Impedance Analysis with Transmission Line Model for Reaction Distribution in a Pouch Type Lithium-Ion Battery by Using Micro Reference Electrode

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Electrochemical impedance spectroscopy (EIS) using an equivalent circuit is a powerful tool in the diagnosis of lithium-ion batteries (LIBs). However, LIBs have been increasingly used in applications requiring power higher than that used for conventional LIBs for portable electric devices. Considering this demand for LIBs, the impedance responses in the electrodes, which raise a reaction distribution under high-power operation, are important. This consequently means EIS analysis should include ionic resistances in the electrodes in equivalent circuits. Additionally, the impedance response of LIBs are too complicated to be analyzed in detail because the impedance response consists of overlapping elemental processes such as chemical reactions and ion migration. This paper therefore presents an analysis of impedance responses, which are independently obtained by a micro reference electrode, by using a transmission line model (TLM) that possesses the ability to count the ionic resistances in the electrodes. Similar to the conventional Randles equivalent circuit, the equivalent circuit with TLM could fit the impedance responses simulated by the equivalent circuit with measured responses. This paper discusses the potential of EIS using an equivalent circuit coupled with a TLM for diagnosis of LIBs in power applications.

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Since the launch of lithium-ion batteries (LIBs) into the market in 1991,1 LIBs have been widely used for portable electric devices because of their higher power and higher energy density compared with those of other batteries. Recently, the application of LIBs has been expanded to hybrid electric vehicles (HEVs) and battery electric vehicles (BEVs) to exploit their high-efficiency energy utilization.2 LIBs have been further proven useful in innovative technologies such as smart grids.3,4 Thus, LIBs are one of the most important devices for a sustainable society. Because rechargeable batteries such as LIBs store and deliver electricity through chemical reactions, the batteries deteriorate with charge–discharge cycles and storage time.5 Therefore, diagnostic technologies for LIBs are important not only for research and development, but also for applications in HEVs, BEVs, and smart grids.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for in situ measurement that does not require disassembly of the battery. It is also powerful in that it can separate a complicated reaction into elementary processes according to differences in time constants. The degraded part of the cell and degree of the degradation in a LIB can be interpreted on the basis of the elementary processes by means of an EIS. Therefore, EIS has been applied in the field of LIB analysis and diagnosis.6–10 However, since information acquired from both the cathode and anode is complex, accurate evaluation of LIBs by impedance analysis is still difficult. Recent developments of LIBs have reduced the impedance and have produced closer time constants, which has resulted in the overlap of impedance responses.20 Therefore, the cathode and anode should be analyzed separately before the impedance response of an entire LIB is to be assessed. Our group proposed two approaches to tackle this difficulty. Our first approach is to implement EIS under controlled temperatures, as low temperatures increase the impedances, thereby facilitating the analysis of LIBs.21 In addition, temperature-controlled EIS can be used to determine the activation energy of elemental processes from which the elemental processes can then be attributed. The second approach involves EIS using a separable cell. Since the separable cell enables us to change the electrodes readily, we could obtain the impedances of the full cell and of the cathode and anode symmetrical cells. Feedback from the results for the cathode and anode symmetrical cells enabled us to analyze LIBs accurately.22 A third approach that has been adopted by many researchers is the use of reference electrodes such as lithium foil for EIS.23,24 Reference electrodes can separate the cathode and anode impedance accurately and concurrently. The reference electrode theoretically must be placed between the cathode and anode to obtain the impedance accurately.19 However, the reference electrode often disturbs the current flow between the cathode and anode during operation. The nonuniform current flow leads to a reaction distribution and consequent abnormal degradation, which is undesirable for degradation testing of LIBs. To avoid this problem, a micro-reference electrode has been applied to LIB evaluation.25–27 Dees et al. demonstrated that a 25 μm diameter reference electrode wire placed between the cathode and anode does not significantly impact the accuracy of EIS; even a 25 μm thick, 1 mm wide reference electrode incurs ca. 10% error for EIS of LIBs.26 Hoshi et al. demonstrated the importance of the position and size of the reference electrode through a finite-element method.15 We also developed a micro-reference electrode made of LiAl, which is electrochemically lithiated.27 The potential of Li4Al is stable in the range of x values of 0.1 to 0.9.28 Although several materials showing stable potential such as Li4Ti5O12 or LiFePO429 and lithiated bismuth30 have been reported, the LiAl reference electrode has the advantage of being easily applied onto commercially available aluminum wire with 25 μm diameter immediately after electrochemical lithiation. In the present study, the cathode and anode impedances of the pouch-type LIB, which were obtained simultaneously with the LiAl micro-reference electrode, were analyzed with an equivalent circuit using a transmission line model (TLM). TLM can be used to analyze the ionic resistance in electrodes that affects the distribution of depth of discharge (DOD) in the depth direction during high current discharging, as illustrated in Figure 1. Because LIBs are used in high-power applications such as those in HEVs, BEVs, and smart grids, the ionic resistance in the electrodes must not be omitted. On the other hand, the conventional Randles-type equivalent circuit, which treats the electrode as a homogeneous system, does not count the ionic resistance in the electrode. If there is a degradation of the electrodes in LIBs, it is possible that it will change the ionic pass in the electrode layer due to the accumulation of decomposed products inside the electrode layer and due to the collapse of the active materials and the micro pores. TLM is effective at evaluating the reaction distribution in electrodes with three-dimensional structure, such as LIBs31–34 and fuel cells.35–38 Previously, we proposed...
an equivalent circuit where a particle size distribution of the cathode is counted to analyze the impedance spectra in the low frequency region (less than 1 Hz).\textsuperscript{16,39} And also, the low-frequency behavior is discussed by several researchers.\textsuperscript{40,41} The present paper discusses the high-middle frequency region to evaluate the possibility of EIS with TLM for LIB that is equipped with a micro reference electrode, comparing with Randles model. For the comparison of the impedance analysis by using Randles model and TLM, we adopted an impedance response, in which a slope of 45° is a typical feature of a reaction distribution in Nyquist plots is hard to be found. If a 45° slope is obvious in the Nyquist plots, then impedance analysis using the Randles model is not applicable.

Experimental

Cell information.— The pouch-type LIB was composed of a LiCoO\textsubscript{2} cathode, a graphite anode (Piotrek Co. Ltd.), and an Al wire reference electrode (ϕ 25 μm, 4 mm) inserted between the cathode and anode, separation of which was achieved with a commercially available polyethylene separator. The mass loading of the cathode material (LiCoO\textsubscript{2} + conductive carbon: polyvinylidene fluoride (PVdF) = more than 90 : less than 10) was 11.3 mg/cm\textsuperscript{2}, and the areal capacity of the cathode sheet was 1.6 mAh/cm\textsuperscript{2}. The thickness of the cathode and anode was 60 μm. The dimensions of the cathode and anode were 70 mm × 70 mm and 72 mm × 72 mm, respectively. The electrolyte was 1 M LiPF\textsubscript{6}/ethylene carbonate–diethyl carbonate solution (50:50 vol.%). The LIB was assembled in a dry room with a dew point of less than −50°C. The LIB was pretreated with two charge–discharge cycles with a current of 7.0 mA (ca. 0.1 C against design capacity) and a cutoff voltage of 4.2 and 3.0 V using a charge–discharge system (HJ-1010SM8, Hokuto Denko). The reference electrode was activated and a cutoff voltage of 4.2 and 3.0 V using a charge–discharge system (Solartron) and a frequency response analyzer (1455, Solartron) system. The charge–discharge test for degradation was carried out at a current of 35.0 mA (ca. 0.5 C against design capacity) and at cutoff voltages of 4.2 V and 3.0 V by using the charge–discharge system.

Design of the equivalent circuit using TLM.— An equivalent circuit was designed by considering the following conditions reported in previous papers:\textsuperscript{32–34,42} conductive materials related to wiring and instruments (Z\textsubscript{i}), ionic resistance of the electrolyte (R\textsubscript{i}), charge transfer resistance of the active material (R\textsubscript{ct}), capacity corresponding to the charge transfer resistance (C\textsubscript{dl}), ionic resistance in the electrode (R\textsubscript{dl}), ionic or electric resistance of the interface between the electrolyte and electrode layer or between the current collector and electrode layer (R\textsubscript{high}, capacity corresponding to R\textsubscript{high} (C\textsubscript{high}), and the constant phase element for diffusion (CPE\textsubscript{diff}). In this paper, C\textsubscript{high} and C\textsubscript{dl} are expressed as CPE\textsubscript{high} and CPE\textsubscript{dl}, respectively.\textsuperscript{43} CPE is composed of two parameters, CPE-T and CPE-P, which are independent of frequency. When p = 1 and p ≠ 1, CPE-T has units of F and s\textsuperscript{-1}Ω, respectively. The equivalent circuit based on these parameters is shown in Figures 2a and 2b. For comparison, a conventional Randles-type equivalent circuit (Fig. 2c) was used. The equivalent circuit for the TLM for the porous electrodes was designed by assuming the porous structure in the electrode a cylindrical structure.\textsuperscript{44} In the calculations for fitting, the cylinder radius (r) and electrode thickness (l) are included in the formula as a variable parameter that is related to R\textsubscript{ct}, R\textsubscript{dl}, and CPE\textsubscript{dl}. R\textsubscript{ct} is derived from the resistivity of the ionic path in the electrode pore (ρ) and the sectional area of the cylinder: R\textsubscript{ct} = ρ/lπr\textsuperscript{2}. ρ was fixed at 100 Ω cm, which is the typical resistivity of organic-solvent electrolytes. Formulas for fitting using TLM (Eqs. 1, 2, 4, and 5) and Randles-type model (Eqs. 1, 2, 3, and 5) are as follows:

\[
Z_{\text{total}} = R_s + Z_L + Z_{\text{high}} + Z_{\text{ct}} + Z_{\text{diff}} \quad [1]
\]

\[
Z_{\text{high}} = \frac{R_{\text{high}}}{1 + (j\omega)^p T_{\text{high}} R_{\text{high}}} \quad [2]
\]

\[
Z_{\text{ct}} = \frac{R_{\text{ct}}}{1 + (j\omega)^p T_{\text{dl}} R_{\text{ct}}} \quad [3]
\]

Electrochemical measurements.— The DOD of the LIB was controlled by discharging to a DOD following a fully charged state at 4.2 V (0% DOD). The DODs were defined as the voltages that were obtained from the discharge curve at the second cycle for pretreatment. EIS was carried out in the frequency range of 100 kHz - 1 mHz and an alternating current (AC) amplitude of 10 mV\textsubscript{AC}, while applying the defined voltages via a multi-channel potentiostat (1470E, Solartron) and a frequency response analyzer (1455, Solartron) system. The charge–discharge test for degradation was carried out at a current of 35.0 mA (ca. 0.5 C against design capacity) and at cutoff voltages of 4.2 V and 3.0 V by using the charge–discharge system.

Figure 1. Schema for a cathode used for demonstrating depth-of-discharge distribution during high current discharging.

Figure 2. (a) Equivalent circuit with the transmission line model (TLM), (b) equivalent circuit of the TLM used for determining the reaction distribution, and (c) a conventional Randles-type equivalent circuit.
Figure 3. Discharge curve of the pouch-type LIB with the LiAl micro-reference electrode at 4.2 to 3.0 V at a C-rate of 0.5 C.

Figure 4. Voltage and potential profiles of the pouch-type LIB with the LiAl micro-reference electrode during the EIS sequence. Solid lines and dashed lines indicate the profiles during discharging and EIS, respectively.

EIS data were fitted with Microsoft Excel Solver to reach the minimum sum of χ² values between the acquired experimental complex impedance data and the impedances calculated with the equivalent circuit using the parameters obtained by fitting for each frequency. In our model, the fitting error is usually <1% (the residual error of |Z|).

Results and Discussion

Figure 3 shows the discharge curve of the pouch-type LIB with the LiAl micro-reference electrode at a C-rate of 0.5 C. The LIB was found to have a discharge capacity of ca. 61 mAh at a C-rate of 0.5 C. The discharge curve shows a typical plateau that may be attributed to the LiCoO₂ cathode. DODs from the discharge curve were translated into voltage values. DODs and voltages are summarized in Table I. In this paper, the defined DODs are used.

The voltages and potential profiles of the pouch-type LIB during the EIS sequence are shown in Figure 4. Consequently, the potential profiles against the LiAl micro reference electrode of both the cathode and anode confirmed that the two were obtained separately. As the voltage of the pouch-type LIB decreased, the potential of the cathode decreased while that of the anode increased. A question that may arise is why the discharge capacity in Figure 4 is higher than that in Figure 3. This difference may be attributed to the capacity during EIS measurement, in which a constant voltage bias was applied to the LIB. Although the DOD shifts during EIS appear to be large, shifts at frequencies of 100 kHz to 100 mHz are within 0.56–3.7%. Figure 5 shows AC impedance spectra for the full cell, cathode, and anode obtained from the pouch-type LIB with various DODs. Impedance spectra of the full cell are composed of overlapping semicircles in the high- and middle-frequency regions and loci related to diffusion at low frequency. At first glance, only two semicircles observable at ca. 10 kHz and ca. 3 Hz can be found in the impedance spectra of the cathode (Figs. 5b and 5c) and anode (Figs. 5d and 5e) separated by the reference electrode are clearly composed of overlapping semicircles in the high- and middle-frequency regions. The separated impedance spectra of the cathode and anode reveal two semicircles observable at ca. 15 kHz and ca. 4 Hz in the impedance spectra of the cathode in Figure 5b. Two semicircles observable at ca. 1.2 kHz and ca. 3 Hz can be found in the impedance spectra of the anode (Fig. 5d). In the literature, the two semicircles for the anode confirmed at several kHz and several Hz are attributed to lithium migration in the solid electrolyte interphase (SEI) and to charge transfer, respectively. The two semicircles for the cathode confirmed at several kHz and several Hz are attributed to lithium migration in the surface film and to charge transfer, respectively. It is noteworthy that a 45 degree slope with respect to the real axis in the limit of a semi-infinitely deep pore was clearly observed in the Nyquist plots enlarged at the region between the high and middle frequency for the cathode (Fig. 6e); whereas, a corresponding slope could not be observed for the anode (Fig. 6f). Thus, we could confirm the impedance separation in the pouch-type LIB using the LiAl micro-reference electrode.

Table I. The values of the LIB voltage defined for the DODs and the LIB voltage, and the cathode and anode potentials at EIS, and DOD range used for the fitting analysis (100 kHz – 100 mHz).

| Depth of discharge/% | 0    | 20   | 40   | 60   | 80   |
|----------------------|------|------|------|------|------|
| Voltage defined for DOD/ V | 4.20 | 3.99 | 3.87 | 3.79 | 3.71 |
| Voltage at EIS/ V    | 4.21 | 4.00 | 3.85 | 3.79 | 3.72 |
| Cathode potential at EIS/ V vs. LiAl | 3.93 | 3.74 | 3.64 | 3.57 | 3.52 |
| Anode potential at EIS/ V vs. LiAl | −0.28 | −0.22 | −0.21 | −0.22 | −0.20 |
| DOD range used for the analysis (100 kHz – 100 mHz) / % | 0.0–0.56 | 12.7–15.7 | 29.8–33.3 | 48.2–51.1 | 65.7–69.4 |
Figure 5. (a) Nyquist plots of the full cell impedance of the LIB with various DODs (×) and the sum of the cathode and anode impedances (♦) obtained by using the LiAl micro-reference electrode in the frequency range of 100 kHz – 1 mHz. Insets indicate the frequencies at the top of two semicircles. (b) and (c) Nyquist plots of the cathode impedance (×) and the spectra fitted by using the equivalent circuit of the TLM and Randles model, respectively, in Fig. 2 (×). (d) and (e) Nyquist plots of the anode impedance (×) and the spectra fitted by using the equivalent circuit with TLM and Randles model in Fig. 2 (×). Cathode and anode impedances, which were obtained by using the LiAl micro-reference electrode, were fitted in the frequency range of 100 kHz – 100 mHz. Insets in (b)–(e) indicate the frequencies calculated from the fitting results related to the two semicircles.

In the present study, we adopted the impedance responses, which may be analyzed by using the Randles model. Hence, differences between the fittings by using the Randles model and the TLM are difficult to see in the Nyquist plots. In order to determine the agreement between the measured data and the fitted data by using the equivalent circuit with TLM and the Randles model, the distance between the plots measured and fitted with Nyquist plot (d), as well as the difference in phase angles between the measured and fitted data (Δθ) were evaluated (Figs. 6a and 6c for the cathode and Figs. 6b and 6d for the anode). The fitted...
data are in good agreement with the measured data, being within the $d$ values for the cathode ($5 \, \text{m}\Omega$) and for the anode ($2 \, \text{m}\Omega$). The $d$ values are almost one order of magnitude lower than the radii of the semicircles in the regions between 10 kHz and 1 Hz, where most elemental processes occur. In addition, the $d$ value from using the equivalent circuit with the TLM was compared with those from the conventional Randles-type equivalent circuit. For the cathode, the $d$ value from using the equivalent circuit with the TLM is less than that from using the conventional Randles-type equivalent circuit. For the anode, the $d$ value from using the equivalent circuit with the TLM is less than or equal to that from using the conventional equivalent circuit. Thanks to the application of the TLM, the $d$ value for the cathode decreased not only in the frequency region characterized by ionic resistance in the electrodes (ca. 100 Hz) but also in the higher frequency region. On the other, the $d$ value for the anode in the same region decreased slightly because a 45° slope with respect to the real axis was not obviously observed or probably because the anode impedance had an inductive response in the high-frequency region. The $d$ value from using the equivalent circuit with the TLM was compared with those from using the conventional Randles-type equivalent circuit. For the anode, the $d$ value from using the equivalent circuit with the TLM is less than or equal to that obtained by using the conventional equivalent circuit. Thus, we demonstrated the applicability of the TLM, especially to the cathode in this LIB. The results are confirmed by the Nyquist plots in Figures 6c and 6d. Similar to the $d$ values, $\Delta \theta$ values from using the equivalent circuit with the TLM were compared with those from using the conventional Randles-type equivalent circuit. For the cathode, $\Delta \theta$ from using the equivalent circuit with the TLM is much smaller than that obtained by using the conventional Randles-type equivalent circuit. For the anode, $\Delta \theta$ from using the equivalent circuit with the TLM is less than or equal to that obtained by using the conventional equivalent circuit. Thus, we demonstrated the applicability of the TLM, especially to the cathode in this LIB. The results are confirmed by the Nyquist plots in Figures 6c and 6d. The fitting error for the Nyquist plots for the cathode, which show a clear 45° slope with respect to the real axis, decreased upon application of TLM. In contrast, that for the Nyquist plots of the anode, which do not have an apparent 45° slope with respect to the real axis, did not improve. Parameters obtained from the fitting using the conventional Randles-type equivalent circuit are summarized in Figure 7. $R_s$ values of the cathode and anode are almost constant. This finding is reasonable because the electrolyte resistance does not depend on the DODs. The $R_{\text{high}}$ value of the anode, which is the resistance of the SEI, seems unchanged by the variations in DODs. Markovsky et al. investigated in detail the impedances of graphite-based anodes. They separated the impedance response into resistance of lithium migration through the film on the electrode, charge-transfer resistance, solid-state diffusion resistance, and lithium accumulation in the bulk of graphites. One may seem that the $R_{\text{high}}$ of the anode has slight tendency to increase during discharging. This increase may be attributed to in-plane shrinkage of SEI accompanied by the shrinkage of the graphite anode due to delithiation. In-plane shrinkage of the SEI thickens the SEI itself, resulting in an increase in the $R_{\text{high}}$ of the anode. Although the $R_{\text{high}}$ of the cathode is considered the resistance of decomposition products on the cathode or the resistance due to electrode structures, it is not clearly understood in this case. The $R_{\text{high}}$ value of the cathode tends
Figure 7. Parameter variation with DODs of $R_s$, $R_{\text{high}}$, $R_{\text{ct}}$, $\text{CPE}_{\text{high}-\text{T}}$, and $\text{CPE}_{\text{ct}-\text{T}}$ values derived by using the conventional Randles-type equivalent circuit.

to increase during discharge; this tendency is also not understood and remains a question to be solved in future. $\text{CPE}_{\text{high}-\text{T}}$ values of the cathode and anode decreased upon discharge (CPEhigh-p values of the cathode and anode are ca. 0.85 and ca. 0.64, respectively). The explanation for the decrease in $\text{CPE}_{\text{high}-\text{T}}$ value of the anode may be similar to that for the $R_{\text{high}}$ of the anode: In-plane SEI shrinkage accompanied with shrinkage of the graphite anode due to delithiation could increase the thickness of the SEI. As the film thickens, the capacity ($C$) decreases, as expressed by the formula $C = \varepsilon S d/w$, where $\varepsilon$ is the dielectric constant, $S$ is the area of the film, and $d$ is the distance related to the film thickness. The decrease in $\text{CPE}_{\text{high}-\text{T}}$ value of the cathode, along with the $R_{\text{high}}$ value of the cathode, is also a question to be solved in the future. $R_{\text{ct}}$ value for the cathode and anode was found to increase during discharging of both. The increase in $R_{\text{ct}}$ value of the cathode is in accordance with results from previous studies.45,49,50 This increase is partly due to the variation of electronic conductivity in the active material, $\text{LiCoO}_2$.45,51,52 The increase in $R_{\text{ct}}$ value of the anode is also in accordance with results in the literature.40,53 It was also explained by Markovsky et al.8 The $\text{CPE}_{\text{ct}-\text{T}}$ value of the cathode was essentially invariant, implying that the surface area of the cathode did not vary during discharge significantly (CPEct-p value of the anode is ca. 0.96). On the other hand, the $\text{CPE}_{\text{ct}-\text{T}}$ value of the anode increased in the deep DOD region (because CPEct-p of the anode is unity, CPE is equal to $C_{\text{ct}}$). This increase may be due to the shrinkage of the anode material. The shrinkage enabled an electric double layer overlapping due to the close proximity of the anode materials to appear, therefore increasing the area of the electric double layer.

Parameters obtained from the fitting using the equivalent circuit with TLM are summarized in Figure 8. Compared with the parameters obtained by fitting using the conventional Randles-type equivalent circuit, all parameters obtained from the former varied during discharge in the same manner. $R_s$ values of the cathode and anode are slightly different from those obtained from the fitting using the conventional Randles-type equivalent circuit. This difference is due to the complicated inductive responses, which cause fitting errors especially in the high-frequency region (over 10 kHz). In fact, the residual errors shown in Figure 6 are scattered in this region. $R_{\text{high}}$ and $\text{CPE}_{\text{high}-\text{T}}$ values of the cathode and anode are in good accordance with the values obtained by using the conventional Randles-type equivalent circuit (CPEhigh-p values of the cathode and anode were ca. 0.95 and ca. 0.64, respectively) because the TLM expresses the response in the charge-transfer region and not in the $R_{\text{high}}$ region. $R_{\text{ct}}$ and $\text{CPE}_{\text{ct}-\text{T}}$ values of the cathode and anode are also highly comparable to the values obtained by using the conventional Randles-type equivalent circuit. Because CPEct-p values of the cathode and anode are unity, the CPE of the cathode and anode represents capacitance. CPEhigh-p and CPEct-p values of the cathode are close to unity because the TLM represents the distortion between the semicircles at high and middle frequencies. $R_s$ values for the cathode and the anode respectively tended to increase and decrease during discharging. This tendency
may be explained by the volume change of the active materials. The active material of the cathode and the anode expand and shrink with discharging, leading to shrinkage and expansion, respectively, of the space for lithium-ion migration in the electrode. Therefore, changes in $r$ value result in changes in $R_i$ as DOD varies. Consequently, the equivalent circuit with the TLM can be used in sensitive evaluation of structural changes in LIBs, specifically, changes in pore volume and tortuosity of the ionic path in the electrodes. In the case of LIB degradation, the space is limited because of SEI formation in the active materials and electron-conducting carbons. Note that the CPEdiff value, which was used just for fitting in the low-frequency region, is not discussed in this paper. This is because the main aim of the present study was to implement a TLM to determine the ionic conductivity in the electrodes, which does not appear in the low-frequency region.

Conclusions

To establish a diagnosis of LIBs for power applications using EIS, we applied TLM onto an equivalent circuit to determine the ionic resistance in the electrodes for the analysis of EIS responses of LIBs, which is an important factor for power applications. The impedance response of LIBs is too complicated to analyze in detail; the impedance response was composed of overlapping elemental processes such as charge transfer for chemical reactions and ion migration. To separate the complicated impedance response, the LiAl micro-reference electrode was thus applied to the pouch-type LIB. We demonstrated the separation of the LIB impedance response into cathode and anode impedance responses using the LiAl micro-reference electrode in various DODs. The separated impedance responses were analyzed by using the equivalent circuit with the TLM to determine the ionic resistance in the electrodes. Results for the analysis using the Randles-type equivalent circuit were compared against those for the equivalent circuit with the TLM, which includes the important parameter $R_i$. The results show that LIB impedances are in close accordance with the values that are derived by using the Randles model, even though the characteristic responses of the reaction distribution are difficult to find in the Nyquist plots. Variation of the parameters with DODs agrees well with previous reports. They are also explained by such reports. In particular, the variation of $R_i$ values for the cathode and anode suggests that the ionic resistance in the electrode depends on the DOD, which is affected by the pore volume and tortuosity of the ionic path in the electrodes. Thus, the present study showed the potential of using EIS, TLM, and a micro-reference electrode to evaluate LIBs for power applications. Detailed diagnosis of LIBs with cycle degradation will be reported in the near future.

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New Energy and Industrial Technology Development Organization of Japan.

List of Symbols

| Symbol | Units | Description |
|--------|-------|-------------|
| Z_L   | Ω     | Inductive impedance related to wire and instruments |
| R_Ω   | Ω     | Ionic resistance of the electrolyte |
| R_high| Ω     | Resistance at high frequency |
| C_high| F     | Capacity corresponding to R_high |
| T_high| s/Ω   | CPE parameter T related to decomposition products (when p_high = 1, CPE-T = C_high) |
| p_high|       | CPE parameter p related to decomposition products |
| R_cl  | Ω     | Charge-transfer resistance |
| C_cl  | F     | Capacity corresponding to R_cl |
| T_cl  | s/Ω   | CPE parameter T related to double-layer capacitance (when p_cl = 1, CPE-T = C_cl) |
| p_cl  |       | CPE parameter p related to double-layer capacitance |
| R_p   | Ω/cm  | Ionic resistance in the pores |
| Z_p   | Ω/cm²| Charge-transfer resistance in the pores |
| r     | cm    | Estimated radius of the pore |
| l     | cm    | Thickness of the electrode |
| CPE_packages | Ω | CPE for diffusion |
| d     | Ω     | Distance between the plots measured and the fitted Nyquist plot |

Greek

| Symbol | Units | Description |
|--------|-------|-------------|
| ρ     | (Ω cm) | Resistivity in the pore |
| Δθ    | (degree) | Difference in phase angles between the measured and fitted data |

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