

Temperature hysteresis in charge–discharge process of LiMn_2O_4 spinel

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Abstract

Quasi-equilibrium potential profiles of stoichiometric LiMn_2O_4 spinel in charge–discharge process have been recorded to investigate temperature dependence in lithium ions intercalation. Temperature of electrodes has been controlled within $273 \leq T \leq 298$ K in this research. Discharge curve reveals anomalous stepwise features when both charge and discharge processes are carried out at low temperature ($T \leq 278$ K). However, discharge curve at 273 K immediately after charge at 298 K does not show stepwise shape but gently slope as potential curve in charge at 298 K. In contrast to this, discharge curve at 298 K immediately after charge at 273 K shows stepwise anomaly. Temperature at discharge does not affect on shape of potential profile at next charge process. This temperature hysteresis has been confirmed repeatedly in several charge–discharge cycles. Temperature at Li ions de-intercalation has a large effect on next intercalation in LiMn_2O_4 spinel.

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1. Introduction

Recently, lithium ion battery has propagated as a power supply for portable machines: cellular phone, notebook computer, digital camera, and so on.

Spinel type lithium manganese oxide, LiMn_2O_4 , has received much attention for a cathode material of lithium ion battery [1–8] as a substitute for LiCoO_2 or LiNiO_2 , and many properties of the material have been studied for practical use. Most of the objective in researches has been mainly improvement of cyclic performance [9–11], and voltage [12–14].

We have reported quasi-equilibrium potential profiles of stoichiometric LiMn_2O_4 at several temperatures from a basic viewpoint of solid state chemistry; understanding exact potential-composition ($\phi - x$; $\text{Li}_x\text{Mn}_2\text{O}_4$) profiles which are excluded effect of polarization overpotential by lithium ions. Then, the anomaly has been found in the $\phi - x$ curves at low temperature ($T \leq 278$ K) as previous reports [15,16]. Characteristic gently slope at $x = 0.5$ in potential profile of $\text{Li}_x\text{Mn}_2\text{O}_4$ becomes very steep at 278 K, and a new voltage step also appears at $x \approx 0.7$ below room temperature (Fig. 1). We have found that the anomalous stepwise feature, especially appearance of the step at $x \approx 0.7$ is

not attributed to dissolution of Jahn–Teller distortion [8] because several non-stoichiometric specimens of lithium manganese spinel oxides, which have no Jahn–Teller distortions also show anomalous curves in our measurements of the $\phi - x$ relationships at $T \leq 278$ K [16]. A lithium-excess type $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4$ ($[\text{Li}]_{8a}[\text{Li}_\delta\text{Mn}_{2-\delta}]_{16d}[\text{O}_4]_{32e}$, $\delta = 0.01$) compound and lithium-deficient type specimens $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ ($[\text{Li}_{1-\delta}]_{8a}[\text{Mn}_2]_{16d}[\text{O}_4]_{32e}$, $\delta = 0.03, 0.05$) show stepwise feature in the $\phi - x$ profile at 273 K and no distortion in DSC measurements.

Furthermore, chromium-substituted lithium manganese spinel $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ ($[\text{Li}]_{8a}[\text{Cr}_y\text{Mn}_{2-y}]_{16d}[\text{O}_4]_{32e}$) also shows an anomalous stepwise feature identical with one of stoichiometric LiMn_2O_4 when the value of y is small enough ($y < 0.2$) at low temperature, despite that the kink at $x \approx 0.7$ becomes weak with increase of the value y (Fig. 2) [17]. The above results suggest that Mn-lattice (16d) in the spinel type structure strongly affect on the step at $x \approx 0.7$.

These $\phi - x$ profiles in the previous measurements have been obtained by de-intercalating of Li ions (charge process). LiMn_2O_4 shows reversible Li ions intercalation/de-intercalation certainly, and these profiles have been recorded with a very weak electric current to suppress overpotential. However, discharge potential profile is rather important for practical utility of lithium ion battery.

At first, in this research, the aim was recording of quasi-equilibrium potential profiles in first discharge process

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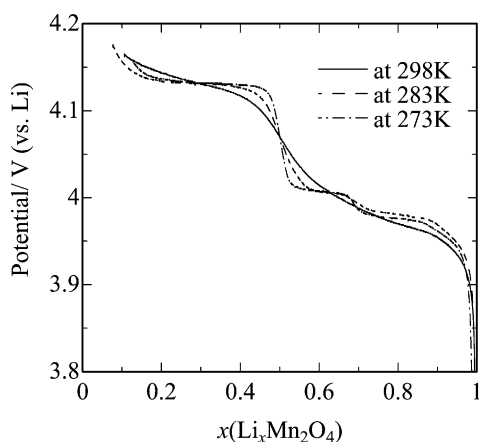


Fig. 1. Anomaly in the potential-composition profile of LiMn_2O_4 spinel below room temperature.

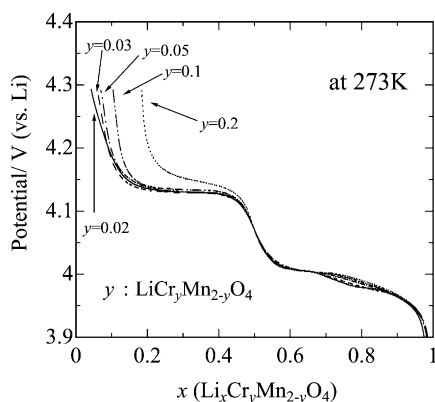


Fig. 2. Gradual change in the potential-composition profiles of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 0.02\text{--}0.2$) at 273 K.

at low temperature, in order to confirm whether the anomaly undergoes or not in discharge curve. The $\phi - x$ profiles recorded in first charge–discharge process at low temperature indicate that the anomalous stepwise feature reveals also in discharge profiles. Then, we have recorded first charge and discharge curves separately at different temperatures in the range of $273 \leq T \leq 298$ K to clarify temperature dependences in charge and discharge processes. As a result, a temperature hysteresis in charge–discharge process has been found. Around room temperature, Li ions intercalating process in LiMn_2O_4 spinel is affected by Li de-intercalation, which is immediately before.

2. Experimental

Synthesis of powder specimen and manner of recording $\phi - x$ profiles in the research are according to previous reports [15,16]. Stoichiometric LiMn_2O_4 has been prepared from Li_2CO_3 and MnCO_3 (both the products of Soekawa Chemical Co.) by conventional solid-state reaction. The specimen is confirmed by powder X-ray diffraction (XRD,

using RIGAKU RINT2000 system) that it is in a single cubic phase ($Fd3m$) at room temperature. We have also confirmed its chemical composition by redox titration [16].

Measurements of the $\phi - x$ profiles are performed using a gas-tight three electrode glass cells. The cells are filled with argon gas, and sealed up tightly. The air-tightness of the glass cells prepared in the research is maintained for more than 3 months around room temperature.

The $\phi - x$ profiles are recorded using HJ-101SM6 system (Hokuto Denko Co.) under a constant current condition. To suppress polarization overpotential, a very small value of the current density, i.e. 0.428 mA per 1 g of each specimen has been used in both charge–discharge processes. Rest time for about 24 h has been kept between charge and discharge. The circuit of the cell was completely opened in the rest time.

The cell temperature has been controlled within ± 0.1 °C using a Peltier thermostatic bath (DW621-A/DR62B, Komatsu Electronics Inc.). When temperature is changed between charge and discharge, measurement restarts after confirmation of sufficient temperature stability inside the thermostatic bath. We have recorded the $\phi - x$ profiles in charge–discharge process at several temperatures for a few cycles by the above method.

3. Results and discussion

Initial feature about LiMn_2O_4 spinel is really important for analysis in potential-composition profile. Lattice parameter of the specimen in this research is 8.2463(23) Å, and state of average manganese valence is 3.50. They do not contradict values in the foregoing reports, and this result indicates that we have synthesized almost stoichiometric LiMn_2O_4 spinel.

In order to confirm whether the anomalous stepwise shape reveals or not in discharge profile of LiMn_2O_4 at low temperature ($T \leq 278$ K), we recorded the $\phi - x$ profile in first discharge at 278 K after charge at 273 K (Fig. 3). As a

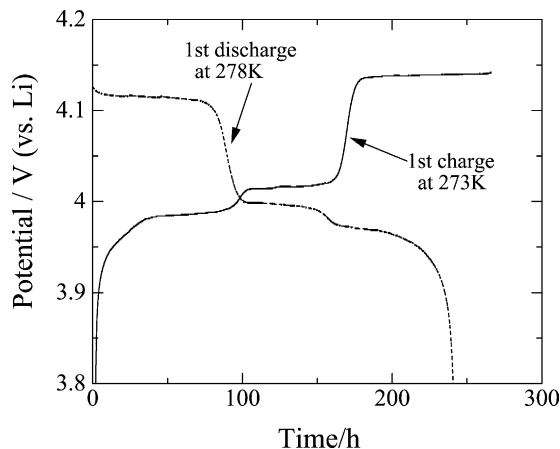


Fig. 3. Anomalous stepwise feature in charge–discharge profile of LiMn_2O_4 at low temperature.

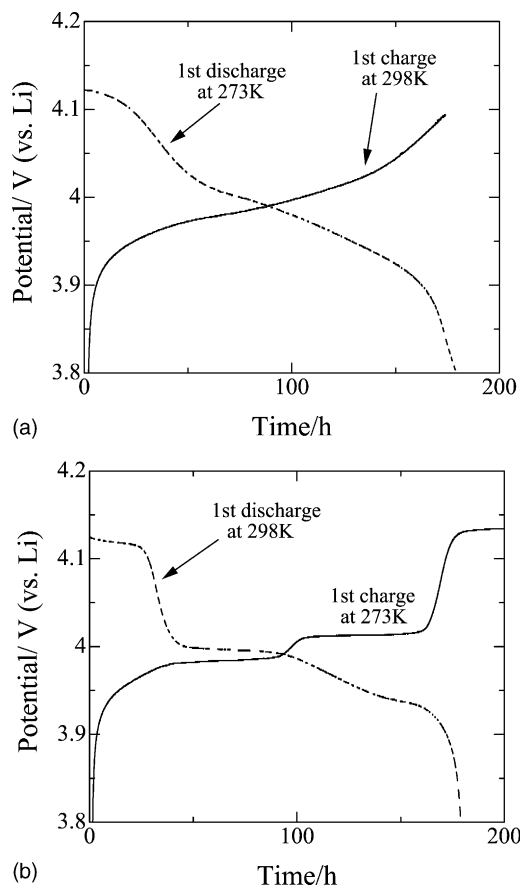


Fig. 4. Temperature hysteresis in first charge–discharge profile of LiMn_2O_4 : (a) charge at 298 K and discharge at 273 K; (b) charge at 273 K and discharge at 298 K.

consequence, the anomaly has been found also in discharge curve. In this case, both first charge–discharge processes were carried out at low temperature.

On the other hand, Fig. 4(a) shows first discharge profile at 273 K after charge at 298 K. The anomaly has never been found in the $\phi - x$ profile here. The profile is different from that of Fig. 3, in spite of the fact that they are recorded at low temperature; $T \leq 278$ K. The shape of discharge curve in Fig. 4(a) shows a gently slope as potential curve in charge at 298 K. Then, Fig. 4(b) describes first discharge profile at 298 K after charge at 273 K. The step at $x \approx 0.7$ (around 120 h here) in the discharge curve becomes indistinct on the condition; however, the discharge profile causes the anomaly as well. The above results demonstrate that LiMn_2O_4 spinel has a hysteresis with temperature in potential–composition profiles of charge–discharge process.

It follows that state of charge process has a large effect on next discharge. On the other hand, discharge process little affects upon next charge. Fig. 5 describes second charge profile at 298 K immediately after first discharge at 278 K (in Fig. 3). The charge profile reveals a usual smooth slope, not a stepwise feature. In contrast to this, potential curve in second charge at 273 K immediately after first discharge at 298 K shows the anomaly.

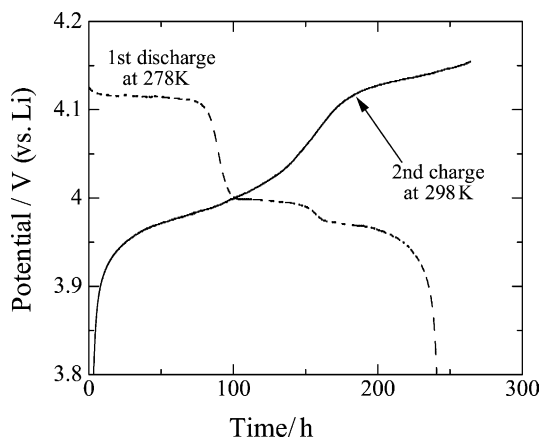


Fig. 5. Neutralization of the temperature hysteresis: second charge profile at 298 K after first discharge at 278 K.

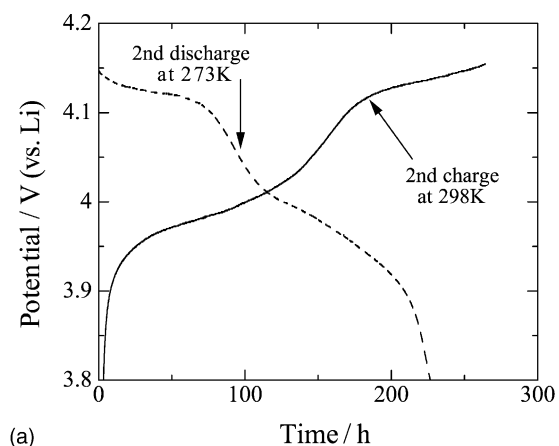
That is, temperature dependence is not completely reversible in charge–discharge profiles of LiMn_2O_4 spinel. The shape of discharge curve reflects previous charge profile within the temperature range of $273 \leq T \leq 298$ K. However, the hysteresis is neutralized when all $8a$ sites in the spinel type structure are filled with lithium ions by discharge. The temperature hysteresis is confirmed repeatedly for several charge–discharge cycles (Fig. 6).

In the hysteresis, it seems that diffusion pass of Li ions in charge (de-intercalation) process remains as it is when Li ions are intercalated in discharge process. From the above results, it is also expected that state of host manganese lattice is strongly related to the anomalous stepwise feature in potential profiles of LiMn_2O_4 , because stoichiometric LiMn_2O_4 spinel and some of manganese oxides show charge–orbital ordering phase with temperature hysteresis around room temperature [18–23].

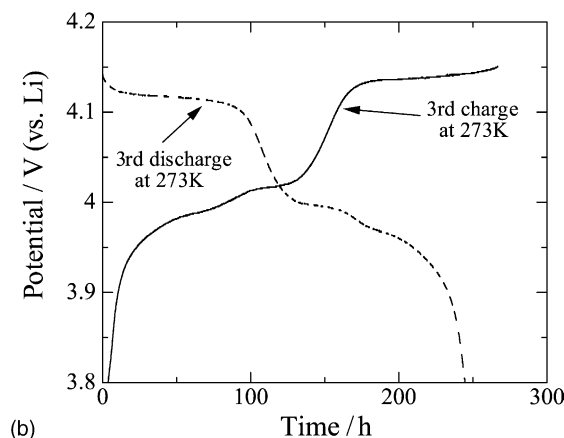
Furthermore, in this research, we have attempted to change temperature when charge was midway. At first, charge profile was recorded to the point, which is corresponding to the anomalous step, $x \approx 0.7$ ($\text{Li}_x\text{Mn}_2\text{O}_4$) at 298 K. Then, charge was restarted after temperature changed to 273 K. When the temperature was changed, a rest time for about 30 min was taken, and circuit of the glass cell and the recording system was completely opened. The Peltier thermostatic bath used in this research can control temperature sufficiently within the rest time.

Fig. 7 describes result of the measurement. In this case, it is attractive that the anomaly is not found in the region at 273 K. As compared with the profile which is recorded continuously at 298 K, they overlap each other in almost all regions.

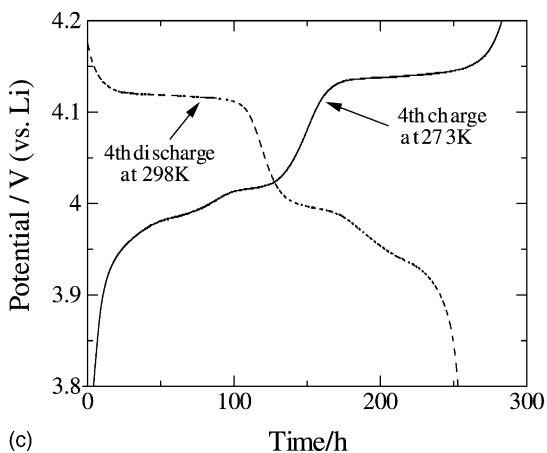
Then, Fig. 8 shows result of opposite case: temperature was changed from 273 to 298 K at the point corresponding to $x \approx 0.7$. In this case, anomalous stepwise feature is found even in the region at 298 K. The results indicate that comparative beginning process in charge ($0.7 \leq x$) decides following charge process ($x \leq 0.7$) in $\text{Li}_x\text{Mn}_2\text{O}_4$.



(a)



(b)



(c)

Fig. 6. The temperature hysteresis recorded in several charge–discharge cycles.

In addition, the anomalous step at $x = 0.5$ has attracted in the profiles. In the past, characteristic gently slope, which is shown in the potential profile of LiMn_2O_4 around room temperature, is speculated as occurrence of a Li ordering phase [24–26], because the host diamond-type lattice has a commensurate ZnS arrangement at $x = 1/2$.

However, it was found that the slope at $x = 0.5$ dramatically becomes perpendicular below room temperature ($T \leq 278 \text{ K}$) by our quasi-equilibrium potential profiles measurements, so we consider a possibility that the “true” Li or-

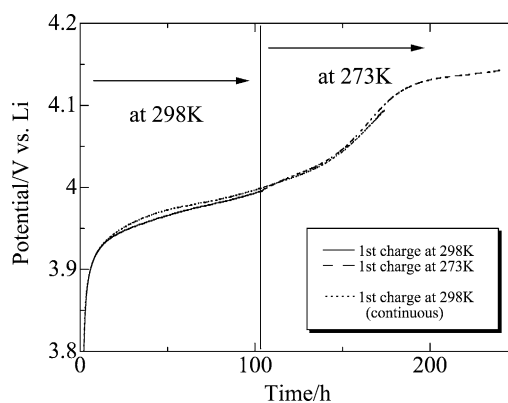


Fig. 7. The potential-composition profile with temperature change from 298 to 273 K at the point corresponding to $x = 0.7$ ($\text{Li}_x\text{Mn}_2\text{O}_4$).

dering phase really occurs at more lower temperature than that was expected so far. We have also demonstrated that the characteristic potential profile in experimental data at 298 K can be reproduced comparatively well by a calculation assuming Li disordered state in the range of $0.5 \leq x \leq 1.0$ ($\text{Li}_x\text{Mn}_2\text{O}_4$) [27–29]. In contrast to this, origin of the step at $x = 0.7$ is not clearly understood by distribution of Li ions, and it is strongly assumed that partial ordering phase in Mn lattice of LiMn_2O_4 ($\text{Mn}^{3+}:\text{Mn}^{4+} = 1.0$) is related [17].

Therefore, assuming that origins of each step ($x = 0.7$ and $x = 0.5$) are different, it can be expected that the slope at $x = 0.5$ becomes very steep not only in discharge profile at 273 K immediately after charge at 298 K but also in the region at 273 K in Fig. 7. However, in this research, both steps at $x = 0.5$ and $x = 0.7$ seem to be likely interlocked, not independent. It predicts a possibility that the steps originate from same mechanism, i.e. charge ordering of Mn (16d) in spinel type structure. It is expected that the step at $x = 0.7$ corresponds to dissolution of ordering phase in LiMn_2O_4 ($\text{Mn}^{3+}:\text{Mn}^{4+} = 1.0$), and the step at $x = 0.5$ is attributed to another charge ordering phase ($\text{Li}_{0.5}\text{Mn}_2\text{O}_4$; $[\text{Li}_{0.5}]_{8a}[\text{Mn}_2]_{16d}[\text{O}_4]_{32e}$, $\text{Mn}^{3+}:\text{Mn}^{4+} = 1:3$). Of course, there is not sufficient evidence for the above interpretation

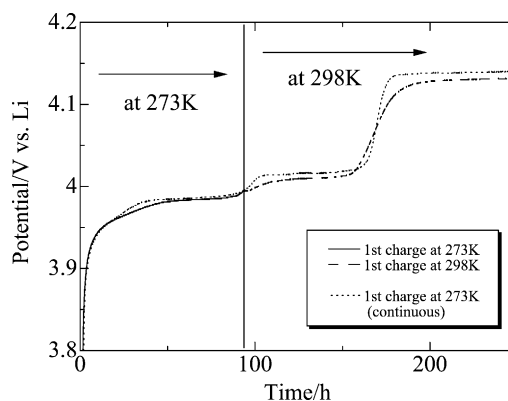


Fig. 8. The potential-composition profile with temperature change from 273 to 298 K at the point corresponding to $x = 0.7$ ($\text{Li}_x\text{Mn}_2\text{O}_4$).

yet. It is very necessary indeed to observe structure at the points of anomalous steps directly in order to solve the detail of anomaly and the temperature hysteresis in charge–discharge process of LiMn_2O_4 . The solution is believed to be also significant for practical application of LiMn_2O_4 spinel as a cathode material for lithium ion battery.

4. Conclusions

As a result of measurement in the temperature range around room temperature ($273 \leq T \leq 298 \text{ K}$), anomalous stepwise feature is also found in potential curve of LiMn_2O_4 spinel in discharge process when both charge–discharge are carried out at low temperature ($T \leq 278 \text{ K}$). However, the anomaly does not reveal in discharge process when the specimen is charged at 298 K.

There is a temperature hysteresis in charge–discharge profile of LiMn_2O_4 , and completion of discharge cancels the hysteresis. It is confirmed repeatedly in charge–discharge cycles.

Li ions de-intercalation process has a large effect on next intercalation in LiMn_2O_4 . Especially, beginning stage in charge process is very important for lithium intercalation/de-intercalation in LiMn_2O_4 spinel. Whether the anomaly reveals or not is determined by process of Li ions de-intercalation in the region $0.7 \leq x$ ($\text{Li}_x\text{Mn}_2\text{O}_4$).

It is also important to solve mechanism of the hysteresis for practical utility of LiMn_2O_4 spinel as a cathode material for lithium ion battery, in relation to cycle performance.

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