

# Microvoltammetry for cathode materials at elevated temperatures: electrochemical stability of single particles

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## Abstract

The electrochemical stability of single particles of cathode materials ( $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_{1.10}\text{Cr}_{0.048}\text{Mn}_{1.852}\text{O}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ ) was investigated by means of a microelectrode technique at 25°C and 50°C. The cycle stability was evaluated by multi-cyclic voltammetry.  $\text{LiMn}_2\text{O}_4$  showed good cycle stability in  $\text{LiClO}_4$ /propylene carbonate (PC) + ethylene carbonate (EC) and  $\text{LiBF}_4$ /PC + EC solutions even at 50°C. On the contrary, in  $\text{LiPF}_6$ /PC + EC, significant capacity fading during charge–discharge was observed at 50°C. The cycle stability of  $\text{LiMn}_2\text{O}_4$  in the latter solution was improved by partial substitution of Mn by Cr and Li. Regarding  $\text{LiCoO}_2$ , its cycle life in  $\text{LiClO}_4$ /PC + EC at 50°C was unsatisfactory when the potential was scanned between 3.60 and 4.30 V. On the other hand,  $\text{LiCoO}_2$  retained 90% of its capacity when the potential scan was limited to 4.00 V.  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  showed similar trend at 50°C. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Microelectrode; Single particle; Cycle stability; Lithium ion battery; Lithium manganese oxide; Lithium cobalt oxide

## 1. Introduction

Lithium batteries are now widely used as the power source of portable electrical appliances [1]. One of the research interests is the cycle life of lithium batteries at elevated temperatures. For the commercial use, it is typically expected for the battery to operate at various temperatures (40–80°C). However, capacity fading during charge–discharge is also observed at elevated temperatures [2–10]. The capacity fading has been ascribed to several possible phenomena, among them the dissolution of  $\text{LiMn}_2\text{O}_4$  provoked by acidic species in the electrolyte [2–8]. The cycling performances were usually investigated by using composite electrodes consisting of cathode materials, organic binder and conductive additives. When the composite electrode is used, changes that occur in inter-particle connection within the composite may affect the cycle life [11]. In fact, it was reported that cell impedance increases during charge–discharge cycles [5]. Such uncertainties of composite electrode can be eliminated by using

a single particle of the cathode material. We have already carried out electrochemical investigations on single particles of battery active materials using a microelectrode technique [11–19]. For example, the electrochemical properties of  $\text{LaNi}_5$  [12],  $\text{LiCoO}_2$  [13,14],  $\text{LiNiO}_2$  [14],  $\text{LiMn}_2\text{O}_4$  [13,15,16] and meso-carbon micro beads [11,17–19] were investigated. By means of this technique, we can focus on changes of electrochemical properties of the cathode material itself during charge–discharge cycles without the influence of additives. In this case, the current is small enough (nA level) so that the  $iR$  potential drop can be neglected. Then, the straightforward electrochemistry of the redox material can be investigated in detail even if the material is highly resistive.

In this work, we investigate the electrochemical stability of single particles of cathode materials at elevated temperatures via a microelectrode technique. The potential cycling behavior of  $\text{LiMn}_2\text{O}_4$  was examined in 1 M  $\text{LiClO}_4$ /propylene carbonate (PC) + ethylene carbonate (EC), in 1 M  $\text{LiBF}_4$ /PC + EC and 1 M  $\text{LiPF}_6$ /PC + EC at 50°C. The effect of water content in electrolytes as a contaminant on the cycle life of  $\text{LiMn}_2\text{O}_4$  was also investigated. Cr-doped  $\text{LiMn}_2\text{O}_4$  was examined in comparison with non-doped  $\text{LiMn}_2\text{O}_4$  at elevated temperatures. In

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addition, the electrochemical stability of  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  has been also investigated.

## 2. Experimental

The single-particle electrochemistry under temperature control was evaluated by using an experimental set-up similar to the one described elsewhere [16]. An electrochemical cell made of Teflon was set on an  $x$ - $y$ - $z$  stage with a remote controllable drive (Chuo Precision Industrial), and the temperature of the cell was controlled by a thermoelectric element (SL-10 W, Nippon Blower). A Pt–Rh filament microelectrode (25  $\mu\text{m}$  in diameter) was used as a current collector, which was coated with a thin film of Teflon (Cytop, Asahi Glass) to minimize background currents. The contact between the microelectrode and a target particle in the electrolyte was achieved by manipulating the  $x$ - $y$ - $z$  stage, and the operation was monitored by an optical microscope (SMZ-U, Nikon).

Spherical  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_{1.10}\text{Cr}_{0.048}\text{Mn}_{1.852}\text{O}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  particles were supplied from Nikki Chemical. Electrolytes were 1 M  $\text{LiClO}_4$ , 1 M  $\text{LiPF}_6$  or 1 M  $\text{LiBF}_4$  in PC and EC (1:1 in volume) solution (Lithium battery grade) supplied from Mitsubishi Chemical. Electrolytes were used as received unless otherwise stated. The content of water in the electrolyte solutions was less than 50 ppm, as measured by Karl-Fisher's method (CA-06, Mitsubishi Chemical). A lithium foil of 1  $\text{cm}^2$  served as reference electrode. All electrochemical measurements were carried out with a potentiostat/galvanostat (HA-150, Hokuto Denko). The measurements were carried out in a dry box filled with dry air ( $-50^\circ\text{C}$  dew point).

## 3. Results and discussion

### 3.1. Cycle stability of $\text{LiMn}_2\text{O}_4$ particle at $50^\circ\text{C}$

The cycle stability of  $\text{LiMn}_2\text{O}_4$  in 1 M  $\text{LiClO}_4/\text{PC} + \text{EC}$ , in 1 M  $\text{LiBF}_4/\text{PC} + \text{EC}$  and in 1 M  $\text{LiPF}_6/\text{PC} + \text{EC}$

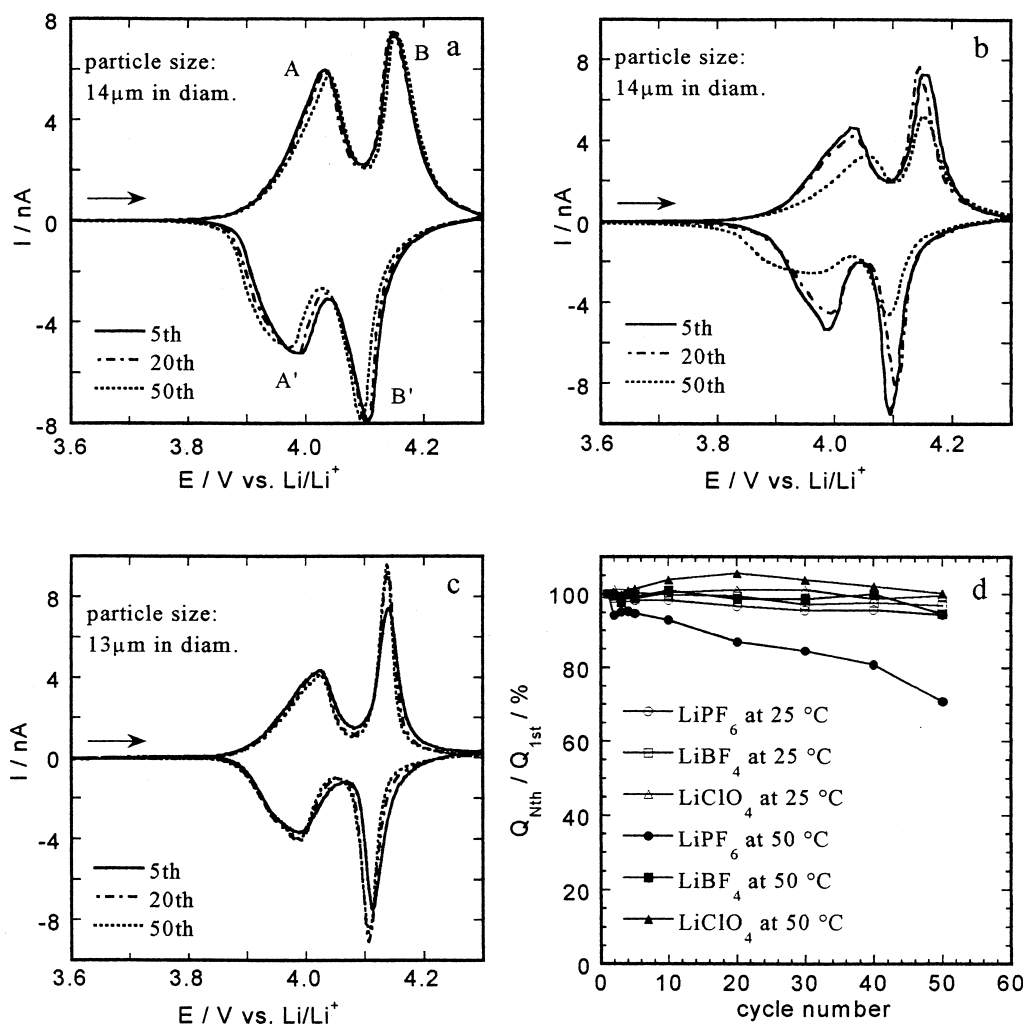
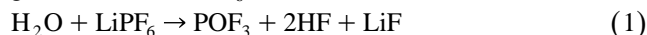


Fig. 1. Cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  single particles at  $0.5 \text{ mV s}^{-1}$  taken in 1 M  $\text{LiPF}_6/\text{PC} + \text{EC}$  at  $25^\circ\text{C}$  (a), 1 M  $\text{LiPF}_6/\text{PC} + \text{EC}$  at  $50^\circ\text{C}$  (b), and 1 M  $\text{LiClO}_4/\text{PC} + \text{EC}$  at  $50^\circ\text{C}$  (c). Relative changes in discharge capacities of  $\text{LiMn}_2\text{O}_4$  particles during CV cycles (d) is also presented.

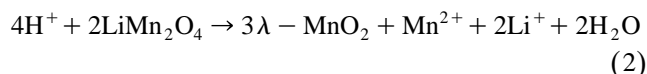
solutions was first evaluated at 25°C. Fig. 1(a) shows the cyclic voltammograms (CVs) of a  $\text{LiMn}_2\text{O}_4$  particle in  $\text{LiPF}_6/\text{PC} + \text{EC}$  at 25°C. Two peaks are clearly observed at 4.00 V (A/A') and 4.15 V (B/B') in both anodic and cathodic scans. The peak currents and the peak potentials did not change significantly during cycling. According to previous reports [20], Li-ion extraction/insertion occur in a homogeneous cubic phase at peak A/A', and the reaction at peak B/B' proceeds under the coexistence of two different cubic phases at room temperature. The CVs recorded in other electrolytes ( $\text{LiBF}_4/\text{PC} + \text{EC}$  and  $\text{LiClO}_4/\text{PC} + \text{EC}$ ) were similar to those in  $\text{LiPF}_6/\text{PC} + \text{EC}$ . In all the electrolytes considered, the  $\text{LiMn}_2\text{O}_4$  particles showed excellent cycle stability at 25°C, and the discharge capacities were maintained more than 95% of the first cycle even after 50 cycles as can be seen in Fig. 1(d).

Fig. 1(b) shows the CVs in 1 M  $\text{LiPF}_6/\text{PC} + \text{EC}$  at 50°C. Although two peaks were clearly recognized as in the case of 25°C, the peak heights gradually decreased during cycling. In order to reveal the effect of electrolyte, Fig. 1(c) illustrates the CVs obtained in 1 M  $\text{LiClO}_4/\text{PC} + \text{EC}$  at 50°C. No significant changes in CV waves were seen until 50 cycles, exhibiting an excellent cycle stability. The cycle stability in 1 M  $\text{LiBF}_4$  solution at 50°C was also investigated and results showed excellent stability as in the case of 1 M  $\text{LiClO}_4$  solution. In Fig. 1(d), the relative capacity changes of  $\text{LiMn}_2\text{O}_4$  particles in different conditions are summarized, showing that the cycle stability of  $\text{LiMn}_2\text{O}_4$  at 50°C in  $\text{LiPF}_6/\text{PC} + \text{EC}$  solution was particularly worse (ca. 30% decrease for 50 cycles) compared with the cases of  $\text{LiClO}_4$  and  $\text{LiBF}_4/\text{PC} + \text{EC}$  solutions. The capacity fading observed in  $\text{LiPF}_6/\text{PC} + \text{EC}$  at 50°C might have been caused by the dissolution of  $\text{LiMn}_2\text{O}_4$  promoted by acidic species generated at elevated tempera-

ture [3]. When  $\text{H}_2\text{O}$  is contained in the electrolyte, HF is generated from  $\text{LiPF}_6$  as follows [21]:



and the proton from HF will dissolve the  $\text{LiMn}_2\text{O}_4$  as follows [22]:



Hence, reactions (1) and (2) will cooperate to accelerate the dissolution at elevated temperatures, even if the content of  $\text{H}_2\text{O}$  in the electrolyte is small. Usually, a very small amount of  $\text{H}_2\text{O}$  is present in the electrolytes as a contaminant. In the cases of  $\text{LiClO}_4$  and  $\text{LiBF}_4$ , this proton-assisted dissolution mechanism seems to not occur. To confirm this point, we performed the following experiments.

### 3.2. The water effect on the cycle stability of $\text{LiMn}_2\text{O}_4$

Electrolytes were intentionally exposed to a humidified atmosphere for 30 min. At this point, each electrolyte contained water of about 2000 ppm (measured by the Karl-Fisher's method). Then, the solutions were left in air-sealing bottles for 10 days at room temperature. After 10 days the water content in  $\text{LiPF}_6/\text{PC} + \text{EC}$  decreased to 200 ppm. On the other hand, no such effect was observed in  $\text{LiClO}_4$  or  $\text{LiBF}_4/\text{PC} + \text{EC}$  solutions. The consumption of water in  $\text{LiPF}_6/\text{PC} + \text{EC}$  can be explained by reaction (1).

Fig. 2(a) shows the CVs of a  $\text{LiMn}_2\text{O}_4$  particle in  $\text{LiPF}_6/\text{PC} + \text{EC}$  solution containing 200 ppm of  $\text{H}_2\text{O}$ . Even at the initial cycles, the CV wave was not sharp and the two classical CV peaks for  $\text{LiMn}_2\text{O}_4$  were not clearly distinguished, the peak separation between anodic peaks and cathodic peaks being large. This suggests that a larger overvoltage is needed for Li-ion extraction and insertion. According to reports [3,4], when the dissolution of  $\text{Mn}^{2+}$

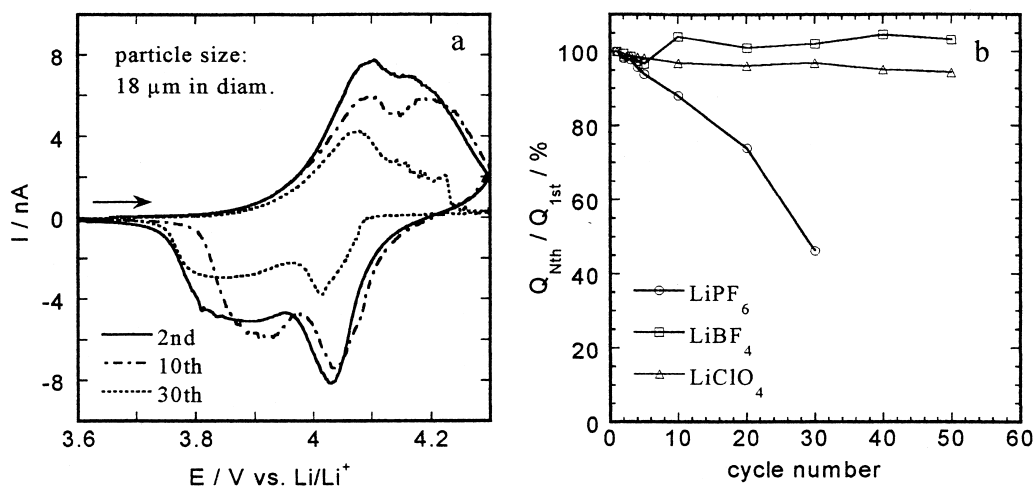


Fig. 2. (a) Cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  single particles at 25°C in  $\text{LiPF}_6/\text{PC} + \text{EC}$  containing 200 ppm  $\text{H}_2\text{O}$ , taken at  $0.5 \text{ mV s}^{-1}$ . (b) Relative changes in discharge capacities of  $\text{LiMn}_2\text{O}_4$  particles during CV cycles in electrolytes, which added water intentionally.

from  $\text{LiMn}_2\text{O}_4$  takes place,  $\text{Li}_2\text{MnO}_3$  and  $\text{Li}_2\text{Mn}_4\text{O}_9$  are formed at the particle surface which are believed to be electrochemically inactive around 4 V. These inactive phases will interfere the Li-ion extraction and insertion, resulting in large overvoltages. The discharge capacity faded rapidly as shown in Fig. 2(b), possibly being caused by the dissolution of  $\text{LiMn}_2\text{O}_4$  by HF.

In contrast, the drastic capacity fading was not seen in cases of  $\text{LiClO}_4$  and  $\text{LiBF}_4$  solutions even in the presence of 2000 ppm of water. The CV waves of  $\text{LiMn}_2\text{O}_4$  in  $\text{LiClO}_4/\text{PC} + \text{EC}$  or in  $\text{LiBF}_4/\text{PC} + \text{EC}$  solution with water were the same as those observed in electrolytes without water, and the discharge capacities are shown in Fig. 2(b). This indicates that  $\text{LiClO}_4$  and  $\text{LiBF}_4$  salts are relatively stable in moist solutions and no acidic species would be generated by adding water.

### 3.3. The effect of partial substitution of Mn in $\text{LiMn}_2\text{O}_4$ by other cations

Fig. 3 shows the CVs of  $\text{Li}_{1.10}\text{Cr}_{0.048}\text{Mn}_{1.852}\text{O}_4$  taken in  $\text{LiPF}_6/\text{PC} + \text{EC}$  at  $50^\circ\text{C}$ . The CV wave did not change upon cycling, in contrast to  $\text{LiMn}_2\text{O}_4$  (Fig. 1(b)). The capacity at the 50th cycle was 95% of the initial capacity. This result indicates that the doping of  $\text{LiMn}_2\text{O}_4$  by cations ( $\text{Cr}^{3+}$  and  $\text{Li}^+$ ) is effective for the improvement of cycle stability of lithium manganese oxide spinel at elevated temperatures. Similar results have been reported by Robertson et al. [4] and Gao and Dahn [9,10]. Since the oxidation state of Mn in solid is increased by doped cations, the disproportionation reaction of  $\text{Mn}^{3+}$  ( $2\text{Mn}_{\text{solid}}^{3+} \rightarrow \text{Mn}_{\text{solid}}^{4+} + \text{Mn}_{\text{solv.}}^{2+}$ ) could be hindered. This may be favorable for the stability of the oxides. In addition, Guohua et al. [23] suggested, on the basis of thermodynamic calculation with Born–Haber’s cyclic process, that the strength of Cr–O bond is stronger than that of Mn–O bond, which may increase the chemical stability of lithium manganese oxide spinel against the attack of acidic species.

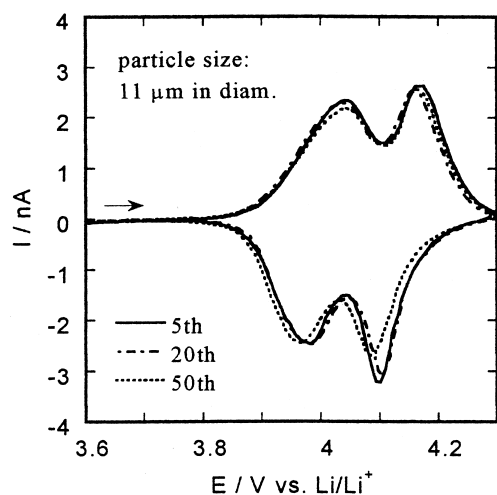


Fig. 3. Cyclic voltammograms of a  $\text{Li}_{1.10}\text{Cr}_{0.048}\text{Mn}_{1.852}\text{O}_4$  particle at  $50^\circ\text{C}$  in  $\text{LiPF}_6/\text{PC} + \text{EC}$ , taken at  $0.5 \text{ mV s}^{-1}$ .

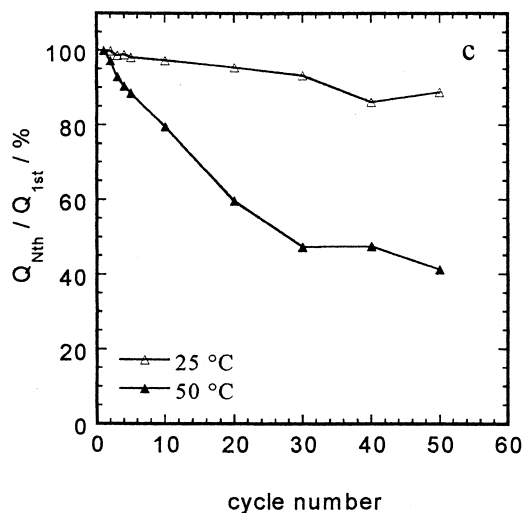
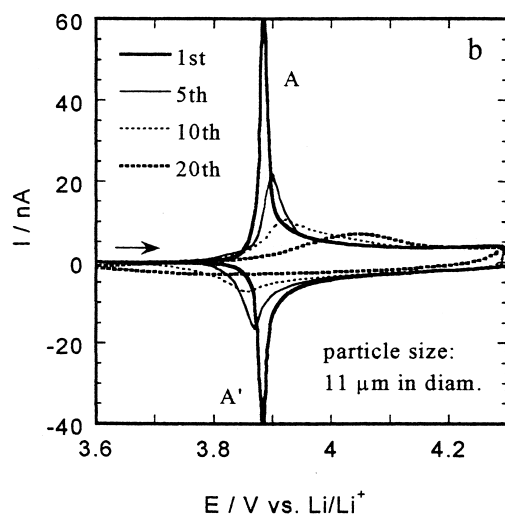
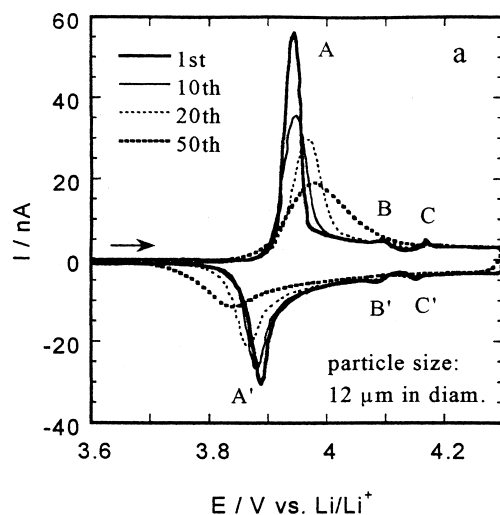


Fig. 4. Cyclic voltammograms of  $\text{LiCoO}_2$  single particles in  $\text{LiClO}_4/\text{PC} + \text{EC}$  at  $25^\circ\text{C}$  (a) and at  $50^\circ\text{C}$  (b), taken at  $1 \text{ mV s}^{-1}$ . The potential was scanned between 3.60 and 4.30 V. Relative changes in discharge capacities of  $\text{LiCoO}_2$  single particles during CV cycles (c).

### 3.4. The cycle stability of LiCoO<sub>2</sub> particles at elevated temperature

Fig. 4(a) shows the cycle stability of single particles of LiCoO<sub>2</sub> in LiClO<sub>4</sub>/PC + EC solution at 25°C. Three reversible peaks (A/A', B/B' and C/C') at around 3.90, 4.08 and 4.15 V are clearly seen at early cycles. It is known that Li-ion extraction and insertion take place under the co-existence of two different hexagonal phases at peaks A/A', while peaks B/B' and C/C' are linked to the phase transformation between hexagonal and monoclinic phases [24,25]. Reimers and Dahn [25] also suggested that the order–disorder process takes place between peaks B/B' and C/C' (around  $x = 0.5$  in Li<sub>1-x</sub>CoO<sub>2</sub>). The peak currents of A and A' decreased; meanwhile, their respective peak potentials shifted to anodic and cathodic regions upon CV cycling when the potential was reversed at 4.3 V. However, capacity fading was not serious as shown in Fig. 4(c). The peaks B/B' and C/C' progressively disappeared during cycling and were barely recognized upon the 50th cycle. The decrease of peak A/A' and the disappearance of B/B' and C/C' are indicative of some degradation of crystal or interface structures of LiCoO<sub>2</sub>. The repetition of crystallographic change during Li-ion extraction and insertion would cause destruction of the crystal structure. Recently, Wang et al. [26] by means of transmission electron microscopy and electron diffraction reported that the structure changes by cycling. They showed that the charge–discharge cycles cause micro-cracks among LiCoO<sub>2</sub> particles and two types of cation disorders. One is defects on octahedral site layers (including cation substitutions and vacancies), and the other is a partial transformation to spinel tetrahedral ordering. Such cation disorder will interfere the order–disorder process around  $x = 0.5$ .

Fig. 4(b) shows the CVs of a LiCoO<sub>2</sub> particle taken at 50°C in 1 M LiClO<sub>4</sub>/PC + EC. In contrast to the case of

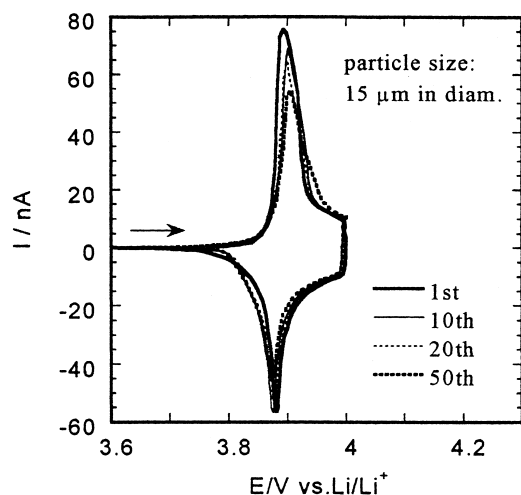


Fig. 5. Cyclic voltammograms of a LiCoO<sub>2</sub> particle in LiClO<sub>4</sub>/PC + EC at 50°C, taken at 1 mV s<sup>-1</sup>. The potential was scanned between 3.60 and 4.00 V.

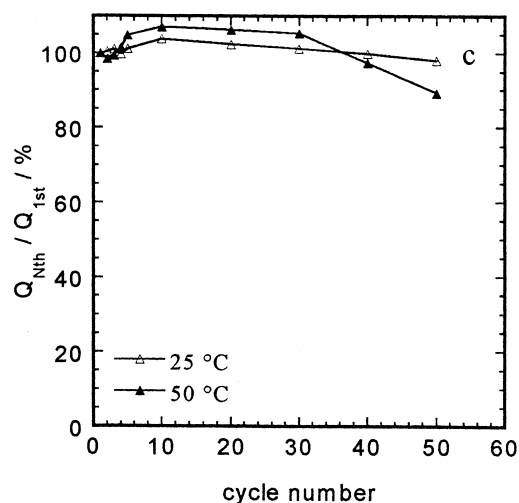
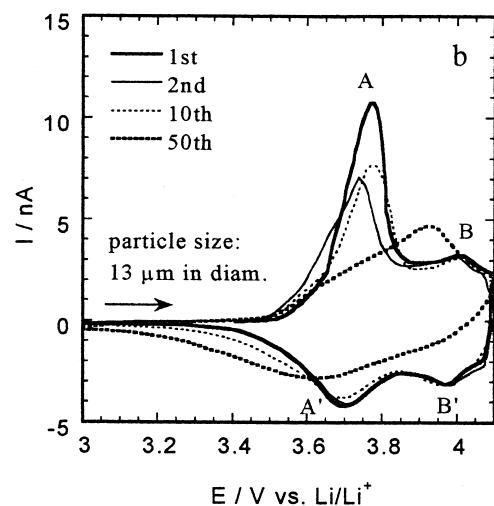
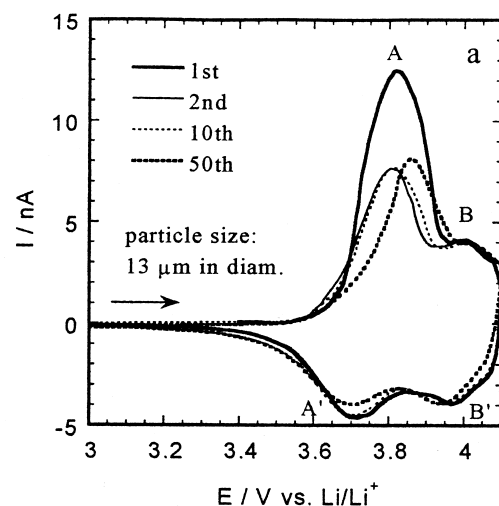


Fig. 6. Cyclic voltammograms of LiNi<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> single particles in LiClO<sub>4</sub>/PC + EC at 25°C (a) and at 50°C (b), taken at 1 mV s<sup>-1</sup>. The potential was scanned between 3.00 and 4.10 V. Relative changes in discharge capacities of LiNi<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> single particles during CV cycles (c).

room temperature, only process A/A' were observed. This result agrees well with previous report by Reimers and Dahn [25], in which in situ XRD analysis proved that phase transitions at peaks B/B' and C/C' did not occur at elevated temperatures. The width of peak A is very narrow probably due to faster Li-ion diffusion in the  $\text{Li}_{1-x}\text{CoO}_2$  particle at 50°C than at 25°C. However, the peak currents of A/A' decreased rapidly and could not be clearly observed at 20th cycle, indicating a great capacity loss as shown in Fig. 4(c). Although the reason for it is unclear at the moment, the destruction of crystal structure such as cation disorder [26] may be accelerated at elevated temperatures and thus the electrochemically inactive parts may increase.

Fig. 5 shows the cycling behavior of  $\text{LiCoO}_2$  examined in the potential range between 3.60 and 4.00 V at 50°C. In comparison with the case of wider potential range (Fig. 4(b)), the decrease in peak current was not rapid and the capacity was maintained about 90% after even 50 cycles. This result indicates that the anodic potential limit at elevated temperatures, namely, the limit of Li-ion extraction severely affects the cycle life of  $\text{LiCoO}_2$ . The destruction of structure may occur mainly at potentials upper than 4.00 V.

### 3.5. The cycle stability of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ particles at elevated temperature

Fig. 6 shows cycle behaviors of single particles of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  in 1 M  $\text{LiClO}_4/\text{PC} + \text{EC}$  solution at 25°C and 50°C. The electrode potential was scanned in the range between 3.00 and 4.10 V because the cyclability of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  was not good when the potential exceeded over 4.20V even at 25°C (results are not shown here). At both 25°C and 50°C, two peaks (A/A' and B/B') in anodic and cathodic scans was ambiguous at early cycles. According to previous reports [27,28], Co-doped lithium nickel oxide such as  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  [28] and  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  [27] do not have phase transition during Li ion extraction and insertion. It is said that the hexagonal phase is preserved. Therefore, the two peaks observed in Fig. 6(a) and (b) did not originate from phase transition. As shown in Fig. 6(c), the loss in discharge capacity is less than 10% even at 50°C. The decrease of peak currents and the shifts of peak potential imply the increase of kinetic irreversibility and can be attributed to the fatigue of crystal structure.

## 4. Conclusions

The electrochemical stability of single particles of  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_{1.10}\text{Cr}_{0.048}\text{Mn}_{1.852}\text{O}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  at 50°C were investigated by using a microelectrode technique.

(i) The cycle stability of  $\text{LiMn}_2\text{O}_4$  at 50°C in  $\text{LiPF}_6/\text{PC} + \text{EC}$ ,  $\text{LiClO}_4/\text{PC} + \text{EC}$  and  $\text{LiBF}_4/\text{PC} + \text{EC}$  was studied comparatively. Significant discharge capacity fading during CV cycling was observed only in  $\text{LiPF}_6/\text{PC} + \text{EC}$  solution at 50°C. The water contamination in  $\text{LiPF}_6$  solutions critically limits the cycle life of  $\text{LiMn}_2\text{O}_4$ . It was confirmed that the dryness of the electrolyte solution is a very important factor for the cycle life of  $\text{LiMn}_2\text{O}_4$ , especially in the case of  $\text{LiPF}_6$  salt-based electrolyte.

(ii) The improving effects of partial substitution of Mn by Cr and Li on the cycle life of lithium manganese oxide spinel at elevated temperature were confirmed.

(iii) The cycle life of  $\text{LiCoO}_2$  particle at 50°C was unsatisfactory in  $\text{LiClO}_4/\text{PC} + \text{EC}$  when the potential was scanned between 3.60 and 4.30 V, while it was relatively good for the potential scan between 3.60 and 4.00 V.

(iv) Although  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  showed an increase in kinetic irreversibility during CV cycles at 50°C, the discharge capacity did not fade rapidly.

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