A Clue to High Rate Capability of Lithium-Ion Batteries Obtained by an Electrochemical Approach Using "Diluted" Electrode

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Abstract

Rate capability of "diluted" electrodes composed of micron-sized particles of an active material, Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO), and a spectator material, Al₂O₃, were investigated to determine the rate-limiting step during discharge accompanied with lithium insertion. Capacity retention based on the current density based on LAMO weight (C-rate) was significantly improved by reducing LAMO contents in the diluted electrodes, whereas no significant difference was found in capacity retention based on area specific current density. These results indicate that the rate-limiting step during discharge is transportation of Li cations and counter anions in the electrodes, not Li-ion diffusion in the active materials. Comparison of amounts of Li⁺ ions inserted to LAMO during charge with that supplied from an electrolyte indicated that rate capability can be improved by increasing the amount of Li ions in the pore of the electrode. The comparison also suggest that transportation of the counter anion causing concentration overvoltage limits the rate capability.

Keywords: lithium-ion battery, rate-capability, diluted electrode

Introduction

Lithium-ion batteries commercialized in 1990s have been used as power sources for portable electronic devices, such as laptop computers, smartphones. Recently, the application areas of lithium-ion batteries expand to electric vehicles and stationary use for solar and wind power generations,¹⁻⁴ in which high input/output power for the batteries is strongly demanded. Thus, a large number of studies have been carried out to improve power capability of lithium-ion batteries. The power capability of lithium-ion batteries mainly depends on the rate capability of electrodes, because the power capability is closely related to the capacity retention at high current density. The rate capability of batteries is generally influenced by the concentration overvoltage caused by decrease in ions concentration resulting from slow transportation and diffusion in solid or liquid phase.^{5,6} The slow lithium-ion diffusion in solid active materials has been regarded as a main factor of the concentration overvoltage of lithium-ion batteries.⁷⁻¹¹

In this context, much effort has been devoted to enhancement of diffusion coefficient and/or reducing diffusion length of lithium ions in active materials to improve rate capability of lithium-ion batteries.¹²⁻¹⁶ Nano-sized materials with shorter diffusion length and larger surface area than those of micro-sized materials have been reported to exhibit superior rate capability.¹⁴⁻¹⁶ Intrinsic diffusion behavior of Li ions in the active material was investigated by using model electrodes, i.e., single-particle electrodes¹⁷⁻²¹ and thinfilm electrodes.^{22,23} Thin-film electrodes exhibited significantly higher rate capability than conventional porous electrodes. Additionally, more than half of discharging capacity can be delivered for single-particle electrodes of LiCoO₂ at the C-rate as high as 300 C- rate (11 s of discharge),¹⁷ LiFePO₄ at 500 C-rate (4 s),¹⁹ and graphite at 1500 C-rate (2 s).²⁰ However, the excellent rate capability of these model electrodes was hardly reproducible with a porous electrode composed of nano- or micron-sized particles, for which sufficient discharging capacity can be delivered at < 10 C-rate.²⁴ The low rate capability of a porous electrode indicates that rate capability depends not only on particle size of active materials, which is related to the diffusion path length of Li ions, but also on another factor. The factor should be clarified to achieve lithium-insertion electrodes with higher rate capability necessary for high-power lithium-ion batteries.

In this research, we clarify the rate-limiting step during discharge using diluted electrodes composed of particles of an active material for lithium insertion-extraction and a spectator with various ratios, where particles of Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) and Al₂O₃ are used as active and spectator materials, respectively. The electrodes termed as "diluted electrodes" can replicate electrode structures ranging from a porous electrode to a single-particle electrode by changing the ratios of the materials without significant changes in an electrode weight, thickness, porosity, amounts of a conductive additive and a binder (Fig. 1). Thus, investigation of electrochemical behaviors of diluted electrodes with various ratios of LAMO and Al₂O₃ particles allows to verify the rate-limiting step during discharge, where Li insertion to the LAMO particles proceeds, providing a clue to high rate capability of lithium ion batteries.

Experimental

All the chemicals were used without further purification. Lithium aluminum

manganese oxide Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O4²⁵ (LAMO; Tosoh) and lithium titanium oxide Li[Li_{1/3}Ti_{5/3}]O4^{26,27} (LTO; Ishihara Sangyo Kaisha, LT855-17C) were used as an active materials. Alumina powder (Al₂O₃; Wako Pure Chemical Industries, Ltd.) with particle size of ca. 30 μ m, acetylene black (AB) and polyvinylidene fluoride (PVdF) were used as a spectator material, a conductive binder and a polymer binder.

Diluted LAMO electrodes consisted of LAMO, Al₂O₃, AB and PVdF with weight ratio of 88-x : x : 6 : 6. Al₂O₃ and AB added to LAMO were mixed in a mortar and pestle for 10 minutes. Slurry obtained by adding PVdF dissolved in N-methylpyrrolidone (NMP) to the mixture was cast on an aluminum foil by a blade. Thereafter, it was dried under vacuum at 80°C for 1 h, and then the temperature was raised to 150°C and maintained for 12 h. The dried electrode was punched into an electrode with a 2 cm²

The electrochemical behavior of diluted LAMO electrode was examined in lithiumion cells with LTO negative electrode which partially reduced in a lithium cell before the cell fabrication. Electrochemical cells and instruments used were the same as those reported previously.²⁵ In the rate-capability test, the cells was charged to 3.1 V at a current density of 0.25 mA cm⁻² and then discharged at current densities in the range from 0.25 to 20 mA cm⁻². After discharging at various discharge rates, the cell was left until the open circuit voltage (OCV) of the cell was stabilized, then discharged again at 0.25 mA cm⁻² to confirm no remarkable change in the reversible capacity of the cell.

Results

LAMO electrodes are mainly composed of Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) and Al₂O₃,

in which the weight ratio of these metal oxides, acetylene black (AB) and polyvinylidene difluoride (PVdF) is 88:6:6. Sizes and morphologies of the main components of LAMO and Al₂O₃ particles were confirmed by scanning electron microscopy (SEM) shown in Fig. 2. The SEM images indicates that the size of spherical LAMO particles is ca. $5\sim10$ µm although the size of primary particles is around 1 µm, and Al₂O₃ particles are rounded shape and ca. 5 µm in size. The LAMO contents in "diluted" electrodes composed of these particles were varied from 88 to 5% in weight. The weight and thickness of all diluted LAMO electrodes were maintained around 30 mg and 120 µm, respectively, because LAMO particles in the porous electrode were partially replaced with a similar amount of Al₂O₃. Thus, the structures of the diluted LAMO electrodes were virtually identical in terms of thickness and density with a similar porosity (Table 1).

Charge and discharge curves of lithium-ion cells employing Li[Li_{1/3}Ti_{5/3}]O₄ (LTO) and a diluted LAMO electrode as negative and positive electrodes, respectively, are displayed in Fig. 3. The cells were operated at the constant current density of 0.5 mA cm⁻² in the voltage range from 1.5 to 3.0 V corresponding to 3.0 to 4.5 V of LAMO electrodes against the Li metal electrode. Decrease in the LAMO amount in diluted LAMO electrodes resulted in decrease in specific capacity based on the geometrical electrode area (Area Specific Capacity; ASC) from 1.59 mAh cm⁻² to 0.08 mAh cm⁻² by reducing the LAMO content from 88 to 5 wt%. Specific capacity of the LAMO electrodes based on the LAMO weight, gravimetric capacity, was more than 90 mAh g⁻¹ irrespective of LAMO contents, indicating that all LAMO particles in the diluted electrodes participate in Li insertion/extraction reactions even when a large amount of the spectator material, Al₂O₃, was added to the LAMO electrodes. Also, the spectator Al₂O₃ material in the diluted electrodes scarcely influences on electrochemical properties of LAMO. Therefore, the electrochemical behavior of diluted electrodes with various LAMO concentrations depends on the structure of LAMO particles agglomerates.

Rate capability tests were performed for LTO/LAMO cells employing diluted electrodes with LAMO contents ranged from 5 to 88 wt% (Fig. 4). The LTO/LAMO cells were discharged at several current densities between 0.25 and 20 mA cm⁻² after charging at the constant current density of 0.25 mA cm⁻². Suitable discharge end voltages of a cell were chosen depending on the current density; 1.5 V (ca. 3.0 V of LAMO electrode against the electrode potential of Li^+/Li) at current density lower than 2.0 mA cm⁻², 1.25 V (2.75 V vs Li⁺/Li) at current density between 2.0 and 5.0 mA cm⁻², and 1.0 V (2.5 V vs Li⁺/Li) at current density higher than 10 mA cm⁻² under consideration of IR drop of the cells. The shape of discharge curves highly depends on the current density; almost flat at slow rates but modest decline at faster rates. Resistance of an electrode estimated from the voltage drop at the beginning of discharging process slightly increased with decreasing the amount of LAMO, although LAMO contents in the diluted electrode were varied in an order of magnitude. Almost full capacity delivered by all the diluted LAMO electrodes at current density less than 2.0 mA cm⁻² indicates that concentration overvoltage is negligible in the electrodes. However, further increase of current density resulted in decrease of discharge capacity. Capacity retention of all the diluted LAMO electrodes based on discharge capacity at low current density was plotted as a function of the current density based on the electrode area (j_A) (Fig. 5). Discharge capacity decreases with increasing the current density for all the LAMO electrodes. The discharge capacity dropped by 30 to 60 % of that obtained at lower current density depending on LAMO contents at the current density of 20 mAh cm⁻². Lower LAMO contents in the diluted LAMO electrodes resulted in higher capacity retention. (Fig.5)

The capacity retention of all the diluted LAMO electrodes was also plotted against the discharge current density based on LAMO weight (j_W) as shown in Fig. 6. Drastic decrease in discharge capacity was observed for diluted electrodes with high LAMO contents. Capacity retention of the electrode without Al₂O₃ was 30 % at the current density as low as 1.3 A g⁻¹. High capacity retention was achieved by decreasing the LAMO contents although all the LAMO electrodes have similar electrode thickness and porosity. Capacity retention of a LAMO electrode with the lowest LAMO content (5 wt%) was as high as 82 % at 13.6 A g⁻¹ and 57 % at 27.2 A g⁻¹. These current densities correspond to be 136 and 272 C-rate, respectively, under the consideration of nominal capacity of 100 mAh g⁻¹ based on LAMO weight, suggesting that 80 % of Li ions are inserted into LAMO materials within 26 seconds, moreover a half of Li ions is inserted within only 13 seconds. Superior rate capability for a diluted electrode with 5 wt% LAMO content was similar to that reported for single particle electrodes,¹⁷⁻²¹ which showed 80 % of capacity retention at more than 100-C rate. Thus, the dilution of active materials with a spectator material in a conventional porous electrode successfully replicates excellent rate capability of single-particle electrodes.

The rate-limiting step during discharge of lithium insertion materials such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ and $LiFePO_4$ with various thickness^{28,29} and

porosity³⁰ has been reported to involve transportation of Li ions. Also, computational calculation^{31,32} in literature supports that transportation of Li ions in a lithium insertion electrode played crucial role upon capacity retention at high current density. Thus, ASCs of the diluted LAMO electrodes with various LAMO contents obtained in the rate capability tests were plotted against j_W of the diluted LAMO electrodes to confirm the rate-limiting step during discharge by LAMO contents of diluted LAMO electrodes (Fig. 7). Constant ASCs at lower current density for each electrode indicates that no concentration overvoltage of the diluted electrodes results in delivering full capacity of LAMO in this region. The ASCs decreased in proportion to j_W with regardless of the LAMO contents indicates that the rate-limiting step during discharge is mass transfer in the lithium insertion electrodes for all the diluted LAMO electrodes.

Discussion

Rate capability of lithium-insertion electrodes is believed to be governed by concentration overpotential at the interface between an active material and a liquid electrolyte. In general, the overpotential is thought to be caused inside active material due to solid-state diffusion of Li ions. If Li-ion diffusion were the rate-limiting step during discharge of the diluted LAMO electrodes, capacity retention of diluted electrodes with various LAMO contents should be dependent on the current density based on the active material of LAMO (j_W). However, the large dependence of rate capability on LAMO contents of the diluted electrodes as was shown in Fig. 6 indicates fast Li-ion diffusion in the solid LAMO electrodes. Moreover, only a diluted electrode with LAMO contents as

low as 5 wt% showed excellent rate capability, 80% capacity retention less than 1 min, as well as single-particle electrode. Thus, the rate-limiting step during discharge is transportation of Li ions in the electrode.

A plausible rate-limiting step during discharge of dilute LAMO electrode is estimated from the amounts of Li ions in electrolyte and inserted into LAMO. The amount of Li ions supplied from electrolyte in the electrode pore, $n_{\rm El}$, was compared with amount of Li ions inserted to the LAMO particles, $n_{\rm Ins}$. $n_{\rm Ins}$ was calculated from the weight of LAMO in a diluted electrode and reversible capacity of LAMO, 100 mAh g⁻¹ (eq. 1).

$$n_{\rm Ins} = w \times (\text{LAMO wt\%}) \times 100 \times 3600 / 96500 \tag{1}$$

where *w* is the weight of LAMO in a dilute electrode.

To calculate $n_{\rm El}$, pore volume in the LAMO electrodes, $V_{\rm Pore}$, was calculated by subtracting volume of materials (LAMO, Al₂O₃, AB and PVdF) from volume of an electrode. Volume occupied by electrode materials were estimated from weight and density of each material.

$$V_{\text{Pore}} = A \times d - w \times \{ (\text{LAMO wt\%}) \times \rho(\text{LAMO}) + (\text{Al}_2\text{O}_3 \text{ wt\%}) \times \rho(\text{Al}_2\text{O}_3) + (\text{AB}) \times \rho(\text{AB}) + (\text{PVdF wt\%}) \times \rho(\text{PVdF}) \}$$
(2)

where *A* is geometrical electrode area, *d* is electrode thickness, and ρ is the true density of each material constituting the electrode; 4.16 g cm⁻³ for LAMO, 3.95 g cm⁻³ for Al₂O₃, 1.9 g cm⁻³ for AB³³ and 1.9 g cm⁻³ for PVdF.³⁴ Amount of Li ions were obtained by pore volume times Li-ion concentration, *C*_{Li}, 1.0 mol dm⁻³ in this study,

$$n_{\rm El} = V_{\rm Pore} \times C_{\rm Li}.$$
 (3)

Calculated results are summarized in Table 1. Pore volume and porosity of all the diluted

LAMO electrodes showed similar values in spite of changing the amount of LAMO by adding a spectator material of Al₂O₃ with different particle size from LAMO.

 n_{Ins} and n_{El} , in a diluted LAMO electrode as a function of LAMO content were shown in Fig. 8. $n_{\text{El}8}$ are virtually the same for all the diluted LAMO electrodes. On the other hand, n_{Ins} drastically decreases with decreasing LAMO contents in the diluted electrode. $n_{\text{El}} / n_{\text{Ins}}$ as small as *ca*. 0.1 in the diluted electrode with 88 wt% LAMO content indicates that Li ions have to be supplied from electrolyte outside the electrode to deliver the full capacity of LAMO. $n_{\text{El}} / n_{\text{Ins}}$ of *ca*. 3 is enough high ratio for delivering the full capacity in the diluted LAMO electrode with the lowest LAMO content (5 wt%). Thus, the ratio of $n_{\text{El}} / n_{\text{Ins}}$ is an indicator to predict rate capability of electrodes. Linear relationship between current densities and the ratio of $n_{\text{El}} / n_{\text{Ins}}$ was observed at 60, 70 and 80% of capacity retention for each LAMO electrode estimated from Fig. 5 (Fig. 9). Parallel three lines suggest that the rate-limiting step during discharge of the diluted LAMO electrode is related to the concentration of Li salts in the electrolyte. The diluted electrode cannot deliver full capacity even for the ratio greater than unity where $n_{\text{El}} / n_{\text{Ins}}$ is as high as ~3.

The capacity retention as low as half at high current density can be elucidated under consideration of another mass transfer process in the diluted LAMO electrodes. Transportation of counter anions, PF_6^- anion in the dilute electrodes, would be involved in the rate-limiting step. The movement of Li ions from an electrolyte to an active material through phase boundary resulted in rapid decrease of Li ions concentration at the surface of active material during discharge at high current density. Counter anions as well as Li ions should move to the electrode for charge compensation (Fig. 10). The results shown

in Fig. 4 can be rationally explained under the assumption; transportation of PF_6^- anion is thought to be kinetically the same in all the diluted LAMO electrode. Therefore, rate capability or capacity retention of the diluted LAMO electrodes depends on current density based on electrode area, j_A . Thus, anion transportation in the electrode is the ratelimiting step, because experimental results shown in Figs. 5 and 9 can be clearly elucidated.

Conclusions

Rate-capability tests of the diluted electrodes in which an active material of LAMO was mixed with a spectator material of Al₂O₃ were performed to reveal factors affecting rate-limiting step during discharge of lithium insertion electrodes. Capacity retention based on the current density in A g⁻¹ (C-rate) was significantly improved by diluting LAMO with Al₂O₃ in an electrode, whereas no significant difference was observed in capacity retention based on current density. These results indicate that the rate-limiting step during discharge of lithium insertion electrodes is transportation of Li cations and counter anions in the electrodes, but not Li-ion diffusion in the active materials. Quantification of Li-ion consumption and supply in the electrodes proved that superior rate capability can be achieved by enrichment of Li ions in the pore of an electrode. The analysis also suggests that transportation of a counter anion causing concentration overvoltage is the rate-limiting step during discharge of lithium insertion electrodes. This finding shed on the light for selection of counter anion in the electrolyte for improving rate capability of lithium-ion batteries.

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	LAMO-Al ₂ O ₃ electrode			
LAMO:Al ₂ O ₃	1:0	1:1	1:3	1:16.6
LAMO in an electrode/ wt%	88	44	22	5
Weight / mg	35.3	32.4	31.5	29.4
Thickness / µm	117	117	133	126
V(Electrode) / mm ³	23.4	23.5	26.6	25.3
V (LAMO) ^{a)} / mm ³	7.47	3.43	1.67	0.35
V(AB) ^{a)} / mm ³	1.11	1.02	0.99	0.93
V(PVdF) ^{a)} / mm ³	1.11	1.02	0.99	0.93
V(Al ₂ O ₃) ^{a)} / mm ³	0	3.61	5.26	6.18
Density / g cm ⁻³	1.51	1.38	1.19	1.17
Porosity (%)	58.5	61.3	66.4	66.7
Free Volume / mm ³	13.7	14.4	17.6	16.8
n _{lns} ^{b)} / μmol	115.9	53.2	25.9	5.5
n _{El} ^{c)} / μmol	13.7	14.4	17.6	16.8
n _{Ins} / n _{El}	0.12	0.27	0.68	3.1

Table 1 Structural properties of the diluted Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) electrodes.

^{a)} Densities of LAMO, acetylene black (AB), polyvinilidene difluoride (PVdF) and Al₂O₃ are 4.16,

1.90, 1.90 and 3.95 g cm⁻³, respectively.

 $^{\rm b)}$ The amount of Li ions inserted into LAMO was 3.73 mmol g $^{\rm -1}.$

^{c)} Li-ion concentration of the electrolyte was 1.0 mmol cm⁻³.



Fig. 1 A schematic illustration of ideal "diluted" electrodes composed of particles of an active material, $Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ (LAMO), and a spectator material, Al_2O_3 , in a porous electrode. Electrode character changes from the porous electrode to single-particle electrode with a similar porous structure by increasing the contents of Al_2O_3 .



Fig. 2 A SEM image of diluted electrode consisted of 44 wt% $Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ (LAMO), 44 wt% Al_2O_3 , 6 wt acetylene black (AB), and 6 wt% polyvinylidene difluoride (PVdF).



Fig. 3 Charge and discharge curves of Li[Li_{1/3}Ti_{5/3}]O₄ (LTO)/Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) cells operated at a rate of 0.5 mA cm⁻² in the voltage (*E*) range from 1.5 to 3.1 V as a function of area specific capacity (ASC). The diluted LAMO electrodes were composed of LAMO : Al₂O₃ : acetylene black (AB) : polyvinylidene difluoride (PVdF) = x : 88 - x : 6 : 6; x = (a) 88, (b) 44, (c) 22, and (d) 5. The electrode weights and thickness were (a) 35.3 mg and 116.8 µm, (b) 32.4 mg and 117.3 µm, (c) 31.5 mg and 132.8 µm and (d) 29.4 mg and 125.8 µm.



Fig. 4 Rate-capability tests of Li[Li_{1/3}Ti_{5/3}]O₄ (LTO)/Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO). Discharge curves were obtained under operation at a rate of 0.25, 1.0, 2.0, 5.0, 10 and 20 mA cm⁻² in the voltage (*E*) range from 1.0, 1.25, or 1.5 to 3.1 V as a function of area specific capacity (ASC). The LAMO contents in the diluted LAMO electrodes were (a) 88, (b) 44, (c) 22 and (d) 5 wt%.



Fig. 5 Capacity retention of the diluted Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) electrodes as a function of discharge current density based on geometrical electrode area (j_A). The LAMO contents in the diluted electrodes were (a) 88, (b) 44, (c) 22 and (d) 5 wt%.



Fig. 6 Capacity retention of the diluted Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) electrodes as a function of discharge current density based on LAMO weight (j_W). LAMO contents in the diluted LAMO electrodes were (a) 88, (b) 44, (c) 22 and (d) 5 wt%.



Fig. 7 Plots of area specific capacity (ASC) of the diluted electrodes composed of $Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ (LAMO) and Al_2O_3 against current density based on LAMO weight (*j*_W) and corresponding C-rate. The contents of LAMO in the electrodes were (a) 88, (b) 44, (c) 22 and (d) 5 wt%.



Fig. 8 (a) Amounts of Li ions inserted to Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O₄ (LAMO) (n_{Ins} , \blacksquare) and (b) amounts of Li ions supplied from the electrodes embedded in electrode pore (n_{El}) as a function of LAMO content in the diluted electrodes (\Box) and (c) the ratio of $n_{\text{El}} / n_{\text{Ins}}$ (\bigcirc).



Fig. 9 Plots of the current density (A g⁻¹) for delivering certain capacity retention at various capacities (*Q*) [*Q* = (a) 80 %, (b) 70 % and (c) 60 %, versus the ratio of $n_{\rm El} / n_{\rm Ins}$].



Fig. 10 A schematic illustration of ions movement in diluted electrodes composed of an active material (LAMO) and a spectator material (Al₂O₃). The rate-limiting step during lithium insertion reaction of LAMO (discharge) is transportation of PF_6^- from the electrode to the electrolyte.