

## Methods for promoting electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for lithium-ion batteries

BAO LiYing<sup>1,2</sup>, CHE HuiQuan<sup>1</sup>, HU DaoZhong<sup>3</sup>, SU YueFeng<sup>1,2\*</sup>, WANG Zhao<sup>1</sup>, LI Ning<sup>1</sup>, CHEN Shi<sup>1,2</sup> & WU Feng<sup>1,2</sup>

<sup>1</sup> Beijing Key Laboratory of Environment Science and Engineering, School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China;

<sup>2</sup> National Development Center of High Technology Green Materials, Beijing 100081, China;

<sup>3</sup> China North Vehicle Research Institute, Beijing 100072, China

Received November 27, 2012; accepted January 1, 2013; published online March 26, 2013

One popular study of the recent research is to develop the cathode materials for lithium-ion batteries. As a new cathode material for lithium-ion batteries, the  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  has drawn widespread attention because of its high capacity, high cut-off voltage and high tap density. Its theoretical capacity is 277.8 mAh/g. The crystal structure of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  is  $\alpha\text{-NaFeO}_2$ . The structural and morphological features of the  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  are introduced in this paper. The emphasis is to present the methods for promoting electrochemical properties. The electrochemical properties and structure characteristics are discussed. And the prospect of layered  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  is forecast in the end.

**lithium-ion batteries, cathode material,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , modification**

**Citation:** Bao L Y, Che H Q, Hu D Z, et al. Methods for promoting electrochemical properties of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  for lithium-ion batteries. *Chin Sci Bull*, 2013, 58: 1869–1875, doi: 10.1007/s11434-013-5758-6

One of the challenges for improving the performance of lithium-ion batteries to meet the increasingly demanding requirements for energy storage is the development of suitable cathode materials [1,2]. The cathode materials have influence on some important properties of batteries like battery voltage, working hours, and stability. Simple calculations show that an increase in cell energy density of 57% can be achieved by doubling the capacity of the cathode materials [3].

So the chances of drastically improving Li-ion cells energy density are mainly rooted in spotting better positive electrode materials. Recently,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  has attracted growing interest because it exhibits high capacity, high cut-off voltage and high tap density. Besides, it has the merits of good security and stability. It is considered to be one of the candidate cathode materials for high energy density lithium batteries [4–6].

The tap density and thermal stability of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) have been improved greatly in recent years. According to statistics, the output of NCM in China is 8500 t, which is 48.1% of the total amount all over the world. However, it is lacking in competitiveness in the international market because of the core technology and patents of NCM having been tightly controlled by America and Canada. It mostly applies to the portable electronic device and some small electric transport in China.

### 1 Structural characteristics and mechanism of charging and discharging

Since  $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$  ( $0 < x < 0.5$ ,  $0 < y < 0.5$ ) is reported in 1991, this cathode material has attracted much attention [7]. Layered NCM was first prepared by a solid state reaction at 1000°C in air in 2001 [8]. NCM shows a rechargeable capacity of 150 mAh/g in 3.5–4.2 V or 200 mAh/g in 3.5–5.0

\*Corresponding author (email: suyuefeng@bit.edu.cn)

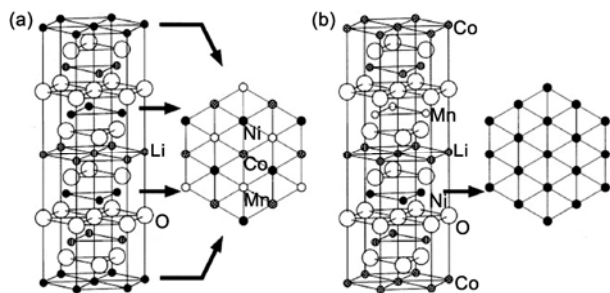
V. Research shows that the NCM has the  $\alpha$ - $\text{NaFeO}_2$  structure, which is the characteristic of the layered  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  structures and shows larger capacity of more than 150 mAh/g in the voltage range of 2.5–4.2 V with excellent cycle ability and no transformation to spinel phase during electrochemical cycling [9–11]. The DSC measurements shows the thermal behavior of NCM is milder than that of  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$  [12].

Figure 1 shows two structural models for NCM [13]. The first model illustrated in Figure 1(a) consists of  $[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]_2\text{O}_2$  slabs of the  $[\sqrt{3} \times \sqrt{3}]R30^\circ$ -type super lattice in Wood's notation based on basal net in triangular lattice of sites. The second model illustrated in Figure 1(b) consists of  $\text{CoO}_2$ ,  $\text{NiO}_2$  and  $\text{MnO}_2$  slabs piled up regularly, called piled-up model hereafter. This structure has Li-ions at the 3a position, the transition metal ions ( $M=\text{Mn}, \text{Co}, \text{Ni}$ ) at 3b position and O ions at 6c position. Layered structure intercalation material provides a 2-dimensional interstitial space, which can facilitate fast mobility of  $\text{Li}^+$  ion in the host materials. The structures with 1-dimensional tunnels, such as olivine [14], encounter the difficulty of Li-ion bulk diffusion. However, some researchers believe that the magnitudes for ionic conductivity in both the two directions and the diffusion coefficient are the same at elevated temperatures [15].

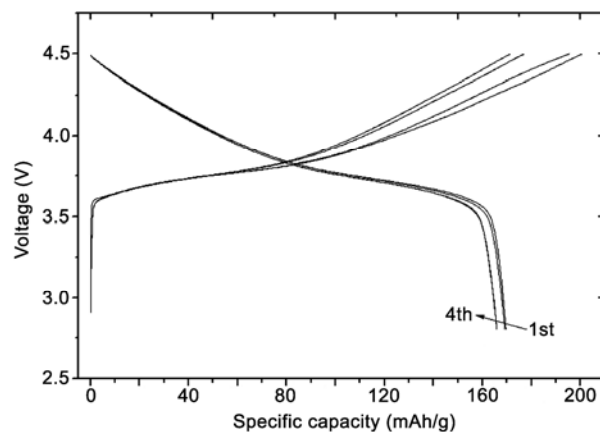
However, data from laboratory, synchrotron, and constant wavelength neutron sources show that  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  does not present any evidence of a  $[\sqrt{3} \times \sqrt{3}]R30^\circ$ -type super lattice [16]. So it is necessary to study the structure of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ .

We tested the charge-discharge properties at 0.1 C current density. The voltage rapidly rose to 3.6 V at first and then rose to 4.5 V slowly. The initial discharge capacity and the irreversible capacity were 173 and 25 mAh/g, respectively. With the increase of the numbers of cycle, the discharge capacity reduced gradually. Typical charge-discharge profile of NCM is shown in Figure 2. This result is similar to the reports [8,17].

Now the high-performance cathode material still has a lot of problems to be resolved, such as cation mixing, capacity decaying too fast at a large current and the transition metal ions dissolving into electrolyte. These issues limit the use of



**Figure 1** Schematic illustration of the framework of NCM. Reprinted from [13] with permission from Elsevier.



**Figure 2** Typical charge-discharge profiles of NCM.

NCM in lithium batteries.

## 2 Methods for promoting electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

A lot of fruitful work has been done by many researchers on solving the problems in order to enhance the electrochemical properties of NCM.

### 2.1 The inhibition effect on cation mixing

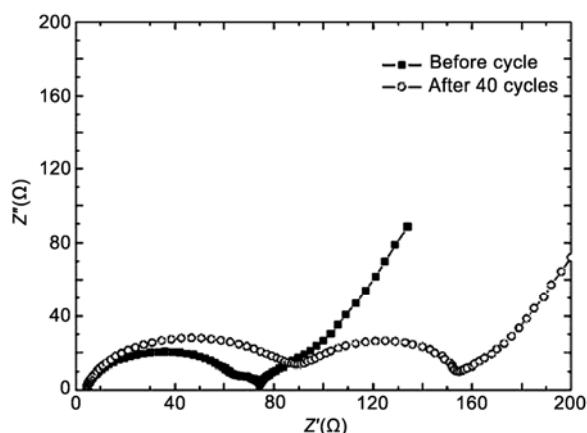
A partial interchange of occupancy of  $\text{Li}^+$  and transition metal ions among the sites (i.e.  $\text{Li}^+$  in 3b and M in 3a sites) would give rise to disordering in the structure called 'cation mixing', which is known to deteriorate the electrochemical performance of the above layered compounds [17]. More  $\text{Ni}^{2+}$  in lithium layer results in harder de-intercalation of  $\text{Li}^+$ , and the electrochemical properties gets worse [18]. The lithium excess cathode is found to exhibit better cyclability and rate capability than the stoichiometric cathode up to a cutoff charge voltage of 4.6 V in lithium cells [19]. The better electrochemical performance of the lithium excess cathode is attributed to a smaller volume change occurring during the discharge-charge cycling and a consequent suppression of lattice strain and impedance growth [20]. The higher Li/M molar ratio on electrochemical performances of layered NCM oxide improved specific capacity, rate performance and the first cycle coulombic efficiency and inhibited the cation mixing.

NCM samples are synthesized based on the homogeneous precursors formed in ethanol [21]. Special synthetic conditions at  $0^\circ\text{C}$  were used to prepare nanostructured NCM via chemical coprecipitation synthesis [22]. NCM with nanostructured shows a well-ordered layered hexagonal lattice with low cation mixing. Galvanostatic testing shows good electrochemical properties and high rate capability. The initial charge and discharge capacities are 208.7 mAh/g and 171.8 mAh/g at a constant current density of 32 mA/g

(0.2 C), respectively. The material shows stable cycling properties and a capacity of 162.5 mAh/g is obtained after 50 cycles. Especially, the discharge capacity obtained at the 4 C rate is 84.2% of that at 0.2 C, which indicates the good high rate performance of the material prepared. A porous cathode material composed of interconnected single crystal NCM nanoparticles was synthesized via nitric acid as a pH value adjuster [23]. The modified sol-gel process results in significant improvement in chemical and physical characteristics. These structural modifications in turn significantly enhance the electrochemical properties of the NCM cathode material, in terms of improved charge/discharge capacity, cyclic stability and rate capability and reduced cation mixing. Layered lithium transition metal oxide cathode materials were synthesized through a simple carbonate co-precipitation method [24]. NCM cathode could deliver a discharge capacity of 190 and 166 mAh/g at constant current density of 25 and 250 mA/g, respectively. Non-spherical NCM powders have been synthesized using a two-step drying method with 5% excess LiOH at 800°C for 20 h [25]. The initial discharge capacity of 167 mAh/g is obtained between 3 and 4.3 V at a current of 0.2 C rate. The capacity of 159 mAh/g is retained at the end of 30 charge-discharge cycle with capacity retention of 95%.

Hydrothermal reaction is another method for synthesizing cathode materials like LiFePO<sub>4</sub> [26]. The materials with best electrochemical properties synthesized via hydrothermal reaction for 30 h and calcined at 850°C for 6 h [27]. The initial charge and discharge capacity is 223.5 and 187.7 mAh/g at a current density of 20 mA/g, respectively. The material shows stable cycling properties. Capacity maintains at 97.9% at 1 C rate after 40 cycles. Cyclic voltammetry tests (Figure 3) show that the cathodic and anodic peak of every cycle is almost at the same place, which indicates the good cycle ability. The electrochemical impedance spectroscopy test shows the impedance after 40 cycles.

LiNi<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>O<sub>2</sub> (1/3 ≤ x ≤ 1/2) electrode powders were prepared by a sol-gel method. It was synthesized and characterized [28]. Increasing the *x* value in the synthesized



**Figure 3** Cyclic voltammogram of NCM. Reprinted from [27] with permission from Elsevier.

LiNi<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>O<sub>2</sub> powders leads to decrease its particle size and increase its cation mixing. The best specific capacity of 192 mAh/g was obtained for the LiNi<sub>0.375</sub>Co<sub>0.25</sub>Mn<sub>0.375</sub>O<sub>2</sub> electrode with good capacity retention among the synthesized materials cycled at 0.1 C in the potential between 3.0 and 4.5 V at room temperature. Although structural parameters of the LiNi<sub>0.375</sub>Co<sub>0.25</sub>Mn<sub>0.375</sub>O<sub>2</sub> powder are similar to those of the NCM powder, its specific capacity is higher due to the increase of the stoichiometry of active site Ni. The increase of Ni and Mn content could reduce cost of the materials. It is found that the cell performance of the LiNi<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>O<sub>2</sub> electrode drops dramatically and its cation mixing increases while the *x* value is higher than 0.4. Layered O<sub>2</sub>-phase lithium manganese oxides was synthesized, Li<sub>2/3</sub>(Ni<sub>1/3-x</sub>Mn<sub>2/3-x</sub>M<sub>2x</sub>)O<sub>2</sub> (M=Cr, Co, x=0.05) by ion exchange of Li<sup>+</sup> for Na<sup>+</sup> in P<sub>2</sub>-Na<sub>2/3</sub>(Ni<sub>1/3-x</sub>Mn<sub>2/3-x</sub>M<sub>2x</sub>)O<sub>2</sub> precursors via sol-gel method [29]. The discharge capacity of O<sub>2</sub>-Li<sub>2/3</sub>(Ni<sub>1/3-x</sub>Mn<sub>2/3-x</sub>Co<sub>2x</sub>)O<sub>2</sub> (x=0.05) is around 188 mAh/g at a current density of 0.2 mA/g.

## 2.2 The capacity attenuation at high current

LiCo<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>2</sub> powders were synthesized using a sol-gel method [30]. The capacity at 1 C rate is 134 mAh/g. This performance was not necessarily expected for this material, since Mn<sup>3+</sup> is a Jahn-Teller ion, which implies that the change of valence Mn<sup>3+</sup> ↔ Mn<sup>4+</sup> is accompanied by local distortions, and thus strains fields, which reduces the life of the battery, especially at high discharge current. For NCM, there is the same Jahn-Teller phenomenon. Researchers use doping anion like fluorine and sulfur to improve the stability of the structure, the cycle performance and lithium ion migration rate. The M-F bond energy is greater than M-O bond energy because the fluorine and oxygen is the element of the same cycle and fluorine ion radius is smaller than the ionic radius of oxygen. So doping a little amount of fluorine could improve the stability of the structure of the NCM and achieve the purpose of improving the cycle performance [31,32].

Li[Ni<sub>0.333</sub>Co<sub>0.333</sub>Mn<sub>0.293</sub>Al<sub>0.04</sub>]O<sub>2-z</sub>F<sub>z</sub> (0 ≤ z ≤ 0.1) were synthesized from a sol-gel precursor [33]. It shows an improved cathodic behavior and discharge capacity retention compared to the undoped samples in the voltage range of 3.0–4.3 V. The electrodes prepared from Li[Ni<sub>0.333</sub>Co<sub>0.333</sub>Mn<sub>0.293</sub>Al<sub>0.04</sub>]O<sub>1.95</sub>F<sub>0.05</sub> delivers an initial discharge capacity of 158 mAh/g and an initial coulombic efficiency is 91.3%, and the capacity retention at the 20th cycle is 94.9%. Though the F-doped samples have lower initial capacities, they show better cycle performances compared with F-free samples. Therefore, this is a promising material for a lithium-ion battery. To improve the electrochemical property of NCM at high upper voltage limit of 4.6 V, fluorine is partly substituted for oxygen. Fluorine is both substituted in bulk and coated on the surface of NCM. It shows stable cycling performance and improvement of high rate capability com-

pared with bare NCM. In addition, fluorine substitution catalyzes the growth of the primary particles, which in turn resulted in high tap density as well as high volumetric capacity [34]. Researchers found that the initial discharge capacity of M-doped ( $M = \text{Mg}^{2+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ce}^{2+}$ ) NCM decreased because the M was not involved in the redox process [35–38]. And the cation mixing phenomenon is serious because the  $\text{Mg}^{2+}$  radius is close to the  $\text{Li}^+$  radius. However,  $\text{Mg}^{2+}$  could improve the the stability of the structure of the NCM and facilitate the cycle stability of materials at high voltage and high current.

An initial search with density functional theory to sort through potential cathode materials based on their  $\text{Li}^+$  intercalation potentials and electronic structures is carried on.  $\text{Fe}^{3+}$  substitution is found to be advantageous. The material shows the lowest voltage at the last stage of the charge [39].

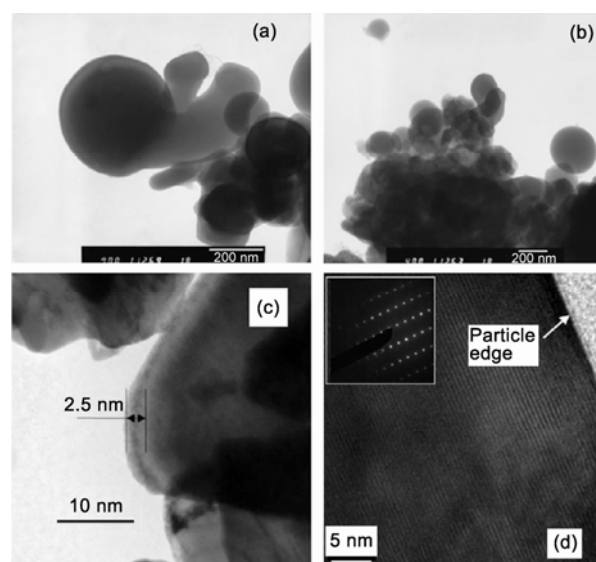
In addition, some researchers modify the cathode materials by coating the compounds [40]. The  $\text{Al}(\text{OH})_3$ -coated NCM shows a capacity retention of 80% at 320 mA/g based on 20 mA/g, while the pristine NCM delivers only 45% at the same current density. Also, unlike pristine NCM, the  $\text{Al}(\text{OH})_3$ -coated  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  cathode exhibits excellent rate capability and good thermal stability.

### 2.3 The inhibition effect on transition metal dissolution

Spontaneous reactions occurring at the surface of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$ -based electrodes during the storage in organic non-aqueous electrolytes ( $\text{LiPF}_6$ , EC, DMC) have been investigated by diffuse reflectance FTIR technique. It is suggested that the products of these reactions create a film on the surface of lithium metal and graphite electrodes. This surface film is found to play an important role in the electrochemical processes occurring during cycling. Therefore, it has attracted great scientific interest. It is often called a “passivating layer” or a “solid electrolyte interphase”(SEI) [41]. Meanwhile, there is a possibility of ionic exchange between  $\text{LiMn}_2\text{O}_4$  and ions such as  $\text{H}^+$  (e.g. coming from unavoidably present HF in  $\text{LiPF}_6$  solutions). This leads to the formation of an inactive mass on the  $\text{LiMn}_2\text{O}_4$  particles. The new compounds formed on  $\text{LiMn}_2\text{O}_4$  particles are organic polycarbonates and polymeric hydrocarbons, and salt-based products are also observed.  $\text{LiF}$  is the main product. Such phenomena results in capacity fading of these electrodes in solutions, especially at elevated temperatures [42,43].

For  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , coating with a compound could improve the electrochemical properties [44,45]. There are some studies about the coating effects on NCM. Some studies show that C,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$  coating on NCM could improve the electrochemical properties [40,46]. Modification which can improve the electrochemical properties is attributed to existence of the coating layer. It can separate the electrolyte from direct contact with the active cathode material and prevent dissolution of the cathode ma-

terials. Surface coating suppresses the interaction between  $\text{LiCoO}_2$  and the electrolyte at the uncharged state and alleviates the electrolyte decomposition at charged states. Modifying the surface of commercial  $\text{LiCoO}_2$  particles with nano- $\text{MgO}$  can suppress chemical reactions on the electrode surface significantly.  $\text{Cr}_2\text{O}_3$ -coated NCM cathode material was synthesized via a novel method [47]. The measured results indicate that surface coating with 1.0wt%  $\text{Cr}_2\text{O}_3$  does not affect the NCM crystal structure ( $\alpha\text{-NaFeO}_2$ ) of the cathode material compared with the pristine material, the surfaces of NCM samples are covered with  $\text{Cr}_2\text{O}_3$  well, and the NCM material coated with  $\text{Cr}_2\text{O}_3$  has better electrochemical performance under a high cutoff voltage of 4.5 V [48]. The coated samples are found to display the improved electrochemical performance, which is mainly attributed to the suppression of the charge-transfer resistance at the interface between the cathode and the electrolyte.  $\text{CeO}_2$ -coated NCM has been synthesized with sol-gel method for Li-ion batteries [49]. It indicates that coating metal oxides is an effective way to improve the electrochemical properties of cathode materials. The improvement of the discharge capacity and cycling characteristics is due to the coating layer that could reduce the direct contact between the cathode material and electrolyte thus protecting the surface of cathode material from harmful reaction with the electrolyte. The effect of the heat treatment of particles at  $600^\circ\text{C}$  with organic substances such as sucrose and starch is investigated [50]. The results indicate that the surface of particles has been modified (Figure 4(a), (b)). The annealing does not lead to any carbon coating but it leads to the crystallization of the thin disordered layer on the surface of NCM (Figure 4(c), (d)). And the capacity at 10C-rate is enhanced by 20%. Polymer-NCM composites are prepared to test. Polymers on



**Figure 4** TEM and HRTEM images of NCM powders for as-grown and heat treated sample with sucrose at  $600^\circ\text{C}$  for 30 min in air. Reprinted from [50] with permission from Elsevier.

the surface of NCM could significantly decrease the charge-transfer resistance of NCM [51,52]. Grapheme was used as a conductive additive to enhance the discharge capacity and rate capability of NCM [53]. The results indicate a better electrochemical performance of the NCM-graphene composite in terms of high discharge capacity (188 mAh/g), good rate capability, and good cycling performance compared with NCM. The improved electrochemical performance of the NCM-graphene composite is attributed to a decrease in the charge-transfer resistance.

### 3 Conclusion

The electrochemical properties of anode materials are better than those of cathode materials [54,55]. And the electrolytes apply widely [56,57]. Therefore, the performance of the cathode material determines the performance of the lithium-ion batteries. NCM is a cathode material with layered crystal structure, good thermal stability, low cost of production and superior electrochemical performance for lithium batteries. It is expected to be a good competitor for the next generation of lithium battery cathode material. Synthesizing NCM with a stable structure and good de-intercalation property, inhibiting cation mixing, promoting the performance of large-current discharge ability and preventing elution of the transition metal is the focus of current research.

### 4 Prospects

We have done a lot of work on NCM system and have got some achievement in recent years. We used activated carbon as a template to synthesize NCM via a sol-gel method. The layered NCM materials with good crystalline are synthesized by a novel method of hydrothermal method followed by a short calcination process [6]. In order to improve the electrochemical properties, we doped metal ions, such as Al, Y, Cr, into the bulk of NCM [58]. And we coated  $Y_2O_3$ ,  $CeO_2$  and  $TiO_2$  on the surface of NCM [59–61]. The Li-rich layered cathode material,  $Li[Ni_{0.2}Li_{0.2}Mn_{0.6}]O_2$ , was synthesized via a “mixed oxalate” method [62].

The lithium-ion batteries have a bright prospect [63]. Meanwhile lithium-ion batteries have to compete with other types of energy storage materials [64–66]. The NCM would become a good competitor for power battery by promoting its special capacity, energy density, rate capability, cycle life, especially the thermal stability properties [67]. The positive temperature coefficient resistors (PTC) are usually equipped as a safety device on the crust of commercial lithium ion batteries to restrict or even prevent current from flowing through the cell under abusive conditions [68].

In recent years, lithium-enriched manganese-based solid

solution  $xLi[Li_{1/3}Mn_{2/3}]O_2 \cdot (1-x)LiMO_2$  is a new cathode material for lithium ion batteries. Researches on these materials still dedicate to promoting the electrochemical properties [69,70].

*This work was supported by the National Basic Research Program of China (2009CB220100), the National Natural Science Foundation of China—Youth Science Fund (51102018 and 21103011) and the National High-tech R&D Program of China (2011AA11A235 and SQ2010AA1123116001).*

- 1 Fergus J W. Recent developments in cathode materials for lithium ion batteries. *J Power Sources*, 2010, 195: 939
- 2 Wu F. Green Secondary Battery and Research Progress in New System (in Chinese). Beijing: Science Press, 2007
- 3 Tarascon J M. Key challenges in future Li-battery research. *Philos Trans Roy Soc A*, 2010, 368: 3227–3241
- 4 Terada N, Yanagi T, Arai S, et al. Development of lithium batteries for energy storage and EV applications. *J Power Sources*, 2001, 100: 80–92
- 5 Zheng J, Chen J J, Jia X, et al. Electrochemical performance of the  $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$  in aqueous electrolyte. *J Electrochem Soc*, 2010, 157: A702–A706
- 6 Wu F, Wang M, Su Y F, et al. A novel method for synthesis of layered  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  as cathode material for lithium-ion battery. *J Power Sources*, 2010, 195: 2362–2367
- 7 Liu Z L, Yu A, Lee J Y. Synthesis and characterization of  $LiNi_{1-x-y}Co_xMn_yO_2$  as the cathode materials of secondary lithium batteries. *J Power Sources*, 1999, 81: 416–419
- 8 Ohzuku T, Makimura Y. Layered lithium insertion material of  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  for lithium-ion batteries. *Chem Lett*, 2001, 30: 642–643
- 9 He Y S, Pei L, Ma Z F. Progress in preparation and modification of layer-structured  $Li[Ni,Co,Mn]O_2$  cathode material for lithium ion batteries (in Chinese). *Prog Chem*, 2007, 26: 337–344
- 10 Wang Y G, Li H Q, He P, et al. Nano active materials for lithium-ion batteries. *Nanoscale*, 2010, 2: 1294–1305
- 11 Okubo M, Mizuno Y, Yamada H, et al. Fast Li-ion insertion into nanosized  $LiMn_2O_4$  without Domain Boundaries. *ACS Nano*, 2010, 4: 741–752
- 12 Yabuuchi N, Ohzuku T. Novel lithium insertion material of  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  for advanced lithium-ion batteries. *J Power Sources*, 2003, 119–121: 171–174
- 13 Koyama Y, Tanaka I, Adachi H, et al. Crystal and electronic structures of superstructural  $Li_{1-x}[Co_{1/3}Ni_{1/3}Mn_{1/3}]O_2$  ( $0 \leq x \leq 1$ ). *J Power Sources*, 2003, 119–121: 644–648
- 14 Wang Y G, He P, Zhou H S. Olivine  $LiFePO_4$ : Development and future. *Energy Environ Sci*, 2011, 4: 805–817
- 15 Ellis B L., Lee K T, Nazar L F. Positive electrode materials for Li-ion and Li-batteries. *Chem Mater*, 2010, 22: 691–714
- 16 Whitfield P S, Davidson I J, Cranswick L M D, et al. Investigation of possible superstructure and cation disorder in the lithium battery cathode material  $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$  using neutron and anomalous dispersion powder diffraction. *Solid State Ionics*, 2005, 176: 463–471
- 17 Shaju K M, Rao S G V, Chowdari B V R. Performance of layered  $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$  as cathode for Li-ion batteries. *Electrochim Acta*, 2002, 48: 145–151
- 18 Sun Y K, Kang H B, Myung S T, et al. Effect of manganese content on the electrochemical and thermal stabilities of  $Li[Ni_{0.58}Co_{0.28-x}Mn_{0.14+x}]O_2$  cathode materials for lithium-ion batteries. *J Electrochem Soc*, 2010, 157: A1335–A1340
- 19 Choi J, Manthiram A. Comparison of the electrochemical behaviors of stoichiometric  $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$  and lithium excess  $Li_{1.03}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.97}O_2$ . *Electrochem Solid-State Lett*, 2004, 7: A365–A368
- 20 Todorov Y M, Numata K. Effects of the Li:(Mn+Co+Ni) molar ratio on the electrochemical properties of  $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$  cathode material. *Electrochim Acta*, 2004, 50: 495–499

- 21 Gao P, Li Y H, Liu H D, et al. Improved high rate capacity and lithium diffusion ability of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  with ordered crystal structure. *J Electrochem Soc*, 2012, 159: 506–513
- 22 Deng C, Zhang S, Wu B, et al. Synthesis and characteristics of nanostructured  $\text{Li}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$  cathode material prepared at 0°C. *J Solid State Electrochem*, 2010, 14: 871–875
- 23 Huang Z D, Liu X M, Oh S W, et al. Microscopically porous, interconnected single crystal  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode material for Lithium ion batteries. *J Mater Chem*, 2011, 21: 10777–10784
- 24 Wang J, Yao X Y, Zhou X F, et al. Synthesis and electrochemical properties of layered lithium transition metal oxides. *J Mater Chem*, 2011, 21: 2544–2549
- 25 Chang Z R, Chen Z J, Wu F, et al. Synthesis and characterization of high-density non-spherical  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  cathode material for lithium ion batteries by two-step drying method. *Electrochim Acta*, 2008, 53: 5927–5933
- 26 Zhou M, Qian J F, Cao Y L, et al. Low temperature hydrothermal synthesis and electrochemical performances of  $\text{LiFePO}_4$  microspheres as a cathode material for lithium-ion batteries. *Chin Sci Bull*, 2012, 57: 4164–4169
- 27 Wu F, Wang M, Su Y F, et al. A novel method for synthesis of layered  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  as cathode material for lithium-ion battery. *J Power Sources*, 2010, 195: 2362–2367
- 28 Chen C H, Wang C J, Hwang B J. Electrochemical performance of layered  $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$  cathode materials synthesized by a sol-gel method. *J Power Sources*, 2005, 146: 626–629
- 29 Wang X, Yang X H, Zheng H G, et al. Layered  $\text{O}_2\text{-Li}_{2/3}(\text{Ni}_{1/3-x}\text{Mn}_{2/3-x}\text{M}_2)_2\text{O}_2$  ( $\text{M}=\text{Cr, Co, } x=0.05$ ) cathode materials for Li-ion rechargeable batteries. *Solid State Ionics*, 2005, 176: 1043–1049
- 30 Abuzeid H A M, Hashem A M A, Abdel-Ghany A E, et al. De-intercalation of  $\text{Li}_x\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_2$ : A magnetic approach. *J Power Sources*, 2011, 196: 6440–6448
- 31 Palacin M R, Le Cras F, Seguin L, et al. *In situ* structural study of 4V-range lithium extraction/insertion in fluorine-substituted  $\text{LiMn}_2\text{O}_4$ . *J Solid State Chem*, 1999, 144: 361–371
- 32 Amatucci G G, Pereira N, Zheng T, et al. Enhancement of the electrochemical properties of  $\text{LiMn}_2\text{O}_4$  through chemical substitution. *J Power Sources*, 1999, 81–82: 39–43
- 33 Liao L, Wang X Y, Luo X F, et al. Synthesis and electrochemical properties of layered  $\text{Li}[\text{Ni}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.293}\text{Al}_{0.04}]\text{O}_{2-x}\text{F}_x$  cathode materials prepared by the sol-gel method. *J Power Sources*, 2006, 160: 657–661
- 34 Kim G H, Kim J H, Myung S T, et al. Improvement of high-voltage cycling behavior of surface-modified  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  cathodes by fluorine substitution for Li-ion batteries. *J Electrochem Soc*, 2005, 152: A1707–A1713
- 35 Yang P, Zhang C F, Dai X, et al. Synthesis of  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3-x}\text{Mn}_{1/3})\text{M}_x\text{O}_2$  ( $\text{M}=\text{Ti, Mg}$ ) cathode material by oxalate precursor and its properties (in Chinese). *Chin J Nonferrous Metals*, 2009, 19: 101–107
- 36 Ren H B, Li X, Peng Z H. Electrochemical properties of  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Al}_{1/3-x}\text{Co}_x]\text{O}_2$  as a cathode material for lithium ion battery. *Electrochim Acta*, 2011, 56: 7088–7091
- 37 Li J B, Xu Y L, Du X F, et al. Improved electrochemical stability of Zn-Doped  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode materials. *Acta Phys Chim Sin*, 2012, 28: 1899–1905
- 38 Zhang Y J, Xia S B, Zhang Y N, et al. Ce-doped  $\text{LiNi}_{1/3}\text{Co}(1/3_{x/3})\text{Mn}_{1/3}\text{Ce}_{x/3}\text{O}_2$  cathode materials for use in lithium ion batteries. *Chin Sci Bull*, 2012, 57: 4181–4187
- 39 Meng Y S, Wu Y W, Huang B J, et al. Combining *Ab initio* computation with experiments for designing new electrode materials for advanced lithium batteries:  $\text{LiNi}_{1/3}\text{Fe}_{1/6}\text{Co}_{1/6}\text{Mn}_{1/3}\text{O}_2$ . *J Electrochem Soc*, 2004, 151: A1134–A1140
- 40 Jang S B, Kang S H, Amine K, et al. Synthesis and improved electrochemical performance of  $\text{Al}(\text{OH})_3$ -coated  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$  cathode materials at elevated temperature. *Electrochim Acta*, 2005, 50: 4168–4173
- 41 Ostrovskii D, Ronci F, Scrosati B, et al. Reactivity of lithium battery electrode materials toward non-aqueous electrolytes: Spontaneous reactions at the electrode-electrolyte interface investigated by FTIR. *J Power Sources*, 2001, 103: 10–17
- 42 Edstrom K, Gustafsson T, Thomas J O. The cathode-electrolyte interface in the Li-ion battery. *Electrochim Acta*, 2004, 50: 397–403
- 43 Aurbach D. Review of selected electrode-solution interactions which determine the performance of Li and Li ion batteries. *J Power Sources*, 2000, 89: 206–218
- 44 Lin H C, Zheng J M, Yang Y. The effects of quenching treatment and  $\text{ALF}_3$  coating on  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  cathode materials for lithium-ion battery. *Mater Chem Phys*, 2010: 519–523
- 45 Yabuuchi N, Lu Y C, Mansour A N, et al. The influence of surface chemistry on the rate capability of  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  for lithium rechargeable batteries. *Electrochem Solid-State Lett*, 2010, 13: A158–A161
- 46 Kim Y, Kim H S, Martin S W. Synthesis and electrochemical characteristics of  $\text{Al}_2\text{O}_3$ -coated  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode materials for lithium ion batteries. *Electrochim Acta*, 2006, 52: 1316–1322
- 47 Wang Z, Hung X, Chen L. Performance improvement of surface-modified  $\text{LiCoO}_2$  cathode materials: An infrared absorption and X-ray photoelectron spectroscopic investigation. *J Electrochem Soc*, 2003, 150: A199–A208
- 48 Li X W, Lin Y B, Lin Y, et al. Surface modification of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  with  $\text{Cr}_2\text{O}_3$  for lithium ion batteries. *Rare Metals*, 2012, 31: 140–144
- 49 Wang M, Wu F, Su Y F, et al. Modification of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode material by  $\text{CeO}_2$ -coating. *Sci China Ser E-Tech Sci*, 2009, 52: 2737–2741
- 50 Hashema A M A, Abdel-Ghany A E, Eid A E, et al. Study of the surface modification of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode material for lithium ion battery. *J Power Sources*, 2011, 196: 8632–8637
- 51 Zhang P X, Zhang L, Ren X Z, et al. Preparation and electrochemical properties of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -PPy composites cathode materials for lithium-ion battery. *Synth Met*, 2011, 161: 1092–1097
- 52 Park J H, Cho J H, Kim S B, et al. A novel ion-conductive protection skin based on polyimide gel polymer electrolyte: Application to nanoscale coating layer of high voltage  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode materials for lithium-ion batteries. *J Mater Chem*, 2012, 22: 12574–12581
- 53 Rao C V, Reddy A L M, Ishikawa Y, et al.  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  graphene composite as a promising cathode for lithium-ion batteries. *ACS Appl Mater Inter*, 2011, 3: 2966–2972
- 54 Hu R Z, Liu H, Zeng M Q, et al. Progress on Sn-based thin-film anode materials for lithium-ion batteries. *Chin Sci Bull*, 2012, 57: 4119–4130
- 55 Wang Y D, Guang X Y, Pan M. Mechanochemical synthesis and high-capacity performances of transition-metal borides as aqueous anode materials. *Chin Sci Bull*, 2012, 57: 4225–4228
- 56 Zhang H, Han H B, Gong S Z, et al. Characterization and properties of the electrolyte using  $\text{Li}[\text{N}(\text{SO}_2\text{OCH}(\text{CF}_3)_2)_2]$  as conductive salt (in Chinese). *Chin Sci Bull (Chin Ver)*, 2012, 57: 2623–2631
- 57 Huang F, Zhao Q, Luo C H, et al. Influence of  $\text{Cr}^{3+}$  concentration on the electrochemical behavior of the anolyte for vanadium redox flow batteries. *Chin Sci Bull*, 2012, 57: 4237–4243
- 58 Wu F, Wang M, Su Y F, et al. A novel layered material of  $\text{LiNi}_{0.32}\text{Mn}_{0.33}\text{Co}_{0.33}\text{Al}_{0.01}\text{O}_2$  for advanced lithium-ion batteries. *J Power Sources*, 2010, 195: 2900–2904
- 59 Wu F, Wang M, Su Y F, et al. Surface modification of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  with  $\text{Y}_2\text{O}_3$  for lithium-ion battery. *J Power Sources*, 2009, 189: 743–747
- 60 Wu F, Wang M, Su Y F, et al. Effect of  $\text{TiO}_2$ -coating on the electrochemical performances of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . *J Power Sources*, 2009, 191: 628–632
- 61 Wu F, Wang M, Su Y F, et al. Surface of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  modified by  $\text{CeO}_2$ -coating. *Electrochim Acta*, 2009, 54: 6803–6807
- 62 Wu F, Lu H Q, Su Y F, et al. Preparation and electrochemical performance of Li-rich layered cathode material,  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ , for lithium-ion batteries. *J Appl Electrochem*, 2010, 40: 783–789
- 63 Tao Z L, Chen J. Secondary battery systems for energy storage in smart grids (in Chinese). *Chin Sci Bull (Chin Ver)*, 2012, 57: 2545–2560

- 64 Yue Y H, Han P X, Dong S M, et al. Nanostructured transition metal nitride composites as energy storage material. *Chin Sci Bull*, 2012, 57: 4111–4118
- 65 Lu J F, Bai J, Xu X B, et al. Alternate redox electrolytes in dye-sensitized solar cells. *Chin Sci Bull*, 2012, 57: 4131–4142
- 66 Zhang Y Q, Xia X H, Kang J, et al. Hydrothermal synthesized porous  $\text{Co}(\text{OH})_2$  nanoflake film for supercapacitor application. *Chin Sci Bull*, 2012, 57: 4215–4219
- 67 Huang Z D, Liu X M, Oh S W, et al. Microscopically porous, interconnected single crystal  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode material for lithium ion batteries. *J Mater Chem*, 2011, 21: 10777–10784
- 68 Xia L, Zhu L M, Zhang H Y, et al. A positive-temperature-coefficient electrode with thermal protection mechanism for rechargeable lithium batteries. *Chin Sci Bull*, 2012, 57: 4205–4209
- 69 Du K, Hu G R. Review of manganese-based solid solution  $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \cdot (1-x)\text{LiMO}_2$  (in Chinese). *Chin Sci Bull (Chin Ver)*, 2012, 57: 794–804
- 70 Yang Y, Gong Z L, Wu X B, et al. Recent progress in cathode materials for Li-ion batteries (in Chinese). *Chin Sci Bull (Chin Ver)*, 2012, 57: 2570–2586

**Open Access** This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.