Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental information

Mathematical Model Based on Staircase Structure for Porous Electrode Impedance

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General theory for resistance and capacitance in AC impedance

When given the voltage (E) and current (I) as a function of AC frequency (ω), the impedance component (Z(ω)) respectively, can be shown as follows [1, 2]:

$$Z(\omega) = \frac{E(\omega)}{I(\omega)} \quad (1)$$

where ω (= 2πf, f is the frequency (Hz)) is the angular velocity.

Here, resistance and capacitance as impedance component are considered (Z_R and Z_C, respectively).

Z_R, consisting of resistance (R), can be expressed by the relation $E(\omega) = RI(\omega)$, as in the following equation:

$$Z_R = R \quad (2)$$

This equation is not affected by AC frequency.

On the other hand, the current I(ω) in the presence of electric double layer capacitance (C_{dl}) can be shown as the following equation using the relation $Q = C_{dl}E(\omega)$ when charge (Q) is differentiated with time (t):

$$I(\omega) = \frac{dQ}{dt} = C_{dl}\frac{\partial E(\omega)}{\partial t} \quad (3)$$

The time derivative of E(ω) in AC results in $j\omega E(\omega)$, so $I(\omega) = j\omega CE(\omega)$. Therefore, Z_C can be shown as follows:

$$Z_C = (j\omega C_{dl})^{-1} \quad (4)$$

where j is an imaginary number. This equation is affected by AC frequency.

These are used as impedance components for equivalent circuit design.

Complex capacitance theory

Impedance ($Z(\omega)$) and complex capacitance ($C(\omega)$) are related as follows [3, 4].

$$C(\omega) = \frac{1}{j\omega Z(\omega)} \tag{5}$$

Based on the definition of complex impedance ($Z(\omega) = Z_{re} + jZ_{im}$), the complex capacitance ($C(\omega) = C_{re} + jC_{im}$) is considered as follows.

$$C(\omega) = \frac{1}{j\omega(Z_{re} + jZ_{im})} \tag{6}$$

Here, the real (C_{re}) and the imaginary (C_{im}) parts are expressed as follows.

$$C_{re} = \frac{-Z_{im}}{\omega|Z(\omega)|^2} \tag{7}$$

$$C_{im} = \frac{Z_{re}}{\omega|Z(\omega)|^2} \tag{8}$$

Program details

Program for Python for impedance spectra of non-Faradaic process in a staircase model

```
import numpy as np # importing modules for using NumPy
import pandas as pd # importing modules for using Pandas
import cmath # importing modules for using imaginary number
import math # importing modules for using pi

# input parameters
Re = 0.001 # input electric resistance
Rion = 0.03 # input ionic resistance
C = 0.001 # input electric double-layer capacitance

# setting the frequency
a = np.arange(91) # generating an isoperimetric sequence
f = 10**(a/10 - 3) # frequency range: 10^-3～10^+3 Hz
w = 2 * math.pi * f # angular velocity

# setting the capacitance
jwc = w * C * 1j # The notation "1j" is used to handle imaginary numbers in Python

# Calculation of impedance using recursive function
i = 100 # number of step
def z_n(i):
    if i < 1:
        return Rion + (Re + 1/jwc) # i=0
    return Rion + (1/(1/z_n(i -1) + 1/(Re + 1/jwc))) # i>1
ans_n = z_n(i)

Rre = ans_n.real - Rion # Real part of impedance
Rim = -ans_n.imag # Imaginary part of impedance
# output data
df_non_faradaic = pd.DataFrame(list(zip(w, Rre, Rim)), columns = ["Frequency (Hz)", "Rre_n-f",
"Rim_n-f"])
df_non_faradaic
```

Program for Python for impedance spectra of Faradaic process in a staircase model

```
import numpy as np # importing modules for using NumPy
import pandas as pd # importing modules for using Pandas
import cmath # importing modules for using imaginary number
import math # importing modules for using pi

# input parameters
Re = 0.001 # input electric resistance
Rion = 0.03 # input ionic resistance
Rct = 400 # input charge-transfer resistance
C = 0.001 # input electric double-layer capacitance

# setting the frequency
a = np.arange(91) # generating an isoperimetric sequence
f = 10**(a/10 - 3) # frequency range: 10^-3～10^+3 Hz
w = 2 * math.pi * f # angular velocity

# setting the capacitance
jwc = w * C * 1j # The notation "1j" is used to handle imaginary numbers in Python

# Calculation of impedance using recursive function
i = 100 # number of step
def z_f(i):
    if i < 1:
        return Rion + (Re + 1/(1/Rct + jwc)) # i=0
    return Rion + (1/(1/z_f(i-1) + 1/(Re + 1/(1/Rct + jwc)))) # i>1
ans_f = z_f(i)

Rre = ans_f.real - Rion # Real part of impedance
Rim = -ans_f.imag # Imaginary part of impedance
# output data
df_faradaic = pd.DataFrame(list(zip(w, Rre, Rim)), columns = ["Frequency (Hz)", "Rre_f",
"Rim_f"])
df_faradaic
```

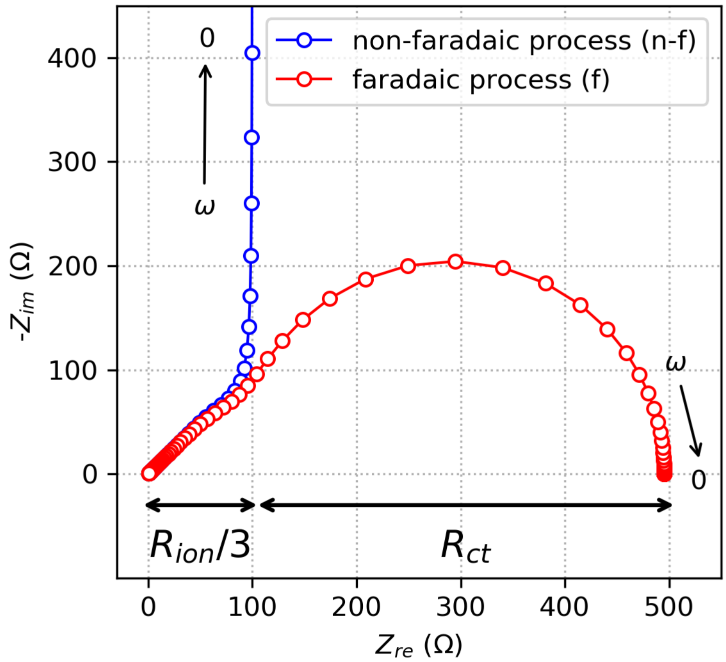

Fig. S1 Nyquist plots of non-Faradaic and Faradaic processes in the transmission line model calculated using Equations (6) and (7). Input parameters: $2\pi r$ = 1 cm, L = 1 cm, R_{sol} = 0 Ω, $R_{ion,\,L}$ = 300 Ω cm^{-1}, $R_{ct,\,A}$ = 400 Ω cm^2, $C_{dl,\,A}$ = 0.1 mF cm^{-2}.

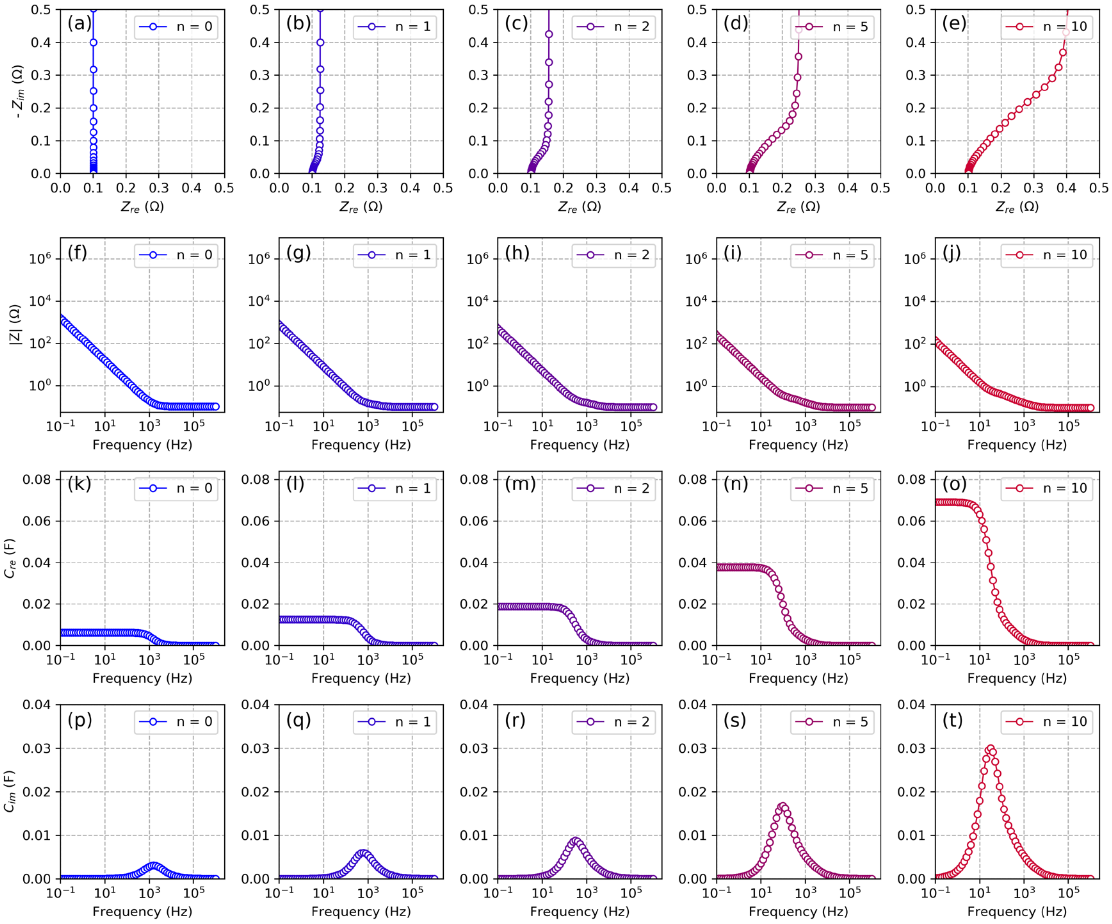

Fig. S2 (a-e) Nyquist plots, and frequency properties of (f-j) absolute value of resistance (|Z|), (k-o) the real part (C_{re}), and (p-t) imaginary part (C_{im}) of complex capacitance for non-Faradaic processes at step numbers (n) = 0, 1, 2, 5 and 10 calculated using the staircase model. Input parameters: $R_{e,\ in}$ = 1 mΩ, $R_{ion,\ in}$ = 0.1 Ω, and $C_{dl,\ in}$ = 1 mF. The calculation results of the frequency characteristics of the capacitance in non-Faradaic process obtained using the complex capacitance theory[3, 4] show that as n is increased, C_{re} reaching at the low frequency region increases, while the peak of the capacitance behaviour of C_{im} shifts to the low frequency. These capacitance behaviours are typical of non-Faradaic process, and are in good agreement with the behaviour when the electrode thickness is increased.[3]

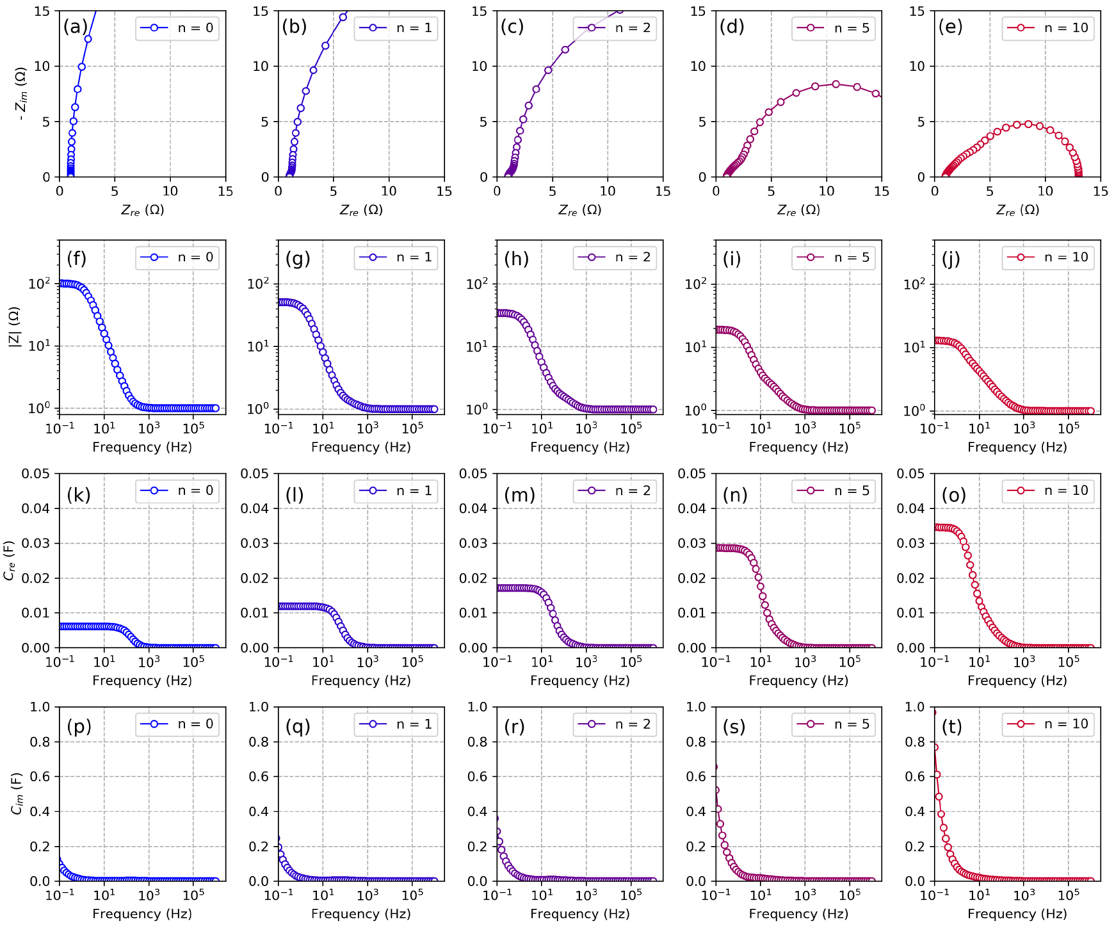

Fig. S3 (a-e) Nyquist plots, and frequency properties of (f-j) absolute value of resistance (|Z|), (k-o) the real part (C_{re}), and (p-t) imaginary part (C_{im}) of complex capacitance for Faradaic processes at n = 0, 1, 2, 5 and 10 calculated using the staircase model. Input parameters: $R_{e,\ in}$ = 1 mΩ, $R_{ion,\ in}$ = 0.1 Ω, $R_{ct,\ in}$ = 100 Ω, and $C_{dl,\ in}$ = 1 mF. In Faradaic process, although C_{re} shows similar behaviour to that of the non-Faradaic process, C_{im} shows a tail toward the low frequency region without a peak. The value of C_{im} for Faradaic process is about two orders of magnitude larger than that for the non-Faradaic process, which is in good agreement with the behaviour reflecting the effect of the current corresponding to Faradaic process.[5]

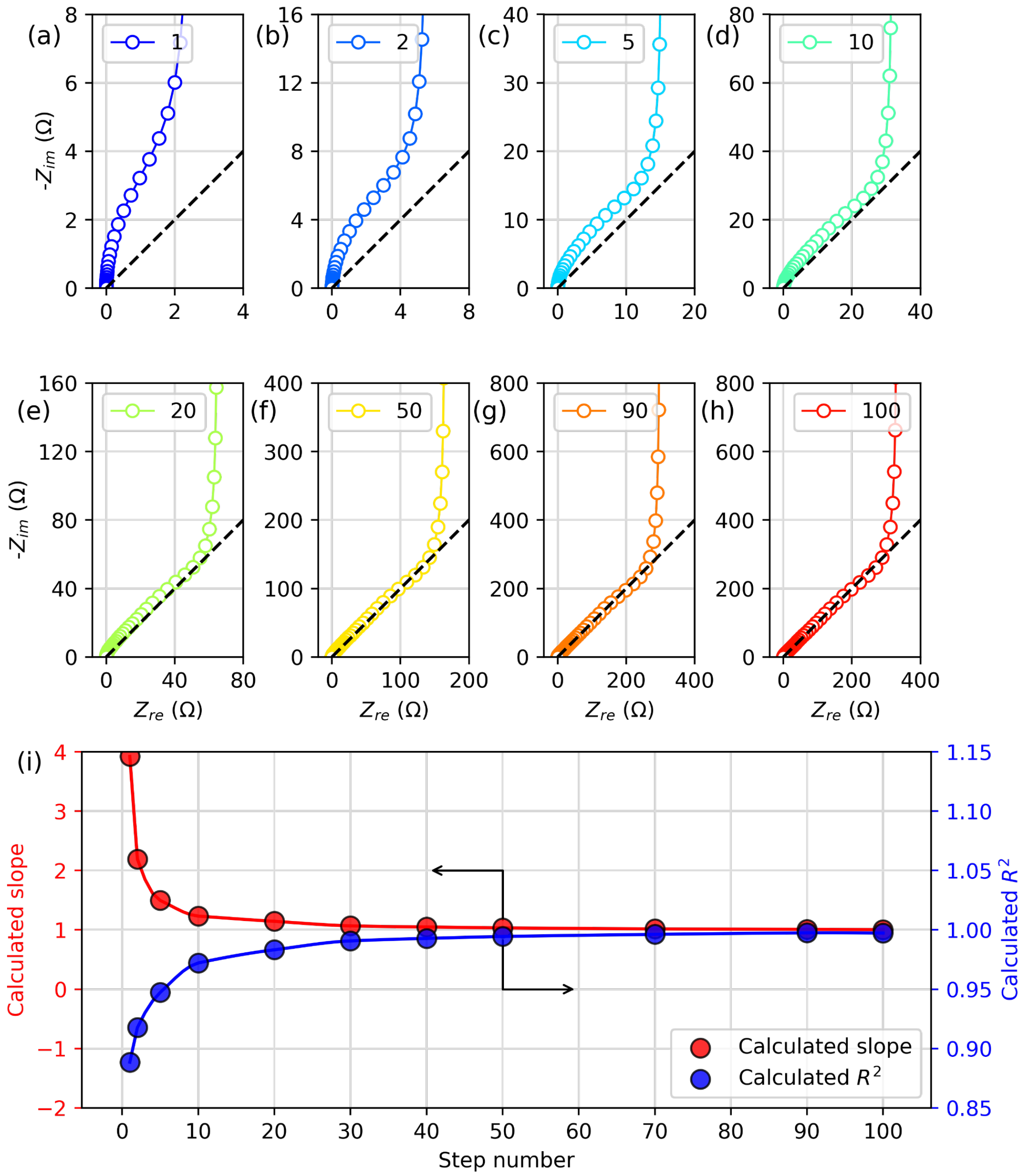

Fig. S4 (a-h) Detailed change in the Nyquist plots of non-Faradaic process in the high-frequency region for different n calculated using the staircase model. (i) Variation in the slope and coefficient of determination (R^2) of the linear approximation in the high-frequency region of the Nyquist plots for non-Faradaic process *vs.* the number of steps. Input parameters: n = 1–100, $R_{e,\,in}$ = 1 mΩ, $R_{ion,\,in}$ = 10 Ω, and $C_{dl,\,in}$ = 1 mF.

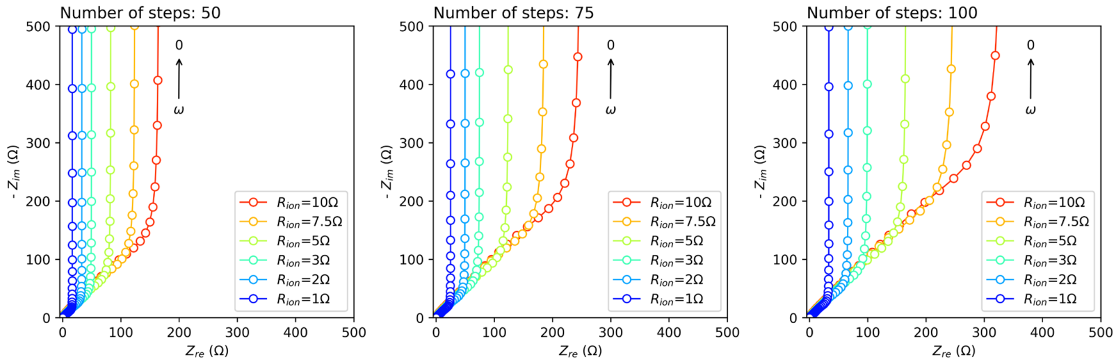

Fig. S5 Nyquist plots of non-Faradaic processes for each $R_{\text{ion, in}}$ at n = 50, 75, and 100 calculated using the staircase model. Input parameters: $R_{\text{e, in}}$ = 1 mΩ, $R_{\text{ion, in}}$ = 1–10 Ω, and $C_{\text{dl, in}}$ = 1 mF.

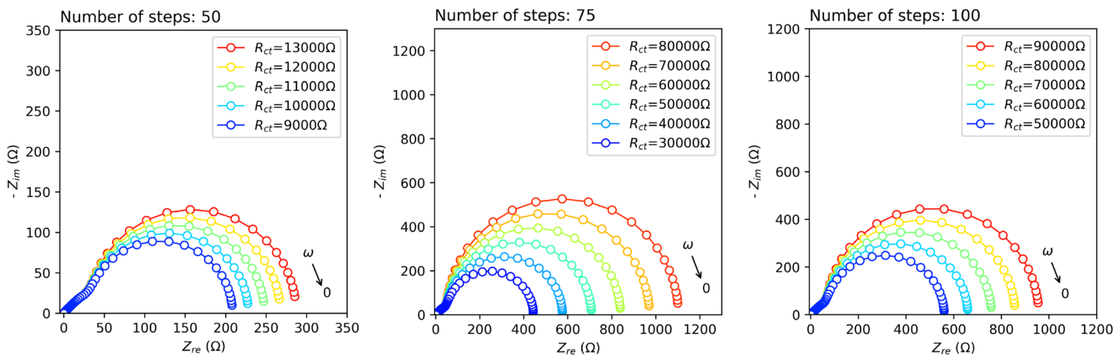

Fig. S6 Nyquist plots of Faradaic processes for each $R_{\text{ct, in}}$ at n = 50, 75 and 100 calculated using the staircase model. Input parameters: $R_{\text{e, in}}$ = 1 mΩ, $R_{\text{ion, in}}$ = 2 Ω, $R_{\text{ct, in}}$ = 9–90 kΩ, and $C_{\text{dl, in}}$ = 1 mF.

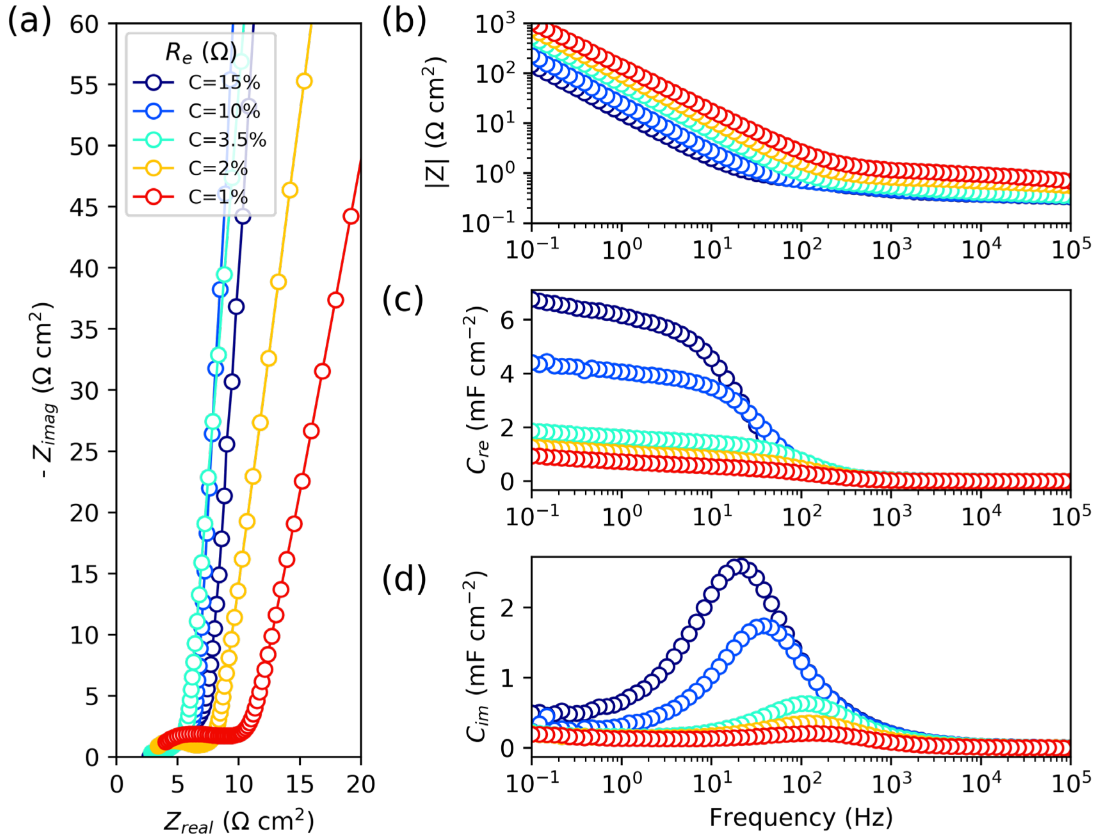

Fig. S7 (a) Nyquist plots, (b) Absolute value of resistance (|Z|), (c) Real part (C_{re}), and (d) Imaginary part (C_{im}) of complex capacitance for symmetric cells using two positive electrodes in 1.0 M $LiPF_6$ in EC/DMC/EMC (30/40/40 volume ratio) at 20 °C. The positive electrode composition was $LiNi_{0.75}Co_{0.15}Al_{0.05}Mg0.0_5O_2$, carbon black, and PVDF at C = 1% (98/1/1), C = 2% (96/2/2), C = 3.5% (94/4/2), C = 10% (85/10/5), C = 15% (80/15/5) (weight ratio). Loading weight: ~10.5 mg cm^{-2}. Electrodes were uncharged (state of charge = 0%).

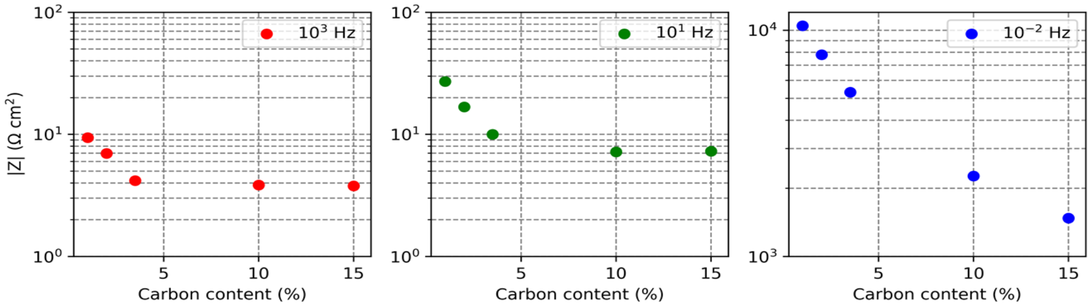

Fig. S8 Dependence of the absolute value of resistance (|Z|) on the conducting carbon ratio at frequencies of 10^3, 10^1, and 10^{-1} Hz for electrochemical impedance spectroscopy measured using the same symmetric cell as in **Fig. S7**(b). With respect to the ratio of conductive carbon, |Z| at low frequencies of 10^{-2} Hz shows linearity, while that at high frequencies of 10^1 and 10^3 Hz show nonlinearity. This suggests that the behavior in the high frequency region due to the electronic resistance is independent of the ratio of the conducting carbon.

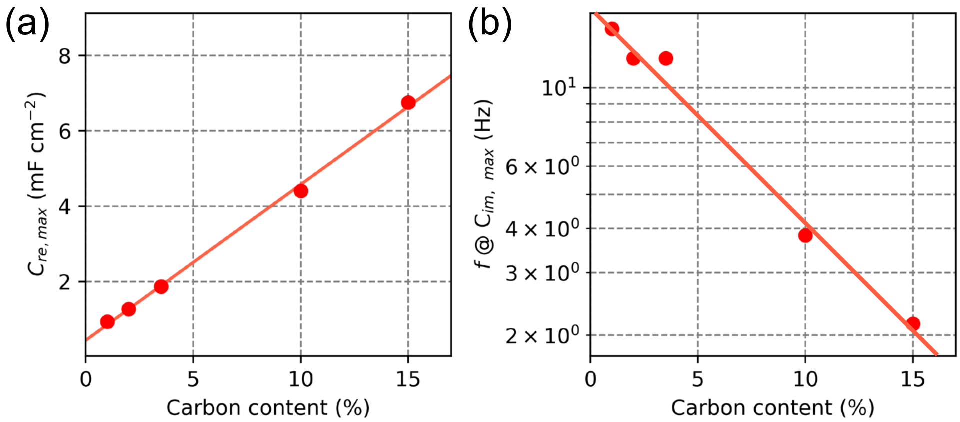

Fig. S9 Dependence of (a) the maximum value of the real part ($C_{\text{re. max}}$) and (b) the frequency showing the maximum value of the imaginary part (f @ $C_{\text{im, max}}$) in the complex capacitance results measured using the same symmetric cell as shown in **Fig. S7**(c) and d, respectively, on the conducting carbon ratio. These relationships mean that $C_{\text{re. max}}$ and f @ $C_{\text{im, max}}$ show linear variation at all conductive carbon ratios.

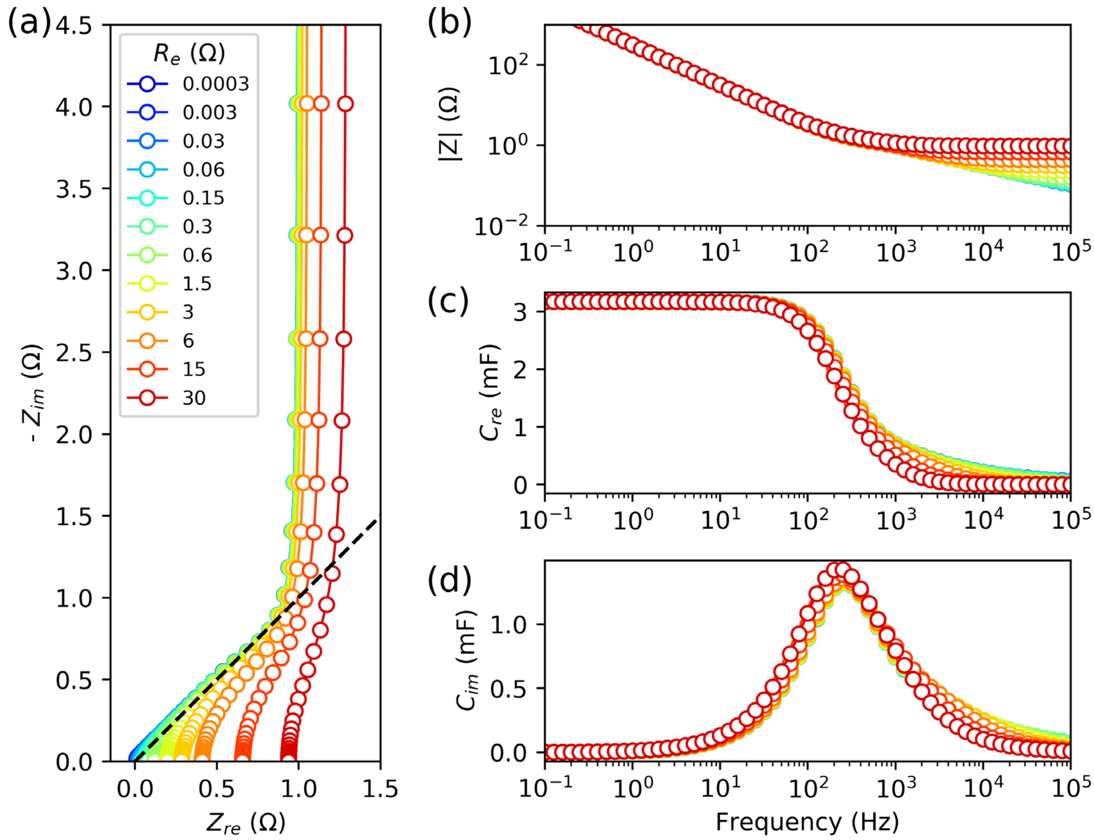

Fig. S10 (a) Nyquist plots, (b) Absolute value of resistance (|Z|), (c) Real part (C_{re}), and (d) Imaginary part (C_{im}) of complex capacitance for non-Faradaic processes when electronic resistance is varied uniformly using the staircase model defined as (i) uniform change in Fig. 7(c). Input parameters: $n = 100$, $R_{e,\ in} = 0.3$ mΩ-30 Ω, $R_{ion,\ in} = 30$ mΩ, and $C_{dl,\ in} = 5$ μF.

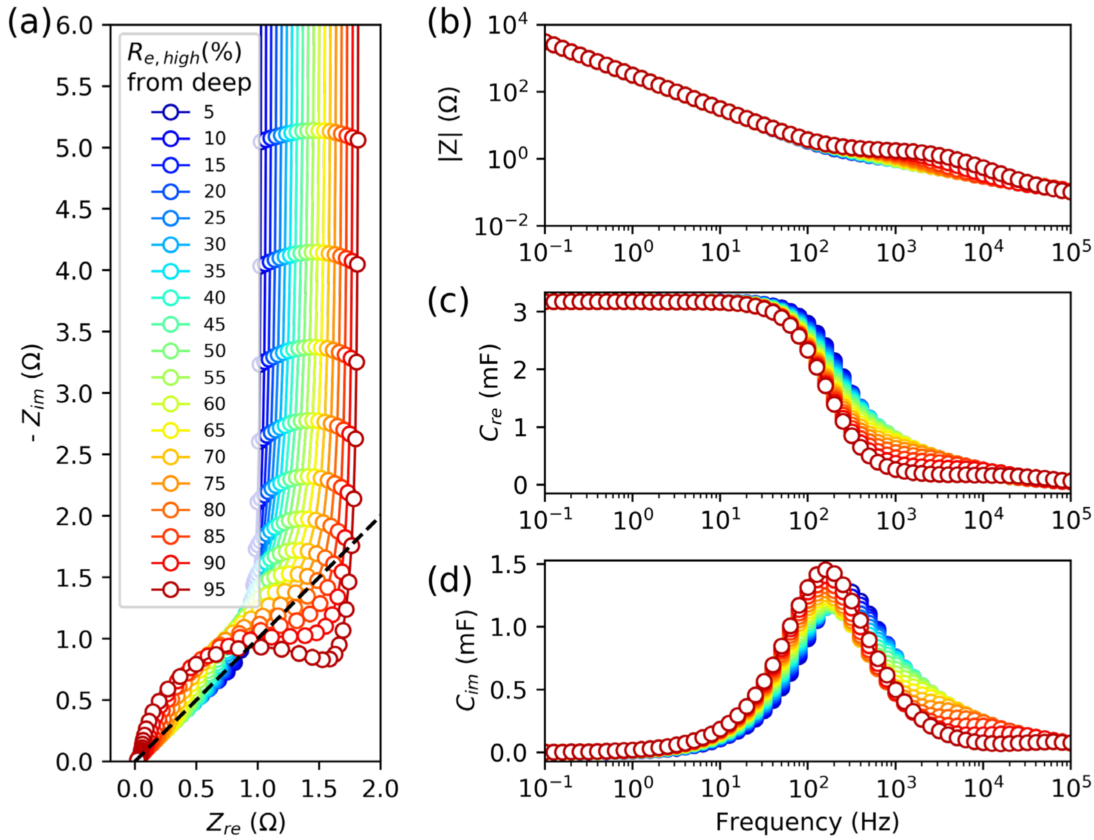

Fig. S11 (a) Nyquist plots, (b) Absolute value of resistance (|Z|), (c) Real part (C_{re}), and (d) Imaginary part (C_{im}) of complex capacitance for non-Faradaic processes when electronic resistance is varied non-uniformly using the staircase model defined as (ii) non-uniform change A in Fig. 7(c). Input parameters: n = 100, Electronic resistance (R_e) for deep/shallow regions = $R_{e,\,high}/R_{e,\,low}$ (5/95 to 95/5), $R_{e,\,high}$ = 90 Ω, $R_{e,\,low}$ = 30 mΩ, $R_{ion,\,in}$ = 30 mΩ, and $C_{dl,\,in}$ = 5 µF.

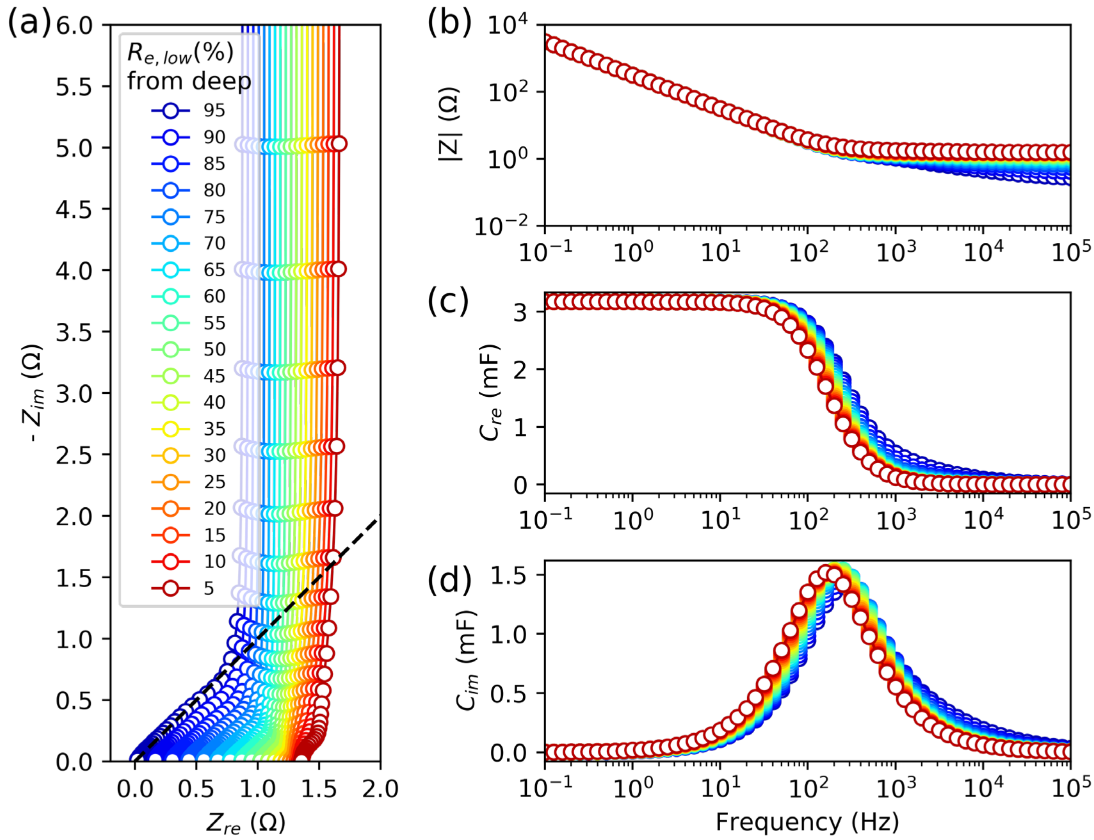

Fig. S12 (A) Nyquist plots, (B) Absolute value of resistance (|Z|), (C) Real part (C_{re}), and (D) Imaginary part (C_{im}) of complex capacitance for non-Faradaic processes when electronic resistance is varied non-uniformly using the staircase model defined as (iii) non-uniform change B in Fig. 7(c). Input parameters: n = 100, Electronic resistance (R_e) for deep/shallow regions = $R_{e,\ low}/R_{e,\ high}$ (95/5 to 5/95), $R_{e,\ high}$ = 90 Ω, $R_{e,\ low}$ = 30 mΩ, $R_{ion,\ in}$ = 30 mΩ, and $C_{dl,\ in}$ = 5 μF.

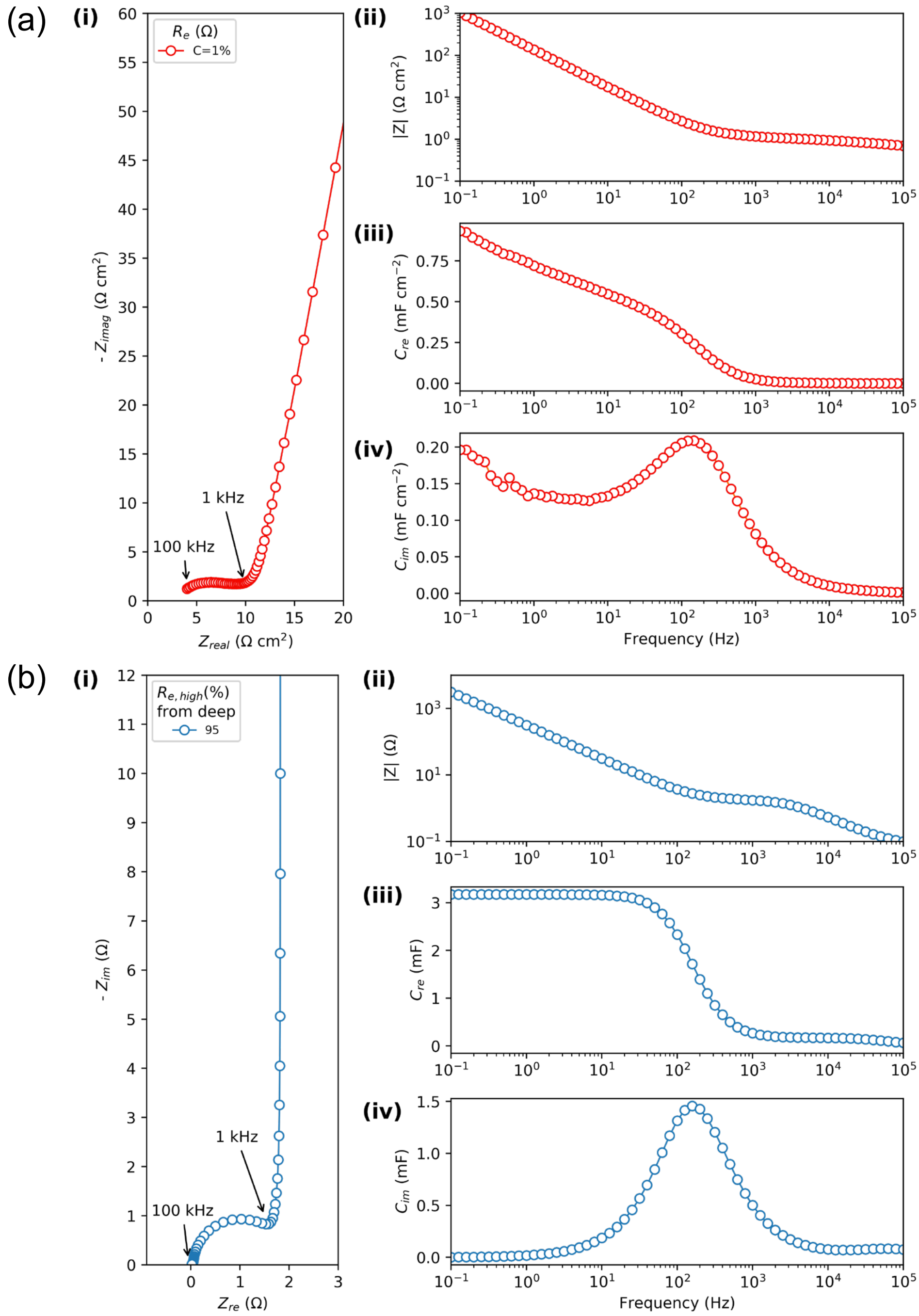

Fig. S13 (i) Nyquist plot, (ii) Absolute value of resistance (|Z|), (iii) Real part (C_{re}), and (iv) Imaginary part (C_{im}) of complex capacitance (a) from the actual experimental result of symmetric cells using positive electrode with low carbon of 1% in **Fig. S7**, and (b) from the calculated result using staircase modes obtained from the condition of non-uniform A at $R_{e,\,high}$ ratio from deep = 95% in **Fig. S11**. Both results show good agreement in the shape similarity in the Nyquist plot from 100 kHz–1 kHz and in the frequency response.

References

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5. J. H. Jang, S. Yoon, B. H. Ka, Y. H. Jung and S. M. Oh, *J. Electrochem. Soc.*, 2005, **152**, A1418-A1422.