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The Difference in the Effects of *IR*-Drop from the Negative Capacitance of Fast Cyclic Voltammograms

Yuanyuan Liu ¹, Koichi Jeremiah Aoki ² and Jingyuan Chen ^{1,2,*}¹ Department of Applied Physics, University of Fukui, Fukui 910-0017, Japan; lyd21003g@u-fukui.ac.jp² Electrochemistry Museum, Fukui 9103115, Japan; d930099@yahoo.co.jp

* Correspondence: jchen@u-fukui.ac.jp or jingyuanchen46@gmail.com; Tel.: +81-9082625425

Abstract: Diffusion-controlled cyclic voltammograms at fast scan rates show peak shifts, as well as decreases in the peak currents from predicted diffusion-controlled currents, especially when the currents are large in a low concentration of supporting electrolytes. This has been conventionally recognized as an *IR*-drop effect due to solution resistance on the peaks, as well as a heterogeneously kinetic effect. It is also brought about by the negatively capacitive currents associated with charge transfer reactions. The reaction product generates dipoles with counterions to yield a capacitance, the current of which flows oppositely to that of the double-layer capacitance. The three effects are specified here in the oxidation of a ferrocenyl derivative using fast scan voltammetry. The expression for voltammograms complicated with *IR*-drop is derived analytically and yields deformed voltammograms. The peak shift is approximately linear with the *IR*-voltage, but exhibits a convex variation. The dependence of some parameters on the peaks due to the *IR*-drop is compared with those due to the negative capacitance. The latter is more conspicuous than the former under conventional conditions. The two effects cannot be distinguished specifically except for variations in the conductance of the solution.

Keywords: *IR*-drop; negative capacitance; double-layer capacitance; fast scan cyclic voltammograms; microelectrode reactions

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1. Introduction

Linear sweep cyclic voltammetry has been conventionally obtained at scan rates v in the range of $0.01 < v < 0.2 \text{ V s}^{-1}$. The slowest scan has been used for hydrodynamic voltammetry [1] and microelectrode voltammetry [1] on the assumption of a steady state. It often provides a well-defined voltammogram, but takes a long period of measurements. An advantage of slow scan rates is able to distinguish faradaic, diffusion-controlled currents from background currents via double-layer capacitance (DLC). For example, the diffusion current at a concentration of 0.5 mM ($\text{M} = \text{mol dm}^{-3}$) of redox species is roughly $I_d = 3v^{1/2} \mu\text{A}$ at a 1 mm^2 planar electrode for v in the unit of V s^{-1} . In contrast, the DLC of a platinum electrode in aqueous solutions, being $C = 30 \mu\text{F cm}^{-2}$, provides a capacitive current $I_c = 0.3v \mu\text{A}$. Since the ratio is $I_c/I_d = 0.1v^{1/2}$, the diffusion currents at $v < 0.2 \text{ V s}^{-1}$ can be distinguished from the background within a 5% error. A disadvantage is the time-consuming measurement, during which, redox species might be altered through chemical complications. If faradaic reactions occur under an adsorbed state, the advantage is not perceptive, because the background current has the same v -dependence as I_c . Slow responses fail to detect kinetic properties.

Studies on homogeneous and heterogeneous kinetics require such a wide range of v that reaction rates can be covered. A range of kinetics is often much wider than that of conventional scan rates ($0.01\text{--}0.2 \text{ V s}^{-1}$); hence, fast scan voltammetry is desirable for kinetic work, principally [2–9] and practically [10–13] for applications in neurotransmitter detection. Unfortunately, the increase in scan rates, which enhances the currents, is associated with at least five problems to be considered. (A) *IR*-drop, in which applied voltage is

insufficient due to solution resistance, makes voltammograms deformed and shifted in a scanned direction [14,15]. It is ascribed not only to ionic conductivity, but also the geometry of cells and electrodes as a solution of the Laplace equation for the voltage. (B) Even if the difference in the v -dependence of I_d and of I_c enables us to evaluate I_d accurately [16], the adsorption-controlled current, I_a , prohibits the extraction of I_a from the observed current because it has the same v -dependence as I_c . (C) The delay of a potentiostat underestimates true currents at a short time [6,7,16]. (D) Heterogeneous kinetics represented by the Butler–Volmer equation make the peak potential shifted and the peak current deviates lower than the predicted diffusion-controlled peak current [17] with an increase in v . (E) Fast scans more than 0.5 V s^{-1} generate a negatively capacitive current, which is caused by the formation of the dipoles of a reaction product with counterions at an electrode [18,19]. These problems result from an enhancement in currents due to an increase in scan rates, and are often encountered in conventional, electrochemical measurements.

A level of these problems depends on the magnitude of v . We suggest three classes; $v < 0.2 \text{ V s}^{-1}$, $v < 5 \text{ V s}^{-1}$, and $v < 500 \text{ V s}^{-1}$. The advantages and possible risks for each class are listed in Table 1.

Table 1. Advantages and risks for three classes for the levels.

Range of v	Advantages	Risks
(I) $< 0.2 \text{ V s}^{-1}$	Small background currents Easy extraction of diffusion currents Usage of low-cost potentiostats Possibility of theoretical analysis	Misleading kinetic reaction mechanisms Time consumption
(II) $< 5 \text{ V s}^{-1}$	Possibility of subtraction of IR -drop Possibility of determining reaction mechanisms Evaluation of heterogeneous kinetics Comparison of the results with those by other rapid electrochemical methods Commercially available potentiostats	Discussion required for peak shifts Deformation of waveform Limited to microelectrodes in order to prevent large currents
(III) $< 500 \text{ V s}^{-1}$	Detection of kinetics with milli-second orders such as neurotransmitters	Empirical search for detecting conditions A loss of theoretical support

The usage of fast scan rates prevents the clear distinction of faradaic reactions from backgrounds. The difficulty in the distinction in class III has been overcome with efforts of trial and error, as exemplified by the rapid detection of neurotransmitters [10–12]. The developed techniques are empirically specific to given redox species under limited conditions. In contrast, those in class II have been carried out on the theoretical basis of the difference in the v -dependence when faradaic reactions proceed in diffusion control. If problems (A)–(E) are intertwined complicatedly, corrections are not easy for the evaluation of accurate voltammograms. For class I, this intertwining is largely solved, except for adsorption in the v -dependence.

We examine here subjects (A)–(E) in detail. Since no stereotyped redox species has been found for Butler–Volmer kinetics yet [20], (D) may be excluded from the present work on ferrocenyl derivatives [21–23]. If we pay attention only to diffusion-controlled currents under category (II), subjects (B) and (C) have been automatically resolved. Both (A) and (E), being necessarily involved in fast scan voltammetry, exhibit similar behavior in spite of their different concepts. We examine in this work how voltammetric peak potentials and currents belonging to class (II) are varied when controlling parameters for (A) and (E) by the use of the fast scan voltammetry of a ferrocenyl derivative. Unfortunately, even the effects of IR -drop (A) have not been discussed systematically yet. Thus, we present here experimental results and the theory.

2. Materials and Methods

2.1. Chemicals

All the chemicals were of analytical grade. Solutions were prepared in doubly distilled water supplied by CPW-100 (Advance, Tokyo, Japan). Aqueous solutions with different concentrations of KCl ($x = 0.005, 0.05, 0.1, 0.5$, and 5 M) were prepared with the aim of varying the solution resistance. The electrochemical charge transfer species was 1 mM (ferrocenylmethyl)trimethyl ammonium (FcTMA).

2.2. Voltammetry

Voltammetry was performed in a three-electrode cell equipped with a working platinum wire electrode 0.03 mm or 0.5 mm in diameter or a 1.6 mm disk electrode. The tip of the wire was inserted into the solution at a given length (ca. 1 mm), which was measured with a microscope. The wire was not sealed with any insulator to expose an active area in order to avoid floating capacitance at the crevices of the electrode | insulator. The electrode was pretreated by being soaked in the mixed acid (0.26 M acetic + 0.33 M nitric acid + 0.73 M phosphoric acid) for 1 min to clean the surface. The counter electrode was a platinum coil. The reference electrode was a homemade Ag | AgCl (x M KCl), where x is the concentration of the test solution in order to minimize the leakage of KCl. A columnar porous glass was fixed to the tip of taper glass tube with a heat shrink tube, into which an Ag | AgCl wire was inserted, together with an x M KCl solution. In order to detect any leakage of chloride ions during the experiment, we measured the resistance values of the solution before and after the experimental test, which were almost the same.

A delay of the potentiostat, Compactstat by Ivium (Netherlands), was examined by using a carbon resistance of 1 k Ω for a dummy cell by applying the voltage with 1 V. The maximum difference in the currents at the forward and reverse scan was 3% at 8 V s $^{-1}$. Our voltammetry for FcTMA and various concentrations of KCl was conducted at scan rate less than 7 V s $^{-1}$. Ac-impedance was performed for the 10 mV amplitude and frequency domain from 1 Hz to 10 kHz. All the measurements were made at temperatures of 25 ± 1 °C.

3. Results

Figure 1A shows the voltammograms at the 0.5 mm platinum wire electrode inserted to 1 mm length into the solution of 1.0 mM FcTMA + 5 mM KCl at several scan rates. FcTMA, or related ferrocenyl derivatives, have been recognized as such fast charge transfer reacting species that voltammetric peak potentials, E_p , may be independent of voltammetric scan rates [18,20,24–27]. However, the peak potential in Figure 1A shifted in the forward direction at fast scan rates. The potential shift has often been attributed to IR -drop. The resistance values were estimated from the inverse slope of the line connecting the peaks (solid lines) [17,25]. The slope for the anodic waves was the same as that for the cathodic one. This equality partially supports the effect of IR -drop on potential shift. The inverse slope was close to the resistance (2.7 k Ω) obtained through Nyquist plots from the ac-impedance. The potential at which the lines were extrapolated to zero current can be regarded as the peak potential without IR -drop. The difference between the extrapolated anodic potential and the cathodic one was 60 mV, indicating diffusion-controlled behavior [17]. The voltammograms in Figure 1B at the disk electrode 1.6 mm in diameter were drawn out to exhibit the peak-connecting line with an inverse slope of 5.5 k Ω , which was larger than the resistance value of 4.2 k Ω with ac-impedance. Except for this point, the behavior was almost the same as that in Figure 1A.

There may have been a reason for the larger values of the slopes of the voltammetric peaks than those of the R_s -values with ac-impedance. Figure 2 shows logarithmic plots of two kinds of the resistance against concentrations of KCl. The R_s -values (a, b) with the ac-impedance were linear with the logarithmic form of [KCl], with a slope of -0.91 , independent of the electrode geometry. The approximately inverse proportion of R_s to [KCl] agrees with the concept of ionic mobility driven by electric fields [27]. The deviation of the slope (-0.91) from the ideal one (-1.0) may have been caused by the frequency dispersion

of the double-layer capacitance, in that the slopes of the Nyquist plots show concentration-dependence [19]. In contrast, the resistances evaluated from the voltammetric peaks (c, d) were kept almost constant for the low salt concentrations. They were provided through the oxidation current of FcTMA rather than the capacitive currents of the electric double layer. The potential shifts only caused by faradaic reactions can be attributed to the effects of (i) electric migration [28–30], (ii) the heterogeneous kinetics of the charge transfer reaction [17], (iii) the following chemical reactions [31,32], and (iv) the negative capacitance associated with the charge transfer reaction [18,19]. We attempt to estimate these effects briefly here.

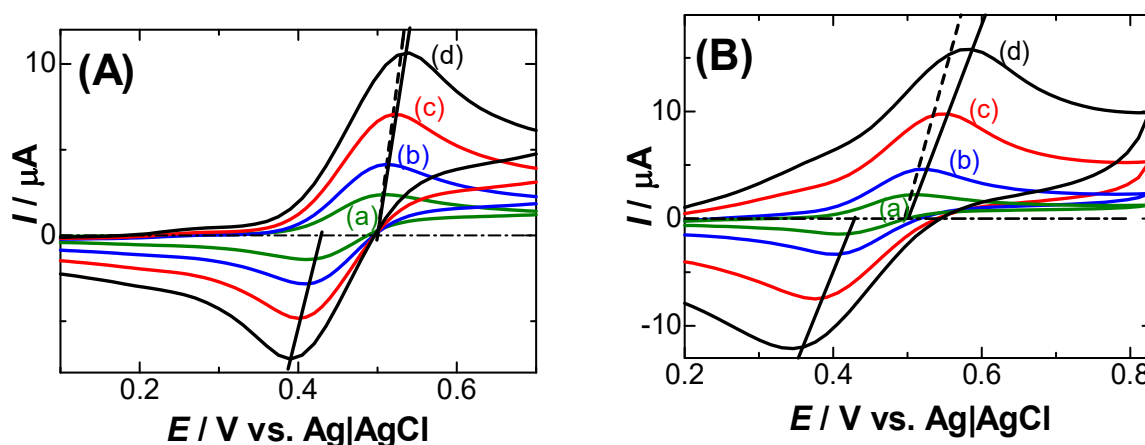


Figure 1. Voltammograms in 1.0 mM FcTMA + 5 mM KCl at the (A) Pt wire 0.5 mm in diameter and 1 mm long, (B) 1.6 mm disk Pt for $v =$ (a) 0.03, (b) 0.1, (c) 0.3, and (d) 0.7 V s^{−1}. The solid lines are connecting lines on the peaks, while the dashed lines are drawn from the solution resistance by ac-impedance.

- (i) The flux of a univalent cationic redox species controlled both by diffusion and electric migration is expressed by the Nernst–Planck equation, $j/F = -Ddc/dx - (DF/RT)c(d\phi/dx)$ [1], where c is its concentration, D is the diffusion coefficient, and ϕ is the potential in the solution at a distance from the electrode of x . It can be approximated to be $j/F = -Dc^*/\delta - (DF/RT)c^*(\Delta\phi/\delta)$, on the basis of the concept of a diffusion layer [33]. Here, its thickness at the peak current, I_p , is given by $\delta = Dc^*FA/I_p$, where A is the electrode area. The ratio of the current component of the migration to that of the diffusion is $(F/RT)\Delta\phi$. When $\Delta\phi$ was replaced by $R_s I_p$, the ratio became less than 0.5% under our experimental conditions. Therefore, migration had no contribution to the potential shift in our case.
- (ii) Electrode kinetics often cause potential shifts. Quantitatively accessible kinetics are represented by the Butler–Volmer equation. The theoretical peak currents and potentials for different scan rates can be obtained from the analytical equation at a given transfer coefficient α and a heterogeneous rate constant k_0 [17]. Figure 3(c–e) shows the variation in I_p with E_p for several scan rates at $\alpha = 0.5$ and some values of k_0 via the use of our software for the kinetics, so that I_p vs. E_p were close to the experimental ones (a). However, the experimental plots (a) were different from the theoretical variations for any different values of k_0 . The inconsistency was also applied to other values of R_s (b). Since no potential shift was found in the 0.1 M KCl solution (b), it is not reasonable to explain the shift in terms of the heterogeneous kinetics. However, an explanation only due to kinetics has often been reported [2–9].
- (iii) A following chemical reaction causes a potential shift, as can be understood from the Nernst equation for reaction rates faster than the voltammetric rates. Ferrocenyl compounds, however, are not satisfied with the condition of the rates; hence, item (iii) is unsuitable for explaining the present potential shifts.
- (iv) The negative capacitance was brought about through the following steps according to Figure 4: a charge-transferred redox species (Fc) was coupled with a counterion (Cl[−])

for electric neutrality by responding to the externally applied field E_{ap} to yield an electric dipole (Fc^+-Cl^-), where Cl^- came from the supporting electrolyte because of the highest concentration of anions: the dipole with the dipole moment p was oriented in the direction for enhancing the external field by $-pc/\epsilon_0$ to yield the effective field E_{ef} , which generated capacitance with a sign opposite to double-layer capacitance [16,34]. Negative capacitance has been obtained for ferrocenyl derivatives [18], ruthenium complex, iridium complex, and hemin [34] with ac-impedance. Since the voltammetric current from the negative capacitance was proportional to the scan rate, it depressed the diffusion tail to cause the potential shift [16]. The negative capacitance varied with electrode areas and scan rates, as the IR -drop did. The similarity in the properties stimulated us to distinguish their properties theoretically.

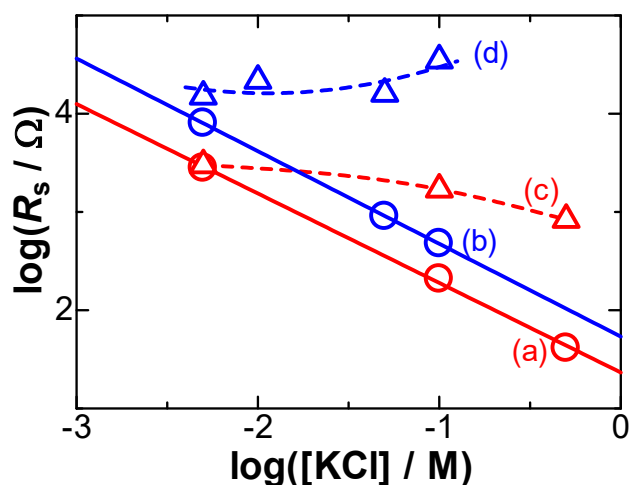


Figure 2. Logarithmic dependence of the solution resistance, R_s on $[\text{KCl}]$ at Pt wires (a,c) 0.5 mm and (b,d) 0.03 mm in diameter and 1 mm in length. R_s (a,b) were obtained with ac-impedance at the polarized potential, whereas (c,d) were obtained from slopes of lines connecting voltammetric peaks in Figure 1.

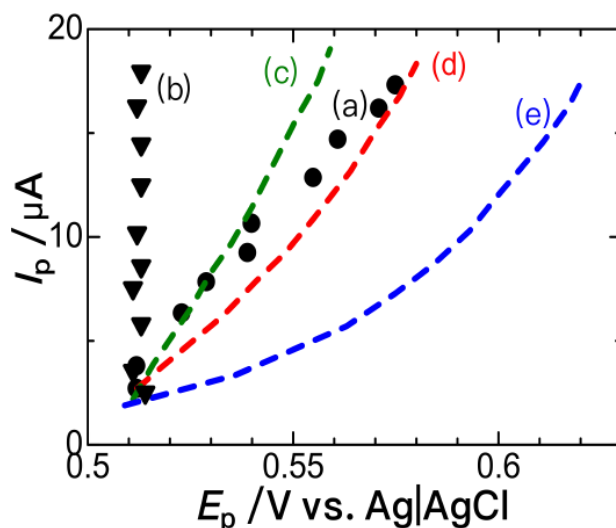


Figure 3. Variations in I_p against E_p at the 0.5 mm Pt wire electrode, 1 mm long in the solution of 1.0 mM FcTMA + (a) 0.005 M and (b) 0.1 M KCl at $0.03 < v < 3 \text{ V s}^{-1}$. The other plots were calculated from the Butler–Volmer typed kinetic equation for $k_0 =$ (c) 0.01, (d) 0.005, and (e) 0.001 cm s^{-1} and $\alpha = 0.5$.

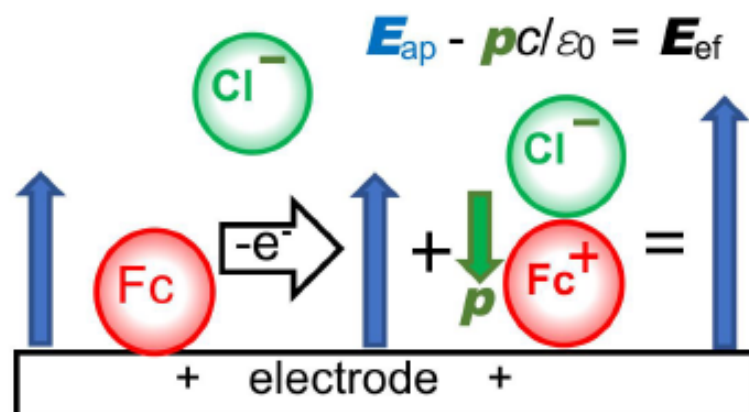


Figure 4. Illustration of generation of a dipole with Cl^- just after the oxidation of the ferrocenyl molecule.

4. Theory of Effects of IR-Drop

The electrode reaction here is a simple Nernstian charge transfer reaction with the mass transfer being controlled by x -directional diffusion. The diffusion coefficient of the reduced species, D , is assumed to have a common value with the oxidized species. Letting the solution resistance between a working electrode and a reference one be R_s , the scan rate be v , and the initial potential be E_{in} , we can express the linearly scanned potential efficiently participating in the oxidation for the current I as $E(t) = E_{\text{in}} + vt - I(t)R_s$ at time t . The common value of D implies that the sum of the concentrations of both species is equal to the bulk concentration, c^* , at any time and any location. Thus, the Nernst equation for the reduced species tends to:

$$c_x = 0 = c^* / \{1 + \exp((E_{\text{in}} + vt - I(t)R_s)F/RT)\} \quad (1)$$

On the other hand, the surface concentration is given by a solution of the diffusion equation [17] as a function of the current density j :

$$c_{x=0} = c^* - F^{-1}(\pi D)^{-1/2} \int_0^t j(t-u)u^{-1/2} du$$

Inserting this equation into Equation (1) and extracting j using the technique previously described [35] yields:

$$j/c^*FD^{1/2} = d \int_0^t (\pi u)^{-1/2} \{1 + \exp[-(E(t-u)F/RT)]\}^{-1} du / dt \quad (2)$$

The application of Leibniz's theorem [36] makes the combination of the integral and the differentiation be reduced to:

$$I/Ac^*FD^{1/2} = (1/4) \int_0^t \{\pi(t-u)\}^{-1/2} \{\text{sech}^2(E(u)F/2RT)\} \{v - R_s dI(u)/du\} (F/RT) du$$

where A is the area of the electrode.

We replace the time with the potential through $y = (E_{\text{in}} + vu)F/RT$, and define the dimensionless current as:

$$f(t) = I(t)/I_{p0} \quad (3)$$

where I_{p0} is the peak current without solution resistance, given by $I_{p0} = 0.446Ac^*F(FDv/RT)^{1/2}$. The current has the dimensionless parameter for the resistance:

$$\rho = I_{p0}R_sF/RT \quad (4)$$

and can be rewritten as:

$$f(t) = \pi^{-1/2} \int_{\zeta_{\text{in}}}^{\zeta_{\text{ap}}} (\zeta_{\text{ap}} - y)^{-1/2} g(y - 2.24\rho f(y)) \{1 - \rho df(y)/dy\} dy \quad (5)$$

where $g(x) = (1/4)\text{sech}^2(x/2)$, and ζ_{in} and ζ_{ap} are the dimensionless initial voltage $E_{\text{in}}F/RT$ and dimensionless applied voltage $(E_{\text{in}} + vt)F/RT$, respectively. Function f was evaluated using numerical computation via the discretization of $\zeta_{\text{ap}} - \zeta_{\text{in}} = nh$ for a small value of h , as was described in the supporting information.

Figure 5 shows the dimensionless voltammograms for several values of resistance parameter ρ (Equation (4)). With an increase in the values of ρ , the voltammograms shift in the positive direction, accompanied by a decrease in the peak currents. An exemplified value of $\rho = 4$ corresponds to $I_{p0} = 0.1$ mA, $R_s = 1$ k Ω .

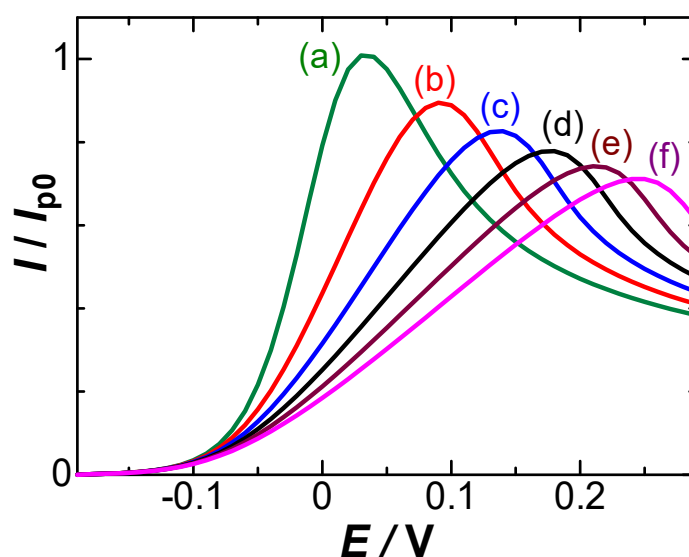


Figure 5. Voltammograms computed from Equation (5) for $\rho =$ (a) 0, (b) 2, (c) 4, (d) 6, (e) 8, and (f) 10.

Peaks were calculated for various values of ρ . The E_p increased from 0.029 V convexly with ρ , as shown in Figure 6(a). The intuitively predicted increase in E_p is $I_{p0}R_s$ or (26 mV) ρ ,

$$(E_p)_{IR, \text{prdict}} = I_{p0}R_s + 0.026 V \quad (6)$$

as shown in the line of Figure 6(b). The tangent line at $\rho = 0$ has the slope, 33 mV (Figure 6(c)). The slight shift from 26 mV is ascribed to the smaller decrease in the current for $E > E_p$ compared to that for $E < E_p$ (see Figure 5), owing to the diffusion tail. Consequently, the E_p -values calculated from Equation (5) for $\rho < 3$ are larger than the line (Equation (6)). Since the variable ρ is proportional to $v^{1/2}$ through I_{p0} , the effect of the IR-drop on the voltammograms is approximately exhibited in the form of the linearity of E_p to $v^{1/2}$ rather than $\log v$.

The peak current normalized with the theoretically diffusion-controlled one decreased with an increase in the resistance, as shown in Figure 7. This decrease can be explained in terms of the following reasons: the shift in the peak potential delayed the arrival at the peak and the delay was equivalent to a substantial decrease in the applied scan rate, v_{ap} , which led a decrease in I_p so that $I_p < I_{p0} = k_1 v_{\text{ap}}^{1/2}$, where $k_1 = 0.446Ac^*F(FD/RT)^{1/2}$. By letting the effective scan rate, v_{ef} , be $I_p = kv_{\text{ef}}^{1/2}$, v_{ef} decreased with ρ , as shown on the right ordinate in Figure 7(b). It varied linearly with $\rho^{1/2}$. The effective rate became less than a half for $\rho > 10$ or $I_{p0}R_s > 0.25$ V. The difference, $0.446 - (I_p/Ac^*F)(RT/FDv_{\text{ap}})^{1/2}$, was

approximately proportional to $\rho^{1/2}$. As a result, the peak current at any value of R_s can be approximated as:

$$I_p/I_{p0} = 1 - 0.09\rho^{1/2} \quad (7)$$

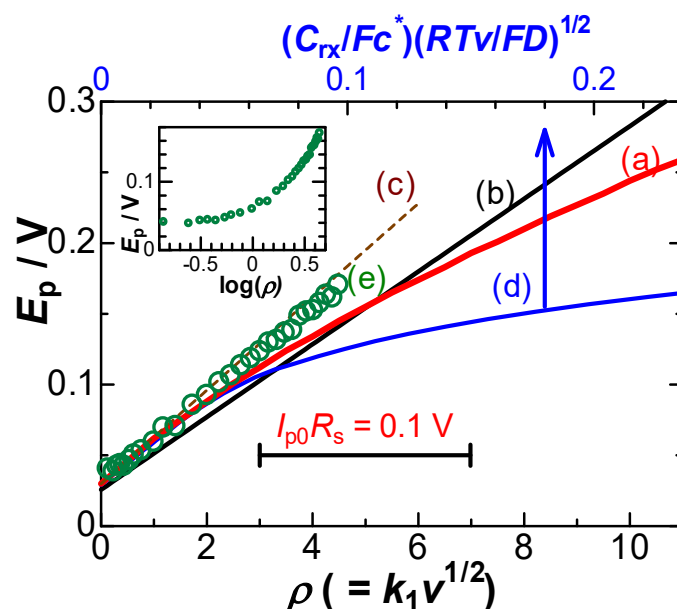


Figure 6. Variations in the peak potential due to (a) the IR -drop with the resistance parameter, (b) the intuitive IR -drop by $I_{p0}R_s$, (c) the tangent line of (a) at $\rho = 0$, (d) the negative capacitance with $(C_{rx}/c^*)(v/RTFD)^{1/2}$, and (e) experimental variations in E_p with ρ where $R_s = 2.7 \text{ k}\Omega$ in 1mM FcTMA + 5 mM KCl at the 0.5 mm wire electrode.

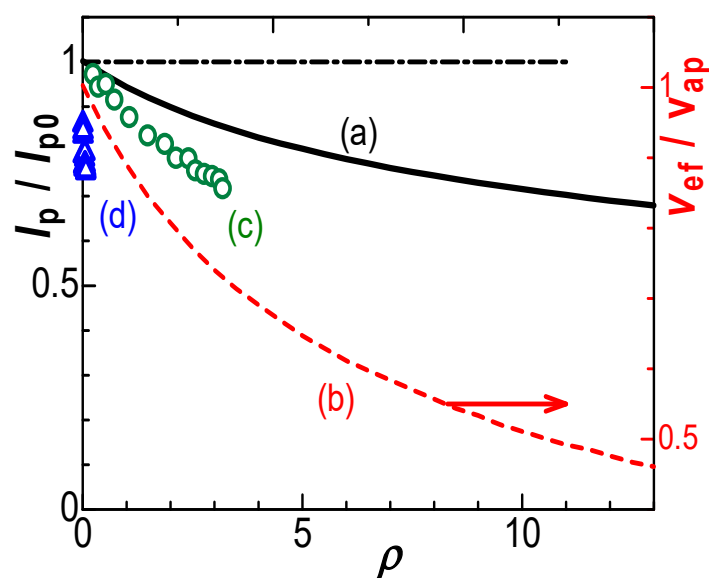


Figure 7. Variations in (a) the peak current, (b) the ratio of effective scan rate, and (c) the experimental peak current with the dimensionless resistance ρ at (circles) $R_s = 2.7 \text{ k}\Omega$ and (d) (triangles) $R_s = 80 \text{ }\Omega$.

This is a new insight into the IR -drop effect that has not been reported yet [6,8]. Since ρ was proportional to $v^{1/2}$ through I_{p0} (Equation (4)), the peak current for the IR -drop could be approximated as $I_p = kv^{1/2} - k_1v^{3/4}$.

It is interesting to compare the effects of the IR -drop on I_p and E_p with those of the negative capacitance (NC), C_{rx} . The E_p due to C_{rx} varied linearly with $\log[(\sigma^*/c^*)^2(v/FRTD)]$ [16] for $E_p - E^0 > 0.06 \text{ V}$, where σ^* is the sum of the surface charge density of the oxidized

and the reduced species, and c^* is the bulk concentration of FcTMA. In contrast, its variation for $E_p - E^0 < 0.1$ V was linear with $(\sigma^*/c^*)(v/FRTD)^{1/2}$, as shown in Figure 6 on the upper abscissa, which was scaled so that the line would overlap with the line for the IR -drop. The line can be approximated as $0.0217(\sigma^*/c^*)(v/FRTD)^{1/2} + 0.03$ in the unit of V for $E_p - E^0 > 0.06$ V. The empirical equality, $C_{rx} = 0.16(F/RT)\sigma^*$, in Equation (13) of [17] can substitute C_{rx} for σ^* to give:

$$(E_p)_{NC, <0.10V/V} = 0.135(C_{rx}/Fc^*)(RTv/FD)^{1/2} + 0.03 \quad (8)$$

When potential shift was small, the observed shift was the sum of the shifts for the IR -drop and the negative capacitance,

$$(E_p) < 0.10V/V = 0.135(C_{rx}/Fc^*)(RTv/FD)^{1/2} + 1.15I_{p0}R_s + 0.03 \quad (9)$$

R_s varied with the geometry of the electrodes at a given conductivity of solution. A disk electrode made R_s be $1/4\Lambda[KCl]a = (\pi/A)^{1/2}/4\Lambda[KCl]$ [37] for the molar conductivity Λ of KCl. R_s at a wire electrode, on the other hand, was inversely proportional to A . Some variables that controlled E_p are summarized in Table 2 for comparing these two effects.

Table 2. Variations in E_p and $I_{p0}-I_p$ with four variables.

Variables	E_p		$I_{p0}-I_p$	
	IR	NC	IR	NC
c^*	c^*	1	$c^{*3/2}$	c^*
$A(\text{disk})$	$A^{1/2}$	1	$A^{5/4}$	A
v	$v^{1/2}$	$v^{1/2}$	$v^{3/4}$	v
R_s	R_s	1	$R_s^{1/2}$	1

The IR -drop contribution to the peak current normalized with I_{p0} is:

$$(I_{p0} - I_p)/I_{p0} \equiv X_{IR} = 0.09(I_{p0}R_sF/RT)^{1/2} \quad (10)$$

On the other hand, the negatively capacitive peak current is given by $I_{NC} = I_{p0} - AC_{rx}v$. The normalized contribution is given by:

$$X_{NC} = AC_{rx}v/I_{p0} \quad (11)$$

Eliminating I_{p0} from Equations (10) and (11) yields:

$$X_{IR} = 0.09(AR_sC_{rx}vF/RTX_{NC})^{1/2} \quad (12)$$

Especially, the relation for the disk is given by:

$$(X_{IR})_{\text{disk}} = 0.06A^{1/4}(C_{rx}vF/RT\Lambda[KCl]X_{NC})^{1/2} \quad (13)$$

Figure 8 shows the variations in $(X_{IR})_{\text{disk}}$ with X_{NC} for some electrode areas at the conventionally experimental conditions of v , κ ($=\Lambda[KCl]$), and C_{rx} . The constant of $X_{IR}^2X_{NC}$ indicates that the effect of the negative capacitance was predominant compared to that of the IR -drop. Furthermore, high scan rates at large electrodes in a low salt concentration should enhance both the IR -drop and the negative capacitance.

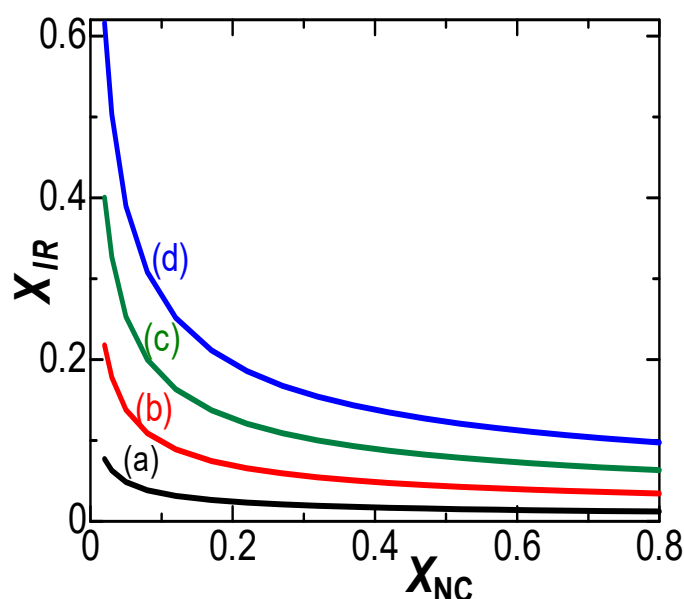


Figure 8. Variations in the fraction of the IR -drop, X_{IR} ($= (I_{p0} - I_p)/I_{p0}$), with that of the negative capacitance, X_{NC} , for A = (a) 0.01, (b) 0.04, (c) 0.09, and (d) 0.16 mm² at $v = 0.1$ V s⁻¹, $\kappa = 0.133$ S m⁻¹ corresponding to [KCl] = 10 mM and $C_{rx} = 50$ μ F cm⁻².

5. Discussion

The experimental values of E_p in the solution of 1 mM FcTMA + 5 mM KCl were plotted against ρ ($= I_p R_s F / RT$) in Figure 6(e), where the value of R_s for ρ was obtained from the Nyquist plot. They were on a line, deviated upward from the theoretical curve in Figure 6(a) of the IR -drop; hence, the potential shift cannot be ascribed only to the IR -drop. The plot of the experimental E_p vs. $\log v$ is shown in the inset of Figure 6, as is often plotted. The non-linearity indicates that the conventionally observed linearity should not explain any IR -drop effect. The addition of voltages does not agree with that of the processes because of the non-linear relation to voltages in electrochemical processes. The experimentally obtained ratio, I_p/I_{p0} , decreased with an increase in v , as shown in Figure 7(c,d) at two values of R_s . The variation in the triangular marks was close to that of the circles if the ρ -axis was expanded. The experimental values Figure 7(c,d), lower than the theory (a), were caused by the effect of the negative capacitance.

It is current that can make arithmetic operations possible through the addition of a current at a parallel process or an inverse current at a series one. In order to confirm the dependence of the IR -drop contribution on the scan rates, we plotted $I_{p0} - I_p$ in solution of 1 mM FcTMA + 5 mM KCl against v logarithmically in Figure 9(a). The plot shows a line with the slope, 0.71, which was close to the theoretical value, 3/4, in Table 2. The value of the slope suggested the control of the IR -drop. On the other hand, the currents at the 0.03 mm wire in 0.1 M KCl (in Figure 2(d)) did not contain any IR -drop effect, as demonstrated in Figure 3(b). The logarithmic plots of $I_{p0} - I_p$ vs. v show a line with slope of 0.92 in Figure 9(b). The value of the slope was close to unity; hence, it should belong to the negative capacitance.

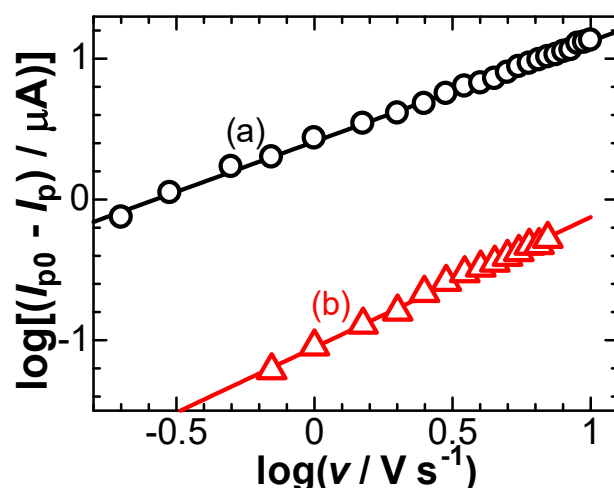


Figure 9. Logarithmic variation in $I_{p0} - I_p$ with v in the solution of (a) 1 mM FcTMA + 0.005 M KCl at the 0.5 mm wire electrode (b) 1 mM FcTMA + 0.1 M KCl at the 0.03 mm wire electrode.

6. Conclusions

Fast scanning for a diffusion-controlled voltammogram in a quiescent solution makes the peak potential shift and the peak current decrease from the known theoretical values. The deviation is not caused by Butler–Volmer typed kinetics, but is caused by combinations of the IR -drop of the solution resistance and the negative capacitance associated with electrode reactions. The two effects are hardly discriminated in terms of scan rate dependence, but a distinction can be made with variations in the concentrations of electrolytes or the size of electrodes. The effect of the negative capacitance is likely to appear more strongly than the IR -drop effect in voltammetric peaks. Wire electrodes less than 0.05 mm in diameter are suitable for suppressing IR -drop effects, even in low concentrations of electrolytes.

The expression for voltammograms complicated by IR -drop is given by a non-linear integral equation as a function of $I_{p0}R_s$. The evaluation has to rely numerical computation through digitization. The peak potential shifts intuitively due to $I_{p0}R_s$. However, the theory predicts that it shows a non-linear relation with $I_{p0}R_s$, because of an asymmetric waveform near the peak. The calculated potential shifts over 0.2 V are smaller than the values of $I_{p0}R_s$. The potential shift delays the time reaching the peak, yielding a decrease in the actual scan rate. As a result, the peak current is observed to be suppressed.

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References

1. Bard, A.J.; Faulkner, L.R. *Electrochemical Methods; Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, NY, USA, 2001; pp. 29, 170–176, 331–332.
2. Howell, J.O.; Goncalves, J.M.; Amatore, C.; Klasinc, L.; Wightman, R.M.; Kochi, J.K. Electron transfer from aromatic hydrocarbons and their π -complexes with metals. Comparison of the standard oxidation potentials and vertical ionization potentials. *J. Am. Chem. Soc.* **1984**, *106*, 3968–3976. [\[CrossRef\]](#)
3. Amatore, C.; Lefrou, C. Is cyclic voltammetry above a few hundred kilovolts per second still cyclic voltammetry? *J. Electroanal. Chem.* **1990**, *296*, 335–358. [\[CrossRef\]](#)
4. Montenegro, M.I.; Pletcher, D. The determination of the kinetics of electron transfer using fast sweep cyclic voltammetry at microdisc electrodes. *J. Electroanal. Chem.* **1986**, *200*, 371–374. [\[CrossRef\]](#)
5. Fitch, A.; Evans, D.H. Use of microelectrodes for the study of a fast chemical step in an electrode reaction. *J. Electroanal. Chem.* **1986**, *202*, 83–92. [\[CrossRef\]](#)

6. Amatore, C.; Maisonhaute, E.; Simonneau, G. Ultrafast cyclic voltammetry: Performing in the few megavolts per second range without ohmic drop. *Electrochem. Commun.* **2000**, *2*, 81–84. [CrossRef]
7. Andrieux, C.P.; Garreau, D.; Hapiot, P.; Pinson, J.; Saveant, J.M. Fast Sweep Cyclic Voltammetry at Ultra-Microelectrodes Evaluation of the Method for Fast Electron-Transfer Kinetic Measurements. *J. Electroanal. Chem.* **1988**, *243*, 321–335. [CrossRef]
8. Wosiak, G.; Coelho, D.; Carneiro-Neto, E.B.; Pereira, E.C.; Lopes, M.C. Numerical Resolving of Net Faradaic Current in Fast-Scan Cyclic Voltammetry Considering Induced Charging Currents. *Anal. Chem.* **2020**, *92*, 15412–15419. [CrossRef]
9. Amatore, C.; Oleinick, A.; Svir, I. Theoretical Analysis of Microscopic Ohmic Drop Effects on Steady-State and Transient Voltammetry at the Disk Microelectrode: A Quasi-Conformal Mapping Modeling and Simulation. *Anal. Chem.* **2008**, *80*, 7947–7956. [CrossRef]
10. Roberts, J.G.; Sombers, L.A. Fast-Scan Cyclic Voltammetry: Chemical Sensing in the Brain and Beyond. *Anal. Chem.* **2018**, *90*, 490–504. [CrossRef]
11. Baur, J.E.; Kristensen, E.W.; May, L.J.; Wiedemann, D.J.; Wightman, R.M. Fast-Scan Voltammetry of Biogenic Amines. *Anal. Chem.* **1988**, *60*, 1268–1272. [CrossRef]
12. Venton, B.J.; Cao, Q. Fundamentals of fast-scan cyclic voltammetry for dopamine detection. *Analyst* **2020**, *145*, 1158–1168. [CrossRef]
13. Puthongkham, P.; Venton, B.J. Recent advances in fast-scan cyclic voltammetry, doi.org/10.1039/C9AN01925A. *Analyst* **2020**, *145*, 1087–1102. [CrossRef]
14. CV Sim: Simulation of Simple Redox Reaction (E) Part 2 Ohmic Drop Effect & Double Layer Capacitance—Application Note 41-2, pp. 1–4. Available online: https://www.biologic.net/wp-content/uploads/2019/08/cv-simulation_electrochemistry-an41-2.pdf (accessed on 5 November 2018).
15. Aoki, K.J.; Chen, J. Tips of Voltammetry. pp. 1–19. Available online: <https://www.intechopen.com/chapters/63917> (accessed on 5 November 2018).
16. Aoki, K.J.; Chen, J.; Liu, Y.; Jia, B. Peak potential shift for fast cyclic voltammograms owing to capacitance of redox reactions. *J. Electroanal. Chem.* **2020**, *856*, 113609. [CrossRef]
17. Matsuda, H.; Ayabe, Y.Z. The theory of the cathode-ray polarography of Randles-Sevcik. *Elektrochimie* **1955**, *59*, 494–503.
18. Aoki, K.J.; Chen, J.; Zeng, X.; Wang, Z. Decrease in double layer capacitance by Faradaic current. *RSC Adv.* **2017**, *7*, 22501. [CrossRef]
19. Wang, R.; Aoki, K.J.; Chen, J. Enhancement of the Negative Capacitance Associated with the Dissolution of Silver by Salt Concentrations by Means of Anodic Stripping Voltammetry. *J. Electrochem.* **2022**, *3*, 397–406. [CrossRef]
20. Aoki, K.J.; Zhang, C.; Chen, J.; Nishiumi, T. Heterogeneous reaction rate constants by steady-state microelectrode techniques and fast scan voltammetry. *J. Electroanal. Chem.* **2013**, *706*, 40–47. [CrossRef]
21. Sun, P.; Mirkin, M.V. Kinetics of electron-transfer reactions at nanoelectrodes. *Anal. Chem.* **2006**, *78*, 6526–6534. [CrossRef]
22. Velmurugan, J.; Sun, P.; Mirkin, M.V. Scanning Electrochemical Microscopy with Gold Nanotips: The Effect of Electrode Material on Electron Transfer Rates. *J. Phys. Chem. C* **2009**, *113*, 459–464. [CrossRef]
23. Smalley, J.F.; Feldberg, S.W.; Chidsey, C.E.D.; Linford, M.R.; Newton, M.D.; Liu, Y.-P. The Kinetics of Electron Transfer Through Ferrocene-Terminated Alkanethiol Monolayers on Gold. *J. Phys. Chem.* **1995**, *99*, 13141–13149. [CrossRef]
24. Nioradze, N.; Kim, J.; Amemiya, S. Quasi-Steady-State Voltammetry of Rapid Electron Transfer Reactions at the Macroscopic Substrate of the Scanning Electrochemical Microscope. *Anal. Chem.* **2011**, *83*, 828–835. [CrossRef] [PubMed]
25. Li, Y.; Bergman, D.; Zhang, B. Preparation and Electrochemical Response of 1–3 nm Pt Disk Electrodes. *Anal. Chem.* **2009**, *81*, 5496–5502. [CrossRef] [PubMed]
26. Zhang, Y.; Zhou, J.; Lin, L.; Lin, Z. Determination of Electrochemical Electron-Transfer Reaction Standard Rate Constants at Nanoelectrodes: Standard Rate Constants for Ferrocenylmethyltrimethylammonium(III)/(II) and Hexacyanoferrate(III)/(II). *Electroanal* **2008**, *20*, 1490–1494. [CrossRef]
27. Atkins, P.; Paula, J.D. *Atkin's Physical Chemistry*, 10th ed.; Oxford University Press: Oxford, UK, 2014; pp. 799–802.
28. Zhou, Y.; Yang, P.; Yuan, C.; Huo, Y. Electrochemical migration failure of the copper trace on printed circuit board driven by immersion silver finish. *Chem. Eng. Trans.* **2013**, *33*, 559–564.
29. Sorbello, R.S. Microscopic driving forces for electromigration. *Mater. Res. Soc. Conf. Proc.* **1996**, *427*, 73–81. [CrossRef]
30. Putra, B.R.; Aoki, K.J.; Chen, J.; Marken, F. A cationic rectifier based on a graphene oxide covered microhole: Theory and experiment. *Langmuir* **2019**, *35*, 2055–2065. [CrossRef]
31. Song, P.; Fisher, A.C.; Wadhawan, J.D.; Cooper, J.J.; Ward, H.J.; Lawrence, N.S. A mechanistic study of the EC' mechanism—the split wave in cyclic voltammetry and square wave voltammetry. *RSC Adv.* **2016**, *6*, 70237–70242. [CrossRef]
32. Nassef, H.M.; Radi, A.-E.; O'Sullivan, C.K. Electrocatalytic sensing of NADH on a glassy carbon electrode modified with electrografted o-aminophenol film. *Electrochem. Commun.* **2006**, *8*, 1719–1725.
33. Molina, A.; Gonzalez, J.; Laborda, E.; Compton, R.G. On the meaning of the diffusion layer thickness for slow electrode reactions. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2381–2388. [CrossRef]
34. Aoki, K.J.; Taniguchi, S.; Chen, J. Participation in negative capacitance of diffusion-controlled voltammograms of hemin. *Omega ACS* **2020**, *5*, 29447–29452. [CrossRef]
35. Aoki, K. Is voltammetric current proportional to the number of transferring electrons of multi-charged ions or 3/2 powers of the number? *Electroanalysis* **2005**, *17*, 1379–1383. [CrossRef]

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36. Abramowitz, M.; Stegun, I.A. *Handbook of Mathematical Functions*; U.S. Government Printing Office: Washington, DC, USA, 1964; p. 11. Available online: <https://personal.math.ubc.ca/~cbm/aands/frameindex.htm> (accessed on 5 November 2018).
 37. Newman, J.S. *Electrochemical Systems*; Prentice-Hall Inc.: Englewood Cliff, NJ, USA, 1991; Chapter 18; pp. 340–345.

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