

## Multi-cycle operations for Lithium Extraction-insertion in the Spinel Manganese Oxide Adsorbents

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### INTRODUCTION

Over the past years, spinel lithium manganese oxides compounds have been proposed as the promising cathode materials in the rechargeable lithium batteries. It is urgent to exploit vast amounts of lithium to supply the industrial requirements. Therefore, recovery of lithium from seawater or other sources became an important issue in the recent years. In this work, spinel lithium manganese oxides synthesized in our laboratory were used as the starting adsorbent materials. Multi-cycle extraction-insertion of lithium was performed in column operations. The lithium adsorptivity and manganese dissolution, as well as the microstructure of the adsorbents were under this investigation.

### EXPERIMENTAL

Spinel-type  $\text{LiMn}_2\text{O}_4$  powder was synthesized from  $\text{MnCO}_3$  and  $\text{Li}_2\text{CO}_3$  ( $\text{Li}/\text{Mn} = 0.5$ ) by solid-state reaction. The experiments of extraction and insertion of lithium were operated in a column at  $25^\circ\text{C}$ . In the extraction step, the lithium was eluted from the adsorbents with  $0.5\text{N HCl}$  solution. Subsequently, the lithium ion was re-inserted into the adsorbent with a  $\text{LiCl}+\text{LiOH}$  solution ( $[\text{Li}^+] = 500\text{ppm}$ ). The valence of manganese was determined by standard sodium oxalate titration method. The analyses of XRD, SEM, EXAFS and atomic absorption spectroscope were used to characterize the adsorbents.

### RESULTS AND DISCUSSION

The lithium adsorptivity decreased with increasing the number of the operation cycle, as shown in Fig. 1. More amounts of manganese were dissolved under multi-cycle operations. As listed in Table 1, the valence of manganese increased after the elution of lithium from the adsorbents. This results revealed that disproportionation reaction, i.e.  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$ , was occurred. Also the  $\text{Mn}^{2+}$  ions would be dissolved in the  $\text{HCl}$  eluent [3]. As the results of EXAFS, the coordination number (CN) of the Mn-Mn decreased in the extraction step. On the contrary, the CN increased in the insertion step. The change in the bond distance of Mn-Mn was consistent with the trend of the CN. From the XRD patterns (Fig. 2), the characteristic peaks shifted to higher angle. It could be comprehensible that lithium was extracted from the tetrahedral interstice of the spinel lattice. When the lithium re-inserted into the spinel lattice, the characteristic peaks returned to lower angle. However, the degree of crystallization was reduced, and the irreversibility of the spinel structure was remarkable after multi-cycle operations. It might be the smaller particle and destruction of the spinel structure.

### CONCLUSION

The results showed that the extraction-insertion of lithium for spinel-type adsorbent was proceeded via redox mechanism. Multi-cycle operations resulted in the lowering of the lithium adsorptivity and collapse the spinel structure. Work on finding eluents with higher Li

uptake and less Mn dissolution is now in progress.

### LITERATURES CITED

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Table1. The valences of manganese and structural parameters calculated from EXAFS analysis for various samples.

Sample	$Z_{\text{Mn}}$	Mn-Mn		Mn-O	
		R (Å)	CN	R (Å)	CN
Parent materials	3.7	2.881	4.46	1.911	7.7
1 <sup>st</sup> -extracted	3.9	2.824	3.74	1.907	9.18
1 <sup>st</sup> -inserted	3.7	2.868	3.89	1.910	8.51
2 <sup>nd</sup> -extracted	3.8	2.825	2.70	1.897	8.49
2 <sup>nd</sup> -inserted	3.6	2.860	3.67	1.907	8.71
3 <sup>rd</sup> -extracted	3.8	2.821	2.16	1.897	7.63
3 <sup>rd</sup> -inserted	3.8	2.828	2.88	1.897	8.35

( $Z_{\text{Mn}}$ : valence of Mn, R: bond distance, CN: coordination number)

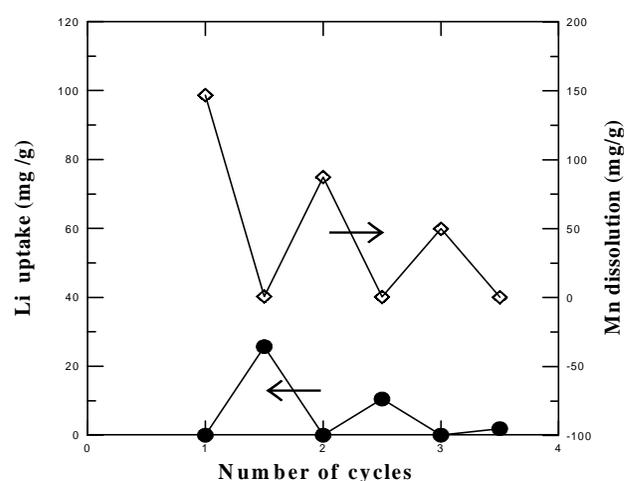


Figure1. The variations of Li uptake and Mn dissolution in the multi-cycle operations.

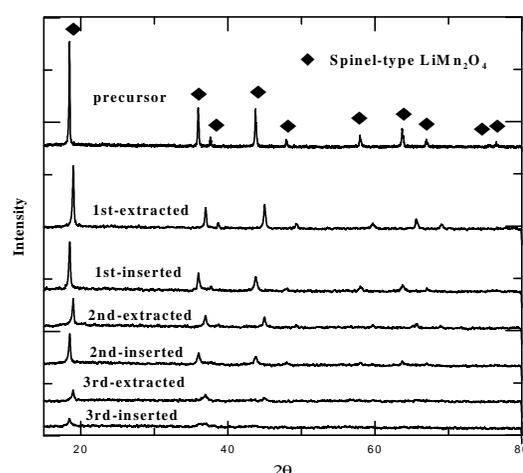


Figure2. XRD patterns of various samples in the multi-cycle operations.