Special Feature: Design of High-power Lithium-ion Batteries with Long Operational Life

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**ABSTRACT** The dependence of the internal resistance of porous electrodes with high loading weight on the electrode thickness was systematically investigated to determine the relationship between the specific energy and power of lithium (Li)-ion batteries. The ionic resistance of pores ($R_{\text{ion}}$) and charge-transfer resistance for Li intercalation ($R_{\text{ct}}$) normalized according to the unit electrode geometric area were examined using a combination of electrochemical impedance spectroscopy with symmetric cells and the transmission line model theory. The changes in $R_{\text{ion}}$ and $R_{\text{ct}}$ and their magnitudes show opposite trends with respect to electrode thickness. For thin electrodes where $R_{\text{ion}}$ is lower than $R_{\text{ct}}$, the total internal resistance is predominantly affected by the charge-transfer resistance, and there is no delay of the response in the depth direction; therefore, the decrease in specific power is slight as the electrode become thicker. In contrast, for thick electrodes where $R_{\text{ion}}$ is higher than or approximately equal to $R_{\text{ct}}$, there is a delay of the reaction in the depth direction. As a result, the power of the battery is dramatically reduced because the total internal resistance is strongly influenced by both $R_{\text{ion}}$ and $R_{\text{ct}}$.

**KEYWORDS** Lithium-ion Battery, Porous Electrode, Electrochemical Impedance Spectroscopy, Transmission Line Model, Thickness, Resistance

1. Introduction

High power and energy density batteries with excellent performance are required for automobile applications, such as hybrid electric, plug-in hybrid, and electric vehicles. To realize such batteries, it is necessary to comprehend the internal resistance of the battery. In this study, a novel electrochemical analysis method is applied to the practical porous electrode of a lithium-ion battery using the transmission line model (TLM). The real electrode of lithium-ion batteries is composed of an insertion material, conductive carbon, binder and pores filled with the electrolyte. Electrochemical impedance spectroscopy (EIS) is a useful technique for analysis of the internal resistance. As a preliminary step, a suitable EIS method is developed to examine the true electrode/electrolyte interface. The internal resistance at a porous electrode can be expressed by four parameters: electrical resistance ($R_e$), electrolyte bulk resistance ($R_{\text{sol}}$), ionic resistance in pores ($R_{\text{ion}}$), and charge-transfer resistance for lithium intercalation ($R_{\text{ct}}$). In a previous study, we examined how to separate resistance components in a porous electrode, such as the electrical resistance, ionic resistance inside pores, and charge-transfer resistance, using a symmetric cell (SC) technique. When the thickness of the electrode is increased, the energy density improves; however, details of the resistance components that influence power density have not yet been sufficiently clarified. Therefore, it is necessary to clarify the relation between electrode thickness and each resistance component with an aim to achieve a high power and energy density battery with excellent performance practically.

In this study, the dependence of the internal resistance on the thickness of intercalated LiNiO$_2$-based electrodes, which are conventionally used in Li-ion batteries, was systematically investigated using EIS-SC and TLM (described in the previous paper in this special feature) to understand the relationship between specific energy and power. In a porous electrode, a change in electrode thickness corresponds to a variation in pore length ($L$) and the reaction surface area ($2\pi rL$), assuming the voids of the electrodes as cylindrical pores. $R_{\text{ion}}$ and $R_{\text{ct}}$ normalized according
to the unit electrode geometric area show different trends as the electrode thickness is increased, i.e., the relative effect of $R_{\text{ion}}$ and $R_{\text{ct}}$ on the total internal resistance changes. We also examine the relationships between the individual internal resistances and power capability of actual Li ion cells as the pore structure parameters change.

2. Dependence of Individual Internal Resistances on Porous Electrode Thickness

2.1 Performance of Cylindrical-type Cells

First, we fabricated cylindrical-type cells (Fig. 1) wound with electrodes of different thickness, as shown in Fig. 2, to investigate the dependence of specific power and energy on thickness. The positive electrode was composed of LiNi$_{0.75}$Co$_{0.15}$Al$_{0.05}$Mg$_{0.05}$O$_2$, a carbon black conductive agent, and polyvinylidene fluoride (PVDF) binder (85:10:5 weight ratio), while the negative electrode was composed of graphite and PVDF (90:10 weight ratio). The cylindrical-type cells were first cycled between 4.1 and 3.0 V at a low current density of 0.05 mA cm$^{-2}$ to determine the energy density. Figure 3 shows the initial charge-discharge curves of cylindrical-type cells with electrodes of different thickness, where the capacity per amount of active material was almost equal.

Figure 4(a) shows the relationship between the specific power and energy of cylindrical-type cells consisting of LiNiO$_2$-based positive and graphite carbon negative electrodes for various electrode thicknesses. The specific energy increases while the specific power decreases with increasing electrode thickness. The increase of specific energy with electrode thickness means that the proportion of active materials in the total volume, including the current collector for both positive and negative electrodes, increases. In contrast, the power decay with increasing electrode thickness occurred differently in two thickness regions, i.e., a slight decline in the thin-electrode region (region I) and a large decline in the thick-electrode region (region II). This means that different factors in terms of internal resistance can affect the power decay. The $I$-$V$ resistance, which was calculated from the polarization obtained from charge and discharge curves and the measured current of the same cylindrical-type cell, decreased dramatically.

Fig. 1 Schematic illustration of cylindrical-type cell.

Fig. 2 Cross-sectional SEM images of LiNiO$_2$-based positive electrodes with various thickness.
in region I and slightly in region II with increasing electrode thickness, as shown in Fig. 4(b). An inverse plot of the $I$-$V$ resistance also shows a non-linear profile as a function of electrode thickness.

AC impedance measurements of the same cylindrical-type cells were conducted to confirm the rate capability and $I$-$V$ resistance are due to the internal resistance. As shown in Fig. 4(c), the Nyquist plots of the full-type cells with different electrode thickness and with a state of charge (SOC) of 50% show two overlapping semicircles at high- ($10^1$–$10^3$ Hz) and low-frequency ($10^0$–$10^1$ Hz) regions for all electrode thicknesses, which is decreased in size with increasing electrode thickness. An equivalent circuit considering a simple planar electrode, which is two parallel circuits in series (inset in Fig. 4(c)), was used for fitting of the Nyquist plots.\(^7\)\(^8\) As shown in Fig. 4(d), the charge-transfer resistance for the positive electrode

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**Fig. 3** Initial charge-discharge curve of the cylindrical-type cell.

**Fig. 4** (a) Relation between power and energy densities for cylindrical-type cells with various electrode thickness, where the numbers indicate electrode thickness ($\mu m$). (b) Dependence of the $I$-$V$ resistance (circles) and the corresponding inverse of the $I$-$V$ resistance (squares) of the same cell on electrode thickness. (c) Nyquist plots for cylindrical-type cells with various electrode thickness at $0^\circ C$. Inset: equivalent circuit for full-type cell. (d) Dependence of charge-transfer resistance of the positive electrode, $R_{ct,\ app.}$ (circles), and the corresponding inverse of $R_{ct,\ app.}$ (squares) on electrode thickness obtained by fitting.
$R_{\text{ct, app}}$, decreased dramatically in region I and slightly in region II with increasing electrode thickness. An inverse plot of $R_{\text{ct, app}}$ shows a linear profile in region I and a non-linear profile in region II, which is the same tendency as the $I-V$ resistance in Fig. 4(b). The profile of $R_{\text{ct, app}}$ in region II cannot be explained by Eq. (7) of the previous paper in this special feature, which indicates that another resistance component that is different from the charge-transfer resistance may contribute to the total internal resistance in region II.

2.2 Symmetric Cell Analysis

The dependence of EIS-SC for the positive electrodes, which were the same lot electrodes as those used in the full-type cells described in Sec. 2.1, on the electrode thickness was conducted at an SOC of 0% and 50% to determine $R_{\text{ion}}$ (Fig. 5(a)) and $R_{\text{ct}}$ (Fig. 5(b)), respectively. With increasing electrode thickness, the length of the 45° slope corresponding to $R_{\text{ion}}$ in the high frequency region increases in the Nyquist plots at SOC = 0% (Fig. 5(a)), and the size of the semicircle corresponding to $R_{\text{ct}}$ in the low frequency region decreases in the Nyquist plots at SOC = 50% (Fig. 5(b)). $R_{\text{ion}}$ and $R_{\text{ct}}$ obtained by fitting had proportional (Fig. 5(c)) and inversely proportional (Fig. 5(d)) relationships with increasing electrode thickness, respectively; therefore, $R_{\text{ion}}$ and $R_{\text{ct}}$ obtained from EIS-SC show opposite trends with respect to electrode thickness. These results agree with Eq. (5) and Eq. (7) of the previous paper in this special feature.

Figure 7 shows the dependence of the internal resistance, $R_{\text{ct, app}}$, decreased dramatically in region I and slightly in region II with increasing electrode thickness. An inverse plot of $R_{\text{ct, app}}$ shows a linear profile in region I and a non-linear profile in region II, which is the same tendency as the $I-V$ resistance in Fig. 4(b). The profile of $R_{\text{ct, app}}$ in region II cannot be explained by Eq. (7) of the previous paper in this special feature, which indicates that another resistance component that is different from the charge-transfer resistance may contribute to the total internal resistance in region II.

Fig. 5 Nyquist plots for symmetric cells with two identical positive electrodes with various electrode thickness measured at 0°C; electrodes prepared at SOC of (a) 0% and (b) 50%. Dependence of each internal resistance on electrode thickness at 0°C: (c) ionic resistance in pores ($R_{\text{ion}}$), and (d) charge-transfer resistance of lithium intercalation reaction ($R_{\text{ct}}$) obtained by fitting (circles) and the corresponding inverse of $R_{\text{ct}}$ (squares).

* This technique is described in detail in the previous paper in this special feature.
resistance on electrode thickness obtained from EIS-SC. The inverse of $R_{\text{ct}}$ is proportional to the electrode thickness. With reference to Eq. (4) of the previous paper in this special feature, the inverse of the total internal resistance, i.e., $R_{\text{ct}}$ plus one third of $R_{\text{ion}}$, $R_{\text{ion}}/3 + R_{\text{ct}}$, shows non-linear behavior. Such non-linear behavior is in agreement with the inverse of the $I-V$ resistance in Fig. 4(b) and the inverse of $R_{\text{ct,app}}$ of the observed cylindrical-type cells in Fig. 4(d). This means the total resistance obtained from EIS-SC reflects the behavior of the actual cylindrical cell well and is greatly affected by the ionic conductivity of the porous structure, especially for thick electrodes with a high loading weight of active materials.

3. Relationship between Battery Performance and Internal Resistance Components

Finally, we consider the relationship between the specific power and the energy change with respect to the electrode thickness in the cylindrical-type cells from the viewpoint of the internal resistance component. The relationship between the specific power and internal resistance of the cylindrical-type cells can be described theoretically using the TLM. The relationship between $R_{\text{ct}}$ and $R_{\text{ion}}$ can be considered as a parallel circuit in the TLM. In this case, the higher resistance, either $R_{\text{ct}}$ or $R_{\text{ion}}$, dominates the rate-determining process. $R_{\text{ion}}$ is lower than $R_{\text{ct}}$ in region I, but higher in region II, as shown in the inset of Fig. 7. When $R_{\text{ion}}$ is lower than $R_{\text{ct}}$ at a thin electrode (region I), the rate-determining process is $R_{\text{ct}}$. Thus, there is essentially no delay in the response of the reaction in the depth direction. As a consequence, the reduction of power is minimal (Fig. 4(a) region I) because only $R_{\text{ct}}$ has an effect. In contrast, when $R_{\text{ion}}$ is higher than or approximately equal to $R_{\text{ion}}$ in a thick electrode (Fig. 7 region II), the rate-determining process is $R_{\text{ct}}$. Thus, there is essentially no delay in the response of the reaction in the depth direction.

4. Conclusions

We have confirmed the contribution of the internal resistance of the charge-transfer reaction $R_{\text{ct}}$ and the dependence of ionic conduction at the porous electrode/electrolyte interface $R_{\text{ion}}$ on the electrode thickness by considering EIS-SC measurements and TLM theory for cylindrical pores. The individual internal resistance components of $R_{\text{ion}}$ and $R_{\text{ct}}$ show opposite trends with respect to electrode thickness.
because $R_{\text{ion}}$ is affected by the pore length, whereas $R_{\text{ct}}$ is inversely affected by the electroactive surface area. We experimentally confirmed that marked power decay occurred when $R_{\text{ion}}$ affected the Li-ion conduction in the electrolyte-filled pores rather than $R_{\text{ct}}$ with increasing electrode thickness; therefore, a porous electrode structure design with suitable ionic-conduction pathways will be necessary to achieve both high energy density and high power density. The results also show that despite its simplicity, our approach will give reasonably accurate results and is sufficient for analysis of the electrochemical characteristics of actual porous electrodes for lithium-ion batteries.

References


Fig. 1

Figs. 2, 4-7

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