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Abstract

To establish the kinetics of the lithium insertion materials used as the electrodes in lithium-ion batteries, it is important to clarify the diffusion phenomena of lithium ions in the solid phase. Since there are two variations of the rate-determining step of a lithium insertion electrode (Li-ion diffusion in solid particles and that in the electrolyte solution), these have to be differentiated in any investigation of the diffusion phenomena of Li ions in a solid. In this study, we calculated the rate capability of diluted electrodes using a charge–discharge simulation program and proved that the transport of Li ions in the solid phase is the rate-determining step for a diluted electrode with an extremely low active material content. In addition, the solid-state Li-ion diffusion coefficient can be calculated by analyzing the results of the rate capability tests. These results reveal that the diluted electrode method is very useful for elucidating the solid-state Li ion diffusion phenomena of lithium insertion materials. As such, the rate capability tests provide a new means of analyzing the solid-state diffusion coefficient.

Keywords: lithium insertion material, solid-state diffusion, rate capability, simulation
1. Introduction

The input- and output-power capability of lithium-ion batteries (LIB) is one of the most important measures of a battery’s performance, especially for automobile applications where rapid charging is a requirement. Among the experimental methods used to evaluate the power capability of an LIB, the “rate capability test,” wherein the capacity retention is measured after charging or discharging at a high current density, is widely used. Since the characteristics of a LIB are significantly determined by the electrode performance of the lithium insertion electrodes used as positive and negative electrodes, the determination of the rate capability of a lithium insertion electrode is essential to materials testing as well as cyclability.

The rate capability of a lithium insertion electrode is determined from the concentration overvoltage; the Li-ion concentration in the electrolyte or the chemical composition (amount of Li ions) in the active materials at an active material/electrolyte interface changes significantly upon the completion of charging or discharging. There are two possible reasons for this concentration polarization.

Case I: A potential change due to the Li-ion concentration in the electrolyte becoming zero (or attaining a saturated concentration) based on the Nernst equation representing the concentration dependence of the electrode potential.

Case II: The chemical composition on the surface of the active material particles changes to the fully charged or discharged state. In this case, the composition dependence of the electrode potential is determined by the reversible electrode potential of the material as a function of the chemical composition (the amount of Li ions).
Thus, in a rate-capability test of a lithium insertion electrode, there are two rate-determining steps; the migration of the Li ions in the solid particles and the transport process of the Li ions in the liquid electrolyte in the pores inside the electrode. Consequently, two different rate characteristics should be observed in a lithium insertion electrode.

In our previous study\textsuperscript{1}, we measured each of these two rate-capabilities using the diluted electrode method. This method, in which the active material particle content can be changed while maintaining the electrode structure, provides useful information on the kinetics of lithium insertion electrodes\textsuperscript{1-3}. For an electrode with a high active material content, the Li-ion transport in the electrolyte solution in the pores is the rate-determining step, while the migration of Li ions in solid particles is the rate-determining step in the case of a dilute electrode with a low active material content. Therefore, the diluted electrode method enables the determination of the solid-state diffusion coefficient of Li ions in a material, based on the rate capability of a dilute electrode with a low active material content.

In the present study, the solid-state diffusion coefficient of the Li ions was estimated based on the simulated results of rate capability tests on diluted electrodes with a low active material content. For conventional LIBs with a liquid electrolyte, solid-state Li-ion diffusion is not very important from either technological or practical viewpoints because the rate-determining step is the Li-ion diffusion in the electrolyte within the pores\textsuperscript{2}. However, solid-state Li-ion diffusion is a very important parameter in an all-solid-state LIB\textsuperscript{4-9}. In solid electrolytes, there is no concentration gradient due to the single-ion transfer. Therefore, the rate-determining step for an all-solid-state LIB should be the Li-ion transfer in the active material. In other words, solid-state Li-ion diffusion in the active material plays a crucial role
in determining rate capability of an all-solid-state LIB.

2. Charge–discharge Simulation

The charge–discharge simulation program (Dualfoil, ver. 5.1) developed by Newman et al.\textsuperscript{10-12} was used to simulate the rate capability tests for a dilute electrode. For the cell configuration, LiAl\textsubscript{0.2}Mn\textsubscript{1.8}O\textsubscript{3.8}F\textsubscript{0.2} (LAMOF)\textsuperscript{13} and Li metal were selected for the positive and negative electrodes, respectively. We selected LAMOF as the positive electrode materials for two reasons: first, LAMOF is the most similar to Li[Li\textsubscript{0.1}Al\textsubscript{0.1}Mn\textsubscript{1.8}]O\textsubscript{4} (LAMO) we have examined so far\textsuperscript{1-3} and, second, the electrochemical reaction of LAMOF comprises a single-phase reaction throughout the region, i.e., no phase boundary in the solid and Li-ion transportation in the solid takes place as a result of diffusion only. The parameters affecting the LAMOF diluted electrode were fixed except for the amount of LAMOF (electrode thickness: 100 \(\mu\)m, LAMOF particle size: 5.0 \(\mu\)m) The solid-state Li diffusion coefficient of LAMOF was set to 2.0 \(\times\) 10\textsuperscript{-14} m\textsuperscript{2} s\textsuperscript{-1} with reference to that of LiMn\textsubscript{2}O\textsubscript{4}\textsuperscript{14}. This paper also examines the case where the diffusion coefficient of LAMOF is changed. The only variable parameter was the volume fraction of the LAMOF (10, 5, and 2 vol\%), in which case the proportion of the spectator material was increased to retain the same porosity of the electrode, that is, 40 vol\% (Fig. 1). Electrolyte properties are also fixed to be 1.0 \(\times\) 10\textsuperscript{-11} m\textsuperscript{2} s\textsuperscript{-1} for diffusion coefficient and 0.4 for transference number of lithium ions\textsuperscript{15}.

3. Results and Discussion

The rate capability tests for the dilute LAMOF electrodes in lithium cells were simulated
The simulation of the discharging cell was performed until the discharge capacity decreased to half of the theoretical capacity as a result of increasing the current density. When the cell was discharged at a low current density, a capacity close to the theoretical value was obtained, even for a diluted electrode with an extremely low LAMOF content. This indicates that all the LAMOF particles were discharged, even in the dilute electrode. By comparing the results based on the current density per geometrical electrode area, $j_A$ (mA cm$^{-2}$), the value of $j_A$ delivering half of the theoretical capability decreased with a reduction in the LAMOF content in the dilute electrodes. However, by comparing the results based on the current density per LAMOF weight, $j_W$ (A g$^{-1}$), the value of $j_W$ delivering half the theoretical capability is low for the dilute electrodes with 10 vol% LAMOF (1.7 A g$^{-1}$), whereas it was the same for the dilute electrode containing ≤ 5 vol% LAMOF (2.4 A g$^{-1}$).

Figure 3 shows the normalized discharge capacity plotted against the current density, based on the LAMOF weight ($j_W$). The rate capability of the dilute electrode with 10-vol% LAMOF was significantly lower than those with 5- and 2-vol% LAMOF. This indicates that the diffusion of the Li ions in the solution still affects the rate capability of the dilute electrode with 10-vol% LAMOF. However, for the dilute electrode with 2- and 5-vol% LAMOF, the rate capabilities are exactly the same, which indicates that in the dilute electrodes with a LAMOF content of ≤ 5 vol%, the diffusion of the Li ions in the solid is the rate-determining step. From these results of the rate capability tests for the dilute electrodes, under the simulation conditions assumed in this study, the LAMOF content should be ≤ 5 vol% to analyze the solid-state Li-ion diffusion phenomena based on the results of the rate
capability tests. It is noticed that the rate capability of the diluted electrode depends on LAMOF particle size because the particle size corresponds to diffusion length of Li ions. If the particle size of LAMOF is small, LAMOF content should be decreased in order to exhibit the solid-state Li-ion diffusion phenomena.

To confirm the rate-determining step for the dilute electrode with 5-vol% LAMOF, the concentration of electrolyte in the electrode and the chemical composition of the solid surface upon the completion of discharge was examined. Figure 4a shows the results when a 5-vol% LAMOF dilute electrode was discharged at a current of 3.0 mA cm$^{-2}$. The Li-ion concentration of the electrolyte in the pores of the electrode changed slightly along the radial direction. However, depletion of the Li salt was not observed; it did not reach zero in every region. This indicates that the supply of Li ions from the electrolytic solution in the pores within the electrode was sufficient and that the diffusion of the Li ions in the electrolyte was not the rate-determining step. In contrast, the chemical composition of the LAMOF particle surface is in the fully discharged state regardless of the depth of the electrode, indicating that discharge of the dilute electrode had completed, as indicated by the compositional change in the LAMOF surface. The compositional change within the LAMOF particles (Fig. 4b) shows that the chemical composition inside the particles changes due to the slow diffusion of Li ions in the solid. The profiles of the chemical composition relative to the radial direction were virtually the same at each electrode depth. This means that the diffusion of the Li ions in the solid is the rate-determining step. Figure 4c illustrates this schematically; the deeper blue color corresponds a high concentration in the electrolyte, whereas the deeper red color
corresponds to the large amount of Li in the solid. In the case of a dilute electrode with an extremely low LAMOF content (< 5 vol%), a sufficient amount of Li ions can be supplied from the electrolyte, because the consumption rate of Li-ion in the electrolyte is very low. Consequently, the diffusion of Li ions in the solid is the rate-determining step in a dilute electrode with ≤ 5 vol% LAMOF.

The diffusion coefficient of the Li ions in the solid was derived from the results of the rate capability test for the dilute electrode with 5-vol% LAMOF. By assuming three-dimensional spherical diffusion in which the reaction proceeds at the surface of each spherical particle in the fully charged state (the initial concentration of particles is zero), the concentration profile is calculated using Eq. (1)\(^16\).

\[
C = \frac{j_WaD}{\alpha^2} \left\{ \frac{3Dt}{2\alpha^2} + \frac{r^2}{2\alpha^2} - \frac{3}{10} - 2\sum_{n=1}^{\infty} \frac{\sin(a_n r)}{a_n^3 a^2 \sin(a_n \alpha)} \exp\left(-Da_n^2 t \right) \right\}
\]  

(1)

where \(D\) is the solid-state diffusion coefficient of the Li ions in LAMOF, \(C\) is the concentration of Li ions within the particle, \(j_W\) is the current density at the particle surface, \(a\) is the particle radius, and \(r\) is the radial distance. When the fourth term in Eq. (1) is ignored, the equation can be simplified, as follows.

\[
C = \frac{F_0aD}{\alpha^2} \left\{ \frac{3Dt}{2\alpha^2} + \frac{r^2}{2\alpha^2} - \frac{3}{10} \right\}
\]  

(2)

Figure 5 shows the verification of the concentration profile as calculated using Eq. (2) by
comparing the result with that obtained with Eq. (1). If $t$ is sufficiently large ($C$ significantly increases), the approximation is reasonably accurate. Therefore, the approximate expression given by Eq. (2) can be applied to estimate the discharge time for the rate capability tests, because the change in $C$ is sufficiently large ($t$ is also large) at the end of the discharge.

The electrode potential of LAMOF is determined from the concentration at the particle surface, $r = a$. Substituting $r$ with $a$ in Eq. (2), we obtain

$$C = \frac{jw a}{D \left( \frac{3Dt}{a^2} + \frac{1}{5} \right)} \quad (3)$$

By transforming Eq. (3), the capacity at the end of discharge, $Q$, is given as

$$Q = jw t = \frac{Ca}{3} - \frac{1}{15 \frac{a^2}{D}} jw \quad (4)$$

The relationship between the discharge capacity, $Q$, and the discharge current density, $jw$, in the rate capability tests can be obtained. From Eq. (4), the discharge capacity is proportional to the current density and its gradient is $(-a^2/15D)$. The simulated results shown in Fig. 3 reveal that $Q$ decreases linearly with respect to $jw$.

To confirm the relationship between $Q$ and $jw$ under any conditions, rate capability tests for the LAMOF dilute electrodes were carried out by changing the values of $a$ and $D$ (Fig. 6). Regardless of the conditions, $Q$ linearly decreased as $jw$ increased. The slope of the lines depends on the value of $a$ and $D$; the slope decreases as the diffusion coefficient increases.
and the particle size decreases. In particular, when the particle size is changed, the change in the slope is significant compared to the change in the diffusion coefficient. This is reasonable because the slope of the lines is linearly proportional to the diffusion coefficient, whereas the dependence of the particle size upon the slope is squared.

Figure 7 shows plots of the slope, as calculated from Fig. 6, against the value of \( (a^2/D) \). All the data fell on a line. The gradient of the line is \(-0.069\), with this value being very close to a coefficient of \(-1/15 = -0.067\) as given by Eq. 4. Therefore, if the particle radius, \( a \), is known, the diffusion coefficient, \( D \), can be determined from the rate capability tests.

4. Conclusions

In this study, we simulated the rate capability of diluted electrodes using a simulation program and showed that it was possible to determine the solid-state diffusion coefficient of the Li ions from the results of the rate capability tests. According to the simulated results, in the rate capability tests applied to the dilute electrode with an extremely small amount of the active material, there was no reaction distribution in the active material particles in the electrode upon the completion of discharge, so that all the particles were in a uniform discharge state. Therefore, in the rate capability test applied to the dilute electrodes, the Li ions in the electrolyte present in the pores within the electrode can always be supplied without being depleted, and therefore the solid-state Li-ion diffusion within the particles is the rate-determining step. When the solid-state Li-ion diffusion is rate-determining, the discharge capacity decreases in proportion to the current density. Furthermore, since the
relationship between $Q$ and $j_w$ is irrelevant to the structure of the electrode, it changes according to the diffusion coefficient and particle size of the material. The determination of the solid-state Li-ion diffusion coefficient in lithium insertion materials using the method described in this paper will be presented in a future paper.

Acknowledgements

This work was partly supported by the Advanced Low Carbon Technology Research and Development Program, Specially Promoted Research for Innovative Next Generation Batteries (ALCA Spring) of the Japan Science and Technology Agency (JST), Japan.

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Figure 1. Schematic illustrations of Li/LAMOF cells for charge-discharge simulation. The diluted LAMOF electrodes contained (a) 10-vol%, (b) 5-vol%, or (c) 2-vol% LAMOF.
Figure 2. Simulated discharge curves for Li/LAMOF cells. The diluted LAMOF electrodes contained (a) 10-vol%, (b) 5-vol%, or (c) 2-vol% LAMOF.
Figure 3. Normalized discharge capacity of Li/LAMOF cells as a function of current density.

The diluted LAMOF electrodes contained (a) 10-vol%, (b) 5-vol%, or (c) 2-vol% LAMOF.
Figure 4. (a) Change in concentration of Li ions in the electrolyte and the chemical composition at the LAMOF particle surface upon the completion of discharge. The diluted LAMOF (5 vol%) electrode was discharged at a rate of 3 mA cm$^{-2}$. (b) Change in the chemical composition of LAMOF particles located at the electrode surface, in the middle of the electrode, or near the current collector. (c) Schematic illustration of diluted LAMOF electrode upon the completion of discharge. The blue and red color gradations indicate the concentration of the electrolyte and the LAMOF chemical composition, respectively. Arrows indicate locations at which chemical composition of LAMOF was shown in Fig. (b).
Figure 5. Change in the concentration in a spherical particle with a radius $a$ for a current density $j_w$ at the surface. The solid and dashed curves were calculated from Eqs. 1 and 2, respectively. The value of $Dt/a^2$ is (a) 0.2, (b) 0.1, (c) 0.05, and (d) 0.01.
Figure 6. Discharge capacity of diluted LAMOF electrode (5 vol%) as a function of the current density. The variables are the solid-state diffusion coefficient of Li ions in the LAMOF particles, $D$, and the radius of the LAMOF particles, $r$. 
Figure 7. Plot of slopes of the lines shown in Fig. 6 (dQ/dj_W) against r^2/D. The gradient in the plot (−0.069) is similar to the theoretical value (−1/15).