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Electrochemical Impedance Analysis of $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ Used as Lithium-Insertion Electrodes by the Diluted Electrode Method

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Abstract

Electrochemical impedance analysis was performed for $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO) used as a lithium-insertion electrode by the diluted electrode method to identify the origin of resistance. Utilization of diluted electrodes, in which some portion of active material, LAMO, was systematically replaced with the same amounts of spectator Al_2O_3 material to maintain the original structure of the LAMO electrode, is a promising method to discriminate between the resistance attributed to the lithium-insertion reaction in LAMO (charge-transfer resistance) and that accompanied by conduction of electron and/or ion in the porous electrodes. Electrochemical impedance spectra of the diluted electrodes consisted of two semicircles. The radius of a semicircle in the lower frequency region depends on the LAMO content in a diluted electrode, indicating that the semicircle is associated with charge-transfer resistance. On the other hand, the radius of the other semicircle in the higher frequency region is independent of the LAMO contents, suggesting that the semicircle is mainly related to the resistance accompanied by the porous structure of electrodes. Thus, the structure of lithium-insertion electrode should be carefully considered in designing high-energy and high-power lithium-ion batteries that employ thick electrodes.

Keywords: electrochemical impedance spectroscopy, lithium-insertion electrode, diluted electrode, charge transfer resistance

1. Introduction

Lithium-ion batteries (LIBs) are receiving considerable attention as power sources for stationary and automobile applications, which demand high energy and power densities and long-life performance. Since the power characteristics of LIBs are determined by the resistances of the positive and negative electrodes and the electrolyte, reducing the resistance of the electrodes is important for improving the power density of LIBs. Among several electrochemical techniques for investigating the resistance of lithium-insertion electrodes, the electrochemical impedance technique is the most powerful tool, because it allows differentiation of several electrochemical processes with different time constants that collectively contribute to the resistance of the electrode [1–3]. However, lithium-insertion electrodes generate complicated impedance spectra, which are difficult to fit with a simple equivalent circuit consisting of a resistance and capacitor connected in parallel (Randles circuit [4]). A complicated equivalent circuit consisting of several resistances and capacitors connected in series or in parallel is necessary to fit the observed impedance spectra of the electrodes. Various equivalent circuits have been proposed to analyze the impedance spectra of lithium-insertion electrodes [5–9]. Although calculated impedance spectra based on these complicated equivalent circuits can be fitted well to the observed spectra, it is difficult to determine which electrochemical process contributes to a given resistance component.

Several theoretical and experimental approaches have been developed to establish an equivalent circuit suitable for lithium-insertion electrodes by identifying the origins of resistance contributors [6,10–13]. In recent years, new insights into the impedance

behavior of lithium-insertion electrodes have been provided through the use of symmetric cells, which can measure the electrochemical impedance spectra of a single electrode without a reference electrode [14–21]. Electrochemical impedance analysis for a symmetric cell revealed that electronic and/or ionic conductivity in porous electrodes contributed to resistance of the electrode in addition to the charge-transfer resistance of the active material [15,18,20,21]. Therefore, the resistance of lithium-insertion electrodes has two components. One component is charge-transfer resistance arising from the lithium-insertion reaction at the surface of an active material. The other is resistance arising from electronic and/or ionic conduction in the porous electrode.

In a previous report [22], we proposed the diluted electrode technique, which can provide useful information about the kinetics of a lithium-insertion electrode. This technique enables to clarify factors affecting the resistance of the electrode because it is possible to arbitrarily change only the ratio of the active material present in the electrode without changing the electrode structure (Fig. 1). By applying the diluted electrode technique to the $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO) electrode, the rate-determining step for the lithium insertion reaction of the electrode was shown to be Li and/or anion transport in the electrolyte within the porous electrode, not solid-state diffusion of Li ions in LAMO.

Fig. 1. A schematic illustration of ideal “diluted” electrodes composed of LAMO active material ($\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}\text{O}_4]$) and a spectator material (Al_2O_3) in a porous electrode. Electrode character changes from that of a porous electrode to that of a single-particle electrode with a similar porous structure by increasing the Al_2O_3 content. (reprinted with permission from [22]. Copyright 2018, The Electrochemical Society).

In the present study, electrochemical impedance analysis of the LAMO electrodes was carried out with the diluted electrode technique. In the electrochemical impedance spectra of the diluted electrodes, resistance originating from the lithium-insertion reaction was expected to be related to the LAMO content of the electrode, while resistance from the porous electrode would be independent of the LAMO content. Analyzing the electrochemical impedance spectra of the diluted electrodes enables to identify which component of electrode resistance relates to the lithium-insertion reaction.

2. Experimental

2.1 Preparation of the diluted LAMO electrodes and electrochemical impedance

spectroscopy of the LTO/LAMO cells

All chemicals were used as received from the manufacturer. Lithium aluminum manganese oxide $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO, Tosoh) and lithium titanium oxide $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LTO, Ishihara Sangyo Kaisha, LT855-17C) were used as the active materials. Alumina powder (Al_2O_3 , Wako Pure Chemical Industries, Ltd.) with a mean particle size of 5 μm was used as the spectator material. Acetylene black (AB) and polyvinylidene fluoride (PVdF) were used as a conductive additive and a polymer binder, respectively. The LTO electrodes consisted of 88 wt% of LTO and 6 wt% AB and 6 wt% of PVdF. The loading weight and thickness of the LTO electrodes were approximately 35 mg and 130 μm , respectively. The diluted LAMO electrodes consisted of LAMO, Al_2O_3 , AB, and PVdF in a mass ratio of x : 88– x : 6: 6. Al_2O_3 and AB were added to LAMO, and the mixture was ground with a mortar and pestle for 10 minutes. PVdF dissolved in *N*-methylpyrrolidone (NMP) was added to the mixture to obtain a slurry. The slurry was spread onto aluminum foil with a blade and dried under vacuum at 80°C for 1 h. The temperature was then raised to 150°C and maintained there for 12 h. Finally, 2-cm² sections of the dried electrode were cut out with a hole punch. Structural properties of diluted-LAMO electrodes were listed in Table S1.

The electrochemical behavior of the diluted LAMO electrode was examined in lithium-ion cells with a partially reduced LTO negative electrode. LTO/diluted-LAMO cells were constructed using a diluted LAMO electrode and an LTO negative electrode partially reduced (approximately 25% of SOC) in a lithium cell prior to cell fabrication. Electrochemical impedance spectroscopy of LTO/diluted-LAMO cells was recorded to

examine the SOC of the cell adjusted to be 50% based on the LAMO electrode. SOC of the LTO electrode is in the range of 25-75 %, where impedance behavior of an LTO electrode is virtually the same [16], because the capacity of an LTO electrode is larger than that of a LAMO electrode in these cells. Electrochemical cells and the instrumentation used for cell performance tests have been described previously [23]. Electrochemical impedance measurements were performed using a 1260 frequency response analyzer (Solartron Analytical, West Sussex, U. K.) with a 1287 potentiostat. A sinusoidal voltage with a peak amplitude of 14.1 mV (RMS value = 10 mV) was superimposed on the open-circuit voltage (OCV) of the cell. The frequency was scanned stepwise at 10 steps per decade from 100 kHz and 10 mHz.

2.2 Calculation of single LAMO electrode impedance from impedances of LTO/LAMO cells

The impedance of an LTO/LAMO cell at angular frequencies can be expressed as $Z_{\text{Cell}}(\omega) = Z_{\text{LAMO}}(\omega) + Z_{\text{LTO}}(\omega)$. In this equation, impedance of the electrolyte is omitted, because the impedance can be assumed to exhibit simple resistance behavior at any frequency. From the above equation, the impedance of the single electrode, such as $Z_{\text{LAMO}}(\omega)$ for the LAMO electrode, can be calculated by subtracting the impedance of the single-LTO electrode from that of the LTO/LAMO cell:

$$Z_{\text{LAMO}}(\omega) = Z_{\text{Cell}}(\omega) - Z_{\text{LTO}}(\omega) \quad \text{Eq. (1).}$$

The impedance of a single-LTO electrode can be measured in a LTO/LTO symmetric cell composed of two LTO electrodes of identical weight and thickness [16,24]. The LTO/LTO

symmetric cell was prepared using fully-oxidized and fully-reduced LTO electrodes prepared in lithium cells, which were disassembled and combined in a fresh cell. The electrochemical behaviors of both LTO electrodes, such as reversible capacity, polarization, and impedance, are consequently also identical. The charge-discharge curves were symmetric at zero volts. The cell capacity after five cycles was 4.77 mAh, or 158 mAh g⁻¹ based on LTO weight. The electrochemical impedance measurements of the LTO/LTO symmetric cells were examined at 50% SOC of the cell, where chemical composition of the LTO electrodes (Li_{3/2}[Li_{1/3}Ti_{5/3}]O₄) was identical. Hence, impedance of the LTO/LTO symmetric cell at this point was twice the impedance of the single-LTO electrodes:

$$Z_{\text{LTO/LTO}}(\omega) = 2 \times Z_{\text{LTO}}(\omega) \quad \text{Eq. (2).}$$

The impedance of a single-LTO electrode is shown in Fig. S1. There is a capacity loop at high frequency, approximately 30 kHz. The electrode exhibited resistive behavior in the frequency range of 1 kHz to 1 Hz. In the range below 1 Hz, $|Z|$ increased gradually, and θ tended to increase. The impedance of the single-LTO electrode was calculated to be half that of the symmetric cell by Eq. 3:

$$Z_{\text{LTO}}(\omega) = Z_{\text{LTO/LTO}}(\omega)/2 \quad \text{Eq. (3).}$$

In this study, the impedance of the diluted LAMO electrodes was obtained by subtracting $Z_{\text{LTO}}(\omega)$ of the single-LTO electrode from $Z_{\text{Cell}}(\omega)$ of the LTO/LAMO cells. $Z_{\text{LAMO}}(\omega)$ of the single-LAMO electrodes was thus calculated by the following:

$$Z_{\text{LAMO}}(\omega) = Z_{\text{Cell}}(\omega) - Z_{\text{LTO}}(\omega) = Z'_{\text{Cell}}(\omega) - Z'_{\text{LTO}}(\omega) + i\{Z''_{\text{Cell}}(\omega) - Z''_{\text{LTO}}(\omega)\}$$

$$\text{Eq. (4).}$$

Therefore, the real (Eq. 5) and imaginary (Eq. 6) parts of Z_{LAMO} were

$$Z_{\text{LAMO}}(\omega) = Z_{\text{Cell}}(\omega) - Z_{\text{LTO}}(\omega) \quad \text{Eq. (5) and}$$

$$Z''_{\text{LAMO}}(\omega) = Z''_{\text{Cell}}(\omega) - Z''_{\text{LTO}}(\omega) \quad \text{Eq. (6).}$$

The absolute value of the impedance $|Z|$ of the single-LAMO electrode was

$$|Z|_{\text{LAMO}}(\omega) = [\{Z_{\text{LAMO}}(\omega)\}^2 + \{Z''_{\text{LAMO}}(\omega)\}^2]^{1/2} \quad \text{Eq. (7),}$$

and the phase shift (θ) at this time was determined by Eq. 8:

$$\theta(\omega) = \arctan\{Z''_{\text{LAMO}}(\omega) / Z_{\text{LAMO}}(\omega)\} \quad \text{Eq. (8).}$$

3. Results and discussion

3.1 Electrochemical impedance measurements of lithium-ion cells with the diluted LAMO-positive and LTO-negative electrodes

Charge-discharge curves of the diluted LAMO electrodes examined in the lithium-ion cells with an LTO electrode are shown in Fig. 2. No significant differences in the voltage profiles of the cells were observed. All the diluted LAMO electrodes showed a reversible capacity of about 100 mAh g⁻¹ at 4 V, which is characteristic of the LAMO electrode [23]. The charge-discharge curves crossed at about half capacity, indicating that polarization of the cells was relatively minimal regardless of LAMO content. Capacity based on geometric electrode area, or area-specific capacity (ASC), decreased with decreasing

Fig. 2. Charge-discharge curves of LTO/Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) cells operated at a current density of 0.5 mA cm⁻² in the voltage range of 1.5 to 3.1 V. The diluted LAMO electrodes were composed of [LAMO : Al₂O₃ : acetylene black (AB) : polyvinylidene difluoride (PVdF)] = [x : 88-x : 6 : 6] in wt%, where x = (a) 88, (b) 44, (c) 22, (d) 5, and (e) 1.

LAMO content. Capacity was 1.55 mAh cm⁻² with 88 wt% LAMO and was reduced to 0.017 mAh cm⁻² with 1 wt% LAMO. ASC decreased proportionally as a function of LAMO loading weight (Fig. S2). From these results, we determined Al₂O₃ had no

discernable effect on the electrochemical reactivity of LAMO. Therefore, the diluted electrode technique enabled reduction of the LAMO loading weight without a significant change in electrode weight, thickness, porosity, or specific capacity in mAh g^{-1} based on LAMO.

Electrochemical impedance measurements were performed with the cells containing the diluted LAMO-positive electrodes and LTO-negative electrodes. Fig. 3 shows the absolute impedance values $|Z|$ and phase angles (θ) as a function of frequency. For the measurements, the state-of-charge (SOC) of each cell was 50%. As can be seen from the figure, $|Z|$ and θ did not vary significantly in the high-frequency region ($f > 100$ Hz). In the high-frequency region, a capacitive loop at approximately 10 kHz was observed with a time constant independent of LAMO content. In the range between 1 kHz and 10 Hz, $|Z|$ remained constant at about $3 \Omega \text{ cm}^2$ and was independent of LAMO content, and θ approached 0° . In the frequency range from 100 Hz to 0.01 Hz, one capacitive loop was observed, and its time constant decreased with decreasing LAMO content. In the lower-frequency range (<10 Hz), the impedance of the cells with the diluted LAMO electrodes grew as the frequency decreased. $|Z|$ depended on LAMO content, as the $|Z|$ values increased with decreasing LAMO content. Capacitance behavior was gradually indicated by θ , and all of the cells converged on the same magnitude from 1 Hz to 0.1 Hz.

Fig. 3. Bode plots of the impedance for LTO/LAMO cells at 50% of the state-of-charge. The LAMO contents (wt%) in the diluted LAMO electrodes were (a) 88, (b) 44, (c) 22, (d) 5, and (e) 1.

3.2 Electrochemical impedance spectra of single LAMO electrode

The electrochemical impedance spectra of the LTO/LAMO cells shown in Fig. 3, which contain information from both the LTO-negative and LAMO-positive electrodes. To obtain the impedance of the single-LAMO electrode, the impedance of the single-LTO electrode obtained by measuring impedance of the LTO/LTO symmetric cell was subtracted from that of the LTO/LAMO cell. Impedance of the single-LAMO electrode cannot be measured by using a symmetric cell method for the diluted LAMO electrodes with low LAMO content (< 5 wt%) because of very rapid capacity fading due to side

reaction currents of diluted LAMO electrodes. Fig. 4 shows the absolute value of impedance $|Z|$ and the phase angle (θ) for the single-LAMO electrodes as a function of frequency. Impedance of the single-LAMO electrodes also indicated two electrochemical processes, one at a high frequency of ~ 30 kHz and the other at a low frequency of 1 Hz. No significant change in $|Z|$ or θ was observed in the high-frequency region. The impedance spectra in the high-frequency region appeared to be independent of LAMO content in spite of some variation in the spectra. The impedance spectra at lower frequencies, on the other hand, obviously showed a dependence on LAMO content. These results indicated there were two electrochemical processes occurring in the single LAMO electrode. One was independent of LAMO content, while the other strongly depended on LAMO content.

Fig. 4. Bode plots of the impedance for single-LAMO electrodes. The LAMO contents (wt%) in the diluted LAMO electrodes were (a) 88, (b) 44, (c) 22, (d) 5, and (e) 1.

The low-frequency (<1 kHz) regions of the complex-plane plots of impedance for the single LAMO electrodes with varying LAMO content are shown in Fig. 5. Area-specific resistance (ASR) based on geometric electrode area, corresponding to the diameters of the semicircles, increased with

Fig. 5. Complex-plane plots of the impedance in the low-frequency region for single-LAMO electrodes. The LAMO contents (wt%) in the diluted LAMO electrodes were (a) 88, (b) 44, (c) 22, (d) 5, and (e) 1.

decreasing LAMO content in the diluted electrodes. ASR was $2.1 \Omega \text{ cm}^2$ at 88 wt% LAMO, $5.4 \Omega \text{ cm}^2$ at 44 wt% LAMO, $10.4 \Omega \text{ cm}^2$ at 22 wt% LAMO, $25 \Omega \text{ cm}^2$ at 5 wt% LAMO, and $105 \Omega \text{ cm}^2$ at 1 wt% LAMO. The ASR clearly depended on the amount of LAMO in the electrode, indicating a process that was attributable to the LAMO lithium-insertion reaction. In other words, the results reflected the charge-transfer resistance of the LAMO material. The ASR values in the low-frequency region estimated from the diameters of the semicircles appeared to be inversely proportional to LAMO content in the electrodes (Fig. S3). The ASR was very small with larger quantities of LAMO, whereas the resistance was drastically increased by reducing the LAMO content. A relationship between the reciprocal of ASR and LAMO loading weight was observed (Fig. 6). The reciprocal of the resistance value increased proportionally with the loading weight of LAMO. The slope of the straight line shown in Fig. 6 is $0.03 \Omega^{-1} \text{ mg}^{-1}$. The charge-transfer resistance of LAMO corresponding to the reciprocal of the slope was calculated to be $33 \Omega \text{ mg}$. This result indicated that ASR could be reduced by increasing the LAMO loading weight, and $\text{ASR } (\Omega \text{ cm}^2) = 33 \Omega \text{ mg} / \text{loading weight } (\text{mg cm}^{-2})$. On the basis of this equation, an electrode with a large LAMO loading weight obtained by increasing electrode density and thickness could improve the power density of the electrode by reducing the ASR.

Fig. 7 shows complex-plane plots of impedance in the high-frequency region for the single-LAMO electrodes. The solution resistance seems to be independent of LAMO content in spite of some variation for 88wt% and 5 wt% LAMO electrodes, probably resulting from variety of inter-electrode pressure. While the ASR in the low-frequency region of the complex-plane plots was related to the LAMO content of the diluted electrode, ASR at high frequencies was independent of LAMO content. Resistance from electrochemical processes at high frequencies ranged from 1 to 3 $\Omega \text{ cm}^2$ regardless of LAMO content. Semicircles in the high-frequency region have also been reported by others [8,10,17,20,21]. There are several interpretations

Fig. 6. Plots of reciprocal ASR of the diluted LAMO electrodes against the loading weight of LAMO in mg cm^{-2} .

regarding the origin of these semicircles. They could arise from contact resistance between the porous electrode and the current collector [8–10] or from resistance at the

interface between the active material and the conductive binder [21]. To determine whether or not the semicircles we observed were related to the LAMO active material, the electrode with no active material that contained only Al_2O_3 powder was examined (Fig. 8). Only one semicircle in the high-frequency region was observed. In the low-frequency region, capacitive behavior without any associated electrochemical process was seen, which was consistent with the polarizable behavior of the alumina electrode.

Fig. 7. Complex-plane plots of the impedance in the high-frequency region for single LAMO electrodes. The LAMO contents (wt%) in the diluted LAMO electrodes were (a) 88, (b) 44, (c) 22, (d) 5, and (e) 1.

Resistance at high frequencies is key for improving the energy and power density of lithium-insertion electrodes by increasing electrode thickness. This is because ASR at high frequencies is constant and independent of the LAMO loading weight, while it is possible to reduce ASR at low frequencies by increasing the loading weight. Thick electrodes have a number of advantages. The quantities of current collectors and separators are reduced, leading to incremental increases in energy density. They are easier to handle, as the electrodes are robust with regard to swelling problems. However, one of the most serious problems with thick electrodes is that their power density is lower than that of thin-film electrodes due to ASR in the high-frequency region. Thicker electrodes exhibit higher resistance per loading weight of the active material. Consequently, ASR at high frequencies is dominant in thicker electrodes, although ASR at low frequencies corresponding to charge-transfer resistance decreases with increasing electrode thickness. This is why thin electrodes are used to design high-power lithium-ion batteries. For thick electrodes, it is thus important to reduce or diminish resistance at high frequencies instead of reducing the charge-transfer resistance of a lithium-insertion material to improve the power density of lithium-insertion electrodes.

Fig. 8. (a) Bode and (b) complex-plane plots of an $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ symmetric cell. The Al_2O_3 electrodes consisted of 88 wt% Al_2O_3 , 6 wt% AB, and 6 wt% PVdF.

4. Conclusion

Electrochemical impedance measurements were carried out to understand the origin of the resistance of lithium-insertion electrodes containing LAMO. The impedance spectra of the diluted LAMO electrodes consisted of two resistance components. Resistance in the lower-frequency region varied with the LAMO content, while resistance

in the high-frequency region was independent of LAMO content. Resistance in the low-frequency region was proportional to the reciprocal of the LAMO loading weight, indicating it corresponded to the charge-transfer resistance of the LAMO materials. Resistance in the high-frequency region was independent of the LAMO content, indicating it was characteristic of the resistance caused by the porous electrode. Impedance spectra from the $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ symmetric cell also contained a single semicircle in the same high-frequency region, which supported the notion that resistance at high frequencies arose from the porous electrode configuration, not from the lithium-insertion reaction. The diluted electrode technique for electrochemical impedance spectroscopy can divide the resistance components of the electrodes into that related to the lithium-insertion reaction and resistance that is not. This is useful information for understanding the origin of the resistance of lithium-insertion electrodes. Notably, resistance in the high-frequency region of an impedance spectrum is a very important consideration in designing high-energy and high-power lithium-ion batteries that employ thick electrodes. The origin of resistance in the high-frequency region is still debatable, however, and electrochemical impedance analysis with $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ symmetric cells is currently underway in our laboratory.

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