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Short communication

Fabrication and electrochemical properties of lithium-ion batteries for power tools

Ru-fu Liang, Zhi-xing Wang *, Hua-jun Guo, Xin-hai Li, Wen-jie Peng, Zhi-guo Wang

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

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Abstract

204056-Type prismatic lithium-ion battery for power tools was developed by using $LiMn_2O_4$ as cathode and CMS (carbonaceous mesophase spheres) as anode. The performance of batteries and their electrodes were characterized by SEM, ac impedance and electrochemical tests. The bulk density of cathode after pressing was selected as a main factor and it effects on high current rate capability and discharge plateau distinctly, which were investigated in details. Being charged/discharged in the voltage range of 2.5–4.2 V, the normal $LiMn_2O_4$ battery with cathode bulk density of 2.7 g cm^{-3} shows excellent electrochemical performances. The discharge capacity at 20*C* rate is 94.1% of that at 1*C* rate, and the capacity retention ratio charged at 1*C* and discharged at 5*C* is 91.7% after 100 cycles at 25 °C. While modified $LiMn_2O_4$ is used as the cathode material, the cycling performance of batteries is better than that of batteries made from normal $LiMn_2O_4$. The capacity retention ratios of modified $LiMn_2O_4$ batteries after 100 cycles at 25 °C and 55 °C are 95.0% and 85.3%, respectively. The discharge capacity at low temperature was tested both at 1*C* rate and 5*C* rate, and the capacities discharged at −20 °C were 96.3% and 94.2% of that at 1*C* at 25 °C. Furthermore, the batteries also show good safety in the test of short circuit, overcharge, and nail penetration.

Keywords: Lithium-ion batteries; $LiMn_2O_4$; High power; Rate capability; Safety

1. Introduction

Li-ion batteries hold a broad prospect in electronic products. During the last decade, there has been a growing interest in lithium insertion materials, largely because they potentially have a wide range of applications as positive and/or negative electrodes in lithium-ion batteries [1]. Especially, high power batteries for power tools possess more attraction recently for their high rate capability. Now the globe demand of high power batteries for power tools is growing increasingly. Obviously, it is necessary to develop high power batteries for their promising utilization.

At present, $LiCoO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$, $LiFePO_4$, and their doped compounds have been most extensively investigated as cathode materials. On account of the poor safety and high cost for $LiCoO_2$ [2] and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ batteries, and low energy density for $LiFePO_4$ batteries [3], batteries based on spinel lithium manganese oxide ($LiMn_2O_4$) has been extensively investigated for power tools, for its high voltage, low cost, good safety, and no toxicity [4–6]. Though $LiMn_2O_4$ has lots of merits, it suffers from severe capacity fading during cycling, which has been a key problem prohibiting the commercialization usage of $LiMn_2O_4$ [7]. The severe capacity fading is due mainly to the Jahn-Teller distortion at the surface of $LiMn_2O_4$ [8–10], the dissolution of manganese in the electrolyte solution [11,12]. To produce power tools with good performances, we selected two commercial $LiMn_2O_4$ cathode materials and studied the effect of materials and the process conditions, such as the bulk density of electrodes, on the electrochemical properties and safety characteristics of batteries in this work.

* Corresponding author. Tel.: +86 731 8836633; fax: +86 731 8836633.
E-mail addresses: liangrufu@163.com (R.-f. Liang), zxwang@mail.csu.edu.cn (Z.-x. Wang), ghj@mail.csu.edu.cn (H.-j. Guo), xhli@mail.csu.edu.cn (X.-h. Li), pwj.csu@163.com (W.-j. Peng), wzg5951578@163.com (Z.-g. Wang).

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Table 1
The parameters of the 204056-type prismatic battery

Exterior dimension (mm)			Material of the can	Nominal capacity (Ah)
Thickness	Width	Height		
20	40	56	Steel	1.8

2. Experimental

2.1. Preparation of electrodes

For cathode fabrication, the normal $LiMn_2O_4$ (marked as LM) or modified $LiMn_2O_4$ (marked as GLM) powders (From Hunan Shanshan Advanced Material Co. Ltd., China) were mixed with 4% of electric carbon and 4% of PVDF (polyvinylidene fluoride) in NMP (*N*-methyl pyrrolidinone) until slurry was obtained. And then, the blended slurries were coated onto an aluminum current collector. The anode was prepared by mixing CMS (From Shanghai Shanshan Technology Co. Ltd., China) powders with 3% electric carbon and 6% bonding agent of LA133 (From Chengdu Indigo Power Sources Co. Ltd., China) in water. Then the mixture was coated onto a copper current collector. Then the anode was dried at 105 °C in the vacuum for 12 h.

2.2. Fabrication and electrochemical tests of 204056-type prismatic batteries

The LM/GLM electrode was coated with a fixed area density, then pressed with different bulk densities which were 2.25, 2.4, 2.55, 2.7, and 2.8 g cm^{-3}. The CMS anode electrode was also pressed with different bulk densities (1.1, 1.15, 1.2, 1.25 and 1.3 g cm^{-3}). Then the cathode and anode were assembled into 204056-type prismatic batteries (Table 1 shows the parameters of the 204056-type prismatic battery) using Celgard 2300 as the separator and 1 mol/L $LiPF_6$ in EC + EMC + DMC (1:1:1 in volume) as the electrolyte. Expressly, the semi-finished batteries were dried at 80 °C for 48 h before they were injected electrolyte.

The batteries were charged/discharged in the voltage range of 2.5–4.2 V and 0.02*C* as cut-off current of charge. Rate capability, cycle performance and safety under short circuit, overcharge, and nail penetration of batteries were characterized.

2.3. Fabrication and electrochemical tests of CR2025 coin-type cells

The cathode or anode electrodes were assembled into CR2025 coin-type cells with the counter electrode of metallic lithium foil in a dry Ar-filled glove box. The separator and electrolyte were the same as the 204056-type prismatic batteries. The cells were charged and discharged for two cycles for activation at 0.2*C* current rate over a voltage range of 3.0–4.2 V versus Li/Li^+ electrode at room temperature, and then the cells were tested by ac impedance.

3. Results and discussion

3.1. Morphology analysis

Fig. 1 shows the SEM images of the sample LM. The sample reveals secondary particle size of 10–25 μm and the disordered primary particles. The primary particles tightly congregate.

Fig. 2 shows the SEM images of GLM sample. The sample reveals smaller secondary particle sizes of 6–14 μm and regular primary particles, and possesses crystalline morphology.

3.2. EIS analysis of LM cathode and CMS anode

Fig. 3 shows that the electrochemical impedance which was tested at half-charged state decreases and then becomes large with the increase of the bulk density of LM electrode from 2.25 g cm^{-3} to 2.8 g cm^{-3}. When the bulk density of LM cathode is 2.55 g cm^{-3}, electrochemical impedance is lowest. This phenomenon can be interpreted from the two aspects of electronic conduction and ion conduction. As the bulk density is low, particles are loose, which results in poor electronic con-

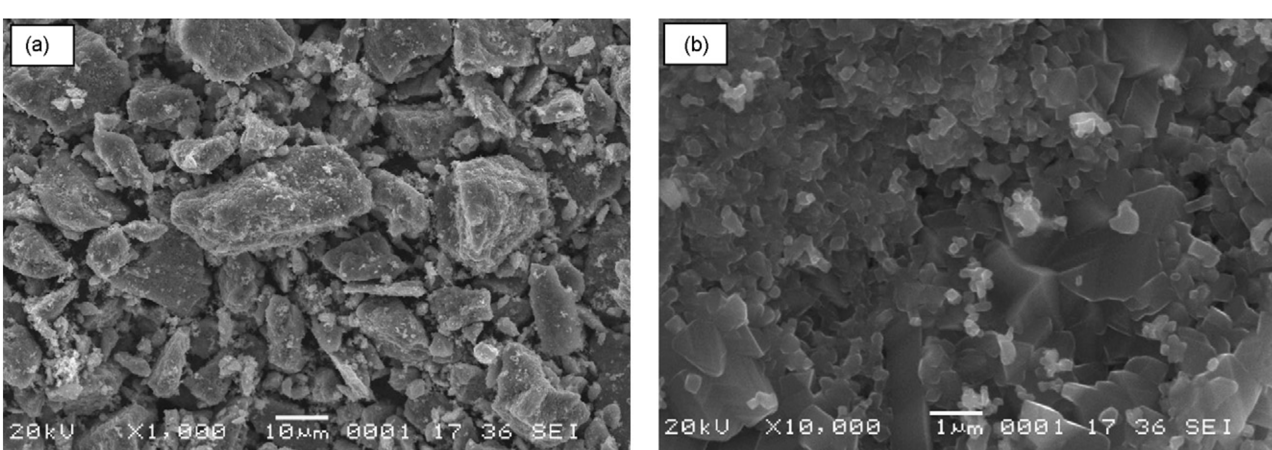

Fig. 1. SEM images of LM sample. (a) ×1000 and (b) ×10,000.

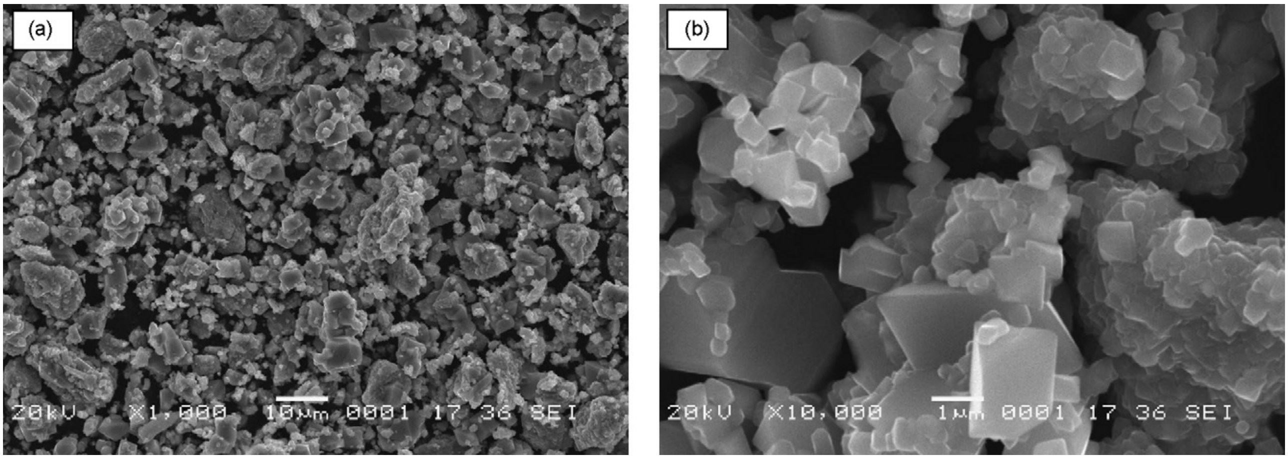

Fig. 2. SEM images of GLM sample. (a) ×1000 and (b) ×10,000.

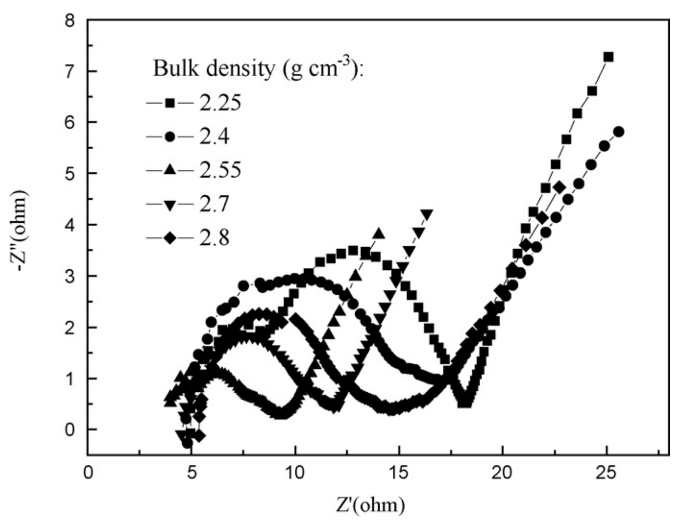

Fig. 3. EIS of LM cathode (tested at half-charged state).

duction. While the bulk density is high, voidage of electrode is small, which is hard for ion conduction.

Fig. 4 reveals the similar phenomenon for the bulk densities of CMS anode from 1.1 g cm^{-3} to 1.3 g cm^{-3}. While the bulk density of CMS anode is 1.25 g cm^{-3}, electrochemical impedance which was tested at half-charged state is lowest.

3.3. The effect of bulk density of LM cathode on electrochemical performances of batteries

Fig. 5 shows that the discharge rate capability of batteries using LM cathode with different bulk densities and CMS anode with fixed bulk density of 1.25 g cm^{-3}. It reveals that the discharge capacity at high rate decreases and then grows high with the increase of the bulk density of LM cathode from 2.25 g cm^{-3} to 2.8 g cm^{-3}, which is similar to the variation of impedance of LM in Fig. 3. However, the discharge plateau voltage increases with the increase of bulk density as shown in Fig. 6. The optimal bulk density of LM cathode is 2.7 g cm^{-3}, under which batteries shows the best rate capability. The discharge capacity at 20*C* rate

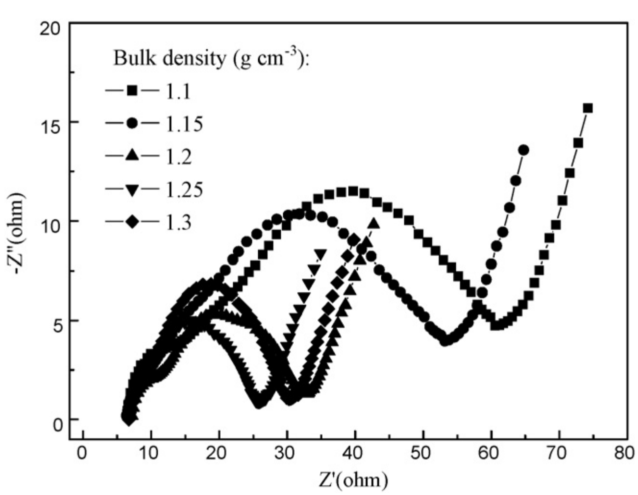

Fig. 4. EIS of CMS anode (tested at half-charged state).

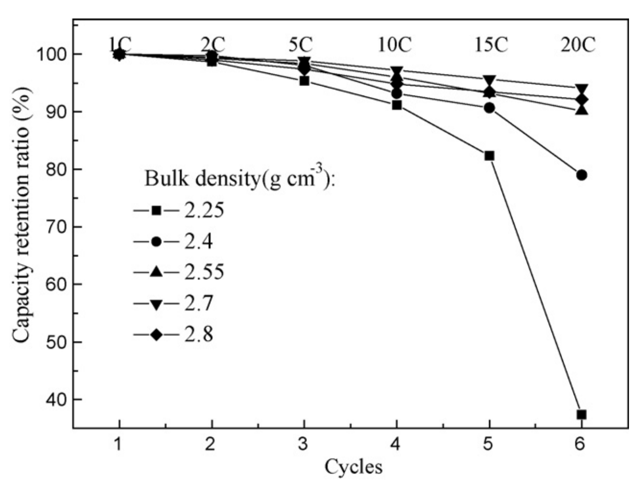

Fig. 5. The discharge capacity ratios of LM batteries with various bulk density of LM cathode at different rates (charge: 1*C*, temperature: 25 °C).

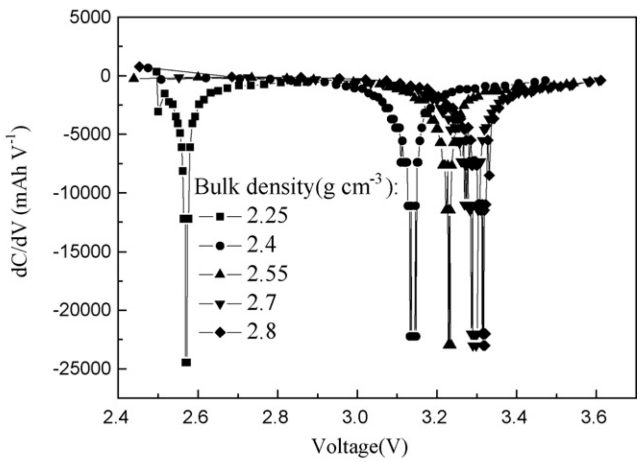

Fig. 6. Plot of differential capacity vs. voltage for batteries made from LM cathode with different bulk density (charge: 1*C*, discharge: 20*C*, temperature: 25 °C).

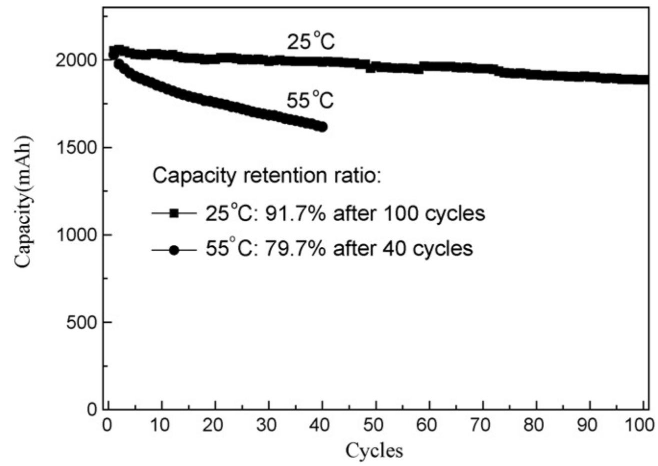

Fig. 8. Cycling performance of batteries made from LM cathode with bulk density of 2.7 g cm^{-3} (charge: 1*C*, discharge: 5*C*).

is 94.1% of that at 1*C* rate, as shown in Fig. 7. Fig. 8 shows that it also has a good capacity retention ration of 91.7% charged at 1*C* and discharged at 5*C* after 100 cycles at 25 °C. While its capacity retention ration is only 79.7% charged at 1*C* and discharged at 5*C* after 40 cycles at 55 °C.

3.4. Electrochemical characteristics of batteries made from GLM cathode material

Fig. 9 shows that the discharge characteristics of batteries made from GLM electrode, which has the same bulk density of 2.7 g cm^{-3} as LM electrode, and CMS anode with the bulk density of 1.25 g cm^{-3}. It reveals that the discharge capacity at 20*C* rate is 90.7% of that at 1*C* rate, which is a little lower than that of LM battery. This may be explained by the SEM images of LM and GLM as shown in Figs. 1 and 2. Because the primary particle sizes of GLM samples are larger than that of LM, the lithium-ion diffusion is a little poorer than that of the later one. However, Figs. 10 and 11 show that the cycling performance of GLM batteries is much more excellent than that of LM batter-

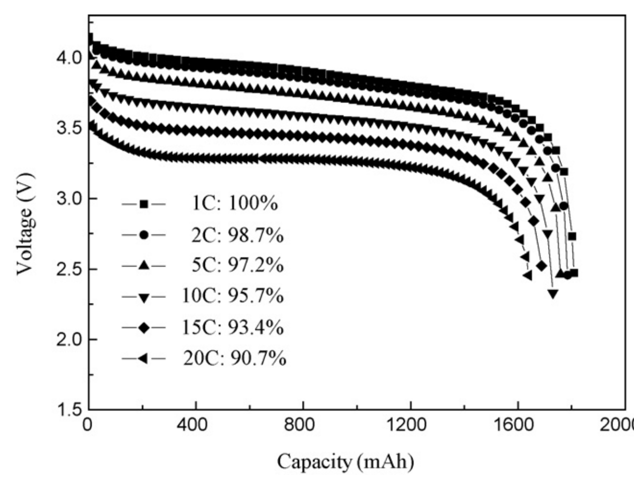

Fig. 9. Discharge curves of batteries made from GLM electrode with bulk density of 2.7 g cm^{-3} at various discharge rates (charge: 1*C*, temperature: 25 °C).

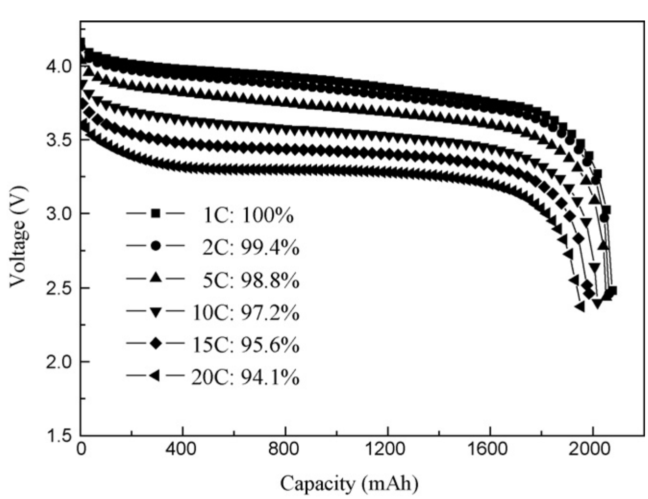

Fig. 7. Discharge curves of batteries made from LM cathode with bulk density of 2.7 g cm^{-3} at various discharge rates (charge: 1*C*, temperature: 25 °C).

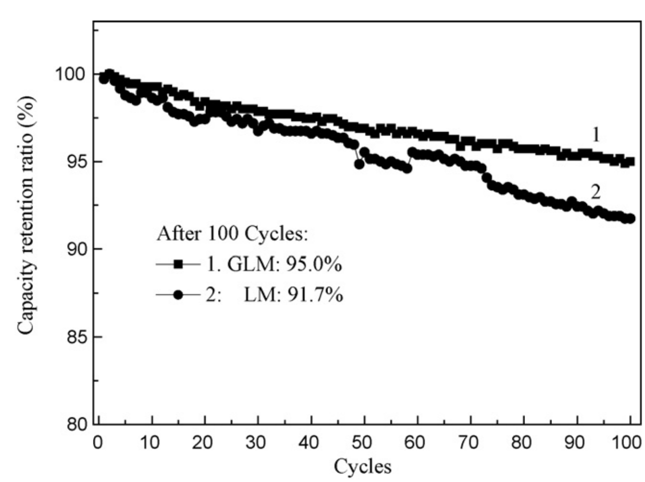

Fig. 10. Cycling performance comparison of batteries made from GLM and LM cathode (charge: 1*C*, discharge: 5*C*, temperature: 25 °C).

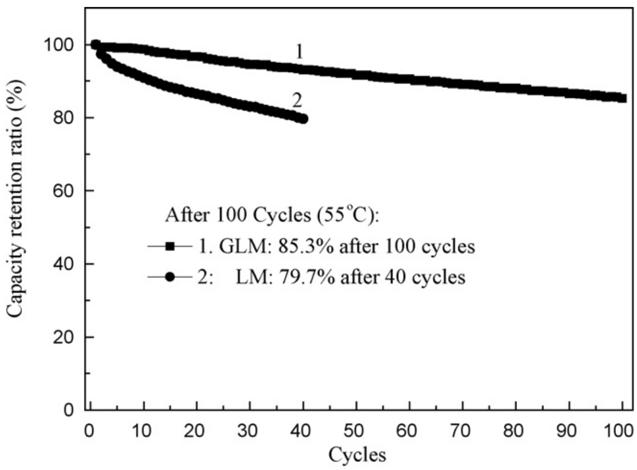

Fig. 11. Cycling performance comparison of batteries made from GLM and LM cathode at high temperature (charge: 1*C*, discharge: 5*C*, temperature: 55 °C).

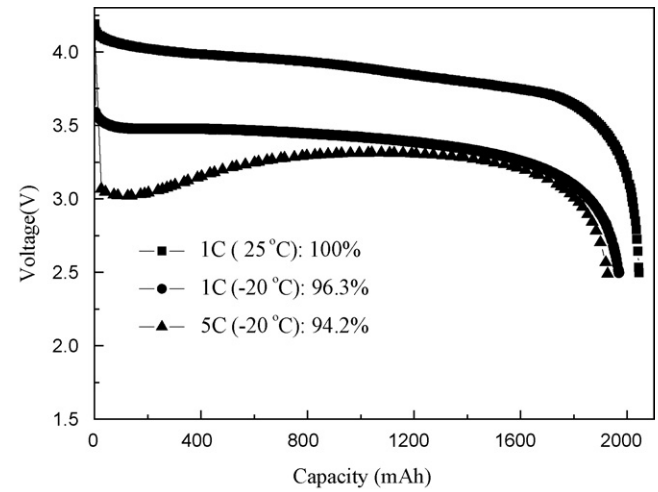

Fig. 12. The discharge characteristic of batteries made from GLM cathode at low temperature (charge: 1*C*, discharge: 5*C*).

ies, and the capacity retention ratios of GLM batteries after 100 cycles at 25 °C and 55 °C are 95.0% and 85.3%, respectively. Besides, Fig. 12 shows that the discharge characteristics of GLM batteries at low temperature are very good. The capacities discharged at 1*C* and 5*C* and at −20 °C are 96.3% and 94.2% of that discharged at 1*C* and at 25 °C, respectively.

3.5. Safety characteristics of GLM batteries

Fig. 13 shows the excellent safety performance of GLM batteries evaluated by short circuit, nail penetration and overcharge measurement. The highest temperature was 104 °C in short circuit, 137 °C in nail penetration and 119 °C in overcharge test

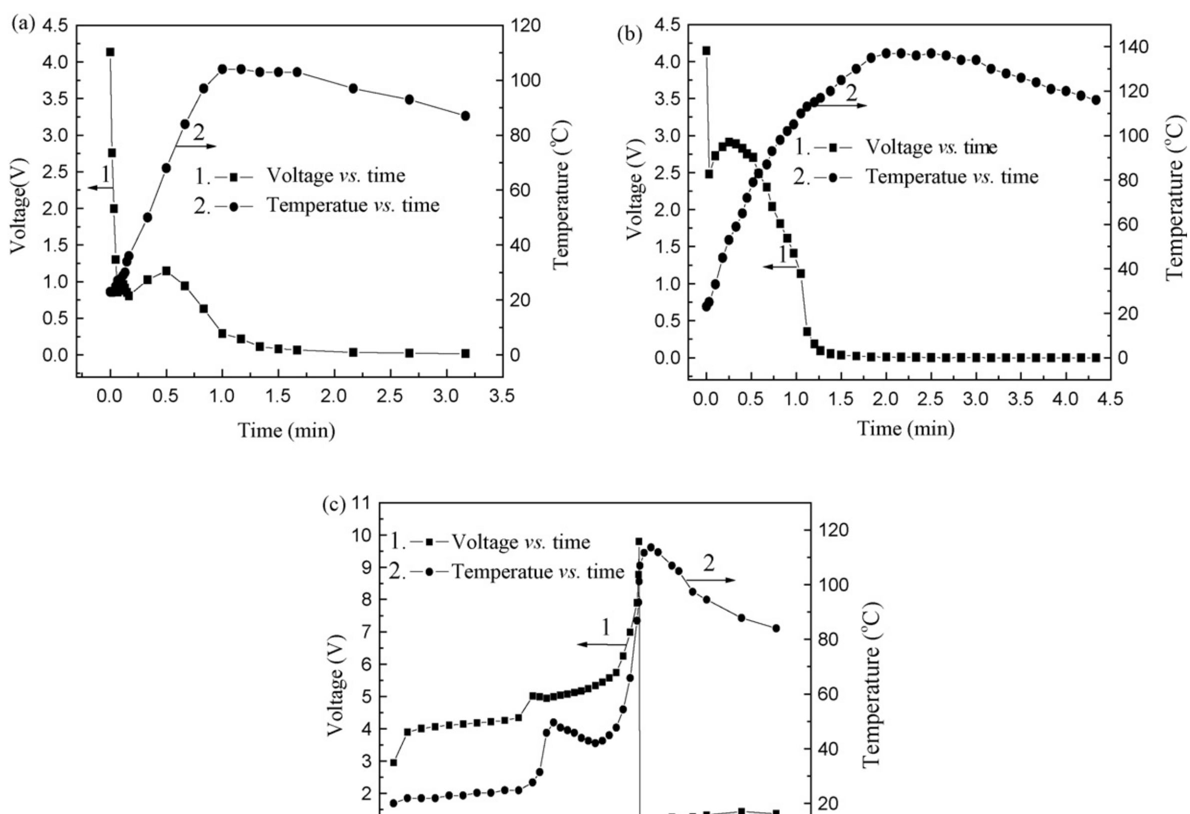

Fig. 13. The safety characteristics test of GLM batteries: (a) short circuit, (b) nail penetration, (c) overcharge: at 3*C* and to 10 V.

(charged at 3*C* and to 10 V). No fire, explosion and black smoke happen.

4. Conclusion

204056-Type prismatic lithium-ion batteries were developed by using LM or GLM as cathode and CMS as anode. When the bulk density of LM cathode is 2.7 g cm^{-3}, the electrochemical performances of batteries are best. The discharge capacity at 20*C* rate is 94.1% of that at 1*C* rate, and the capacity retention ratio charged at 1*C* and discharged at 5*C* is 91.7% after 100 cycles at 25 °C.

While GLM is used as the cathode material, the cycling performance of batteries is better than that of batteries made from LM. The capacity retention ratios of GLM batteries after 100 cycles at 25 °C and 55 °C are 95.0% and 85.3%, respectively. It also shows good discharge performance at low temperature and excellent safety properties.

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