Determination of the number of electrons by chronoamperometry at small electrodes

Toyohiko Nishiumi, Motin Md. Abdul, Koichi Aoki *

Department of Applied Physics, University of Fukui, 3-9-1 Bunkyo, Fukui-shi 910-8507, Japan

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Abstract

The number of electrons transferred, \( n \), was determined by taking the ratio of the square of the slope to the intercept of Cottrell plots by chronoamperometry at a small disk electrode without knowing values of diffusion coefficients. The intercept is ascribed to the contribution of spherical diffusion. This technique is useful for estimating reaction mechanisms of unstable species of which lifetime is shorter than the period of bulk electrolysis. It takes advantage not only of getting the simultaneous acquisition of two independent variables (the slope and the intercept) in one chronoamperometric curve but also of evaluating the dependence of \( n \) for multi-step charge transfer reactions on electrode potentials. Ferrocene and \( N,N'\)-bis(4-methoxyphenyl)-\( N,N'\)-diphenyl-1,4-phenylenediamine were used for redox species at \( n = 1 \) and \( 2 \), respectively. Chronoamperometric currents were obtained at the platinum disk electrode 50 \( \mu \)m in radius for the time less than 3 s, responding to the various stepped potential values. Values of \( n \) were obtained at each potential even for sluggish charge transfer reactions.

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1. Introduction

The number of electrons, \( n \), for an electrode reaction is significant information of analyzing multiple charge transfer reactions. The significance has recently enhanced as redox particles become bigger, exemplified by fullerene, redox proteins, redox polyelectrolytes, metal nanoparticles and redox colloids. There are basically two types of multiple steps: consecutive [1–3] and concomitant charge transfer reactions [4,5]. The former can be regarded as a specific case of the latter in that there is no electric interaction between redox centers [6,7]. The former is equivalent voltammetrically to the system of the one-electron reaction with \( n \)-times concentration. Thus, the shape of the voltammogram is the same as the conventional wave except for the \( n \)-times values of the peak current [8].

Values of \( n \) have been electrochemically determined by a slope of a Nernst plot, the difference between voltammetric cathodic and anodic peak potentials, evaluation of the amount of redox charge by bulk electrolysis, or the diffusion-controlled current. The first two methods are based upon the Nernst equation, whereas, the last two result from the proportionality of \( n \) with the current. Coulometry by the bulk electrolysis seems to provide the most reliable values of \( n \). It is, however, not only operatively time-consuming but also yields incorrect results owing to mixing of products and reactants, disproportionation, involvement of side reactions for the long time electrolysis, and insufficient potential control by solution resistance. In contrast, the diffusion-controlled current ought to evaluate accurately \( n \) if values of a diffusion coefficient and concentration are known. Nevertheless, \( n \) has not been estimated in most redox systems until diffusion coefficients, \( D \), and concentrations can be determined.

The chronoamperometric technique of evaluating \( n \) or \( D \) without knowing a value of either \( D \) or \( n \) was devised...
by Kakihana et al. [9], and has been applied to accurate evaluation of $D$ [10–12] rather than $n$ [13]. The technique is based on taking the ratio of the slope to the intercept in the Cottrell plots (current vs. inverse of the square-root of the electrolysis time) at a microelectrode. The advantage has been justified by other research groups [14–18]. When chronoamperometry is performed at various potentials, as is for normal pulse voltammetry, values of $n$ thus obtained at each potential provide a potential dependence of the redox states. This technique may be useful not only for determination of potential-dependence of multi-valence states [6,19–21] but also estimation of the degree of the partial charge of redox colloids [22,23]. The present report is devoted to obtaining the $n$ vs. potential curve by chronoamperometry at a small electrode.

2. Concept

A chronoamperometric curve at a disk microelectrode varies from the Cottrell behavior to the steady state current. When potential is stepped to a diffusion-controlled potential domain at the disk electrode with radius, $a$, in the solution including electroactive species with the concentration, $c^*$, and the diffusion coefficient, $D$, the responding current, $I$, at the electrolysis time, $t$, has been expressed as [24,25]

$$I = 4nFc^*Da(1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2}),$$

$$I = 4nFc^*Da(\pi/4\tau)^{1/2} + \pi/4 + 0.094t^{1/2},$$

where $\tau = 4Dt/a^2$. Eqs. (1) and (2) are valid for $\tau > 1.44$ and $\tau < 0.82$, respectively. Some expressions for the chronoamperometric curves obtained by finite difference or the related methods [9,26–31] are closed to Eqs. (1) and (2). When $\tau$ is small enough to neglect the third term in Eq. (2), the potential-depending current for the reversible case is expressed by

$$I = (\pi^{1/2}nFD^{1/2}a^2t^{-1/2} + \pi nFDa)c^*(1 + e^{-z})^{-1},$$

where

$$z = (F/RT)(E - E^0),$$

The Cottrell plot ($I$ vs. $t^{-1/2}$) gives the slope and the intercept, respectively.

$$s = \pi^{1/2}nFD^{1/2}a^2c^*(1 + e^{-z})^{-1},$$

$$p = \pi nFDc^*(1 + e^{-z})^{-1},$$

The ratio of the square of the slope to the intercept is

$$s^2/p = nF^2a^2c^*(1 + e^{-z})^{-1} \text{ or } n(1 + e^{-z})^{-1} = s^2/pF^2a^2c^*.$$

This equation does not include $D$, and hence is the basic equation of evaluating $n$ without knowing $D$ from the chronoamperometric curves.

3. Experimental

3.1. Chemicals

Ferrocene (Wako) was purified by sublimation before use. Tetra-$n$-butylammonium perchlorate (TBAP) and tetra-$n$-butylammonium tetrafluoroborate (TBABF$_4$) as supporting electrolyte were from TCI and Aldrich, respectively, and used as received. Acetonitrile was of analytical grade (Kanto).

3.2. Synthesis

$N,N'$-Bis(4-methoxyphenyl)-$N,N'$-diphenyl-1,4-phenylene-diamine (MPA), as is shown in Fig. 1, was synthesized from $N,N'$-diphenyl-1,4-phenylenediamine (Kanto) and 4-idoanisole (TCI) via the Ullmann reaction according to the literature [32]. The purification was carried out by silica gel column chromatography and recrystallization. The product was identified by $^1$H NMR, $^{13}$C NMR and IR to be MPA.

3.3. Electrochemistry

The platinum disk 50 $\mu$m in radius was purchased from BAS and was used as a working electrode for voltammetry and potential step experiments. The electrode surface was polished with 0.05 $\mu$m alumina before each run. The auxiliary electrode was a coiled platinum wire. The reference electrode was an Ag/Ag$^+$ electrode. The potentiostat was an HECS-318C (Fuso, Kawasaki). A 12 bit AD/DA converter (PCI-3521, Interface) was used as a function generator and a recorder connected to the potentiostat. Oxygen was purged from the one-compartment cell before electrochemical run.

![Fig. 1. Structure of: (a) MPA, (b) cation radical stabilized by resonance, and (c) dication.](image-url)
4. Results and discussion

4.1. Ferrocene

Fig. 2 shows cyclic voltammograms of ferrocene at the small disk electrode for slow and fast scan rates. The voltammetric peaks disappeared with a decrease in the scan rate, as is known theoretically [33]. Chronoamperometry was made through the potential step from –0.2 V to various values of potential ranging from 0.0 to 0.5 V in the time domain from 0.1 to 10 s. The linearity of the Cottrell plot was poor over the whole time-domain. When the background current was subtracted, the Cottrell plot showed an approximately linear relation in the time domain from 0.3 to 3.0 s. The current at the time longer than 3.0 s is ascribed to the contribution of the third term in Eq. (2). All the Cottrell plots in the domain from 0.3 to 3.0 s exhibited a slightly concave variation, as is shown in Fig. 3.

In order to evaluate accurately \( s \) and \( p \), large values of the currents should have the same contribution to a regression line as small values have in the Cottrell plot. Thus the currents were weighed by \( r^{-1/2} \) for the regression. Inserting values of \( s \) and \( p \) of the plot and \( a = 0.05 \) mm into Eq. (4), we evaluated \( n(1 + e^{-z})^{-1} \). The concave variation increased errors in \( n \); i.e., a larger contribution in the short time domain increases \( s \) and decreases \( p \), leading to overestimation of \( n \). We express this ambiguity as the standard deviation of \( n \), which is propagated from the standard deviations for \( s \) and \( p \) through Eq. (4). The variances of the slope and the intercept are, respectively, given by

\[
\sigma_s^2 = \left[ \frac{\sum (st_i^{-1/2} + p - I_i)^2}{N \sum t_i^{-1} - (\sum t_i^{-1/2})^2} \right]
\]

\[
\sigma_p^2 = \left[ \frac{\sum (st_i^{-1/2} + p - I_i)^2 (\sum t_i^{-1})}{N^2 \sum t_i^{-1} - N(\sum t_i^{-1/2})^2} \right]
\]

where \( N \) is the number of the data points, and \( I_i \) is the current at the time \( t_i \). The error included in \( n(1 + e^{-z})^{-1} \) is \( (2\sigma_s + \sigma_p)/Fa z e^z \) from Eq. (4).

Values of \( n(1 + e^{-z})^{-1} \) and the errors thus obtained are plotted against the potential in Fig. 2. When the potential step domain was more than 10 mV of the peak potential, values of \( n \) were determined within 5% errors. However, the Nernst plot for \( n(1 + e^{-z})^{-1} = z \), i.e., \( \ln [z(1 - z)] \) vs. \( E \), was too scattered to determine a value of \( nF/RT \).

4.2. \( N,N'-\text{Bis}(4\text{-methoxyphenyl})-N,N'-\text{diphenyl}-1,4\text{-phenylenediamine (MPA)} \)

Fig. 4 shows cyclic voltammograms of MPA at three scan rates. Two well-defined waves appeared. The first oxidation is ascribed to formation of the cation radical from one of the two amines (Fig. 1(b)). Since the cation radical has resonance structure as is depicted in Fig. 1(b), it is stabilized before the second oxidation. The difference between the corresponding peak potentials ranged from 0.09 to 0.12 V at 0.5 V s\(^{-1}\). The charge transfer steps of the first and the second oxidation are complicated by sluggish charge transfer reactions. However, the slow steps were not revealed in the dependence of the peak potentials on the scan rates for less than 0.5 V s\(^{-1}\). This is because the anodic peak potential shifts in the positive direction with a decrease in the scan rate [33].

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Fig. 2. Cyclic voltammograms of 2.0 mM ferrocene + 0.2 M TBAP in acetonitrile at scan rates of: (a) 0.5 and (b) 0.005 V s\(^{-1}\) in the left ordinate. Values of \( n(1 + e^{-z})^{-1} \) (○ in the right ordinate) obtained from the Cottrell plot (Fig. 3) through Eq. (4) from 1.0 mM Ferrocene + 0.1 M TBABF\(_4\) in acetonitrile. The error bars were evaluated from Eqs. (5) and (6).

Fig. 3. Cottrell plots of the background-subtracted currents for 1.0 mM ferrocene + 0.1 M TBABF\(_4\) when the potential was stepped from –0.2 to: (a) 0.4, (b) 0.3, (c) 0.1, (d) 0.05, (e) –0.05 V.
Chronoamperometry was made by stepping potentials from \(-0.2\) to various values up to 0.8 V. The Cottrell plots of the background-subtracted current are shown in Fig. 5. Those for the diffusion-controlled potentials (0.3 and 0.8 V) fell on each straight line in the time domain from 0.3 to 3.0 s. The linearity was valid also for the plots when potential was stepped to the potentials for the charge transfer control (0.1 and 0.5 V). Since the current at a short time is controlled more by the charge transfer step than diffusion, it should be smaller than Eq. (3) and hence the Cottrell plot should take theoretically a convex form. However, the quality of the linearity was similar to that of ferrocene (Fig. 3). The time domain (0.3–3.0 s) may be too narrow to reveal the difference between the diffusion control and the charge transfer control.

We estimated \(n\) from the values of the slope and the intercept by use of Eq. (4) on the assumption of \(f \to 1\), which is valid for the potential domain of the limiting current. Values of \(n\) are plotted against the potential in Fig. 6. Taking into account only the data in the potential domain of the limiting current, we obtained either \(n = 1\) or \(n = 2\), as predicted from the reaction scheme in Fig. 1. The variation of \(n\) with the potential corresponds well to the steady-state voltammogram. However, the agreement is not reasonable for points at \(n = 1.1\) and 1.8, because we assumed the diffusion-controlled limit (\(f \to 1\)) for the analysis.

5. Conclusion

Chronoamperometry at the electrode 50 \(\mu\)m in radius allowed us to evaluate \(n\) from the ratio of the square of the slope to the intercept of the Cottrell plot in which chronoamperometric data were selected in the time domain of 0.3–3.0 s. These conditions were examined by use of the oxidation of ferrocene as a standard redox reaction. A significant point of this technique is to eliminate ambiguity of conditions of bulk electrolysis, such as difficulty in subtraction of background current, mixing of products and reactants, disproportionation, involvement of side reactions for the long time electrolysis, insufficient potential control by solution resistance, and big noises owing to stirring the solution. New points presented here are to obtain the variation of \(n\) with potential, to evaluate \(n\) even for the multiple charge transfer sluggish reactions, and to assess errors of \(n\) including the slope and the intercept.

References