via the immobilised redox centres whose spatial separation is a priori, unknown (but decidedly dependent upon film thickness), it is customary to postulate an electron hopping mechanism and characterise the hopping process in terms of an 'electron diffusion coefficient'.  $D_{et}$  is experimentally obtained using chronocoulometry\*\* as

$$D_{et} = \frac{S^2\pi}{(2nFC)^2} \quad (1)$$

where  $S$  is the slope of the 'Anson Plot' and  $C$  is the mediator concentration in the film which is proportional to the loading value  $\Gamma$ . If hopping is the mechanism by which electron transfer is postulated to occur, we may intuitively perceive that the more the number density of redox centres, the more facile should be the hopping process. This physical intuition has served as the basis for

\* While electron transport takes place between immobilised redox centres, it is accompanied by the flow of counter ions etc. so as to maintain electroneutrality. Added to this, the segmental motion of the polymer chain may occur either preceding or succeeding the movement of constituent species [1] and hence the noncommittal term, 'charge transport' is employed.

\*\* The precise choice of the experimental techniques, transient as well as steady-state methods to characterise the charge transport phenomena is being debated [3-7].

employing the classical Dahms - Ruff model [8-10] which predicts a linear increase in  $D_{et}$  with the concentration of redox centres viz.

$$D_{et} \sim k_{ex}(r^2)C_0 \quad (2)$$

While a large number of experimental studies have supported the above simple equation, the exceptions are too many and too varied, to demand a closer scrutiny, even in cases where it is found to be obeyed. The fact that the 'concentration' dependence of  $D_{et}$  as predicted by equation (2) is too simplistic has been recognised (cf. Fig. 27 of [1] and repeated cautions\* of Anson et al [11-13]. Had a monotonic increase with  $C_0$  been realistic, mere loading with the maximum number of redox centres would suffice for the preparation of an efficient electrocatalyst! However, as  $C_0$  increases, other factors such as reduction in the electron self exchange rate or decrease in the rate of short range diffusive motion may come into play, thereby making the translation of  $D_{et}$  into  $K_{ex}$  values unclear [14] and may even cause a change in the rate determining step, thus invalidating the analysis in terms of  $D_{et}$  itself. Diverse number density dependences of  $D_{et}$  have been experimentally observed [11-22] and a quantitative theory is still lacking. A recent report [21] concerning the charge transfer kinetics of  $[Ru(NH_3)_6]^{3+/2+}$  complex confined in montmorillonite clay coatings on graphite electrodes indicates the diffusion coefficient reaching a maximum as a function of  $C_0$ .

We hasten to add here that in most of the analysis ([21] being an exception) concerning the use of equation (2) to obtain  $D_{et}$ , the mean nearest neighbour distance ( $r$ ) is assumed to be constant irrespective of the incorporated number density of redox centres. To realise the qualitative consequences of this assumption we recall the classical result [24] for the mean nearest neighbour distance for point molecules, viz.

$$\langle r \rangle = \Gamma(4/3)(3/4\pi n)^{1/3} \quad (3)$$

and

$$\langle r^2 \rangle = \Gamma(5/3)(3/4\pi n)^{2/3} \quad (4)$$

By using equation (4), we may obtain as a first approximation

$$D_{et} \sim k_{ex}C_0^{1/3} \quad (5)$$

thereby demonstrating the nonlinear increase with  $C_0$ .

While this indicates the nontrivial manner in which ( $r$ ) can qualitatively influence the behaviour of  $D_{et}$ , the role of  $K_{ex}$  is not insignificant. For example, in [12], the diffusion coefficient of  $C_0(bpy)_3^{2+}$  in Nafion coatings was measured both by reducing to  $C_0(bpy)_3^+$  ( $D_{2/1}$ ) and by oxidising to  $C_0(bpy)_3^{3+}$  ( $D_{2/3}$ ). While the diffusion coefficient  $D_{2/1}$  showed a significant increase with concentration,  $D_{2/3}$  decreased with concentration somewhat moderately. Furthermore, it is even suggested [15] that  $K_{ex}$  in equation (2) can be replaced by the classical expression for the observed rate constant  $k$  as

$$1/k = 1/k_{ex} + 1/k_d \quad (6)$$

\* Equation (2) is valid only when  $D_{ox} = D_{red}$  and is in fact, a simplified version of the more general equation [9].

where  $k_d$  denotes the diffusion limited rate constant\*.

Thus He and Chen [15] indicate that while  $k_{ex}$  for  $Ru(bpy)_3^{2+/3+}$  is  $\sim 10^9 M^{-1} sec^{-1}$ , the diffusion controlled rate constant  $k_d$  is  $\sim 10^4 M^{-1}sec^{-1}$ . Hence if we replace  $k_{ex}$  of equation (2) by  $k$  and incorporate the enhancement factor  $f$ , so as to include the probability of finding more than one acceptor in the given 'hemisphere' equation (2) gets modified as

$$D_{et} \propto k(r^2) f^2 C_o \quad (7)$$

where  $f$  has an involved dependence on  $C_o$ . This modification alone is shown to yield an exponential increase of  $D_{et}$  with  $C_o$  and explain the observed  $D_{et}$  in the case of charge transport of  $Ru(bpy)_3^{2+/3+}$  and  $Os(bpy)_3^{2+/3+}$  in Nafion films. Faulkner et al [19] have considered a more sophisticated version of the above approach [15] by including a distance-dependent rate constant and the random distribution of hard spheres/disks and quantitatively explained observed exponential increase of  $D_{et}$  with concentration, in certain metalloprotein and steroid spacer systems. We also note nearly similar values of diffusion coefficients for  $Co(bpy)^{2+}$  and  $Ru(bpy)_3^{2+}$  reported in Nafion coatings [17] even though the self-exchange rate constants of the latter is  $\sim 10^8$  times the former.

We reiterate, therefore, that both the system parameters entering into equation (2) viz.  $\langle r \rangle$  and  $k_{ex}$  are amenable for further modelling thus obviating at least partially, the need for invoking changes in rate-determining steps in an effort to explain away the experimental behaviour.

#### DISTRIBUTION OF NEAREST NEIGHBOUR DISTANCES

The classical result for the mean nearest neighbour distance in a random distribution of point molecules is given by equation (3). Its extension to hard spheres and hard disks for moderate number densities is relatively recent and is due to Faulkner et al [19] viz.,

$$\langle r \rangle = r_o \eta^{-1/3} \exp(\eta) \Gamma(4/3, \eta) \quad (8)$$

where  $\Gamma(a, x)$  denotes the incomplete Gamma function and  $\eta = 4\pi r_o^3 n/3$  and  $r_o$  denotes the hard sphere diameter. Elsewhere [35], we have extended this result further and reported  $\langle r \rangle$  and  $\langle r^2 \rangle$  as

$$\langle r \rangle = r_o (\eta^*)^{-1/3} \exp(\eta^*) \Gamma(4/3, \eta^*) \quad (9)$$

where  $\eta^* = 4\pi r_o^3 n^*/3$  and  $n^* = n/[1 - r_o(n/2)^{1/3}]^3$ . Further,  $\langle r^2 \rangle$  for hard spheres follows as

$$\langle r^2 \rangle = r_o (\eta^*)^{-2/3} \exp(\eta^*) \Gamma(5/3, \eta^*) \quad (10)$$

The significance of the above equation for  $\langle r \rangle$  is that it reproduces the classical result for point molecules as well as that of Faulkner et al [19] at low concentrations. Further, at close packing density  $\langle r \rangle \rightarrow r_o$ , the hard sphere diameter. Though the above equation may be further improved, our main emphasis in the above formalism is to point out the involved functional dependence of  $\langle r \rangle$  on  $C_o$ , and hence of  $D_{et}$  even if  $K_{ex}$  is not<sup>†</sup> dependent on  $\langle r \rangle$ . If we assume an exponentially decreasing distance-dependence for rate constants, we obtain [29]

$$\langle r^2 \rangle = \int_0^\infty y^2 \exp(-\beta y) w(y) dy \quad (11)$$

\* Lest it should be presumed that  $k_d$  is not influenced by probabilistic notions, we emphasize that in diffusion limited reactions, the rate constant may be represented [23] as  $k_a w(y)$  dy where  $k_a$  is the activation controlled rate constant and  $w(y)$  is the probability distribution of the 'encounter pair'

† In the field of many body theory [26-28] concerning transport in disordered systems, the crucial parameter of interest is the time dependence of  $\langle r^2(t) \rangle$  and the analysis of  $(d/dt) \langle r^2(t) \rangle$  furnishes enlightening insights into the dynamics of the process.

where  $w(y)$  denotes the distribution of hopping distances.

Since electron hopping is postulated\* to occur among the (randomly distributed) redox centres, the rate at which hopping takes place depends upon the distance of separation. In line with studies concerning electron transfer in biological system [33] hopping conduction [34] in amorphous materials, let us consider the following form for the rate constant  $k(r)$ , viz.,

$$k(r) \sim A(\Delta\phi) \exp(-\alpha r) \quad (12)$$

where the pre-exponential factor  $A$  in our context is dependent upon the appropriate potential differences which is, strictly speaking a function of the (mean) distance between redox centres. To obtain an ensemble averaged rate constant, the distribution of hopping distances is required. By assuming the familiar Hertz distribution in three dimensions, for point molecules ( $k(r)$ ) becomes\*\*

$$\langle k(r) \rangle = A[1 - z \text{Hi}(-z)] \quad (13)$$

where

$$\text{Hi}(z) = (1/\pi) \int_0^\infty \exp(-t^{3/3} + zt) dt \quad (14)$$

denotes a type of Airy function [25].  $z$  in equation (13) is dependent on number density of redox centres  $n$  as  $z = \alpha/(4\pi n)^{1/3}$ . Further, if we combine equations (4) and (13) and employ, as a first approximation, \*

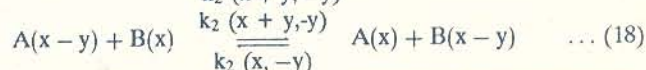
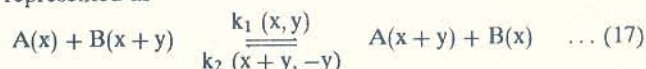
$$D_{et} = \langle k(r) \rangle \langle r^2 \rangle / 6 \quad (15)$$

several types of number density dependence of  $D_{et}$  are obtained. Our main aim in this endeavour has been to indicate, what one should anticipate if one were to model the hopping rate constant and the mean nn distances stochastically. The results for  $D_{et}$  perforce have now become nonanalytical.

The foregoing formalistic analysis has, however, not taken into account the interaction between sites and their influence on  $D_{et}$  [37], nor has the potential distribution been modelled. To tackle these issues at a conceptual level, we briefly indicate the derivation of diffusion migration equation.

#### A GENERALISED DIFFUSION - MIGRATION EQUATION

The scheme for distance dependent self exchange reactions may be represented as



wherein the hopping distance  $y$  is a continuous random variable. Incorporating the potential and distance dependences into the rate constants and keeping for the sake of generality the parameters  $m$  and  $n$  as reaction orders with respect to  $A$  and  $B$ , we obtain

\* Doblhofer et al have consistently [30-32] maintained the view that the contribution of electron hopping to charge transport phenomena is not significant.

\*\*For an arbitrary distribution  $F(r)$ ,  $\langle k(r) \rangle$  is

$$\langle k(r) \rangle = A \int_0^\infty \exp(-\alpha r) F(r) dr \quad (16)$$

whereas the analysis of [19] approximates (i)  $\langle k(r) \rangle$  as  $A \exp(-\alpha \langle r \rangle)$  and (ii)  $\langle r^2 \rangle$  as  $(\langle r \rangle)^2$

\* A more microscopic description would start with the generalised master equation for the time evolution of a given site and derive [36] the frequency dependent diffusion coefficient using lattice gas models, as a function of the effective jump rate and the concentration of the particles.

$$\frac{\partial A}{\partial t} = k_0 \langle x^2 \rangle \left\{ m \frac{\partial}{\partial x} [A^{m-1} B^n A'] - n \frac{\partial}{\partial x} [A^m B^{n-1} B'] + (F/RT) \partial / \partial x \right. \\ \left. [A^m B^n \Gamma] \right\} \quad \dots (19)$$

where A', B' and  $\Gamma$  denote, respectively,  $\partial A / \partial x$ ,  $\partial B / \partial x$  and  $d \phi / dx$ . Interestingly,  $\langle r^2 \rangle$  is obtained as

$$\langle r^2 \rangle = \int_0^{\infty} y^2 \exp(-\beta y) w(y) dy \quad \dots (11)$$

wherein  $w(y)$  denotes the probability distribution of hopping distances. We may note [29] the flexibility this approach offers in deriving several types of number density dependences of  $D_{et}$  solely based on models\* for  $w(y)$ . Further, the substitution in equation (19) of (i)  $m = 0$  and  $n = 1$  leads to the classical Nernst Planck equation\*\* [39] and (ii)  $m = n = 1$  leads to the transport equation of [38].

The aforesaid discussion, though by no means complete, serves to illustrate the interesting features concerning the modelling of  $D_{et}$ . Several finer aspects, such as the region of validity of Cottrell plots, the influence of electrodynamic effects etc. remain to be investigated in order to obtain a comprehensive picture.

## REFERENCES

1. R W Murray In *Electro-analytical Chemistry*, (Ed) A J Bard, Vol 13, Marcel Dekker, New York, (1983) p 191
2. L R Faulkner, *Electrochim Acta*, **34** (1989) 1699
3. B Lindholm, *J Electroanal Chem Interfacial Electrochem*, **250** (1988) 341
4. B Lindholm, *J Electroanal Chem Interfacial Electrochem*, **289** (1991) 85
5. X Chen, P He and L R Faulkner, *J Electroanal Chem Interfacial Electrochem*, **222** (1987) 223
6. Seung Mo Oh and R Faulkner, *J Electroanal Chem Interfacial Electrochem*, **269** (1989) 77
7. R H Schmehl and R W Murray, *J Electroanal Chem Interfacial Electrochem*, **152** (1983) 97
8. H Dahms, *J Phys Chem*, **72** (1968) 362
9. I Ruff and V Freidrich, *J Phys Chem*, **75** (1971) 3297
10. I Ruff, *Electrochim Acta*, **15** (1970) 1059
11. Y M Tsou and F C Anson, *J Phys Chem*, **89** (1985) 3818
12. D A Butry and F C Anson, *J Amer Chem Soc*, **105** (1983) 685
13. K Shigehara, N Oyama and F C Anson, *J Amer Chem Soc*, **103** (1981) 2552
14. J Facci and R W Murray, *J Phys Chem*, **85** (1981) 2870
15. P He and X Chen, *J Electroanal Chem Interfacial Electrochem*, **256** (1988) 353
16. J Ochmanska and P G Pickup, *J Electroanal Chem Interfacial Electrochem*, **297** (1991) 197
17. D A Butry and F C Anson, *J Electroanal Chem Interfacial Electrochem*, **130** (1981) 333
18. L R Whiteley and C R Martin, *J Phys Chem*, **93** (1989) 4650
19. I Fritsch - Faules and L R Faulkner, *J Electroanal Chem Interfacial Electrochem*, **263** (1989) 237
20. J S Facci, R H Schmehl and R W Murray, *J Amer Chem Soc*, **104** (1982) 4959
21. T Okajima, T Ohsaka and N Oyama, *J Electroanal Chem Interfacial Electrochem*, **315** (1991) 175
22. N Oyama, S Yamaguchi, Y Nishiki, K Tokuda, H Matsuda and F C Anson, *J Electroanal Chem Interfacial Electrochem*, **139** (1982) 371
23. See for example, S A Rice Diffusion Limited Reactions in *Comprehensive Chemical Kinetics*, Vol 25 (Ed) C H Banford and R G Compton, Chapter 2
24. S Chandrasekar, *Rev Mod Phys*, **15** (1943) 1
25. *Handbook of Mathematical Functions*, (Ed) M Abramovitz and I A Stegun, Dover, New York (1972)
26. H Scher and M Lax, *Phys Rev*, **B 7** (1973) 4491
27. H Scher and M Lax, *Phys Rev*, **B 7** (1973) 4502
28. See for example, G Zumofen and A Blymen, *J Chem Phys*, **76** (1982) 3713 and references therein
29. L Srinivasa Mohan and M V Sangaranarayanan (to be published)
30. K Doblhofer, H Brawn and R Lange, *J Electroanal Chem Interfacial Electrochem*, **206** (1986) 93
31. R Lange and K Doblhofer, *J Electroanal Chem Interfacial Electrochem*, **216** (1987) 241
32. K Doblhofer and R Lange, *J Electroanal Chem Interfacial Electrochem*, **229** (1987) 239
33. *Photo Induced Electron Transfer*, (Ed) M A Fox, M Chanon, Elsevier, Amsterdam (1988) Vols. A D
34. *Electronic Properties of Doped Semi Conductors*, (Ed) B I Shklovskii and A L Eforos, Springer Verlag, (1984)
35. L Srinivasa Mohan, M V Sangaranarayanan and S K Rangarajan, Extended Abstracts of the 180th ECS meeting, Phoenix, Arizona (Oct. 1991) Abst No 730
36. R Granek and A Nitzan, *J Chem Phys*, **92** (1990) 1329 and references therein
37. C E D Chidsey and R W Murray, *J Phys Chem*, **90** (1986) 1479
38. J M Save'ant, *J Electroanal Chem Interfacial Electrochem*, **201** (1986) 211
39. J Helfferich, *Ion Exchange*, McGraw Hill, New York (1981)
40. M L Kagan, R Kosloff, O Citri and D Avnir, *J Phys Chem*, **93** (1989) 2728
41. G Nicolis and V Altares, *J Phys Chem*, **93** (1989) 2861
42. Raima Larter, *Chem Rev*, **90** (1990) 355 and references therein

\* The study of concentration dependence of diffusion coefficient is a regular feature in the analysis of spatial patterns in reaction-diffusion systems [40,41].

\*\*The mathematical analysis of the Nernst Planck equation is interesting in its own right in that it can give rise to oscillatory instabilities when applied to ion exchange membranes (cf[42]).