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Capacity of layered cathode materials for lithium-ion batteries – a theoretical study and experimental evaluation

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Abstract

The theoretical capacity and the vacancy concentration of metal-ion-doped layered compounds such as $LiCoO_2$, $LiNiO_2$, and $LiMnO_2$, acting as cathodes in high-voltage lithium-ion batteries are calculated. The capacity shows strong dependence on valency of the doped metal ion and vacancy concentration. Experimental verification carried out to check the validity of the proposed equation for aluminium substitution into the potential layered materials shows good agreement between the experimental and theoretical capacity values. The vacancy concentration values of doped layered compounds have been found to be high when compared with that of the doped spinel compounds.

Keywords: Lithium-ion batteries; Doped compounds; Layered cathodic materials; Theoretical capacity; Vacancy concentration

1. Introduction

With an increase in the demand for batteries having extended life and higher power output for various portable applications, research in the development of lithium batteries satisfying these requirements has been intensified. In the lithium battery system the energy storage is mainly associated with a reversible lithium intercalation into positive electrode materials, i.e., cathodes. Various cathode materials have been under close scrutiny for the last 25 years since the discovery of intercalation compounds [1]. Sony launched the commercial lithium-ion cell in 1991, using layered $LiCoO_2$ as the positive material [2]. $LiMn_2O_4$ and $LiNiO_2$ are also being investigated intensively for possible application as positive materials for commercial Li-ion cells. This makes the battery environmentally benign and cheap, as cobalt in $LiCoO_2$ is toxic and expensive. The practical problem that prevents $LiMn_2O_4$ from reaching the commercial stage is its reduced capacity as the number of cycles is increased. In the case of $LiNiO_2$, the synthesis of pure phase itself is a problem because of the coexistence of NiO. Apart from layered $LiCoO_2$ and $LiNiO_2$ and spinel $LiMn_2O_4$, there is one technologically significant layered compound $LiMnO_2$, but the synthesis of the pure phase of this compound is again posing great difficulty. A few groups have reported the synthesis of this compound via an ion-exchange process [3].

Many attempts have been made to eliminate the difficulties that prevent these potentially suitable materials from reaching the commercial stage [4–6]. Doping of metal ions into cathode materials has proven successful with respect to both $LiMn_2O_4$ [7] and $LiNiO_2$ [8]. These studies have led to the identification of a new layered compound $LiCo_yNi_{1-y}O_2$ $(0<y<0.9)$, which is at the threshold of commercial exploitation [9]. For all these newly synthesised materials the parameter of great practical importance is the capacity of the material.

This work reports the calculation of the theoretical capacity of the doped layered compounds which crystallise in α-$NaFeO_2$ structure. An experimental study has also been performed to verify the validity of the proposed equation for theoretical capacity. An attempt has already been made to evaluate the theoretical capacity of spinel $LiMn_2O_4$ [10].

2. Theoretical aspects

In the layered compounds of the general type $LiMeO_2$, which are of α-$NaFeO_2$ structure, the transition metal ions and lithium ions occupy 3(a) and 3(b) sites, respectively and oxygen ions occupy the 6(c) sites. The oxygen ions form a closed cubic packing, i.e., the structure can be described as

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a layered structure in which lithium cation sheets and MeO_2 sheets are piled up alternately [11]. Here we assume that the doped metal ions occupy only the 3(a) site of the transition metal ions. Experimental evidence by XRD crystal Reitveld refinement has proved the presence of aluminium ions in the nickel ion site in $LiAl_yNi_{1-y}O_2$ [8] supporting the above assumption. If the doped metal ions 'M' with valency '*Z*' occupy the octahedral 3(a) sites, the chemical formula can be represented as

$$[Li_x\square_{1-x}]_{3(b)}\ (Me(III)_p\, Me(IV)_q\, M(Z)_r\, \square_s)_{3(a)}\ O_2 \quad (1)$$

where *x*, *p*, *q*, *r* and *s* show the numbers of ions at the 3(b) and 3(a) sites and □ represents the vacancy.

Now, let us define

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

and

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

where *n* is the mole fraction of Li and *f* is the mole fraction of doped metal ions with respect to the total metal ions present.

The charge balance and total number of ions at the 3(a) sites lead to

$$x+3p+4q+rZ=4 \quad (4)$$

$$p+q+r+s=1 \quad (5)$$

since, we have synthesised our compounds with a Li-to-metal ion ratio as unity, $n=1$, then

$$x=1-s \quad (6)$$

Since all layered compounds such as $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$ have the Li-to-metal ion ratio as unity, we have from Eqs. (4) and (6)

$$p=1-5s+r(Z-4) \quad (7)$$

$$q=4s-r(Z-3) \quad (8)$$

Now the theoretical capacity due to the reaction $Me^{3+}\rightarrow Me^{4+}+e^-$, using Faraday's law, is

$$C_T=26.8\ p/F \quad (9)$$

$$C_T=26.8[1-5s+r(Z-4)]/F \quad (10)$$

where C_T is the theoretical capacity in mAh g^{-1} and *F* is the molecular weight of the layered compound.

On combining Eqs. (3), (7) and (8), we have

$$C_T=26.8[1-5s+f(1-s)(Z-4)]/F \quad (11)$$

wherein

$$p=1-5s+f(1-s)(z-4) \quad (12)$$

$$q=4s-f(1-s)(z-3) \quad (13)$$

Eq. (11) signifies that the capacity depends on the vacancy content *s* and the dopant concentration *f* when the valency of the doped cation is constant.

3. Experimental

The synthesis of aluminium-doped $LiCoO_2$ has been done by the sol-gel method and details have been given elsewhere [12]. The synthesised compound was analysed for its phase purity using Cu Kα X-ray diffraction studies. The electrochemical studies were performed in a glass cell with lithium metal as negative electrode and doped $LiCoO_2$ as positive electrode in 1 M $LiPF_6$/EC/DEC electrolyte. The synthesised cathode materials were mixed with 5% acetylene black and 2% PVDF as binder, and made into a slurry coated onto an aluminium mesh which was used as a current collector. The above cell was assembled inside an argon-filled glove box.

4. Results and discussion

4.1. $LiCoO_2$

The theoretical capacity of trivalent-ion-doped $LiCoO_2$ was calculated for various values of vacancy concentrations *s* and valency *Z* using Eq. (11). For experimental verification, doped $LiAl_yCo_{1-y}O_2$ was synthesised [12]. The experimental capacity of the synthesised aluminium-doped $LiCoO_2$ behaves as predicted by Eq. (11) and the first charging capacities were 152, 157, 141 and 84 mAh g^{-1} for $y=0.05$, 0.1, 0.25, and 0.5, respectively, in $LiAl_yCo_{1-y}O_2$. There is a decrease in capacity with an increase in aluminium concentration and a small deviation in this experimental value of capacity for $y=0.1$. This deviation is very much within the region of acceptable experimental error. A typical charge–discharge curve using the synthesised compound $LiAl_{0.25}Co_{0.75}O_2$ as cathode, Li metal as anode and 1 M $LiPF_6$/EC/DEC as electrolyte is shown in Fig. 1. It shows an equilibrium voltage of 4.4 V. The voltage plateau between 4 and 4.4 V remains flat with increase in aluminium content [12]. This voltage of 4.4 V is very high when compared to pure $LiCoO_2$ (voltage range of 3.7 V); however, in both cases the active redox couple is Co^{3+}/Co^{4+}. In the case of aluminium-doped $LiCoO_2$ the increase in voltage is due to the presence of constant valent Al^{3+} ions, which also force electron exchange with oxygen during topotactic reactions [13].

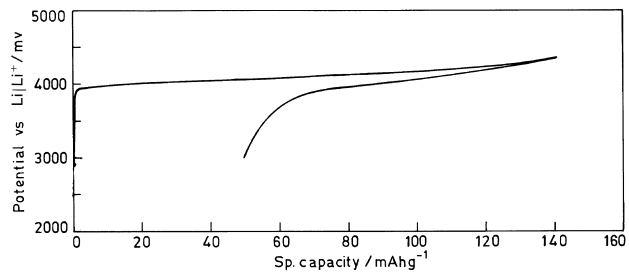

Fig. 1. Typical charge–discharge curve of $LiAl_{0.25}Co_{0.75}O_2$ at *C*/100 rate.

The discharge capacities obtained for synthesised compounds [12] show a linear decrease with increase in aluminium content. The change in capacity for aluminium-doped $LiCoO_2$ may be attributed to the change in the active redox couple Co^{3+}/Co^{4+} ratio. In this, Co^{4+} is a Jahn–Teller ion, which has an adverse effect on the CoO_6 octahedra. The lithium ion intercalation is mainly dependent on the maintenance of the host structure. Hence, the increase in Co^{4+} ions will affect the structure of the $LiCoO_2$ which reflects on the intercalation process, reducing the capacity.

For divalent dopant ions, our theoretical calculation predicts a decrease in capacity with increase in dopant concentration as in Fig. 2(a) for doped $LiCoO_2$. This may be due to increase in Co^{4+} content and the corresponding decrease in Co^{3+} content. The increase in Co^{4+} content reflects directly on the spontaneous disruption of the CoO_6 octahedra, resulting in a structural change, which hinders the lithium intercalation. The reduction in Co^{3+} content is also reflected in the decrease in capacity. Similar results have been observed in pristine $LiCoO_2$, wherein the Co^{4+} is the Jahn–Teller ion responsible for the spontaneous deformation from O_h symmetry of CoO_6 octahedra [5]. The observed capacity of aluminium-doped $LiCoO_2$ matches the capacity calculated using Eq. (11) for a vacancy concentration between $s = 0.06$ and $s = 0.08$, and $Z = 3$ for all studied values except for the mole fraction value of 0.5, wherein the deviation may be due to mixed-phase [12] formation which is not accounted for in our calculation of the theoretical capacity C_T (Fig. 2(b)).

With the increase in valency of the dopant ion Z, the theoretical capacity increases. This increase can be explained by the fact that doping of metal ion M with a higher valency leads to increase in p in Eq. (1), which is the Me^{3+} ion concentration. Since the capacity is mainly due to the active redox couple Me^{3+}/Me^{4+} the increase in Me^{3+} leads to the higher theoretical capacity, C_T. The slope of the curve of capacity versus dopant concentration f decreases gradually, reaches zero for $Z = 4$ and then increases with increase in Z for metal-ion-doped $LiCoO_2$, which is evident from Eq. (11). For dopant valences of $Z < 4$, the theoretical capacity decreases with increase in dopant concentration f: this is because an increase in f decreases the number of Me^{3+} ions, which reduces the capacity for dopants. When $Z = 4$, the number of Me^{3+} ions (p), remains the same, independent of f, and hence a constant capacity line has been observed. For $Z > 4$, the number of Me^{3+} ions (p) increases with increase in f which accounts for the increase in capacity. However, we expect this trend of increase in C_T with increase in f is only valid up to a particular value of f, the limit of which is observed in our calculations by the negative values of p and q (not given). When this limit of f is exceeded, the dopant forms a separate oxide phase as shown by our XRD for $LiAl_{0.5}Co_{0.5}O_2$ [12]. This phase segregation disrupts the electrochemical activity.

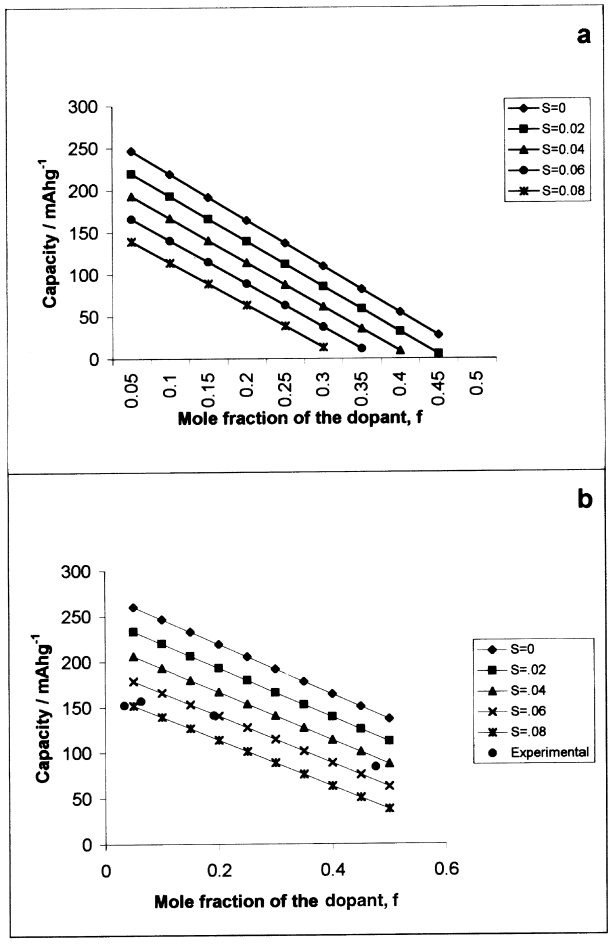

Fig. 2. Capacity vs. mole fraction of the dopant for doped $LiCoO_2$: (a) $Z = 2$; (b) $Z = 3$.

4.2. $LiNiO_2$ and $LiMnO_2$

Calculated capacities for aluminium substitution in $LiNiO_2$ have been done for $Z = 3$ for various vacancy concentrations. For divalent-ion-doped ($Z = 2$) $LiNiO_2$, a similar behaviour is observed as in Fig. 2(a). The observed capacity [8]

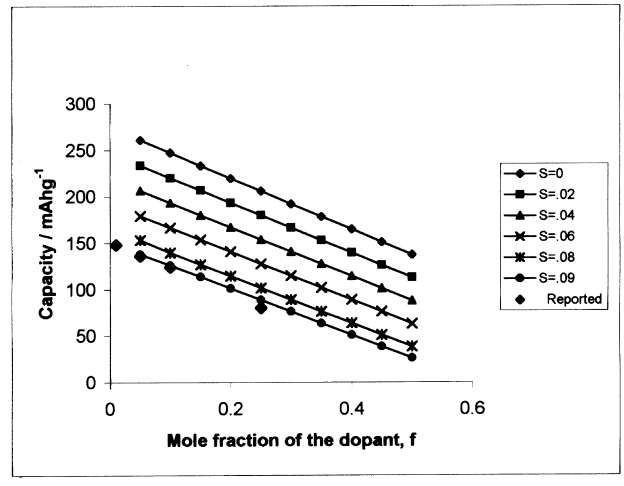

Fig. 3. Capacity vs. mole fraction of the dopant for doped $LiNiO_2$ for $Z = 3$.

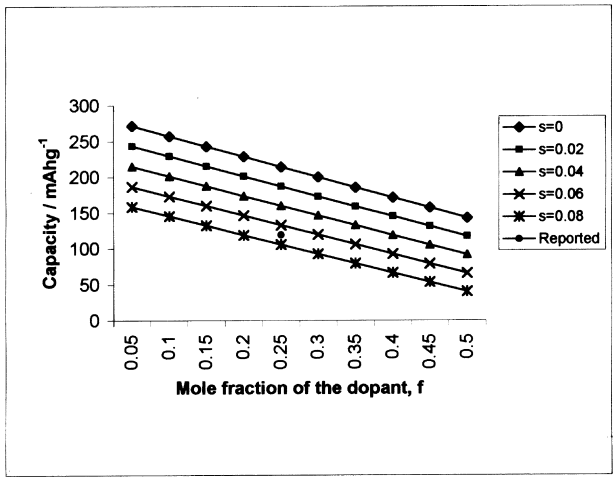

Fig. 4. Capacity vs. mole fraction of the dopant for doped $LiMnO_2$ for $Z=3$.

matches our calculated capacity for a vacancy concentration of $s=0.09$ and $Z=3$, as shown in Fig. 3. As per our calculated capacities, increase in capacity is attributed to increase in Ni^{3+} ion, which is the Jahn–Teller ion in the active redox couple Ni^{3+}/Ni^{4+}. However, for doped compounds, there is a predominant absence of cooperative Jahn–Teller effect. A monoclinic phase which results from the cooperative Jahn–Teller effect of low-spin Ni^{3+} is not observed in the entire range of $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$, probably due to a microscopic stress induced by the substitution of nickel ions for aluminium ions [5]. For metal-ion-doped $LiMnO_2$ also, theoretical capacities were calculated for $Z=2$ and $Z=3$ for various vacancy concentrations. For divalent-ion-doped ($Z=2$) $LiMnO_2$ a similar behaviour is observed as in Fig. 2(a). The reported capacity [14] for doped $LiMnO_2$ matches the calculated values for a vacancy concentration of $s=0.06$ and $Z=3$, as shown in Fig. 4 for $LiAl_{0.25}Mn_{0.75}O_2$. This experimental evidence indicates that metal-ion-doped layered compounds have vacancy concentrations ranging from 0.06 to 0.09. The vacancy concentrations of the layered compounds seem to be high when compared to that of spinel $LiMn_2O_4$ with a vacancy concentration of 0.01–0.03 [10].

4.3. Theoretical capacity and cycling

The theoretical capacity calculated using Eq. (11) is the first-cycle charging capacity, since we base our calculations of C_T upon p which is the number of Me^{3+} ions in the cathode materials prepared as such. We expect the p/q ratio, i.e., number of Me^{3+}/Me^{4+} to vary with the cycles and reach a steady value [14]. It has been experimentally shown for $LiAl_{0.25}Mn_{0.75}O_2$ that, with cycling, the capacity increases progressively and saturates after about 15 cycles at 148 mAh g^{-1} [14]. In the case of layered $LiMnO_2$ substituted with cobalt [15] the capacity fading due to the Jahn–Teller effect of Mn^{3+} ions is very much reduced. This capacity ranges between 200 and 210 mAh g^{-1} for nearly 20 cycles. Of this observed capacity only a proportion is delivered above 4 V versus $Li|Li^+$. The remaining portion of the capacity is delivered in the 3 V region. From this it may be concluded that the doping of non-transition metal ions into the potential layered compounds yields higher voltage at the cost of capacity [13], whereas the doping of transition metal ions results in the increase of capacity at the cost of voltage [15].

5. Conclusions

The theoretical capacity of layered cathode materials for lithium batteries has been calculated. Experimental verification has been done by the substitution of constant valent aluminium in the $LiCoO_2$ matrix. Similar experimental work reported in the literature for $LiNiO_2$ and $LiMnO_2$ was considered for the verification of our calculated capacities. From the study the following conclusions have been derived:

1. Theoretical capacity of the doped layered compound increases with increase in valency Z of the dopant ion.
2. Of all the layered materials studied, $LiMnO_2$ shows higher capacities than other materials, because it has a lower vacancy concentration.
3. The substitution of non-transition metal ions into the layered compounds results in higher voltage with a reduced capacity, whereas transition metal ion doping yields a higher capacity with a lower voltage profile.
4. The experimental values of the capacity of layered materials match the capacities calculated from our proposed equation. The vacancy concentration of the doped layered compounds has been found to be high when compared with that of the doped spinel compounds.

Hence, a synthesis procedure which yields a lower vacancy concentration for a higher valent doped layered compound will yield better capacity.

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