

Dissolution behavior of chromium-ion doped spinel lithium manganate at elevated temperatures

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Abstract

The dissolution behaviors of manganese and chromium-ions of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ have been investigated at various temperatures. When the $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ powders were soaked in the LiPF_6 -containing electrolyte, the dissolution of manganese-ions as well as chromium-ions took place. With an increase of chromium-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$, the amounts of dissolved manganese-ions significantly decreased at room and elevated temperatures. This indicates that doping chromium-ions in LiMn_2O_4 can suppress the dissolution reaction of manganese-ions at elevated temperatures, thereby leading to lowered degree of capacity deterioration. On the other hand, raising the immersion temperature significantly increased the amounts of dissolved manganese and chromium-ions. It was also demonstrated that operation temperatures play an important role in the dissolution in both undoped and chromium-ion doped LiMn_2O_4 .

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1. Introduction

The spinel-structure lithium manganate has been considered to be one of the most promising cathode materials for lithium-ion secondary batteries owing to its low material cost and good environmental benignity [1–3]. However, the spinel-structured lithium manganate suffers from a serious capacity deterioration problem after cycling at elevated temperatures. Moreover, the discharge capacities diminish significantly with long-term cycling. These shortcomings limit the commercial application of LiMn_2O_4 to lithium-ion secondary batteries. In order to improve the cycleability, the structure of LiMn_2O_4 has been modified by doping other transition metal (TM)-ions into the original skeleton [4,5]. Several research groups have confirmed that the capacity fading after long-term cycling of TM-ion doped lithium manganate is considerably inhibited [6,7]. Furthermore, the electrochemical performance of the chromium-ion doped specimens cycled at elevated temperatures is markedly enhanced [8,9]. For elucidating the capacity fading of the batteries containing LiMn_2O_4 , several deterioration mechanisms have been proposed, i.e. Jahn-Teller distortion [10], dissolution of the active materials [11], decomposition of the electrolyte [12], lithium deposition [13], and the passive film

formation. Since the dissolution of active materials is regarded as the primary problem for the capacity loss in the lithium-ion batteries, it is imperative to examine the dissolution behavior of LiMn_2O_4 doped with other TM-ions.

In this study, the dissolution behavior of manganese and chromium-ions from the cathode materials $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ into the electrolyte was investigated. $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ powders were immersed in the LiPF_6 -containing electrolyte. The relations between the concentrations of TM-ions in the electrolyte and the reaction temperatures as well as the immersion duration were discussed. Normalized concentrations of manganese and chromium-ions were used to quantify the actual dissolved amounts in the electrolyte.

2. Experimental

$\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0, 0.05, 0.10, \text{ and } 0.15$) powders were synthesized via a solid-state process. Lithium hydroxide (LiOH), manganese dioxide (MnO_2), and chromium oxide (Cr_2O_3) were used as the starting materials. The starting powders with appropriate ratios were thoroughly mixed and heated at 800°C for 8 h in air. The crystal structure of the calcined specimens was characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation. Field emission scanning electron microscopy (FESEM) was performed to determine the particle size and morphology of the heated powders.

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To investigate the dissolution behavior of TM-ions in LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$, the obtained powders were soaked in the electrolyte consisting of 1 M LiPF_6 dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) at ambient and elevated temperatures. The weight of the immersed cathode powders was 0.08 g, and the volume of the electrolyte was 20 ml. After immersing the calcined powders for various durations, the resulted electrolytes were analyzed via atomic absorption spectroscopy (AAS) to determine the concentrations of the dissolved TM-ions.

3. Results and discussion

The XRD patterns of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0, 0.05, 0.10,$ and 0.15) powders calcined at 800°C for 8 h are shown in Fig. 1. All the diffraction peaks of calcined specimens were characterized as the pure spinel phase with a space group of $Fd\bar{3}m$. Fig. 2 shows the SEM photos of the $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ powders. It was clearly observed that the particle size of the calcined powders decreased with increasing the doping amount of chromium-ions. For LiMn_2O_4 , the average particle size was measured to be $1.34\ \mu\text{m}$. When x in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ increased from 0.05 to 0.15, the particle size decreased from 0.24 to $0.20\ \mu\text{m}$.

Fig. 3 illustrates the relation between the concentrations of dissolved cations and the immersion duration. The 800°C -calcined powders for $x = 0$ and 0.10 were soaked

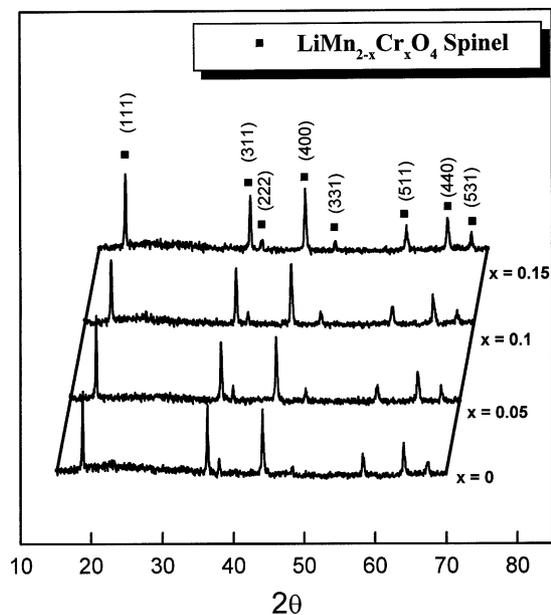


Fig. 1. XRD patterns of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ ($x = 0, 0.05, 0.10,$ and 0.15) powders calcined at 800°C for 8 h. The figure shows the corresponding lattice parameter of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$.

in the LiPF_6 -containing electrolyte at 55°C . In Fig. 3a, the apparent concentrations of manganese-ions (abbreviated as C_{Mn}) increased with prolonging the immersion duration. It was found that more manganese-ions were dissolved from undoped LiMn_2O_4 powders than from $\text{LiMn}_{1.9}\text{Cr}_{0.1}\text{O}_4$

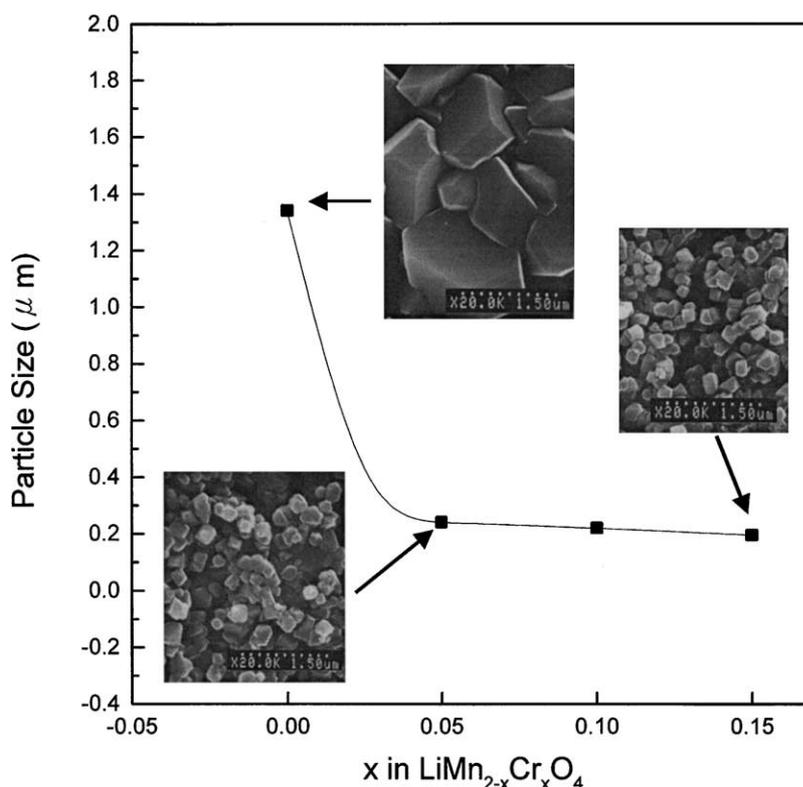


Fig. 2. SEM photographs and the corresponding particle size of the 800°C -calcined $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ powders.

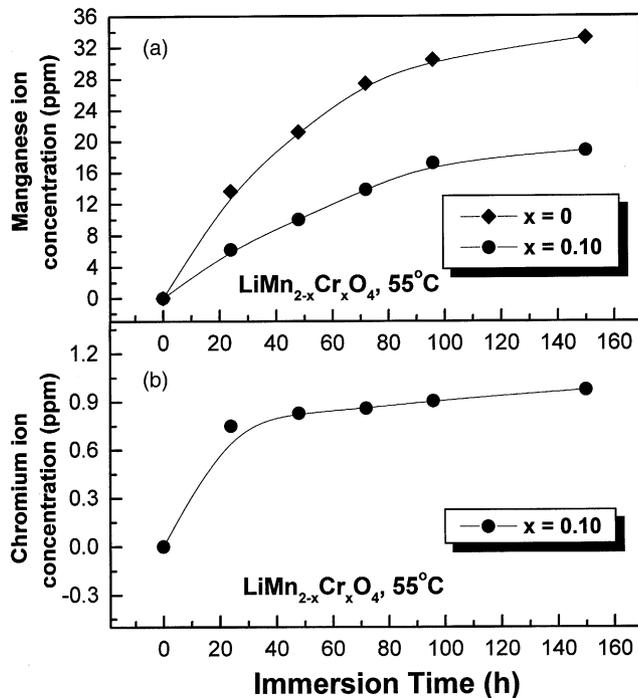


Fig. 3. Relationships between the apparent concentrations of dissolved TM-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ and the immersion time: (a) apparent Mn-ion concentrations (C_{Mn}) with $x = 0$ and 0.10 and (b) apparent Cr-ion concentrations (C_{Cr}) with $x = 0.10$.

powders, demonstrating that doping chromium-ions into the spinel lithium manganate could suppress the dissolution of manganese-ions at elevated temperature. Fig. 3b shows the concentration curve of dissolved chromium-ions in $\text{LiMn}_{1.9}\text{Cr}_{0.1}\text{O}_4$ samples. It was also observed that chromium-ions were also dissolved in the LiPF_6 -containing solution. The apparent concentrations of dissolved chromium-ions (abbreviated as C_{Cr}) increased with prolonging the immersion duration. It is worth noting that C_{Cr} increased more rapidly in the initial stage of the soaking process than in the final stage. This result indicates that chromium-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ mainly dissolved in the early period of the immersing process. With extending the immersing time, the dissolving rate of chromium-ion gradually decreased. It seems that the surface of the particles have less stable structure than the interior of the particles.

For accurately quantifying the dissolving amounts of manganese and chromium-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ with various doping amounts of chromium-ions, the measured concentrations of two TM-ions in the electrolytes were normalized according to the following equation:

$$N_{\text{TM}} = \frac{C_{\text{TM}}}{W \times (P_{\text{TM}}/M)} \quad (1)$$

where N_{TM} is the normalized concentration of corresponding TM-ions, C_{TM} the apparent concentration of TM-ions measured by AAS, W the weight of the immersed powders, M the molecular weight of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$, and P_{TM} the

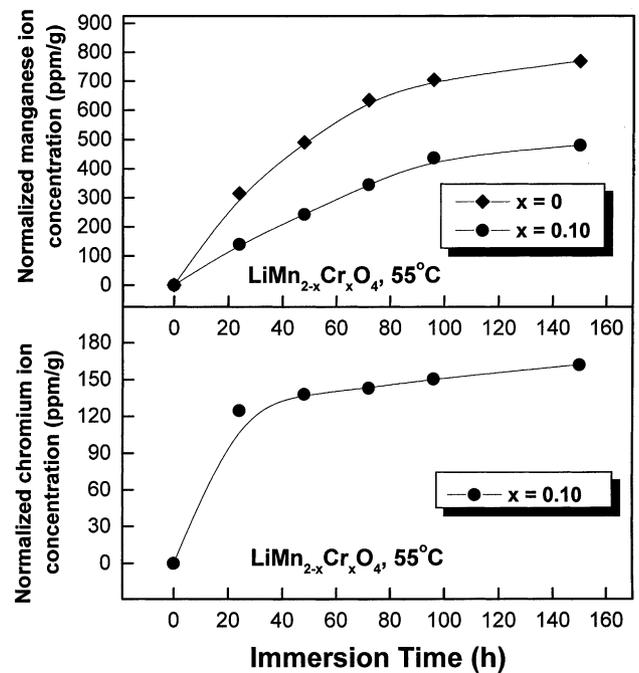


Fig. 4. The normalized results of dissolved TM-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$: (a) normalized Mn-ion concentrations (N_{Mn}) with $x = 0$ and 0.10 and (b) normalized Cr-ion concentrations (N_{Cr}) with $x = 0.10$.

weight of manganese or chromium-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$. The normalized results of the 55°C -immersed specimens ($x = 0$ and 0.10) are shown in Fig. 4. The values of N_{TM} represent the concentrations of TM-ions in the LiPF_6 -containing electrolyte per gram of the TM-ions in the cathode materials. In this study, N_{TM} was used to discuss the relationship between the concentrations of TM-ions in the electrolyte and the doping amounts of chromium-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$.

Fig. 5 depicts the normalized concentrations of manganese and chromium-ions when $\text{LiMn}_{1.9}\text{Cr}_{0.1}\text{O}_4$ powders were soaked in the electrolytes at 25, 35 and 55°C . From Fig. 5a and b, it was found that only small amounts of manganese and chromium-ions were dissolved from $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ at 25°C . However, the concentrations of the dissolved manganese and chromium-ions greatly increased with a rise in the immersion temperatures. This result revealed higher immersion temperatures significantly accelerated the dissolution reactions of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ powders. It was reported that doping chromium-ions into the spinel LiMn_2O_4 can effectively improve the cycleability at elevated temperatures [8]. However, based on the results of Fig. 5, chromium-ions were also found to dissolve into the electrolyte, which will affect the structural stability of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$.

To investigate the effects of chromium-ion doping on the dissolution of TM-ions, the 800°C -calcined powders with various doping amounts of chromium-ions were soaked in the electrolyte at 55°C . Fig. 6 illustrates the normalized

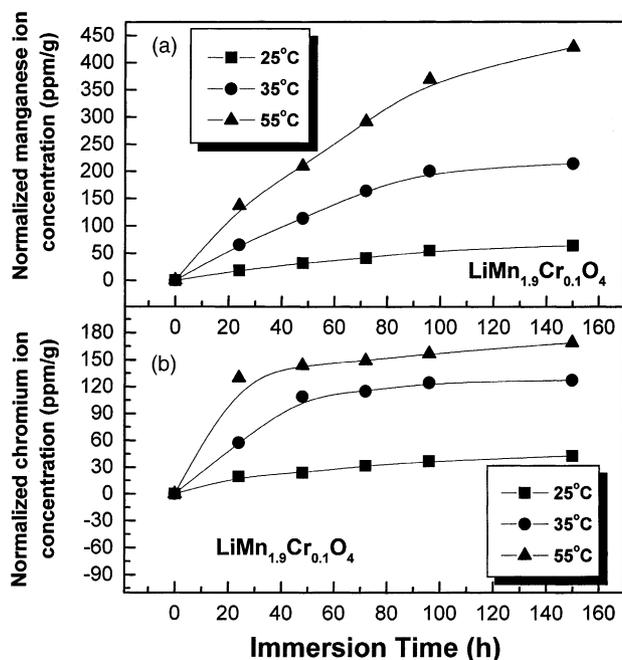


Fig. 5. Normalized concentration curves of the 800 °C-calcined $\text{LiMn}_{1.9}\text{Cr}_{0.1}\text{O}_4$ powders soaked in LiPF_6 -containing electrolytes at 25, 35 and 55 °C, respectively for 150 h.

concentrations of TM-ions measured after immersing the powders for 150 h. In Fig. 6a, it is clearly shown that the concentrations of dissolved manganese-ions decreased with increasing the doping amounts of chromium-ions. With a rise in the doping concentrations of chromium-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$, the normalized chromium-ion concentration

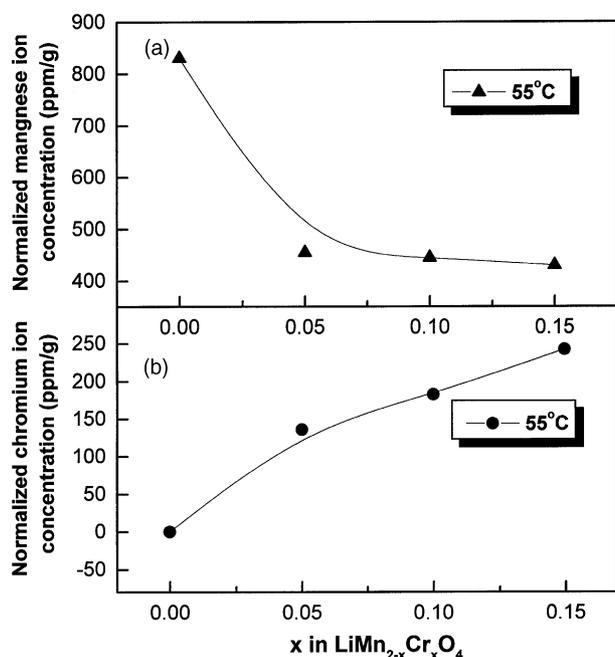


Fig. 6. Normalized concentration curves of TM-ions: (a) normalized Mn-ion concentrations and (b) normalized Cr-ion concentrations with various x in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ after immersing the powders for 150 h at 55 °C.

rose. These results indicate that the dissolution reaction of manganese-ions from the spinel structure can be suppressed by the doping of chromium-ions, and increasing the chromium-ions can reduce the dissolved manganese-ions. On the other hand, when the content of chromium-ions in the spinel structure increases, the amount of the dissolved chromium-ions also increases. From the FESEM micrographs in Fig. 2, doping chromium-ions into the spinel compound reduced the particle size of the cathode powders. However, the amount of dissolved manganese-ions did not increase when the particle size of the chromium-ions doped cathode powders became small. It implies that the structural stability plays a more important role than surface area in controlling the dissolution reactions of the spinel compounds. The relation between the molar ratio of dissolved chromium-ions to manganese-ions in the electrolyte and that of chromium-ions to manganese-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ is illustrated in Fig. 7. It was found that the molar ratio of dissolved chromium to manganese-ions increased when more chromium-ions were doped in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$. In addition, the molar ratio of dissolved chromium to manganese-ions decreased with higher temperatures in all samples. It is revealed that raising temperature had more profound effects on the Mn dissolution than increasing the doping amount of chromium-ions.

According to the previous studies, the capacity fading problems of pure spinel lithium manganate cathode powders at elevated temperatures are mainly dominated by the dissolution of manganese-ions [13–15]. Doping chromium-ions into the spinel structure can effectively improve the cycleability at elevated temperatures [8]. This study demonstrated that the Cr-doping in LiMn_2O_4 can suppress the reaction of Mn dissolution at elevated temperatures, thereby leading to lowered degree of the capacity deterioration.

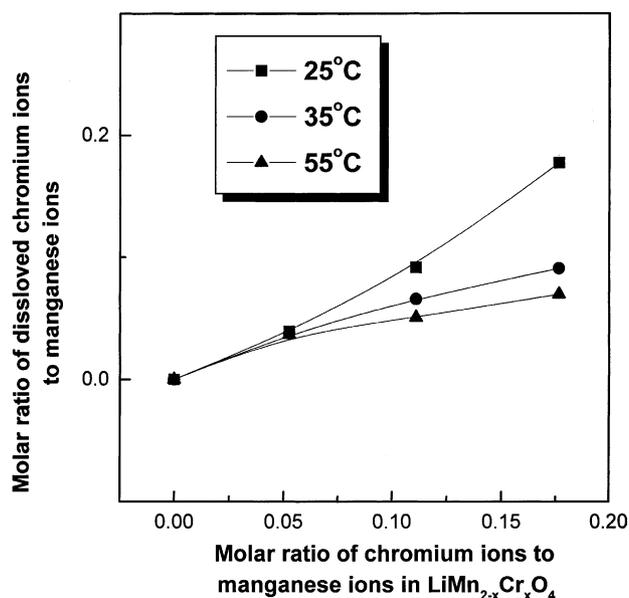


Fig. 7. Molar ratio of dissolved chromium-ions to manganese-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$.

However, it was also found that chromium-ions also dissolve into electrolyte after the long-term reaction at elevated temperatures. Therefore, additional studies on other appropriate dopants and co-dopants in spinel lithium manganate powders are still needed for further improving the electrochemical properties and structural stability of LiMn_2O_4 .

4. Conclusions

The dissolution behavior of the TM-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ at various temperatures has been investigated in this study. The amounts of dissolved manganese-ions in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ significantly decreased with an increase in the doping amounts of chromium-ions at ambient and elevated temperatures. It is indicated that doping chromium-ions in LiMn_2O_4 can suppress the dissolution reaction of manganese-ions at elevated temperatures, thereby leading to lowered degree of capacity fading. Increasing the doping amounts of chromium-ion in $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ also increased the amounts of dissolved chromium-ions in the electrolytes. In addition, raising the temperatures markedly accelerated the dissolution reaction of $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ powders.

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