

The Quantitative Analyses of the Dissolved Manganese in the Electrolyte of Li/LiMn₂O₄ Cell Using by Ion Chromatography

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The emphasis on green technology for electric vehicle application has provided much emphasis on lithium battery research work based on Li/LiMn₂O₄ battery system.¹⁻⁵ Even though the cathode LiMn₂O₄ has environmentally benign elements with low cost benefit, it inherits low cycle life compared to cobalt and nickel based cathodes. The cycle capacity is also affected when the cells are cycled at higher temperature conditions especially above 50 °C.⁶⁻¹⁰ The reason for the capacity fading at high temperature is believed to be due to factors such as: i) the decomposition of electrolyte at the high voltage region; ii) the particle fracture due to repeated cycling. The dissolution of manganese during cycling is believed to take place when the cathode encounters low discharge voltage where the presence of large amount of Mn³⁺ is believed to form through 1) the disproportionation reaction: $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$, 2) the reduction of Mn³⁺ by the electrolyte: $\delta \text{Mn}^{3+} + \delta e^- (\text{electrolyte}) \rightarrow \delta \text{Mn}^{2+}$.^{9,11,15} The capacity fading upon cycling was at first described by Thackeray *et al.*¹¹ as due to the dissolution of Mn from the electrode into the electrolyte. Recently, Oh *et al.*^{9,12-15} have analyzed quantitatively the dissolution of manganese ions for the spinel compound using differential pulse polarography method. They have found that the manganese dissolution causes the capacity loss by two ways, one is the material loss of the loaded spinel, and another is the polarization loss due to the cell resistance increment. They have also investigated the influence of electrolyte on spinel dissolution in the subsequent paper in which they demonstrated that the protons generated in the electrolyte as a result of solvent oxidation, play a key role in spinel dissolution.¹³ Yoshio *et al.* also reported that for the spinel LiMn₂O₄, there exist two-phase structure regions in the high-voltage range which is very sensitive to temperature.⁸ The manganese dissolution occurs as a result of a transformation of unstable two phases into single-phase structure. They have indicated

that the capacity loss is due to Mn dissolution which accounts for 34% of the overall capacity loss. According to Yoshio¹⁶ and Wakihara¹⁷ groups the LiMn₂O₄ is transformed to Li_{1+x}Mn_{2-x}O₄ accompanied by Mn dissolution which explains that during Mn dissolution from 16d site of the spinel leads to a vacant position during charging process. This vacant position might probably be occupied by Li⁺ ion as a part of charge compensation process. The studies on the manganese dissolution phenomena were performed by many researchers.¹⁸⁻²⁰

This paper describes experimental details and use of Ion Chromatography as a tool to quantitatively analyze the dissolved manganese in the electrolyte of Li/LiMn₂O₄ cell between different cycle intervals. The technique of Ion Chromatography²¹ could be used as the method of qualitative and quantitative analyses of ions in range of ppm or ppb level. Ion Chromatography could be used to analyze the cations of Li, Na, Mg, Al, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ag, Cd, Ba, Pb and the anions of B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Sb, I, V, Cr, Mo, W using by the appropriate stationary and moving phases. The principle of Ion Chromatography is same as the general chromatography to be different using the supporting electrolyte as the eluent solution. Each ion including cation and anion can be freely eluted without any restriction by the sufficient counter ion which is the oppositely charged ion. A graphical concept of the cation elution was depicted in Fig. 1.

Experiment

The LiMn₂O₄ cathode was prepared by coating a viscous mass made out of LiMn₂O₄ (Allied signal no. 13070, D₅₀ 10 μm), Super Pure black (TIMCAL) and PVDF (polyvinylidene fluoride) in the weight ratio 90 : 10 : 10 using NMP (*N*-methyl pyrrolidone) over aluminum foil and dried in air oven of 110 °C for 30 minutes. Then the coated foil was pressed using a hydraulic press to 70% of the original thickness and dried in vacuum oven for 6 hours. The density of electrode composite was 3.7 g/cm³. The LiMn₂O₄ cathode coated on single side of aluminum foil was then cut in size 5 × 2 cm² containing 110 mg of LiMn₂O₄ and wound in the form of a hollow cylindrical electrode with aluminum lead provision for electrical contact. This hollow cylindrical electrode was kept inside another lithium foil (Cyprus Foote mineral Co., t = 300 μm) cylinder provided with Nickel lead wire for providing electrical connection. In order to prevent electrical short circuit a separator with an area 3 × 6 cm² folded like a cylinder was kept between the anode and the cathode. The electrolyte was used 20 mL of

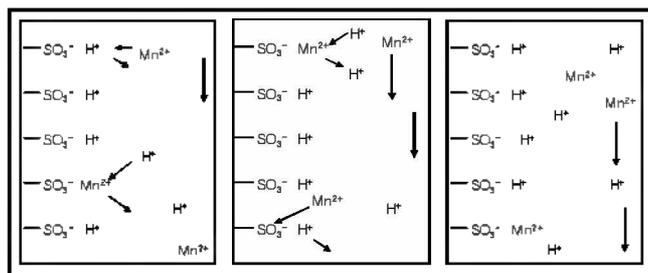


Figure 1. The graphical concept of the cation elution in Ion Chromatography.

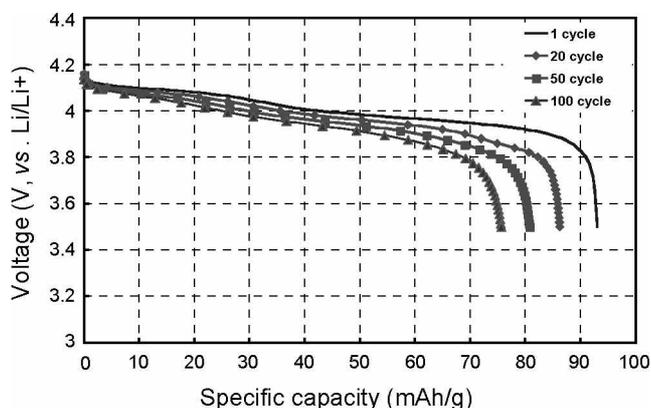
Table 1. The experimental conditions employed for carrying out the analyses of Ion Chromatography.

ICapillary column	METROSEP C2 150 150/4.0 mm
Eluent	5 mmol/L tartaric acid 0.09 mmol/L dipicolinic acid 1 mmol/L ascorbic acid
Flow rate	1.0 mL/min
Sample volume	10 μ L
Temperature	25 $^{\circ}$ C
Run time	20 min

1.12 M LiPF_6 with 2 wt% vinylene carbonate (VC) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed in 1 : 1 (v/v) ratio. Cell assembly was performed in a dryroom to have the Dewpoint of -65 $^{\circ}$ C. The test cell so constructed was subjected to electrochemical charge-discharge study using a Versatile Modular Potentiostat (Princeton Applied Research) at a constant current of 140 mA/g (1 C rate) for voltage range of 3.0 ~ 4.4 V (Li/Li^+) and ran the cell for 100 cycles. The electrolytes of 1 ml in the tube cells were collected at different cycle intervals. Since the electrolyte required for Ion Chromatography is only 1 mL, the Mn concentration in the experimental cell will not be affected. The electrolyte was collected at periodic intervals using a syringe. The collected electrolyte was diluted 50 times by the deionized water. Each IC (Metrohm 861) analysis uses 1 mL of the diluted aqueous solutions. A calibration curve for manganese ion was evaluated using standard manganese ion solutions of 1 ppm, 5 ppm and 10 ppm in 0.5 M HNO_3 (Fluka no. 17075). The Ion Chromatography conditions are presented in the form of Table 1. The eluent solution contained some extent of tartaric acid, dipicolinic acid and ascorbic acid. Ascorbic acid could be used as a mild reductant.

Results and Discussion

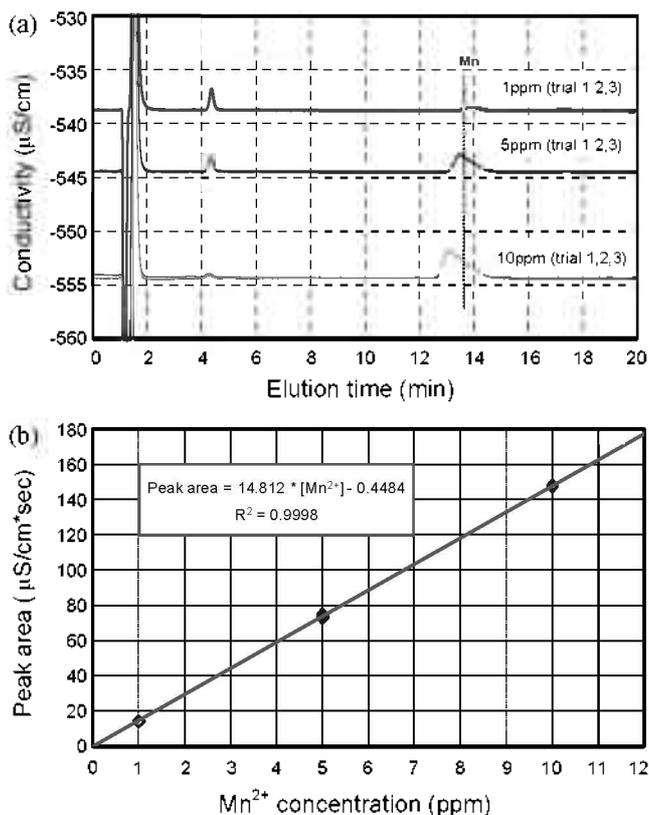
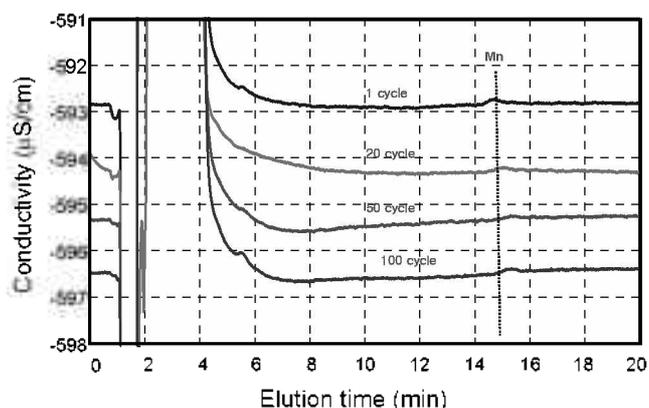
The capacity values at different cycle intervals and the voltage behaviors of each discharge were given as Fig. 2. The specific capacity decreases as the cycle number increases. The capacity decline with cycling may be attributed to the loss

**Figure 2.** The voltage behaviors against the specific capacity of $\text{Li/LiMn}_2\text{O}_4$ cell for the various cycle intervals.

of electrical contact between the electrode particles due to particle fracture with cycling and due to manganese dissolution as described by early researchers.^{3,8,11,13,17,22}

A chromatogram of the standard solution of 1, 5 and 10 ppm of Mn^{2+} ion by $\text{Mn}(\text{NO}_3)_2$ was presented in Fig. 3a. The retention time of Mn^{2+} for a given condition of Ion Chromatography was 14 minute. A calibration curve of Mn^{2+} ion was drawn as Fig. 3b with a correlation of empirical equations (1) and (2).

$$\text{Peak area } (\mu\text{Scm}^{-1}\text{s}^{-1}) = 14.812 \times \text{Mn}^{2+} \text{ concentration (ppm)} - 0.4484 \quad (1)$$

**Figure 3.** (a) The cation chromatograms and (b) the standard calibration curve of the standard manganese solutions.**Figure 4.** The cation chromatograms of the electrolyte of $\text{Li/LiMn}_2\text{O}_4$ cell for the various cycle intervals.

$$\text{Mn}^{2+} \text{ concentration (ppm)} = 0.06751 \times \text{Peak area } (\mu\text{Scm}^{-1}\text{s}^{-1}) + 0.0303 \quad (2)$$

An ion chromatogram of the electrolytes of different cycle intervals in Li/LiMn₂O₄ cell was presented in Fig. 4. Data of the chromatograms were analyzed by the use of the analytical program (IC net 2.3) and the calibration curve of Eq. (1) or (2) to give results of Table 2 and Fig. 5. The manganese concentrations in the electrolyte were 18 ppm after the first cycle, 23 ppm after 50th cycle and 31 ppm after 100th cycle, respectively. The rapid increasing of the manganese concentration during the 1st cycle was retarded for prolonged cycles to show 28% increasing at 50th cycle and 72% increasing at 100th cycle. Retarded increases of manganese ion content in electrolyte may be attributed to the buffer action provided by the manganese ions present in the electrolyte.

Table 2. The analytical results of the manganese dissolution in the electrolyte of Li/LiMn₂O₄ cell with various cycle intervals using Ion Chromatography.

Cycle number	Discharge capacity (mAh/g)	Capacity loss (%)	Mn ²⁺ concentration by IC (ppm)
1	93	0	0.18
20	86	7	0.23
50	81	12	0.23(5)
100	76	17	0.31

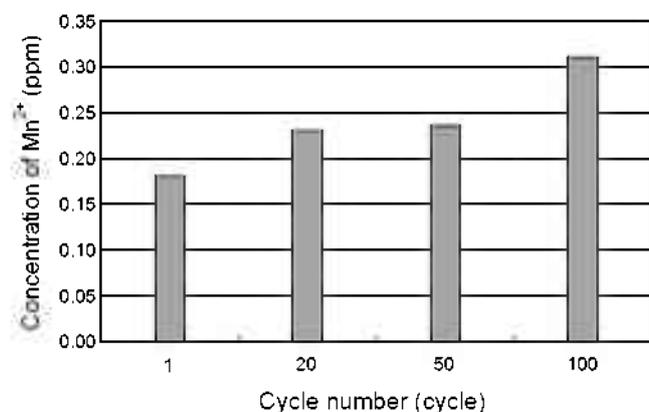


Figure 5. The manganese concentrations of the electrolyte of Li/LiMn₂O₄ cell for the various cycle intervals.

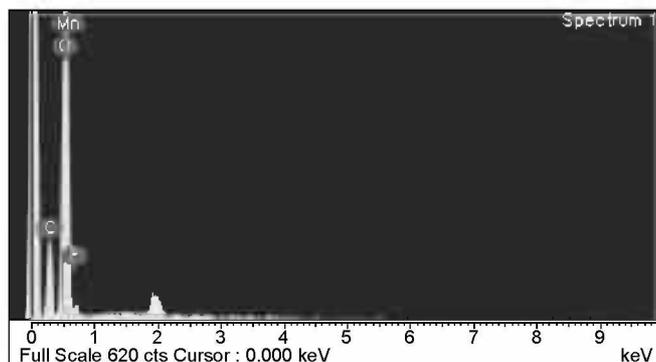


Figure 6. The EDX spectrum of the lithium anode of Li/LiMn₂O₄ cell.

to the buffer action provided by the manganese ions present in the electrolyte. Dissolved manganese ion from LiMn₂O₄ cathode can be deposited at the surface of lithium anode, which is fully enough to give reducing power to manganese ion. The deposition of manganese on an anode was confirmed by an energy dispersive X-ray spectrum (EDX) as shown in Fig. 6. Therefore, the concentration of manganese ion in the electrolyte could be maintained to certain range. The high capacity fading at the prolonged cycle may be attributed to the disintegration/loss of electrical contact among the electrode particles due to the manganese dissolution.

Results of this study is to serve one new method of quantitative analysis of Mn²⁺ ion dissolved in the organic electrolyte of lithium ion battery by Ion Chromatography. The technique of Ion Chromatography can be used as the method of quantitative analysis of Li, Co, Ni and Fe ions as the major components of cathode materials for lithium ion batteries. Furthermore, Ion Chromatography can be used in the field of anion analyses.

Conclusion

The use of Ion Chromatography for the direct quantification of manganese content in the electrolyte of Li/LiMn₂O₄ cell was reported. The manganese concentrations in the electrolyte were 18 ppm after the first cycle, 23 ppm after 50th cycle and 31 ppm after 100th cycle, respectively. The rapid increasing of the manganese concentration during the 1st cycle was retarded for prolonged cycles to show 28% increasing at 50th cycle and 72% increasing at 100th cycle. The buffering action on the manganese concentration in the electrolyte solution was provided by the continuous dissolution from the Li₂Mn₂O₄ electrode and deposition to the lithium electrode. The higher capacity losses at the prolonged cycles have been originated by the disintegration of the electrode particles by the manganese dissolution.

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