

Comparison of structure and electrochemistry of Al- and Fe-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

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Abstract

$\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{M}_x\text{Mn}_{1/3}\text{O}_2$ ($\text{M} = \text{Fe}$ and Al ; $x = 0, 1/20, 1/9$ and $1/6$) have been synthesized by firing the co-precipitates of metal hydroxides. The impacts of Fe and Al doping on the structure and electrochemical performances of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are compared by means of powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and galvanostatic charge/discharge test as cathode materials for lithium ion batteries. These materials keep the same layered structure as the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ host. It is found that Fe- and Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ show different characteristics in lattice parameter and cycling voltage plateau with increasing dopant dose. More interestingly, low Al doping ($x < 1/20$) improves the structural stability while Fe doping does not have such effect even at low Fe content.

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1. Introduction

In recent years, layer-structured $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ has been extensively studied as a candidate to replace the costly LiCoO_2 cathode material. The predominant oxidation states of Ni, Co, Mn in these materials are +2, +3 and +4, respectively. During delithiation, the Ni^{2+} ions are oxidized to Ni^{4+} while the oxidation state of Mn^{4+} remains unchanged. It is believed that the presence of Mn^{4+} stabilizes the structure of the material and improves its electrochemical reversibility during cycling [1]. Therefore, the electrochemical performances and safety of these materials are comparable or even superior to that of LiCoO_2 [2–4].

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is an important member of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ family ($x = 1/3$) [5]. An initial discharge capacity of 160 mAh/g was obtained in the cutoff voltage range of 2.5–4.4 V [1,6]. The reversible capacity can be further raised to 200 mAh/g if the material is charged to 4.6 V versus Li^+/Li [1,7–9]. As the Co^{3+} ion will not be oxidized to Co^{4+} until ca. 4.6 V [1], the available capacity of this material is expected to increase if the delithiation potential can be lowered.

Partial substitution has been proved an effective method in modifying the electronic structure and improving the electrochemical performances of the cathode materials. Recently, the Ceder's group in MIT and other scientists in the world reported a series of interesting theoretical studies on predicting the electrochemical performances of the cathode materials, such as Al doping to improve its electrochemical stability of LiNiO_2 or $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ [10,11].

Cr doping into LiFePO_4 to increase its electric conductivity [12] and Fe doping into $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ to lower its delithiation potential [13]. These studies, with the help of experimental investigations, greatly shortens the development cycle of materials. However, in most cases, what the scientists concern the most is the general performances of a material. Predicted improvement of one or a few aspects of the properties of a material may sometimes bring new and even more severe problems in other aspects. A good example for this is that Cr doping for Li in LiFePO_4 increases the electronic conductivity but the doped Cr atoms hinder the diffusion of the Li^+ ions and finally deteriorates the rate performance of this material [14]. In this paper, we will compare the impacts of two typical elements, Fe^{3+} and Al^{3+} (Fe^{3+} doping lowers the delithiation voltage while Al^{3+} doping raises the delithiation voltage), on the electrochemical performances and structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and show some revelatory results.

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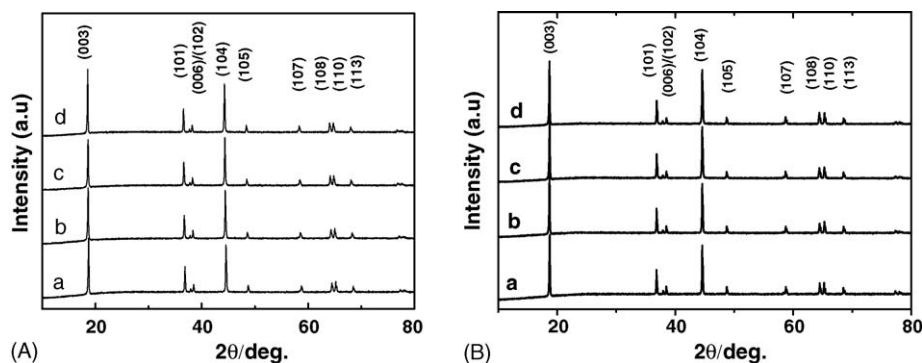


Fig. 1. X-ray diffraction patterns of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$ (A) and $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ (B) with $x=0$ (a), $x=1/20$ (b), $x=1/9$ (c) and $x=1/6$ (d).

2. Experimental

$\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (all are 99.9% in purity) and $\text{Mn}(\text{NO}_3)_2$ (50% aqueous solution) were used as starting materials for $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$. The aqueous solution of the metal nitrates and LiOH were dripped and mixed in a stirred reactor. The pH value of the mixture was regulated to 11 by changing the dripping rate of the two solutions. $\text{NH}_3\cdot\text{H}_2\text{O}$ can also be used as the chelating agent. The temperature, pH value and the concentration of the solution as well as the stirring speed of the mixture were controlled carefully. This led to the precipitation of hydroxides of Ni, Co, Fe and Mn with a homogeneous cation distribution. The precipitate was dried at 140°C for 8 h after rinsing and filtering. The dried powder was then mixed with a stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ and ball-milled sufficiently. The solid mixture was heated at 450°C for 5 h. By sintering the powder at 900°C for 20 h was the final product obtained. All the above operations were carried out in air.

On preparing $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$, dried Ni, Co, and Mn hydroxides were mixed with stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ (99%; $\text{Al}(\text{OH})_3$ will be dissolved in an alkaline solution) by sufficient ball milling. $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ was obtained by treating the powder as that for $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$.

Powder X-ray diffraction (Panalytical, X'pert Pro MPD) with $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase of the products. XRD data were collected in the 2θ range of $10\text{--}80^\circ$. The morphology of the material was observed on Philips FEG XL30 scanning electron microscope (SEM).

Slurries containing 85 wt.% active material, 5 wt.% polyvinylidene fluoride PVDF dissolved in *n*-methyl-2-pyrrolidinone (NMP) and 10 wt.% acetylene black were spread evenly on a piece of Al foil. The sheet was subsequently dried at 100°C for 10 h and then was cut into pieces as cathode. One mole per liter of LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DEC) containing (1:1, v/v) was used as the electrolyte solution. Coin cells were assembled with metallic Li as the counter electrode and Celgard 2400 as the separator in an Ar-filled glove box. The cells were cycled between 2.5 and 4.4 V versus Li/Li^+ galvanostatically (C/10 rate) on Land CT2001A battery tester (Wuhan, China) at room temperature.

3. Results and discussion

The X-ray diffraction patterns of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ are shown in Fig. 1. All the peaks in each pattern can be indexed to the $\alpha\text{-NaFeO}_2$ structure ($R\bar{3}m$, 166), indicating that all the obtained materials are well crystallized and pure in phase.

Table 1 compares the a and c values of all the prepared materials. It can be found that both the a and c values all increase with increasing Fe content in $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, indicating that the volume of the unit cell increases with the Fe content. As the radius of the Fe^{3+} ion is larger than that of Co^{3+} , it is reasonable that substitution of Fe^{3+} for Co^{3+} in $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ leads to lattice expansion in the a and c directions. The c value of the Al-substituted $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ increases with increasing Al content while its a value slightly decreases with the increasing Al content, indicating that the influence of Al doping on the structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is not remarkable. This is attributed to the similarity of Al^{3+} and Co^{3+} in ionic radius.

Figs. 2 and 3 show the SEM images of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{M}_x\text{Mn}_{1/3}\text{O}_2$ ($M=\text{Fe}$ and Al), respectively. The particle size of the Al- and Fe-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ lies between 200 and 500 nm and does not vary with the dopant or the doping content.

More attention was paid to the electrochemical aspects of the doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Fig. 4A shows that both the charge and discharge capacities of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$ decrease with increasing Fe content in the material. Part of the reason is that the Fe^{3+} ion cannot be oxidized until rather high voltage (4.4 V versus Li^+/Li). As the cutoff voltage range in this work is

Table 1
The lattice parameters of Fe- and Al-substituted $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

Compounds	Crystal parameters	
	a	c
$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$	2.862	14.249
$\text{LiNi}_{1/3}\text{Co}_{1/3-1/20}\text{Fe}_{1/20}\text{Mn}_{1/3}\text{O}_2$	2.868	14.258
$\text{LiNi}_{1/3}\text{Co}_{2/9}\text{Fe}_{1/9}\text{Mn}_{1/3}\text{O}_2$	2.874	18.263
$\text{LiNi}_{1/3}\text{Co}_{1/6}\text{Fe}_{1/6}\text{Mn}_{1/3}\text{O}_2$	2.880	18.275
$\text{LiNi}_{1/3}\text{Co}_{1/3-1/20}\text{Al}_{1/20}\text{Mn}_{1/3}\text{O}_2$	2.861	14.251
$\text{LiNi}_{1/3}\text{Co}_{2/9}\text{Al}_{1/9}\text{Mn}_{1/3}\text{O}_2$	2.858	14.254
$\text{LiNi}_{1/3}\text{Co}_{1/6}\text{Al}_{1/6}\text{Mn}_{1/3}\text{O}_2$	2.856	14.258

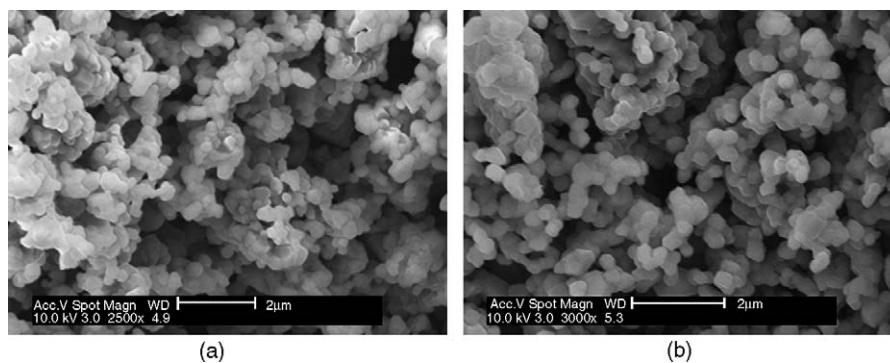


Fig. 2. SEM images of LiNi_{1/3}Co_{1/3-x}Fe_xMn_{1/3}O₂ with $x = 1/20$ (a) and $x = 1/6$ (b).

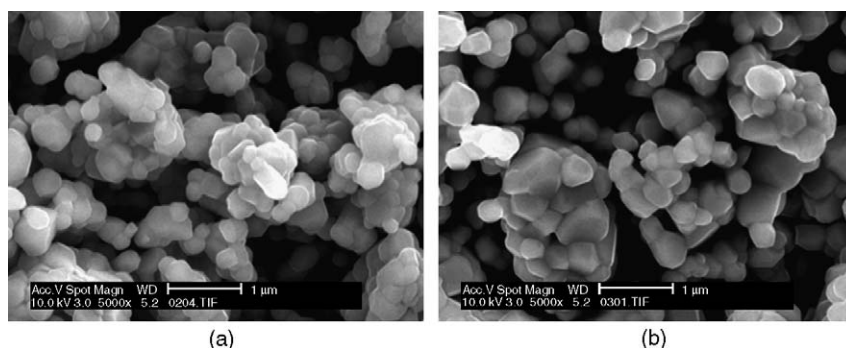


Fig. 3. SEM images of LiNi_{1/3}Co_{1/3-x}Al_xMn_{1/3}O₂ with $x = 1/20$ (a) and $x = 1/6$ (b).

2.5–4.4 V, these Fe³⁺ ions are actually electrochemically inactive. Further investigation to Fig. 4 indicates that the discharge capacity in the first cycle decreases quicker than the charge capacity with increasing Al content. The discharge capacity and coulombic efficiency of the Fe-doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ also decrease with increasing Fe content but the coulombic efficiency does not drop as obvious as the Al-doped samples. The coulombic efficiency for all the Fe- and Al-doped materials keeps ca. 96% in the second and subsequent cycles and does not vary with the doping content any more.

Fig. 5 compares the profiles of voltage versus normalized capacity of Fe³⁺- and Al³⁺-doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ in the 3rd cycles. The voltage plateau at ca. 3.75 V for LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ ($x = 0$) is assigned to its Ni²⁺/Ni⁴⁺

reaction. It is seen that the delithiation (charge) plateau rises monotonously when x increases from 0 to 1/6 for LiNi_{1/3}Co_{1/3-x}M_xMn_{1/3}O₂ ($M = \text{Al or Fe}$). The lithiation (discharge) plateau also rises with the Al content (Fig. 5A) but does not with the Fe content (Fig. 5B). This implies that the rise of charge voltage plateau of Fe-doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ results from the polarization effect rather than from the drop of chemical potential of the material due to Fe doping. Actually Ceder and co-workers [13] predicted that Fe doping lowers the operation voltage of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. The polarization effect becomes more severe with increasing Fe content.

Although the reversible capacities of Fe- and Al-doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ decrease with the increasing doping dose, their reasons are different. The decreased specific capacity

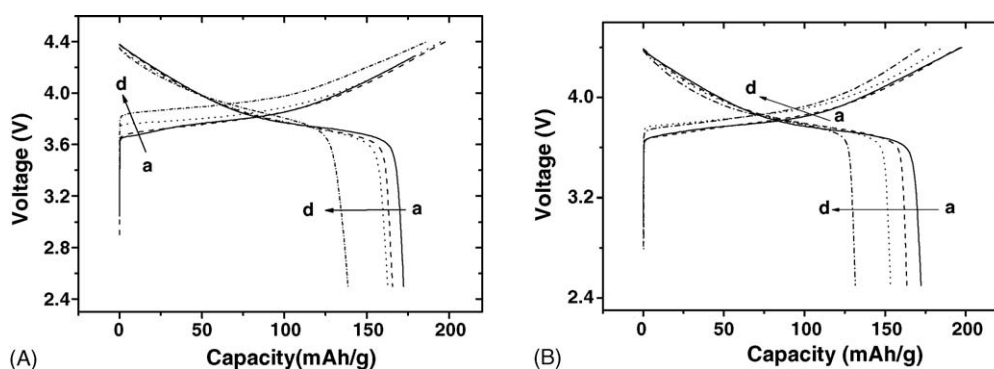


Fig. 4. Comparison of the voltage profiles of LiNi_{1/3}Co_{1/3-x}Fe_xMn_{1/3}O₂ (A) and LiNi_{1/3}Co_{1/3-x}Al_xMn_{1/3}O₂ (B) ($x = 0$ (a), $x = 1/20$ (b), $x = 1/9$ (c), $x = 1/6$ (d)) in the first cycle.

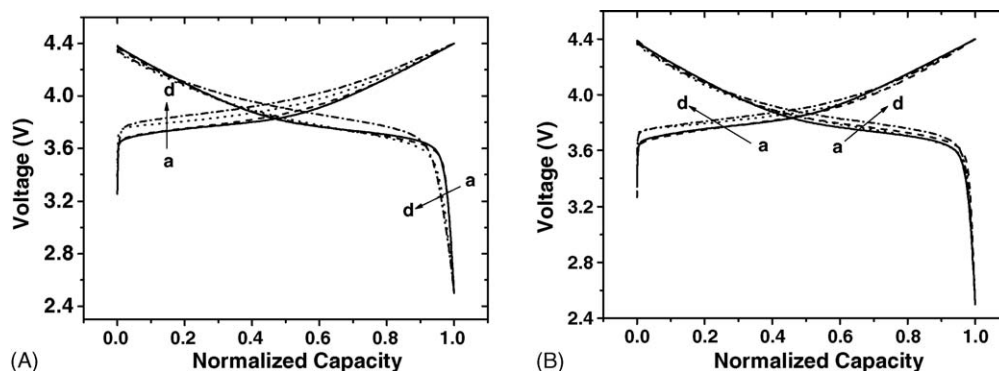


Fig. 5. The third charge curves of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$ (A) and $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ (B) cycled between 2.5 and 4.4 V at room temperature ($x=0$ (a), $x=1/20$ (b), $x=1/9$ (c), $x=1/6$ (d)).

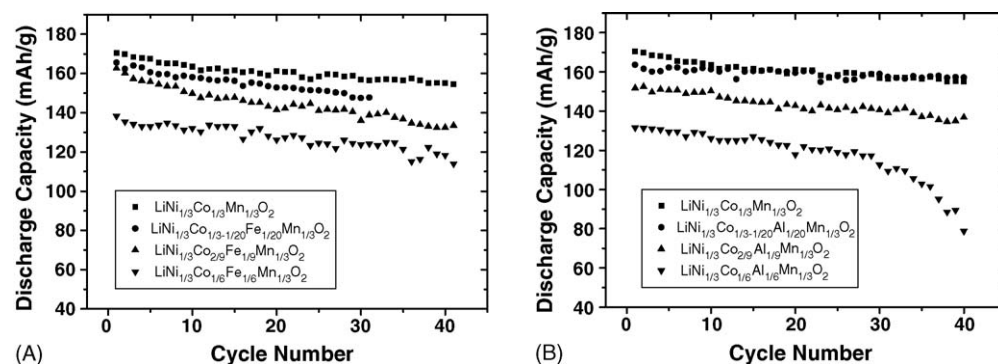


Fig. 6. Cycling performances of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$ (A) and $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ (B) cycled between 2.5 and 4.4 V.

for the Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ might be for two reasons. On one hand, Al^{3+} is electrochemically inactive in $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ as cathode material. Therefore, substitution of Al^{3+} for Co^{3+} in $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ decreases the content of its active species. On the other hand, both the charge and discharge voltage plateaus of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ obviously increase with increasing Al^{3+} content. This phenomenon has been experimentally observed by Jang et al. in Al-doped LiCoO_2 [15]. As a result, the rise of the discharge and charge voltage plateaus for the Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ should be attributed to the real drop of chemical potential of the material. However, the cutoff voltage is not obviously

correspondingly elevated in the charge process in this work for the purpose of comparison with that of the Fe-doped samples.

The reason for the decreased capacity of the Fe-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is more complicated. On one hand, similar to the Al^{3+} ions, the Fe^{3+} ion is also electrochemically inactive for the cutoff charge/discharge voltages in this work (2.5–4.4 V). Therefore increasing Fe^{3+} content means decreasing the active species in $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. On the other hand, it is reported that the doped Fe atoms tend to occupy the 3a sites as well as the 3b sites, especially after deep charge of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Fe}_x\text{Mn}_{1/3}\text{O}_2$. The Fe atoms at the 3a sites

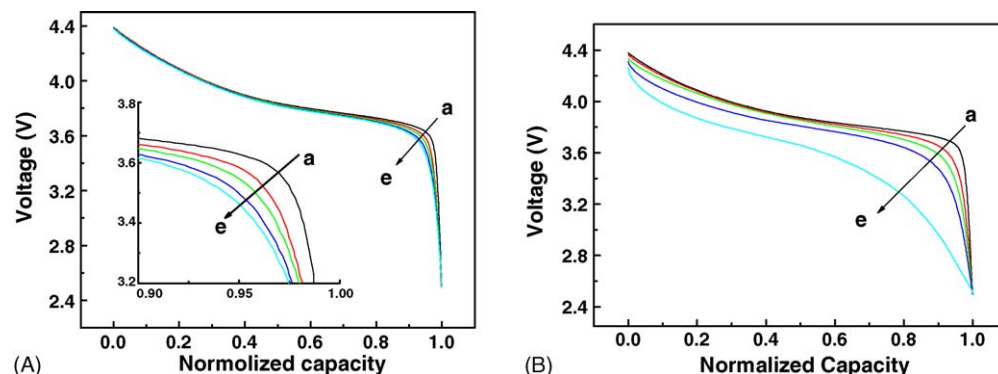


Fig. 7. Comparison of voltage profiles vs. normalized capacity of low (A, $x=1/20$) and high (B, $x=1/6$) Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ between 4.4 and 2.5 V at C/10: (a) 1st cycle, (b) 10th cycle, (c) 20th, (d) 30th cycle, (e) 40th cycle.

hinder the diffusion of the Li ions also located at the 3a sites. This will lead to decrease of ionic conductivity and increase of polarization of the material. Because of this, a sudden decrease of Li ion mobility takes place. This will lead to “irreversible capacity” [16,17]. This phenomenon can occur for both the Al- and Fe-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. However, as the mobility of the Li^+ ions decreases more for the Fe-doped host than for the Al-doped one, the discharge capacity of Fe-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is more obvious. The lost capacity for this reason can be recovered by sufficiently decreasing the current density for discharge [18] (therefore, Dahn et al. regarded the phrase “lost capacity” as a misnomer).

Jang et al. believed that Al-doping enhances the Li diffusivity and suppresses the cycling-induced lattice strain in $\text{Li}_{1-x}\text{Al}_x\text{Co}_{1-y}\text{O}_2$. Fig. 6 compares the cycling performances of $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$ ($x=0, 1/20, 1/9, 1/6$) between 2.5 and 4.4 V versus Li/Li^+ at room temperature. Indeed Al-doping is effective in enhancing the cycling performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ when the doping dose is low ($x < 1/20$). Nevertheless, both the reversible capacity and capacity retention decrease when more Al ($x > 1/20$) is doped. At $x = 1/6$, the capacity fades to about 80 mAh/g after 40 cycles.

In order to find out the reason for the quick deterioration of the cycling performance of $\text{LiNi}_{1/3}\text{Co}_{1/3-1/20}\text{Al}_{1/20}\text{Mn}_{1/3}\text{O}_2$ with high Al content, the voltage profiles of $\text{LiNi}_{1/3}\text{Co}_{1/3-1/20}\text{Al}_{1/20}\text{Mn}_{1/3}\text{O}_2$ (Fig. 7A) and $\text{LiNi}_{1/3}\text{Co}_{1/6}\text{Al}_{1/6}\text{Mn}_{1/3}\text{O}_2$ (Fig. 7B) experiencing various galvanostatic cycles are compared. It is seen that the voltage profiles of low Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material almost overlap with each other for 40 cycles, corresponding to the excellent capacity retention or the stable structure of the material. The shape of the voltage profile of the high Al-doped material in the first discharge, however, is very different from the one that has experienced 40 cycles. The voltage profiles are well separated, showing clearly that both the average discharge voltage and the available capacity decrease quickly. Meanwhile, the polarization effect of the cell is very obvious. As soon as the charge process is ended, the voltage drops from 4.4 to ca. 4.2 V (Fig. 7B). This is a phenomenon very similar to that observed in most other cathode materials though its exact reason is still unknown. Structural degradation is supposed to be responsible for the deteriorated cycling performance of highly Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3-x}\text{Al}_x\text{Mn}_{1/3}\text{O}_2$. However, this structural degradation is not detectable with XRD. Similar phenomena were also observed for the Fe-doped materials but the doping-induced polarization is not as obvious as the Al-doped materials do.

As Al^{3+} is introduced into $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by mixing the co-precipitates of Ni^{2+} , Co^{3+} and Mn^{4+} with fine $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ powder in this work, it becomes difficult for the Al^{3+} ions to distribute homogeneously in the final product when the Al content is high. This might be also an important reason for the poor cycling performance of high-content Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/6}\text{Al}_{1/6}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/6$). Between these two critical points, the impacts of Al- and Fe-doping are similar—Al and Fe doping show similar effects: doping reduces the discharge capacity but does not influence the cycling performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

4. Conclusions

Al- and Fe-substituted $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ have been prepared by firing the co-precipitates of Ni, Co and Mn hydroxides. All the prepared materials have $\alpha\text{-NaFeO}_2$ structure as $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ does. The lattice parameters a and c of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ increase with increasing Fe content but roughly keeps unchanged with the Al content. Comparison of the electrochemical performances of Fe- and Al-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ indicates that both series of materials show similar discharge capacities and rather good reversibility. The discharge capacity of Co-substituted $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ drops for different reasons. Fe doping lowers the delithiation potential plateau of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ but hinders the diffusion of its Li^+ ion due to disordered occupation of the doped Fe ions at the 3a sites. It seems that Fe doping cannot improve the electrochemical performances of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. In contrast, low-content ($x < 1/20$) Al doping improves the capacity retention of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. However, the capacity retention becomes poor because homogeneous distribution of Al^{3+} ions in the material becomes impossible at high-dose doping ($x > 1/6$) with the present method.

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