ORIGINAL PAPER

Effect of lithium boron oxide glass coating on the electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

Junqing Dou · Xueya Kang · Tuerdi Wumaier · Hongwei Yu · Ning Hua · Ying Han · Guoqing Xu

Abstract The effect of the lithium boron oxide glass coating on the electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been investigated via solution method. The morphology, structure, and electrochemical properties of the bare and coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ are characterized by scanning electron microscopy, X-ray diffraction, electrochemical impedance spectroscopy, and charge–discharge tests. The results showed that the lattice structure of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is not changed after coating. The coating sample shows good high-rate discharge performance (148 mAh g^{-1} at 5.0 C rate) and cycling stability even at high temperature (with the capacities retention about 99% and 87% at room and elevated temperature after 50 cycles). The Li^+ diffusion coefficient is also largely improved, while the charge transfer resistance, side reactions within cell, and the erosion of Hydrofluoric Acid all reduced. Consequently, the good electrochemical performances are obtained.

Keywords Lithium boron oxide glass · Coating · Cathode material · Lithium-ion batteries

J. Dou · X. Kang (✉) · T. Wumaier · H. Yu · N. Hua · Y. Han · G. Xu
Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, China
e-mail: kangxy@ms.xjb.ac.cn

J. Dou
Graduate University of Chinese Academy of Sciences, Beijing 100049, China

J. Dou · X. Kang · T. Wumaier · N. Hua · Y. Han · G. Xu
Xinjiang Key Laboratories of Electronic Information Materials and Devices, Urumqi, Xinjiang 830011, China

Introduction

Lithium-ion batteries have been widely applied in hybrid electric vehicle, laptop, mobile phone, and others due to their long cycle life and high energy density [1, 2]. $LiCoO_2$ is still the most widely used cathode material in commercial lithium-ion batteries, because of its easy synthesis, high electronic conductivity, excellent cycling performance, and reasonable rate capability. However, the disadvantages, such as the high cost, limited capacity, and toxicity, limit its further development and application [3, 4]. With the increasing market demand, it is necessary to search for new cathode materials of the lower cost, lower toxicity, and, also, ease in preparation to replace $LiCoO_2$.

$LiNi_xCo_yMn_{(1-x-y)}O_2$, a combination of cations Ni, Co, and Mn, has been reported as a most promising next cathode material for rechargeable Li-ion batteries. These materials belong to α-$NaFeO_2$ type. The valences of nickel, cobalt, and manganese ions are +2, +3, and +4, respectively. But only nickel ions and cobalt ions are electro-active [5]. It is reported that a high discharge capacity 200 mAh g^{-1} can be obtained [6, 7]. Among $LiNi_xCo_yMn_{(1-x-y)}O_2$ systems, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) is the most investigated one since first synthesized by Ohzuku and Makimura in 2001 [6]. However, the unreasonable rate and cycling performance are still the main difficulties in developing a large-scale battery using NCM as cathode material until now.

It's well known that surface modification on cathode materials with electrochemically inactive metal oxides such as Al_2O_3 [8, 9], ZrO_2 [10, 11], TiO_2 [12, 13], and ZnO [14] could prevent dissolution of transition metals, unwanted reactions between cathode and electrolyte, and also improve their electrochemical performances to some extent. These results indicated that the surface treatment method is

an effective way for improving the electrochemical performances of cathode materials.

In addition, according to the report of Amatucci and coworkers [15], lithium boron oxide (LBO) glass was particularly suitable for surface treatment. And due to LBO glass with a good lithium ionic conductivity, it has already been investigated as solid lithium ionic conductor (or fast-ion conductor) for a long time [16–18]. The molten LBO compositions exhibited good wetting properties and relatively low viscosity, which make it easy to homogeneously coat on the surface with powders. Furthermore, electrochemical studies have shown that these materials are stable against the high oxidation potentials of the 4 V cathode electrode materials used in Li-ion batteries today [15]. Finally, such a material coating has a relatively low treatment temperature, which is only about 500 °C.

Chan et al. [19] has reported that spinel lithium manganese oxide cathode material coated with LBO via solid-state method exhibited relatively good cycling performance; the capacity fade was 2.63% after ten cycles at a current rate of 0.1 C. Şaban Patatet et al. [20] also investigated the effect of the LBO glass coating on the charge–discharge cycling performance of spinel powders ($LiMn_2O_4$) via a solution method. The coated $LiMn_2O_4$ exhibited an excellent cycling performance; it retained about 100% of the original capacity after 30 cycles at a current rate of 1.0 C with a cut-off voltage of 3.5–4.5 V. J. Ying et al. [21], by coating LBO glass on the surface of $LiNi_{0.8}Co_{0.2}O_2$, effectively increased the reversible capacity, decreased the irreversible capacity loss, stabilized the cycling performance, and reduced the self-discharge of the $LiNi_{0.8}Co_{0.2}O_2$ powders. The reports indicated that surface modification with LBO glass on cathode materials can improve their electrochemical performances effectively, but only a few reports can be found about $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ coating with LBO glass. Therefore, we attempted to enhance the electrochemical performances of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ by LBO glass coating.

In this study, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was successfully coated with LBO glass layer via solution method, and the good cycling stability, high rate, and high temperature performances are obtained. In comparison, the morphology, structure, and electrochemical performances of the bare and coated NCM materials are discussed in detail.

Experimental

The layered NCM powder was synthesized via carbonate co-precipitation from a solution containing nickel, cobalt, and manganese sulfates by the addition of sodium carbonate solution and ammonia as a chelating agent solution, as described by S.H. Park et al. [22].

The LBO glass coating was prepared using a solution method. All the reagents used in experiment were of analytical purity and used without further purification. Stoichiometric $LiOH·H_2O$ and H_3BO_3 (1:2 in molar) was dissolved in deionized water under strong stirring. Then, the base material powder NCM was added into the solution and was stirred continually, and gently heated to 80 °C until the solvent completely evaporated. Then, the mixture was heated at 500 °C for 10 h. After the mixture cooled to room temperature, the homogeneous coating with LBO glass powders was obtained. The weight ratio of the precursor of LBO glass to the NCM powders was 3 wt.% in this experiment.

The crystalline phase was analyzed using X-ray diffraction (XRD, RINT-2500 V, Rigaku Co.) with Cu Kα radiation (λ=1.5418 Å) in the range of $10° \leq 2\theta \leq 90°$ with a scanning rate of 2° per minute.

The particle morphology of the prepared bare and coated NCM powders was determined by scanning electron microscopy (SEM, LEO-1430VP).

Electrochemical performances of the bare and coated NCM powders were investigated by using CR2025 coin cell. The cathode was fabricated from a mixture of the prepared powders, acetylene black, and polyvinylidene fluoride with a weight ratio 80:15:5, and the electrolyte was 1 M $LiPF_6$ in a mixture of ethyl carbonate, diethyl carbonate, and dimethyl carbonate (volume ratio, 1:1:1). The slurry was then casted on aluminum foil and dried at 120 °C overnight under vacuum. The cells (CR2025) were assembled in an argon-filled glove-box using lithium metal foil as the counter electrode. The cells were charged and discharged between 2.5 and 4.5 V on a charge–discharge apparatus (BTS-51, Neware, China). Electrochemical impedance spectroscopy (EIS) was also tested using a CHI650 electrochemical working station.

Results and discussion

Figure 1 showed the XRD patterns of the bare and coated NCM powders. The strong and narrow diffraction peaks and the clear peak splits of (006)/(102) and (018)/(110) indicates the layered $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode material are successfully synthesized in the experiment [23]. All the diffraction peaks can be indexed on the basis of the hexagonal α-$NaFeO_2$ structure with a space group 166, R-3 m. In addition, the spectrum of the coated sample is almost the same as the bare one, and no other peaks such as H_3BO_3 and $LiOH·H_2O$ diffraction peaks are found, indicating that the coating layer (LBO glass) did not destroy the lattice of $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$, and the LBO glass may exists in amorphous state.

The morphology of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ has great influence on their electrochemical performance. SEM analyses of the prepared bare and LBO-coated NCM were
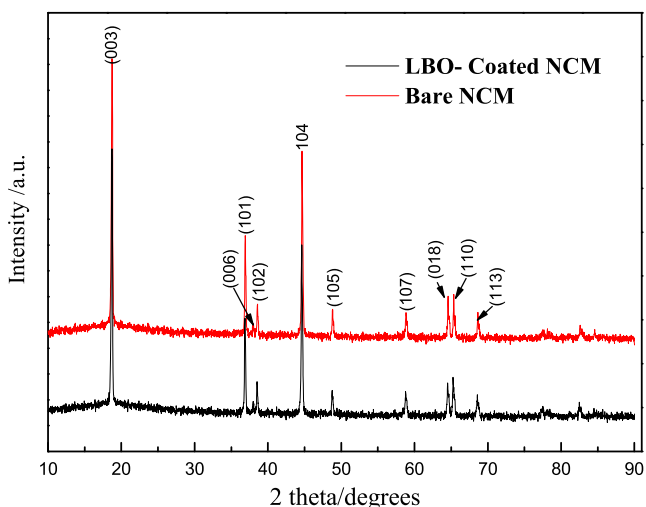
Fig. 1 XRD patterns of the bare and coated NCM powders

carried out. The SEM images of the two samples are shown in Fig. 2. It can be seen that the bare and coated sample shows a similar surface morphology. However, there exist some crystal edges on the surface of the bare NCM, while the LBO-coated NCM become blurry and most of the
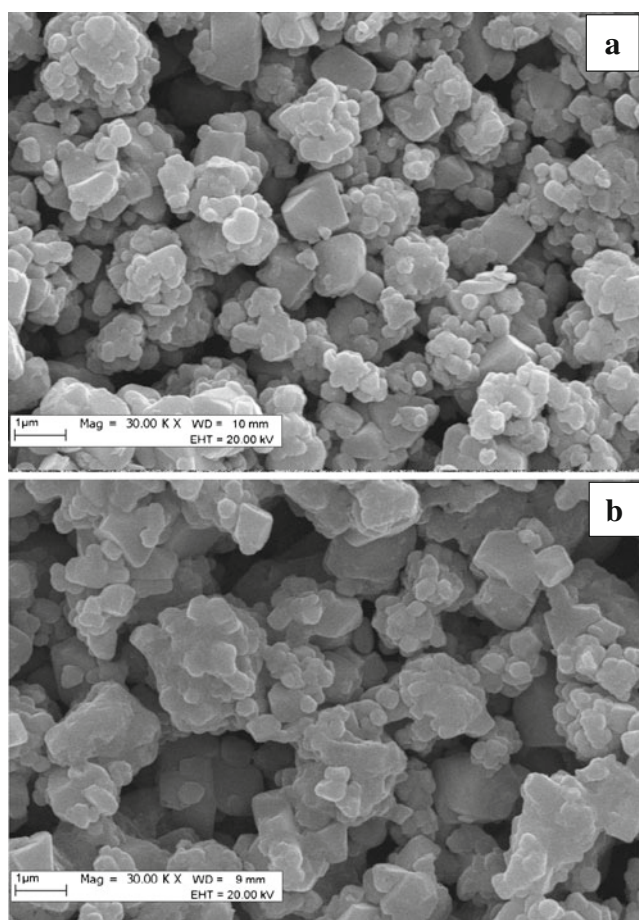

Fig. 2 SEM images of the bare (a) and coated (b) NCM powders

angular features have been rounded. Moreover, from Fig. 2, also find that the particles of the both samples distributed uniformly, but the particle size of the coated one is lager than the bare NCM. As we know, a larger size particle always has a smaller special surface area, which can reduce the contact area between cathode and electrolyte, and further reduce the corrosion of active material due to present Hydrofluoric Acid (HF) in electrolyte. In addition, the fact that no other phases revealed in the XRD pattern illustrates that the LBO was homogeneously coated on the surface of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles as an amorphous glass phase as we expected.

The charge–discharge curves of the bare and coated NCM powders at 0.5 C rates (1 C=200 mA g^{-1}) are shown in Fig. 3. Both samples show a gradually decreased discharge voltage from 4.5 to 3.6 V, which is the main characteristic of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode material. However, at the same special capacity, the charge voltage of the coated NCM is lower than the bare one, while the discharge voltage is opposite. This phenomenon indicates that the smaller electrode polarization exists in the coated one. The rate performances of both samples are also investigated at 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 C rates within 2.5–4.5 V, as shown in Fig. 4. It is seen that with the current density increasing gradually, the discharge capacity of both samples are rapidly reduced. But the coated one exhibits a better rate performance. The initial discharge capacities are 181, 171, 164, 158, 155, and 148 mAh g^{-1} at 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 C rates for the coated one and 183, 169, 160, 152, 145, and 132 mAh g^{-1} are obtained for the bare one. At the same time, when recovering the former testing rate (1.0 C rate in the experiment), the discharge capacities of the coated one show almost no decrease, which indicates the good cyclic reversibility of the electrodes [24] due to the LBO glass coating layer. And these are
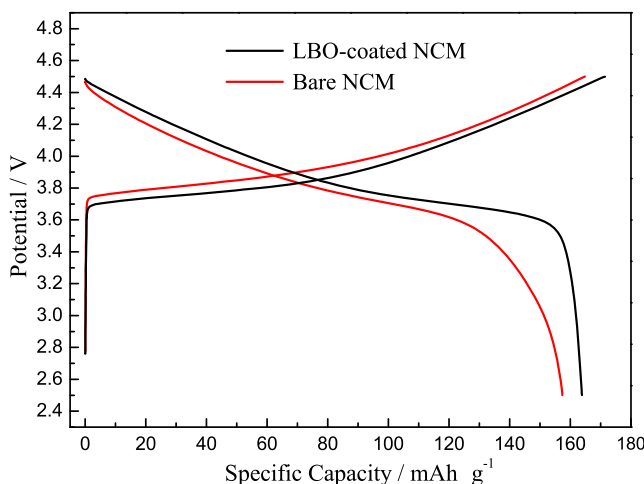

Fig. 3 The charge–discharge curves of the bare and coated NCM powders at 0.5 C rate
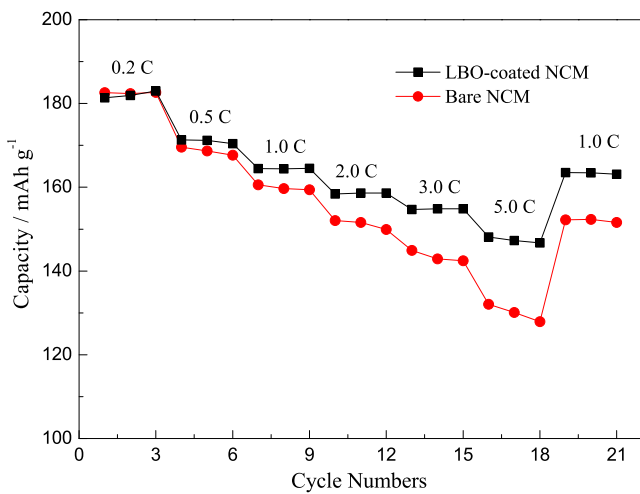
Fig. 4 Cycle performance of the bare and coated NCM powders at various rates within 2.5–4.5 V

Fig. 6 Cyclic curves of the bare and coated NCM powders at 0.5 C rate between 2.5 and 4.5 V at elevated temperature

directly related to the high Li$^+$ ions' conductivity in the electrode during charge–discharge progress after coating. It is confirmed that the LBO coating layer on the surface of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ can enhance the conductivity effectively.

The cycling profiles of the bare and coated electrodes within 2.5–4.5 V at 0.5 C rates and room temperature for 50 cycles are shown in Fig. 5. Due to the presence of the electrochemical inactive LBO glass layer on surface of the cathode electrode, the initial discharge capacity of the coated material is decreased. But the LBO-coated NCM exhibits a batter cycling stability. The bare sample delivered a capacity 165.92 and 154.91 mAh g^{-1} of the first and 50th cycles. In comparison, the coated sample delivers a capacity 162.41 mAh g^{-1} after 50 cycles with about 99% capacity retention. In addition, the cycling stability of both samples at elevated temperature (60 °C in the experiment) is also tested within 2.5–4.5 V at 0.5 C rate and the cycling profiles are
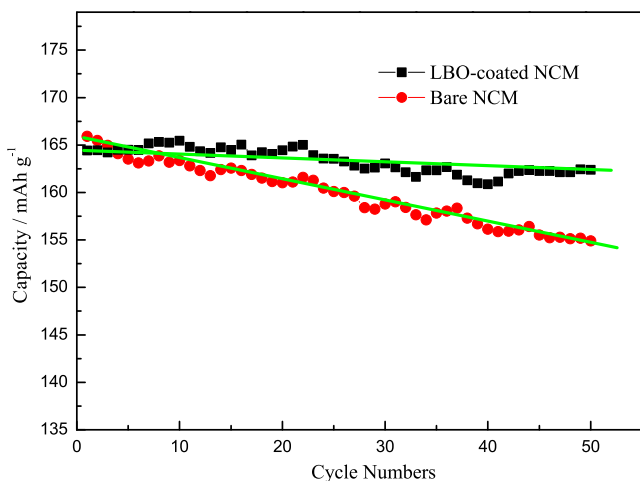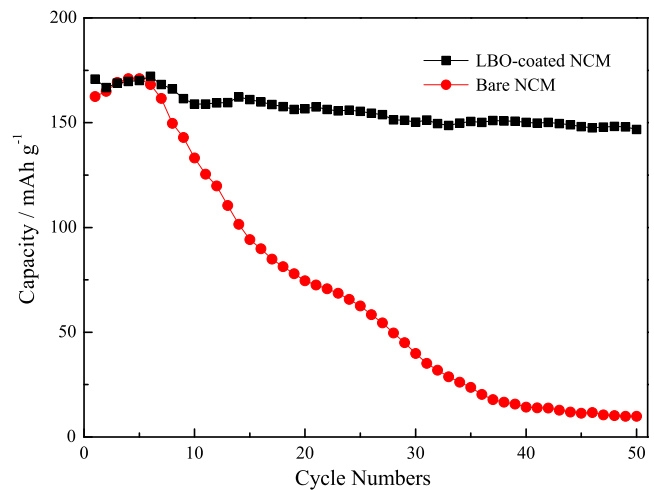
shown in Fig. 6. The bare and coated samples show 150 and 22 mAh g^{-1} capacity drops after 50 cycles with the capacities retention about 10% and 87%, respectively. It is clearly shown that the high temperature performance of the NCM is improved significantly after coating.

To understand the coating layer effect on the kinetics process of the electrode materials, EIS was employed to analyze the impedance of the electrodes. The fully discharged coin cells (CR2025, 2.5 V) were measured in the experiment. The Nyquist plots of the bare and coated samples are given in Fig. 7. The curves are both comprised of one semicircle in high-to-medium frequency and an inclined line in low frequency. Generally, the semicircle in high-to-medium frequency semicircle is attributed to the charge transfer resistance (R_{ct}), and the inclined line at low frequencies is attributed to Warburg impedance that is associated with Li$^+$ diffusion in electrodes [25].
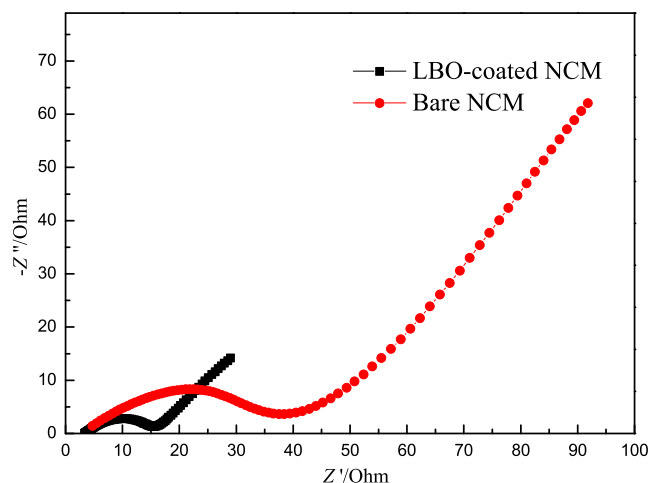

Fig. 5 Cyclic curves of the bare and coated NCM powders at 0.5 C rate within 2.5–4.5 V at room temperature

Fig. 7 The Nyquist plots of the bare and coated NCM powders tested at full discharge (CR2025, 2.5 V)
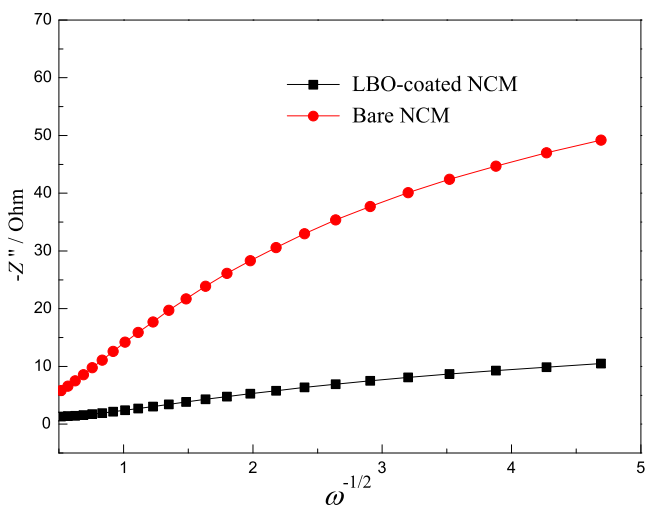
Fig. 8 The relationship between Z'' and $\omega^{-1/2}$ for the bare and coated NCM powders

Generally speaking, the R_{ct} can be measured by the diameter of the semicircle in the high-to-medium frequency range [11]. By comparing the diameter of the semicircle, the charge-transfer resistance for the coated material is about two times smaller than the bare one, owing to the LBO glass coating, as shown in Fig. 7. The lower R_{ct} of the coated one indicates a lower electrochemical polarization, faster electrode/electrolyte interface reaction, and lithium diffusion processes.

According to the literature [26], the lithium diffusion coefficient could be calculated by the following two equations:

$$D_{Li} = \frac{R^2 T^2}{2n^4 F^4 C^2 \sigma^2} \tag{1}$$

$$Z'' = \sigma \omega^{-\frac{1}{2}} \tag{2}$$
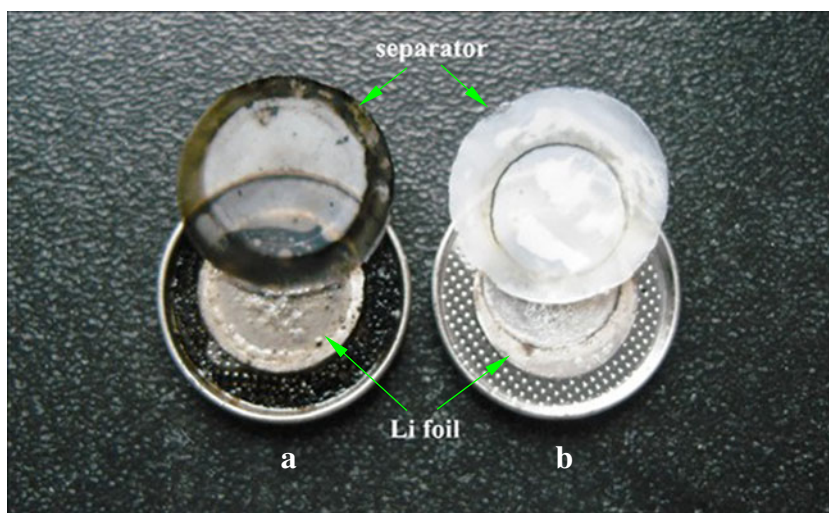
where D_{Li} is the lithium-ion diffusion coefficient (Eq. 1), R is the gas constant, T is the absolute temperature, n is the number of electrons per species reaction, F is the Faraday constant, C is the concentration of lithium ion, and σ is the Warburg factor which could be obtained by Eq. 2. Thus, the lithium-ion diffusion coefficient is inversely proportional to σ^2. Figure 8 shows the relationship between Z'' and square root of frequency $\omega^{-1/2}$ in the low frequency region, the value of σ could be obtained from the slope. Form these dates, we can get $D_{Li, coated} \approx 14.85\, D_{Li, bare}$, indicating that the LBO coating layer can improve the Li-ion conductivity of NCM significantly. The effect on Li^+ ion diffusion conductivity is more pronounced than other coating material such as Al_2O_3 and TiO_2, etc. [27, 28]. That is because the LBO glass is a fast-Li^+ ion conductor; it could provide the tunnel for Li^+ ion transportation during charge–discharge processes, while other conventional coating materials are generally inactive to lithium ion and have low lithium-ion conductivity [28].

Generally, the irreversible capacity loss (ICL) can be ascribed to the transition metal ion dissolution or the side reaction between electrode and electrolyte due to the present of HF [11]. And Jang et al. [29] also confirmed that HF will be generated during cycling when using $LiPF_6$-based electrolyte easily. The generated acid, HF, could corrode the active material as the cycle goes by, causing large ICL. At the same time, the low Li^+ diffusion conductivity can probably also induce some ICL [30]. As mentioned above, the LBO glass has a high stability against the high oxidation potentials of 4 V [15]. Meantime, as a metallic oxide, LBO also could react with HF. So, the LBO glass may act as both HF scavenger and physical protection layer. As HF scavenger, LBO glass will preferentially react with HF and hence delay the corrosion of cathode materials in the $LiPF_6$-based electro-

Fig. 9 The images of the separator in the testing coin cell based on bare (**a**) and coated (**b**) electrodes after 50 cycles

lyte and then reduced the transition metal ion dissolution, as demonstrated in Fig. 9. Figure 9a, b shows the images of the separator in the testing coin cell based on bare and coated electrodes after 50 cycles. It is clearly shown that the separator (Fig. 9a) is covering some black substance (it is the dissolved cathode material), while the separator (Fig. 9b) remains clean. It can be concluded the LBO glass coating layer does prevent the corrosion and dissolution of the NCM cathode material. Furthermore, the LBO glass also acts as a physical protection layer to prevent the direct contact between cathode material and liquid electrolyte. It minimizes the side reactions within the battery, stabilizes the structure of the charged NCM, and then reduces the ICL due to the erosion of HF. On the other hand, from the EIS test, we know that the LBO layer can weaken the electrode polarization, enhance the Li^+ diffusion coefficient, and then reduces the ICL due to the low Li^+ conductivity, as mentioned in the article [30].

In summary, the LBO coating layer can improve the Li^+ diffusion coefficient, enhance the electrode/electrolyte interface reaction and lithium diffusion processes, reduce the R_{ct}, minimize the side reactions within cell,, and reduce the erosion of HF; these are all in favor for improving the electrochemical performance of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. Therefore, the higher discharge capacity, the better the high-rate performance and cycling stability even at high temperatures obtained.

Conclusions

The coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with LBO glass was successfully prepared using a solution method. And the effect of coating on the electrochemical performances of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was investigated. XRD and SEM measurement indicated that the amorphous LBO glass layers are coated on the surface of the layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles. The electrochemical performance testing results showed that the lattice structure of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is not changed after coating. The coating sample shows good high-rate discharge performance (148 mAh g^{-1} at 5.0 C rate) and cycling stability even at high temperature (with the capacities retention about 99% and 87% at room and elevated temperature after 50 cycles). The obtained excellent electrochemical performances of the LBO-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ should enable the wide accep-

tance and application in long-life lithium ion batteries with high power and high energy density.

References

1. Park SH, Yoon CS, Kang SG, Kim HS, Moon SI, Sun YK (2004) Electrochim Acta 49:557–563
2. Cheng F, Liang J, Tao Z, Chen J (2011) Adv Mater 15:1695–1715
3. Thomas MGSR, Bruce PG, Goodenough JB (1985) Solid State Ionics 17:13–19
4. Goodenough JB, Kim Y (2010) Chem Mater 22:587–603
5. Cho TH, Park SM (2005) J Power Sources 142:306–312
6. Ohzuku T, Makimura Y (2001) Chem Lett 30:642–643
7. Mahmoud A, Saadoune I, Amarilla JM, Hakkou R (2011) Electrochim Acta 11:4081–4086
8. Oh YH, Ahn DG, Nam SH, Park BW (2010) J Solid State Electrochem 14:1235–1240
9. Xiang JF, Chang CX, Yuan LJ, Sun JT (2008) Electrochem Commun 10:1360–1363
10. Li JG, Zhang Q, Liu C, He XM (2009) Solid State Ionics 15:493–496
11. Huang YY, Chen JT, Ni JF, Zhou HH, Zhang XX (2009) J Power Sources 188:538–545
12. Wu F, Wang M (2009) J Power Sources 191:628–632
13. Zheng JM, Li J, Zhang ZR, Guo XJ, Yang Y (2008) Solid State Ionics 179:1794–1799
14. Tan L, Liu HW (2011) Russ J Electrochem 47:156–160
15. Amatucci GG, Tarascon JM (1997) Solid State Ionics 104:13–25
16. Eddrief M, Dzwonkowski P, JuLien C, Balkansk M (1991) Solid State Ionics 45:77–82
17. Ito Y, Miyauchi K, Tetsu OI (1983) J Non-Cryst Solids 57:389–400
18. Horopanitis EE, Perentzis G, Pavlidou E, Papadimitriou L (2003) Ionics 9:88–94
19. Chan HW, Duh JG, Sheen SR (2004) Surface Coatings Technol 188:116–119
20. Şahan H, Göktepe H, Patat Ş, Ülgen A (2008) Solid State Ionics 178:1837–1842
21. Ying J, Wan C, Jiang C (2001) J Power Sources 102:162–166
22. Park SH, Kang SH, Belharouak I, Sun YK, Amine K (2008) J Power Sources 177:177–183
23. Ohzuku T, Ueda A, Nagayama M (1993) J Electrochem Soc 140:1862–1870
24. Peng WX, Jiao LF, Gao HY, Qi Z, Wang QH, Du HM, Si YC, Wang YJ, Yuan HT (2010) J Power Sources 196:2841–2847
25. Liu L, Sun K, Zhang N, Yang T (2009) J Solid State Electrochem 13:1381–1386
26. Fang XS, Li J, Huang KL, Liu SQ, Huang CH Zhuang SX, Zhang JB (2011) Synthesis and electrochemical properties of K-doped LiFePO$_4$/C composite as cathode material for lithium-ion batteries. J Solid State Electrochem. doi:10.1007/s10008-011-1426-4
27. Huang YY, Chen JT, Cheng FQ, Wan W, Liu W, Zhou HH, Zhang XX (2010) J Power Sources 195:8267–8274
28. Chen ZH, Qin Y, Amine K, Sun KY (2010) J Mater Chem 20:7606–7612
29. Jang DH, Shin YJ, Oh SM (1996) J Electrochem Soc 143:2204–2221
30. Xia H, Wang H, Xiao W, Lu L, Lai MO (2009) J Alloys Compd 480:696–701