Theoretical Formulation for Charge / Discharge Efficiencies of Electric Double Layer Capacitors and Their Experimental Verification

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Abstract

To predict charge/discharge efficiencies of electric double layer capacitors, theoretical formulation as a function of time is established under various constraining conditions for nonideal capacitors with series- and parallel-resistors in addition to ideal capacitors. For charging, one of the constraining conditions is charging using a constant voltage source. Another is charging using a constant current source. To confirm the theoretical models, experiments of constant voltage charging, constant current charging and constant resistance discharging have been conducted. Good agreements for all the comparison data have been obtained between the theory and the experiments only by assuming an equivalent circuit with series- and parallel-resistors for the capacitor. Good agreements support that both theoretical formulation and experimental measurements are correct. To determine charge- and discharge-efficiencies for non-ideal capacitors, it is necessary to determine all the values of capacitance, capacitor series resistance, and capacitor parallel resistance. For capacitance evaluation, among the 5 methods we compared, constant current charge experiment, in which capacitance is given by the constant current divided by the slope of the linear fit to the voltage-time graph, is considered to give most accurate capacitance since there is no need to know the series resistance in the circuit. Nevertheless, all the capacitance values obtained agree within 10% above 1 V. The series resistance is determined as the ratio of the voltage jump at the beginning of charge to the current. The parallel resistance is determined as the ratio of the time constant of the self-discharge decay to the capacitance. In conclusion, it is theoretically and experimentally confirmed that charge efficiency under constant current condition can closely reach unity while that under constant voltage condition cannot exceed 1/2.

1. Introduction

Capacitors have been widely used as one of the essential electrical components having a certain value of capacitance. Basically, capacitors have a simple structure consisting of a pair of flat electrodes facing each other charged with opposite polarity. One of the features is that its impedance is ideally inversely proportional to the frequency of the alternating current (AC) applied to the capacitor. For the AC applications, the phase of the current flowing the capacitor ideally leads the phase of the voltage applied to the capacitor by one fourth the period. Therefore, there is no power dissipation in the capacitor while it has an impedance.

In addition to such AC properties, capacitors have a feature of energy storage [1]. Electric double layer capacitors (EDLC) [2-7] meet such needs since they have extraordinary larger capacitance by several orders of

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magnitude than the traditional capacitors.

At the beginning of the EDLC application history, one of the most common applications has been in the field of memory backup [8]. As the markets expand, the performances of EDLC, especially energy storage capacity increases. Nevertheless, practical use of EDLC is still very limited. Compared to batteries, EDLCs are regarded to have advantages of higher power density, simpler structure, wider operating temperature range, longer cycle life, faster charge and discharge capabilities etc. However, they are regarded to have disadvantages such as non-constant voltage output, lower energy density. There exists a trade-off for EDLCs; higher energy density products have higher internal series resistance [9-11].

In such a situation, Okamura et al. proposed from 1990s "Energy Capacitor System" in which capacitors with high energy density but high series resistance combined with electronical circuit[15-17] were used, and demonstrated realizing high charge and discharge efficiencies. The key point is the use of current source as a charger and take longer charging and discharging time than the CR constant where C is the EDLC capacitance and R is the series resistance.

Thus, Okamura et al. triggered and accelerated application-oriented research and developments such as for hybrid vehicles, uninterruptible power supplies etc. They reported that they often used SPICE (Simulation Program with Integrated Circuit Emphasis) to simulate the operation of EDLC systems. Instead, there are few reports, to our knowledge, on detailed analytical formulations for EDLC to cover various charge- and discharge-conditions.

Therefore, we aim firstly to formulate analytical equations to derive charge- and discharge-efficiencies of EDLCs at various constraint conditions such as constant voltage, constant current taking account of nonideal properties (series- and parallel-resistors), and secondly to conduct verification experiments.

2. Theoretical

In this section, analytical equations for some parameters including charge- and discharge-efficiencies are formulated under several conditions.

Charging conditions: One of the conditions is charging using a constant voltage (termed as CV hereafter) source. This condition is considered in sections 2.1 and 2.2. Another is charging using a constant current (termed as CC hereafter) source. This is considered in sections 2.3 and 2.4.

Discharging conditions: The most common case that a constant resistance load is simply connected to a charged capacitor is considered in sections 2.5 and 2.6. In addition, the case that a constant resistance load is connected to a charged capacitor through a resistance-controlled device to maintain the voltage across the load constant (can be termed as CV or CC load) is considered in section 2.7.

Assumption for the capacitor: In sections 2.1, 2.3 and 2.5, we assume for the capacitor that the series resistance is zero and that parallel resistance is infinite. On the other hand, in sections 2.2 and 2.4, we consider on actual capacitors with series- and parallel-resistances based on simple equivalent circuits.

2.1 CV Charge efficiency

The circuit is shown in Fig. 1 where the capacitor with capacitance, C, is charged from the constant voltage source supplying constant voltage, V, through the shunt resistance, R.

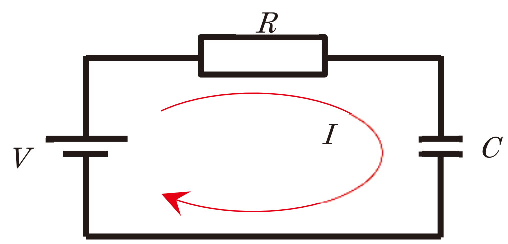

Fig. 1 Circuit for charge efficiency measurement using a constant voltage source.

In general, charge efficiency can be defined as follows

$$\eta_c = \frac{W_C}{W_R + W_C} = \frac{W_C}{W_S}, \quad (1)$$

where W_C, W_R and W_S ($= W_R + W_C$) are the energy stored in the capacitor, the energy dissipated in the resistor, and the energy supplied from the source, respectively.

Let the charging time be t. Current flowing in the circuit, I, is given by

$$I = \frac{V}{R} e^{-\frac{t}{CR}}. \tag{2}$$

W_C is given by

$$W_C = \frac{Q^2}{2C} = \frac{\left(\int_0^t I dt\right)^2}{2C} = \frac{V^2\left(\int_0^t e^{-\frac{t}{CR}} dt\right)^2}{2CR^2}, \tag{3}$$

where Q is the charge stored in the capacitor.

W_S is given by

$$W_S = V\int_0^t I dt = \frac{V^2}{R}\int_0^t e^{-\frac{t}{CR}} dt. \tag{4}$$

By substituting Eqs. (3) and (4) for Eq. (1), charge efficiency using a constant voltage source, η_c^{CV}, becomes,

$$\eta_c^{CV} = \frac{1}{2CR}\int_0^t e^{-\frac{t}{CR}} dt = \frac{1 - e^{-\frac{t}{CR}}}{2}. \tag{5}$$

The efficiency converges to 1/2 regardless of the values of C and R at the limit of infinite t.

2.2 CV charge efficiency of a capacitor with series- and parallel-resistances

The circuit is shown in Fig. 2 where equivalent circuit of the actual capacitor is composed of serial resistor, r_C, connected to a paralleled pair of capacitor, C, and parallel resistor, R_C. The capacitor expressed by the above equivalent circuit is charged from the constant voltage source supplying constant voltage, V_S, through the shunt resistance, r.

By letting $r' = r + r_C$, the voltage across the capacitor, V_C is given by,

$$V_C = V_S - Ir', \tag{6}$$

where V_C and I are expressed as follows.

$$V_C = \frac{\int_0^t I_C dt}{C} = I_R R_C, \tag{7}$$

$$I = I_C + I_R, \tag{8}$$

where I_C, I_R are the current flowing through C and the one through R_C, respectively.

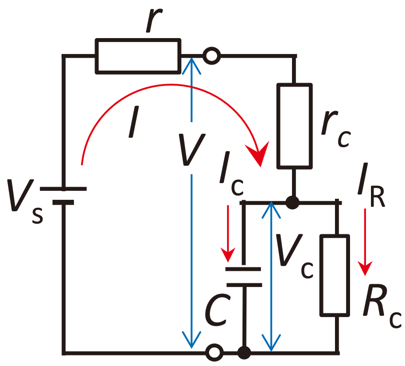

Fig. 2 Equivalent circuit for charge efficiency measurement of capacitors with series- and parallel-resistances using a constant voltage source.

By combining Eqs. (6), (7) and (8), we obtain

$$\frac{\int_0^t I_C dt}{C} = V_S - r'\left(I_C + \frac{\int_0^t I_C dt}{CR_C}\right). \tag{9}$$

Differentiating both sides with respect to t leads to the following equation.

$$I_C = -CR'\frac{dI_C}{dt}, \tag{10}$$

where

$$R' = \frac{1}{\frac{1}{r'} + \frac{1}{R_C}}. \tag{11}$$

Solution to the differential equation becomes,

$$I_C = \frac{V_S}{r'} e^{-\frac{t}{CR'}}. \tag{12}$$

Therefore,

$$I_R = \frac{\int_0^t I_C dt}{CR_C} = \frac{R'V_S}{R_C r'}\left(1 - e^{-\frac{t}{CR'}}\right), \tag{13}$$

$$I = I_C + I_R = \frac{R'V_S}{R_C r'}\left(1 - e^{-\frac{t}{CR'}}\right) = \frac{V_S}{r'}\left\{\left(1 - \frac{R'}{R_C}\right)e^{-\frac{t}{CR'}} + \frac{R'}{R_C}\right\} \approx \frac{V_S}{r'} e^{-\frac{t}{CR'}}. \tag{14}$$

The approximation holds under the condition of $r + r_C \ll R_C$, which is easily justified in actual products.

By using Eq. (14), the apparent capacitor voltage, V, is expressed as follows.

$$V = V_S - Ir$$
$$= V_S\left[1 - \frac{r}{r'}\left\{\left(1 - \frac{R'}{R_C}\right)e^{-\frac{t}{CR'}} + \frac{R'}{R_C}\right\}\right]$$
$$\approx V_S\left(1 - \frac{r}{r'}e^{-\frac{t}{CR'}}\right), \quad (15)$$

The approximation holds for $R' << R_C$, which is also easily justified.

By using Eq. (13), the true capacitor voltage, V_C is expressed as follows.

$$V_C = I_R R_C$$
$$= \frac{R'V_S}{r'}\left(1 - e^{-\frac{t}{CR'}}\right). \quad (16)$$

Charge efficiency is defined as a ratio of capacitor stored energy, W_C, to the supplied energy, W_S, and is given by

$$\eta_C^{CV'} = \frac{W_C}{W_S}$$
$$= \frac{\frac{CV_C^2}{2}}{V_S\int_0^t I_C dt}$$
$$= \frac{1 - e^{-\frac{t}{CR'}}}{2\left(1 + \frac{r + r_C}{R_C}\right)}. \quad (17)$$

The efficiency converges to $\frac{1}{2\left(1+\frac{r+r_C}{R_C}\right)}$ at the limit of infinite t. Actually, the efficiency converges closely to 1/2 since $r + r_C << R_C$ easily holds for real products.

2.3 CC charge efficiency

The circuit is shown in Fig. 3 where the capacitor with capacitance, C, is charged from the constant current source supplying constant current, I, through the resistance, R. Charge, Q, accumulated in the capacitor during charging time, t, is expressed as $Q = It$, sine I is constant in this case.

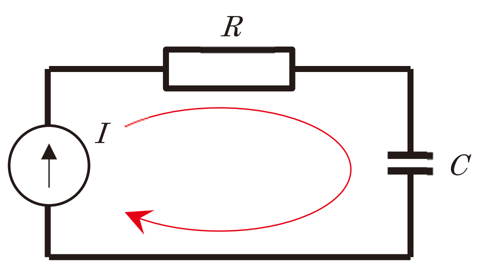

Fig. 3 Circuit for charge efficiency measurement using a constant current source.

Therefore, W_C, W_R are simply given as follows.

$$W_C = \frac{Q^2}{2C}$$
$$= \frac{I^2t^2}{2C}, \quad (18)$$
$$W_R = I^2Rt. \quad (19)$$

The CC charge efficiency is also given by the definition of Eq. (1) and becomes

$$\eta_C^{CC} = \frac{1}{\frac{2CR}{t} + 1}. \quad (20)$$

The efficiency converges to 1 at the limit of infinite t. It should be noted that charge efficiency under constant current can closely reach unity while that under constant voltage cannot exceed 1/2.

2.4 CC charge efficiency of a capacitor with series- and parallel-resistances

The circuit is shown in Fig. 4. The difference between Fig. 2 and Fig. 4 is that the voltage source is only replaced with the current source.

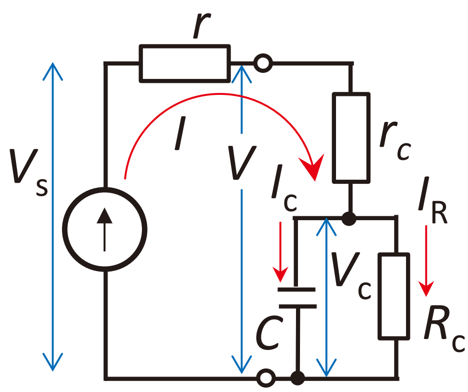

Fig. 4 Equivalent circuit for charge efficiency measurement of capacitors with series- and parallel-resistors using a constant current source.

The following equations hold.

$$I = I_C + I_R, \quad (21)$$
$$V_C = \frac{\int_0^t I_C dt}{C}$$
$$= I_R R_C. \quad (22)$$

By combining these equations, we obtain

$$\int_0^t I_C dt = CR_C(I - I_C). \quad (23)$$

Differentiating both sides with respect to t leads to

$$I_C = -CR_C\frac{dI_C}{dt}, \quad (24)$$

Solution to the differential equation becomes,

$$I_C = Ie^{-\frac{t}{CR_C}}. \quad (25)$$

Therefore, the following equations are derived.

$$I_R = I\left(1 - e^{-\frac{t}{CR_C}}\right), \quad (26)$$

$$V_C = I_R R_C = IR_C\left(1 - e^{-\frac{t}{CR_C}}\right), \quad (27)$$

$$V = V_C + Ir_C = \frac{I}{C}\int_0^t e^{-\frac{t}{CR_C}}\,dt + Ir_C = I\left\{R_C\left(1 - e^{-\frac{t}{CR_C}}\right) + r_C\right\}, \quad (28)$$

and

$$V_S = V + Ir = I\left\{R_C\left(1 - e^{-\frac{t}{CR_C}}\right) + r_C + r\right\} \approx I\left(\frac{t}{C} + r_C + r\right). \quad (29)$$

The approximation holds under the condition of $CR_C >> 0$, which is easily justified in actual products

Supply energy, W_S, and stored energy in the capacitor, W_C, are given as follows.

$$W_S = I\int_0^t V_S\,dt \approx I\int_0^t \left(\frac{t}{C} + r_C + r\right)dt = I^2(r_C + r) + \frac{I^2t^2}{2C}, \quad (30)$$

$$W_C = \frac{\left(\int_0^t I_C dt\right)^2}{2C} = \frac{I^2\left(\int_0^t e^{-\frac{t}{CR_C}}\,dt\right)^2}{2C} = \frac{1}{2}I^2R_C^2C\left(1 - e^{-\frac{t}{CR_C}}\right)^2 \approx \frac{I^2R_C^2C}{2}\left(\frac{t}{CR_C}\right)^2 = \frac{I^2t^2}{2C}. \quad (31)$$

Therefore, the efficiency is obtained as follows.

$$\eta_c^{CC'} = \frac{W_C}{W_S} \approx \frac{1}{1 + \frac{2C(r_C + r)}{t}}. \quad (32)$$

This also shows that the charge efficiency converges to 1 at the limit of infinite t.

2.5 Discharge efficiency for a constant resistance load

The circuit is shown in Fig. 5. The voltage across the capacitor is expressed as

$$V_C = V_0e^{-\frac{t}{CR}}. \quad (33)$$

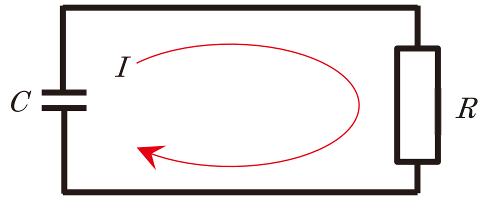

Fig. 5 Circuit for discharge efficiency measurement for a constant resistance load.

Discharge efficiency is defined as follows

$$\eta_d^{CR} = \frac{W_R}{W_{CS}}, \quad (34)$$

where W_{CS}, W_R are supply energy from the capacitor and consumed energy at the resistor, respectively. They are given as follows.

$$W_{CS} = \frac{C}{2}(V_{C0}^2 - V_C^2) = \frac{CV_{C0}^2}{2}\left(1 - e^{-\frac{2t}{CR}}\right), \quad (35)$$

$$W_R = \frac{1}{R}\int_0^t V_C^2\,dt = \frac{V_{C0}^2}{R}\int_0^t e^{-\frac{2t}{CR}}\,dt = \frac{CV_{C0}^2}{2}\left(1 - e^{-\frac{2t}{CR}}\right). \quad (36)$$

where, V_{C0} and V_C are capacitor initial voltage before discharging, and capacitor voltage at time t, respectively.

Therefore, the efficiency is always,

$$\eta_d^{CR} = 1. \quad (37)$$

2.6 Discharge efficiency from a capacitor with series- and parallel-resistances to a constant resistance load

The circuit is shown in Fig. 6. Combined resistance seen from the capacitor, R', is given by

$$R' = \left(\frac{1}{R_C} + \frac{1}{r_C + R}\right)^{-1}. \quad (38)$$

Therefore, the capacitance voltage decays with time constant of CR' as,

$$V_C = V_{C0}e^{-\frac{t}{CR'}}, \quad (39)$$

where V_{C0} is the initial value of the capacitance voltage. V_C is also expressed by

$$V_C = V_{C0} - \frac{\int_0^t I_C dt}{C} \quad (40)$$

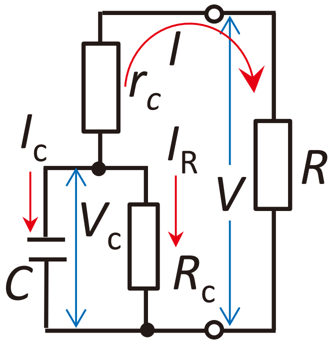

Fig. 6 Circuit for discharge efficiency measurement for a constant resistance load.

From Eqs. (38), (39) and (40) we obtain

$$\int_0^t I_C dt = CV_{C0}\left(1 - e^{-\frac{t}{CR'}}\right) \quad (41)$$

Differentiating both sides with respect to t leads to

$$I_C = \frac{V_{C0}}{R'} e^{-\frac{t}{CR'}} \quad (42)$$

Current flowing through the resistor, I_R, is given by

$$I_R = \frac{V_C}{R_C} = \frac{V_{C0}}{R_C} e^{-\frac{t}{CR'}}. \quad (43)$$

Concerning the currents, the following equation holds.

$$I = I_C - I_R \quad (44)$$

By substituting Eq. (42) and Eq. (43) for Eq. (44), I becomes

$$I = V_{C0}\left(\frac{1}{R'} - \frac{1}{R_C}\right) e^{-\frac{t}{CR'}} = \frac{V_{C0}}{r_C + R} e^{-\frac{t}{CR'}} \quad (45)$$

Supply energy from the capacitor, W'_{CS} is given by

$$W'_{CS} = \frac{C}{2}(V_{C0}^2 - V_C^2) = \frac{CV_{C0}^2}{2}\left(1 - e^{-\frac{2t}{CR'}}\right), \quad (46)$$

Consumed energy at the load resistor is expressed by

$$W'_R = R\int_0^t I^2\, dt \quad (47)$$

Substitution of Eq.(45) for Eq. (47) gives

$$W'_R = R\left(\frac{V_{C0}}{r_C + R}\right)^2 \int_0^t e^{-\frac{2t}{CR'}} dt = CR'R\left(\frac{V_{C0}}{r_C + R}\right)^2 \quad (48)$$

Therefore, the discharge efficiency is given by

$$\eta_d^{CR'} = \frac{W'_R}{W'_{CS}} = \frac{R'R}{(r_C + R)^2} = \frac{1}{\left(1 + \frac{r_C}{R}\right)\left(1 + \frac{R + r_C}{R_C}\right)} \quad (49)$$

Note that the efficiency is constant for t.

2.7 Discharge efficiency for CV load

The circuit is shown in Fig. 7 where the capacitor with capacitance, C, is discharged to a resistor load through an additional series resistor (active device such as a transistor in reality to enable feedback control), whose resistance is variable so that the voltage across the load is kept constant at V. Since the current flowing in the load resistor becomes constant as well, the section title can be also expressed as “Discharge efficiency for CC load”.

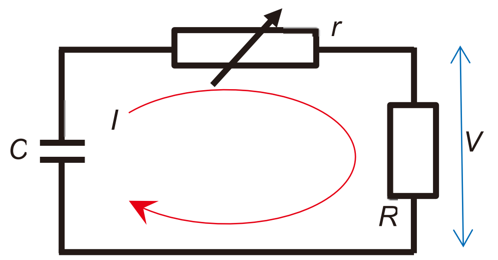

Fig. 7 Circuit for discharge efficiency measurement for a constant voltage load.

Capacitor voltage, V_C, is expressed as

$$V_C = V_0 - \frac{I}{C}t = V_0 - \frac{V}{CR}t. \quad (50)$$

Supply energy from the capacitor, W''_{CS}, is given by

$$W''_{CS} = \frac{C}{2}(V_0^2 - V_C^2) = \frac{V_0 V}{R}t - \frac{V^2}{2CR^2}t^2, \quad (51)$$

where, V_0, V_C and V are capacitor initial voltage before discharging, capacitor voltage and resistor voltage, respectively.

Since consumed energy at the resistor, W''_R, is given by

$$W_R'' = \frac{V^2 t}{R}, \tag{52}$$

the efficiency is formulated as

$$\eta_d^{CR''} = \frac{W_R''}{W_{CS}''} = \frac{1}{\frac{V_0}{V} - \frac{t}{2CR}}. \tag{53}$$

The efficiency starts to decrease as t increases from V/V_0 and converges to 0 at the limit of infinite t.

3. Experimental

Experiments to characterize EDLCs, specifically, charge experiment using a constant voltage source and a constant current source together with discharge experiment with a constant resistance load have been conducted. Specimens and major instruments used are listed in Table 1 together with some nominal specifications.

Table 1. Specimens and major instruments used

	Manu-facturer	Model	Specifications etc.
EDLC	NEC/ TOKIN	FYD0H1 05ZF	5.5 V, 1.0 F
Power supply	KIKUS UI	PMC18-2	DC 18 V, 2 A
Logger	GRAPH TEC	GL100-4VT	CH1, CH4: 10 V range (4 digits)
Calibra-tor	YOKOG AWA	CA11E	± (0.01%+0.8 μA) for 20 mA source
Tester	FLUKE	179	± (0.09 % + 2) for DCV

Using the CV or CC source, a nominal 1 F (maximum rated voltage 5.5 V) electric double-layer capacitor was connected through a nominal 3 Ω resistor and charged. Low resistance of the shunt resistor was measured by 4-terminal method by which voltage drop across the resistor under test is measured by the tester (FLUKE 170) while constant current is fed by the calibrator (YOKOGAWA CA11). Resistance of the shunt resistor was determined to be 2.93 ± 0.01 Ω.

The capacitors were initially shorted at both ends to be in a discharged state, and charging began after removing the short wiring. Data recording was performed using the data logger GL100 recording CH1: voltage across the capacitor terminals, and CH4: resistor terminal voltage (used to derive current based on Ohm's law). Data sampling period was set to 1 s. After charging was complete, the power supply was disconnected and then the capacitor voltage decay due to the self-discharge was also recorded.

3.1 CV charge experiment

The experiment was carried out based on the circuit of Fig. 1 where $C = 1$ F, $R = 3$ Ω and V = 5.3 V (all the values are nominal ones). Current flowing in the circuit is derived by dividing the measured voltage across the shunt resistor with its resistance (2.93 Ω). Measured voltage and current curves are shown in Fig. 8 together with analyzed curves. True capacitor voltage is derived by correcting the voltage drop due to the series resistance inside the capacitor. The curve denoted by $V+V_r+V_p$ should be equal to the source voltage and it is supported.

Constant voltage charging starts at 0 s and ends at 93 s. Since charging is ended by disconnecting the cable to the capacitor, the slow decay in the voltage is interpreted to be caused by self-discharge due to the parallel resistor inside the capacitor. Determination of the parallel resistance will be described later in section 3.2.

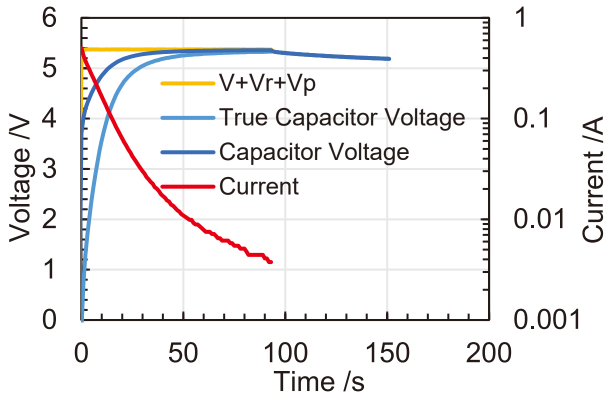

Fig. 8 Temporal change in capacitor voltage, current etc. for constant voltage charging. V : capacitor voltage, Vr : shunt resistor voltage. Vp : parasitic resistance such as contact resistance. Current is derived by Vr/r where r is the shunt resistor resistance. True Capacitor Voltage is calculated based on the assumed equivalent circuit.

Fig. 9 is an expanded graph near the

beginning of constant voltage charging to show the details of the change in voltage and current. For the current, exponential function is fitted and its equation is also shown together with its coefficient of determination (denoted by R^2). The voltage jump-up at the beginning of discharge indicates the presence of series resistance inside the capacitor. Its resistance is calculated by dividing the voltage at $t = 0$ (corresponding to the voltage step height) by the current at $t = 0$. The result is 8.19 Ω, which is even larger than the external series resistor. In such a case, it is necessary to use the model taking account of the effect of series- and parallel-resistances inside the capacitor as described in section 2.2.

According to the theory, current decays exponentially with time. Since the ordinate for the current in Fig. 8 is logarithmic, the curve should be linear. The deviation from the straight line in the low-level current might be caused by an offset of the data logger. As in Fig. 9, the first 20 seconds part results in a very good fit and gives a time constant of 1/9.978E-2 = 10.02 s.

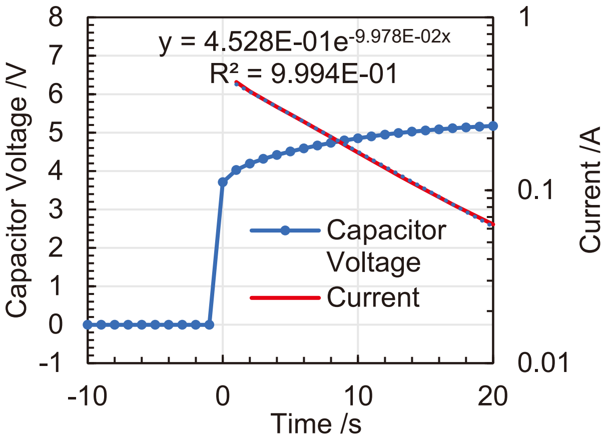

Fig. 9 Temporal change in voltage and current expanded at the beginning of constant voltage charging. Voltage drop due to the capacitor series resistor is clearly observed at the beginning of discharge.

Fig. 10 shows a modified graph for capacitor voltage by taking $1-V/V_0$, where V_0 is the maximum (saturated) voltage at the end of the measurement, to obtain time constant for voltage increase. The first 20 seconds part fitting for the voltage change gives a time constant of 1/1.031E-1 = 9.696 s, which is smaller than the current fitting result by 3.2%.

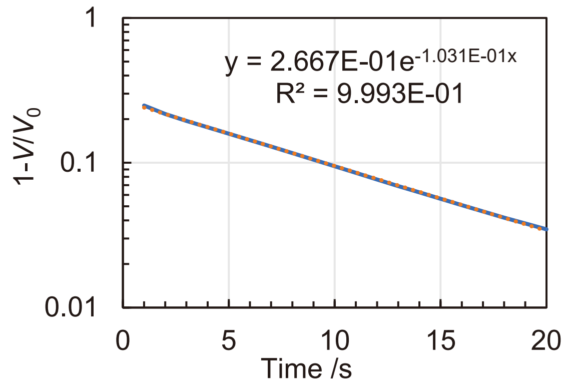

Fig. 10 Temporal change in $1-V/V_0$ where V and V_0 are capacitor voltage at time t and saturated capacitor voltage during the charge. Linear approximated line is also shown for determination of voltage decay constant. *CR* decay constant is given by using the slope as 1/0.1031.

3.2 Self-discharge experiment

As mentioned on Fig. 8 in section 3.1, voltage slow decay was observed during no-load (though the data logger itself provided some load with a 1 MΩ input resistance). When parallel resistance inside the capacitor is denoted by R_C, decay time constant is simply given by CR_C.

Fig. 11 shows an expanded graph in which an exponential fitted curve is added with its formula. From the fitting, the time constant is obtained to be $T = 1/(4.535\text{E-}4\ \text{s}^{-1}) = 2205$ s. As for C, the value obtained by using the slope of the voltage linear increase in time during CC charge is considered to be most accurate as will be discussed in section 3.3. By using this value of $C = 0.939$ F, R_C is determined to be 4.07 kΩ.

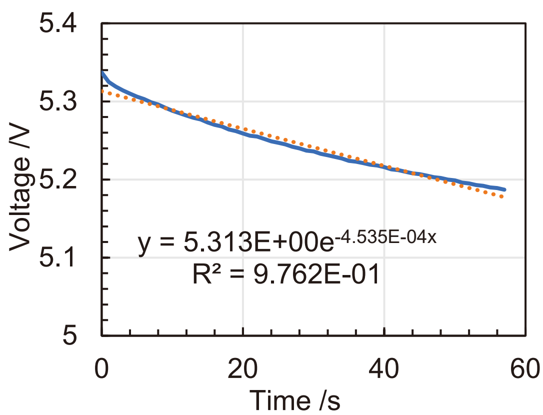

Fig. 11 Temporal change in capacitor voltage and current during self-discharging (without a load).

Charge efficiency experimentally obtained using a constant voltage source is shown in Fig.

12 together with the theoretical curve based on Eq.(17) in section 2.2. Both curves agree satisfactorily. This proves not only the correctness of the formulation but also the one of the measurements. However, it should be noted that such a good agreement is not obtained by using a simple model with an ideal capacitor as described in section 2.1.

As noted in sections 2.1 and 2.3, the efficiency never exceeds 1/2.

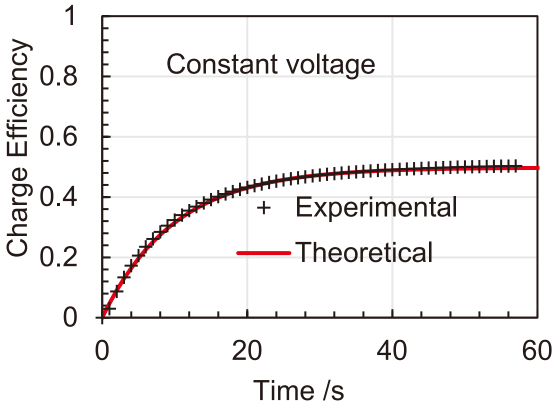

Fig. 12 Temporal change in charge efficiency during constant voltage charging. Experimental results are compared with theoretical ones.

3.3 CC charge experiment

The experiment was carried out based on the circuit of Fig. 3 where $C = 1$ F, $R = 3$ Ω and $I = 0.1$ A (all the values are nominal ones).

Fig. 13 shows all the sequential data of capacitor voltage and current during not only charging but also following self-discharging and constant resistance discharging. Constant current charging starts at 0 s and ends at 40 s.

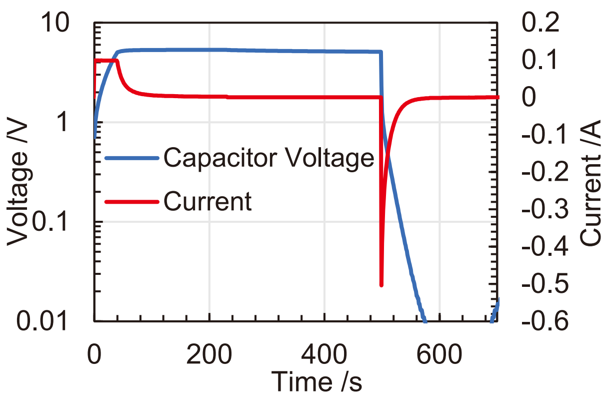

Fig. 13 Temporal change in capacitor voltage and current for constant current charging, self-discharging and constant resistance discharging.

Temporal change in capacitor voltage and current under constant current charging is shown in Fig. 14.

Voltage jump at the beginning of charge is also observed. Similarly to the procedures of CV charge, series resistance is determined by dividing the voltage jump by the current. The result is 8.15 Ω, which is nearly equal to the value of 8.19 Ω for the CV charge measurement.

Theoretically, capacitor voltage, V, is expressed as $V = It/C = at$ where I is the constant current, t is the charge time and a is the slope(V/t) in the V-t graph. As expected, the measured voltage data are on a straight line. By using the measured slope ($a = 0.1054$ V/s) and the current ($I = 0.09899$ A), capacitance can be determined to be $C = I/a = 0.939$ F. This determination method (denoted by $I/(V/t)$ method hereafter) for capacitance is considered to be more accurate than the time constant (CR) determination method used in section 3.1.

For the latter, a product of C and R is obtained in the first place from exponential decay or saturating curve. In the second place, R must be determined to obtain C. However, R is not equal to the resistance of externally connected series resister for the actual case where there exist a series- and parallel-resistor. Therefore, it is necessary to determine all these resistances by separate measurements as described in section 3.1 and it brings increased uncertainty.

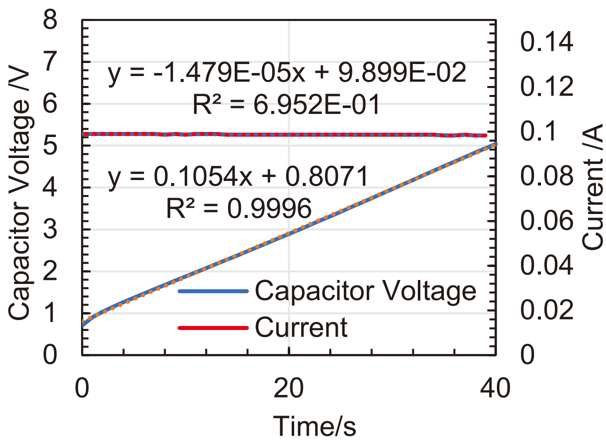

Fig. 14 Temporal change in capacitor voltage and current under constant current charging. Linear approximated lines are also shown for determination of capacitance and equivalent series resistance.

For capacitance evaluation, we tested and compared 5 different methods, which are listed as follows with equations used and the explanations.

1. T/R : Dividing the time constant T of the current or voltage change in time during charging and discharging by the resistance R.
2. $\Delta W_C/\Delta V/V$: Dividing the change in capacitor energy ΔW_C by the product of the capacitor voltage V and its change ΔV.
3. $2W_C/V^2$: Dividing the accumulated energy W_C in the capacitor by the square of the capacitor voltage V.
4. Q/V : Dividing the accumulated charge Q by the capacitor voltage V.
5. $\Delta Q/\Delta V$: Dividing the change in the accumulated charge ΔQ by the capacitor voltage change ΔV.

Fig. 15 shows a comparison in capacitances determined by the 4 methods except method 1 as a function of the true capacitor voltage. The $I/(V/t)$ method to use the voltage slope for CC charge can be categorized to method 4 although its result is not shown in Fig. 15 since it cannot be expressed as a function of the capacitor voltage. All the results agree within 10% above 1 V. The deviation below 1 V is likely to be caused by offset of the logger etc.

For integral quantities such as Q and W, they are calculated by time integration of current and power, respectively using the trapezoidal rule. For differential quantities such as ΔW, ΔV and ΔQ, they are numerically calculated using the adjacent values.

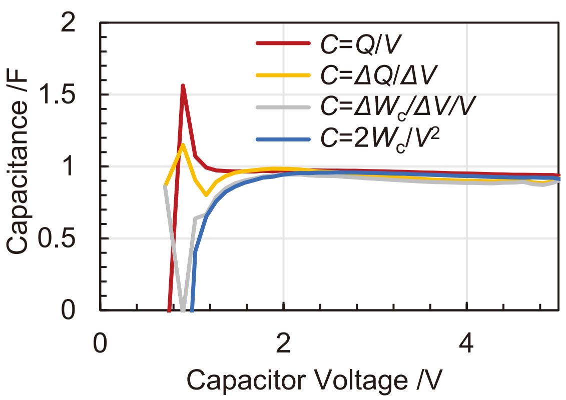

Fig. 15 Capacitances derived from 4 different equations during constant current charging as a function of true capacitor voltage.

Charge efficiency experimentally obtained using a constant current source is shown in Fig. 16 together with the theoretical curve based on Eq.(32) in section 2.4. Again, both curves agree satisfactorily showing that both theoretical formulation and experimental measurements are correct. Prominent difference from the CV charging as shown in Fig. 12 is that the charge efficiency for CC charge can exceed 1/2 and can approach unity as close as possible.

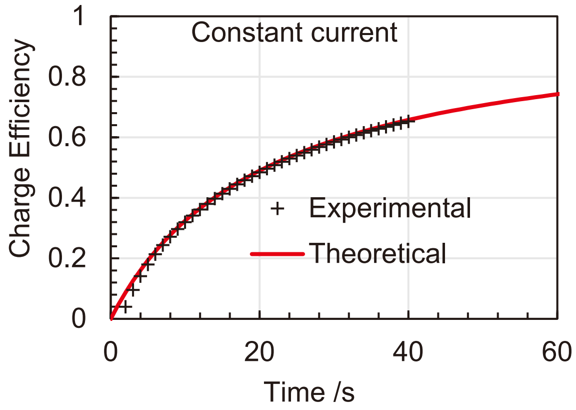

Fig. 16 Temporal change in charge efficiency during constant current charging. Experimental results are compared with theoretical ones.

3.4 Discharge experiment using a constant resistance load

The experiment was carried out based on the circuit of Fig. 5 where C = 1 F and R = 3 Ω (both values are nominal ones).

Fig. 17 shows measured voltage and current together with corrected true voltage as a function of time. Discharge starts at 0 s and ends at 182 s. Soon after the discharge ends, the voltage gradual increase is observed in spite of the no-load condition, which cannot be explained by the assumed equivalent circuit model.

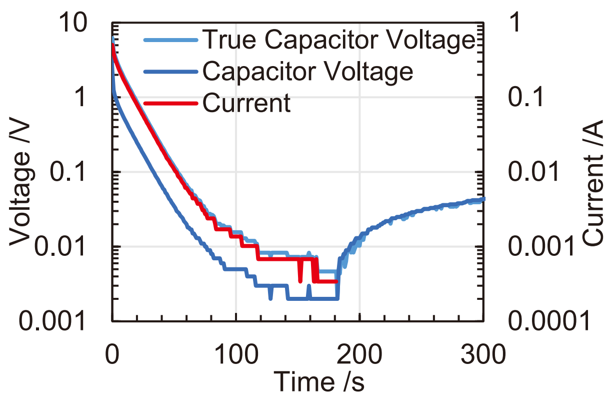

Fig. 17 Temporal change in Measurement results for constant resistance discharging.

Expanded graph in the time range from -20 s till 20 s is shown in Fig. 18. Voltage sudden fall at the beginning of discharge is observed. Similarly to the procedures of CV- and CC-charge, series resistance is determined by dividing the voltage step by the current. The result is 7.78 Ω, which is smaller than the preceding results in section 3.1 by about 0.4 Ω but is almost comparable.

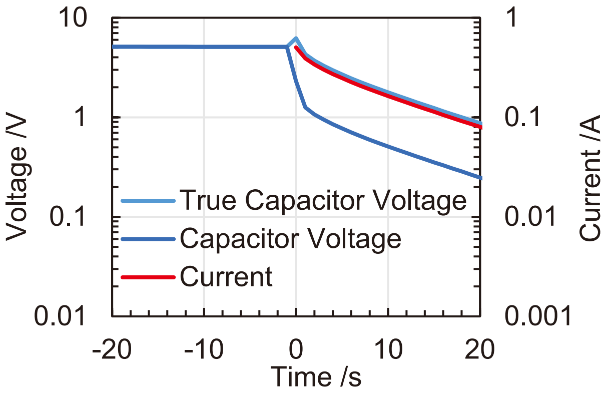

Fig. 18 Expanded graph for temporal change in measurement results for constant resistance discharging. Voltage drop due to the capacitor series resistor is clearly observed at the beginning of discharge.

Discharge efficiency experimentally obtained for a constant resistance load is shown in Fig. 19 together with the theoretical curve based on Eq.(49) in section 2.6. Although the experimental values are higher than the theoretical ones by about 5%, time independent feature is observed experimentally as well.

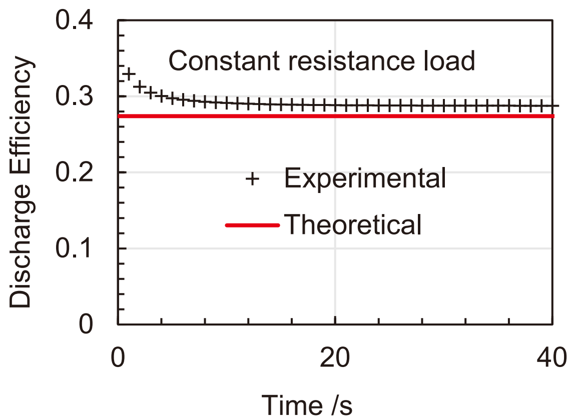

Fig. 19 Temporal change in discharge efficiency for a constant resistance load. Experimental results are compared with theoretical ones.

4. Conclusion

Both theoretical and experimental characterization to determine charge- and discharge-efficiencies of electric double layer capacitors are conducted.

Analytical equations are formulated under several conditions: 1) Charge using a constant voltage source for an ideal capacitor, 2) Charge using a constant voltage source for a capacitor with series- and parallel-resistances, 3) Charge using a constant current source for an ideal capacitor, 4) Charge using a constant current source for a capacitor with series- and parallel-resistances, 5) Discharge from an ideal capacitor to a constant resistance resistor, 6) Discharge from a capacitor with series- and parallel-resistances to a constant resistance resistor, and 7) Discharge from an ideal capacitor to a constant resistance resistor via a variable resistor keeping constant voltage.

For comparison with the theory, experiments, where capacitors are not ideal but are assumed to have series- and parallel-resistors, have been conducted under the following conditions: 2) Charge using a constant voltage source, 4) Charge using a constant current source and 6) Discharge to a constant resistance load. All the experimental results on efficiencies agree well to the theoretical ones. This supports that both theoretical formulation and experimental measurements are correct.

To determine charge- and discharge-efficiencies for non-ideal capacitors, it is necessary to determine all the values of capacitance, C, capacitor series resistance, r_c, capacitor parallel resistance, R_c. As for C determination, 5 different methods as a function of the true capacitor voltage are compared. Although all the results agree within 10% above 1 V, the $I/(V/t)$ method under CC charge is considered to give most accurate capacitance since there is no need to know the series resistance in the circuit.

Equations and methods to experimentally determine each parameter are as follows. $C = I/(V/t)$: to divide constant current I by the slope of the linear fit to the V-t graph in CC charge experiment. $r_C = \Delta V/I$: to divide a voltage step ΔV observed in the capacitor voltage right after charging completion, by the charging current just before charging completion. $R_C = T/C$: to divide a time constant of self-discharge by the known capacitance determined by the $I/(V/t)$ method.

Theoretical analysis shows that charge efficiency using a constant voltage source converges to 1/2, as known well, regardless of the values of C and R at the limit of infinite t. This is confirmed by the experiment. On the contrary, charge efficiency using a constant current source converges to 1. Therefore, CC charging should be used especially for high energy applications.

The cause of the difference is understood as follows. For CV charge, Joule loss is inevitable because there always exists voltage difference between the source and the capacitor and therefore a series resistance (including the one inside the capacitor) is an essential component to absorb the voltage gap. Especially at the beginning of charging, both voltage and current have largest values and such Joule loss is inevitable. For CC charge, in principle, no external series resistor is necessary since voltage across the CC source is automatically adjusted so as tomatch the load (capacitor) voltage. Therefore, the resistor generating Joule loss can be limited to a series resistor inside the capacitor.

With this study, it has been confirmed that analytical equations are useful and give a sharp perspective for better understanding. Good agreements obtained between theory and experiment proves that experiments are reliable enough. Therefore, for instance, a new system design in which analytical equations are not ready can be evaluated experimentally.

In addition to the discussion points in this paper, the effective key to reduce Joule loss is to replace the series resistor with a switching regulator[18] where the average current is regulated by an electronic switch which controls the duty ratio of on-time and off-time. In such a case, it is necessary to characterize and optimize not only DC properties but also AC properties of capacitors.

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