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## Rapid evaluation of charge/discharge properties for lithium manganese oxide particles at elevated temperatures

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**Abstract** A microelectrode technique was applied to investigate the electrochemical properties of  $\text{LiMn}_2\text{O}_4$  particles at elevated temperatures. Cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  were measured after the particles were exposed to the electrolytes. This technique results in rapid and precise evaluation of the redox behavior of the materials. A significant capacity fading was observed in 1 M  $\text{LiPF}_6/\text{EC}+\text{PC}$  electrolytic solution, which indicates that both  $\text{LiMn}_2\text{O}_4$  and  $\text{LiPF}_6$  participate in the reaction to produce an inert material on the particle surface. Next, the capacity fading for two different BET surface area particles were compared using 1 M  $\text{LiPF}_6/\text{EC}+\text{PC}$  at 50 °C. The reaction was found not to be controlled by the surface area. Finally, a  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  particle was employed. The fading in discharge was ca. 10% for 50 cycles even at 50 °C, which means that the partial substitution of Mn in  $\text{LiMn}_2\text{O}_4$  by Li substantially enhanced the capacity stability.

**Keywords** Microelectrode technique · Lithium manganese oxide spinel · Charge/discharge properties · Elevated temperature

### Introduction

Lithium manganese oxide spinel ( $\text{LiMn}_2\text{O}_4$ ) has been extensively investigated during the last 10 years as a 4-V cathode (positive electrode) for lithium-ion cells [1]. The merits of the relative abundance of Mn, its moderate

cost and low toxicity have made this material more attractive than other materials such as cobalt or nickel. However,  $\text{LiMn}_2\text{O}_4$  is well known to exhibit significant capacity fading during charge-discharge cycles, particularly at elevated temperatures [2, 3, 4, 5, 6, 7, 8, 9]. For independent  $\text{LiMn}_2\text{O}_4$ , the mechanism is usually interpreted by a disproportionation reaction of  $\text{Mn}^{3+}$  into the electrolyte (i.e.,  $2\text{Mn}^{3+}_{\text{solid}} \rightarrow \text{Mn}^{4+}_{\text{solid}} + \text{Mn}^{2+}_{\text{solv}}$ ) [10, 11]. Generally, the material performance is evaluated using a whole cell construction having a binder resin and some additives such as a conductive carbon. Therefore, decomposition of the solvent molecules at the carbon surface and manganese dissolution by the reaction product often occur [12, 13]. The cathode (and of course, the anode also) is thus complicated; it is very difficult to reveal the intrinsic electrochemical characteristics of the electrode material itself.

From a microscopic viewpoint, we have recently developed an electrochemical measurement method for a single particle of electrode materials using a microelectrode technique. We have demonstrated its ability to evaluate rapidly the electrochemical characteristics of single particles, especially electrode active materials, without any influence of the binder resin or electrically conductive additives such as carbon [14, 15, 16, 17, 18, 19, 20, 21]. Thus far, these experiments were conducted only at room temperature, because temperature control seems to be difficult with microelectrode manipulation in a dry box. Very recently, we succeeded in improving the electrochemical apparatus for elevating the cell temperature and reported some basic thermal properties for some kinds of electrode active materials, including  $\text{LiMn}_2\text{O}_4$  [22, 23].

In this report, we further investigate the thermal properties of lithium manganese oxide using this microvoltammetric technique in order to reveal unique electrochemical characteristics of a single particle of  $\text{LiMn}_2\text{O}_4$  at elevated temperatures from the standpoint of practical use [24, 25]. Firstly, the cyclic voltammetry behavior was measured with a single particle influenced by the exposure time in electrolyte solution prior to the

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measurement. Next, the effect of the surface area of the particle was investigated. Moreover, the electrochemical stability of  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  was also compared with that of  $\text{LiMn}_2\text{O}_4$ .

## Experimental

Two types of  $\text{LiMn}_2\text{O}_4$  particles were used in this study. One was supplied from Nikki Chemical (Japan), the particle being ideally spherical. The BET surface area of the  $\text{LiMn}_2\text{O}_4$  was found to be  $0.6 \text{ m}^2/\text{g}$  using  $\text{N}_2$  absorption/desorption measurements (ASAP2010, Shimadzu, Japan). The other was synthesized using the so-called "citrate process". Stoichiometric amounts of  $\text{LiNO}_3$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in distilled water containing citric acid (twice the  $\text{LiNO}_3$  amount), and then the resulting solution was evaporated in a rotary evaporator at  $80 \text{ }^\circ\text{C}$  for at least 24 h. The pink powdery precursor of the citrate complex was obtained. The final product,  $\text{LiMn}_2\text{O}_4$ , was obtained from the calcination of the resultant precursor at  $700 \text{ }^\circ\text{C}$  for 12 h in oxygen. The BET surface area of the obtained  $\text{LiMn}_2\text{O}_4$  was assessed to be  $10.43 \text{ m}^2/\text{g}$  using  $\text{N}_2$  absorption/desorption measurements.

The apparatus for the electrochemical measurement of a single particle is shown in Fig. 1. A thermoelectric element (SL-10W, Nippon Blower, Japan) was placed on an  $x$ - $y$ - $z$  axis remotely controllable stage (model M9103, Chuouseiki, Japan), and an electrochemical cell made of Teflon was placed on it. The wall of the cell was covered with alumina wool to prevent heat loss. The cell temperature was controlled by a thermal controller in combination with the thermoelectric element and a Cu-W thermocouple. In a preliminary experiment, the temperature difference between the solution in the cell and the wall of the cell was within  $\pm 0.5 \text{ }^\circ\text{C}$ . The constant temperature was achieved within 20 min after the heater element was used.

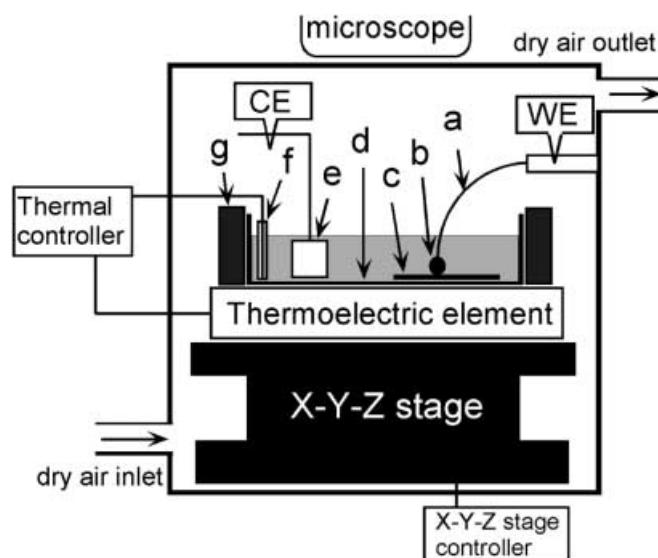
The electrochemical measurement was carried out by the following procedure. A Pt-Rh filament microelectrode ( $25 \text{ }\mu\text{m}$  in diameter) was used as a current collector, which was coated with a thin film of Teflon (Cytop, Asahi Glass, Japan) to minimize background current. The contact of the microelectrode with a target particle was achieved by manipulating the  $x$ - $y$ - $z$  stage, and

the operation was monitored by a stereomicroscope (SMZ-U, Nikon, Japan). A Li foil attached to a Ni mesh ( $9 \times 6 \text{ mm}^2$ ) served as both the counter and reference electrodes. The electrolyte was  $1 \text{ M LiClO}_4$  or  $1 \text{ M LiPF}_6$  in a mixture of 50/50 vol% ethylene carbonate (EC) and propylene carbonate (PC) (Li ion battery grade, Mitsubishi Chemical, Japan). Electrolytes were used as received unless otherwise stated. The water content in the electrolyte solutions was less than 50 ppm, as measured by the Karl-Fischer method (CA-06, Mitsubishi Chemical, Japan). All electrochemical measurements were carried out with a potentiostat/galvanostat (HA-150, Hokuto Denko, Japan) in a glove box ( $-70 \text{ }^\circ\text{C}$  dew point) filled with air dried by a dryer (model 75-20, Balston).

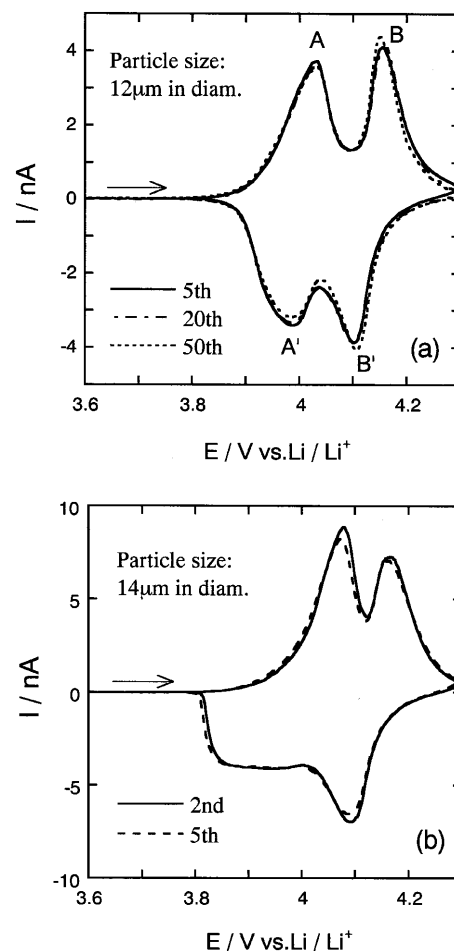
## Results and discussion

### The exposed time effect of $\text{LiMn}_2\text{O}_4$ in electrolytes

In practical use, lithium-ion batteries will be used after a long time exposure to a high-temperature environment. We focused on the change in voltammograms of  $\text{LiMn}_2\text{O}_4$  (Nikki Chemical) after the particle was left in the electrolyte at elevated temperature. The experiment was carried out as follows. Single particles were



**Fig. 1** Schematic illustration of apparatus for electrochemical investigation of single particles: *a* Pt-Rh filament, *b* single particle, *c* Teflon mesh, *d* Teflon cell, *e* Li foil, *f* Cu-W thermocouple, *g* alumina wool



**Fig. 2** Cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  single particles at  $0.5 \text{ mV s}^{-1}$  measured after immediate immersion in  $1 \text{ M LiClO}_4/\text{PC} + \text{EC}$  at  $25 \text{ }^\circ\text{C}$  (a) and after exposure at  $50 \text{ }^\circ\text{C}$  for 1 month (b)

dispersed on a Teflon mesh, and the mesh was placed in the Teflon cell which was filled with 1 M LiClO<sub>4</sub>/PC+EC or 1 M LiPF<sub>6</sub>/PC+EC. The cell was then sealed to protect it from humidity and then placed into an incubator adjusted at 25 °C or 50 °C. After 1 week or 1 month, the cell was subjected to microvoltammetry measurement at a temperature of 25 °C.

Figure 2a shows typical cyclic voltammograms (CVs) for a single particle (12 μm in diameter) in 1 M LiClO<sub>4</sub>/PC+EC at 25 °C prior to a long time exposure to the electrolyte. Two sets of peaks, defined as A/A' and B/B', were respectively observed at ca. 4.0 V and 4.1 V vs. Li/Li<sup>+</sup> [26]. It is clear that the peaks B/B' are sharper than the peaks A/A'. Both A/A' and B/B' correspond to the Mn<sup>3+</sup>/Mn<sup>4+</sup> redox reaction coupled with Li<sup>+</sup> extraction/insertion from/into the tetrahedral sites. No significant change in the peaks in the CV was observed during the potential cycling over 50 cycles.

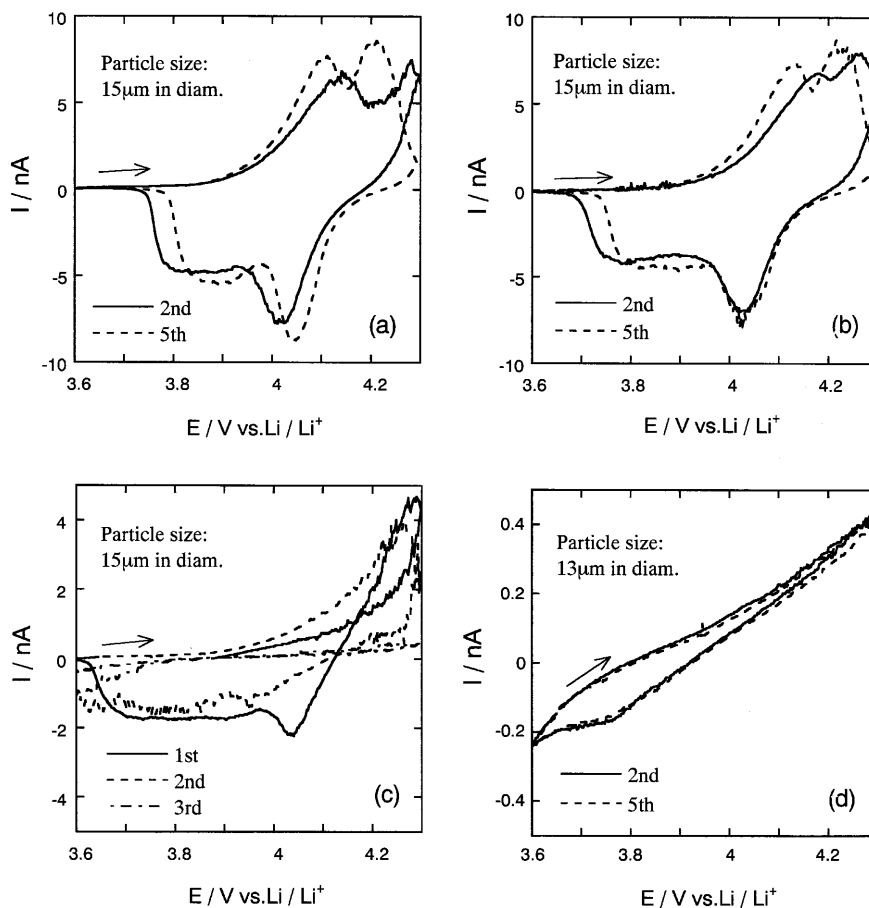
Figure 2b shows the CVs for a single particle (14 μm in diameter) obtained after 1 month exposure to 1 M LiClO<sub>4</sub>/PC+EC at 50 °C. The CV was stable in cycling and the profile was almost the same as that in Fig. 2a. However, the profile of A/A' is slightly different between Fig. 2a and b, which can be explained by a small amount of an inert film on the particle surface. In addition, after 1-month immersion at 25 °C, no substantial change in the CV was observed. Consequently, it is believed that

the LiMn<sub>2</sub>O<sub>4</sub> particle is stable in 1 M LiClO<sub>4</sub>/PC+EC, even at elevated temperature for a long time.

Next, we employed the 1 M LiPF<sub>6</sub>/PC+EC electrolyte. Figure 3a shows the CVs for a single particle after treatment at 25 °C for 1 week. The difference in potential between the anode and cathode peaks of both A/A' and B/B' became larger, which means that the overpotentials of Li<sup>+</sup> extraction/insertion have increased. Further, after 1 week at an elevated temperature of 50 °C, the same kind of CV profile was observed as indicated in Fig. 3b. The peak potential difference for the two couples became much larger compared to those in Fig. 3a. Furthermore, the CVs measured after 1 month at 25 °C and 50 °C are displayed in Fig. 3c and d, respectively. As shown in Fig. 3c, the peak-shaped wave drastically changed, where the anodic peak potential shifted in the anodic direction, and the two peaks in the anodic current were still not apparent. Moreover, in the case of 50 °C for 1 month, the peaks completely disappeared, and only small currents of at least one order of magnitude smaller flowed, which meant that the Li<sup>+</sup> extraction/insertion was not taking place.

According to these results, it was shown that this spinel suffers some significant changes during the extraction/insertion at the particle level even at room temperature when using LiPF<sub>6</sub> in the electrolyte. The mechanism of the change in overpotential is thought to

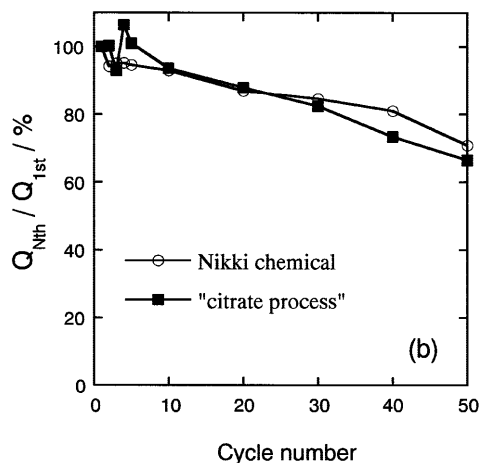
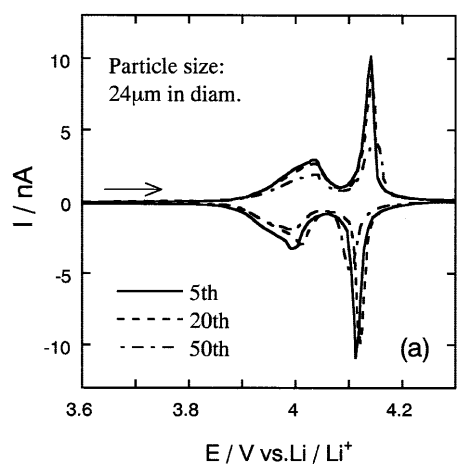
**Fig. 3** Cyclic voltammograms of LiMn<sub>2</sub>O<sub>4</sub> single particles at 0.5 mV s<sup>-1</sup> measured after exposure to 1 M LiPF<sub>6</sub>/PC+EC at 25 °C for 1 week (a), 50 °C for 1 week (b), 25 °C for 1 month (c) and 50 °C for 1 month (d)



be due to the particle surface of  $\text{LiMn}_2\text{O}_4$  being changed to an electrochemically inert material by a chemical reaction [27, 28]. The reaction has been accelerated at  $50^\circ\text{C}$  for one month, and thus the generated surface products would prevent the  $\text{Li}^+$  extraction/insertion. Amatucci et al. [29] reported that  $\text{LiMn}_2\text{O}_4$  in moistened  $\text{LiPF}_6$  electrolytes produces manganese ion and HF at  $55^\circ\text{C}$ . Such a chemical reaction might produce an electrochemically inert material on the particle surface.

#### The surface area effect of the $\text{LiMn}_2\text{O}_4$ particle

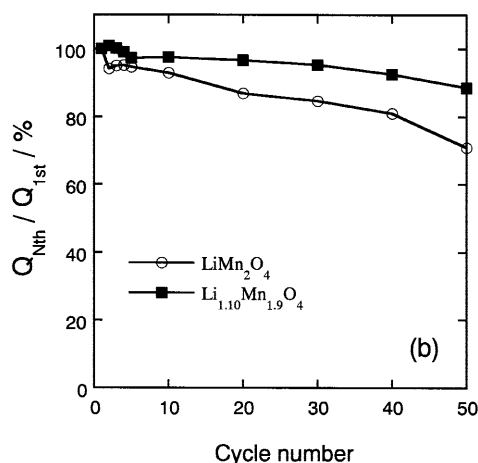
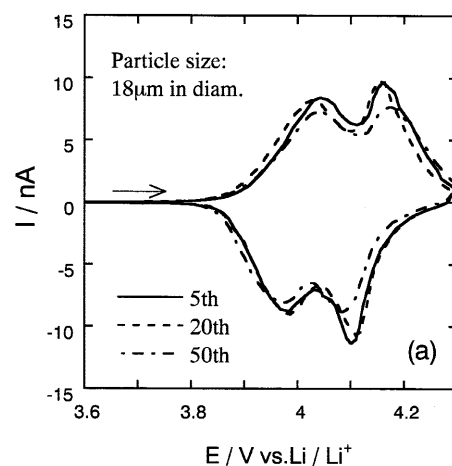
Based on the above results, both the  $\text{LiMn}_2\text{O}_4$  particle and  $\text{LiPF}_6$  used in the electrolyte participate in the reaction at the surface of the particle to produce an inert material. Thus, we compared the reaction in terms of the BET surface area of two different particles. Here we employed home-made samples obtained by the citrate process in combination with 1 M  $\text{LiPF}_6/\text{EC} + \text{PC}$  electrolyte at elevated temperature.



**Fig. 4** **a** Cyclic voltammograms of a  $\text{LiMn}_2\text{O}_4$  single particle (synthesized by the citrate process) at  $50^\circ\text{C}$  in 1 M  $\text{LiPF}_6/\text{PC} + \text{EC}$  taken at  $0.5\text{ mV s}^{-1}$ . **b** Relative changes in discharge capacities of  $\text{LiMn}_2\text{O}_4$  particles during CV cycles

Figure 4a shows the CVs of a  $\text{LiMn}_2\text{O}_4$  particle prepared by the citrate process at  $50^\circ\text{C}$ . The two sets of peaks are sharper than those of the single particle supplied by Nikki, in profile. The peak heights gradually decreased during cycling, and the peak separation in each set of anodic and cathodic peaks increased. This is to say, the reversibility of the  $\text{Li}^+$  extraction/insertion changes to irreversible.

Figure 4b represents the relative capacity changes of these two  $\text{LiMn}_2\text{O}_4$  particles during CV cycles. The capacity faded monotonously in accordance with the cycle number, but no significant disparity was recognized between the two. From the results, it could be understood that the deterioration reaction is controlled neither by the surface area of the particle nor the number of  $\text{LiPF}_6$  molecules present at the surface. If we presume that the reversibility of the  $\text{Li}^+$  extraction/insertion is affected by the number of surface inert materials, the kinetic order of the deterioration reaction is suggested to be 0th order [30].



**Fig. 5** **a** Cyclic voltammograms of a  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  single particle at  $50^\circ\text{C}$  in 1 M  $\text{LiPF}_6/\text{PC} + \text{EC}$  taken at  $0.5\text{ mV s}^{-1}$ . **b** Relative changes in discharge capacities of  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  particles during CV cycles

### Cyclic stability of a $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ particle at 50 °C

According to the above observations, the performance-decay causing reaction in which both  $\text{LiMn}_2\text{O}_4$  and  $\text{LiPF}_6$  participate is not controlled by the surface area of the particle; that is, the bulk phase of the solid is involved. Thus, we employed a  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  particle instead of  $\text{LiMn}_2\text{O}_4$ , expecting its cycling stability in 1 M  $\text{LiPF}_6/\text{EC} + \text{PC}$  electrolyte at elevated temperature.

The CVs of the  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  particle measured at 50 °C are shown in Fig. 5a. The two sets of peaks are somewhat broader than those of the single  $\text{LiMn}_2\text{O}_4$  particle. The  $\text{Li}^+$  extraction/insertion potential is determined by the energy level of 8 (a) sites in the  $\text{LiMn}_2\text{O}_4$  structure, whereas with  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ , Li with 16 (d) sites is considered to affect the energy distribution and influence the CV in shape [31].

Figure 5b shows the relative capacity changes of these two  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  particles during CV cycles. The fading in discharge is ca. 10% even at 50 °C. Obviously, the partial substitution of Mn in  $\text{LiMn}_2\text{O}_4$  by Li enhanced the cycling stability. Thus, we employed X-ray diffraction and obtained a lattice constant of 8.2240 for  $\text{LiMn}_2\text{O}_4$  and of 8.2166 for  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ . This implies that the smaller magnitude of lattice constant exhibits the cycling stability. A possible mechanism is proposed to be (1) the stability of the crystal structure or (2) the suppression of Mn dissolution. Regarding the former, the average oxidation number is increased by Li substitution, which could restrain the Jahn-Teller stress. On the other hand, Yoshio et al. [32] proposed that the coupled  $\text{Li}^+$  extraction/insertion at the second set of peaks ( $\text{B}/\text{B}'$ ), which occurs under the coexistence of two crystal phases, reduces the cycling stability at elevated temperature, while the extraction/insertion functions as it does in a homogeneous phase of  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  [31]. As for the latter proposal (2), the crystal structure is significantly stiffened by the substitution of Mn for Li so as to prevent the dissolution. The scope of the present data does not allow us to determine the nature of the stabilization.

### Conclusions

The electrochemical cycling stability of  $\text{LiMn}_2\text{O}_4$  single particles was studied by means of a microvoltammetry method. The conclusions are summarized as follows.

1. The rapid electrochemical evaluation of charge-discharge properties for battery materials at a single particle level has been demonstrated at elevated temperatures.
2. Cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  particles were measured sequentially after the particle was soaked in the electrolytes for given periods. When 1 M  $\text{LiPF}_6/\text{EC} + \text{PC}$  was used as the electrolyte, significant ca-

capacity fading was observed at 50 °C, which indicates that both  $\text{LiMn}_2\text{O}_4$  and  $\text{LiPF}_6$  participate in the reaction to produce an inert material on the particle surface.

3. To elucidate the reaction producing the capacity fading, two particles having different BET surface areas were compared in combination with 1 M  $\text{LiPF}_6/\text{EC} + \text{PC}$  at 50 °C. As a result, it was found that the deterioration is not controlled by the surface area of the  $\text{LiMn}_2\text{O}_4$  particle.
4. To prevent the deterioration, a  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  particle was employed in the 1 M  $\text{LiPF}_6/\text{EC} + \text{PC}$  electrolyte. The fading in discharge was found to be ca. 10% even at 50 °C, which means that the partial substitution of Mn by Li in  $\text{LiMn}_2\text{O}_4$  substantially enhanced the capacity stability.

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