Determination of Constant Phase Element Parameters under Cyclic Voltammetry Conditions Using a Semi-theoretical Equation

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ABSTRACT

An electrical double layer typically behaves as a constant phase element (CPE) rather than a pure capacitor. To separate the non-faradaic current contributed by the electrical double layer from the total current, which is obtained from cyclic voltammetry using modeling, the CPE parameters—the CPE parameter (Y_0) and the CPE exponent (γ)—need to be determined. In this work, a semi-theoretical equation for directly evaluating the CPE parameters from cyclic voltammetry experiments was developed by investigating cyclic voltammetry performed under a narrow potential window. The experiments were performed using a ferri/ferrocyanide solution with a cylindrical graphite electrode. The obtained parameters were quantitatively different from those obtained from electrochemical impedance spectroscopy analysis. However, the obtained parameters were in an excellent agreement with cyclic voltammograms. This suggested that to model a non-faradaic current using a CPE in cyclic voltammetry, it is important to evaluate the CPE parameters using cyclic voltammetry. An application of the CPE parameters for simulating cyclic voltammograms that contain both faradaic and non-faradaic currents is also presented. The results show that the model can satisfactorily simulate entire cyclic voltammograms.

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1. Introduction

Cyclic voltammetry is an electroanalytical method that is used to determine parameters such as electron transfer kinetics, diffusivity of active species, and electrode effective surface area.^{1–3} In cyclic voltammetry, a cyclic triangular potential scan is applied to an electrode that is submerged in an unstirred analyte, and the total current is measured as a response of the system. The total current consists of two parts: one is the faradaic current generated from the reaction of interest, and the other is the non-faradaic current contributed by an electrical double layer. Although non-faradaic current fades with time in a potential step experiment, it behaves differently in potentiodynamic measurements such as cyclic voltammetry. Non-faradaic current always flows continuously in cyclic voltammetry, and it can be simply described by Eq. (1) as follows:

$$I_{nf} = C \frac{dE}{dt} \quad (1)$$

where C is the ideal capacitance of the electrical double layer (F), E is the potential (V), and t is the time (s). However, it is widely recognized that, the electrical double layer behaves as a constant phase element (CPE) rather than a pure capacitor in the above-mentioned equation.^{4–6} Non-faradaic current from an electrical double layer governed by a CPE can be expressed in a fractional derivative form as

$$I_{nf} = Y_0 \frac{d^\gamma E}{dt^\gamma} \quad (2)$$

where Y_0 is the CPE parameter ($\text{Fs}^{\gamma-1}$), and superscript γ is the CPE exponent.

To determine parameters such as the reaction rate constant and the electrode effective surface area, it is essential to model the entire voltammogram to characterize complex mechanisms. If the analytical relationships between the peak potentials or currents

and scan rates are used conventionally without considering the non-faradaic current and ohmic drop effects, this can lead to incorrect parameters. Therefore, it is important to distinguish between faradaic and non-faradaic currents. However, the non-faradaic current is not linear with the applied potential, and it is also coupled with the faradaic current through ohmic drop effects.^{7,8} In addition, if the ohmic drop effect is appreciable compared to the accuracy of the measurement, the faradaic peak potential is flattened and shifted more toward the irreversible regime because of the non-linear scan rate. Usually, ohmic drop effects can be minimized by either lowering the scan rate, reducing the electrode surface area,^{9–11} or increasing the supporting electrolyte concentration. Nonetheless, they are not preferable in certain cases.

To distinguish between faradaic and non-faradaic currents in cyclic voltammograms, a model that includes the combined effects of ohmic resistance, CPE, mass transfer, and faradaic processes has been proposed.⁷ A set of equations such as Fick's second law and the Butler–Volmer equation were used to solve for the faradaic current, while the non-faradaic current was calculated using the time-domain response of a CPE. By adopting the equivalent circuit concept, the total current can be obtained. This model has several advantages because it considers both ohmic resistance and CPE effects. Important parameters can still be evaluated using this model, although both the ohmic resistance and CPE effects are appreciable. However, CPE parameters are required as inputs in this model.

Several theoretical and experimental studies have been conducted to understand the origin of the CPE. However, there is no consensus on the physical meaning of the CPE.^{12,13} First, it was believed that the CPE originates from interface irregularity. Le Mehaute and Crepy¹⁴ introduced the concept of fractal geometries to the electrochemical impedance. This concept was used by Nyikos and Pajkossy¹⁵ to show that γ is a function of the fractal dimension. When the fractal dimension equals 2, which corresponds to a perfectly smooth surface, the relation results in a γ of 1 (i.e., a pure capacitor), whereas CPE behavior ($\gamma < 1$) was observed when the

fractal dimension was higher than 2 in their study. Thus, this suggested that capacitance dispersion on solid electrodes is caused by surface irregularities. This assumption has been confirmed by several studies, which showed that γ is a function of surface roughness.^{16–20} Besides the fractal approach, de Levie²¹ suggested a pore model based on a V-shaped groove to describe the rough surface of an electrode. In their model, the double layer capacitance was assumed to be uniform over the true surface and the current lines were perpendicular to the macroscopic surface of the electrode. The impedance of the groove is analogous to a transmission line, and the phase angle of the impedance changes from $\pi/2$ to $\pi/4$ in the limit of low and high frequency. The branched transmission line suggested by Scheider²² leads to an impedance with a phase angle of $(3/4) \times (\pi/2)$. The important characteristics of transmission lines are that they produce a constant phase angle and the phase angle is not restricted to $\pi/4$ like a Warburg element, which is the characteristic behavior of a CPE. Nonetheless, Bates et al.²³ experimentally found no correlation between γ and the fractal dimension. They suggested that γ is not just a function of the fractal dimension of the electrode, which concurred with the report by Kaplan et al.²⁴ Conversely, Martin and Lasia²⁵ suggested the idea of surface irregularity and showed that an increase in γ occurs with an increase in surface roughness. A qualitative experiment conducted by Kerner and Pajkossy^{26,27} revealed that the capacitance dispersion was caused by heterogeneities on the atomic scale rather than geometric irregularities (surface roughness). Some studies^{28,29} also supported the idea of the relationship between capacitance dispersion and surface heterogeneity. However, CPE behavior has been also attributed to electrode porosity,^{30–32} variations in coating composition,³³ and slow adsorption reactions,³⁴ which clearly underlined that the physical meaning of this element is not clear.

The conventional method for evaluating CPE parameters is electrochemical impedance spectroscopy (EIS) analysis. EIS is a very powerful tool used to study electrochemical properties and aging mechanisms of electrochemical converters.^{35–42} This measurement is based on the principle of applying an alternating signal of a small amplitude to an electrode that is submerged in an electrolyte. The applied signal is compared with the measured response to evaluate the impedance of a system.^{43,44} Because the impedance of a system is obtained instead of directly evaluating the CPE parameters, applying EIS analysis is difficult because it involves selecting an equivalent circuit to describe the impedance to obtain the CPE parameters. There are several equivalent circuit models available for simulating the electrical characteristics of a system. One of the most common models used for describing the electrochemical interface of a flat rough electrode exposed to an electrolyte solution is the Randles model, which treats the electrode as a homogeneous system. In this model, the equivalent series resistance, which represents the sum of resistances from the electrode, electrolyte, and electrical contacts, is in series to a parallel connection of faradaic impedance and double layer capacitance, which is often replaced by a CPE. To increase the performance of energy storage or generation devices, highly porous electrodes are typically used to increase the specific surface area. In this type of electrode, the reaction does not simply occur on the surface of the electrode, like on a flat rough electrode. This consequently leads to a non-uniform distribution of solution resistance and current on the electrode. The electrochemical characteristics of this kind of electrode can be expressed by the transmission line model.

Nevertheless, Zheng et al.⁴⁵ compared cyclic voltammetry and EIS as techniques for analyzing double layer capacitances. The researchers observed that, in some cases, there are quantitative differences between the charge transfer resistance and the capacitance of an electrical double layer obtained from cyclic voltammetry and those obtained from EIS. They suggested that these differences can be attributed to different levels of surface reactivity supported by

the measurement conditions of the two techniques.^{45,46} In addition, the ohmic resistance from EIS is often much smaller than that evaluated using the galvanostatic methods.^{47–50} Therefore, to distinguish between the faradaic and non-faradaic currents in cyclic voltammograms, it is important to directly determine the CPE parameters from cyclic voltammetry. Although several studies have investigated the time-domain response of a CPE,^{5–8,51,52} few studies have focused on obtaining the CPE parameters in cyclic voltammetry experiments.⁵³ However, those approaches were limited to the case when a large faradaic current is not present in the first cycle. In our study, a semi-theoretical equation for time-domain responses of a CPE in voltammetry was introduced to estimate the CPE parameters under cyclic voltammetry conditions. A numerical investigation of the time-domain responses of a CPE was conducted to develop the semi-theoretical equation. The CPE parameters obtained from the semi-theoretical equation were compared against the parameters obtained from EIS data using complex nonlinear least-squares regression (CNLS). Furthermore, the parameters obtained from both methods were applied to a numerical model to validate the experimental data. The proposed method has the advantage of being straightforward for determining CPE parameters. Application to an actual electrochemical system is also presented.

2. Determining CPE Parameters under Voltammetry Conditions

The system considered in this work was a stationary cylindrical electrode that was submerged in an unstirred electrolyte. The faradaic current was contributed by the simple electrode reaction, $R \rightleftharpoons O + ze^-$, which occurs at the surface of the electrode. The non-faradaic current generated by an electrical double layer is governed by a CPE. The impedance of the CPE in the Laplace domain can be expressed as

$$Z_{CPE}(s) = \frac{1}{Y_0 s^\gamma} \quad (3)$$

where s is the Laplace variable.

2.1 Linear sweep voltammetry

To determine CPE parameters using cyclic voltammetry, linear sweep voltammetry was first considered. In linear sweep voltammetry, ohmic drop effects can be controlled by the scan rate. A lower scan rate results in a lower total current and thus a lower ohmic drop. Assuming that the ohmic drop effect is negligible, the assumption of a constant scan rate holds true. From Eq. (3), applying the Ohm's law, setting the constant scan rate, and taking the inverse Laplace transformation, the responses of a CPE to a linear potential scan can be expressed as

$$I_{nf}(t) = \frac{Y_0 v}{\Gamma(2-\gamma)} t^{1-\gamma} = \frac{Y_0 v^\gamma}{\Gamma(2-\gamma)} E_{app}^{1-\gamma} \quad (4)$$

where subscript nf indicates the non-faradaic condition, v is the scan rate (V/s), E_{app} is the potential applied to the system (V), and Γ is the gamma function.

Theoretically, the abovementioned equation can be applied to a system in which the faradaic current is absent to determine the CPE parameters, e.g., the electrical double layer capacitor and electrochemical systems when only one species initially appear in the system. When only one active species is present in an electrolyte, it is possible to prevent the presence of faradaic current by carefully selecting the potential window. However, in practical cases, the faradaic current may not be avoided because both reduced and oxidized species may appear in the system before conducting linear sweep voltammetry.

2.2 Cyclic voltammetry

The model presented here was proposed by Charoen-amornkitt et al.⁷ The faradaic current was solved through the Butler–Volmer equation and Fick’s second law, which account for the mass transfer and faradaic processes. The non-faradaic current was calculated using the time-domain response of the CPE. Using the equivalent circuit concept, these currents can be combined, and ohmic drop effects are included. For the faradaic part, the diffusion of active species is governed by Fick’s second law, which can be expressed in a general form as

$$\frac{\partial c_j}{\partial t} = \nabla \cdot (D_j \nabla c_j) \quad (5)$$

where subscript j indicates the electroactive species R or O , c_j is the species concentration (mol/cm³), and D_j is the diffusivity of the species (cm²/s).

Equation (6), the Butler–Volmer equation, is used to describe the rate of an electrochemical reaction,

$$\frac{j}{zF} = k_0(c_R)_s \exp\left(\frac{(1-\alpha)zF\eta}{RT}\right) - k_0(c_O)_s \exp\left(\frac{-\alpha zF\eta}{RT}\right) \quad (6)$$

where j is the current density from the reaction of interest (A/m²), z is the electron transferred, F is the Faraday constant (C/mol), k_0 is the reaction rate constant (m/s), subscript s indicates the electrode surface, α is the charge transfer coefficient, R is the universal gas constant (kg·m²/(s²·K·mol)), T is the temperature (K), and η is the overpotential (V).

The current density at the electrode surface can also be expressed by the diffusion flux as

$$\frac{j}{zF} = D_R \nabla(c_R)_s = -D_O \nabla(c_O)_s \quad (7)$$

The electrode potential is initially held at E_i and is swept linearly with time. Thus, the applied potential at any time can be given by

$$E_{app} = E_i + vt \quad (8)$$

The initial conditions are

$$c_R = c_R^*, \quad c_O = c_O^* \quad \text{at } t = 0 \quad (9)$$

with

$$c_R(t) + c_O(t) = c_R^* + c_O^* \quad (10)$$

where the * superscript denotes the initial condition.

For the non-faradaic current, applying Eq. (3) and Ohm’s law, allowing the actual applied potential to be any function of time, and taking the inverse Laplace transformation, the responses of the CPE in the time domain can be obtained as

$$I_{nf}(t) = \frac{d\bar{E}_{act}(t)}{dt} * A(t) + \bar{E}_{act}(0)A(t) \quad (11)$$

with

$$A(t) = \frac{Y_0 t^{-\gamma}}{\Gamma(1-\gamma)} \quad (12)$$

where $\bar{E}_{act}$ is the actual applied potential deviated from the initial value (V), and the * symbol denotes the convolution operation. Taking the convolution, Eq. (11) can be written as

$$I_{nf}(t) = \int_0^t \frac{d\bar{E}_{act}(\tau)}{d\tau} A(t-\tau) d\tau + \bar{E}_{act}(0)A(t) \quad (13)$$

The first term on the right-hand side of Eq. (13) is the Caputo fractional derivative. By uniformly discretizing the time interval, the approximate form of Eq. (13) can be expressed as follows:⁷

$$I_{nf}(t) = \frac{A(\Delta t)}{(1-\gamma)} \sum_{j=0}^k [\bar{E}_{act}(t_{k+1-j}) - \bar{E}_{act}(t_{k-j})] [(j+1)^{1-\gamma} - j^{1-\gamma}]$$

$$+ \bar{E}_{act}(0)A(t) \quad (14)$$

However, clearly, the equation governing the responses of a CPE (Eq. (14)) has a complicated form. Thus, it is difficult to apply Eq. (14) for determining CPE parameters. To model the total current, a Randles equivalent circuit is assumed. The total current flows through the CPE, connecting in parallel to the faradaic impedance, and through a resistance, connecting in series to those CPE and faradaic impedance. The total current can be expressed as follows:

$$I_{total} = I_{nf} + I_f \quad (15)$$

Because of the presence of an ohmic drop effect, the actual potential applied to the electrode depends on the total current, and it can be expressed as

$$E_{act} = E_{app} - I_{total}R_\Omega \quad (16)$$

A flowchart of the numerical algorithm for calculating cyclic voltammograms can be found elsewhere.⁷

There is a conventional method for estimating the differential capacitance of an electrode using cyclic voltammetry, which operates under a narrow potential window.^{54,55} It is known that by performing cyclic voltammetry under a well-selected narrow potential window, faradaic current can be avoided.⁵⁶ Numerical investigation on cyclic voltammetry with a narrow potential window was conducted to confirm whether it is possible to experimentally obtain the non-faradaic current alone. To ensure that the simulation is realistic, the properties and parameters used in this simulation, i.e., the effective surface area (A_{eff}), formal potential (E°), diffusivity of the active species (D), reaction rate constant (k_0), and charge transfer coefficient (α), were obtained from the experiments using a cylindrical graphite electrode submerged in a ferri/ferrocyanide solution. The values of Y_0 and γ were approximated from the results of Charoen-amornkitt et al.⁷ A low scan rate of 10 mV/s was selected to minimize the ohmic drop effects. Furthermore, both the reduced and oxidized species were set to be present in the initial electrolyte so that the faradaic current could not be avoided.

The numerical response of an electrochemical system, which consists of both reduced and oxidized species in an initial electrolyte, is depicted in Figs. 1a–d. Figure 1a shows a cyclic voltammogram with a wide potential window of an electrochemical system. Clearly, in this system, non-faradaic current was also involved and superimposed on faradaic current. During the forward scan, the initially applied potential was 0.50 V. The potential was swept negatively with a scan rate of 10 mV/s to generate both non-faradaic and faradaic currents. The very high positive current in the first few potentials, which is faradaic current, was evidence of the presence of reduced species. The formal potential of the reaction was approximately 0.25 V, which resulted in the cathodic and anodic peak potentials at approximately 0.22 V and 0.28 V, respectively. Cyclic voltammograms for the same system in different narrow potential windows are presented in Fig. 1b. In this case, it was not possible to evaluate the CPE parameters using the approach proposed by Sagüés et al.⁵³ Because there were also oxidized species in the electrolyte, in the cyclic voltammogram with a potential range of 0.00–0.10 V, a very large negative current in the first few potentials was observed. Very large currents were also observed in the other potentials. However, those were caused by the presence of reduced species. Furthermore, the shapes of the cyclic voltammograms with potential ranges of 0.00–0.10 V and 0.40–0.50 V were similar after performing cyclic voltammetry for several cycles. However, the response in the 0.20–0.30 V range was different.

This difference can be explained using Figs. 1c–d, which show the faradaic and non-faradaic currents of the cyclic voltammograms in Fig. 1b. In Fig. 1c, the magnitude of the faradaic current in

Figure 1. Numerical solutions of (a) total current in a wide potential window, (b) total current, (c) faradaic current, and (d) non-faradaic current in different narrow potential windows under the conditions of $A_{eff} = 33.5 \text{ mm}^2$, $E^{\circ'} = 0.25 \text{ V vs. Ag/AgCl}$, $Y_0 = 0.002 \text{ Fs}^{-1}$, $\gamma = 0.7$, $D = 7 \times 10^{-6} \text{ cm}^2/\text{s}$, $k_0 = 7 \times 10^{-5} \text{ m/s}$, $\alpha = 0.5$, $T = 298 \text{ K}$, $\nu = 10 \text{ mV/s}$, $c_O^* = 1 \text{ mM}$, and $c_R^* = 1 \text{ mM}$.

regions that are sufficiently far from the formal potential gradually decreased as the cyclic voltammetry experiment proceeded. However, the magnitude of the faradaic current that was obtained near the formal potential remained the same. After applying the cyclic triangular potential scan for several cycles, the faradaic currents in the potential ranges of 0.00–0.10 V and 0.40–0.50 V were not completely absent but were independent of the applied potential; hence, their effects were suppressed. The non-faradaic currents for the three different potential ranges are presented in Fig. 1d. Clearly, there were no differences between each potential range. The non-faradaic current in Fig. 1d and the total current in Fig. 1b had similar shapes when the cyclic voltammetry was performed in the potential windows of 0.00–0.10 V and 0.40–0.50 V. Although the faradaic current was still included in the obtained total current, the total current obtained after performing cyclic voltammetry until the periodic responses was observed, as shown in Fig. 1b, which represented the non-faradaic current. In principle, because the non-faradaic current can be obtained using experiments, it is possible to convert the experimental response to the CPE parameters.

2.3 A semi-theoretical approach

From Section 2.1, it is known that CPE parameters can be obtained from linear sweep voltammograms by fitting experimental data with a power regression model because Eq. (4) is a power formula. Section 2.2 shows that by performing cyclic voltammetry for several cycles the periodic responses were observed. The obtained current was mainly a non-faradaic current and did not significantly change as a function of the number of cycles. Combining these two ideas, if the periodic responses follow the

power formula, fitting them with the power function would provide the CPE parameters.

Because the total current that is obtained after performing cyclic voltammetry under a narrow potential window for several cycles is mainly non-faradaic current, faradaic processes can be neglected. Moreover, the ohmic resistance can be ignored if an electrode has a sufficiently small surface area and if the scan was performed at a low scan rate. When the faradaic current is absent and the ohmic resistance is negligible, Fig. 2a shows a cyclic voltammogram of the CPE calculated from Eq. (14). The red curves highlight the first and tenth positive sweeps. The results of fitting them with the power regression model are shown in Figs. 2b and 2c. As shown from the coefficient of determination, the results of the first positive sweep perfectly fit the power regression model. However, the results of the tenth positive sweep did not show a perfect fit; however, it was a sufficiently good fit ($R^2 = 0.998$). However, the pre-power factor and the exponent of the fitted equation obtained from the responses of the tenth positive sweep were different from those obtained from the responses of the first sweep because the responses of a CPE always contain the effect of historical responses, as described by Eq. (14). To determine the CPE parameters, the fitted pre-power factor and the exponent of the tenth positive sweep required some factors to convert them back to the values in the first positive sweep. Thus, the semi-theoretical equation for determining the CPE parameters using cyclic voltammetry can be written similar to Eq. (4) as

$$\bar{I}_p(\bar{E}_{app}) = \frac{aY_0\nu^\gamma}{\Gamma(2-\gamma)} \bar{E}_{app}^{(1-\gamma)b} \quad (17)$$

Figure 2. (a) A cyclic voltammogram in a narrow potential window, where the red lines indicate the curves selected for fitting with the power regression model: (b) the curve from the first positive sweep and (c) the curve from the tenth positive sweep, where the square symbol ($\square$) are the data taken from (a), and the red line is the fitting line.

where $\bar{I}_p$ is the difference between the current during the positive sweep and the minimum current of the latest negative sweep after the periodic responses were observed, $\bar{E}_{app}$ is the difference between the applied potential during the positive sweep and the minimum potential of the latest negative sweep, a is the factor for the pre-power factor, and b is the factor for the exponent. These factors were obtained by performing a numerical investigation on the effects of Y_0 , γ , and the sweep rate. Factors a and b from different potential ranges are presented in Tables 1 and 2, respectively. These factors can be approximately described as factors that include historical

Table 1. Factors b .

Fitted exponent	Potential ranges (mV)			
	200	100	50	20
0.0873	0.873	0.869	0.861	0.846
0.174	0.871	0.867	0.859	0.845
0.261	0.870	0.866	0.859	0.846
0.348	0.870	0.867	0.860	0.849
0.436	0.872	0.869	0.864	0.854
0.527	0.878	0.875	0.871	0.864
0.622	0.888	0.887	0.884	0.879
0.725	0.907	0.906	0.904	0.902
0.845	0.939	0.939	0.938	0.938
1.00	1.00	1.00	1.00	1.00

Table 2. Factor a .

CPE exponent	Potential ranges (mV)			
	200	100	50	20
1.0	2.00	2.00	2.00	2.00
0.9	1.88	1.86	1.84	1.81
0.8	1.76	1.73	1.69	1.62
0.7	1.64	1.59	1.53	1.45
0.6	1.52	1.46	1.39	1.29
0.5	1.40	1.33	1.26	1.15
0.4	1.28	1.21	1.14	1.04
0.3	1.17	1.11	1.04	0.944
0.2	1.08	1.02	0.963	0.887
0.1	1.01	0.971	0.934	0.885
0.0	1.00	1.00	1.00	1.00

response effects. The tenth positive sweep was selected to be the reference cycle in this study because both factors changed less than 0.05% compared to those of the cycle before. This suggested that they converged. Therefore, they are not limited to specific cases. If the non-faradaic current is obtained under the condition that the faradaic current and the ohmic resistance can be ignored, then experimentalists can simply apply this approach to evaluate the CPE parameters from experiments regardless of electrode structure or solution type. A flowchart for the procedure for estimating CPE parameters using this approach is summarized in Fig. 3.

Of note, from the derivation by Sagüés et al.,⁵³ the current during the first reverse scan ($t_0 < t \leq 2t_0$) can be expressed as

$$I_r = \frac{Y_0 \nu t^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{2Y_0 \nu (t-t_0)^{1-\gamma}}{\Gamma(2-\gamma)} \quad (18)$$

where I_r is the current during the reverse scan. Clearly, as shown by Eq. (18), the time-domain response of a CPE under CV conditions always contains historical responses. To suppress the effects of the faradaic current shown in Fig. 1, in our approach, the current was modified by subtracting the current at the switching potential. The current can be written as

$$\bar{I}_r = \frac{Y_0 \nu t^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{2Y_0 \nu (t-t_0)^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{Y_0 \nu t_0^{1-\gamma}}{\Gamma(2-\gamma)} \quad (19)$$

The modified current can be expressed as a function of potential by substituting $t = \frac{2v_0 - E(t)}{v}$ and $t_0 = \frac{E_0}{v}$. Assuming that v is positive, we obtain

Figure 3. Flowchart of the proposed procedure used to estimate the CPE parameters.

$$\begin{aligned} \bar{I}_r &= \frac{Y_0 v^\gamma (2\bar{E}_0 - \bar{E})^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{2Y_0 v^\gamma (\bar{E}_0 - \bar{E})^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{Y_0 v^\gamma \bar{E}_0^{1-\gamma}}{\Gamma(2-\gamma)} \\ &= \frac{Y_0 v^\gamma}{\Gamma(2-\gamma)} [(2\bar{E}_0 - \bar{E})^{1-\gamma} - 2(\bar{E}_0 - \bar{E})^{1-\gamma} - \bar{E}_0^{1-\gamma}] \quad (20) \end{aligned}$$

where $\bar{E}_0$ is the potential window. Equation (20) can be approximately expressed as Eq. (17). However, as shown in Fig. 1, the current in the first few cycles will be affected by the faradaic current. While Eq. (20) represents an analytical solution for the modified current in the first cycle, the current that occurs when the response insignificantly changes with the number of cycles is more preferable. Although it may be possible to obtain the analytical solution of the current when the response insignificantly changes with the number of cycles, Sadkowsky suggested that there are no such solutions for obtaining the time-domain response of a CPE, and numerical calculations are needed.⁵¹ However, the current when the response insignificantly changes with the number of cycles can be approximately represented by Eq. (17), which is relatively more simple and easy to use. The main equations presented in this work are summarized in Table 3.

3. Experimental

A platinum electrode and a Ag/AgCl electrode were used as the counter and the reference electrodes in a conventional three-electrode system, respectively. Cylindrical graphite electrodes with a diameter of 0.56 mm were selected as the working electrode because

they are easy to implement.^{57–59} Two different solutions were prepared to show that the application of this approach is not limited only to one system. A 64 wt% sulfuric acid (H₂SO₄) solution from KISHIDA Chemical was used to prepare sulfuric acid at a desired concentration of 0.5 M. A 1 mM ferri/ferrocyanide solution in 1.0 M potassium chloride (KCl) was prepared by potassium ferricyanide (K₃[Fe(CN)₆]), potassium ferrocyanide (K₄[Fe(CN)₆]), potassium chloride, and deionized water supplied by KISHIDA Chemical. Before beginning the experiments, the ferri/ferrocyanide solution was deaerated by nitrogen purging into the solution for 20 min and, during the experiments, the system was tank-blanketed with nitrogen.

All electrochemical measurements were conducted using a Solartron analytical 1280Z electrochemical test system. EIS measurements were measured with an AC signal of 5 mV from 20 kHz to 0.1 Hz at 10 points per decade. A linear Kronig–Kramers transform test was also performed to ensure that the experimental data were of good quality. The equivalent circuit used for evaluating the CPE parameters was the Randles circuit. Cyclic voltammetry measurements with a narrow potential window were run at 10, 15, 20, 25, and 50 mV/s for 10 cycles. The number of cycles was selected by considering that the responses did not change with the number of cycles. The experimental data were fitted using the power regression model and applied to the semi-theoretical equation to obtain the CPE parameters as described in Fig. 3. The CPE parameters were evaluated at each scan rate and averaged. The potential windows of 0.55–0.65 V and 0.40–0.50 V were selected to measure the current contributed by the electrical double layer in sulfuric acid and ferri/ferrocyanide solution, respectively. Cyclic voltammetry experiments with a narrow potential window were also performed before each cyclic voltammetry scan with a wide potential window. In the wide potential range experiments, the measurements were conducted at several scan rates of 2, 5, 10, and 20 mV/s. The initial potential was 0.45 V, and the switching potential was 0 V.

4. Results and Discussion

EIS measurements were conducted to estimate the CPE parameters to compare them to those obtained from the semi-theoretical approach. Figures 4a and b show example Nyquist and Bode plots, respectively, of the system with the sulfuric acid and the ferri/ferrocyanide solutions. In the low-frequency region, the system exhibited different behaviors. While the sulfuric acid system showed a behavior of a CPE that is close to a capacitor with no faradaic contribution, the system with the ferri/ferrocyanide solution displayed an angle of approximately 45° between the low frequency impedances and the x-axis, which clearly suggested that it is Warburg element (CPE with an exponent of 0.5) behavior. The presence of Warburg behavior coincided with the results presented in previous studies.^{60–63} The solid lines represent the fitted curves.

The CPE parameters describing the electrical double layer, which were obtained from the EIS data, were compared to those obtained

Table 3. Summary table of equations presented in this work.

Analytical solution	Linear sweep voltammetry	$I_{nf}(t) = \frac{Y_0 v}{\Gamma(2-\gamma)} t^{1-\gamma} = \frac{Y_0 v^\gamma}{\Gamma(2-\gamma)} E_{app}^{1-\gamma}$
	Modified current in the first reverse scan	$\bar{I}_r = \frac{Y_0 v^\gamma}{\Gamma(2-\gamma)} [(2\bar{E}_0 - \bar{E})^{1-\gamma} - 2(\bar{E}_0 - \bar{E})^{1-\gamma} - \bar{E}_0^{1-\gamma}]$
Approximate solution	Cyclic voltammetry	$I_{nf}(t) = \frac{A(\Delta t)}{(1-\gamma)} \sum_{j=0}^k [\bar{E}_{act}(t_{k+1-j}) - \bar{E}_{act}(t_{k-j})] [(j+1)^{1-\gamma} - j^{1-\gamma}] + \bar{E}_{act}(0)A(t)$
	Semi-theoretical equation	$\bar{I}_p(\bar{E}_{app}) = \frac{aY_0 v^\gamma}{\Gamma(2-\gamma)} \bar{E}_{app}^{(1-\gamma)b}$

Figure 4. (a) Nyquist and (b) Bode representations for the sulfuric acid and ferri/ferrocyanide solutions, where in (b), the square symbol ($\square$) indicates the phase angle, and the circle symbol ($\circ$) indicates the magnitude of the impedance. The solid lines are the fitting curves obtained from the modified Randles circuit shown in (a).

from the proposed approach in Figs. 5a and b. In this figure, the results from Sagüés et al.⁵³ were also included. From Fig. 5a, although Y_0 from both approaches seemed to agree well, the Y_0 determined from the semi-theoretical approach can be approximately 2–3 times higher than that determined from the system impedance. Sagüés et al.⁵³ also showed that obtaining the CPE parameters using cyclic voltammetry measurements can result in Y_0 , which is approximately two times larger than that obtained from EIS by CNLS. For γ , a significant difference is clearly shown in Fig. 5b. The results found here are similar to those of Zheng et al.⁴⁵ In their work, a comparison of the differential capacitances obtained from cyclic voltammetry and EIS was presented. Carbon nanotube and glassy carbon electrodes were studied in 1-ethyl-3-methyl imidazolium ethylsulfate, $[\text{EMIM}]^+[\text{EtSO}_4]^-$. The results showed that the charge transfer resistance and capacitance of an electrical double layer determined by two different measurements—cyclic voltammetry and EIS—can be quantitatively different. They suggested that if the results from the two techniques do not mutually agree, the capacitance of the electrical double layer from cyclic voltammetry should be used as the primary reference because it does not require an additional model.

To further discuss the validity of the CPE parameters determined by these methods, CPE parameters obtained using the proposed approach and CNLS were applied to the model⁷ and validated against the experimental data obtained from cyclic voltammetry with a narrow potential window. Figures 6a and b show an example of the validation. Because the selected potential windows were sufficiently far from the formal potential, the total currents obtained

Figure 5. Comparison of (a) CPE parameter Y_0 and (b) CPE exponent γ obtained from different approaches, where the circle symbol ($\circ$) indicates the results of this study, and the square symbol ($\square$) indicates the results from Sagüés et al.³⁰

using cyclic voltammetry with the narrow potential window were mainly non-faradaic currents, as discussed earlier. The figure clearly shows good agreement between the numerical results, which applied the CPE parameters determined using the semi-theoretical approach, and the experimental data from both systems. However, the parameters from EIS analysis failed to predict the non-faradaic current. The EIS analysis not only failed to predict the current from the CPE parameters but also the shapes of the cyclic voltammograms, which are governed by γ . Clearly, to apply CPE parameters to a model for predicting cyclic voltammograms, it is important to directly estimate the CPE parameters from cyclic voltammetry.

As known, a system responds differently to the DC bias potential in EIS.⁴⁵ Therefore, EIS measurements were conducted to investigate its effects on the fitted CPE parameters and to examine whether it is possible to obtain CPE parameters that can reproduce the non-faradaic currents in cyclic voltammograms. Figures 7a and b depict Nyquist and Bode plots for the system using the ferri/ferrocyanide solution as the electrolyte at different potentials. The results revealed that the impedance of the system was not considerably different, except the one taken at 0.25 V vs. Ag/AgCl. Figures 8a and b present Y_0 and γ determined using EIS at several DC bias potentials and those determined using cyclic voltammetry with a potential window of 0.4–0.5 V vs. Ag/AgCl. The CPE parameters evaluated using these two approaches were at different levels. Although Y_0 that was evaluated at the formal potential was relatively larger than the others, it was still approximately two times lower than that measured using cyclic voltammetry. EIS measurements also predicted that CPE parameters are possibly different at

Figure 6. Comparison between the calculated non-faradaic current and the experimental results in (a) sulfuric acid and (b) ferri/ferrocyanide solution by applying the CPE parameters obtained from different approaches.

each applied bias potential. However, there is only a slight difference in this case. Furthermore, the CPE parameters obtained from EIS measurements at 0.45 V vs. Ag/AgCl were also different from those obtained by the semi-theoretical approach for a potential window of 0.4–0.5 V vs. Ag/AgCl. Based on the evidence presented here combined with the previous studies,^{45,53} we conclude that CPE parameters obtained from cyclic voltammetry may be different from those obtained by EIS analysis.

The difference between the CPE parameters obtained from these two methods may be due to the fact that in EIS measurements, they are obtained by fitting an equivalent circuit to the impedance of the system over a large range of frequencies, whereas in cyclic voltammetry, they are measured directly in the low-frequency region (scan rate), which is close to the condition used in cyclic voltammetry with a wide potential window. Our proposed approach attempted to suppress the faradaic current by carefully selecting a potential window that was sufficiently narrow and far from the formal potential in the cyclic voltammetry experiments. When the faradaic current is negligible, the system can be represented by an R-CPE circuit because only the non-faradaic current remains. Therefore, CPE parameters can be directly evaluated. However, in EIS analysis, the equivalent circuit of such a system cannot be simplified as the R-CPE circuit. These differences may be the reasons of different CPE parameters.

To further show the importance of this approach, an application for modeling cyclic voltammetry is presented. Cyclic voltammetry of a cylindrical graphite electrode in a ferri/ferrocyanide solution covering the faradaic processes was carried out at different scan rates. Prior to each scan, cyclic voltammetry with a narrow potential

Figure 7. (a) Nyquist and (b) Bode representations for the ferri/ferrocyanide solution at different DC bias potentials, where in (b), the square symbol ($\square$) indicates the phase angle, and the circle symbol ($\circ$) indicates the magnitude of the impedance. The solid lines are the fitting curves.

window was applied to determine the CPE parameters that were used as inputs in the model.⁷ Therefore, the properties and parameters obtained from the experiments, i.e., cyclic voltammetry and EIS measurements, and previous studies were used in this simulation. Table 4 summarizes the properties and parameters used the model. The CPE parameters and ohmic resistance measured before each scan are presented in Table 5. Note that Y_0 and γ were assumed to be constant throughout the potential window. Figure 9a displays a comparison between the numerical results and experimental data. Excellent agreement between the numerical solutions and experimental results was clearly observed. Although cyclic voltammetry with a narrow potential window was conducted in a potential window of 0.4–0.5 V, the CPE parameters obtained in that region can satisfactorily represent the CPE parameters of the entire potential window. Thus, the assumption of constant CPE parameters was confirmed to be reasonable in this case. In this model, it is possible to separate the faradaic and non-faradaic currents from the total current in the cyclic voltammograms, as shown in Figs. 9b and c. Hence, the kinetic and thermodynamic parameters can be conveniently estimated.

The results of this study suggest that to model cyclic voltammetry, which consists of both faradaic and non-faradaic currents, measuring the CPE parameters using cyclic voltammetry is important. EIS approach, which measures the impedance of a system in the frequency domain, failed to provide the CPE parameters that can reproduce the non-faradaic current in the cyclic voltammetry experiments in this case. Additionally, one difficulty of applying EIS analysis is the selection of a suitable equivalent circuit to describe the system. However, the semi-theoretical approach presented in this

Figure 8. Comparison of (a) CPE parameter Y_0 and (b) CPE exponent γ obtained from EIS analysis at different DC bias potentials and those obtained from the semi-theoretical approach.

Table 4. Properties and parameters used in the simulation.

Parameters		Units
Electrode diameter (D_i)	0.560	mm
Boundary diameter (D_o)	1.56	mm
Active surface area (A_{eff})	33.5	mm 2
Formal potential (E^0)	0.25	V vs. (Ag/AgCl)
Ohmic resistance (R_Ω)	4.41–4.54	Ω
Y_0	0.354–0.378	mFs $^{-1}$
γ	0.678–0.741	
Diffusivity (D)	7×10^{-6}	cm 2 s $^{-1}$
Reaction rate constant (k_0)	7×10^{-4}	m s $^{-1}$
Charge transfer coefficient (α)	0.5	
Temperature (T)	298	K
Scan rates (ν)	2–20	mV s $^{-1}$
Initial potential (E_i)	0.45	V vs. (Ag/AgCl)
Oxidized species concentration (c_o)	1	mM
Reduced species concentration (c_R)	0	mM

work provided satisfactory results in terms of both accuracy and cost. The approach is simple and straightforward. Ongoing studies include determining the effective surface area, reaction rate constant, and diffusivity of active species when a non-faradaic current and ohmic drop are also involved in the cyclic voltammogram.

Table 5. Parameters obtained from EIS and the semi-theoretical approach.

Parameters	2 mV s $^{-1}$	5 mV s $^{-1}$	10 mV s $^{-1}$	20 mV s $^{-1}$	Units
Ohmic resistance (EIS)	4.54	4.49	4.41	4.49	Ω
Y_0 (The semi-theoretical approach)	0.378	0.355	0.354	0.361	mFs $^{-1}$
γ (The semi-theoretical approach)	0.741	0.694	0.695	0.678

Figure 9. Comparison between numerical solutions and experimental data from (a) cyclic voltammograms, consisting of the (b) faradaic current and (c) non-faradaic current at different scan rates.

5. Conclusion

A method for determining CPE parameters using cyclic voltammetry combined with a semi-theoretical equation was successfully developed. Validation of this approach was also conducted, and excellent agreement between the calculated responses and the experimental data was clearly observed. Therefore, to apply CPE parameters to a model for simulating cyclic voltammetry, it is important to directly determine the CPE parameters from cyclic voltammetry. By determining the CPE parameters in a narrow potential window and applying them to the model, the model can satisfactorily simulate the cyclic voltammograms that contain both faradaic and non-faradaic currents. This proposed approach for determining CPE parameters using cyclic voltammetry can not only be applied to one specific system but also provides several advantages, e.g., accuracy of the CPE parameters and easy implementation.

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