ELSEVIER

Phase transition observed in potential–composition profiles of $Li_xMn_2O_4$

Hironobu Abiko [a,*], Mitsuhiro Hibino [b], Tetsuichi Kudo [b]

[a] *Department of Human Engineering, National Institute of Industrial Health, 6-21-1 Nagao, Tama ward, Kawasaki, Kanagawa 214-8585, Japan*
[b] *Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan*

Abstract

Open circuit voltage (OCV) profiles of spinel type lithium manganese oxide $Li_xMn_2O_4$ ($x \leq 1$) have been recorded at several temperatures (243 K $\leq T \leq$ 323 K) using a single three-electrode glass cell. Deintercalation of Li ions from $Li_xMn_2O_4$ has been carried out at low temperature (243 K), and then OCV profile has been measured at both the processes of raising and descending temperatures on each state of lithium content (x).

Quasi-equilibrium potential profiles above room temperature (298 K $\leq T$), which are results of continuous measurements by first charge, overlap with OCV profiles in the process of raising temperature well. However, around $x = 0.5$, quasi-equilibrium potential profiles and OCV profiles do not overlap at low temperature ($T \leq$ 278 K). This result indicates that the low-temperature phase at $x = 0.5$ in $Li_xMn_2O_4$ is very sensitive to temperature change.

Temperature dependence of OCV profiles in the process of descending temperature corresponds to a simulation based on assumption that distribution of Li ions is disordered in $Li_xMn_2O_4$ ($0.5 \leq x < 1$).
© 2003 Elsevier B.V. All rights reserved.

Keywords: Phase transition; Temperature hysteresis; Temperature dependence; Lithium ion battery; $LiMn_2O_4$; Battery material

1. Introduction

Spinel type lithium manganese oxide $LiMn_2O_4$ has received much attention for a cathode material of lithium ion battery [1–5], and its characteristic potential profile has been attracted very much from a viewpoint of structural study in deintercalation/intercalation of Li ions. In order to understand in detail, there have been several in situ or ex situ structural reports with XRD or neutron diffraction measurements [6–9]. In addition, realization of the characteristic potential profile of $Li_xMn_2O_4$ by a simulation based on theoretical calculations has been studied frequently [10–16].

Accurate measurements of potential–composition (ϕ–x; $Li_xMn_2O_4$) profiles are very important for realization and precision of the calculations. Of course the measurements are also extremely useful for structural study of $Li_xMn_2O_4$. We have measured quasi-equilibrium potential profiles of $Li_xMn_2O_4$ at several temperatures, and clarified their temperature dependence around room temperature (~298 K).

Especially as a result, drastic change at 278 K in the profile has been found; the slope at $x = 0.5$ in $Li_xMn_2O_4$ becomes far steeper, and a new voltage step appears at $x \fallingdotseq 0.7$ in the profile [17,18].

Until now, the characteristic potential profile of $Li_xMn_2O_4$, a gentle slope around $x = 0.5$ is often assumed appearance of Li-ordering phase, because the host diamond-type lattice has a commensurate ZnS arrangement at $x = 0.5$. Most of above-mentioned theoretical calculations have been carried out based on an assumption that Li-ordering phase exists in the region around 298 K [10–15].

In contrast to this, we have proposed a different opinion that the Li-ordering phase at $x = 0.5$ appears at lower temperature more than that was expected, as is shown in the result of quasi-equilibrium potential measurements. That is, distribution of Li ions in $Li_{0.5}Mn_2O_4$ is disordered above room temperature (298 K $\leq T$). This interpretation reaches that the gentle slope in potential profiles of $Li_xMn_2O_4$ does not originate from ordering of Li ions in 8a sites of spinel type structure (Fd3m).

Further, Kudo and Hibino [16] have shown comparative good accordance between their simulation based on disordered distribution of Li ions in $Li_xMn_2O_4$ ($0.5 \leq x < 1$) and

---

* Corresponding author. Tel.: +81-44-865-6111; fax: +81-44-865-6124.
E-mail address: abiko@niih.go.jp (H. Abiko).

a real potential profile data at room temperature. In recent years, some structural and thermal reports about $Li_xMn_2O_4$ in charge/discharge process have indicated that Li-ordering phase at $x = 0.5$ is not found around 298 K [8,19]. They support our opinion concerning ordering of Li ions and potential profiles of $LiMn_2O_4$.

In this research, we have measured quasi-equilibrium potential profiles above 298 K at first, and compare the slopes at $x = 0.5$. Assuming that Li-ordering phase exists at 298 K, the slope is expected to become more gentle at higher temperature. And then we have recorded open circuit voltage (OCV) profiles at several temperatures (243 K $\leq$ $T \leq$ 323 K) using a single cell, which is the same type used in the measurements of quasi-equilibrium potential profiles.

Charge/discharge process of $Li_xMn_2O_4$ have temperature dependence [17] and temperature hysteresis [20]. That is, behavior of Li-deintercalation/intercalation is considerably and complicatedly affected by temperature change. Taking into account of this point, we have measured OCV at both processes of raising (243 K $\rightarrow$ 323 K) and descending (323 K $\rightarrow$ 243 K) temperatures on each state of lithium content (x; $0.5 \leq x < 1$). In this paper, we will report consideration concerning order/disorder phase transition, which is expected at $x = 0.5$, from a standpoint of potential profiles on the function of state of charge based on the results of above-mentioned measurements.

2. Experimental

Both measurements for quasi-equilibrium potential–composition (ϕ–x) profiles and OCV profiles are performed using gas-tight three-electrode glass cells, with almost stoichiometric $LiMn_2O_4$ as a cathode material in this research. The cells are filled with argon gas, and sealed up tightly. The cell temperature has been controlled within $\pm 0.1\,^{\circ}C$ using a Peltier thermostatic bath (DW621-A/DR62B, Komatsu Electronics). All these profiles are gained as a process of Li-deintercalation from $LiMn_2O_4$ (first charge).

Powder specimen of $LiMn_2O_4$ has been prepared from Li_2CO_3 and $MnCO_3$ (both the products of Soekawa Chemical) by conventional solid-state reaction [17,18]. 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 [18].

Preparation of the cathode electrode and construction of the cells are according to the previous report [17]. The electrolyte is 1 M $LiClO_4$/propylene carbonate (PC) solution (supplied by Kishida Chemical or Mitsubishi Chemical), and lithium foil (Soekawa Chemical) pressed onto a nickel mesh (Nilaco) is used as the anode and the reference electrodes.

Manner of recording the ϕ–x profiles in the research is also according to the previous report [17]. The ϕ–x profiles are recorded using HJ-101SM6 system (Hokuto Denko) under a constant current condition. To suppress polarization

over potential, a very small value of the current density, i.e., 0.428 mA per 1 g of each specimen ($LiMn_2O_4$) has been used in first charge. The ϕ–x profiles are recorded by continuous charge with a very weak electric current, thus in the strict sense, these profiles are different from OCV profiles.

OCV profiles in this research are recorded in a manner as follows. Li ions are deintercalated from $Li_xMn_2O_4$ ($x \leq$ 1) to the appointed lithium content (x) at 243 K with the same electric condition as measurements of the ϕ–x curves. And then OCV has been measured at both processes of raising (243 K $\rightarrow$ 253 K $\rightarrow$ 263 K $\rightarrow$ 273 K $\rightarrow$ 278 K $\rightarrow$ 283 K $\rightarrow$ 285 K $\rightarrow$ 288 K $\rightarrow$ 298 K $\rightarrow$ 303 K $\rightarrow$ 313 K $\rightarrow$ 323 K) and descending (323 K $\rightarrow$ 313 K $\rightarrow$ 303 K $\rightarrow$ 298 K $\rightarrow$ 288 K $\rightarrow$ 285 K $\rightarrow$ 283 K $\rightarrow$ 278 K $\rightarrow$ 273 K $\rightarrow$ 263 K $\rightarrow$ 253 K $\rightarrow$ 243 K) temperatures on each state of lithium content (x). Rest time for about 1 h has been kept before measurement of voltage at each temperature, and the circuit of the cell is completely opened in the rest time. We have repeated a sequence of operations and gained OCV profiles at several temperatures in the region $0.5 \leq$ $x < 1$, in which $Li_xMn_2O_4$ is single spinel phase around 298 K [7].

3. Results and discussion

It is very important to improve effectiveness of $LiMn_2O_4$ in a cathode material in order to record accurate relation between potential and lithium content (x) in $Li_xMn_2O_4$, besides suppression of polarization over potential. That is, conductivity of $LiMn_2O_4$ is not sufficient for function as a cathode electrode at all, so conductive additive (mainly carbon) is indispensable indeed. Further, insulator as binder in cathode material, for example PTFE (polytetrafluoroethylene) can be a factor that reduces effectiveness of $LiMn_2O_4$, so net weight of binder is desirable to be small as possible. Taking account of these points, cathode electrode in the cell used in this research has been prepared for better contact between cathode material and electrolyte [17].

Fig. 1 shows the ϕ–x profile in this research and some OCV profiles in the foregoing reports at room temperature ($T \cong$ 298 K) [7,21]. The ϕ–x profile in this research corresponds with other OCV data by other researches approximately, and shows a feature which undergoes in lower voltage region compared with the OCV data. This indicates that the ϕ–x profile by our measurements is suppressed polarization over potential and reveals more accurate potential–composition profile in $Li_xMn_2O_4$ at 298 K.

In contrast, recently Thomas et al. [22] have reported a potential profile of $Li_xMn_2O_4$ ($x \leq$ 1), which is different from ones reported in the previous reports. They asserted that the profile was mitigated experimental error (side reactions or self-discharge) and corrected by their calculations. Their study is attractive, but we take notice in preparation of cells in the report. In the cathode electrode, compared with the previous reports of OCV profiles and our research, rate
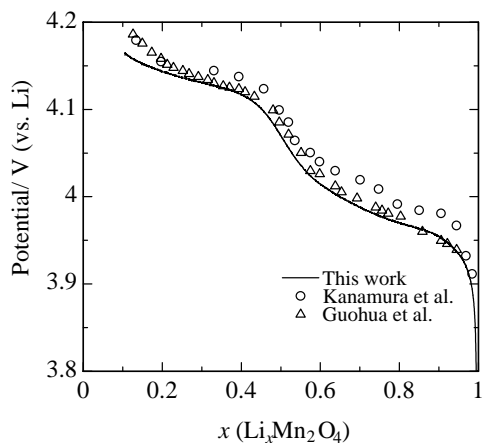
Fig. 1. The ϕ–x profile in this research and some OCV profiles in the foregoing reports [7,21] at room temperature ($T \cong 298$ K).

of conductive additive (carbon) was extremely low (7 wt.%; 30 wt.% by Kanamura et al., 20 wt.% by Guohua et al., 29.9 wt.% by ours), and on the other hand, rate of binder was comparatively high (10.6 wt.%; non-fixed rate (very small quantity) by Kanamura et al., 5 wt.% by Guohua et al., 0.5 wt.% by ours). Actually, the profile in their report seems to shift to higher lithium content region. Similar indication can be applied to an early study about $LiMn_2O_4$ [6].

The ϕ–x profiles in this research also contain small amount of uncertainty. They are quasi-equilibrium potential, so polarization over potential is not completely excluded especially in the region $x \fallingdotseq 0$ and $x \fallingdotseq 1$ more than OCV after all. They are gained by continuous charge process, though it is carried out with a very weak electric current. However, we have confirmed that an experimental error caused by using many cells in measurements is not so large in this research. And then we have continued to apply the method, because it can record charge (or discharge) process, which reflects structure of $Li_xMn_2O_4$ on each state minutely, much better than OCV profiles. Moreover, around 298 K the ϕ–x profile overlaps with OCV, which is measured by intermittent mode very well.

At first, Fig. 2(a) shows the ϕ–x profile at 288 K. Potential–composition profile of $LiMn_2O_4$ has temperature dependence especially below room temperature ($T \leq 298$ K), and low-temperature phase appears at $x = 0.5$ and $x \fallingdotseq 0.7$ certainly. In the ϕ–x profile at 288 K, a weak plateau (or kink) at $x \fallingdotseq 0.7$ is observed and the slope at $x = 0.5$ seems to slightly change from gentle state at 298 K. In Fig. 2(b), the step at $x = 0.5$ and $x \fallingdotseq 0.7$ become clear in the ϕ–x profile at 283 K. This confirms that occurrence of the low-temperature phase at $x = 0.5$ and $x \fallingdotseq 0.7$ cause at 278 K $\leq T < 288$ K in detail. Next, Fig. 3 shows several ϕ–x profiles at 298 K $\leq T$; 298, 303 and 313 K. The three-electrode glass cell in the research cannot be used in measurements for the ϕ–x profile at 323 K $\leq T$, because it is able to keep air-tightness for less than about 2 days in the temperature region.
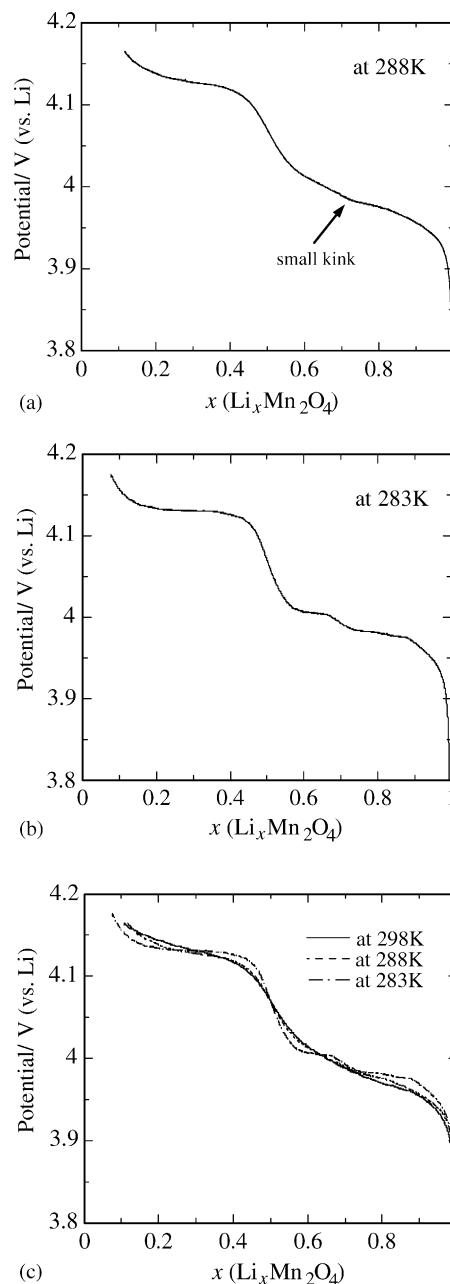

Fig. 2. Phase transition observed in the ϕ–x profile at: (a) 288 K; (b) 283 K; (c) 283 K $\leq T \leq$ 298 K.

In Fig. 3, the slope at $x = 0.5$ seems to be almost constant at 298 K $\leq T \leq 313$ K. On the other hand, potential profile at $x \leq 0.45$ or $0.6 \leq x$ have dependence on temperature obviously. Thus, weakening of the slope at $x = 0.5$ is not brought about at 298 K $< T \leq 313$ K. The result raises doubts about assumption that Li-ordering phase exists at $x = 0.5$ and $T \cong 298$ K, which has been often expected so far.

Further, we have recorded OCV profiles at several temperatures (243 K $\leq T \leq 323$ K) in order to exclude effect of polarization over potential more carefully. The measurements have been carried out with the same type cell used in
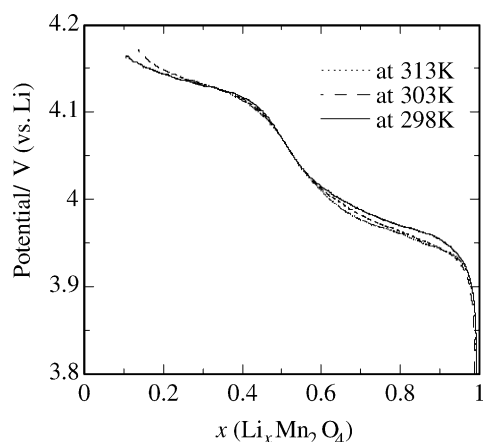
Fig. 3. Quasi-equilibrium potential–composition profiles at 298, 303 and 313 K.

the measurements of quasi-equilibrium potential profiles, for sufficient removal of an experimental error originates from using many cells. Charge/discharge process of $LiMn_2O_4$ have not only drastic temperature dependence around room temperature, but also temperature hysteresis [20]. Behavior of potential profiles in $Li_xMn_2O_4$ is considerably and complicatedly affected by temperature change. From these results, it is easily expected that OCV on each state of lithium content (x) at process of heating is different from one at process of cooling. OCV profiles in this research have been recorded at both processes of raising (243 K → 253 K → 263 K → 273 K → 278 K → 283 K → 285 K → 288 K → 298 K → 303 K → 313 K → 323 K) and descending (323 K → 313 K → 303 K → 298 K → 288 K → 285 K → 283 K → 278 K → 273 K → 263 K → 253 K → 243 K) temperatures on each state of lithium content.

Fig. 4 is the results of a series of OCV measurements. Each figure shows OCV profile in both heating and cooling processes, and some figures also show continuous ϕ–x profile measured with another cell at an aimed temperature. These figures reveal that there is difference between two processes in OCV at low temperature certainly ($T \leq 278$ K). These differences correspond to temperature hysteresis in deintercalation/intercalation of Li ions in $Li_xMn_2O_4$. In addition, the slope at $x = 0.5$ in OCV profiles contradicts the steep slope in the ϕ–x profiles at low temperature. This phenomenon means that the low-temperature phase at $x = 0.5$ is very sensitive to temperature change, and it is different from the low-temperature phase at $x \doteqdot 0.7$, which appears also in OCV profiles of heating process. On the other hand, OCV profiles of both heating and cooling processes overlap at 298 K $\leq T$. Moreover, both OCV profiles overlap with the ϕ–x profile especially at 298 K. So the ϕ–x profile in this research is extremely almost equilibrium potential–composition profile near around 298 K.

Making a comparison between two processes in OCV profiles in the region $0.6 \leq x$, heating process is reflected

by the appearance of low-temperature phase, but in cooling process, the effect is lost completely. Fig. 5 shows only OCV profiles in cooling process at several temperatures (243 K $\leq T \leq$ 323 K). In the profiles, order of potential which depends on temperature reverses at $x = 0.7$ as boundary, and OCV potentials seem to come to convergence at $x = 0.5$. Kudo et al. had once shown a simulation, which realizes comparative good accordance with real data. This is based on disordered distribution of Li ions and the configuration entropy such as the form analogous to the exact entropy of the one-dimensional lattice [16]. There have been some studies of simulation concerning the characteristic potential profile of $Li_xMn_2O_4$. They are based on assumption that Li-ordering phase exists at $x = 0.5$ in $Li_xMn_2O_4$ around 298 K, and mainly focused on realization of the slope at $x = 0.5$ in calculated profiles. On the other hand, they did not confirm correspondence between simulation and real data of potential curves, or showed a calculated profile, which was quite different from real profile in the whole region of lithium content [10–15].

The profile calculated by Kudo et al. is worthy of mention that it can realize the characteristic shape of potential profile of $Li_xMn_2O_4$ in the region $0.5 \leq x < 1$, in which $Li_xMn_2O_4$ is a single spinel phase around 298 K, and corresponds with a real profile data very well (Fig. 6). Furthermore, it also has made reference to temperature dependence of potential profiles of $Li_xMn_2O_4$ (Fig. 7) [23,24]. To the best of our knowledge, there is no parallel to the study until now. Of course, the results of calculations by Kudo et al. contradict to real ϕ–x profiles at $T \leq 278$ K, which are affected by appearance of low-temperature phase in $Li_xMn_2O_4$, because there are no considerations about ordering of Li ions in the spinel type structure, charge ordering in Mn-lattice and so on in the simulations.

However, temperature dependence of OCV profiles in cooling process, in which expected that effect of low-temperature phase is lost completely, corresponds with calculation by Kudo et al. very much. It is hard to take this as only an accidental correspondence. This experimental result indicates appropriation of simulation based on theoretical calculation by Kudo et al., except for anomaly in potential–composition profile of $LiMn_2O_4$ at low temperature ($T \leq 278$ K).

Recently, Liu et al. [8] have reported that Li-ordering phase is not confirmed in $Li_{0.5}Mn_2O_4$ by in situ study with neutron diffraction experiments. Also, Kobayashi et al. [19] have reported that complete site preference (thus complete Li-ordering phase) at $x = 0.5$ does not agree with entropy change in thermal experiments, using coin type cells. These reports support that our opinion concerning Li-ordering phase at $x = 0.5$ ($Li_xMn_2O_4$).

Further, the result suggests the characteristic shape of potential profiles of $Li_xMn_2O_4$ does not originates from Li-ordering phase at $x = 0.5$. The shape of potential curves may be hold in disordered distribution of Li ions, at comparatively high temperature.
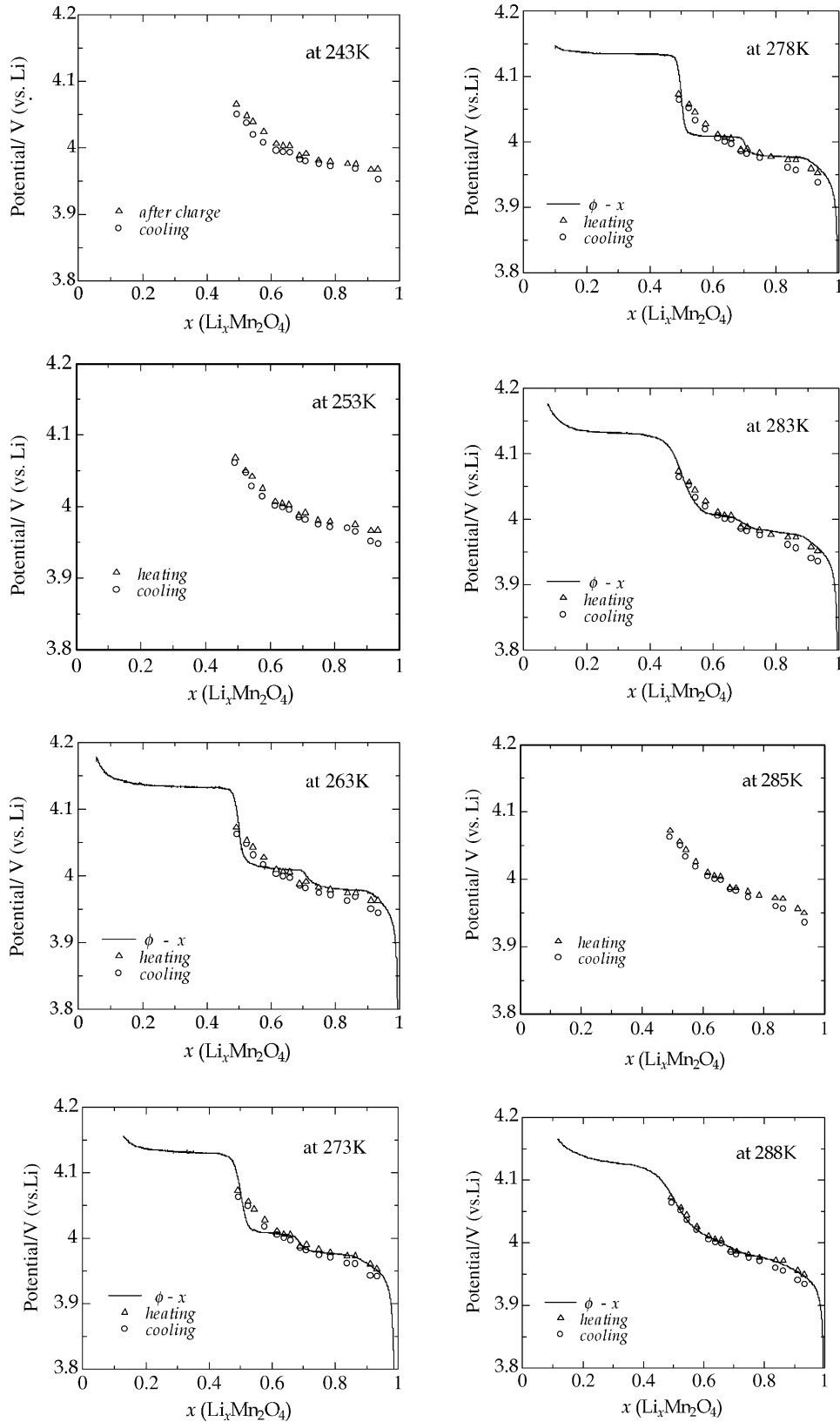
Fig. 4. OCV profiles of both heating and cooling processes (243 K ≤ T ≤ 323 K), compared with the φ–x profile at 263 K ≤ T ≤ 313 K.
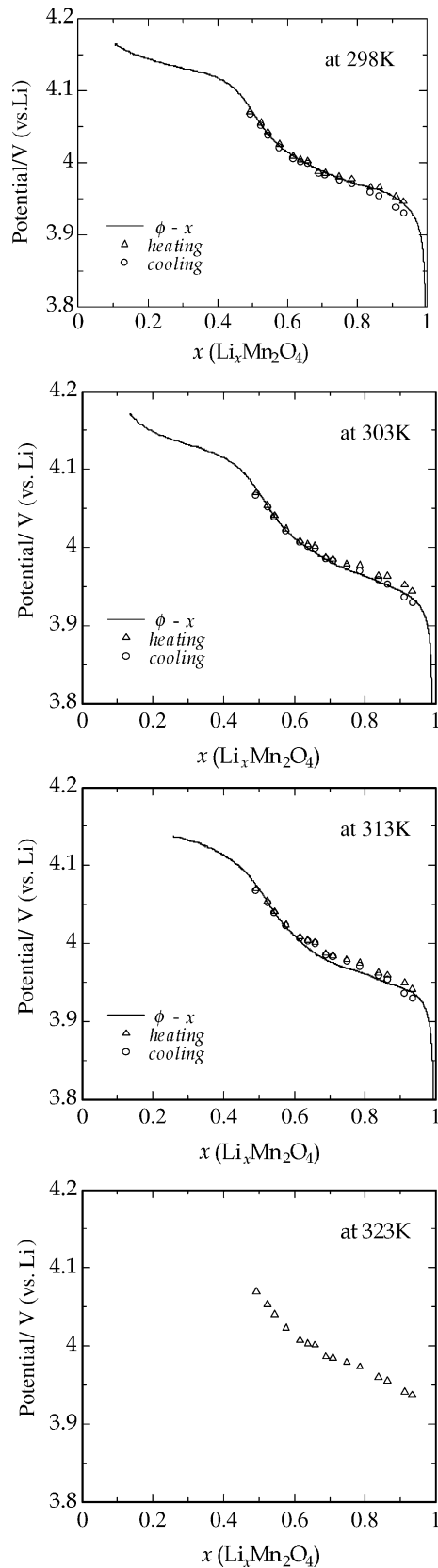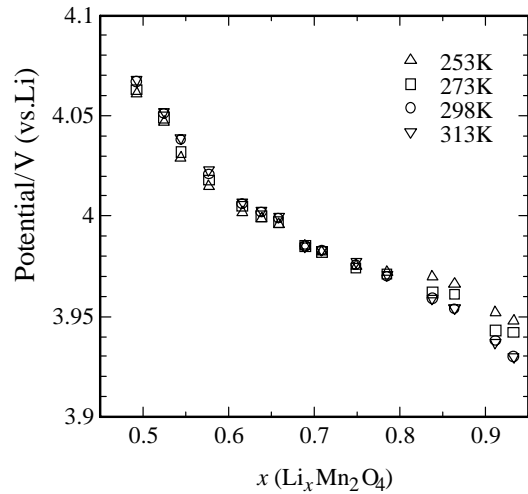
Fig. 4. (*Continued*).

Fig. 5. Temperature dependence of OCV profiles measured in cooling process.

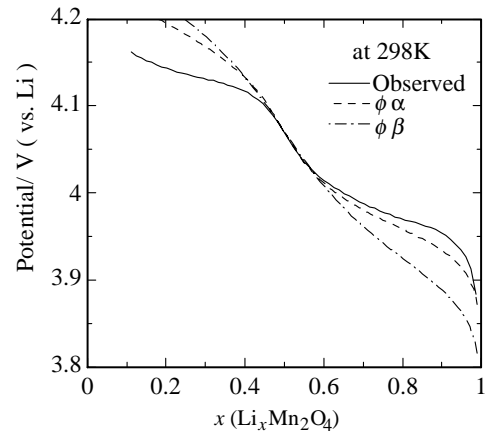

Fig. 6. Simulation of potential–composition profile by Kudo et al. [16,23,24] and real data at 298 K. ϕ_α: 1D approximation, $E_S = -4.17$ eV, $u = J/kT = 1.86$. ϕ_β: Bethe's approximation, $E_S = -4.22$ eV, $u = J/kT = 2.63$ (E_S is the site energy, J is the repulsive interaction between adjacent Li ions).
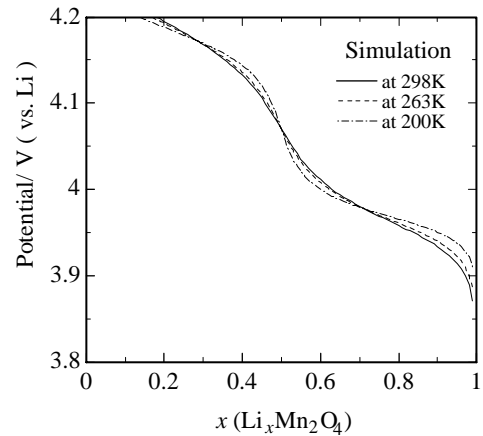

Fig. 7. Temperature dependence of potential–composition profile simulated with 1D approximation by Kudo et al. [23,24] ($E_S = -4.17$ eV, $u = J/kT = 1.86$).

Structure and distribution of Li or Mn ions in $Li_xMn_2O_4$ in Li-deintercalation (or intercalation) is not solved enough in detail yet. However, these structural changes in $Li_xMn_2O_4$ are fully in detail reflected in the ϕ–x profiles or OCV profiles in each process, which have been measured in the research.

4. Conclusions

Deintercalation/intercalation of Li ions in lithium manganese spinel oxide is affected by temperature very complicatedly and sensitively. There is difference between heating and cooling process in OCV profiles of $Li_xMn_2O_4$ ($0.5 \leq x < 1$, $243\,K \leq T \leq 323\,K$), especially in the temperature region $T \leq 278\,K$. This is attributed to an effect of temperature hysteresis in deintercalation of Li ions. Further, at $T \leq 278\,K$, the quasi-equilibrium potential–composition profiles contradict to both OCV profiles in the slope at $x = 0.5$. This phenomenon indicates that the low-temperature phase at $x = 0.5$ is very sensitive and delicate to temperature change on the lithium content.

The OCV profiles in descending temperature is expected to be not affected by appearance of the low-temperature phases, both at $x = 0.5$ and $x \doteqdot 0.7$ in $Li_xMn_2O_4$. These profiles show the same temperature dependence simulated with the calculation by Kudo et al., which assumes disordered distribution of Li ions in 8a sites of $Li_xMn_2O_4$. In addition, the quasi-equilibrium potential–composition profiles at $298\,K < T \leq 313\,K$ have shown no weakening in the slope at $x = 0.5$. These results suggest that the characteristic potential profiles of $LiMn_2O_4$ around room temperature ($T \cong 298\,K$) does not originate from Li-ordering phase at $x = 0.5$ in $Li_xMn_2O_4$.

References

[1] R.J. Gummow, A. de Kock, M.M. Thackeray, Solid State Ionics 69 (1994) 59.
[2] D. Guyomard, J.M. Tarascon, Solid State Ionics 69 (1994) 222.
[3] Y. Gao, J.R. Dahn, J. Electrochem. Soc. 143 (1) (1996) 100.
[4] C. Masquelier, M. Tabuchi, K. Ado, R. Kanno, Y. Kobayashi, Y. Maki, O. Nakamura, J.B. Goodenough, J. Solid State Chem. 123 (1996) 255.
[5] R. Kanno, A. Kondo, M. Yonemura, R. Gover, Y. Kawamoto, M. Tabuchi, T. Kamiyama, F. Izumi, C. Masquelier, G. Rousse, J. Power Sources 81–82 (1999) 542.
[6] T. Ohzuku, M. Kitagawa, T. Hirai, J. Electrochem. Soc. 137 (3) (1990) 769.
[7] K. Kanamura, H. Naito, T. Yao, Z. Takehara, J. Mater. Chem. 6 (1) (1996) 33.
[8] W. Liu, K. Kawal, G.C. Farrington, J. Electrochem. Soc. 145 (2) (1998) 769.
[9] X.Q. Yang, X. Sun, S.J. Lee, J. McBreen, S. Mukerjee, M.L. Daroux, X.K. Xing, Electrochem. Solid-State Lett. 2 (4) (1999) 157.
[10] Y. Gao, J.N. Reimers, J.R. Dahn, Phys. Rev. B 54 (6) (1996) 3878.
[11] G. Ceder, A. Van der Ven, Electrochim. Acta 45 (1999) 131.
[12] A. Van der Ven, C. Marianetti, D. Morgan, G. Ceder, Solid State Ionics 135 (2000) 21.
[13] V.I. Kalikmanov, M.V. Koudriachova, S.W. de Leeuw, Solid State Ionics 136–137 (2000) 1373.
[14] V.I. Kalikmanov, S.W. de Leeuw, Solid State Ionics 116 (7) (2002) 3083.
[15] V.I. Kalikmanov, S.W. de Leeuw, Solid State Ionics 154–155 (2002) 195.
[16] T. Kudo, M. Hibino, Electrochim. Acta 43 (7) (1998) 781.
[17] H. Abiko, M. Hibino, T. Kudo, Electrochem. Solid-State Lett. 1 (3) (1998) 114.
[18] H. Abiko, M. Hibino, T. Kudo, Solid State Ionics 135 (2000) 115.
[19] Y. Kobayashi, H. Miyashiro, N. Terada, T. Ohta, H. Kawai, M. Shirakata, The Electrochemical Society Meeting Abstracts, vol. 99, No. 2, Honolulu, HI, October 17–22, 1999 (Abstract No. 299).
[20] H. Abiko, M. Hibino, T. Kudo, J. Power Sources 123 (1) (2003) 48.
[21] L. Guohua, H. Ikuta, T. Uchida, M. Wakihara, J. Electrochem. Soc. 143 (1996) 178.
[22] K.E. Thomas, C. Bogatu, J. Newmann, J. Electrochem. Soc. 148 (6) (2001) A570.
[23] T. Kudo, H. Abiko, M. Hibino, Extended Abstracts of the 12th International Conference on Solid State Ionics, Sani, Halkidiki, Greece, June 1999, pp. 29–30.
[24] T. Kudo, H. Abiko, M. Hibino, Denchi Gijutsu (Battery Technol.) 12 (2000) 41 (in Japanese).