

Short communication

# A mixture of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiCoO}_2$ as positive active material of LIB for power application

Xingjiang Liu\*, Guangyan Zhu, Kai Yang, Jiqiang Wang

Tianjin Institute of Power Sources, Tianjin 300381, China

Available online 30 June 2007

## Abstract

Layered  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  has been synthesized by heating its precursor of  $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$  and  $\text{Li}_2\text{CO}_3$  at the temperature around of 900 °C in air, and applied in high-power lithium-ion secondary cells by mixed with  $\text{LiCoO}_2$  in mass ratios of 1:1 and 1:2. The lithium-ion secondary cells with mixture of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiCoO}_2$  showed a potential change similar to that of cell with pure  $\text{LiCoO}_2$  under low-rate discharge condition. The ICR18650 LIB with the mixed positive electrode is capable of discharge at 15 C current rate with a better electrochemical performance compared to that of pure  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . Especially, the ICR18650 LIB with the mixed positive electrode exhibits improved safety performance during overcharge period compared to  $\text{LiCoO}_2$ . Therefore, the mixture of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiCoO}_2$  is a promising alternative material to  $\text{LiCoO}_2$  for high-power LIB.

© 2007 Published by Elsevier B.V.

**Keywords:** High-power;  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ; Positive active material; Mixture; Lithium-ion secondary cells

## 1. Introduction

High-power lithium-ion batteries (HP-LIB) are promising candidate as energy storage and power output for HEV including plug-in HEV (PHEV) and power tools [1]. However, application of HP-LIB is limited by thermal abuse characteristics and the other safety issues.  $\text{LiCoO}_2$  has been widely applied as positive active material for LIB, due to its excellent electrochemical properties, higher density, easy to synthesize [2,3]. Nevertheless, the  $\text{LiCoO}_2$  has some disadvantages such as poor thermal stability, overcharge characteristics and high cost, thus the  $\text{LiCoO}_2$  usually applied in small capacity LIB for cellular phone, notebook computer and other mobile electronics. Spinel  $\text{LiMn}_2\text{O}_4$  and olivine  $\text{LiFePO}_4$  exhibit better anti-overcharge characteristics and lower heat generation, thus are applied in large sized LIB or HP-LIB for EV, PHEV and power tools [4–7], even though energy density is lower than that with  $\text{LiCoO}_2$ . Kitao et al. have reported lithium-ion cells using a mixture of  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and  $\text{Li}(\text{NiCoMn})\text{O}_2$ , they found that the cells showed a improved storage characteristics, and investigated the spinel  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  content in the range of 20–60% is most effective [8]. Layered  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  possesses larger

specific capacity, the excellent safety characteristics with much lower heat generation, but slightly lower in high-rate discharge capability compared to  $\text{LiCoO}_2$  [9–12]. Therefore, positive active material is the key in LIB for different application, and using mixed positive active material is an effective way to deal with the balance between energy density, power density and safety performance for HP-cell application. In this work, layered  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  will be prepared though a heat treatment after a soft chemical process. And the mixture of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiCoO}_2$  was attempted as positive active material of LIB for power application.

## 2. Experimental

The  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  was prepared by reacting stoichiometric amounts of coprecipitated mixed hydroxides of nickel, cobalt and manganese with lithium carbonate at the temperature around 900 °C for 12 h in air. The second-particle of  $\text{LiCoO}_2$  was provided by Superhoo Industries Co. Ltd., China, and the features of active materials used in this work were summarized in the Table 1. ICR18650 cells were subjected to evaluation tests using  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ,  $\text{LiCoO}_2$  and mixture of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiCoO}_2$  as positive active material and composite graphite as negative active material, 1.2 mol  $\text{dm}^{-3}$   $\text{LiPF}_6$  in mixture of EC: DMC: DEC (1:1:2 in vol-

\* Corresponding author.

E-mail address: [liuxj@tips.ac.cn](mailto:liuxj@tips.ac.cn) (X. Liu).

Table 1  
Features of active materials

Material	LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>	LiCoO <sub>2</sub>	MCMB	Gr.
Maker	TIPS, China	Superhoo Industries Co. Ltd., China	Osaka Gas	Schunk
Particle size (μm)	8–12	6–10	20–25	20
SSA (m <sup>2</sup> g <sup>-1</sup> )	0.6	0.3–0.6	1.2	1.0
Tap density (g cm <sup>-3</sup> )	2.4	2.5	0.9	0.65

ume) as electrolyte [12]. The mixture of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> and LiCoO<sub>2</sub> has prepared by mechanical mixing in NMP solution of PVdF. The cell capacities were measured at 0.2 C rate; Rate performance test was carried out at 1, 5, 10 and 15 C in the voltage range of 4.2–2.75 V. Overcharge experiment was performed at 1 C charge current rate. ac impedance measurements were performed at OCV after fully charged (100%SOC); the frequency was ranged from 20 kHz to 5 mHz (Solartron 1287).

SEM observation was applied for confirming morphology of the material; the DSC measurement was performed in the temperature range from ambient temperature to 400 °C at a heating rate of 5 °C min<sup>-1</sup>. for checking the thermal stability of the material in electrolyte solution.

### 3. Results and discussion

#### 3.1. Characteristics of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>

Fig. 1 represents the image of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> synthesized by us. Clearly, the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> particles show ball-like appearance with an average diameter of 10–15 μm, the other typical features are described in Table 1. The spherical LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> particles are easy to coat and form a high-density electrode because of high mobility and high tap density; and the small specific area is helpful to suppress reaction between LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> and electrolyte solution.

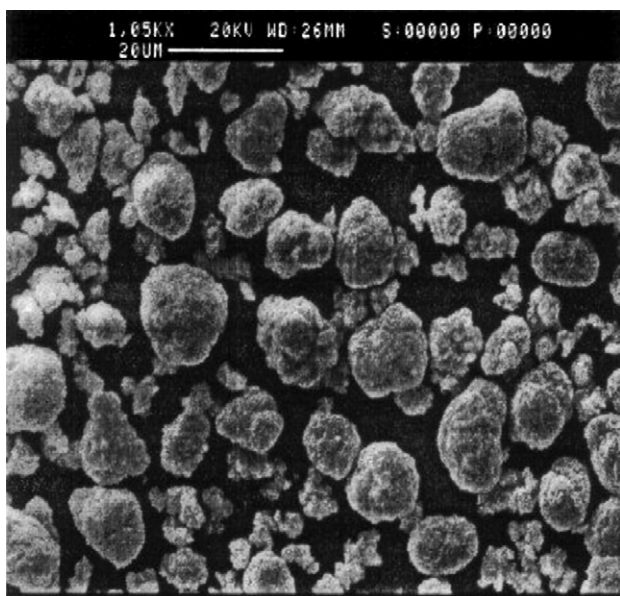


Fig. 1. SEM image of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>.

In order to know thermal stability of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> in the cell, a mixture of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> and electrolyte was subjected for DSC measurement. Fig. 2 shows the DSC curves for LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> before and after charging. It was found that the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is very stable before charge, but the fully charged LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> shows two exothermic peaks at 152.3 and 258.4 °C, respectively. On contrast, the LiCoO<sub>2</sub> possesses larger heat generation at more low temperature of about 220 °C (not shown). It means that the thermal stability of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> superior to that of LiCoO<sub>2</sub> in electrolyte solution.

#### 3.2. Electrochemical performance of the ICR18650 cells

To evaluate electrochemical performance of the cells with various positive electrodes, the cell was charged to 4.2 V at 0.2 C rate in CC–CV mode, then discharged to 2.75 V at 0.2 C rate for cell capacities measurement; high-rate discharge performance was tested at various current rates after charged at same charging rate of 0.5 C with CC–CV mode. Fig. 3 shows the discharge characteristics of 18650 cells with pure LiCoO<sub>2</sub>, pure LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, and mixture of LiCoO<sub>2</sub> and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> in different mass ratios. Clearly, the average voltage/potential of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is lower than that of LiCoO<sub>2</sub> in the voltage range of 4.2–2.75 V, but the mixed electrode given a voltage/potential changes similar to the LiCoO<sub>2</sub>. These results signify that the potential of mixed electrode depend on the material with more positive potential, and the voltage change of the cell observed during low-rate discharge period which mainly related to LiCoO<sub>2</sub>.

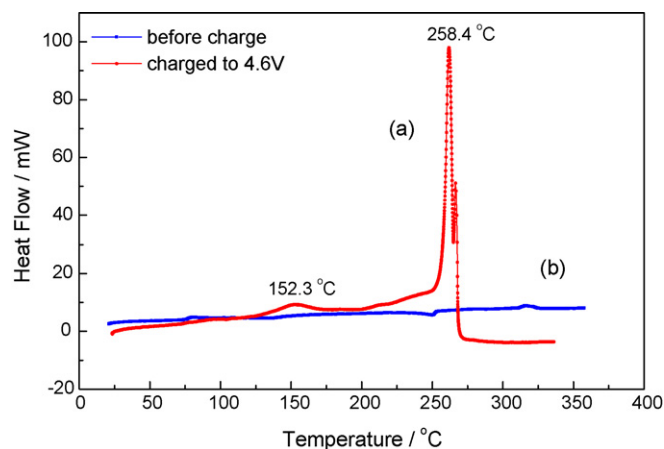


Fig. 2. DSC curves for LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> before charge (a) and after charged to 4.6 V vs. Li/Li<sup>+</sup> (b) with electrolyte solution. The heating rate is 5 °C min<sup>-1</sup>.

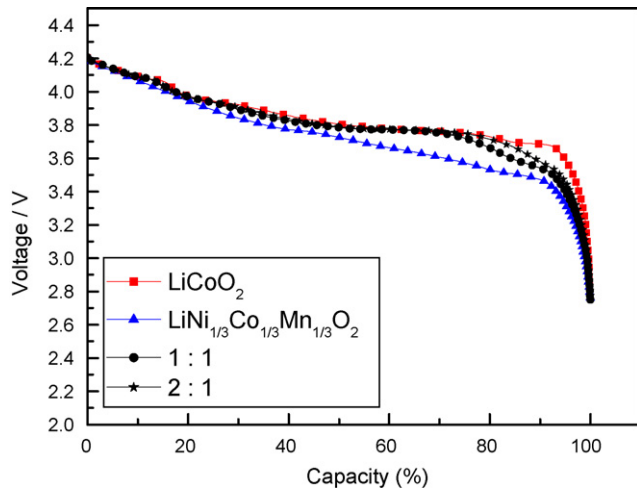


Fig. 3. Discharge characteristics of positive electrode with various mass ratios of  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . The cells were discharged at 0.2 C at ambient temperature.

Fig. 4 shows the high-rate discharge performance of the cells with  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , respectively. The result indicates that the cell with  $\text{LiCoO}_2$  exhibit a high-rate discharge characteristics better than that with  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . The difference in high rate performance is mainly caused by the diffusion coefficient and particle size. The  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  possesses lower diffusion coefficient and larger particle size compared to  $\text{LiCoO}_2$  in this work, which result in different rate performance. As shown in Fig. 5, The average discharge voltage and capacity become lower as increasing the content of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  in the positive electrode at 10 C current rate. Although the rate-performance of cells using mixed positive active material is slightly inferior to  $\text{LiCoO}_2$  as shown in Fig. 4, also capable of discharged at 15 C rate as shown in Fig. 6. The discharge curve shows a minimum voltage appearance at initial period while discharge the cell at high-rate of 15 C, which caused by the changes in Li-ion diffusion rate in solid phase and electrolyte. The cell temperature will increase

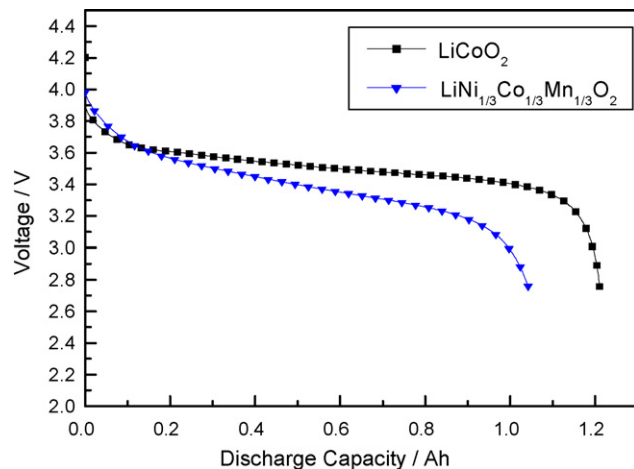


Fig. 4. Comparison of high rate discharge performance for cells with  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . The cells were discharged at 10 C at ambient temperature.

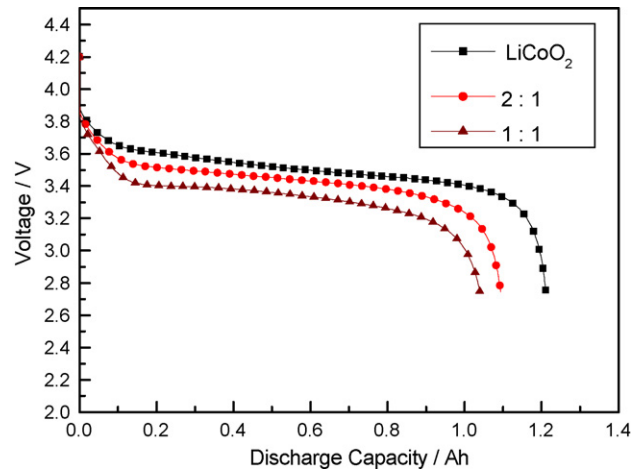


Fig. 5. Discharge performance of the cell using positive electrode with pure  $\text{LiCoO}_2$  (■), mixture of  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  in mass ratio of 2:1 (●) and 1:1 (▲), respectively.

as high-rate discharge, and improve the Li-ion diffusion rate. However the high-rate discharge ability is enough for power use in HEV and power tools.

Fig. 7 compare the cycleability for the cells with pure  $\text{LiCoO}_2$ , pure  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and their mixture at 10 C discharge rate. The cell cycling test has performed with five cycles 10 C-discharge and one cycle 0.2 C-discharge for cell recondition. The better capacity retentions over 90% were achieved for all of the cells after 100 cycles at 10 C (the initial discharge capacity of the cell at 10 C was defined as 100%). Fig. 8 shows the Cole–Cole plots at initial cycle and after 100 cycles measured at full-charged state. All of the plots show the serious loops contribute negative and positive electrode including SEI and kinetic components. The ohmic resistance (real axis intercept) includes electrolyte resistance, electrode bulk resistance, separator resistance, etc., it is small (ca. 12 mΩ) at initial state for all of the cells. Impedance come from positive electrode/electrolyte, it assigned second half circle corresponding

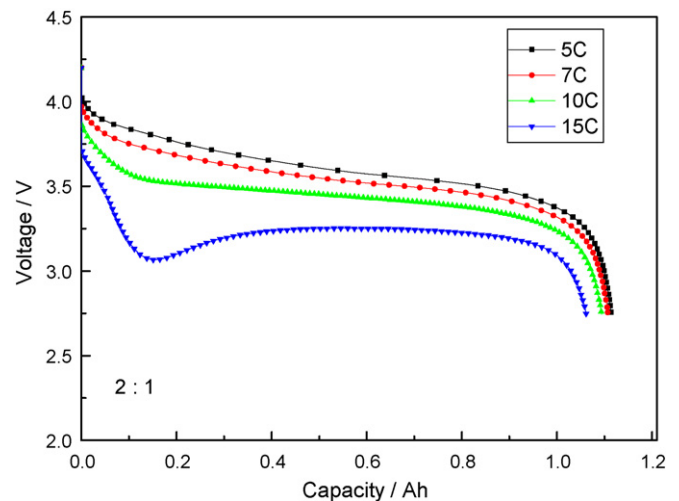


Fig. 6. Rate-discharge performance of the cell using mixture of  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  with mass ratio of 2:1. All of the cells were charged at 0.5 C, and then discharged at 5, 7, 10 and 15 C, respectively.

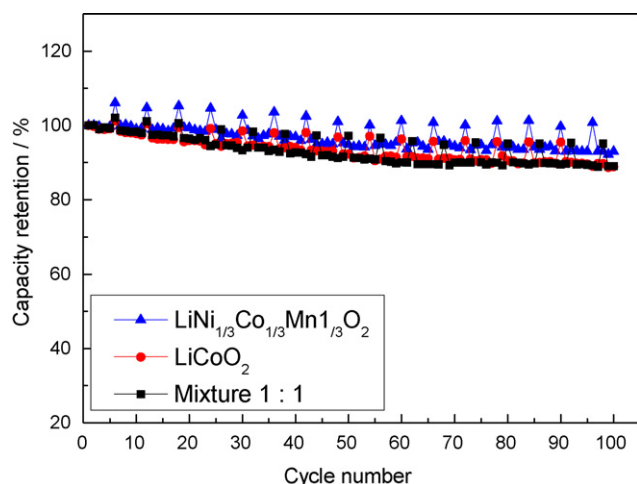


Fig. 7. Comparison of cycleability for LIB with different positive active material. (●) LiCoO<sub>2</sub>; (■) LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>; (▲) Mixture of LiCoO<sub>2</sub> and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> with mass ratio of 2:1.

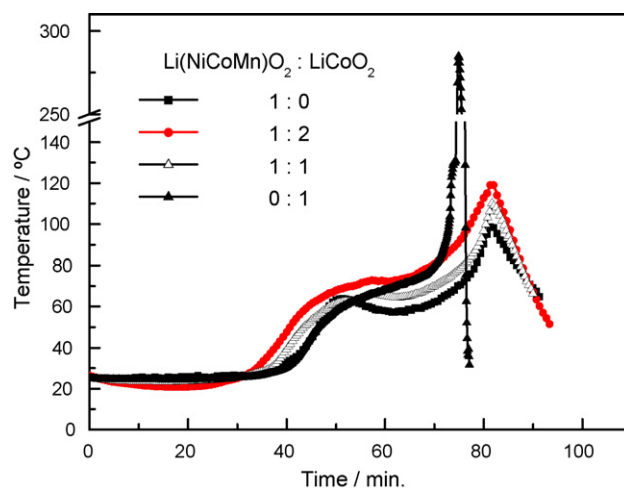


Fig. 9. Temperature change with overcharge time for the cells at 1 C charge current. The mass composition for the positive electrode was shown in the figure.

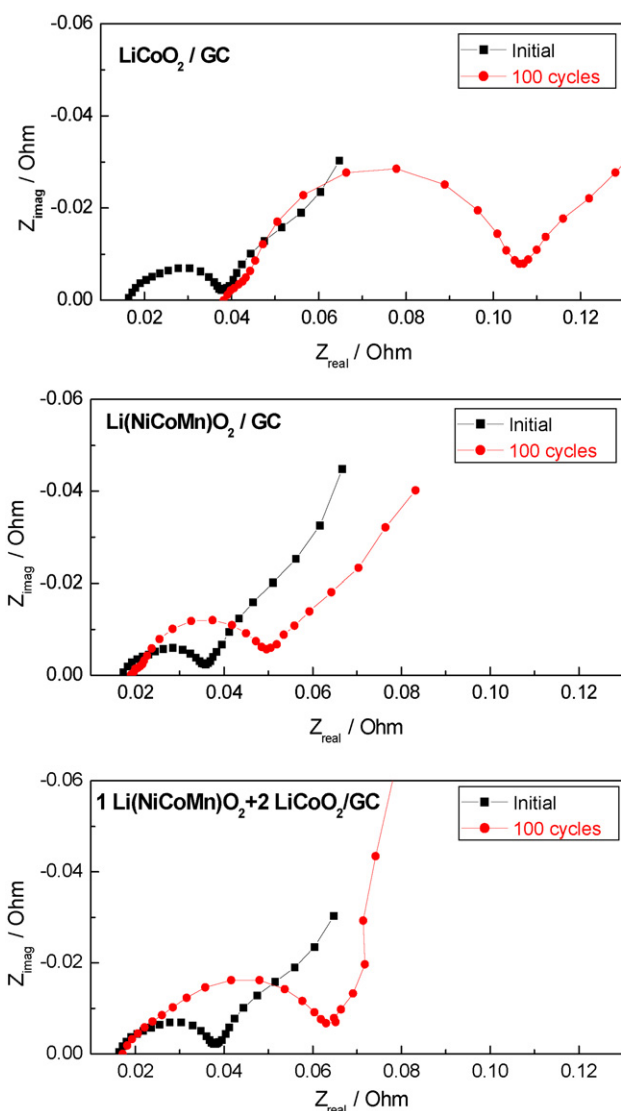


Fig. 8. Cole–Cole plots of the cell with LiCoO<sub>2</sub> (a), LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (b) and mixture of LiCoO<sub>2</sub> and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (c) at initial state and after 100 cycles at full-charged state.

lower frequency. Clearly, positive electrode impedance becomes larger significantly after 100 cycles, especially in the case of LiCoO<sub>2</sub>. It was recognized the LiCoO<sub>2</sub> is thermal unstable at upped temperature in electrolyte solution. However, the cells with positive electrode containing LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> exhibit smaller impedance changes as shown in Fig. 8. These results confirmed that the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is a more thermal stable material.

### 3.3. Safety performance

Fig. 9 shows the overcharge characteristics of the cells with different positive active materials. In the case of full-charged LiCoO<sub>2</sub>, the cell fire up after over charge about 75 min at 10 C. However, the cells with positive electrode containing LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> did not fire or smock or electrolyte leak as well as with pure LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>.

Therefore, the mixture of LiCoO<sub>2</sub> and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> could be used as alternative positive active material for high-power LIB with better electrochemical performance together with improved safety properties.

## 4. Conclusions

Layered LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> has been synthesized by heating its precursor of Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>(OH)<sub>2</sub> and lithium source of Li<sub>2</sub>CO<sub>3</sub> in atmosphere at the temperature around of 900 °C, and applied in high-power lithium-ion cells by mixed with LiCoO<sub>2</sub>. The lithium-ion cells with mixture of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> and LiCoO<sub>2</sub> showed a potential change similar to that of cell with pure LiCoO<sub>2</sub> under low-rate discharge condition. The ICR18650 lithium-ion cell with the mixed positive electrode is capable of discharge at 15 C rate with a better performance compared to that of pure LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>. Especially, the ICR18650 lithium-ion cell with the mixed positive electrode exhibits high safety performance during overcharge period compared to LiCoO<sub>2</sub>. Therefore, the mixture of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> and

LiCoO<sub>2</sub> is a promising alternative material to LiCoO<sub>2</sub> for high-power LIB.

## References

- [1] T. Ikeya, H. Miyazaki, Proceedings of the 46th Battery Symposium in Japan, 2005, 1HEV-01.
- [2] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, Mater. Res. Bull. 15 (1980) 783.
- [3] T. Ohzuku, A. Ueda, J. Electrochem. Soc. 141 (1994) 2972.
- [4] G. Li, H. Ikeda, T. Uchida, M. Wakihara, J. Electrochem. Soc. 143 (1996) 178.
- [5] D. Song, H. Ikuta, M. Wakihara, Solid State Ionics 117 (1999) 151.
- [6] A.K. Padhi, K.S. Nanjund Aswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (4) (1997) 1188–1194.
- [7] M. Thuckera, Nat. Mater 2 (2002) 81–82.
- [8] H. Kitao, T. Fujihara, N. Nakanishi, T. Ikemachi, T. Nohuma, Proceedings of the 44th Battery Symposium in Japan, Sakai, Japan, 2003, p. 308.
- [9] Z. Lu, D.D. MacNeil, J.R. Dhan, Electrochem. Solid-State Lett. 4 (2001) 200.
- [10] N. Tran, L. Croguennec, C. Jordy, P. Biensan, C. Delmas, Proceedings of the 12th International Meeting on Lithium Batteries, Nara, Japan, 2004, Abs. 314.
- [11] N. Yabuuchi, T. Ohzuku, J. Power Sources 119–121 (2003) 174.
- [12] Xingjiang LIU, Guangyan ZHU, Kai YANG, Zhebo ZHANG, Xuesheng LIU, Jiqiang WANG, Chin. J. Power Source, submitted for publication.