Short communication

Determination of theoretical capacity of metal ion-doped $LiMn_2O_4$ as the positive electrode in Li-ion batteries

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Abstract

The theoretical capacity and cation vacancy of metal ion (M)-doped $LiMn_{2-x}M_xO_4$ spinel compounds serving as positive electrodes in a 4-V lithium ion batteries are calculated. The capacity depends strongly on the mole fraction of doped metal ion and vacancies. The theoretical capacity increases with increasing oxidation number of the doped metal ion in the 16d site of $LiMn_2O_4$ at the same doping fraction. The validity of the proposed equation for calculation of the capacity has been initially confirmed using a metal ion with well-known valence, such as the Al ion. The oxidation state of Co, Ni and Cr ions in the spinel structure is found to be trivalent, divalent and trivalent, respectively. Analysis shows that metal ion-doped spinel compounds with low vacancy content promote high capacity. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

$LiMn_2O_4$ spinel is an attractive candidate material for positive electrodes in lithium ion batteries. The cycleability of optimized $LiMn_2O_4$ at room temperature is excellent, for example, the capacity on the first and 100th cycle is 130 and 120 mAh g^{-1}, respectively [1,2]. On the other hand, prolonged cycling of $LiMn_2O_4$ at high temperature results in capacity fading [2,3]. Numerous attempts have been made to improve the cycle life of the spinel by partial substitution of Mn by Co, Ni and Al ions [4–6]. Encouraging results have been reported for Ni- and Co-doped spinels. The role of the doping metal ion is to prevent the formation of λ-MnO_2 in the charged state [2]. This technique always leads, however, to a reduction in the reversible capacity to below the predicted value. To explain this phenomenon, we propose a method to calculate the reversible capacity of metal ion-doped spinel. Using the assumption that vacancies exist in the 16d sites of the spinel structure, we have derived an explanation for the reduced reversible capacity.

2. Theoretical aspects

If it is assumed that the oxygen-rich spinel compound, in which the doped metal ion M with oxidation number z occupies only the 16d site of the spinel structure, then the chemical formula is:

$$[Li_x \square_{1-x}]_{8a}[Mn(III)_p Mn(IV)_q M(z)_r \square_s]_{16d}O_4, \quad (1)$$
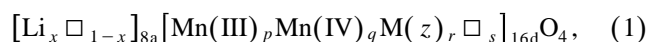
where x, p, q, r and s show the number of molecules in the 8a or 16d sites, and $\square$ denotes the vacancy.

If n equals the mole ratio of Li/total metal ion, $[Li]/([Mn] + [M(z)])$, and f the mole fraction of foreign ion, $[M(z)]/([Mn] + [M(z)])$, then the following equations can be formulated:

$$x/(p + q + r) = n, \quad (2)$$

$$r/(p + q + r) = f. \quad (3)$$

Consideration of the charge balance and the total number molecules in the 16d sites yields:

$$x + 3p + 4q + zr = 8, \quad (4)$$

$$p + q + r + s = 2. \quad (5)$$

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As we have prepared spinel compounds with $n = 1/2$, then:

$$x = 1 - 0.5s. \tag{6}$$

From Eqs. (2)–(6), we can obtain:

$$p = 1 - (9s/2) + (z - 4)r, \tag{7}$$

$$q = 1 + (7s/2) - (z - 3)r. \tag{8}$$

Using Faraday's law, the theoretical capacity, C_T, in the 4-V region (due to the reaction: Mn(III) → Mn(IV)) of the spinel compounds can be presented as follows:

$$C_T = 26.8\,p/F$$
$$= 26.8(1 - (9s/2) + (z - 4)r)/F, \tag{9}$$

where C_T is in Ah g^{-1} and F denotes the molecular weight of the spinel.

By combination with Eqs. (3) and (5), Eq. (9) becomes:

$$C_T = 26.8(1 - (9s/2))/F + 26.8(2 - s)(z - 4)f/F. \tag{10}$$

This relationship shows that the slope of C_T vs. f (fraction of doped metal ion) is proportional to $(z - 4)$ when s is kept constant. The oxidation number of the doped metal ion and the number of vacancies in the 16d site can be determined from the curve of observed capacity against mole fraction (f), as shown later.

3. Experimental

The test compounds were prepared using LiOH, Al(NO$_3$)$_3$, Co(NO$_3$)$_2$, Ni(NO$_3$)$_2$, Cr$_2$O$_3$ and Mn$_3$O$_4$ as precursors. LiOH, Mn$_3$O$_4$ and the given metal nitrate (or Cr$_2$O$_3$ in case of Cr-doped spinels) were mixed in appropriate ratios using a pestle and mortar. The resulting mixture was heated at 470°C for 5 h, followed by heating at 750–800°C for 20 h in air by the melt-impregnation method [7]. The chemical composition of the product was determined by chemical analysis [8].

The crystal structure of the compounds was analyzed by means of a Rigaku RINT1000 X-ray diffractometer (Rigaku, Japan) with Fe K$_\alpha$ radiation, and monochromated by a graphite crystal. All the samples had a single-phase spinel structure and no impurities were identified in the X-ray diffraction (XRD) patterns.

Charge and discharge tests were performed on CR2030 button-type cells. Each cell consisted of a positive electrode and a lithium-metal negative electrode that were separated by a polypropylene separator (Celgard 2501). The lithium metal was in excess. The positive electrode comprised 25 mg active material and 15 mg conducting binder pressed on to a 2.5 cm^2 stainless-steel screen. The electrolyte was 1 M LiPF$_6$-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 by volume). The cut-off voltages were 3.5 and 4.5 V vs. Li/Li$^+$. The typical charge/solidus discharge current rate was 0.1 mA cm^{-2} (10 mA g^{-1}).

4. Results and discussion

The plots in Fig. 1 show the relationship between the theoretical capacity of trivalent ion-doped spinel compounds and the mole fraction of doped metal ion with different s values, i.e., $s = 0$, 0.01, 0.015, 0.025. Eq. (10) was used to calculate the theoretical capacity. The molecular weight for the spinel compound was taken as 181, which is the value of pure LiMn$_2$O$_4$. To check the validity of the proposed equation, it was necessary to prepare a spinel doped with a metal ion which has a defined and stable valence. Such a metal ion is the aluminum ion, which has an oxidation number of three. The Al-doped spinel compounds were subjected to charge–discharge tests. As shown in Fig. 1, the measured initial charge capacity of aluminum-doped spinel is 133, 125, 117 and 108 mAh g^{-1} for f values of 0.022, 0.048, 0.062 and 0.090, respectively. The observed capacities lie on the line of $z = 3$ and $s = 0.015$ and 0.020, depending on the different ratio. Thus, the proposed method is confirmed to be useful for the determination of the oxidation number of the doped metal ion and the vacancy content in the metal ion-doped spinel. As shown in Fig. 2, the capacity decreases with increase in the content of doped metal ion. The capacity decline of spinels doped with Al, Cr or Co is similar, but is somewhat larger for Ni ion-doped spinels.

Cobalt and nickel ions usually exist as divalent ions in oxides. On the other hand, chromium ion exists in various
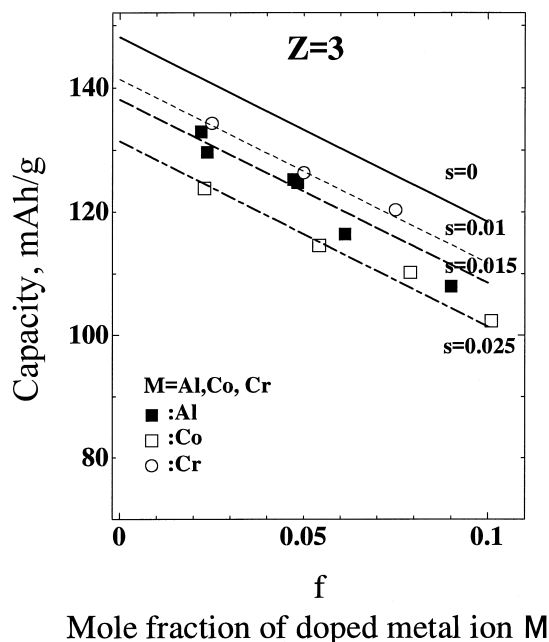

Fig. 1. Theoretical capacity for trivalent metal ion ($z = 3$)-doped spinels and measured capacity for Al-, Co- and Cr-doped spinels; s = vacancy content.
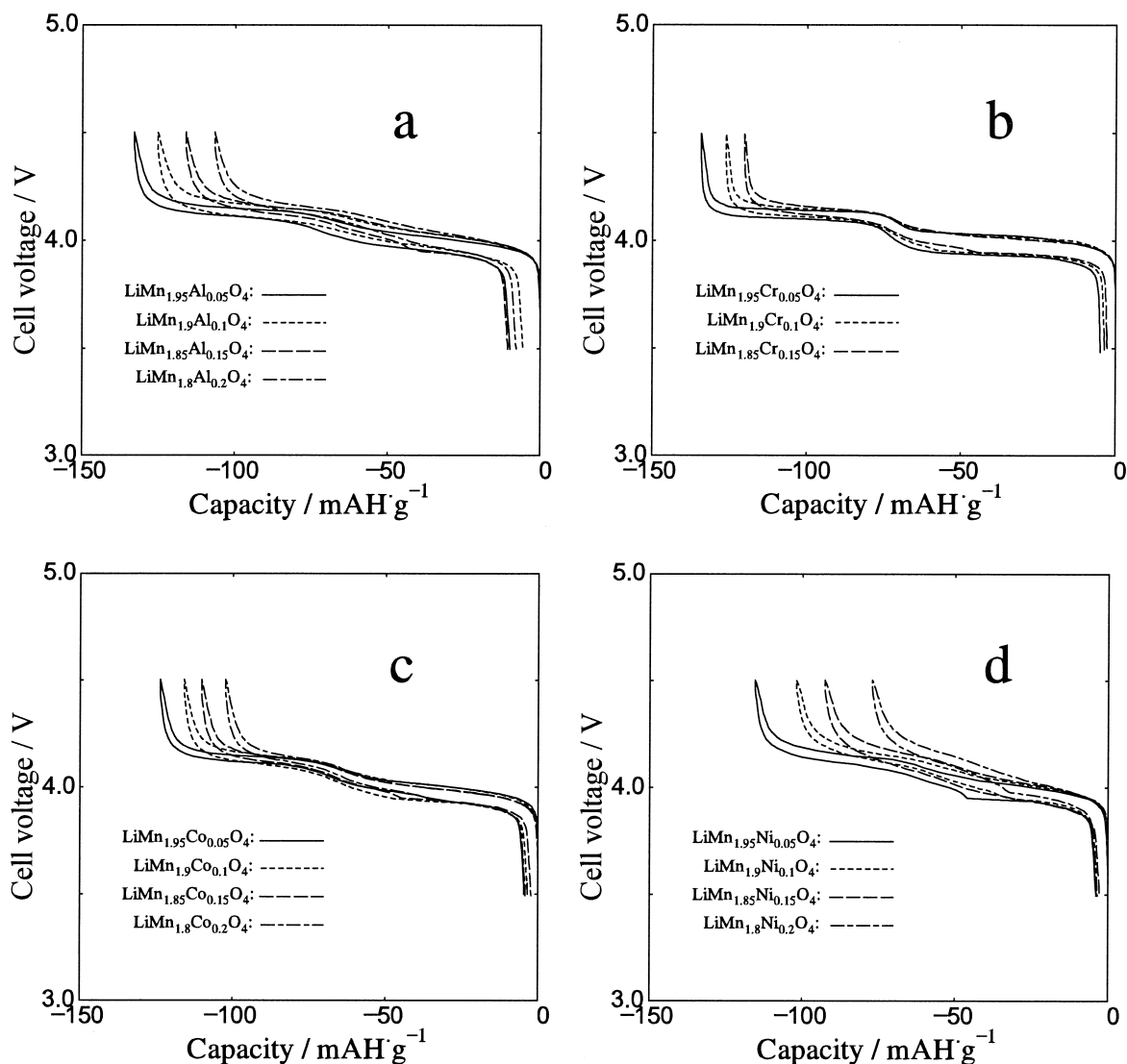
Fig. 2. First charge–discharge curves of (a) Al-, (b) Cr-, (c) Co- and (d) Ni-doped spinels.

oxidation states from $2+$ to $6+$. To determine the oxidation number of these metal ions in the spinel phase, a slope analysis based on Eq. (10) was undertaken; the resulting plots are presented in Figs. 1 and 3. As can be seen in Fig. 1, the Cr-doped spinels follow the same relation as the Al-doped spinels and lie exactly on the line $s = 0.01$ and $z = 3$. The valence of cobalt ion and chromium ion in the spinel phase is found to be trivalent, and that of nickel ion is divalent. The valence of nickel in spinel agrees with that obtained by XPS analysis [9] and leaching of lithium from doped spinel by acid treatment [4]. Further, the valence of chromium also agrees with that determined by EELS analysis [10]. In the other words, the usefulness of the method for the determination of oxidation number of doped ion is supported by the results of other analyses. Moreover, the slope analysis gives reliable data about the oxidation state of the metal ion into the bulk of the spinel, whereas the surface state is determined by XPS analysis.

The number of vacancies in Cr-doped spinel is in the range $s = 0.008$ to $s = 0.011$. By contrast, the number of vacancies in Co-doped spinel is in the range $s = 0.022$ to $s = 0.025$. The vacancy content in Ni-doped spinel is slightly larger ($s = 0.02$ to 0.03) than that of Co-doped spinel. If the vacancy content can be neglected (i.e., $s = 0$), the theoretical capacity of doped spinel can be calculated at various doping levels as summarized in Table 1. These

Table 1
Theoretical capacity (mAh g^{-1}) of doped metal ion spinel, Li-$Mn_{2-x}M_xO_4$

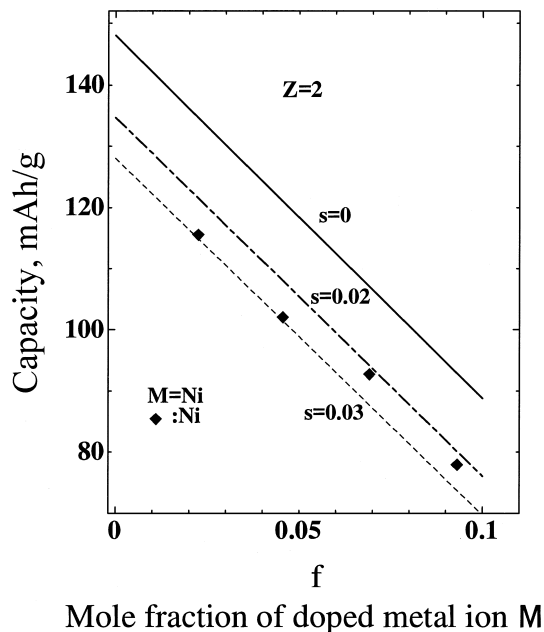| Doped metal ion	Fraction of doped metal ion (f = x/2)		
	0.025	0.05	0.1
Monovalent (Li)	126	104	59
Divalent (Ni)	133	118	89
Trivalent (Al, Cr or Co)	141	133	118

Fig. 3. Theoretical capacity for divalent metal ion ($z = 2$)-doped spinels and measured capacity for Ni-doped spinels; s = vacancy content.

vacancy content would produce a spinel with high stable reversible capacity. Doping with a high valence metal, such as Co(III) and Cr(III), will yield a stable spinel with high reversible capacity.

5. Conclusion

A slope method of analysis has been developed to determine the real oxidation state of the doped metal ion M in $LiMn_{2-x}M_xO_4$ spinel compound.

data show that metal ion-doped spinel with high valence yields higher capacity. The capacity shows strong dependence on the existence of vacancies. To obtain a capacity above 120 mAh g^{-1} at a fraction (f) of 0.05 for trivalent ion, the vacancy should be less than 0.02. The vacancy content in the 16d site for trivalent metal ion (Co, Cr, Al)-doped spinel is lower than that for divalent ion (Ni)-doped spinel. Thus, a synthesis process which reduces the

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