

Electrochemical and calorimetric approach to spinel lithium manganese oxide

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Abstract

A simultaneous electrochemical and calorimetric measurement was conducted on a spinel lithium manganese oxide (LiMn_2O_4)-cathode, carbon-anode prismatic lithium ion cell. From the comparison of thermal behavior at room temperature (25°C) and at an elevated temperature (40°C), a pronounced exothermic thermal behavior was observed during charging in the high voltage region ($0.2 < x < 0.5$ in $\text{Li}_x\text{Mn}_2\text{O}_4$) at elevated temperatures. The degraded cell that was operated at 40°C indicated that the capacity fading occurred mainly in the same high voltage region in advance of lower region. The irreversible thermal behavior observed by calorimetry clearly indicates the degradation of LiMn_2O_4 at elevated temperatures. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium ion cell; Spinel lithium manganese oxide; Calorimetry; Capacity fading

1. Introduction

Spinel lithium manganese oxide (LiMn_2O_4) is currently one of the most promising cathode materials for large-scale lithium secondary batteries [1] because of the advantages of natural abundance and material safety. However, the improvement of the pronounced capacity fading of LiMn_2O_4 on cycling at elevated temperatures and proper thermal management of cells are problems that must be resolved prior to electric vehicles (EV) and load leveling applications. Some irreversible reactions at elevated temperatures were proposed, but these were obtained from post analysis [2,3]. An in situ technique was also used, but specific cell configurations were required [4].

The electrochemical and calorimetric method involves the precise heat generation or absorption observation from the outer surface of the cell during charge/discharge. This method requires no special cell configuration. Furthermore, the correlation between cell voltage and thermal behavior can be analyzed in order to extract the irreversible reaction during cell operation. Calorimetry of a lithium secondary battery has previously been used on a chevrel compound $\text{Li}_x\text{Mo}_6\text{Se}_8/\text{Li}$ metal [5] and the $\text{LiCoO}_2/\text{carbon}$ system [6–8]. In this study, the irre-

versible thermal behavior of LiMn_2O_4 -cathode/carbon-anode cells during charge/discharge cycles at elevated temperature was investigated by calorimetry for the first time.

2. Experimental

Commercially available prismatic lithium ion cells with a nominal capacity of 600 mA h (NEC MP-5A 260948) were used as samples. This cell system consisted of a carbon-anode, a LiMn_2O_4 -cathode and liquid electrolytes. As a reference of the LiMn_2O_4 system, Sony US18650 (1250 mA h) which consisted of a carbon-anode, a LiCoO_2 -cathode system was used. In the LiMn_2O_4 system, operation range of the cell voltage was between 4.2 V and 3.0 V. In the LiCoO_2 system, operation range was between 4.2 and 2.5 V.

The heat flow during charge/discharge was measured using a Calvet-type conduction microcalorimeter (MMC-5111-U Tokyo Riko, Tokyo). An aluminum vessel was touched to the cell surface to maintain smooth heat transfer and was used as an anode current collector (Fig. 1). A cathode current collector was electrically isolated from the aluminum vessel. A thermomodule was placed between the bottom of the vessel and an aluminum heat sink controlled within an accuracy of $\pm 0.0001^\circ\text{C}$ in an air bath.

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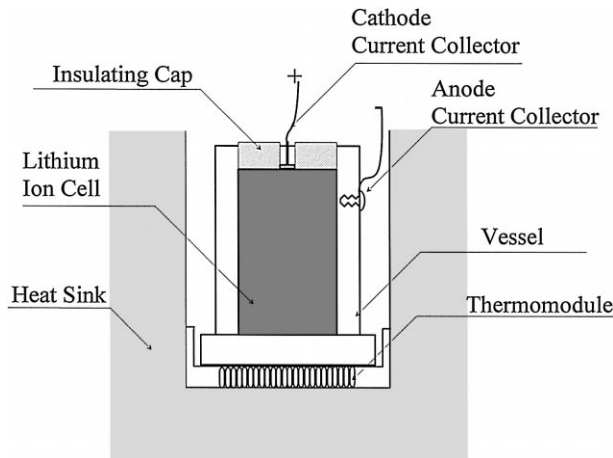


Fig. 1. Design of the vessel for calorimetry measurement of lithium ion cell.

The heat flow output is the differential value between a sample and the reference thermomodule. The detection limit of heat flow from the cell was $1 \mu\text{W}$ and the time constant of the heat transfer was about 600 s. Cells were operated from 10 to 50 h rate that was sufficiently slower than the time constant of the heat transfer in this system. The surrounding temperature was controlled at 25°C as the room temperature, and from 40°C to 60°C as elevated temperatures.

X-ray diffraction experiments of LiMn_2O_4 were carried out using a Mac Science MXP-18 diffractometer with $\text{Cu-K}\alpha$ radiation. LiMn_2O_4 samples at each SOC were disassembled and extracted from the cell. The lattice parameter at each SOC was calibrated with a silicon internal standard. All of the disassembly experiments were conducted in an argon atmosphere.

3. Results and discussion

Fig. 2 shows the cycle performances of LiMn_2O_4 (a) and LiCoO_2 (b) systems. The charge/discharge rate was $1/5\text{C}$. The LiMn_2O_4 system had a lower cycle performance than LiCoO_2 system. In particular, the LiMn_2O_4 system showed poor cycle characteristics at elevated temperatures.

Fig. 3 shows typical heat flow of the cell during charge/discharge at 25°C (solid line) and 40°C (dashed line). During charge at 25°C (A), the observed heat flow was mainly endothermic after iR correction up to 3.9 V (region I). However from 3.9 V to 4.2 V (region II), the heat flow became exothermic. During discharge at 25°C (B), the corresponding thermal behavior was almost reversible compared with that during charge. Considering the heat generated from internal resistance, the observed thermal behavior was mainly derived from the reversible chemical reaction during charge/discharge.

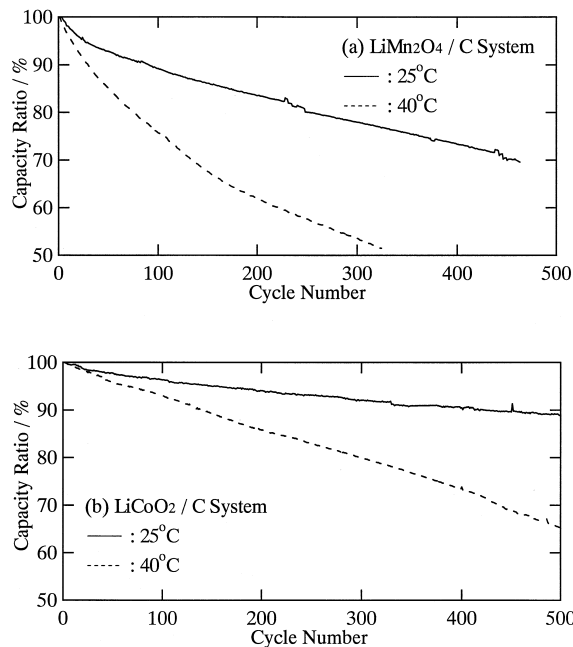


Fig. 2. Typical cycle performances of (a) LiMn_2O_4 and (b) LiCoO_2 system lithium ion cells at 25°C (solid line) and 40°C (dashed line).

At 40°C , a pronounced exothermic behavior was observed in region II. The corresponding endothermic behavior was similar to that at 25°C (region III), and in other regions (I, IV), the thermal profiles were almost the same.

In order to compare the thermal behavior of LiMn_2O_4 with that of LiCoO_2 during charge, Fig. 4 shows the thermal profiles at room temperature and at elevated temperatures of LiMn_2O_4 (a) and LiCoO_2 (b). In the LiMn_2O_4

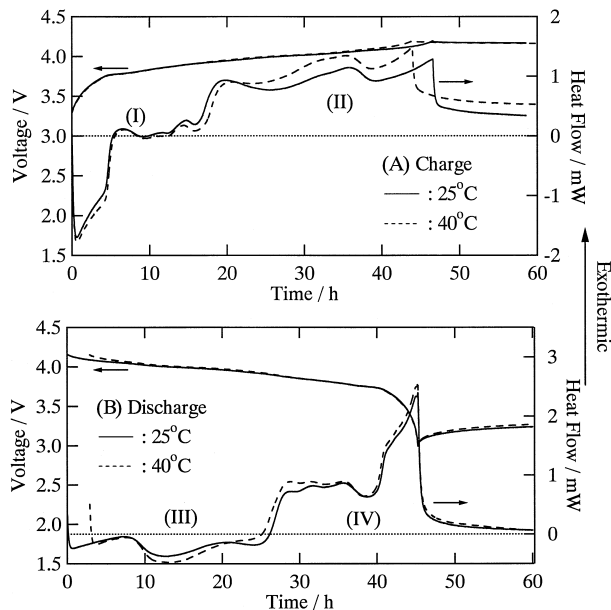


Fig. 3. Charge/discharge curves and corresponding heat flow of LiMn_2O_4 /carbon lithium ion cell at 25°C (solid line) and 40°C (dashed line). Rate: $1/50\text{C}$.

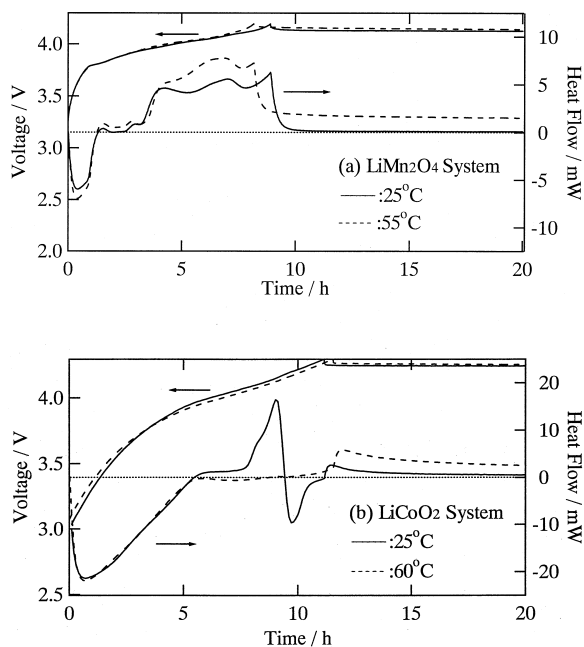


Fig. 4. Observed heat flow during charge at room and elevated temperatures. (a): LiMn_2O_4 /carbon system at 25°C (solid line) and 55°C (dashed line). (b): LiCoO_2 /carbon system at 25°C (solid line) and at 60°C (dashed line). Rate: 1/10C.

system (a), pronounced exothermic behavior was observed in region II at elevated temperatures. However, in the LiCoO_2 system (b), thermal behavior was remarkably different. At room temperature, a reversible phase transition from hexagonal to monoclinic was observed in region II, disappeared at elevated temperatures [6,9]. We also found the fact that the thermal behavior of the phase transition was not observed at 60°C. No pronounced exothermic or endothermic thermal behavior was observed at elevated temperatures which indicates that the operation in region II is not the main factor causing the degradation of the LiCoO_2 system at elevated temperatures. Therefore, the observed pronounced exothermic behavior of over 3.9 V (region II) in the LiMn_2O_4 system was found to be due to the irreversible reaction which occurred during charge.

From the analysis of ex situ XRD patterns (Fig. 5), the lattice constants (a axis) of LiMn_2O_4 were found to change linearly from 8.20 Å at the end of discharge to 8.06 Å at the end of charge. The x values of $\text{Li}_x\text{Mn}_2\text{O}_4$, which were estimated from the lattice parameters, changed from 0.8 to 0.2 [3]. Comparing the thermal behavior with the x values in $\text{Li}_x\text{Mn}_2\text{O}_4$, thermal behavior in region I ($0.8 < x < 0.5$) was endothermic during charge. Lithium intercalation into carbon was reported to be an exothermic reaction [10]; therefore, the endothermic/exothermic behavior in region I/IV was due mainly to the reversible deintercalation–intercalation reaction of lithium ions to LiMn_2O_4 . In region II ($0.5 < x < 0.2$), the thermal behavior changed to exothermic, which indicates that the deintercalation reaction from LiMn_2O_4 may decrease endothermic heat or

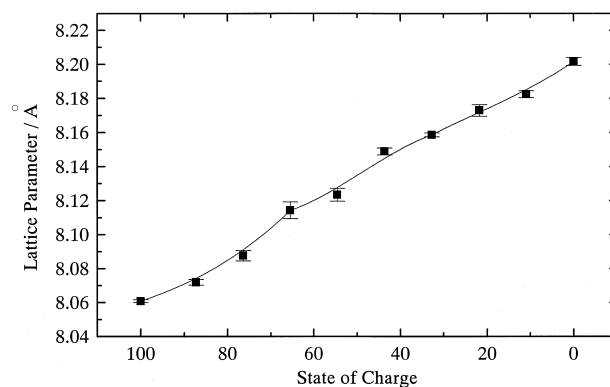


Fig. 5. Variation of the a -axis lattice parameter as a function of Li deintercalation for LiMn_2O_4 .

become exothermic. In regions II and III, accelerated capacity fading on cycling of LiMn_2O_4 was reported [11]. It is assumed that the pronounced exothermic behavior at 40°C in region II is due to the irreversible side reaction in LiMn_2O_4 system.

After 330 charge/discharge cycles at 40°C, the results of which are shown in Fig. 2(a), the thermal behavior of the degraded cell was compared with that of the new cell at 25°C (Fig. 6). The capacity of the degraded cell was about half that of the new cell. The capacities of the endothermic region I during charge and the corresponding exothermic region IV during discharge of the degraded cell were comparable to those in the same regions of the new cell.

However, the capacities of the exothermic region II during charge and the corresponding endothermic region

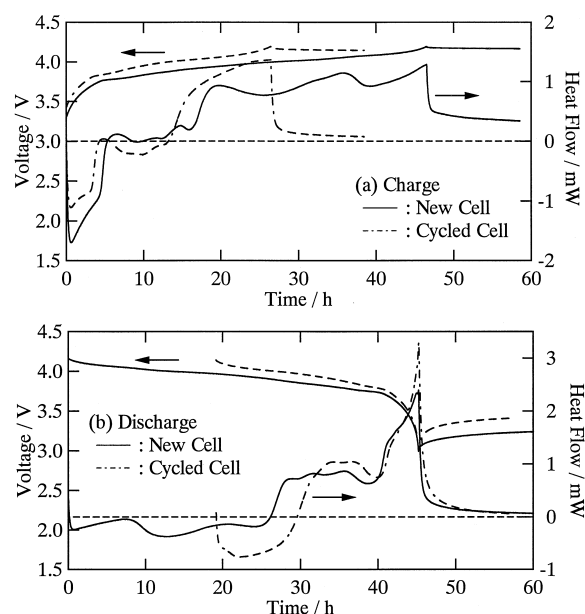


Fig. 6. Charge/discharge curve and corresponding heat flow of the degraded cell (dashed line) and the new cell (solid line). Rate: 1/50C.

III during discharge of the degraded cell were less than half that of the new cell. Thus, capacity fading at elevated temperatures was mainly caused by the irreversible reaction over 3.9 V ($0.2 < x < 0.5$ in $\text{Li}_x\text{Mn}_2\text{O}_4$).

4. Conclusion

By the application of calorimetry to the LiMn_2O_4 -cathode, carbon-anode system, the irreversible thermal behavior at elevated temperatures was observed during cell operation. The irreversible reaction occurred mainly at over 3.9 V ($0.2 < x < 0.5$ in $\text{Li}_x\text{Mn}_2\text{O}_4$) during charge. Our results were derived from a small number of cycles at different temperatures. Thus we conclude that simultaneous electrochemical and calorimetric analysis is a highly sensitive method for measuring the degradation characteristics of encapsulated lithium batteries.

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