Potential Step for Double-Layer Capacitances Obeying the Power Law

Koichi Jeremiah Aoki, Jingyuan Chen,* and Ridong He

ABSTRACT: Potential-step chronoamperometry was made at a platinum wire electrode in KCl aqueous solution at the aim of finding the behavior of the power law of the time or the constant phase element for the double-layer (DL) capacitances. The logarithmic current decays linearly with the time shorter than 0.1 ms, and then it obeys the power law in which it has a linear relation with the logarithmic time in the millisecond time domain. The transition from the exponential decay to the power law was expressed theoretically for the model of a series combination of the resistance and the DL capacitance. The expression predicts that the double logarithmic plots of the current—time provide a capacitance value at 1 s from the intercept, independent of the resistance. This prediction was demonstrated experimentally in KCl solutions of which concentrations ranged from 1 mM to 0.5 M. The capacitance can be evaluated simply by chronoamperometry on a 1 s time scale without considering any resistance effect. The capacitance values did not vary with the applied potential.

1. INTRODUCTION

Double-layer (DL) capacitors have been used industrially for electric storage with large charge density and large current density.1,2 Their performance is revealed in charge and discharge profiles, which consist of voltage vs time curves responding to constant currents applied to the capacitors. The voltage vs time curves take approximately a triangular waveform,3 the charging voltage increases with the time, whereas the discharging voltage decreases. The variation looks linear, but the increasing or decreasing speed is suppressed at a long time. The nonlinearity has been ascribed to space charge effects,4 solution resistance,5,6 morphology of electrodes,7 charge of adsorbed species,8 distributed resistance and capacitance,9 participation in redox reactions,10,11 and frequency dispersion.12 An equivalent circuit of the DL capacitance in salt solution has been supposed to be a series combination of the capacitance $C$ and the solution resistance $R$. Then the observed voltage $V$ responding to a constant current $I$ is represented as $V = (1/C) \int I \, dt + IR$ or $V = (1/C) I \, t + IR$, which means that the resistance makes the line only shifted vertically without any effect on the linearity. The time variation of the speed may be caused by an increase in $C$ with the time.

The time variation of $C$ is called frequency dispersion and has been interpreted as a concept of the constant phase element (CPE).13–19 High ac-frequency decreases the imaginary impedance; that is, a shorter time decreases the capacitance. This behavior can be expressed in terms of the power law of the frequency14–20 or the mathematical treatment of the concept of CPE. It is independent of concentration of ions and can be ascribed to the orientation of dipoles of solvent molecules.20–22 The frequency dispersion has been recognized even at frequencies as low as 1 Hz. Therefore, it is not caused by simple inversion of the dipoles on a molecular scale by the external electric field but should include the thermodynamically collective behavior,18 which can be attributed to a cooperative phenomenon.19 The power number close to 0.1 has been theoretically assigned to the ratio of equilibrium energy of the orientation to the activation energy of the orientation kinetics.20 The time variation of the capacitance has been applied to galvanostatic electrolysis to explain the deviation from linear voltage—time curves of charge—discharge steps for commercial supercapacitors.12 Since observed properties of commercial supercapacitors are superimposed with various effects, they are not always voltammetric features of DL capacitors.

If DL impedance in ionic solution is regarded as an equivalent circuit of a series combination of a time-independent DL capacitance, $C$, and a solution resistance, $R_s$, the current responding to the step potential, $V$, decays with time, $t$, obeyed by $I = (V/R_s) \exp(-t/R_s C)$.20,21 When $C = 30 \ \mu F \ cm^{-2}$ and $R_s = 100 \ \Omega$ under typical voltammetric conditions, the current values at $t = 0.01, 0.1$, and 1 ms are $1 \ mA$, $50 \ nA$, and $2 \times 10^{-51}$, respectively. In other words, the current decreases drastically and becomes actually zero at time

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less than 0.1 ms. Although this time domain is much shorter than the conventional voltammetric time domain except for ac voltammetry, we often have to pay attention to subtracting capacitive currents. The rapid exponential decay should make pulse voltammetric current much smaller than fA even at a pulse width of 1 ms, whereas background currents by actual pulse voltammetry have more than the order of 10 nA.\textsuperscript{22,23} As a result, the exponential decay is not realistic. The power law of the DL capacitance, represented by $C_\text{DL} f^{-\lambda}$ for a positive constant $\lambda$ close to zero, implies that the capacitance may have the time dependence of $t^\lambda$, where $f$ is the frequency of applied ac-voltage. Then the potential step chronoamperometric response may decay with the power law of the time rather than the rapid exponential decay.

Some electrochemists consider that capacitance values determined by potential steps are different from those by ac-impedance because not only of difference in the timescale but also of that of applied voltages. Ideal capacitances should be independent of time domains as well as voltages according to the definition of capacitance, i.e., the ratio of electric charge to voltage. We made preliminary experiments for a DL capacitance and a capacitance of electric element. Figure 1 shows the Nyquist plots (A) and current–time curves (B) for (a) a 1 M KCl solution at the Pt wire and (b) a series combination of a 6.6 $\mu$F paper capacitor and a 10 $\Omega$ carbon resistance.

![Figure 1](https://example.com/fig1.png)

Figure 1. Nyquist plots (A) and chronoamperometric curves (B) of (a) 1 M KCl solution at the Pt wire and (b) a series combination of a 6.6 $\mu$F paper capacitor and a 10 $\Omega$ carbon resistance.

shows the Nyquist plots (A) and current–time curves (B) for (b) a series combination of a nearly ideal electric capacitance with a resistance and (a) the DL capacitance. The Nyquist plots of (b) fall on a vertical line like the ideal behavior, whereas those of (a) exhibit a slant characterized by the frequency dispersion. Log $I$ for (b) in the chronoamperometry varies linearly with $t$, while that for (a) shows complicated behavior, although the DL capacitance value (a) is similar to the electric element of the capacitance (b) at 1 kHz. The difference may be ascribed to the frequency dispersion. This is our concern in this report.

We address here chronoamperometry in a circuit of series combination of a frequency-dispersed DL capacitance and a solution resistance. The expression for the chronoamperometric curves is derived analytically, and then the curves are measured at a platinum wire in KCl solution in the time domain from 50 ns to 3 s. We will find the exponential decay only at a short time, which transits gradually to the power law. Furthermore, we will show a technique of evaluating the parameters of the DL capacitance from the chronoamperometric curves without resistive effects.

2. RESULTS AND DISCUSSION

First of all, we pay attention to the short time responses of current–time curves in the two-electrode system, which is predicted to exhibit the exponential decay with the RC constant. Figure 2 shows variations of log $I$ with $t$ in three concentrations of KCl solutions for the response to the 0.1 V voltage step. Values of log $I$ fell on each line only at short times and then deviated upward from the line, as predicted from the theoretical variation in Figure 6 (Theoretical Section). The deviation begins at 130, 2, and 0.4 ms for 0.001, 0.01, and 0.1 M KCl solutions. Since these time domains are too short for the conventional voltammetric conditions, the exponential decay has not often been recognized. These variations hold also for voltage steps of 0.2 and 0.3 V.

The slope and the intercept of the lines in the exponential decay are given by $-1/R_C$, $C_\text{DL}$, and $\log(V/R_s)$, respectively, which were applied to the data of Figure 2. We evaluated $R_s$ from the real part of the ac-impedance at infinite frequency by Nyquist plots to be 4550, 480, and 66.5 $\Omega$ for concentrations of 1, 10, and 100 mM, respectively. Figure 3 shows the plot of the intercept values for three concentrations and three voltages against the logarithms of known values of $V$ and $R_s$. Since nine points fell on a line with the slope 0.97 and the almost zero intercept, the plots should be satisfied with the exponential decay.

![Figure 3](https://example.com/fig3.png)

Figure 3. Plots of the intercepts against $\log(V/R_s)$ for known values at $V$ = (circles) 0.1, (triangles) 0.2, and (squares) 0.3 V for three concentrations of KCl solutions, where $R_s$ was evaluated from the Nyquist plot by ac-impedance.

Figure 4 shows double logarithmic plots of the currents and the time for three concentrations at the 0.1 V step voltage. The shape of the variations is similar to that of Figure 8 (Theoretical Section) in that the currents at the short time take a convex depending on $R_s$ and that those at time longer than $t_0$ fall on a common line irrespective of $R_s$, i.e., concentrations of KCl. A similar variation was found also at 0.2 and 0.3 V. By applying the slope of the common line to eq 8, we evaluated $\lambda = 0.07$. The intercept provided $C_\text{DL}$ from eq 8. These values are listed in Table 1 for $V = 0.1, 0.2,$ and 0.3 V.
3. CONCLUSIONS

Chronoamperometric currents of DL capacitances responding to a potential step can be represented by the power law of the time with a type of \( t^x \) in the time domain longer than 1 ms rather than the well-known exponential decay with the RC constant. The power law is consistent with that obtained by the ac-impedance technique if the chronoamperometric time is converted to the frequency. Since the relaxation time is much longer than that of the exponential decay, the capacitive currents do not extinguish soon in conventional voltammetry, as we have frequently experienced.

The currents at time longer than 1 ms are independent of solution resistance, in contrast to the exponential decay. In other words, they are independent of the concentration of salts. Consequently, they are not controlled by ionic distribution at all, being different from Poisson–Boltzmann’s ionic distributions such as Gouy–Chapman’s theory. The double logarithmic plots fall a line, of which the slope and intercept provide \( \lambda \) and \( C_{i0} \), respectively. Values of \( \lambda \) and \( C_{i0} \) do not vary with applied potentials and are consistent with the results by ac-impedance techniques.

4. EXPERIMENTAL SECTION

Aqueous solution of KCl was prepared with analytical-grade KCl and distilled and deionized water. A working electrode was a platinum wire 0.5 mm in diameter without any seal. An electrode sealed with an insulator material often gives rise to floating capacitive current owing to imperfect boundaries between the electrode and the insulator. The wire electrode was immersed into solution by a given length, ca. 8 mm. The accurate length was determined with an optical microscope. The counter electrode was a platinum wire with an area 100 times larger than that of the working electrode, and the reference electrode was Ag/AgCl in saturated KCl solution. The test solution, 0.5 M KCl, was deaerated for 20 min before chronoamperometry.

The potentiostat was a Compactstat (Ivium, Netherlands) for cyclic voltammetry, ac-impedance measurements, and chronoamperometry. Chronoamperometry for a capacitor always causes an overload of the current immediately after a potential step. In order to examine the effect of the overloading currents, we carried out chronoamperometry for a dummy cell composed of a 4.7 \( \mu \)F film condenser connecting a 51 \( \Omega \) carbon resistance in series. So far, as the current range of the potentiostat was within the maximum current, log I had a linear relation to \( t \) (<1.5 ms). The RC values were in agreement with the theoretical value within 1.5%. The instrumental delay was examined both in the two-electrode system and the three-electrode one. Although the delay for the latter was larger than the former, we selected a current range less than the predicted maximum, V/R.

5. THEORETICAL SECTION

We derive here expressions for the current responding to a voltage step, which flows through an electric circuit of a series combination of the resistance \( R \) and the DL capacitance \( C \). First of all, chronoamperometric curves are estimated qualitatively. Immediately after the voltage step, electric charge is so rapidly stored at the capacitance that the capacitive impedance \( t/C \) is negligibly small or that the time variation of \( C \) can be neglected. Thus, the capacitance works as an ideal one. Then the current may be represented by an exponential

Figure 4. Double logarithmic plots of the current–time curves observed at the 0.1 V voltage step in the solution of concentrations of (a) 0.1, (b) 0.01, and (c) 0.001 M KCl.

Figure 5. Variations of (circles) \( C_{\text{thr}} \) and (triangles) \( \lambda \) with stepped potential, determined chronoamperometry in the time domain from 0.04 to 4.0 s in 0.1 M KCl solution.

| \( E \) (V) | \( \lambda \) | \( C_{i0} \) (\( \mu \)F cm\(^{-2} \)) | \( C_{\text{thr}} \) (\( \mu \)F cm\(^{-2} \)) |
|---|---|---|---|
| 0.1 | 0.07 | 40 | 35 |
| 0.2 | 0.09 | 39 | 33 |
| 0.3 | 0.07 | 47 | 41 |

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decay with the time constant, RC. As the current decreases with time, it is getting to be controlled by the capacitive impedance so that the frequency dispersion may be conspicuous. The current decays to be controlled by the power law of the time. Conclusively, the logarithmic current is predicted to show a linear variation with time initially and then is altered to a linear relation with logarithmic time.

According to ac-impedance experiments, the capacitance has been empirically expressed by

\[ C = C_{1}t^{x} \]

where \( C_{1} \) is the capacitive value at \( t = 1 \) s, given by \( C_{1} = (2\pi)^{x}C_{1\text{Hz}}. \) When current \( I \) flows through the series circuit of \( R \) and \( C \), the voltage \( V \) between the terminals is given by

\[ V = IR + \frac{1}{C} \int_{0}^{t} I dt \]

Multiplying eq 2 by \( C \) and carrying out the time differentiation for the voltage step yield

\[ \frac{V}{C} = R I + \frac{1}{C} \int_{0}^{t} \frac{dI}{dt} dt \]

The time differentiation \( dC/dt \) by use of eq 1 yields \( dC/dt = \lambda C/t, \) which can rewrite eq 3 as

\[ \frac{dI}{dt} = \left( \frac{1}{RC} + \frac{\lambda}{t} \right) I + \frac{V}{Rt} \]

This is a differential equation for \( I \) with respect to \( t \). Taking \( t = 0 \) in eq 2 yields the initial condition, \( I_{\text{eq0}} = V/R. \) A solution of eq 4 has been derived in the Appendix and is given by

\[ \frac{RI}{V} = \frac{\lambda}{1 - \lambda} \int_{0}^{t} (1 - x)^{(2\lambda - 1)/(1 - \lambda)} e^{-k/(1 - \lambda)x} \, dx \]

where \( k(t) = t^{(1 - \lambda)}/RC_{1}\lambda(1 - \lambda). \) The dimensionless current varies with time through the integral that includes \( k(t). \) Two extremes are examined here. For a long time or a large value of \( k, \) the integration near \( x = 0 \) is significant because of the preference of the term \( e^{-kx} \) over the term \( (1 - x)^{(2\lambda - 1)/(1 - \lambda)}. \) Integrating \( e^{-kx} \) by regarding \( 1 - x \) as unity in eq 5, we obtain

\[ \frac{RI}{V} \approx \frac{\lambda}{1 - \lambda} k = \lambda RC/t \]

This is equal to the time derivative of the charge stored in the capacitance, \( d(CV)/dt = CV_{1}\text{Hz}(dt'/dt) = AVC_{1}\text{Hz}t^{x-1} = AVC/t. \) On the other hand, the limit \( t \to 0 \) causes a singularity at \( x = 1 \) in the integrand of eq 5. Taking \( x \) to be 1 only in \( e^{-kx} \) and carrying out the integration of \( (1 - x)^{(2\lambda - 1)/(1 - \lambda)} \) yield

\[ \frac{RI}{V} \approx e^{-k/x}/(1 - \lambda) \left( \left( 2\lambda - 1 \right)/\left( 1 - \lambda \right) + 1 \right) = e^{-k} \text{or} I \to (V/R)\exp \left[-t^{(1 - \lambda)}/RC_{1\lambda}(1 - \lambda) \right]. \]

This is the well-known exponential decay when \( t \to 0. \)

The integral was evaluated numerically by dividing the integral domain of 1 into \( N \) equi-domains. The integral from 0 to 1/N was approximated by integrating only \( e^{-kx} \) for a constant \( (1 - x)^{-b} \), where \( b = (1 - 2\lambda)/(1 - \lambda) \), while those from \( n/N \) to \( (n + 1)/N \) at \( 2 \leq n < N \) were approximated by integrating only \( (1 - x)^{-b} \) for a constant \( e^{-k(x+1/2)/N}. \) As a result, we have

\[ \frac{RI}{V} \approx \left( 1 - \frac{1}{2N} \right) \left( 1 - e^{-k/\lambda} \right) \left( \frac{1}{k(1 - \lambda)} \right) \]

\[ + \sum_{n=2}^{N} \left( 1 - \frac{n - 1}{N} \right)^{1/1 - \lambda} - \left( 1 - \frac{n}{N} \right)^{1/1 - \lambda} \]

\[ e^{-k/(2\lambda - 1)/2N} \]

(7)

Values of \( RI/V \) were calculated from eq 7 at various combinations of \( t, R, \) and \( \lambda \) under conditions close to our experiments. We have confirmed that they did not vary with \( N \) over 5. An example of the dimensionless, chronoamperometric curves for \( t < 20 \text{ ms} \) is shown in the inset of Figure 6 for \( \lambda = 0.1, \) exhibiting only a decay.

The logarithms of the currents were plotted against the time in Figure 6 for some values of \( \lambda. \) A linear relation was found near \( t = 0, \) suggesting the exponential decay of the current with the RC time constant, i.e., \( I = I_{0}\times e^{-t/RC}. \) Values of the time constants in the linearity are listed in Table 2 for some values of \( \lambda. \) They are smaller than the theoretical value, 3.6 ms. With an increase in \( \lambda, \) the time constant determined from the linear variation decreases owing to the time dependence of the capacitance. In other words, values of the RC constant obtained from the plots of log \( I vs \) \( t \) are smaller than the true one.

In order to examine whether the power law is revealed in the chronoamperometric curves or not, we plotted log\(^{(RI)/V\)} against log \( t \) on a wide time scale in Figure 7 for some values of \( \lambda. \) Linear behavior, a question may occur on whether a round part in Figure 7 can in coalitions of \( \lambda, I, \) and \( R \) under conditions close to our experiments. We have confirmed that they did not vary with \( N \) over 5. An example of the dimensionless, chronoamperometric curves for \( t < 20 \text{ ms} \) is shown in the inset of Figure 6 for \( \lambda = 0.1, \) exhibiting only a decay.

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log(t/s) > −1.5. Numerical calculations demonstrated no effect. In fact, the exponential decay for a long time tends to zero, according to the comparison of (b) with (a) in Figure 1B.

Figure 8 shows the variation of the log(I/V) with log t for some values of R at λ = 0.1. Attention should be paid to the dependence of the curves on R. The currents at a short time are obviously proportional to R−1, but those at a long time merge into a common line when the time is longer than t0 = 8 × 10−6R1/(1−λ), where the units of t0 and R are second and ohm, respectively. The independence of the line from R can be proven from eq 6, which is rewritten as

\[ \log I \approx \log(\lambda V C_I t) = \log(\lambda V C_{I_0}) - (1 - \lambda) \log t \]  

(8)

We can evaluate \( \lambda \) and \( C_{I_0} \) from the slope and the intercept for known values of \( V \) and \( R \), respectively. This technique will be realized in analysis of the experimental results.

■ APPENDIX A

The differential eq 4 is solved here by the method of variation of parameters.\(^{24}\) The homogeneous type of eq 4, i.e., \( V = 0 \), has a form of separation of variables, \( dI/dt = -(\lambda / t + t^{\lambda - 1}/RC_{I_0})I \). The integration yields \( \ln I = -\lambda \ln t - t^{\lambda - 1}/RC_{I_0}(1 - \lambda) + A' \) for a constant \( A' \) or \( I = A g(t) \), where

\[ g(t) = t^{\lambda - 1} \exp[-t^{\lambda - 1}/RC_{I_0}(1 - \lambda)] \]  

(A1)

and \( A = e^{A'} \). When the particular solution \( (Ag(t)) \) is inserted into eq 4 by regarding \( A \) as a function of \( t \), we have the differential equation for \( A \):

\[ g(t)(dA/dt) = \lambda V/Rt \]  

(A2)

A solution of eq A2 is

\[ A = \frac{\lambda V}{R} \int_0^t \frac{du}{ug(u)} + B \]  

(A3)

where \( B \) is a constant. The combination of \( Ag(t) \) with eq A3 is a general solution of eq 4. The integral of eq A3 for a short time has the order of \( t_0 \), while the current should tend to \( V/R \) by the initial condition. Therefore, \( B = 0 \), and we obtain

\[ \frac{RJ}{V} = \lambda g(t) \int_0^t \frac{du}{ug(u)} = \lambda t^{\lambda - 1} \int_0^t u^{\lambda - 2} \exp\left[-u^{\lambda - 2} + u^{1-\lambda}\right] du \]  

(A4)

When \( u \) is replaced by \( x \) through \( x = 1 - (u/t)^{1-\lambda} \), eq A4 becomes eq 5.

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Notes

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