Factors Affecting Voltammetric Responses for Redox-active Solid Layers of Li$_3$Ti$_5$O$_{12}$ Coated on Electrodes

Noboru OYAMA,* Shuichiro YAMAGUCHI, Yasumasa MOCHIZUKI, Tomoo SARUKAWA, Takeshi SHIMOMURA

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology (2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan)

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Instead of W. R. McKinnon$^1$ theory based on interaction energy in lattice-gas model, which has been used widely to analyze the charge-discharge curve for electrode materials of lithium ion battery, Laviron$^{2,3}$ and Matsuda$^4$ theoretical treatments about the cyclic voltammetry (CV) for the electro-active molecular confined on an electrode are applied for clarifying the experimentally accessible physical quantities, i.e. the parameters of electrostatic interaction between redox sites and of electrode kinetics for the Li$_3$Ti$_5$O$_{12}$ (LTO) solid-state layers. From the width at half height ($\Delta E_{1/2}$) of the reversible CV at lowest potential scan-rate, the corresponding attractive force in their active-materials was evaluated as $W/RT = 1.64$ (4.07 kJ mol$^{-1}$), being an identical factor for the interaction energy evaluated by the lattice-gas model. From the shift of peak potential and the changes of $\Delta E_{1/2}$ and peak current for the irreversible CVs against the moderate potential scan-rates, the values of the rate constant ($k$ s$^{-1}$) and the transfer coefficients ($\alpha$) regarding a redox-electrode reaction process were evaluated as $6.7 \times 10^{-2}$ and 0.47-0.48, respectively. The interaction parameter $\Delta W^{1/RT}$ being related to the kinetics of the electrode process was evaluated as $-4.28 \sim -4.68$.

**Key Words**: Analysis of Voltammogram, Solid Layers of Li$_3$Ti$_5$O$_{12}$, Evaluation of Interaction Parameters, Material for Lithium Ion Battery.

1 Introduction

Generally, lattice-gas model, according to W. R. McKinnon$^1$ theory, is applied for understanding the curve of voltage ($E$) vs. composition and the cyclic voltammogram (CV) obtained for a solid-state thin redox-electrode of the LiCoO$_2$, LiCoO$_{1.4}$Ni$_{1.6}$Mn$_{1.3}$O$_2$ and the Li$_3$Ti$_5$O$_{12}$ (LTO), being electrode active-materials for lithium-ion battery. Cell voltage ($E$) for a solid-state redox reaction of the corresponding substrates demonstrates a delicate dependence on the degree of the Li$^+$ content ($\chi$) in the solid matrix, which does not obey the Nernst equation. The responses of $E$ vs. $\chi$ and the electrochemical density of states ($\partial \chi / \partial E$) vs. $E$ are explained by a thermodynamics model, in which a nearest neighbor attractive or repulsive force of active sites is taken into account. A number of theoretical and experimental researches have been done to explain these responses, but not necessarily succeed in giving the reasonable interpretation about the responses, especially ($\partial \chi / \partial E$) vs. $E$. Here, the thermodynamics for the redox-electrode has been applied for the interpretation about the responses. However, except for the static force of active sites, the kinetics of the electrode reactions and the phase-transition should be generally considered to electrochemical responses through redox-active materials fixed on electrode substrate (current collector) soaked in an electrolyte solution, even if the diffusion-less condition is established experimentally.

In the present paper, we report that analysis of the CV for the redox-material coated electrode being simply prepared is the important first step in their characterization for the corresponding active materials. In order to add the contribution of the kinetic parameters to thermodynamics for the CV, we apply the concept of the kinetics for the electrode reactions, that is, E. Laviron theory$^{4-7}$ for the organic molecular confined on an electrode, for battery active-materials. We present the rationality of Laviron$^4$ and H. Matsuda$^8$ theories, by analyzing the CV obtained for the LTO. The LTO which has the unique characteristics of so-called zero-strain material is selected for the present research, since the over-potential required for the phase-transition can ignore with the theoretical treatment for the LTO and therefore our analysis can be simplified.

2 Experimental

2.1 Chemicals

Li$_3$Ti$_5$O$_{12}$ (LTO) was gifted from Ishihara Sangyo Kaisha Ltd. and its surface area was 33.5 m$^2$ g$^{-1}$.

2.2 Electrochemical measurements

Cyclic voltammetry (CV) was carried out with a Hokuto Denko model HZ-3000 or HZ-5000 potentiostat/ galvanostat. The voltammetric measurements were performed in a three-electrode cell configuration using a glassy carbon disk electrode (GCE) (BAS, diameter: 3.0 mm), a Pt coil counter electrode, and an Ag/Ag$^+$ (inner solution of propylene carbonate (PC) containing a 0.05 M AgClO$_4$ and 1.0 M LiPF$_6$) reference electrode. The
described potentials are cited after converting the potentials for the Ag/Ag⁺ to those for the Li/Li⁺ (1.0 M LiPF₆ in PC) reference electrode. To characterize the redox behavior of LTO, experiments regarding the active material coated GCE were carried out at room temperature (25°C) in an electrolyte of PC containing 1.0 M LiPF₆, which was thoroughly deoxygenated using argon gas. Preparation of the LTO-coated electrodes was performed as follows: Slurries were prepared by mixing 85.5% active material coated LTO, 6.0% PVdF, and 8.5% Ketjen black (KB) in 1-methyl-2-pyrrolidinone (NMP), where KB (EC 600JD) is produced by Lion Co., having specific surface area of 1270 m² g⁻¹ and averaged diameter of 34 nm. The resulting slurry was coated on a GCE, followed by vacuum drying at 100°C for 2 hours. The thicknesses of the coating were 0.20 ~ 2.0 μm at each of electrodes.

3 Results and Discussion

CVs in Fig. 1(a) and (b) were observed with the same coated electrode at the different potential scan rates. The CV obtained at a slow scan rate is significantly narrower at half-peak current and has a somewhat greater total area than its counterpart recorded at a high scan rate. Figure 2 summarized the results for a series of measurements of the charge under CVs which were recorded between +1.200 and +1.900 V vs. Li/Li⁺ reference electrode alternatively, when an applied potential scan rate was changed. The difference in the charges observed at the slow scan rate less than 70 mV s⁻¹ could not be observed. Since the theoretical capacity of 175 mAh g⁻¹ for the LTO is ascertained to be observable,²² coverages of the LTO coating in Fig. 2 are 2.3 × 10⁻² and 3.0 × 10⁻² mole cm⁻², when the values of charges observed in the CVs are 1.57 and 2.05 mC cm⁻². The thickness of the LTO thin layer coated on electrode was ca. 0.79 μm with the case of 1.57 mC cm⁻² coating, when the density of the LTO layers is estimated to 1.27 g cm⁻³, and also confirmed by observation of SEM. Though the LTO solid layers are approximately a thousand of monomolecular layer and a fraction of the redox-active centers in the LTO particles are probably located at some distance away from the electrode surface, almost all active centers are oxidized and reduced simultaneously within the time-scale of electrolysis at the scan rates less than 70 mV s⁻¹. It means that the diffusion less condition against the CV responses is established experimentally under the slow scan rate of less than 70 mV s⁻¹. However, as the scan rate increased, the effects of diffusion within the coating appeared in the quantities integrated from the CV responses. In this case, the CV responses will be complicated, because not only the electrode kinetics and linear diffusion in a finite space but also the effects of finite diffusion and inhomogeneity of the coating should be considered.²⁰ The variation of the CV behavior with KB content (from 4.0 to 15.0 weight %) was not observed. Therefore, we can consider that most of redox centers for the coated LTO anticipate directly in the electron transfer reaction with the electrode and the remainder is oxidized and reduced through the electron-exchange reaction among redox centers of coating particle.²¹,²²

Although the charges observed in the range of scan rate 0.005 to 70 mV s⁻¹ are almost constant, the anodic and cathodic peak currents are not proportional to the potential scan rates. Here, we notice that the observed peak currents with 0.20 mV s⁻¹ are larger than those estimated from 𝑛²𝐹²𝐴ΓΤ/4𝑅𝑇 expected for an ideal reversible surface shape of the CV (dotted line in Fig. 1).²⁰ Furthermore, as shown in Fig. 1, the values of the width (Δ𝐸p/2) at half height of peak potentials for the

![Fig. 1] CVs for LTO coated electrode in PC containing 1.0 M LiPF₆ at the scan rate of (a) 20 mV s⁻¹, and (b) 0.20 mV s⁻¹. The dotted curve is estimated from 𝑛²𝐹²𝐴ΓΤ/4𝑅𝑇.

![Fig. 2] Dependence of the charge ((○, ▲) 𝑞ₜ) flowing during the potential sweep from 1.200 to 1.900 V and that ((○, △) 𝑞ₜ) flowing during the potential sweep from 1.900 to 1.200 V on the potential sweep rate (𝑛) for two electrodes (circle#1 and triangle #2) coated with different coverage of LTO.
CV with 0.20 mV s⁻¹ were very small, e.g. 20 mV for the anodic scan and 22 mV for the cathodic scan, respectively, being significantly smaller than 90.6 mV for ideal response. Therefore, we can see that the attractive interaction is present among redox-active centers. Figure 1 also demonstrates that the ΔE⁺₁/₂ became larger at the scan rate 20 mV s⁻¹, e.g. ca. 130 mV for the both scan direction. These phenomena mean that the special interaction among the active-sites for LTO must be taken into account for the interpretation of the CV responses.

Such an interaction among the reactants has been considered in a theory about the CV for a surface redox-electrode reaction by Laviron. In his treatment, the surface standard potential (E⁰) of the redox-couple confined to an electrode surface should be known. However, if the redox-couple species is insoluble in the electrolyte solution, the E⁰ cannot be determined. Therefore, after that, H. Matsuda group rearranged and extended Laviron’s theory using an experimentally determinable E⁺ being named as the conditional potential, which is the equilibrium potential when η₀ = η₁ = 1/2 being a half for the surface mole fractions of R and O.

Although not shown, the minimum of ΔE⁺₁/₂ were 10.8 mV for the anodic scan and 9.5 mV for the cathodic scan at the scan rate 0.0020 mV s⁻¹. When the CV observed at the slow scan rate is reversible case, the values of Λ or k⁺ tends to infinity and then the following equations are obtained from eqn. (18) in ref. 8 by Matsuda, as

\[ E = E^+ + \frac{(RT/nF)}{\ln \left( \frac{\chi_0}{\chi_0} \right)} - \frac{(RT/nF)}{\ln \left( \frac{\chi_0}{\chi_0} \right)} = E^+ + \frac{(RT/nF)}{\ln \left( \frac{\chi_0}{\chi_0} \right)} \]  

The half-height width (ΔE⁺₁/₂) is given by

\[ ΔE⁺₁/₂ = \frac{(2RT/nF)}{\ln \left( \frac{\chi_0}{\chi_0} \right)} \left( \frac{1}{1 - \rho} \right) - \left( \frac{\chi_0}{\chi_0} \right) \]  

where

\[ \rho = \left( \frac{1}{2} - \frac{1}{2} \right) \left( \frac{1}{2} - \frac{1}{2} \right) \]  

By using the theoretical curve of ΔE⁺₁/₂ against Ξ expressed by eqn.(2), the value of Ξ that is, the parameter W/RT is examined. Thus, we have +1.64 ± 0.02 for the W/RT from ΔE⁺₁/₂ (an average value of 10.2 mV) for reversible responses of the CV. The interaction energy is attractive. The parameter W/RT is exactly the same as the parameter U used by McKinnon and Φ, used by T. Ohzuku.

As increasing the potential scan rate, the peak potentials of the CV shift to more positive for the anodic scan and more negative for the cathodic scan, respectively, as shown in Fig. 3. With the scan rate 70 mV s⁻¹, the difference between the values observed with anodic and cathodic scan was above 393 mV. Therefore, the observed behavior reflects the influence of electrode kinetics. In Fig. 3, the linear part of the plot obtained at the scan rates of 7.0 to 70 mV s⁻¹ can be regarded as that for an irreversible process, where the charges shown in Fig. 2 are almost constant under all of the scan rates less than 70 mV s⁻¹, that is, diffusion-less condition is experimentally established. From the slopes of the plots, the cathodic and anodic transfer coefficients (αc and αa for the cathodic and anodic reactions, respectively) were evaluated as 0.47 and 0.48, respectively, the sum of these values (0.95) being close to unity. When the anodic electrode process is irreversible, from eqn. (17) in ref. 8, the dependence of Ψ⁺/αc and E⁺ on Ξ + ΔΞ is simplified and then expressed by the approximate equations of (42) and (43) in ref. 8, as

\[ ψ = \frac{d\chi_0}{d\chi_0} = \frac{(2RT/nF)}{\ln \left( \frac{\chi_0}{\chi_0} \right)} = \frac{1}{2} (\chi_0) \exp \left( \frac{-\chi_0}{\chi_0} \right) \frac{1}{2}(\chi_0 - \chi_0) \]  

\[ Ψ⁺/αc = 0.1240 + 0.01023(Ξ + ΔΞ) + 0.2345(Ξ + ΔΞ)^2 + 0.0260(Ξ + ΔΞ)^2 \]  

Furthermore, the variations of ΔE⁺₁/₂ E⁺ + E⁺ + ΔΞ can be expressed by the approximate equations of (51), (52) and (53) in ref. 8, as

\[ ΔE⁺₁/₂ = (RT/αcηF) \left\{ \begin{array}{l} \text{[1.8217 - 1.0197(Ξ + ΔΞ)]} \\ + 0.6216 \exp \left[ 0.4395(Ξ + ΔΞ) \right] \\ - 0.0183(Ξ + ΔΞ)] \end{array} \]  

\[ E⁺ = \frac{(RT/αcηF) \left\{ \begin{array}{l} \text{[1.8217 - 1.0197(Ξ + ΔΞ)]} \\ + 0.6216 \exp \left[ 0.4395(Ξ + ΔΞ) \right] \\ - 0.0183(Ξ + ΔΞ)] \end{array} \]  

\[ ΔE⁺₁/₂ = (RT/αcηF) \left\{ \begin{array}{l} \text{[1.8217 - 1.0197(Ξ + ΔΞ)]} \\ + 0.6216 \exp \left[ 0.4395(Ξ + ΔΞ) \right] \\ - 0.0183(Ξ + ΔΞ)] \end{array} \]  

\[ E⁺ - E⁻ = \frac{(RT/αcηF) \left\{ \begin{array}{l} \text{[1.8217 - 1.0197(Ξ + ΔΞ)]} \\ + 0.6216 \exp \left[ 0.4395(Ξ + ΔΞ) \right] \\ - 0.0183(Ξ + ΔΞ)] \end{array} \]  

\[ E⁺ - E⁻ = \frac{(RT/αcηF) \left\{ \begin{array}{l} \text{[1.8217 - 1.0197(Ξ + ΔΞ)]} \\ + 0.6216 \exp \left[ 0.4395(Ξ + ΔΞ) \right] \\ - 0.0183(Ξ + ΔΞ)] \end{array} \]
Table 1 Kinetic parameters evaluated for the electrode reaction of Li$_2$Ti$_3$O$_7$ solid layers.

<table>
<thead>
<tr>
<th>Analytical equation$^1$</th>
<th>$W/RT$</th>
<th>$\Delta W/RT$</th>
<th>$\alpha_e$</th>
<th>$\alpha_c$</th>
<th>$k^+$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2$^6$</td>
<td>$1.64 \pm 0.02$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>7</td>
<td>$1.64 \pm 0.02$</td>
<td>$-4.28$</td>
<td>$0.47$</td>
<td>$0.48$</td>
<td>$6.9 \times 10^4$</td>
</tr>
<tr>
<td>8 and 9</td>
<td>$1.64 \pm 0.02$</td>
<td>$-4.40$</td>
<td>$0.47$</td>
<td>$0.48$</td>
<td>$6.7 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td>$1.64 \pm 0.02$</td>
<td>$-4.68$</td>
<td>$0.47$</td>
<td>$0.48$</td>
<td>$6.2 \times 10^4$</td>
</tr>
</tbody>
</table>

$^1$ Denoting the used quotation number in ref. (8). In addition, analytical equations are transferred for cathodic irreversible processes.

$^2$ The equation is the exactly the same as one used by Laviron,$^7$ McKinnon$^3$ and Ohzuku$^9$ in references.

When the cathodic electrode reaction is irreversible, the corresponding equations for an anodic reaction described above can be simply replaced.$^8$ By using the equations introduced above, the values of $(W + \Delta W)/RT$ and $(W - \Delta W)/RT$ can be evaluated and then the interaction parameters of $W/RT$ and $\Delta W/RT$ can be determined, if either the half-peak width ($\Delta E_{p1/2}$), the differences between the peak potential ($E_p$) and the half-peak width ($\Delta E_{p1/2}$), or the peak current functions ($\Psi_p$) for totally irreversible reaction process are known. Accordingly, the value of $k^+$ (the formal rate constant) can be calculated by using the value of the determined $\alpha, E_p$ and $E_{p2}$ for eqn. (43) in ref. 8. The determined parameters are summarized in Table 1, in which kinetic parameter of $\Delta W/RT$ was calculated with the CV response observed at the scan rate of 70 mV s$^{-1}$. Interpretation about the determined parameters will be given in elsewhere.$^9$

4 Conclusion

In the field of chemical modified electrode, Laviron$^7$ has historically dealt with the problems of interaction between redox sites existing throughout the whole region of the thin film and of electrode reaction for the thin film and proposed a general equation of the linear potential sweep voltammogram in the case of diffusionless. In the present paper, we found that his theoretical treatment is applicable to analysis of electrochemical solid-state behaviors observed for the redox-electrode materials of inorganic lithium-intercalation compounds. Evaluations of both the thermodynamic interaction and the kinetics of the electrode reaction for redox-electrode materials of lithium-ion battery were performed, for the first time in our knowledge, for the responses of reversible and irreversible CVs. Note that in the present case, the feature in CV response does not represent phase transition to a disordered or an ordered structure. However, for many redox active materials, it is well known that the interaction between ions and electrons produces the crystalline form or disordered form.$^3$

Therefore, more study is needed of systems where the phase transition is induced by the density of oxidation-states.

Acknowledgement

The authors express their thanks to Ishihara Sangyo Kaisha, Ltd. for gifting well-characterized LTO.

References


Appendix

1. Symbols listed below have the following meaning described in the sentences and equations.

   $\Delta E_{p1/2}$ half-height width
   $E_{c1}$ surface standard potential
   $E^\circ$ conditional potential
   O oxidized site
   R reduced site
   $\Gamma_T$ superficial concentration of the sum of O and R coverage defined by $\theta_T = \Gamma_T/\Gamma_m$
   $\Gamma_m$ the maximum superficial concentration
   $\chi_R$ surface mole fraction of R
   $\chi_O$ surface mole fraction of O
   $k_c$ rate constant
   $\alpha_e$ anodic transfer coefficient
   $\alpha_c$ cathodic transfer coefficient
   $k^+$ formal rate constant for surface redox-electrode reaction
   $\xi$ dimensionless electrode potential defined by $\xi = (nF/RT)(E - E^\circ)$
   $W$ interaction energy related to the equilibrium potential
   $\Delta W/RT$ the same as the parameter $vG$ used by Laviron interaction energy related to the kinetics of the electrode processes
   $\Delta \xi$ interaction parameter affecting the electrode potential for a reversible electrode reaction: $(W/RT) \theta_T$
Δξ***

interaction parameter related to the kinetics of
the electrode processes: \((ΔW^*/RT)θ_ξ\)
p
interaction parameter used by Laviron
r
interaction parameter used by Laviron
v
interaction parameter used by Laviron
w
interaction parameter used by Laviron
E
applied potential
v
potential sweep rate
Ψ
dimensionless current function: \(i/(wFvAT\gamma/RT)\)
Λ
dimensionless kinetic parameter: \(k^*/(nFv/RT)\)
Ψa
anodic current function, dimensionless
Ψc
cathodic current function, dimensionless
i\text{a}
anodic current
i\text{c}
cathodic current
Ψ\text{ap}
anodic peak current, dimensionless
Ψ\text{cp}
cathodic peak current, dimensionless

2. Symbols and subscripts denoted on a cyclic voltammogram used for the parameter evaluation.