

# The improved physical and electrochemical performance of $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ cathode materials by the Cr doping for lithium ion batteries

Yucheng Sun<sup>a,b</sup>, Yonggao Xia<sup>b</sup>, Hideyuki Noguchi<sup>b,\*</sup>

<sup>a</sup> Venture Business Laboratory, Saga University, Honjo-1, Saga 840-8520, Japan

<sup>b</sup> Department of Applied Chemistry, Saga University, Honjo-1, Saga 840-8520, Japan

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## Abstract

We have successfully prepared the layered structure  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents by a co-precipitation method. Many measurement methods have been applied to characterize the physical and electrochemical properties of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ , such as XRD, SEM, BET and electrochemical test. SEM showed that the addition of Cr has obviously changed the morphologies of their particles and increased the size of grains. The specific surface area of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  decreases linearly from  $4.9 \text{ m}^2 \text{ g}^{-1}$  ( $x=0$ ) to  $1.8 \text{ m}^2 \text{ g}^{-1}$  ( $x=0.1$ ) with the increasing of Cr contents. Moreover, we have found that the Cr doping can greatly improve the density of the powder, which is beneficial to solve the problem of lower electrode density for these layered  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  cathode materials. Electrochemical test indicated that the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  can be significantly improved with the increasing of Cr contents, although the initial discharge capacity of the sample has a little decrease.

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**Keywords:** Lithium ion batteries; Cathode materials; Cr doping; Tap density; Cycling performance

## 1. Introduction

Until now, many compounds have been studied as cathode materials for lithium ion batteries such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFePO}_4$ , as well as  $\text{LiMnO}_2$  and their derivatives [1–7]. Among these materials,  $\text{LiCoO}_2$  have been widely used in commercial lithium ion batteries. In order to further improve the energy density of lithium ion batteries to meet the need of mobile electric devices, more and more interests are focused on the layered  $\text{LiMO}_2$  ( $M = \text{Ni}, \text{Co}, \text{Mn}$ ) cathode materials with a higher reversible capacity and lower cost [8–16]. Moreover, its thermal stability can be greatly improved by the addition of Mn in the layered structure.

Ohzuku and Makimura [8] and Dahn and co-workers [9] have, respectively, reported a series of layered compounds based on Ni–Mn oxides. These materials have a higher reversible

capacity and good structural stability even charged to 4.6 V. However, the poor rate capability and lower tap density of these layered compounds are the main obstacles to be applied as cathode materials in lithium ion batteries [13,14,17–20]. Our previous experimental results showed that the addition of Co can greatly improve the rate capability of these layered Li–Ni–Mn–O cathode materials [16,21]. The lower tap density, which is another disadvantageous feature of these compounds, can lead to low electrode density and ultimately to the low volumetric energy density of practical lithium ion batteries. Many preparation techniques have been adopted to improve the tap density of these compounds by preparing a high tap density precursor with a large-size spherical particle and heightening the sintering temperature [18–20,22]. Sun and co-workers [18] prepared the spherical  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  with a high density by sintering  $\text{LiOH}\cdot\text{H}_2\text{O}$  and a spherical nickel, manganese and cobalt hydroxide precursor, which is produced by controlling the co-precipitate conditions such as pH, concentration of  $\text{NH}_4\text{OH}$  and stirring speed. And then, M. Yoshio and co-workers [19,20] applied carbonate co-precipitation to prepare a homogenous

\* Corresponding author. Tel.: +81 952 28 8674; fax: +81 952 28 8591.  
E-mail address: [noguchih@cc.saga-u.ac.jp](mailto:noguchih@cc.saga-u.ac.jp) (H. Noguchi).

layered spherical  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  with a high tap density. Moreover, Dahn and co-workers have adopted a sintering agent  $\text{B}_2\text{O}_3$  to increase the density of  $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  and studied the effects of addition of a few weight percent of boron oxide on the preparation, structure, morphology, density and electrochemical behaviors of cathode materials [23].

In the previous experiments, we have mainly studied the Cr effects on the physical properties of the layered Li–Ni–Mn–O materials [24]. In this paper, we have adopted the doping Cr in layered Li–Ni–Co–Mn–O compounds to improve the physical properties especially the tap density and the electrochemical performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ .

## 2. Experimental

$\text{LiOH}\cdot\text{H}_2\text{O}$  (>98%, Wako),  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (>98%, Aldrich),  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (>99%, Wako),  $\text{Mn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (98%, Wako) and  $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (>95%, Wako) were used as the starting materials. A 1 M aqueous solution of the transition metal nitrates, a 2 M LiOH aqueous solution and 1 M  $\text{NH}_3\cdot\text{H}_2\text{O}$  solutions were slowly dripped into a stirred reactor. The PH value was kept at 11 by adjusting the amount of LiOH aqueous solution. This causes the precipitation of triple hydroxide of Cr, Ni, Co and Mn with a homogeneous cation distribution. The precipitate was filtered out and washed three times with additional distilled water to remove the residual LiOH and the formed  $\text{LiNO}_3$ . The precipitate was dried in air at  $120^\circ\text{C}$  overnight. A series of layered  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  compounds were prepared by heating a mixture of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and a co-precipitate of Cr, Ni, Co and Mn at  $800^\circ\text{C}$  in air for 3 h.

Powder X-ray diffraction (XRD, Rint-1100, Rigaku, Japan) measurement using  $\text{Cu K}\alpha$  radiation was employed to identify the crystalline phase of the synthesized materials. XRD data were obtained ( $2\theta = 15\text{--}70^\circ$ ) with a step size of  $0.02^\circ$ . The as-prepared powders were observed using a scanning electron microscope (SEM, JSM 5200, JEOL, Japan) to get an understanding of their morphology. The specific surface area of the sample was measured by BET method (Micromeritics FlowsorbIII, SHIMADZU).

Pellet density (PD) was obtained by making 16 mm diameter pellets with about 1.0 g of ground powder under the pressure of 20 MPa. The thickness and diameter of the pellet after pressing was measured and the density was then calculated. This PD is well correlated with the achievable electrode density.

The charge/discharge tests were carried out using a CR2032 coin-type cell, which consists of a cathode and lithium metal anode separated by a Celgard 2400 porous polypropylene film. The electrolyte was 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio. The cathodes were prepared by blending 20 mg  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  and 12 mg the conducting binder of teflonized acetylene black (TAB-2). The mixture was pressed onto a nickel screen and dried at  $150^\circ\text{C}$  for 5 h in a vacuum state. The cell was assembled in an argon-filled glove box and tested using a constant charge–discharge current density of  $20\text{ mA g}^{-1}$ .

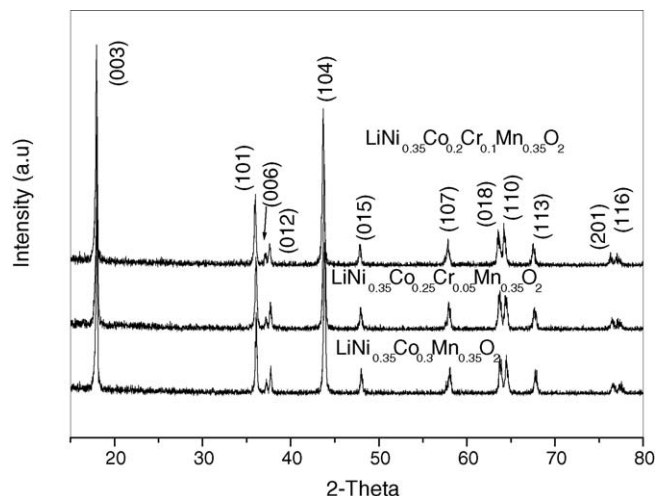


Fig. 1. XRD patterns of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents.

## 3. Results and discussion

XRD diffraction patterns of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents were recorded and shown in Fig. 1. There are no impurity peaks for  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with  $x = 0, 0.05$  and  $0.1$ . All the diffraction lines of these samples can be indexed based on a hexagonal  $\alpha\text{-NaFeO}_2$  structure (space group:  $R\bar{3}m$ , 166), indicating that a single phase is obtained. Table 1 indicated the calculated the structure parameters for the synthesized materials  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ . With the increasing of Cr content, the lattice parameters  $a$ ,  $c$  and  $V$  correspond to become large. Moreover, the colors of the prepared powders change from the brown-black of  $\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$  to blue-dark of  $\text{LiNi}_{0.35}\text{Co}_{0.20}\text{Cr}_{0.1}\text{Mn}_{0.35}\text{O}_2$  with the increasing of Cr content.

Fig. 2 shows the SEM micrographs for  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents. With the increasing of Cr content, the grains of the powder sample become gradually larger and larger. Moreover, the agglomeration of the grains is more and more tightly, which is beneficial to the improvement of tap density.

In order to further study the effects of Cr content on the physical properties of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  cathode materials, we have measured their specific surface areas, indicated in Fig. 3. It is found that the specific surface areas of the samples have linearly decreased with the increasing of Cr content in  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  from  $4.9\text{ m}^2\text{ g}^{-1}$  for  $x = 0$  to  $1.8\text{ m}^2\text{ g}^{-1}$  for  $x = 0.1$ . The reduction of the specific surface

Table 1  
The calculated structure parameters for the synthesized materials  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$

Composition	Lattice parameters		$c/a$	Volume ( $\text{\AA}^3$ )
	$a$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )		
$\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$	2.875	14.310	4.977	102.47
$\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$	2.897	14.437	4.983	104.95
$\text{LiNi}_{0.35}\text{Co}_{0.2}\text{Cr}_{0.1}\text{Mn}_{0.35}\text{O}_2$	2.903	14.465	4.983	105.59

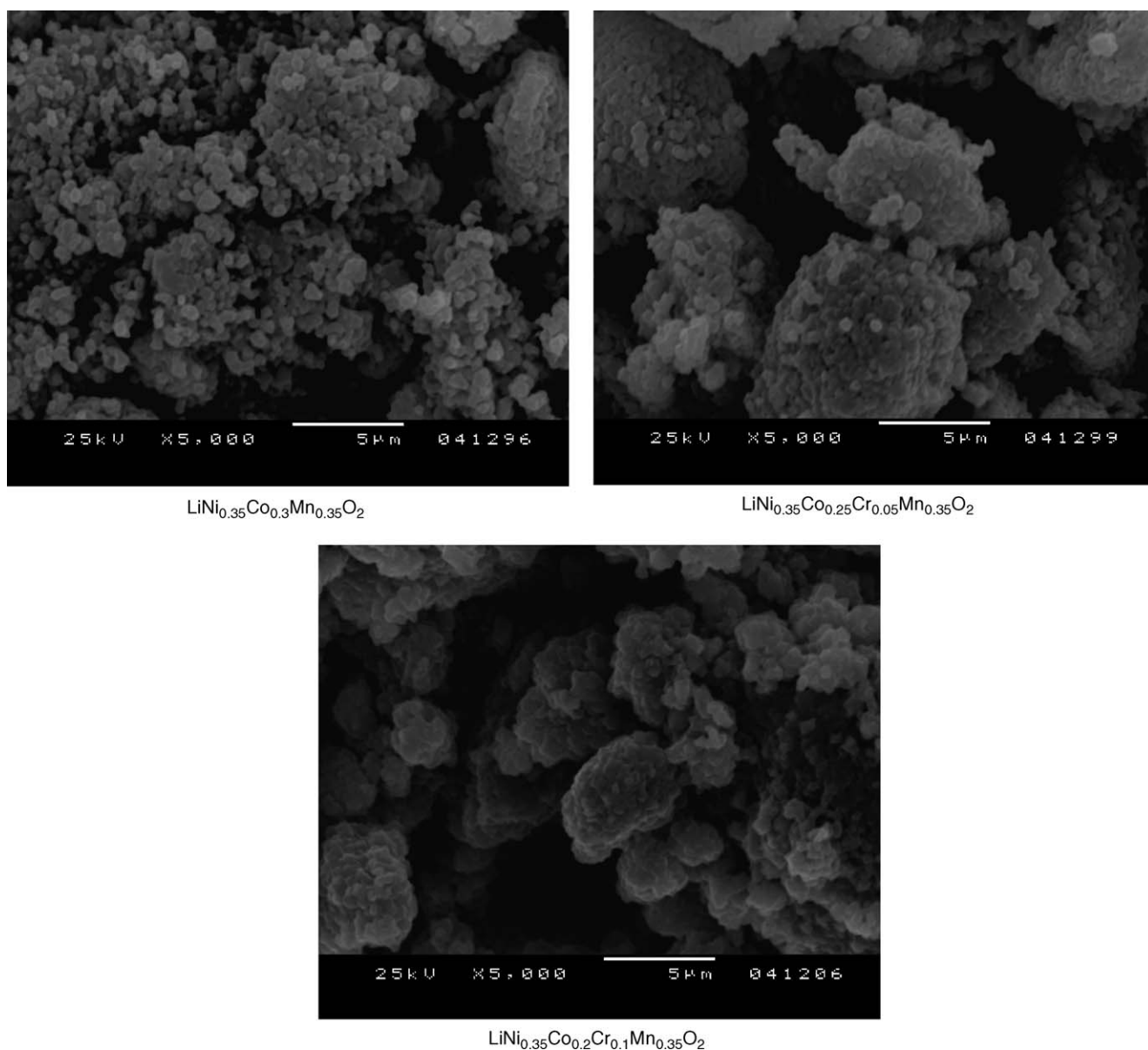


Fig. 2. SEM micrographs for  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents.

areas is ascribed to the increasing of the grains and more tightly agglomeration of the grains, as shown in Fig. 2. It is believed that the less specific surface area can reduce the contact area between the active particles and electrolyte, which can improve the cycling performance and safety properties of cathode materials.

Fig. 3 also indicates the pellet density change of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr content. The PD of the samples has lineally increased with the addition of Cr in  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ . For example, the PD value is only  $2.3 \text{ g cm}^{-3}$  for  $\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$ , but it increases to  $3.1 \text{ g cm}^{-3}$  for  $\text{LiNi}_{0.35}\text{Co}_{0.2}\text{Cr}_{0.1}\text{Mn}_{0.35}\text{O}_2$ . Generally speaking, the PD is related with the size of grains and the agglomeration of the grains. The growth of the grain size and the more tight agglomeration of the primary particles could be found with the increasing of Cr content, as shown in Fig. 2, which

is beneficial to the improvement of its pellet density. Moreover, we have measured the PD of  $\text{LiMn}_{0.35}\text{Co}_{0.3}\text{Ni}_{0.35}\text{O}_2$  and  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ . Experimental results showed that the PD value is only  $2.4 \text{ g cm}^{-3}$  for  $\text{LiMn}_{0.35}\text{Co}_{0.3}\text{Ni}_{0.35}\text{O}_2$ , approaching to that of  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  ( $2.37 \text{ g cm}^{-3}$ ), which means that the addition of Co in  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  can not improve the density of the samples although it can greatly improve the rate capability of  $\text{LiMn}_{0.5-x}\text{Co}_{2x}\text{Ni}_{0.5-x}\text{O}_2$  [21]. However, the doping of Cr can significantly improve the particle morphologies and density of the samples, which is beneficial to obtaining a high density electrode and the excellent processing characteristics of electrode preparation. Generally speaking, layered Li–Ni–(Co)–Mn–O compounds were usually prepared at above  $900^\circ\text{C}$  and the sintering time was over 10 h. If we added a little Cr in a Li–Ni–(Co)–Mn–O compound, the sample with a high density and pure layered structure can be obtained even at  $800^\circ\text{C}$

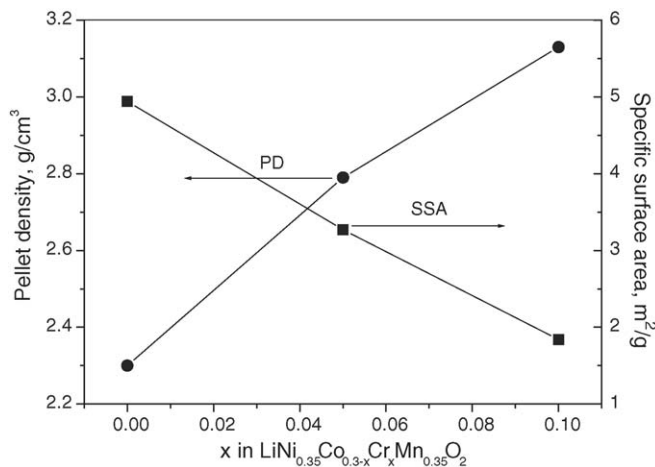


Fig. 3. The specific surface area (SSA) and the pellet density (PD) of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents.

and 3 h of the sintering time. Therefore, the addition of Cr can significantly lower the sintering temperature and sintering time.

Moreover, we have studied the effects of Cr contents on the electrochemical performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  cathode materials. Fig. 4 indicates the first charge and discharge curves of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with the various Cr contents in the voltage ranges of 2.5–4.5 V at room temperature. The charge voltage of the sample has a decrease with the addition of Cr. The discharge capacities of the samples gradually decrease from  $187 \text{ mAh g}^{-1}$  for  $x=0$  to  $165 \text{ mAh g}^{-1}$  for  $x=0.1$  with the increasing of Cr content. However, the discharge capacity of  $\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$  still attains to  $185 \text{ mAh g}^{-1}$ , which means that the addition of a little Cr has not obviously affected the discharge capacity of the samples. The first charge and discharge efficiency of the sample gradually drops from 90.8% for  $x=0$  to 87.7% for  $x=0.1$  with the increasing of Cr content in  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ .

Fig. 5 shows the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents in the voltage ranges of 2.5–4.5 V at room temperature. The Cr existence

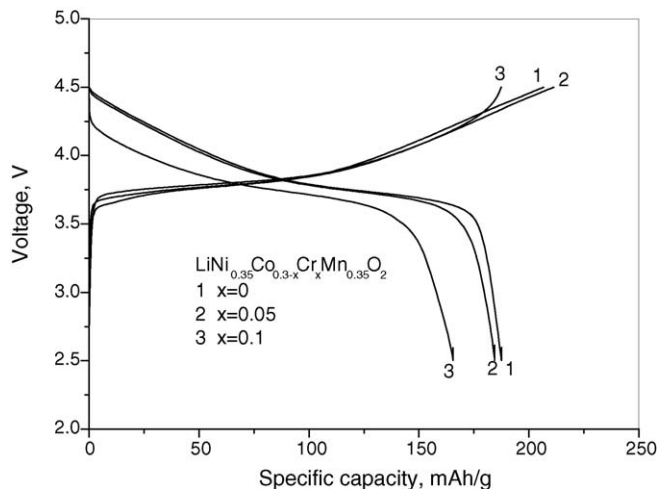


Fig. 4. The first charge and discharge curves of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents.

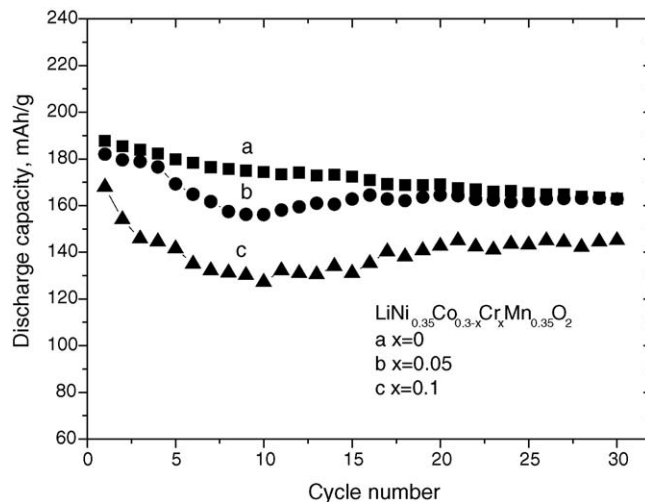


Fig. 5. Showed the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents in the voltage ranges of 2.5–4.5 V at room temperature.

has caused the significant improvement of the cycling performance for  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ . The discharge capacity of  $\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$  gradually decreased with the increment of cycle number from  $187$  to  $163 \text{ mAh g}^{-1}$  after 30 cycles. But for  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with  $x=0.05$  and  $0.1$ , the discharge capacity of the samples decreases at the beginning, and then has some increases. After 15 cycles, the discharge capacity keeps constant. In order to show the cycling performance of the samples more clearly, the charge and discharge curves at various cycles are displayed in Fig. 6. For  $\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$ , its charge voltage gradually increases and the discharge voltage slowly decreases with the increment of cycle number, which means that the electrode polarization become larger and larger. But for  $x=0.05$  and  $0.1$  in  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ , the polarization of electrode gradually increase at the initial 10 cycles, and then it begin to drop from the 10th cycle. After 20 cycles, the charge and discharge curves basically keep constant. For  $\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$ , the charge and discharge curves of the 20th and 30th cycles are almost overlapped. Therefore, the addition of Cr has greatly affected the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  cathode materials and the reason is unknown.

Fig. 7 shows the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  cathode materials in the voltage range of 2.5–4.8 V. Although the discharge capacity of  $\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$  attains to  $213 \text{ mAh g}^{-1}$ , it decreases down to  $148 \text{ mAh g}^{-1}$  after 25 cycles. However, the discharge capacity of  $\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$  still reaches  $172 \text{ mAh g}^{-1}$  after 25 cycles although its initial discharge capacity is  $203 \text{ mAh g}^{-1}$ , which is slightly lower than that of  $\text{LiNi}_{0.35}\text{Co}_{0.3}\text{Mn}_{0.35}\text{O}_2$ . With the increasing of Cr content, the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  cathode material continues to be improved while the reduction of the initial discharge capacity becomes more obviously. For  $\text{LiNi}_{0.35}\text{Co}_{0.2}\text{Cr}_{0.1}\text{Mn}_{0.35}\text{O}_2$ , its initial discharge capacity decreases down to  $179 \text{ mAh g}^{-1}$  and the capacity retention attains to 97% from 2nd to 25th. Fig. 8 indicates the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$  cathode materials

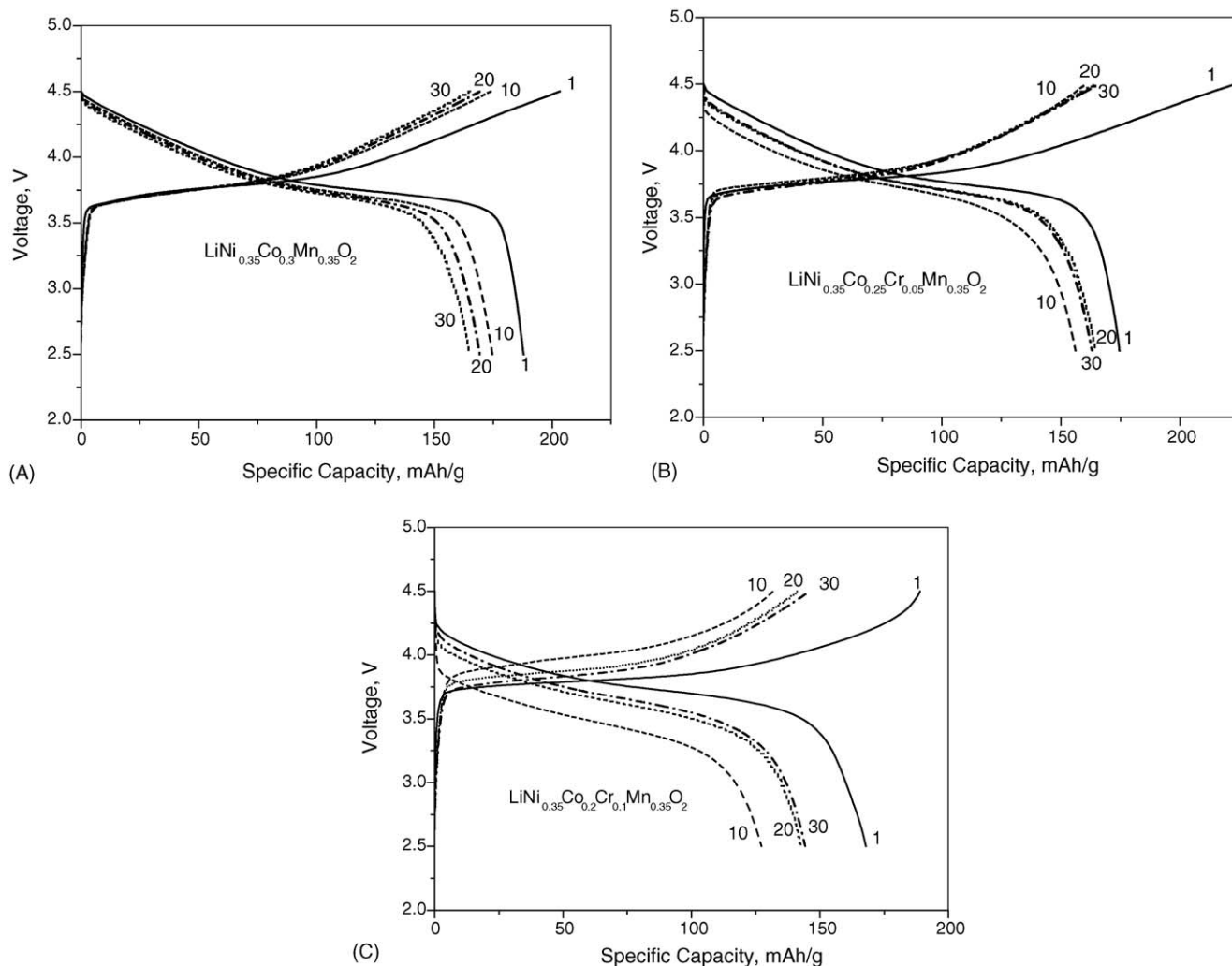


Fig. 6. The charge and discharge curves of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents. (A)  $x=0$ ; (B)  $x=0.05$ ; (C)  $x=0.1$ .

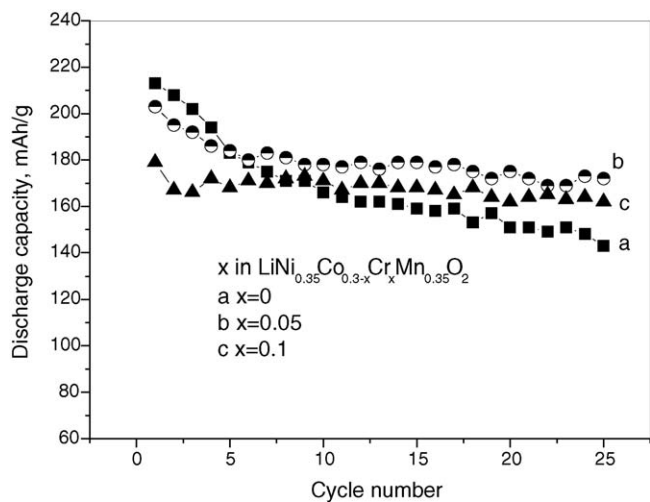


Fig. 7. The cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  with various Cr contents in the voltage range of 2.5–4.8 V.

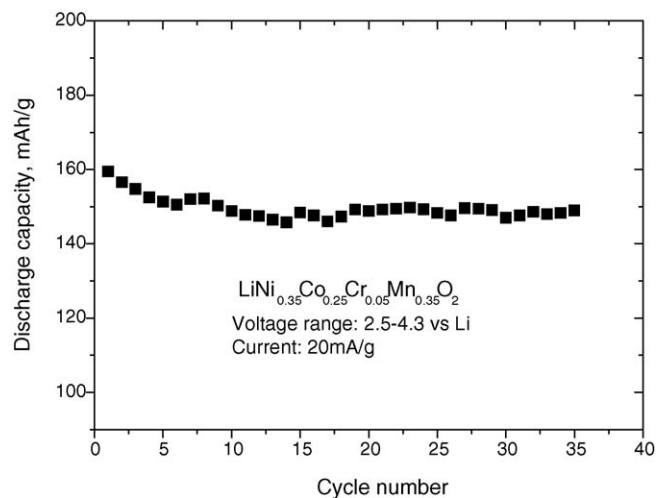


Fig. 8. The cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$  with the charge and discharge voltage range from 2.5 to 4.3 V.

at the charge and discharge voltage between 2.5 and 4.3 V. The reversible capacity of the sample attains to  $160 \text{ mAh g}^{-1}$ , higher than that of  $\text{LiCoO}_2$  (about  $150 \text{ mAh g}^{-1}$ ). After 35 cycles, the discharge capacity is still  $150 \text{ mAh g}^{-1}$  and the retention of capacity is 94%. The capacity loss has mainly occurred at the starting 5 cycles. In order to get the excellent electrochemical performance of the sample, the Cr content should be lower than 10 mol.% in  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ .

Therefore, the above experimental results showed that the doping of Cr and Co have different roles in improving the performance of layered Li–Ni–Mn–O compounds. It is believed that the addition of Cr and Co at the same time can not only improve the rate capability but also increase the density and processing characteristics of prepared electrode [21]. A layered  $\text{LiNi}_{0.35}\text{Co}_{0.25}\text{Cr}_{0.05}\text{Mn}_{0.35}\text{O}_2$  compound is a promising cathode material for lithium ion batteries.

#### 4. Conclusions

Our experimental results revealed that the addition of Cr has an important effect on the physical and electrochemical performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$ . It has changed the morphologies of particles and increased the sizes of grains. Moreover, the existence of Cr in  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  decreases the specific surface of the samples and greatly improves the density of the powder. Electrochemical test indicated that the addition of Cr can significantly improve the cycling performance of  $\text{LiNi}_{0.35}\text{Co}_{0.3-x}\text{Cr}_x\text{Mn}_{0.35}\text{O}_2$  although its initial discharge capacity has a little drop.

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