Is Voltammetric Current Proportional to the Number of Transferred Electrons for Multi-Charged Ions or to 3/2 Power of the Number?

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Abstract
Particles with a large number of electrons to transfer, such as nanoparticles and colloidal redox particles, give voltammetric currents that were demonstrated theoretically to be proportional directly to the number of the electrons, \( n \), rather than to \( n^{3/2} \). The latter quantity is included in the conventional expression for voltammetric peak currents of multi-charge transfer processes. This apparent contradiction appears depending on whether the charge transfer occurs concurrently \( n^{3/2} \) or consecutively \( n \). The expression for the linear sweep voltammetric current was derived from a combination of the diffusion equation for large particles with \( n \) electrons and the Nernst equation for the \( n \)-time consecutive one-electron reactions at the electrode. The power in \( n \) for the peak currents, in several voltammetric techniques, was demonstrated to be ascribed to the convolution of the Nernst equation and the diffusion equation.

Keywords: Voltammetric current, Peak current, Nanoparticles, Colloidal suspensions, Mass transport, Diffusion, Multi-charge transfer process

Devoted to the Memory of Professor Robert (Bob) Osteryoung

1. Introduction
Voltammetric peak currents are known to be proportional to some powers of the number of electrons transferred, \( n \) [1]. For example, a peak current of linear sweep voltammetry is proportional to \( n^{3/2} \) rather than to \( n \) [2–4], even if the process is controlled by a slow charge transfer [5]. Peak currents of differential pulse voltammetry [6] and square-wave voltammetry [7–9] vary with \( n^x \) in complex ways of the applied time-voltage sequence, where \( x \) is a number higher than unity. A peak current of AC reversible voltamograms is proportional to \( n^2 \), whereas the AC-voltammetric peak for sluggish reactions varies with \( n^x \) depending on the rate constant [10–11]. Voltammetric peak currents, generally, exhibit the dependence on \( n^x \). A primitive question arises on why the \( n^x \)-dependence is exhibited while the reaction proceeds with the \( n \)-electron transfer step. Since the \( n^x \)-dependence varies with the applied voltage sequences, it seems to be related to the mass transfer modes.

This question is so classical in the context of mass transfer that it may have already been solved in principle. However, it becomes a new subject when the attention is paid to large particles with multiple charge transfer such as dendrimers [12–13], nanoparticles of metal [14–20], redox polyelectrolytes [21–25], redox latex particles [26–34] and redox polymers [35–37]. Since the voltammetric currents play an important role in determining the structure of large particles through \( n \) [31, 33, 34] it is necessary to discuss in detail the relation between the peak current and \( n \). In this paper we derive expressions for voltammetric currents at any time-potential sequence under the diffusion-control of a large particle with \( n \) transferring electrons on the assumption of the Nernst equation for \( n \)-time consecutive one-electron reactions.

2. Theory
2.1. Reaction Model
Multi-charge transfer reactions with a single standard potential can be observed in the electroactive latex such as mono-dispersed polystyrene latex particle with a number of immobilized ferrocenyl moieties which is suspended in water. Since one latex particle is of 1 \( \mu \)m in diameter and has ca. \( 10^7 \) ferrocenyl moieties, the average concentration of the ferrocenyl moiety is ca. 50 mM within the latex particle. This value may allow ignoring a distribution or a shift of the standard potential of the ferrocenyl group caused by the interactions between neighboring ferrocenyl moieties. This system can be regarded as multi-charge transfer reaction with a simple standard potential.

We consider the overall electrochemical oxidation of the redox particle \( R_n \) to \( O_n \) with \( n \) electrons transferred;

\[
R_n \rightarrow O_n + n \, e^-
\]  

(1)

The redox particle is composed of \( n \) redox sites, on which the elementary reaction is assumed to occur independently.
Fig. 2. Illustrative model of the multiple charge transfer reaction
at big particles for \( k = 0 \) and \( n = 4 \).

\[
j = -F \sum_{k=1}^{n} D(k (\partial c_k / \partial x))_{x=0} \tag{7}
\]

We assumed that Reactions 2 and 3 occur sufficiently rapidly so the Nernst equation holds at the electrode surface \( (x = 0) \). The equilibrium ought to be established with all the contributions of \( A_k \). The concentrations of the oxidized and the reduced species of \( A_k \) are given by \( k c_k \) and \( (n-k)c_k \), respectively, because \( k \) oxidized sites and \( n-k \) reduced sites participate in the establishment of the Nernst equilibrium (see Fig. 1). Their sums from \( k = 0 \) to \( n \) provide the surface concentration of the oxidized and the reduced species for the Nernst equation, and hence

\[
\sum_{k=0}^{n} k(c_k)_{x=0} / \sum_{k=0}^{n} (n-k)(c_k)_{x=0} = \exp[F(E - E^*)/RT] \equiv e^\varsigma
\tag{8}
\]

where \( \varsigma \) is the dimensionless potential: \( F(E - E^*)/RT \).

2.2. Mass Transport Problem

We assume that all the particles are transported under one-dimensional diffusion-control with a common value of the diffusion coefficient, \( D \). This common value suggests there is no change in the hydrodynamic radii of the particles after the electron transfer. The time-dependent diffusion equation for the particle \( A_k \) at concentration \( c_k \) is given by

\[
\partial c_k / \partial t = D(\partial ^2 c_k / \partial x^2)
\tag{4}
\]

Since all the particles are initially in the reduced form, \( A_0 \), the concentration of which is \( e^* \), the initial and boundary conditions in the bulk are given by

\[
t = 0, \ x \rightarrow \infty : c_0 = e^*, \ c_k = 0 \ for \ k = 1, \ldots, n
\tag{5}
\]

as it is shown in Figure 2. The total fluxes for all the \( A_k \) vanish at the electrode surface because there is no accumulation. Consequently we have

\[
\sum_{k=0}^{n} D(\partial c_k / \partial x) = 0
\tag{6}
\]

The oxidation current that leads to the formation of \( A_k \) from \( A_0 \) is related to the \( k \)-electron transfer. An example for the case of \( k = 0 \) and \( n = 4 \) is shown in Figure 2. Thus the oxidation current is the sum of the fluxes of \( A_k \) for \( k = 1 \) to \( n \)

\[
e_{x=0} = \int_{0}^{t} \frac{j_k(u)}{\sqrt{t-u}} \ du
\tag{9}
\]

and for \( k = 0 \)

\[
e_{x=0} = e^* - \int_{0}^{t} \frac{j_0(u)}{\sqrt{t-u}} \ du
\]

Summing \( (c_k)_{x=0} \) for \( k = 0 \) to \( n \) yields

\[
\sum_{k=0}^{n} (c_k)_{x=0} = e^* - \int_{0}^{t} \frac{j_0(u)}{\sqrt{t-u}} \ du
\]

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According to Equation 6, the right hand side of Equation 11 equals to $e^n$. Since the summation of $nc_z$ in Equation 8 becomes $ne^n$, Equation 8 is reduced to

$$\sum_{z=-i}^{n} k(c_z)_{z>0} = \frac{ne^n}{1 + e^{-z}}$$

(12)

Inserting Equation 9 into Equation 12, we obtain

$$-\sum_{z=-i}^{n} \int_{0}^{t} k_z(u) \frac{du}{\sqrt{t-u}} = e^n nF \sqrt{\pi D} \frac{1}{1 + e^{-z}}$$

(13)

By combining $j_z = FD(\partial c_z/\partial x)_{z>0}$ with Equation 7 we obtain the convoluted expression for the oxidation current density:

$$\int_{0}^{t} \frac{j(u)}{\sqrt{t-u}} du = e^n nF \sqrt{\pi D} \frac{1}{1 + e^{-z}}$$

(14)

The Abel type of the integral equation can be solved by the ordinary method [38] to give

$$j(t) = e^n F \sqrt{D/\pi} \frac{d}{dt} \int_{0}^{t} \frac{1}{1 + e^{-z(\omega)}} \frac{du}{\sqrt{t-u}}$$

(15)

where $\zeta(t) = F[\epsilon(t) - \epsilon']/RT$ is a function of time for any time-potential sequence, depending on the voltammetric technique used.

3. Discussion

3.1 Ordinary Voltammetric Techniques

Equation 15 has been derived with an assumption of: (i) the $n$-time consecutive one-electron transfer reaction for $n$-redox charged particles, (ii) the Nernst equation with a common standard potential, and (iii) the diffusion-controlled mass transport with a common diffusion coefficients. Equation 15 has a form similar to the conventional relation [39] between the convoluted current and the electrode potential for the reversible case except for the restriction of the number of electrons to one in the dimensionless potential, $\zeta = F(E - \epsilon')/RT$. We apply Equation 15 to selected voltammetric techniques.

Normal pulse (NP) voltammograms are composed of currents sampled at the end of potential pulses of increased amplitude [40]. If the measurements are done in such a way that the actual current is independent of the previous one [41], then, each individual NP current is actually a chronoamperometric current measured at a sampling time, $t$. The chronoamperometric curve at a given potential is obtained from Equation 15 to yield

$$j_{NP} = e^n F \sqrt{D/\pi}(1 + e^{-z})^{-1}$$

(16)

The current-potential curve is obviously sigmoid with the one-electron transfer step. Extracting the potential with the use of the limiting current density, $j_{NP,L} = e^n F \sqrt{D/\pi}$, we obtain

$$E = E' + \frac{RT}{F} \ln \frac{j_{NP}}{j_{NP,L} - j_{NP}}$$

(17)

The current-potential curve does not contain $n$.

Differential pulse voltammetry and square-wave voltammetry are combinations of potential pulses with the same mass transport mode as in normal pulse voltammetry. Therefore, differential pulse and square-wave voltammetric currents are $n$ times larger than the conventional voltammograms for the one-electron transfer, without any dependence of the voltammetric shape on $n$.

Linear potential sweep voltammograms (LSV) may show $n$-time values of the conventional voltammograms for the one-electron transfer. We dare to derive here the expression for the linear sweep voltammogram, because the derivation may make the mechanism of multiple electron transfer reactions clear. Exchanging the order of the differentiation and the integration, we obtain

$$j(t) = e^n F \sqrt{D/\pi} \int_{0}^{t} \frac{e^{-z(u)}}{(1 + e^{-z(\omega)})} \frac{d\zeta(u)}{du} \frac{du}{\sqrt{t-u}}$$

$$+ e^n F \sqrt{D/\pi} \frac{v}{(1 + e^{-z(\omega)})} \frac{d\zeta}{\sqrt{t}}$$

(18)

Changing variables, $\zeta = F(E - \epsilon')/RT = F(vt + E_i)/RT$ and $\zeta' = F(vu + E_i)/RT$ and taking the initial potential $E_i$ to be $-\infty$, we obtain

$$j_{LSV} = \frac{1}{4} e^n F \sqrt{D/\pi} \frac{Fw}{RT} \int_{-\infty}^{t} \frac{d\zeta'}{\sqrt{\zeta - \zeta}}$$

(19)

The voltammetric waveform depends only on the integral in Equation 19 which does not include $n$. Therefore, the waveform is independent of $n$. The numerical integration of Equation 19 gave the same dimensionless waveform as the conventional one-electron transfer reaction, as is shown in Figure 3a. The invariance of the linear sweep waveform with $n$ has been demonstrated experimentally for silver nanoparticles [14–16] redox latexes [26–34] and redox polymers [35–37]. The number of $n$ has been already determined from the equation similar to Equation 20, which had been obtained intuitively [31]. The values of $n$ were consistent with values estimated from bulk electrolysis [27–31], spectroscopy [34], thermal analysis [15] and chemical analysis [14]. If $n$ were to be included in $\zeta$ of the form $nF(E - \epsilon')/RT$, the voltammogram should take a sharp peak, as is shown by the dotted line in Figure 3b. The integration provides the expression for the peak current

$$j_{LSVP} = 0.446ne^n F \sqrt{DFV/RT}$$

(20)
for $E_p = E^* + 0.0285 \text{ V at } 25 \, ^\circ \text{C}$. This equation shows the proportionality of the peak current to $n$ rather than $n^{3/2}$. If $n$ were to be included in $\zeta$, the peak current should be proportional to $n^{3/2}$.

Flanagan et al. presented a reaction model similar to Reactions 1–3 for redox polymer of poly(vinylferrocene) [35]. Since they applied the statistically modified Nernst equation to polymers and focused only on the redox reaction sites, they have not taken into account size, weight or concentration of polymer molecules. In contrast, Equation 8 has been derived from the thermodynamics with a specific molecular image, including concentrations of big redox particles.

### 3.2. Limitations of the Model

We focus our attention on some limitations of the present model or over-simplification of the model. Dispersion in particle size is often observed no matter how much effort has been made to synthesis of redox latex particles and metal nanoparticles. We first consider the effect of the size-distribution on the voltammetric current. Variables relevant to the size in Equation 20 are $n$, $c^*$, and $D$. A value of $nc^*$ is equivalent to the average concentration of the redox site, and has often been determined with UV spectroscopy after dissolving the particles completely. So far as a value of $nc^*$ is given, the size-distribution by $nc^*$ has no effect on the voltammetric current. On the other hand, the diffusion coefficient exhibits an effect of the size-distribution because it is inversely proportional to the particle diameter through the Stokes-Einstein equation. Small particles provide large current. Consequently, smaller particles should be exhaustively removed from the solution.

The overall $n$-electron transfer, Equation 1, has been assumed to consist of the consecutive $n$ one-electron transfer steps that occur reversibly. If a particle is so large that the Nernstian equilibrium is valid only at a domain contacting with the electrode, some redox moieties far from the contacting point may be left behind the Nernstian equilibrium. As a result, the peak currents are observed to be smaller than the value evaluated from UV-vis spectroscopy or macro-electrolysis, retaining the diffusion-controlled behavior (proportionality of $I_{\text{peak}}$ to $v^{1/2}$). Indeed, the values of $n$ evaluated from the peak currents for the ferrocene-coated latex particles have decreased with an increase in the radius of the particles. The partial charge transfer actually observed is caused by the finite size of the particles, whereas the mass transport in Equation 4–8 holds for infinitely small particles.

Real voltammograms of redox latex suspensions show broader waves than the peak in Figure 3a. The broadness may be caused not only by slow charge propagation steps from the contact point with the electrode to the inner latex sphere but also by distribution of standard potentials varying with the circumstances of the redox sites. Since the former includes kinetics of charge exchange reactions, it is beyond the present subject. We consider here the latter on the assumption of a distribution of standard potentials owing to the charge-charge interaction.

As an example of the charge-charge interaction, we take into account the oxidation of ferrocenyl moiety to ferricenium ion, both being immobilized in a polystyrene latex particle. Neighboring ferricenium ions repulse electrostatically and show the coulombic energy with the inverse proportionality to the separation distance. In other word, the energy is proportional to the cubic root of the concentration of the oxidized moiety. Then the formal potential including the interaction is expressed by

$$E^* = E^*_{\text{int}} + \lambda \left( \sum_{k \in d} k c_k \right)^{1/3}$$

where $\lambda$ is a constant. Defining a new dimensionless variable of the potential:

$$\zeta = (E - E^*_{\text{int}})/RT$$

we can rewrite the dimensionless potential by use of Equation 12 as

$$(E - E^*) \frac{F}{RT} = \left[ E - E^*_{\text{int}} - \lambda \left( \frac{nc^*}{1 + e^{-\zeta}} \right)^{1/3} \right] \frac{F}{RT}$$

$$\approx \zeta - \lambda_1 (1 + e^{-\zeta})^{-1/3}$$

where $\lambda_1$ is a constant given by $\lambda (nc^*)^{1/3}$. Then Equation 15 can be written as

$$I_{\text{LSV, int}}(t) = c^* n F \sqrt{D/\pi} \frac{d}{dt} \frac{1}{\sqrt{t - u}}$$

Replacing the time by the scanned potential, we obtain the expression for LSV:

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\[ j_{\text{LSV.lin}} = \frac{1}{4} \frac{e^a n F \sqrt{D}}{\pi} \sqrt{\frac{Fv}{RT}} \times \int_{-\infty}^{\lambda_1} \text{sech}^2 \left( \frac{z}{2} - \lambda_1 \left(1 + e^{-z}\right)^{-1/2} \right) \frac{dz'}{\sqrt{\lambda_1 - z'}} \]  

(25)

Since the integral does not include \( n \) explicitly, the current is proportional to \( n \) rather than \( n^2 \). The voltammograms calculated from Equation 25 are drawn in Figure 3 for two values of \( \lambda_1 \). The peaks shift in the positive direction and become slightly broad with an increase in \( \lambda_1 \).

4. Conclusions

The peak current of a big redox particle undergoing a large number of one-electron transfer steps in linear sweep voltammetry is proportional to \( n \) rather than to \( n^2 \) if the overall step of Reaction 1 is composed of \( n \) consecutive reactions 3. The voltammogram shape is the same as that for the one-electron transfer reaction. Although reaction 2 combined with reaction 3 resembles the overall reaction, the one-electron transfer reaction. Therefore, the former is different from the latter in the Nernst equation as can be seen by comparing Equation 8 for \( n \geq 2 \) with Equation 8 for \( n = 1 \). The former eq. contains \( n \) in the dimensionless potential of the Nernst equation whereas the latter one does not. Consequently, the Nernst term in Equation 15, \( (1 + e^{-z})^{-1} \), has no possibility of relating \( n \) with the delay by the diffusion term, \( (t-u)^{1/2} \).

Since Equation 15 demonstrates that the current is proportional to \( n \) being independent of applied potential-time sequence, the proportionality is valid for the voltammetric peak currents in differential-, square-wave-, alternating current-, and linear sweep voltammetries. When the voltammogram curves of large particles with multiple transferring electrons have a conventional waveform, the rate-determining step is the one-electron transfer, regardless of the number of transferring electrons. It is possible to evaluate \( n \) from the peak current if values of \( c^* \) and \( D \) are known.

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6. References