Nernst equation complicated by electric random percolation at conducting polymer-coated electrodes

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Abstract

The Nernst equation in a stochastic process is defined when an electrode is coated with a conducting polymer. The electrode potential is determined by the ratio of the number of conductive (oxidized) species to that of the insulating (reduced) species experienced at the interface which is formed by electric percolation of the conductive domain to the substrate electrode. Examples of evaluating the potential are presented for the case where the film has a random distribution of the conductive and insulating species, in the following three models: a one-dimensional model, a seven-cube model and a cubic lattice model. In the one-dimensional model, which is a series connection of conductive and insulating rectangles on the substrate electrode, the electrode potential is obtained analytically as a function of the probability of finding the conductive species, \( p \), in the film. It reduces to the ordinary Nernst equation. The seven-cube model consists of six cubes surrounding a conductive cube. When some of the six cubes are conductive, pairs of conductive/conductive and insulating/conductive interfaces are counted for all configurations. For \( p < 0.4 \), the potential shifts positively from the ordinary Nernst equation. More realistic is the cubic lattice model, in which conductive sites are randomly distributed in a cubic lattice by the Monte Carlo method. The potential is evaluated numerically by tracing conductive domains percolated electrically to the electrode. The potential-\( p \) curve exhibits an angular variation at \( p = 0.31 \), indicating a second-order phase transition. The structure of the two phases is discussed in terms of the size of conductive clusters and the distribution of the clusters. Conductive sites for \( p < 0.31 \) are localized to the electrode, whereas those for \( p > 0.33 \) are uniform over the film. Conductive sites near the transition are fractal. The volumes and areas of the conductive clusters are expressed, respectively, by the 2.3 and 1.3 powers of the average radii of the clusters.

INTRODUCTION

A conducting polymer film synthesized on an electrode is easily interconverted between a conductive and an insulating state by redox reactions under electrochemical control [1,2]. The film, in general, does not take either state entirely, but is often
a mixture of both states depending on the electrode potential [3]. The potential of
the mixture may be given by the Nernst equation, as for a soluble redox couple [4].

A significant difference of the conducting polymer from a conventional redox
couple is the function of the electric conductive domain as an electrode for redox
reactions involving the interconversion. When current flows in the direction of
increasing the conductive domain, the insulating species in contact with the conduc-
tive domain may be converted electrochemically into the conductive species [5–10].
Then the conductive domain grows from the substrate electrode to the interface
between the film and the solution under charge-transfer control. A study on the
oxidation of polypyrrole films has demonstrated visually [10] that a well-defined
boundary between the conductive and the insulating domain moves from the
substrate to the top of the film.

The function of the conductive domain as an electrode may also play a role in
providing a redox potential under equilibrium. If a conductive micro-domain is
enclosed with the oxidized species, it exhibits a more positive potential than that at
a micro-domain surrounded mainly by the reduced species. Thus, the local potential
depends on the distribution of the redox species. If a micro-conductive domain is
isolated in an island form, it does not take part in determining the electrode
potential because of the loss of electric contact with the substrate electrode.
Consequently, only the domains with electric connection can work as an electrode
for determining the potential.

The simplest distribution is a random dispersion of the redox couple in a given
lattice. The statistical physics developed recently [11] has reported that a random
distribution provides extraordinary behaviour such as phase transitions due to
percolation. This paper is devoted to exploring the relation between the equilibrium
electrode potential and the fraction of the conductive species, by means of Monte
Carlo simulation at one- and three-dimensional cubic lattice models when the
conductive species is distributed randomly in a conducting polymer film.

MODELS AND SIMULATION

Definition of electrode potential

The system treated here is an electrode coated with a conducting polymer in a
solution involving an excess of dopant ions and supporting electrolyte. It is assumed
that the conductive site consists of the oxidized species, whereas the insulating site is
the reduced form and that both species are randomly distributed in the film.

The state of species $i$, where $i$ stands for the oxidized species O, the reduced
species R or an electron e, in a local volume of the film is expressed by the
electrochemical potential, $\mu_i$, which is given by the sum of the chemical potential
and the inner potential, $\phi$. When the film has a microscopically non-uniform
distribution of the redox couple, the chemical potential may be influenced by
fluctuation of the local activity. It is better to use the probability, $p_{O}$, of finding the
species in the local volume rather than the concentration because the activity or
concentration is conventionally defined as a macroscopic quantity. Then the electrochemical potential is given by

\[ \bar{\mu}_i = \mu_i^{\circ} + RT \ln \gamma_i \rho_i + z_i F \phi_i \quad (i: \text{O, R or e}) \]  

(1)

where \( \mu_i^{\circ} \) denotes the formal chemical potential of the species \( i \) whose activity coefficient is \( \gamma_i \) and whose charge number is \( z_i \). Under the local equilibrium, we have \( \bar{\mu}_R = \bar{\mu}_O + \bar{\mu}_e \). Considering the local potential defined by \( E_{\text{local}} = \phi_O + \phi_e - \phi_R \), we obtain

\[ E_{\text{local}} = E^{\circ} + (RT/nF) \ln \left[ \rho_O / \rho_R \right]_{\text{local}} \]  

(2)

where \( n \) is the number of electrons transferred. Here \( E^{\circ} \) is the formal potential defined by \( \mu_O^{\circ} + \mu_e^{\circ} - \mu_R^{\circ} + (RT/nF) \ln(\gamma_O / \gamma_R) \). It is assumed that \( \gamma_O / \gamma_R \) is independent of \( \rho_o \). This assumption is valid when interactions between O and O, O and R, and R and R are smaller than those arising from the dispersion forces.

In order to measure the local potential by the substrate electrode, the local site should be connected electrically to the substrate electrode through a conductive network. Otherwise, there might be no means of knowing the local potential to the substrate electrode. Equation (2) is then applicable only to the sites having the electric connection. The entire potential measured at the macroscopical substrate electrode is not always an algebraic average of \( E_{\text{local}} \) over such connected sites. The measured potential is given by the expected number of oxidized species, \( N_O \), or the reduced one, \( N_R \), found on the local interface. Let \( w(k) \) be the area of the interface on which the species \( i \) is found in the \( k \)-th site with the probability \( \rho_i(k) \). Then the expected number on the \( k \)-th interface is given by \( w(k) \rho_i(k) \). \( N_O \) and \( N_R \) are expressed by the integration of \( w(k) \rho_i(k) \):

\[ N_i = \int w(k) \rho_i(k) \, dk \quad (i: \text{O or R}) \]  

(3)

where the integration is carried out over the surface of all the conductive sites connected electrically to the substrate electrode. This expresses a macroscopic surface concentration. The potential, \( E \), measured at the substrate electrode is given by

\[ E = E^{\circ} + (RT/nF) \ln \left[ \int w(k) \rho_O(k) \, dk / \int w(k) \rho_R(k) \, dk \right] \]  

(4)

The distributions of \( \rho_O \) and \( \rho_R \) are assumed to be random in the present paper. The randomness corresponds to neglecting electrostatic interactions, aggregation force, and the difference in ion-pair formation. Introduction of the lattice is helpful for reducing the huge number of possible combinations of \( w(k) \) to a restricted number. In the following three sections, electrode potentials are evaluated at a random distribution in a one-dimensional model, a seven-cube model and a cubic lattice model.
Fig. 1. One-dimensional rectangular model.

One-dimensional model

This model is a linear array of conductive and insulating rectangles on the substrate electrode, as shown in Fig. 1. Each rectangle is assumed to be the smallest unit that can maintain the switching properties of the bulk polymer. The unit is not necessarily one polymer molecule. The interfaces determining the electrode potential are O/E, R/E, O/O' and R/O', where R denotes the insulating reduced species, O the conductive oxidized species, O' a conductive domain working as an electrode, and E is the electrode. O is the same as O' in the sense of the substance relevant to the redox reaction but is different in the function of the electrode. If either domain in a pair of O/O' plays a role in the redox function, the other one does in the electrode function. The interface R/R' cannot participate in determining the potential because of the loss of electric contact from the interface to the electrode. The length of the interface O/E or R/E of each unit is set to be a, while that of O/O' or R/O' is \( h \) (see Fig. 1).

The upper integral in eqn. (4) is proportional to the expected lengths of O/E and O/O' while the lower integral is proportional to those of R/E and R/O'. The expected lengths are now evaluated by distributing randomly all the rectangles on the electrode in a compact series. Let \( p \) be the fraction of the number of conductive units in all the rectangles. The expected lengths for the O/E and R/E interfaces are obviously \( pa \) and \( (1-p)a \), respectively. The probability of finding O/O' and R/O' can be evaluated inductively as follows: When there are two insulating units on both sides of a conductive unit, i.e. R/O'/R, two interfaces of R/O' are generated. Then the probability of making this configuration is \( p(1-p)^2 \). When indistinguishable \( k \) conductive units are arranged in a series lying between two insulating units, the probability is given by \( kp^k(1-p)^2 \), where the factor \( k \) has come from \( k \) arbitrary choices for the arrangements of the conductive units. Then \( k-1 \) pairs of the O/O' and two pairs of the R/O' interface are generated. The expected length of O/O' is \( k(k-1)p^k(1-p)^2h \), and that of R/O' is \( 2kp^k(1-p)^2h \). Since the arrangement is random, \( k \) ranges from unity to infinity. Thus, the expected length of O/O', \( L_{OO} \), and that of R/O', \( L_{RO} \), are expressed by

\[
L_{OO} = \sum_{k=1}^{\infty} k(k-1)p^k(1-p)^2h
\]

\[
L_{RO} = \sum_{k=1}^{\infty} 2kp^k(1-p)^2h
\]
The summation in eqn. (6) was obtained by the relation

\[
\sum_{k=1}^{\infty} kp^k = p \frac{d}{dp} \sum_{k=1}^{\infty} p^k = p \frac{d}{dp} \frac{p}{1-p} = p(1-p)^{-2}
\]

(7)

The summation in eqn. (5) was carried out by replacing the differentiation in eqn. (7) by double differentiation of \( p^k \). Then

\[
L_{OO} = 2p^2(1-p)^{-1}h
\]

(8)

\[
L_{RO} = 2ph
\]

(9)

The total length for O/E and O/O' is expressed by \( pa + 2p^2(1-p)^{-1}h \), whereas that for R/E and R/O' is given by \( (1-p)a + 2ph \). Taking the ratio of these two lengths and using eqn. (4) yields the electrode potential:

\[
E = E^{o'} + \frac{RT}{nF} \ln \frac{pa + 2p^2(1-p)^{-1}h}{(1-p)a + 2ph} = E^{o'} + \frac{RT}{nF} \ln \frac{p}{1-p}
\]

(10)

This is identical to the Nernst equation. Consequently, the one-dimensional arrangement has no specific influence on the electrode potential.

Seven-cube model

This model is an assembly of seven conducting polymer cubes, the centre of which is surrounded by six cubes on its six faces, as illustrated in Fig. 2. The centre cube is supposed to work as an electrode and hence should be the conductive state. The other six cubes randomly take either conductive or insulating states and have a common weight of the probability for every configuration.

We count the number of events of all the configurations that the six cubes can take. When all six cubes are insulated, there is no electric path connecting the centre cube to the substrate electrode. This configuration makes no contribution to the
TABLE 1

<table>
<thead>
<tr>
<th>k</th>
<th>m</th>
<th>Probability for O/O'</th>
<th>Probability for R/O'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>6p^2(1-p)^2</td>
<td>30p^2(1-p)^3</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>30p^2(1-p)^4</td>
<td>60p^4(1-p)^6</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>60p^4(1-p)^3</td>
<td>60p^6(1-p)^2</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>60p^4(1-p)^2</td>
<td>30p^6(1-p)^2</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>30p^6(1-p)</td>
<td>6p^6(1-p)</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>6p^6</td>
<td>0</td>
</tr>
</tbody>
</table>

* k denotes the number of conductive sites involved in the six elements.

* m denotes the multiplicity of a given configuration.

determination of the potential. When one of the six cubes is conductive, there are six configurations of the cluster depending on the location of the conductive cube. They are essentially the same except for their rotation. Then the probability is given by 6p^2(1-p)^2, where the 6 denotes the multiplicity of the configuration. This configuration has one conductive/conductive (O/O') interface and five insulating/conductive (R/O') interfaces. Thus, the expected number which form the O/O' interface is 6p^2(1-p)^2, whereas that which form the R/O' interface is 30p^2(1-p)^2. Applying this procedure to the other events that m(m = 2 - 6) conductive cubes are dispersed to the six sites, we evaluated the probabilities of forming the O/O' and R/O' interfaces and listed them in Table 1.

The sums of the values in the third and fourth columns correspond to the expected areas of forming the O/O' and R/O' interfaces, respectively. Inserting the values of the area into eqn. (4) and using the following dimensionless potential:

\[ \xi = \frac{nF(E - E^{\circ})}{RT} \]  

we have

\[ \xi = \ln \frac{(1-p)^2 + 5p(1-p)^4 + 10p^2(1-p)^3 + 10p^3(1-p)^2 + 5p^4(1-p) + p^5}{5(1-p)^2 + 10p(1-p)^4 + 10p^2(1-p)^3 + 5p^3(1-p)^2 + p^4(1-p)} \]  

(12)

Figure 3 shows the dependence of \( \xi \) on \( p \) calculated from eqn. (12). The curve for \( \xi > 0 \) is identical to the ordinary Nernst equation \( \cdots \). On the contrary, the potential for \( \xi < 0 \) deviates positively from the Nernst equation. The potential at \( p = 0 \) in eqn. (12) is \( -(RT/nF) \ln 5 + E^{\circ} \) instead of \( -\infty \). The difference comes from overestimation in counting at least one conductive site used for the electric connection to the substrate electrode no matter how small the values of \( p \). The minimum value of \( p \) that involves no difference is 2/7, where 2 denotes the sum of one unit for the electric connection and the centre unit. The value of \( \xi \) in eqn. (12) at \( p = 2/7 \) is \( -0.711 \), while that in the ordinary Nernst equation is \( -0.916 \). The potential still has a positive shift. The shift may be ascribed to the restriction that
the centre unit is the oxidized species which enhances the probability of generating the $O/O'$ interface.

When the cluster is near the substrate electrode, the electric connection is more likely to occur at a site with the shortest approach to the electrode (S in Fig. 2) than at one with the farthest approach (F in Fig. 2). Thus, in a more accurate approach, the multiplicity in Table 1 should be replaced by a function of the distance from the cluster to the electrode. The multiplicity may be valid only for clusters far from the substrate electrode. This is a limitation of the present model.

Cubic lattice model by computer simulation

It is really impossible to evaluate analytically the expected areas in a large cluster model including the distance from the electrode. The strategy of the evaluation is to use computer simulation by the Monte Carlo technique.

The processes of the simulation were as follows:
(A) Conductive sites were randomly distributed in the cubic lattice by the Monte Carlo method so that the ratio of the number of conductive elements to that of all the lattice elements was $p$. This process usually forms clusters of conductive domains [12].
(B) An electrically percolated conductive domain was obtained by successively marking conductive sites adjacent to the percolated domain which had already been marked, as described previously [12].
(C) The numbers of interfaces of $O/O'$ and $R/O'$ in every percolated site were counted by testing whether the site adjoins R or O.
(D) Electrode potentials were evaluated from eqn. (4) with these numbers for various values of $p$. 

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The simulation was carried out by a work station, SUN-4 (Sun Microsystems). The maximum number of lattice elements was \(10^6\). In order to minimize fluctuation of the potential associated with the Monte Carlo technique, the numbers of interfaces in ten runs for different sets of random numbers were averaged. When a lattice size varied from \(20 \times 20 \times 20\) to \(50 \times 50 \times 50\) for various combinations of the length, height and width of the lattice, the averaged dimensionless potential was independent of the lattice size. With an increase in the lattice size, the fluctuation more or less decreased.

Figure 3 shows the dependence of \(p\) on \(\xi\) thus computed. When \(\xi > 0\) and \(\xi < -3\), the curve was almost the same as the ordinary Nernst equation. The potential at small values of \(p\) was shifted in the positive direction from the ordinary Nernst equation, as was observed in the seven-cube model. The maximum potential shift was 0.30, corresponding to 7.8 mV at 25°C for a one-electron transfer. The unrealistic behavior of \(\xi \rightarrow -\ln 5\) as \(p \rightarrow 0\) in the previous model has been corrected in the present model.

An interesting characteristic of the curve is the appearance of a slope change at \(p = 0.31\), where a phase transition is known to occur according to the percolation theory [11]. The variation is a second-order phase transition. In order to know the difference in structure of the two phases, the cluster size, \(s\) was obtained, which is defined by the number of conductive elements in a conductive cluster connected electrically to the substrate electrode. Let the sum of a given cluster size be \(I_s\): 
\[I_s = i s,\]
where \(i\) is the number of clusters with the cluster size \(s\). Variations of \(I_s\) with \(\log s\) are shown in Fig. 4 for \(p = 0.30\) (A) and 0.32 (B). The characteristic at \(p = 0.32\) is the appearance of large clusters ranging from \(s = 500\) to 3200, and hence the distribution at \(p = 0.32\) is more structural than that at \(p = 0.30\).

Figure 5 shows the number of clusters, \(i (= I_s/s)\), with the size \(s\) at \(p = 0.32\). Most values of \(i\) for \(s > 10^2\) were unity, and hence the values of \(I_s\) for \(s > 10^2\) were identical to those of \(s\). On the contrary, the plot for \(s < 10^{1.5}\) fell on a straight line.

![Fig. 4. Variations of \(I_s\) with \(\log s\) at \(p = 0.30\) (A) and 0.32 (B) in the same lattice as in Fig. 3.](image-url)
with a slope of $-1.9$, suggesting that $i = k/s^{1.9}$. The power, referred to as Fisher's number [11], for simple percolation in the cubic lattice is reportedly 2.2 [11]. The smaller value in Fig. 5 indicates that there are many more small clusters than predicted from the power of 2.2. Since percolated clusters of size $s$ cannot extend over the $s$-th layer from the electrode, smaller clusters are apt to be localized more closely to the electrode. In order to confirm the localization, we obtained the distribution of conductive elements averaged along a plane parallel to the electrode, and plotted it in Fig. 6. The distribution has been normalized by the number of all conductive elements at each $p$. For $p < 0.31$, conductive elements are localized to the electrode and hence the film is not uniform in conductivity. When $p$ is more
than 0.32, conductive sites are percolated over the film and the density distribution becomes uniform.

Another structural feature is the average radius of a cluster, which is defined by the square mean of the distance between the centre of each cube involved in the cluster and the geometrical centre of the cluster. The evaluation technique has been described elsewhere [12]. The radius, $r$, of the cluster size $s$ is plotted against $s$ in Fig. 7 on a log scale and shows excellent proportionality. Then $s$ is expressed by $s = 4.19r^{2.27} + 0.09$ and $s = 3.89r^{2.36} + 0.12$ for $p = 0.30$ and 0.32, respectively. On considering that the cluster size corresponds to the volume of the cluster and the radius to the characteristic length of the cluster, then the volumes are expressed by fractional powers of the length, indicating fractal formation [13,14]. The powers are slightly larger than the fractal dimension (2.13) of the random percolation in the cubic lattice at the threshold [11]. This is probably due to blocking of the growth of large clusters by the finite size (50 × 50 × 50) of the lattice. Indeed, the plot of points only for $s < 10^{3}$ in curve B decreases the power.

The area of the R/O' interface was obtained for each cluster at several values of $p$ near the threshold. The area varied linearly with $s$: that is, it was proportional to $r^{1.3}$. Thus, the area is also fractal. However, the fractal nature both in the volume and in the area is not a significant feature in the phase transition.

An experimental method of obtaining the relation between $p$ and $E$ is to measure the amounts of charge consumed by partial interconversion during galvanostatic electrolysis. However, linear sweep or cyclic voltammetry is more favourable in terms of accuracy than the galvanostatic electrolysis because the capacitive component can be eliminated approximately by a mathematical process [5]. The anodic current density, $j$, in linear sweep voltammetry is expressed by

$$j = jF^2 \frac{d\Pi}{dt} = \frac{n^2F^2\nu^{*}}{RT} \frac{dp}{dx}$$

(13)
where \( t \) is the time, \( \Gamma_0 \) is the amount of oxidized species, \( \Gamma^* \) is the sum of the amounts of oxidized and reduced species, and \( v \) is the potential sweep rate. In order to minimize scatter in the numerical differentiation of \( \xi \) with respect to \( p \), ten curves of \( p \) vs. \( \xi \) were averaged. The numerical differentiation yielded a voltammogram as shown in Fig. 8. The currents at \( \xi < -0.5 \) showed a large scatter in spite of the averaging. The scatter may be due to fluctuation occurring when large conductive clusters contact the electrode randomly. The currents stepped up discontinuously at \( \xi = -0.5 \), decreased rapidly without scatter, and then approached the ordinary Nernst equation. The discontinuous increase may result from a drastically rapid growth of clusters associated with the phase transition.

CONCLUSION

In the one-dimensional combination of the redox units, the relation between \( p \) and \( \xi \) resulted in the ordinary Nernst equation. On the contrary, the three-dimensional combination made the potential deviate positively from the Nernst equation for \( p < 0 \). The deviation can be explained from the analysis in the seven-cube model as follows: consider the numbers of pairs of \( O|O \), \( O|R \) and \( R|R \), denoted respectively by \( k_{O|O} \), \( k_{R|O} \) and \( k_{R|R} \). The logarithmic term in the ordinary Nernst equation is then \( \ln[(2k_{O|O} + k_{R|O})/(2k_{R|R} + k_{R|O})] \), where the factor 2 denotes a double count in \( O|O \) and \( R|R \). If a pair of \( R|R \) does not come in contact with the electrode or a percolated conductive domain, \( k_{R|R} \) does not contribute to the potential and hence the potential becomes more positive. This is pronounced when \( R \) is large or \( p \) is small. In the seven-cube model, a pair of \( R|R \) was eliminated a priori by the presupposition that the centre cube should be conductive. In the cubic
lattice model, the pair is out of the conductive clusters and hence makes no contribution to the determination of the potential.

Since thermal motion of particles, in general, gives rise to random dispersion of species, the conductive units may be distributed uniformly in the film, as has been employed in the three models. However, in the cubic lattice model for \( p \leq 0.31 \), the units participating in the determination of the potential were localized in the vicinity of the electrode surface. Localization was brought about by blocking the electric percolation due to the small clusters.

Immediately after \( p \) reaches the threshold value (0.31) of the percolation, the percolation theory predicts that the maximum radius of a cluster increases rapidly up to the film thickness. This concept explains the drastic changes in the conductive clusters from the localized distribution to the uniform one in Fig. 6. Since a small change in \( p \) near the threshold causes a tremendous variation in the amount of effective charge, a sharp peak appeared in the linear sweep voltammogram.

REFERENCES