Lithium-ion battery (LIB) as one of major power sources is widely used in electronic equipment on account of their high energy density, no memory effect, relatively good safety and cycling-life performance. The performance of LIB is affected mainly by the components weight ratio of cathode slurry among the other three variables particles dispersion, production processes and processing conditions. This results from that the components weight ratio of the cathode slurry plays a significant role in determining LIB slurry characterizations during LIB production process. In order to investigate LIB slurry characterizations, three methods which are microscopic morphology measurement, rheological rheometer measurement and electrochemical impedance spectroscopy (EIS) measurement are typically used as the effective methods. Cho K Y et al. points out the relation between the internal structure configuration which is referred to the network structure of active particles and the electrical pathways of the conductive additive and the physical properties which are thixotropic, storage modulus and loss modulus of LIB slurry by using the microscopic morphology and rheological rheometer measurements methods. Moreover, Kwon Y J et al. verified the rheological rheometer measurement results of LIB slurry by using the microscopic morphology measurement method. They concluded that the network of active material was broken-down with increasing of time and agitation. However, the morphology and rheometer measurement methods are not capable of acquiring the insight characterizations of LIB slurry. To compensate this deficiency, a non-invasive, continuous and on-line EIS approach is utilized due to its capability of measuring the electrochemical characterizations which are reactance, resistance and relaxation frequency of materials and their interfaces directly. The measurements are run over a wide range of frequencies, which allows frequency dependent responses to be properly characterized. In this regard, Bai S J et al. analyzed the electrochemical characterizations of LiCoO₂ slurry by fitting EIS Nyquist and Bode plots with an 8-parameter electrical equivalent circuit (EEC) which was constructed according to the internal structure of LIB slurry. They concluded that the resistances of LiCoO₂ particles, Carbon Black (CB) conductive additives and PVDF binders are increased with time elapse. Nevertheless, in terms of EIS measurement method, the 8-parameter EEC has an elaborate structure configuration with a combined LiCoO₂ particles and CB resistance parameter, resulting in the difficulty to distinguish the electrochemical characterizations of each component in LIB slurry. Therefore, the EEC with more parameters is essential to be constructed.

In this paper, firstly, in order to verify the accuracy of a newly proposed 10-parameter EEC, Nyquist and Bode plots fitted by the 10-parameter and 8-parameter EECs are compared with those obtained from the electrochemical responses of LIB slurry under different components weight ratio of three samples which are PVDF-NMP solution, CB absent slurry and CB present slurry. Lastly, relaxation frequencies of LiCoO₂-NMP interface dispersion, CB absent slurry and CB present slurry. Secondly, in order to understand the electrochemical responses mechanism of the electrical double layer (EDL) of LIB slurry, the resistance and reactance of EDL are analyzed by changing components weight ratio of LIB slurry. Thirdly, in order to clarify the relationship between the electrochemical responses of EIS Nyquist and Bode plots and the parameters of the 10-parameter EEC, the EIS Nyquist and Bode plots of three samples are fitted by the 10-parameter EEC. Lastly, in order to investigate the relaxation mechanism in LIB slurry, the relaxation frequencies calculated from the 10-parameter EEC are compared with those obtained from EIS experiment.
organic solvent. The averaged diameters of LiCoO₂ particles and CB were 10 μm and 50 nm. Table I shows the experimental conditions, which are “Case #1 to investigate PVDF weight ratio effect in PVDF-NMP solution”, “Case #2 to investigate LiCoO₂ weight ratio effect in CB absent slurry” and “Case #3 to investigate LiCoO₂ weight ratio effect in CB present slurry”. In Case #1, the weight ratio of PVDF \( w_{\text{PVDF}} \) was set to 0%, 5%, and 10%. As for Case #2, the slurry comprises of PVDF-NMP solution and LiCoO₂ particles. The weight ratio of LiCoO₂ \( w_{\text{LiCoO₂}} \) was defined as 44%, 61% and 71% under fixed \( w_{\text{PVDF}} = 10\% \). Case #3 comprises PVDF-NMP solution, LiCoO₂ particles and CB. Herein, \( w_{\text{LiCoO₂}} \) was set to 22%, 45% and 68%, \( w_{\text{PVDF}} = 10\% \) and the weight ratio of CB \( w_{\text{CB}} = 3\% \). For the preparation process of PVDF-NMP solution, PVDF with different weight ratios was added into NMP solvent to obtain PVDF-NMP solution. Moreover, the preparation processes of CB absent and present slurries were shown as follows: (1) PVDF and NMP solvent were blended into PVDF-NMP solution in advance. (2) LiCoO₂ particles (CB absent slurry) or CB and LiCoO₂ particles (CB present slurry) were mixed as solid ingredients. (3) The mixed solid ingredients were added into this PVDF-NMP solution to get LIB slurry by mixing for 30 minutes manually.

Impedance analyzer was used to measure the electrochemical responses of three samples under experimental conditions (Case #1, Case #2 and Case #3). The impedance analyzer was calibrated with open and short standards at 25 °C room temperature. An Alternating Current (AC) with an averaged excitation voltage \( V = 1 V \) and the frequency range from \( f = 4 \) Hz to 5 MHz were applied to these three samples. Meanwhile, the measurement was conducted three times with frequency points \( n = 201 \) at each time. The three-time averaged impedance spectra were utilized to reduce the measurement error. The impedance spectra of Case #1, Case #2 and Case #3 were shown by Nyquist plots which are reactance to resistance plots and Bode plots which are reactance to frequency plots.

### Experimental Results

**PVDF weight ratio effect in NMP solution.**—Fig. 2 and Fig. 3 show Electrochemical Impedance Spectroscopy (EIS) Nyquist and Bode plots of Case #1. In Fig. 2, it is clear that the Nyquist plots of each PVDF-NMP solution have only one semi-circle, and the diameter of each semi-circle is decreased as the weight ratio of PVDF \( w_{\text{PVDF}} \) is increased. Namely, the resistance and reactance of PVDF-NMP solution are gradually decreased as \( w_{\text{PVDF}} \) is increased. In Fig. 3, specifically, in Case #1-1: \( w_{\text{PVDF}} = 0\% \), the peak value of the reactance of PVDF-NMP solution \( Z'_{\text{relax}} = 1.61 \times 10^6 \Omega \) is at the frequency \( f_{\text{relax}} = 1.28 \times 10^4 \) Hz. Moreover, in Case #1-2: \( w_{\text{PVDF}} = 5\% \), \( Z'_{\text{relax}} = 8.436 \times 10^5 \Omega \) is at \( f_{\text{relax}} = 2.41 \times 10^4 \) Hz. Furthermore, in Case #1-3: \( w_{\text{PVDF}} = 10\% \), \( Z'_{\text{relax}} = 6.344 \times 10^5 \Omega \) is at \( f_{\text{relax}} = 2.77 \times 10^4 \) Hz. Therefore, \( Z'_{\text{relax}} \) is decreased and \( f_{\text{relax}} \) is slightly increased as \( w_{\text{PVDF}} \) is increased. The \( f_{\text{relax}} \) was referred to the frequency corresponding to the peak value of the reactance of PVDF-NMP solution. This variation trend is represented by the red arrow in Fig. 3.

### Table I. Experiment conditions.

<table>
<thead>
<tr>
<th>Components</th>
<th>Case #1-1</th>
<th>Case #1-2</th>
<th>Case #1-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>41.3 g</td>
<td>40.35 g</td>
<td>20.07 g</td>
</tr>
<tr>
<td>PVDF</td>
<td>2.29 g</td>
<td>2.2 g</td>
<td>2.23 g</td>
</tr>
<tr>
<td>( w_{\text{PVDF}} ) = ( m_{\text{PVDF}} / (m_{\text{PVDF}} + m_{\text{NMP}}) ) × 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case #2 LiCoO₂ weight ratio effect in CB absent slurry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMP+10%PVDF</td>
<td>26.03 g</td>
<td>15.85 g</td>
<td>12.85 g</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>20.45 g</td>
<td>24.79 g</td>
<td>31.47 g</td>
</tr>
<tr>
<td>( w_{\text{LiCoO₂}} ) = ( m_{\text{LiCoO₂}} / (m_{\text{LiCoO₂}} + m_{\text{PVDF-NMP}}) ) × 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case #3 LiCoO₂ weight ratio effect in CB present slurry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMP+10%PVDF</td>
<td>62.25 g</td>
<td>36.05 g</td>
<td>17.01 g</td>
</tr>
<tr>
<td>Carbon Black (CB)</td>
<td>2.49 g</td>
<td>3.31 g</td>
<td>1.76 g</td>
</tr>
<tr>
<td>( w_{\text{CB}} ) = ( m_{\text{CB}} / (m_{\text{LiCoO₂}} + m_{\text{PVDF-NMP}} + m_{\text{CB}}) ) × 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tilde{Z} ) = ( m_{\text{LiCoO₂}} / (m_{\text{LiCoO₂}} + m_{\text{PVDF-NMP}} + m_{\text{CB}}) ) × 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. The schematic diagram of EIS experiment.

Figure 2. Nyquist plots of PVDF-NMP solution.
LiCoO$_2$ weight ratio effect in CB absent slurry.—Fig. 4 and Fig. 5 show EIS Nyquist and Bode plots of Case #2. As a reference, PVDF-NMP solution with the weight ratio of PVDF $w_{PVDF} = 10\%$ in Case #1-3 is also shown in Fig. 4 and Fig. 5. In Fig. 4, the Nyquist plots of CB absent slurry are composed of two semi-circles, the left semi-circle in the high frequency range represents the LiCoO$_2$-NMP interface dispersion which is caused by the different permittivity and conductivity of the LiCoO$_2$ particle and the surrounding PVDF-NMP solution; while the right semi-circle in the low frequency range represents the PVDF-NMP solution dispersion which is caused by the polarization of the counterions in PVDF-NMP solution. The resistance and reactance of CB absent slurry in the high frequency range are slightly changed as $w_{LiCoO2}$ is increased. Furthermore, in Fig. 5, specifically, in the low frequency range, the peak value of the reactance of CB absent slurry is around $Z''_{relax} = 810 \, \Omega$. Meanwhile, the relaxation frequency of CB absent slurry keeps a constant value $f_{relax,low} = 65 \, Hz$ under these three cases. However, in the high frequency range, in Case #2-1: $w_{LiCoO2} = 44\%$, the peak value of reactance $Z''_{relax} = 948.27 \, \Omega$ corresponds to the high frequency $f_{relax,high} = 9.82 \times 10^4 \, Hz$. Moreover, in Case #2-2: $w_{LiCoO2} = 61\%$, $Z''_{relax} = 367.13 \, \Omega$ corresponds to the high frequency $f_{relax,high} = 1.60 \times 10^5 \, Hz$. Furthermore, in Case #2-3: $w_{LiCoO2} = 71\%$, $Z''_{relax} = 182.53 \, \Omega$ corresponds to the high frequency $f_{relax,high} = 2.12 \times 10^3 \, Hz$. Obviously, the resistance $Z''_{relax}$ and reactance $Z'$ of Case #2 are smaller than that of Case #1-3. In addition, the relaxation frequencies of Case #2-1 $f_{relax,low} = 65 \, Hz$ and $f_{relax,high} = 9.82 \times 10^4 \, Hz$ are considerably different from that of Case #1-3 $f_{relax,low} = 2.77 \times 10^3 \, Hz$. Therefore, LiCoO$_2$ particles have the ability to largely decrease $Z''_{relax}$ and $Z'$ and to change $f_{relax}$ of Case #1-3. In addition, the peak value of the reactance $Z''_{relax}$ in low frequency range keeps constant while the peak value of $Z''_{relax}$ in high frequency range is decreased as $w_{LiCoO2}$ is increased. The relaxation frequencies of PVDF-NMP solution dispersion $f_{relax,low}$ keeps constant while the relaxation frequency of LiCoO$_2$-NMP interface dispersion $f_{relax,high}$ is slightly increased as $w_{LiCoO2}$ is increased as shown by the red arrow.

LiCoO$_2$ weight ratio effect in CB present slurry.—Fig. 6 and Fig. 7 show EIS Nyquist and Bode plots of Case #3. As a reference, PVDF-NMP solution with the weight ratio of PVDF $w_{PVDF} = 10\%$ in Case #1-3 is also shown in Fig. 6 and Fig. 7. In Fig. 6, the Nyquist plots of CB present slurry are composed of two semi-circles with a straight line. The left semi-circle in high frequency range represents the LiCoO$_2$-NMP interface dispersion; while the right semi-circle in low frequency range denotes the PVDF-NMP solution dispersion. This dispersion mechanism is the same as Fig. 4. However, compared with Fig. 4, Fig. 5 also shows a straight line after these two semi-circles. Hence, it is the CB that causes the straight line in the
Nyquist plots of CB present slurry. This linear section at low frequency range results from the CB-electrode interface polarization in CB present slurry. In Fig. 7, specifically, in Case #3-1, the peak reactance of CB present slurry $Z_{\text{rel}}$ is at low frequency $f_{\text{rel}, \text{low}} = 1.02 \times 10^3$ Hz and $Z'_{\text{rel}}$ is at high frequency $f_{\text{rel}, \text{high}} = 2.14 \times 10^6$ Hz. Moreover, in Case #3-2, $Z_{\text{rel}}$ is at low frequency $f_{\text{rel}, \text{low}} = 6.31 \times 10^5$ Hz and $Z_{\text{rel}}$ is at high frequency $f_{\text{rel}, \text{high}} = 2.00 \times 10^7$ Hz. Furthermore, in Case #3-3, $Z_{\text{rel}}$ is at low frequency $f_{\text{rel}, \text{low}} = 3.55 \times 10^5$ Hz and $Z'_{\text{rel}}$ is at high frequency $f_{\text{rel}, \text{high}} = 1.74 \times 10^6$ Hz, respectively. Obviously, the resistance $Z_{\text{rel}}$ and reactance $Z'_{\text{rel}}$ of Case #3 are smaller than that of Case #1-3. Meanwhile, $f_{\text{rel}, \text{low}} = 1.02 \times 10^3$ Hz of Case 3-2 is smaller than that of Case #1-3 $f_{\text{rel}, \text{low}} = 2.77 \times 10^5$ Hz, $f_{\text{rel}, \text{high}} = 1.74 \times 10^6$ Hz of Case 3-3 is larger than that of Case #1-3 $f_{\text{rel}, \text{high}} = 2.77 \times 10^5$ Hz. As a result, the resistance $Z_{\text{rel}}$ and reactance $Z'_{\text{rel}}$ of PVDF-NMP solution dispersion are increased as $w_{\text{LiCoO}_2}$ is increased. In contrary, the resistance $Z_{\text{rel}}$ and reactance $Z'_{\text{rel}}$ of LiCoO$_2$-NMP interface dispersion are decreased as $w_{\text{LiCoO}_2}$ is increased. Furthermore, out from Fig. 7, it is clear that the relaxation frequencies of PVDF-NMP solution dispersion $f_{\text{rel}, \text{low}}$ and LiCoO$_2$-NMP interface dispersion $f_{\text{rel}, \text{high}}$ are slightly decreased as $w_{\text{LiCoO}_2}$ is increased. This variation trend is represented by the red arrow in Fig. 7. Therefore, LiCoO$_2$ particles and CB have the ability to largely decrease $Z_{\text{rel}}$ and $Z'_{\text{rel}}$ and to change $f_{\text{rel}}$ of Case #1-3.

10-Parameter Equivalent Circuit (EEC) Fitting Analysis

10-parameter EEC for three samples.---Fig. 8a and Fig. 8b show the Scanning Electron Microscope (SEM) images of Lithium-ion battery (LIB) slurry in Case #3-1 and Case #3-3, respectively. The amount difference of those LIB slurry is that the weight ratio of LiCoO$_2$ particle $w_{\text{LiCoO}_2}$ is 22% in Fig. 8a, while $w_{\text{LiCoO}_2}$ equals 68% in Fig. 8b. It is clear that the size of LiCoO$_2$ particles is in micro-scale, while the size of CB is in nano-scale. Moreover, the size of individual LiCoO$_2$ particles is much larger than that of the cluster of PVDF chains and CB particles, thus PVDF and CB tend to fill the open space among closely packed LiCoO$_2$ particles. Furthermore, PVDF and CB provide an electrical conductive paths to link LiCoO$_2$ particles together, which forms an interconnected coagulate network in LIB slurry. Specifically, out from Fig. 8a and Fig. 8b, it is shown that the concentration of LiCoO$_2$ particles is remarkably increased with increasing of $w_{\text{LiCoO}_2}$. In Fig. 8a, the mixture of PVDF and CB is sufficient to coat on each surface of LiCoO$_2$ particles. In this regard, a continuous network can be found in LIB slurry in the case of $w_{\text{LiCoO}_2} = 22\%$. Conversely, in Fig. 8b, the mixture of PVDF and CB is not enough to coat on each surface of LiCoO$_2$ particles. Thus, a discontinuous network is produced in LIB slurry in the case of $w_{\text{LiCoO}_2} = 68\%$.

By combining the internal structure of LIB slurry and the electrochemical responses of three samples which are PVDF-NMP solution, CB absent slurry and CB present slurry shown from Fig. 2 to Fig. 7, a 10-parameter EEC of LIB slurry is gradually constructed. Firstly, in Fig. 9a and Fig. 10a, the electrochemical characteristics of PVDF-NMP solution can be expressed as ohmic resistance $R_{\text{OHM}}$ and capacitance $C_{\text{SP}}$ on account of the charged ions in PVDF-NMP solvent.$^8$ Meanwhile, a resistor $R_{\text{RT}}$ is also taken into consideration because PVDF polymer chain has the electronically insulating property, which can be dissolved into the NMP solvent as loops and tails.$^{11}$ In this regard, the charge transfer resistance of PVDF-NMP solution is represented by $R_{\text{RT}}$. Therefore, the EEC of PVDF-NMP solution can be expressed as a resistor $R_{\text{RT}}$ connected in series with the parallel installed resistor $R_{\text{OHM}}$ and capacitor $C_{\text{SP}}$. Secondly, compared with Fig. 9a and Fig. 10a, Fig. 9b and Fig. 10b use a resistor $R_{\text{RT}}$ and a constant phase element (CPE$_p$) to describe the electrochemical characterizations of LiCoO$_2$ particles in CB absent slurry because a network is formed around LiCoO$_2$ particles by PVDF. Namely, the resistance of conductive path of LiCoO$_2$ particles network is described by a resistor $R_{\text{RT}}$, and the constant phase element (CPE$_p$) is used to attain a better fitting results to EIS Nyquist plots. Thirdly, as shown in Fig. 9c and Fig. 10c, all components of LIB slurry are taken into consideration. Fig. 9c illustrates the internal structure of LIB slurry. PVDF has a function of binding LiCoO$_2$ particles, which results in the establishment of the network among LiCoO$_2$ particles. Moreover, according to the fact that CB is not homogeneously distributed on the surface of LiCoO$_2$ particles, electrical double layer (EDL) is formed around the LiCoO$_2$ particles to provide an interconnecting conductive network by the PVDF and CB film.$^{11}$ Thus, EDL is able to be modeled by the combination of $R_{\text{RT}}$, C$_{\text{DL}}$[F] and constant phase element CPE$_p$,$^{12}$ in which $R_{\text{RT}}$ is the resistance of the EDL, C$_{\text{DL}}$[F] is the Warburg diffusion reactance of EDL, and the capacitance of EDL around particles is represented by $T_{\text{DL}}$[F] in CPE$_p$. Consequently, the

Figure 7. Bode plots of reactance of CB present slurry and PVDF-NMP solution with PVDF weight ratio $w_{\text{PVDF}} = 10\%$.

Figure 8. SEM images of LIB slurry in Case #3-1 (a) ($w_{\text{PVDF}} = 10\%$; $w_{\text{CB}} = 3\%$; $w_{\text{LiCoO}_2} = 22\%$) and Case #3-3 (b) ($w_{\text{PVDF}} = 10\%$; $w_{\text{CB}} = 3\%$; $w_{\text{LiCoO}_2} = 68\%$).
whole impedance of the 10-parameter EEC $Z_{10-p}$ for LIB slurry is expressed as follows:

$$Z_{10-p} = R_{CT} + \frac{R_{SO}}{1 + j\omega R_{SO} C_{SO}} + \frac{R_p}{1 + (j\omega)^2 R_p T_p} + \frac{R_{dl} C_{dl} (\omega - j\omega)^{\alpha}}{C_{dl} \omega + T_{dl} (R_{dl} C_{dl} \omega - j\omega)^{\alpha}}$$

where, $\omega = 2\pi f$ is the frequency of the applied alternating current (AC), the components $P_p$ and $P_d$ are in the range from 0 to 1, $T_p$ and $T_d$ are the constants of CPEp and CPEd. In addition, Fig. 11 shows a conventional 8-parameter EEC constructed by Bai et al.\(^4\) according to the internal structure of LIB slurry. In this 8-parameter EEC, $R_{CT}$ is charge transfer resistance; CPE$_{E}$ and CPE$_{B}$ denote Warburg impedance and capacitance of binder, respectively; $C_{dl}$ represents electrical double layer capacitance; $R_{SO}$ is the resistance of solvent and $R_{A&C}$ is the conductive additives and active materials. Obviously, the circuit elements number of the 10-parameter EEC is more than that of the 8-parameter EEC, therefore the 10-parameter EEC is capable providing a better insight into the electrochemical characterizations of LIB slurry. The whole impedance of the 8-parameter EEC $Z_{8-p}$ is shown as follows:

$$Z_{8-p} = R_{CT} + \frac{R_{SO}}{1 + j\omega R_{SO} C_{SO}} + \frac{1}{R_p C_{dl} \omega + T_{dl} (R_{dl} C_{dl} \omega - j\omega)^{\alpha}}$$

The iteration process of unknown parameters vector is expressed as:

$$x^{k+1} = x^k + \Delta x^k$$

where, $\Delta x^k \in C^m$ is the increment of unknown parameters vector. Moreover, the impedances $Z_{exp}(f)$ measured by EIS approach are represented as:

$$Z_{exp}(f) = \left[Z_{CT}(f), Z_{SO}(f), Z_{E}(f), Z_{dl}(f), Z_{A&C}(f), Z_{B}(f), Z_{RSO}(f), Z_{PB}(f)\right]$$

where, $Z_{CT}(f)$, $Z_{SO}(f)$, $Z_{E}(f)$, $Z_{dl}(f)$, $Z_{A&C}(f)$, $Z_{B}(f)$, $Z_{RSO}(f)$, $Z_{PB}(f)$ are the measured impedances at each applied frequency point. Furthermore, the impedances $Z^k(x^k, f)$ fitted by the 10-parameter and the 8-parameter EECs are shown as follows:

$$Z^k(x^k, f) = \left[Z^{CT}(x^k, f), Z^{SO}(x^k, f), Z^{E}(x^k, f), Z^{dl}(x^k, f), Z^{A&C}(x^k, f), Z^{B}(x^k, f), Z^{RSO}(x^k, f), Z^{PB}(x^k, f)\right]$$

where, $Z^{CT}(x^k, f)$, $Z^{SO}(x^k, f)$, $Z^{E}(x^k, f)$, $Z^{dl}(x^k, f)$, $Z^{A&C}(x^k, f)$, $Z^{B}(x^k, f)$, $Z^{RSO}(x^k, f)$, $Z^{PB}(x^k, f)$ are the fitted impedances at each frequency point $i$ under a specific $x^k$. As a result, the difference between the measured impedances and the fitted impedances is represented by an error vector $e(x^k, f) \in C^m$:

$$e(x^k, f) = e(x^k, f) + j e''(x^k, f)$$

where, $n$ denotes the number of EIS measurement points, $f \in R^m$ represents the applied frequency vector, $e(x^k, f) \in R^{8}$ and $e''(x^k, f) \in R^{8}$.
where, \( Z^{exp}(\mathbf{x}) \) and \( Z^{fit}(\mathbf{x}) \) denote the real and imaginary of impedances obtained from EIS experiment, while \( Z^{fit}(\mathbf{x}, \mathbf{f}) \) and \( Z^{fit}(\mathbf{x}^*, \mathbf{f}) \) are the real and imaginary of impedances fitted by the 10-parameter or 8-parameter EECs. At the present work, the Levenberg-Marquardt method is used to obtain \( \Delta \mathbf{x} \in \mathbb{C}^n \). The definition is shown as follows:

\[
\Delta \mathbf{x} = (J^T_{ex,f}(\mathbf{x}))^{-1}J^T_{ex,f}(\mathbf{x}) e(\mathbf{x}, \mathbf{f})
\]

where, \( \mathbf{f} \) is the iteration coefficient, \( J_{ex,f}(\mathbf{x}) \in \mathbb{C}^n \times m \) is Jacobian matrix, which is expressed as:

\[
J_{ex,f}(\mathbf{x}) = \begin{bmatrix}
\frac{\partial e'(\mathbf{x}, \mathbf{f})}{\partial x_1} & \cdots & \frac{\partial e'(\mathbf{x}, \mathbf{f})}{\partial x_n} \\
\vdots & \ddots & \vdots \\
\frac{\partial e''(\mathbf{x}, \mathbf{f})}{\partial x_1} & \cdots & \frac{\partial e''(\mathbf{x}, \mathbf{f})}{\partial x_n}
\end{bmatrix}
\]

Eventually, the averaged error \(|E(\mathbf{x}, \mathbf{f}))|\) is calculated by the following expression:

\[
|E(\mathbf{x}, \mathbf{f}))| = \frac{1}{n} \left( \frac{1}{n} \sum_{i=1}^{n} e'(\mathbf{x}, \mathbf{f})_i \right)^2 + \frac{1}{n} \left( \frac{1}{n} \sum_{i=1}^{n} e''(\mathbf{x}, \mathbf{f})_i \right)^2
\]

where, \( E'(\mathbf{x}, \mathbf{f}) \) and \( E''(\mathbf{x}, \mathbf{f}) \) are the real and imaginary of \( E(\mathbf{x}, \mathbf{f}) \).

The procedure of fitting EIS Nyquist and Bode plots by using the 10-parameter and 8-parameter EECs is summarized in Fig. 12. Firstly, the real and imaginary error vectors \( e'(\mathbf{x}, \mathbf{f}) \) and \( e''(\mathbf{x}, \mathbf{f}) \) are calculated by using the initialized \( \mathbf{x}^0 \) which is obtained from an empirical values. Secondly, the initial increments \( \Delta \mathbf{x} \) is solved by Eq. 11 with \( \lambda = 0.001 \). Afterwards, the differences between \( |E'(\mathbf{x}, \mathbf{f})| \) and \( |E'(\mathbf{x}, \mathbf{f})| \) and between \( |E''(\mathbf{x}, \mathbf{f})| \) and \( |E''(\mathbf{x}, \mathbf{f})| \) are compared to determine the step size of the iteration coefficient \( \lambda \). Finally, in the case that \( |E(\mathbf{x}, \mathbf{f}))| \) is less than 1.0 × 10^-3, the iteration is finished. By using the above-mentioned fitting procedure, \( \mathbf{x}^k \) can be estimated.

Discussion of Electrochemical Characterizations of LIB Slurry with 10-Parameter EEC

In order to have an insight of the electrochemical characterizations which are reactance, resistance and relaxation frequency in LIB slurry, EIS Nyquist and Bode plots of LIB slurry are fitted by the newly proposed 10-parameter EEC. The main discussion points are briefly shown in Fig. 13. Firstly, to verify the accuracy of the 10-parameter EEC, the standard deviation S of the 10-parameter EEC is compared with that of a conventional 8-parameter EEC. After fitting EIS Nyquist and Bode plots with the 10-parameter EEC, the detailed electrochemical characterizations which are resistance, reactance and relaxation frequency are individually analyzed with changing of components weight ratio in LIB slurry. Then, the reactance \( C_{dl} \) and resistance \( R_{dl} \) of electrical double layer (EDL) are investigated in CB present slurries, which is followed by clarifying resistances of charge transfer \( R_{CT} \), PVDF-NMP solution \( R_{SO} \) and conductive path \( R_p \) in three samples. Lastly, relaxation frequencies of LIB slurry obtained from EIS Nyquist and Bode plots are compared with those calculated from the 10-parameter EEC. The above-mentioned four aspects regarding to the present work are specifically discussed in the following subsections.

Accuracy analysis of the 10-parameter and the 8-parameter EECs.—Fig. 14 shows that the Nyquist plots fitted by the 10-parameter (Fig. 14a) and the 8-parameter (Fig. 14b) EECs are compared with these obtained from EIS experiment. In order to quantitatively evaluate the difference between the Nyquist and Bode plots fitted by the 10-parameter and the 8-parameter EECs and obtained from EIS experiment, a standard deviation S is utilized. In terms of Eq. 6 and Eq. 7, S is calculated by the following equation:

\[
S = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{|Z_{exp}(\mathbf{f}_i)| - |Z_{fit}(\mathbf{x}, \mathbf{f}_i)|}{|Z_{fit}(\mathbf{f}_i)|} \right)^2 \times 100\%
\]

where \( \mathbf{x} \) is the eventual unknown parameters vector.

Out from Fig. 15, it is obvious that \( S = 14.9\% \) in Case #3-1, 10.4\% in Case #3-2 and 17.7\% in Case #3-3 in the case of calculating the 10-parameter EEC, while \( S = 28.9\% \) in Case #3-1, 27.2\% in Case #3-2 and 17.7\% in Case #3-3.

Figure 12. The fitting procedure of the Nyquist plots of EIS experiment by using the 10-parameter and 8-parameter EECs.

Figure 13. Discussion points of the electrochemical characterizations of LIB slurry.
Discussion of reactance $C_{dl}$ and resistance $R_{dl}$ of electrical double layer (EDL) in CB present slurry.—Fig. 16 illustrates the variation of the reactance $C_{dl}$ and resistance $R_{dl}$ of Electrical Double Layer (EDL) around LiCoO$_2$ particles in CB present slurry. It is clear that $C_{dl}$ is decreased as the weight ratio of LiCoO$_2$ particles $w_{LiCoO2}$ is increased. This variation tendency is highly related to the components weight ratio of LIB slurry due to the ratio of PVDF binder to carbon additives significantly determines cathode conductivity. In terms of CB present slurry, the ratio of PVDF to CB is gradually decreased from 2.50 to 0.967 when $w_{LiCoO2}$ is increased from 22% to 68%. Thus, the conductivity of CB present slurry is increased, however, the thickness of EDL is decreased as $w_{LiCoO2}$ is increased, which result in the decrement of $C_{dl}$. Moreover, $R_{dl}$ is firstly increased and then decreased as $w_{LiCoO2}$ is increased. In order to explain this phenomenon, LiCoO$_2$-PVDF ratio effect is proposed, which is that in the case of the small ratio of LiCoO$_2$ to PVDF 18.26:6.23 where $w_{LiCoO2}$ varies from 22% to 45% with a fixed PVDF weight ratio $w_{PVDF} = 10$%, a coagulated network among LiCoO$_2$ particles is well formed by the connection of PVDF and CB. Thus, the increased network structure leads to the increment of $R_{dl}$. In the case of the large ratio of LiCoO$_2$ to PVDF 39.9:1.70 where $w_{LiCoO2}$ varies from 45% to 68% with a fixed $w_{PVDF} = 10$%, PVDF is insufficient to maintain EDL which is formed by PVDF and CB. This causes the destruction of the network structure, resulting in the decrement of $R_{dl}$.

Discussion of charge transfer resistance $R_{CT}$, PVDF-NMP solution resistance $R_{SO}$ and conductive path resistance $R_{p}$ in three samples.—The Nyquist and Bode plots of three samples obtained from EIS experiment have been shown from Fig. 4 to Fig. 7. To determine the relationship between the Nyquist and Bode plots obtained from EIS experiment and fitted by 10-parameter EEC, main parameters of three samples fitted by the 10-parameter EEC are analyzed. In Fig. 17, the charge transfer resistance $R_{CT}$ of Case #1 is increased as the weight ratio of PVDF $w_{PVDF}$ is increased since PVDF insulates the charge migration in NMP solvent. Thus, PVDF-NMP solution resistance $R_{SO}$ of Case #1 is decreased as $w_{PVDF}$ is increased. This is because higher content of PVDF enables PVDF chains to form more interconnection network. Moreover, as shown in Fig. 18, $R_{CT}$ and $R_{SO}$ of Case #2 and Case #3 are decreased as the weight ratio of LiCoO$_2$ particles $w_{LiCoO2}$ is increased. For Case #2, a network structure of LiCoO$_2$ particles is well formed by the interaction between PVDF and LiCoO$_2$ particles as $w_{LiCoO2}$ is increased. The network provides charge transfer pathways to break the ion-blocking properties of PVDF, which decreases $R_{CT}$ and $R_{SO}$ in Case #2 and Case #3. Meanwhile, $R_{CT}$ of Case #3 is much smaller than that of Case #2 due to the formation of electrical pathways among CB by PVDF. Furthermore,
the resistance of conductive path formed by LiCoO₂ particles $R_p$ is decreased in Case #2 and increased in Case #3 as wt$_{LiCoO₂}$ is increased. The decrement of $R_p$ in Case #2 results from the network structure of LiCoO₂ particles. However, in Case #3, on the one hand, most of alternating current (AC) easily flows through conductive agents CB as the impedance of CB is lower than that of LiCoO₂ particles; on the other hand, a coagulated network structure is established by EDL formed by PVDF and CB around LiCoO₂ particles, which differs from that of Case #2. As a result, $R_p$ of Case #3 is increased as wt$_{LiCoO₂}$ is increased. After corresponding $R_{SO}$ and $R_p$ to Nyquist and Bode plots of LIB absent slurry in Case #2 and CB present slurry in Case #3, it is clear that the variation tendencies of $R_{SO}$ and $R_p$ are the same as that of the dispersions of LiCoO₂-NMP interface and PVDF-NMP solution. This illustrates that $R_{SO}$ and $R_p$ fitted by the 10-parameter EEC are the resistances of the dispersions of LiCoO₂-NMP interface and PVDF-NMP solution obtained from EIS experiment.

**Discussion of the relaxation frequencies in CB absent and present slurries.** In order to clarify the relaxation mechanism of LIB slurry, relaxation frequencies of CB absent and present slurries calculated from the 10-parameter EEC are compared with that obtained from EIS experiment. As the relaxation frequencies of CB absent and present slurries obtained from EIS experiment are shown from Fig. 4 to Fig. 7, it is necessary to calculate the relaxation frequencies from 10-parameter EEC. Out from Eq. 1 and Eq. 2, three types of impedances ($Z_{10-p1}$, $Z_{10-p2}$ and $Z_{10-p3}$) are shown as follows:

$$Z_{10-p} = Z_{10-p1} + Z_{10-p2} + Z_{10-p3} \quad [15]$$

**Figure 18.** Variation of the resistance of charge transfer $R_{CT}$ and PVDF-NMP solution $R_{SO}$ with increasing of the weight ratio of LiCoO₂ particles wt$_{LiCoO₂}$ in Case #2 and Case #3.

After getting the 10 unknown parameters from the fitting procedure of the 10-parameter EEC, three types of relaxation frequencies can be calculated by solving the maximum imaginary of Eq. 16, Eq. 17 and Eq. 18. These three relaxation frequencies are shown as follows:

$$f_{relax1} = \frac{1}{2\pi R_{SO} C_{SO}} \quad [19]$$

$$f_{relax2} = \frac{1}{2\pi R_P T_P} \quad [20]$$

$$f_{relax3} = \frac{T_{dl}}{2\pi C_{dl}(T_{dl} R_{dl} + 1)} \quad [21]$$

where $f_{relax1}$, $f_{relax2}$ and $f_{relax3}$ are the relaxation frequencies calculated from $Z_{10-p1}$, $Z_{10-p2}$ and $Z_{10-p3}$.

Fig. 20 compares the relaxation frequencies obtained from EIS experiment and calculated from the 10-parameter EEC in CB absent (Case #2) and present (Case #3) slurries. In Case #2 of Fig. 20a, the paths for charge to reach an equilibrium state are increased as wt$_{LiCoO₂}$ is increased. This results in the well-constructed network among LiCoO₂ particles. Commonly, the relaxation frequency of LiCoO₂-NMP interface dispersion $f_{relax,high}$ is a measure of the time required for charges in electrolyte solution to recover their equilibrium distribution after ceasing an external perturbation. In this regard, the time required for charges to reach an equilibrium state is decreased. Thus, as the relaxation frequency of LiCoO₂-NMP interface dispersion $f_{relax,high}$ obtained from the EIS experiment in Case #2 and $f_{relax}$ calculated from the 10-parameter EEC are increased with increasing of wt$_{LiCoO₂}$. However, in Case #3 of Fig. 9a, an EDL is produced around LiCoO₂ particles. Actually, CB and PVDF form a film provided an interconnected conductive network to link LiCoO₂ particles together. The quantity of EDL is increased, but its thickness is decreased as wt$_{LiCoO₂}$ is increased. In this regard, the size of EDL that is coated onto LiCoO₂ particles decreases, while the time needed for relaxation frequencies is increased. Hence, as the relaxation frequency of LiCoO₂-NMP interface dispersion $f_{relax,high}$ obtained from EIS experiment in Case #3 and calculated from 10-parameter EEC $f_{relax}$ are decreased as wt$_{LiCoO₂}$ is increased.

In Case #2 of Fig. 20b, LiCoO₂ particles are added into PVDF-NMP solution, a poor binder/particle interfacial adhesion is produced around LiCoO₂ particles which is regarded as a weak network. LiCoO₂ particles are firstly surrounded by a part of PVDF, and then LiCoO₂ particles are connected by the rest of PVDF, which contributes to the network formation. As wt$_{LiCoO₂}$ is increased, the surface area of LiCoO₂ particles is definitely increased. Thus, the network is capable of promoting PVDF-NMP solution dispersion in CB absent slurry. Because the relaxation frequency of PVDF-NMP solution dispersion $f_{relax,low}$ is a function of particle size, the variation of wt$_{LiCoO₂}$ does not have a large influence on $f_{relax,low}$. Thus, as the relaxation frequency of PVDF-NMP solution dispersion $f_{relax,low}$ obtained from EIS in Case #2 and $f_{relax,low}$ calculated from the 10-parameter EEC keep a constant value regardless of the variation of wt$_{LiCoO₂}$. However, in Case #3 of Fig. 19b, according to DLVO theory, the total interaction energy between the repulsive electrostatic energy and the attractive van der Waals energy determines the agglomeration or dispersion status of CB present slurry. As the repulsive electrostatic energy is less than...
The resistance of electrical double layer (EDL) covered by CB particles increases as the weight ratio of LiCoO₂ particles is increased. This phenomenon can be explained by the LiCoO₂-PVDF ratio effect which is that a network is well formed by connecting PVDF and CB in the case of the small ratio of LiCoO₂ to PVDF 18.26:6.23; while PVDF is insufficient to maintain EDL in the case of the large ratio of LiCoO₂ to PVDF 39.9:1.70. In addition, the reactance \( C_{\text{dl}} \) of EDL is decreased as \( wt_{\text{LiCoO2}} \) is increased because of the reduction of the thickness of EDL.

The electrochemical characterizations of Lithium-ion battery (LIB) slurry are evaluated by using a 10-parameter Electric Equivalent Circuit (EEC) to fit Electrochemical Impedance Spectroscopy (EIS) Nyquist and Bode plots with Levenberg-Marquardt method. The 10-parameter EEC is constructed by combining the internal structure of LIB slurry and the electrochemical responses of three samples which are Polyvinylidenefluoride (PVDF)-NMP solution, Carbon Black (CB) absent slurry and CB present slurry. In addition, EIS Nyquist and Bode plots fitted by the 10-parameter EEC are compared with these fitted by a conventional 8-parameter EEC. The conclusions are shown as follows:

1. The standard deviation \( S \) of the 10-parameter EEC \( \left< S_{p,0} \right> \) is 14.3% lower than that of the 8-parameter EEC \( \left< S_{p,8} \right> \) as \( \Delta \text{S} = 16.3\% \). It illustrates that the newly proposed 10-parameter EEC is more accurate to evaluate LIB slurry than the 8-parameter EEC.

2. The resistance of electrical double layer (EDL) \( R_{\text{dl}} \) is initially increased and then decreased as the weight ratio of LiCoO₂ particles is increased. This phenomenon can be explained by the LiCoO₂-PVDF ratio effect which is that a network is well formed by connecting PVDF and CB in the case of the small ratio of LiCoO₂ to PVDF 18.26:6.23; while PVDF is insufficient to maintain EDL in the case of the large ratio of LiCoO₂ to PVDF 39.9:1.70. In addition, the reactance \( C_{\text{dl}} \) of EDL is decreased as \( wt_{\text{LiCoO2}} \) is increased because of the reduction of the thickness of EDL.

3. PVDF-NMP solution resistance \( R_{\text{SO}} \) of three samples are decreased with increasing of PVDF weight ratio \( wt_{\text{PVDF}} \) in PVDF-NMP solution and with increasing of LiCoO₂ particles weight.

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Figure 19. Variation of the resistance of conductive path \( R_p \) with increasing of the weight ratio of LiCoO₂ particles \( wt_{\text{LiCoO2}} \) in Case #2 and Case #3.

Figure 20. Relaxation frequencies of calculated from 10-parameter EEC and obtained from EIS experiment in Case #2 and Case #3 (a) in high frequency range, (b) in middle frequency range, (c) in low frequency range.
ratio $wt_{LiCoO_2}$ in CB absent and present slurries. Meanwhile, resistance of conductive path $R_p$ is decreased in CB absent slurry and increased in CB present slurry as $wt_{LiCoO_2}$ is increased. Those variation tendencies of $R_{SO}$ and $R_p$ are consistence with those of LiCoO$_2$-NMP interface dispersion and PVDF-NMP solution dispersion in EIS Nyquist and Bode plots. It is concluded that $R_{SO}$ and $R_p$ are the resistances of LiCoO$_2$-NMP interface dispersion and PVDF-NMP solution dispersion in LIB slurry.

4. Relaxation frequencies of LiCoO$_2$-NMP interface dispersion $f_{relax,high}$ and PVDF-NMP solution dispersion $f_{relax,low}$ obtained from EIS Nyquist and Bode plots can be represented by those of $f_{relax1}$ and $f_{relax2}$ calculated from the 10-parameter EEC based on the fact that $f_{relax,high}$ and $f_{relax,low}$ are decreased as $wt_{LiCoO_2}$ is increased in LIB slurry. Moreover, the relaxation frequency of CB-electrode interface dispersion $f_{relax3}$ uniquely calculated from the 10-parameter EEC is increased as $wt_{LiCoO_2}$ is increased in LIB slurry.

Eventually, our proposed 10-parameter EEC is capable of proving insight electrochemical characterizations for LIB slurry, which has a potential to realize an on-line measurement of LIB slurry with the aim of improving the performance of LIB.

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References