

The Effective Capacitance of a Constant Phase Element with Resistors in Series

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ABSTRACT

The power of energy storage devices is characterized by capacitance and the internal resistance. The capacitance is measured on an assumption that the charges are stored at the electrode interface and the electric double layer behaves like an ideal capacitor. However, in most cases, the electric double layer is not ideal so a constant phase element (CPE) is used instead of a capacitor to describe the practical observations. Nevertheless, another problem with the use of the CPE is that CPE does not give capacitance directly. Fortunately, a few methods were suggested to evaluate the effective capacitance in the literature. However, those methods may not be suitable for supercapacitors which are modeled as an equivalent circuit of a CPE and resistor connected in series because the time constant of the equivalent circuit is not clearly studied. In this report, in order to study the time constant of the CPE and find its equivalent capacitor, AC and DC methods are utilized in a complementary manner. As a result, the time constants in the AC and DC domains are compared with digital simulation and a proper equation is presented to calculate the effective capacitance of a supercapacitor, which is extended to an electrochemical system where faradaic and ohmic processes are accompanied by imperfect charge accumulation process.

Keywords: Impedance, Constant phase element, Capacitance, Electrochemical process

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1. Introduction

Electrochemical methods are categorized in two types according to the electric signal types. One is the DC method using constant or sweeping signals of potential or current and the other one is the AC method using AC wave signals. They have pros and cons over each other. DC methods are intuitive, easy and simple while AC methods are more sophisticated but provide richer information which DC methods cannot. Therefore, both methods are utilized in compromised ways, or sometimes complementary.

Among the AC methods, electrochemical impedance spectroscopy (EIS) is most widely used because it is a powerful electrochemical technique which can resolve a complex electrochemical observation into its elementary processes [1]. For example, when an electrochemical system is activated by electric poten-

tial, an electrochemical current is generated as an overall result mixed of electron transfer, mass transfer, charge accumulation and interactions of those processes. While DC methods such as chronoamperometry and linear sweep voltammetry can only measure the all-inclusive monotonic currents, electrochemical impedance spectroscopy can separate and analyze the mixed processes responding differently to frequencies [2]. Y. Zhang *et al.* presented a method for reconstruction of relaxation time distribution using EIS and applied the method to solid oxide fuel cells [3]. J. P. Schmidt *et al.* also used the distribution of relaxation time for Li-ion batteries [4]. B. A. Boukamp claimed that the use of distribution function for relaxation times has advantages and disadvantages by comparing the analysis method of complex nonlinear least square [5]. M. B. Effat *et al.* developed the Bayesian-based deconvolution framework for the time distribution from the data of electrochemical impedance spectroscopy [6].

Another method for analyzing EIS is the equivalent circuit presentation method which depicts a complex electrochemical process as a model consisting of

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resistors, capacitors and other appropriate electric elements and works best with the complex nonlinear least square fitting [7]. Then, resistance of the resistors can explain rates of mass, charge and electron transfers, and capacitance of the capacitors can evaluate the charging properties. Inductance is also used to describe properties such as releasing charges or electric energy. However, the circuit modeling method has limitations because the general electric elements are only equivalent to the ideal electrochemical processes. No electric component could represent the diffusion of molecules, so the Warburg impedance was created. The electric double layer is not perfectly capacitive, therefore a constant phase element has been practically used instead of a capacitor in many cases [8].

The constant phase element (CPE) is a variation of a capacitor. It was invented to describe impedance observed only in electrochemical systems. The impedance of the CPE, Z_{CPE} , is expressed below as a function of ω , the angular frequency [9].

$$Z_{CPE} = \frac{1}{(j\omega)^n Y_0} \quad (1)$$

where n and Y_0 are parameters characterizing the CPE.

A CPE almost inherits properties from a capacitor, but a slight difference in phase shift and magnitude responding to AC signals distinguishes the CPE from a capacitor. The degree of the phase shift of a capacitor is $\pi/2$ while that of a CPE is $n\pi/2$, where n ranges from 0 to 1 (practically 0.8 to 1). These phase shifts are also related to the magnitude values of a capacitor and a CPE which are referred to capacitance and Y_0 , respectively. When $n = 1$, the CPE is an ideal capacitor and the Y_0 presents its capacitance. Otherwise, the CPE deviates from a capacitor and the Y_0 does not directly present the capacitance any longer.

The origin of the deviation from the ideal capacitive property for the CPE is not exactly discovered but it is admitted that the practical capacitive property is well described by the CPE rather than a capacitor [8]. Over the advantage of using the CPE, a problem is faced when the physical meaning of the CPE is studied. For example, when a capacitance of an energy storage system is of interest, the deviation above should be considered: Y_0 is not exactly the same as capacitance. To estimate the capacitance of a CPE, there have been several methods suggested [10-13]. C. H. Hsu *et al.* used a characteristic frequency

at which the imaginary part is the maximum in order to find the effective capacitance and B.-Y. Chang found the effective capacitance by projecting the depressed semi-circle onto part of a perfect semi-circle. Both methods have limitations that the CPE is parallel with the resistor to make a semi-circle on the Nyquist plot. On the other hand, for a CPE with resistors in series and parallel, B. Hirschorn *et al.* used the equivalent time constant to derive an equation for the effective capacitance below,

$$\tau_n = (Y_0 \cdot R)^{1/n} = C_{eff} \cdot R \quad (2)$$

There are more reports where the equivalent time constant is used to find the effective capacitance. Even though Eq. (2) is widely used in many publications, no direct evidence is provided to support the equivalence relationship of the time constants for the capacitor and the CPE. In fact, the time constant is a parameter that is measured in DC currents, however, the time constant of a CPE has not been shown in DC currents and just used in AC methods with the formula above. This evidence for Eq. (2) is important not only to confirm the relationship, but also to evaluate the electrochemical processes modeled as an equivalent circuit of a CPE and a resistor connected both in series and parallel. A typical example of such a system is a pseudocapacitor which stores electric energy as a result of faradaic reactions and it is frequently modeled as an equivalent circuit of a CPE and a resistor connected in series [14]. The CPE represents the accumulation of charges at the electrode/electrolyte interface and the resistor does the transfers of charges such as electrons, molecules, and ions through the electrolyte and at the interface. In this case, the CPE does not directly provide the capacitance from its values and needs to be calculated to result in the effective capacitance.

In this report, we show that the time constants of a capacitor and a CPE, even though they are not the same, are equivalent in DC currents, and derive an equation to find the effective capacitance of a CPE connected to a resistor in series. Here, the equation is derived based on both AC and DC techniques of electrochemical analysis: the former is electrochemical impedance spectroscopy (EIS) and the latter is chronoamperometry. EIS with the complex nonlinear least square fit evaluates the CPE and a resistor of the system of which a chronoamperometric curve

results in the time constant equivalent to that of a capacitor and a resistor system. As a result, a simple equation is suggested for the conversion of the CPE to an equivalent capacitor. The equation is extended to a combination of serial and parallel resistors to generalize the CPE conversion. Those separate serial and parallel equations are unified to be applied to a general complex system composed of charge transfer and accumulation with an ohmic flow such as pseudo-capacitors.

2. Theory

When the electrified interface such as the electric double layer and a pseudo-capacitive layer behaves like an ideal capacitor, the electrochemical system is described as an equivalent circuit composed of a capacitor and a resistor in series. Upon a potential step applied, the electrochemical system produces a chronoamperometric curve decaying exponentially along the time. In the DC domain, the time constant (τ) of the exponential-decaying curve is defined by the time when the current reaches $1/e$ of the instant current at $t = 0$, and formulated as below with the components measured in the AC domain,

$$\tau = C_{dl} \cdot R_s \quad (3)$$

However, in most cases, the electrified interface does not behave like an ideal capacitor, and its non-ideal capacitive property is usually represented by a constant phase element (CPE) in the place of the capacitor. As the CPE has parameters of Y_0 and n , the time constant should be a function of these parameters as expressed below,

$$\tau_n = f(Y_0, n, R_s) \quad (4)$$

Once the time constant is determined, it can be used to estimate the effective capacitance of the capacitor-resistor system equivalent to the CPE-resistor one which has the equivalent time constant. Thus, by combing Eq. (3) and (4), we learn that the effective capacitance can be calculated below,

$$C_{eff} = \frac{f(Y_0, n, R_s)}{R_s} = \frac{\tau_n}{R_s} \quad (5)$$

As we know that τ_n is a measured value in the DC domain, the mathematical formula for τ_n should be

represented by a function of time which might be derived by solving partial derivative equations for the current generated upon electric potential. However, it is impossible to obtain a closed-form solution. Instead, we can approach using numerical analysis if only we are interested in the time constant. As mentioned above, the current generated upon a potential step decays by the factor of $1/e$ at $t = \tau$. Therefore, the time constant can be measured from the decayed current of the electrochemical system. For the system modeled as a circuit of a CPE and a resistor in series, its chronoamperometric curve $i(t)$ is obtained by digital simulation which utilizes the inverse discrete Fourier transform to the impedance spectrum of the circuit.

$$Z(\omega) = R_s + \frac{1}{(j\omega)^n Y_0} \quad (6)$$

$$i(t) = \text{FT}^{-1} \left[\frac{E(\omega)}{Z(\omega)} \right] \quad (7)$$

3. Experimental

In order to find the time constants determined by precisely controlling the CPE with resistors, digital simulations are carried out by a home-made program coded in Python 3.8. For the digitized signals of $Z(\omega)$ and $E(\omega)$ in Eq. (7), suitable frequencies (ω) ranging from $\frac{1}{M\Delta t}$ to $\frac{1}{2\Delta t}$ are selected as defined by the Nyquist theorem, where Δt is the sampling interval and M is the total number of sampling. The numbers of Δt and M are dependent on the memory capacity of the computing system. $E(\omega)$ is obtained from discrete Fourier transform of the following equation

$$E(t) = \frac{4}{\pi} \sum_{m=1}^M \frac{1}{2m-1} \sin(2m-1)\omega t \quad (8)$$

Next, the current in the frequency domain is calculated by Ohm's law, $i(\omega) = E(\omega)/Z(\omega)$. Then, it is converted to $i(t)$ by inverse discrete Fourier transform as expressed below,

$$i(t) = \sum_{\omega} |i(\omega)| \cdot \sin(\omega t - \phi) \quad (9)$$

where ϕ is the phase angle. The time constants are measured at the time when $i(t) = i(0)e^{-1}$.

In order to confirm the theory and simulation

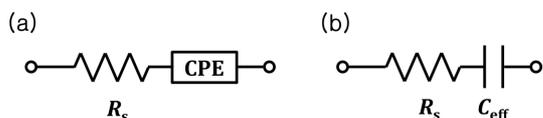


Fig. 1. (a) A circuit composed of a constant phase element (CPE) and a resistor connected in series. (b) A circuit composed of an effective capacitor and a resistor which has the equivalent time constant.

results, a commercially available supercapacitor (BCAP0005, Maxwell Technologies Korea Co., Ltd.) and polyaniline on an ITO electrode are measured to obtain its capacitance. BCAP0005 is purchased and Polyaniline is electrochemically synthesized by applying a potential sweep from -0.2 to 1.2 V vs. Ag|AgCl at 100 mV/s in an aqueous solution containing 30 mM aniline and 0.50 M H_2SO_4 [15]. The electrochemical impedance spectra are acquired with SP-200 (Biologic, France). BCAP0005 is directly connected through wires and polyaniline on ITO is in 0.50 M H_2SO_4 . The acquired data are fitted to the equivalent circuit in Fig. 1(a) using a commercial software, ZSimpWin (AMETEK, USA).

4. Results and Discussion

For numerical analysis, a potential step of $\Delta E = 1$ V is made by Eq. (8) and applied on the circuit in Fig. 1(a) with parameters $R_s = 10 \Omega$, $Y_0 = 10 \mu s^n/\Omega$ and n from 1 to 0.6 . Here, n is theoretically from 0 to 1 , but practically 0.8 to 1 to gain the capacitive property. Using the inverse discrete Fourier transform of Eq. (7), chronoamperometric curves are obtained and shown in Fig. 2. For $n = 1$, the current curve is the same as the theoretical one for a capacitor and a resistor in series, however for $n < 1$, the currents decay steeper as n decreases in Fig. 2. It indicates that the capacitive property is decreased with n even though Y_0 is constant. Keeping in mind that the decaying current decreased by the factor of $1/e$, or 0.368 , the times of those currents, τ_n , are measured for each n value. Logarithms of the measured times are plotted against $1/n$, which shows a linear relationship in Fig. 3. By varying the values of R_s and Y_0 , respectively, the slope of the linear line is learned to be proportional to $\log R_s$ and $\log Y_0$, respectively. Collecting the numerical analysis results, the following equation is confirmed.

$$\log \tau_n = \frac{1}{n} \log(Y_0 \cdot R_s) \quad (10)$$

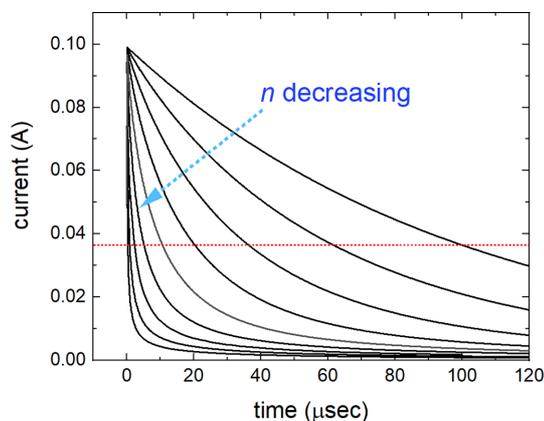


Fig. 2. Chronoamperometric curves of electrochemical systems modeled as the circuit in Fig. 1(a) are obtained by digital simulations based on Eq. (6) to (9). The used parameters are $\Delta E = 1$ V, $R_s = 10 \Omega$, $Y_0 = 10 \mu s^n/\Omega$ and $n = 1, 0.95, 0.9, 0.85, 0.8, 0.75, 0.7, 0.65$ and 0.6 , respectively. The red dot line indicates the current decreased by the factor of $1/e$.

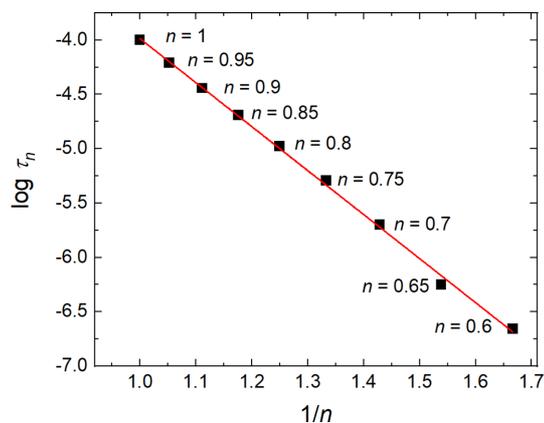


Fig. 3. Plots of $\log \tau_n$ against $1/n$ and their linear fitting curve.

We also need to notice that this equation is the same as the time constant for the circuit of a CPE and a resistor in *parallel* [10]. Now, Eq. (5) is defined as following,

$$C_{eff} = \frac{\tau_n}{R_s} = \frac{(Y_0 \cdot R_s)^{1/n}}{R_s} \quad (11)$$

While it is obtained by the chronoamperometric approach in the DC domain, this equation is consistent with that presented by B. Hirschorn *et al.* which was obtained by equivalent circuit calculation in the

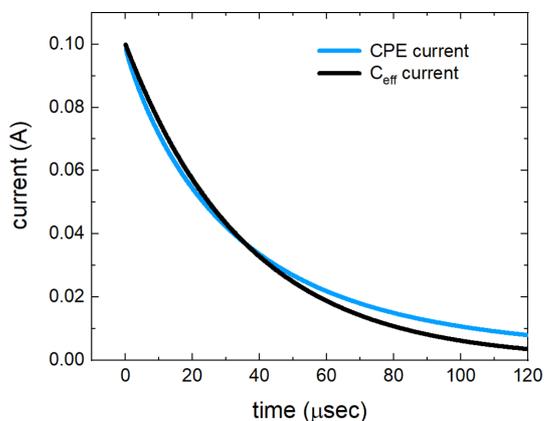


Fig. 4. (Blue) A Chronoamperometric curve of the circuit in Fig. 1(a) with $R_s = 10 \Omega$, $Y_0 = 10 \mu s^n/\Omega$ and $n = 0.9$. (Red) A Chronoamperometric curve of the circuit in Fig. 1(b) having the equivalent time constant calculated by Eq. (11).

AC domain [13]. Using this equation, the effective capacitances are calculated for the systems of which parameters are $R_s = 10 \Omega$, $Y_0 = 10 \mu s^n/\Omega$ with different n values in Table 1. Fig. 4 compares the currents of the CPE and the equivalent capacitor when $R_s = 10 \Omega$, $Y_0 = 10 \mu s^n/\Omega$ with $n = 0.9$ and $C_{\text{eff}} = 3.61 \mu\text{F}$. As shown in the figure, the current of the equivalent capacitor is not the same as that of the CPE, but it effectively reflects the capacitive property in terms of the relaxation time as a result of the charge accumulation process.

In order to confirm the theory, a commercially available supercapacitor (BCAP0005, Maxwell Technologies Korea Co., Ltd.) is measured SP-200 (Biologic, France) to find the capacitance. The electrochemical impedance spectrum is displayed on the Nyquist plot in Fig. 5(a). The supercapacitor, not a perfect capacitor but having high capacitance, shows a typical straight line tilted from the vertical axis. By fitting the plot to the circuit in Fig. 1(a), the values of Y_0 , n , and R_s are obtained $4.79 s^n/\Omega$, 0.971 and 0.0568Ω , respectively. The results are applied to Eq. (11) to yield the effective capacitance, 4.71 F , which is the same value as the printed capacitance of the product,

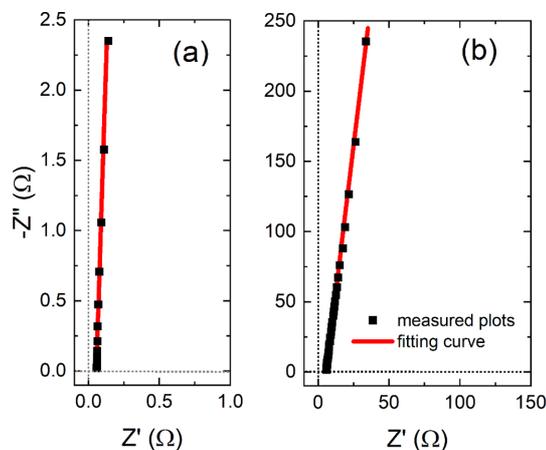


Fig. 5. Electrochemical impedance for a commercial supercapacitor (BCAP0005, Maxwell Technologies Korea Co., Ltd.) and polyaniline on an ITO electrode are measured by SP-200 (Biologic, France). The results are plotted on the Nyquist plane and fitted to the circuit in Fig. 1(a) as indicated by the red curve.

5 F (-10% to +20% tolerance). For practical application, electrochemical impedance of polyaniline is measured. Polyaniline is conducting polymer and one of the best materials for supercapacitors [16]. Once the polyaniline is electrochemically synthesized on an indium tin oxide (ITO) electrode, its electrochemical impedance spectrum is measured in $0.50 \text{ M H}_2\text{SO}_4$ solution and the Nyquist plot of the impedance is displayed in Fig. 5(b). It also shows a typical straight line of a supercapacitor and the fitting process yields $Y_0 = 0.0938 s^n/\Omega$, $n = 0.924$, and $R_s = 5.61 \Omega$, respectively. The effective capacitance calculated by Eq. (11) is 89 mF/cm^2 .

Even though the method that a CPE is converted to its equivalent capacitor based on the chronoamperometric approach is successful with a connection to a resistor either in series, it should be applicable to a system modeled as a combination of serial and parallel connections for the general purpose. The simplest equivalent circuit is shown in Fig. 6. The electrode is covered with a porous material which can accumulate charges with faradaic reaction taking place simulta-

Table 1. The time constants and the effective capacitances of the currents in Fig. 2 are calculated by Eq. (10) and (11)

n	1	0.95	0.9	0.85	0.8	0.75	0.7	0.65	0.6
$\tau (\mu s)$	100	61.6	36.1	20.3	10.6	5.1	2.0	0.6	0.2
$C_{\text{eff}} (\mu\text{F})$	10	6.16	3.61	2.03	1.06	0.51	0.20	0.06	0.02

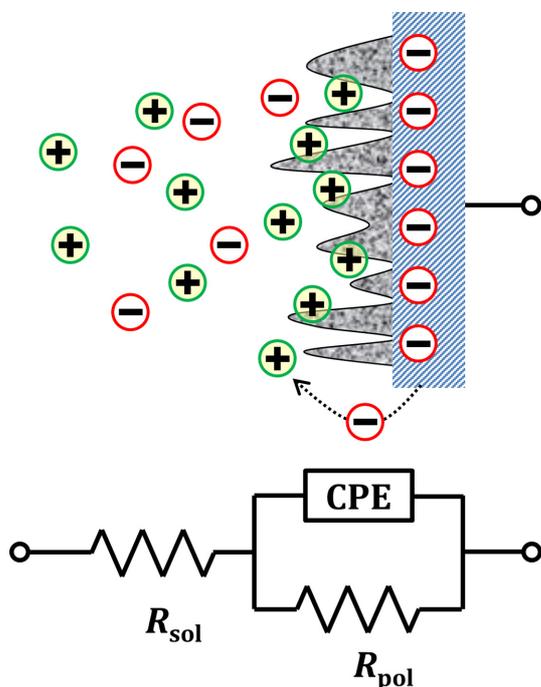


Fig. 6. An interface between an electrolytic medium and a pseudocapacitive layer electrode which accumulates charges with faradaic reactions. The processes at the interface and through the medium can be described by an equivalent circuit shown below.

neously in a conductive medium: the whole processes are described as a CPE, a polarization resistance (R_{pol}) in parallel and a solution resistance (R_{sol}) in series, respectively. According to Thevenin theorem [17] this equivalent circuit can be re-organized to the circuit in Fig. 1 by converting R_{sol} and R_{pol} to R_s and C_{eff} of which the resistance and the effective capacitance are following,

$$R_s = \frac{R_{sol} \cdot R_{pol}}{R_{sol} + R_{pol}}, \quad (12)$$

$$C_{eff} = \frac{\left(Y_0 \cdot \frac{R_{sol} \cdot R_{pol}}{R_{sol} + R_{pol}} \right)^{1/n}}{\frac{R_{sol} \cdot R_{pol}}{R_{sol} + R_{pol}}} = (Y_0)^{1/n} \cdot \left(\frac{R_{sol} \cdot R_{pol}}{R_{sol} + R_{pol}} \right)^{n-1}. \quad (13)$$

This equation also gives the same results that B. Hirschorn *et al.* presented even though the approaches are different [13]. When $R_{pol} \gg R_{sol}$, the circuit model approaches a serial CPE- R_s model and Eq. (13) becomes Eq. (11). On the other hand, when $R_{pol} \ll R_{sol}$, the model approaches a parallel CPE- R_p

Table 2. The effective capacitances of the CPE with changing R_{sol} values. The used parameters are $R_{pol} = 10^3 \Omega$, $Y_0 = 10 \mu s^h/\Omega$ and $R_{sol} = 10^1, 10^2, 10^3, 10^4$ and $10^5 \Omega$, respectively. The unit of the capacitance values in the table is μF

R_{pol}/R_{sol}	n	1	0.95	0.9	0.85	0.8
0.01	10.00	10.00	6.16	3.59	1.96	1.00
0.1	10.00	10.00	6.92	4.59	2.91	1.74
1	10.00	10.00	7.57	5.55	3.93	2.66
10	10.00	10.00	7.81	5.93	4.36	3.09
100	10.00	10.00	7.84	5.99	4.43	3.15

model and Eq. (13) becomes the equation suggested by Mansfield [10].

It is important that the effective capacitance of a CPE is dependent on both the polarization resistance by the faradaic processes at the electrified interface and the ohmic resistance in the electrolyte [18]. Table 2 summarizes the effect of the relative resistance of R_{pol} and R_{sol} according to the n value of the CPE. It is notable that the ideal capacitor ($n = 1$) is not affected by the parallel R_{pol} , but CPEs have higher effective capacitance as R_{pol} increases. It is known that the imperfect capacitive property of the CPE is related to the current leakage through the dielectric material described as leakage resistance [19]. This hidden resistor provides a new pathway that charges prefer to take when the parallel R_{pol} is increased. Then, the increased amount of charges through the CPE cause to increase the effective capacitance.

4. Conclusions

Conversion of a constant phase element (CPE) to its equivalent capacitor is necessary when charge accumulation is more important than charge transfer at the electrode interface. There are conversion methods already reported in the literature, but they may not be suitable to high density energy storages such as supercapacitors being modeled as a double-layer-like CPE with internal resistance. In the present report, a proper conversion method is provided to find the effective capacitance of a CPE with a resistor in series describing practical supercapacitors from the aspect of time constant. While the CPE is an element in frequency domain, the time constant is measured in time domain. In order to overcome this

discrepancy, the AC and the DC methods are exploited in a complementary way. As a result, a simple conversion equation is obtained. Not restricted to supercapacitors, electrochemical systems are more complex and can be modeled as a combination of serial and parallel resistors according to pathways of charge and mass transfer. In order to generalize the CPE conversion methods, an extended equation is also suggested based on the DC approach. Based on this equation, it is also learned that the effective capacitance of a CPE is dependent on the parallel charge transfer process while that of a capacitor is not.

Acknowledgements

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References

- [1] B.-Y. Chang and S.-M. Park, *Annu. Rev. Anal. Chem.*, **2010**, 3, 207-229.
- [2] L. E. Helseth, *J. Energy Storage*, **2021**, 35, 102304.
- [3] Y. Zhang, Y. Chen, M. Yan, and F. Chen, *J. Power Sources*, **2015**, 283, 464-477.
- [4] J. P. Schmidt, P. Berg, M. Schönleber, A. Weber, and E. Ivers-Tiffée, *J. Power Sources*, **2013**, 221, 70-77.
- [5] B. A. Boukamp, *Electrochim. Acta*, **2015**, 154, 35-46.
- [6] M. B. Effat and F. Ciucci, *Electrochim. Acta*, **2017**, 247, 1117-1129.
- [7] W. Choi, H.-C. Shin, J. M. Kim, J.-Y. Choi, and W.-S. Yoon, *J. Electrochem. Sci. Technol.*, **2020**, 11(1), 1-13.
- [8] J. R. Macdonald and W. B. Johnson, *Fundamentals of impedance spectroscopy, Fundamentals of impedance spectroscopy: Theory, experiment, and applications, 2nd Edition*, John Wiley & Sons, New York, **2005**.
- [9] Y. Huang, H. Shih, and F. Mansfeld, *Mater. Corros.*, **2010**, 61(4), 302-305.
- [10] C. H. Hsu and F. Mansfeld, *Corrosion*, **2001**, 57(9), 747-748.
- [11] B.-Y. Chang, *J. Electrochem. Sci. Technol.*, **2020**, 11(3), 318-321.
- [12] E. P. M. van Westing, G. M. Ferrari, and J. H. W. de Wit, *Corros. Sci.*, **1993**, 34(9), 1511-1530.
- [13] B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur, and M. Musiani, *Electrochim. Acta*, **2010**, 55(21), 6218-6227.
- [14] C. Yun and S. Hwang, *ACS Omega*, **2021**, 6(1), 367-373.
- [15] S.-Y. Hong and S.-M. Park, *J. Phys. Chem. B*, **2007**, 111(33), 9779-9786.
- [16] H. Li, J. Wang, Q. Chu, Z. Wang, F. Zhang, and S. Wang, *J. Power Sources*, **2009**, 190(2), 578-586.
- [17] C. K. Alexander and M. N. O. Sadiku, *Fundamentals of Electric Circuits*, McGraw-Hill, New York, **2000**.
- [18] N. Mohanapriya, M. Kumaravel, and B. Lalithamani, *J. Electrochem. Sci. Technol.*, **2020**, 11(2), 117-131.
- [19] X. Vendrell, J. Ramírez-González, Z.-G. Ye, and A. R. West, *Commun. Phys.*, **2022**, 5, 9.