*Int. J. Electrochem. Sci.*, 14 **(2019)** 7925 – 7936, doi: 10.20964/2019.08.17

**International Journal of**
**ELECTROCHEMICAL**
**SCIENCE**
www.electrochemsci.org

# Preparation and Electrochemical Performance of Spherical Mesophase Soft Carbon Materials Composite Anodes for Lithium-ion Batteries

*Hao Lin*[1], *Qinghai Zhao*[2], *Hongxin Zhang*[1,2,*]

[1] School of Mechanical and Electrical Engineering, Qingdao University, Qingdao, 266071, China
[2] Power Integration and Energy Storage System Engineering and Technology Center, Qingdao University, Qingdao, 266071, China
[*]E-mail: qduzhx@126.com

*Received:* 25 Janaury 2019 / *Accepted:* 27 May 2019 / *Published:* 30 June 2019

---

It is imperative to develop lithium battery anode materials with high power performance. In this paper, by improving the preparation process, a novel micro-nano composite structure spherical mesophase soft carbon material was developed as the anode material of a lithium-ion battery. The structure and surface morphology were observed by SEM and XRD. The material was assembled into a button battery and a power battery for performance testing and safety testing. The experimental results indicate that the prepared soft carbon material has excellent surface properties and a uniform shape distribution. The first coulombic efficiency of the button battery is 87.5%. The charging capacity and discharging capacity ratios at 2C/1C are 84.8% and 85.9%, respectively. The capacity retention rate after 50 cycles at 0.5C is 99.9%. The discharge capacity of the battery decreases with increasing discharge ratio. After 500 cycles at 0.5C, 93.96% of the capacity is maintained. In low-temperature testing at –20°C, the discharge rate is 98.94%, while in high-temperature testing at 60°C, the discharge rate is 99.74%. The battery does not catch fire under needle punching, extrusion or overcharging. Therefore, the new soft carbon battery has excellent working performance and can be used as a new energy storage battery.

---

**Keywords:** Lithium ion battery, Soft carbon anode, Cyclic performance, Working performance

## 1. INTRODUCTION

Green, low-carbon, and circular development will be a standard social development strategy in the future. At present, the most widely used lead-acid batteries have a low energy density and cause serious pollution. Although lithium-ion power batteries offer a high energy density and power density, their large-scale development and application is limited due to service life [1,2] and cost [3-5]. Soft carbon is a carbon material obtained by low-temperature carbonization [6] and has attracted attention due to its low cost, long life, and excellent high- and low-temperature performance. To date, there have been many studies on non-graphitized mesophase carbon microspheres [7-10]. The microcrystalline structure of such microspheres has a high lithium-embedding capacity. These spherical structures can achieve close packing to obtain a high volume-specific energy, long cycle life, high safety, and excellent charge-discharge performance [11-14]. Therefore, a spherical mesophase soft carbon material (SMSC) with a micro-nano composite structure has been developed as a negative electrode material for lithium-ion batteries. The material is rich in nano-pores, which is beneficial to the rapid diffusion of lithium ions and improves the charge-discharge performance. The solid-electrolyte interface (SEI) film formed after low-temperature carbonization enhances the stability of the electrode/electrolyte interface, which is conducive to long-term cycle performance in batteries. The bulk density increased after the material was spheroidized, which improved the volume and energy density of the battery. The low specific surface area of the material is conducive to reducing side reactions in the charging and discharging process and improving the safety performance of the battery. The spherical soft carbon material greatly reduces the proportion of material cost in the overall cost of the battery through its simple polycondensation reaction and carbonization. The material can be assembled into a power battery with excellent performance, which has considerable application value [15].

In this paper, the surface characteristics of the new materials were analysed. The performance of a button battery and full battery was tested through experiments, the results of which provide adequate data support for the development and application of soft carbon batteries.

## 2. EXPERIMENTS AND CHARACTERIZATIONS

### *2.1 Preparation of the SMSC with micro-nano composite structure*

The particle size and morphology of a material can be controlled by adjusting the processing technology and technological parameters of the material.

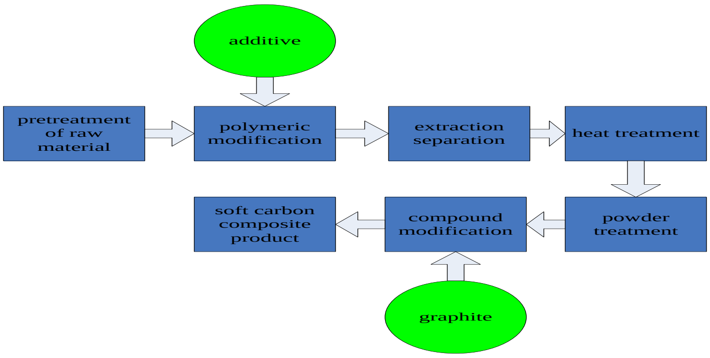


**Figure 1.** Preparation process of soft carbon

During the formation of the mesophase microspheres, the pellets are prevented from polymerizing into large spheres by the addition of additives. The formation of mesophase carbon microspheres with an internal microporous structure improves the high current performance of soft carbon. The composite technology combines soft carbon and graphite to improve the capacity and first columbic efficiency under the premise of ensuring the phase structure and electrochemical performance of the soft carbon.

Accordingly, the preparation process of the material is shown in Fig. 1. Through the pretreatment of raw materials, asphalt is melted to form carbon microspheres with a rich internal pore structure. After carbonization and powder processing, the material is combined with graphite to form the desired SMSC.

### *2.2 Physical characterization and electrochemical characterization*

X-ray powder diffraction (XRD) was performed by using a D/MAX-2500 diffractometer from Rigaku Corporation of Japan with Cu-Kα as the radiation source. The tube pressure and tube flow were set to 40 KV and 100 mA, respectively. Scanning electron microscopy (SEM) was performed by using a Japanese Hitachi S-488 FE-SEM. Battery electrochemical performance was tested by an E-TH-1000L8 programmable thermostatic test chamber.

### *2.3 Preparation of button battery and full battery*

$LiFePO_4$:carbon black (SP):poly(vinylidene fluoride) (PVDF) was mixed in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 91.6:1.8:6.6 and evenly coated on copper foil. After drying at 100°C for 24 hours, the electrode was cut into 14 mm pole pieces. The lithium piece was used as the counter electrode. Celgard 2400 and Jinniu JN-WN-1405 were selected as the diaphragm and electrolyte, respectively. A 2025 button battery was assembled in an argon-filled glove box. $LiFePO_4$ and SMSC were used as the cathode material and anode material, respectively, of 3.7 V/50 Ah batteries. The batteries were charged and discharged at currents varying from 0.5C to 1C between 0 and 3.7 V on a battery testing station at room temperature.

## 3. RESULTS AND DISCUSSION

### *3.1 Material surface characteristics*

#### *3.1.1 Porosity analysis*

The nitrogen adsorption-desorption isotherm of SMSC, as shown in Fig. 2, is type IV. Nitrogen adsorption and desorption isotherms at low relative pressure ($P/P0<0.40$) suggest the existence of many micropores [16]. A hysteresis loop is apparent at relative pressures between 0.6 and 0.9 P/P0, indicating that the material has a mesoporous structure according to the IUPAC classification [17-18]. The pore size distributions were calculated from the adsorption branch according to the Barrett-Joyner-Halenda (BJH) method. The pore size distribution diagram shown in Fig. 3 shows that the material has a large number of mesopores in the range of 2-4 nm and 5-50 nm. Mesopores are conducive to the adsorption and transport of electrolyte ions during the charging and discharging process. The existence of these pores strongly favours the rapid diffusion and transport of lithium ions, which can improve the electrochemical performance of materials at higher current densities.

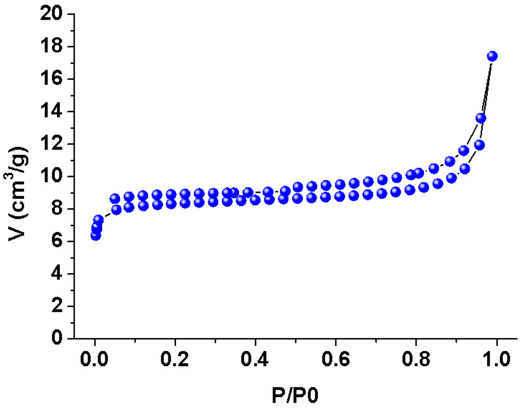


**Figure 2.** Nitrogen adsorption-desorption isotherm of SMSC

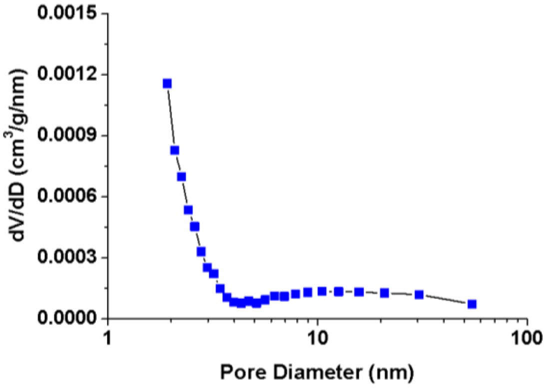


**Figure 3.** Pore size distribution data calculated with the BJH method

### *3.1.2 SMSC section morphology*

SEM analysis was performed to observe the shape of the material more clearly. Fig. 4 shows an SEM image of the SMSC precursor; the size of the composite spheres is 7~ 15 µm. Clearly, the SMSCs have excellent surface properties, a narrow particle size distribution and a large number of pore channels. These channels provide a path for lithium-ion diffusion, which is consistent with the results of pore size distribution analysis. The abundant pore structure is beneficial to the adsorption and transport of electrolyte ions and the accumulation of electric charge, thereby improving the electrochemical performance of the material [19-21].

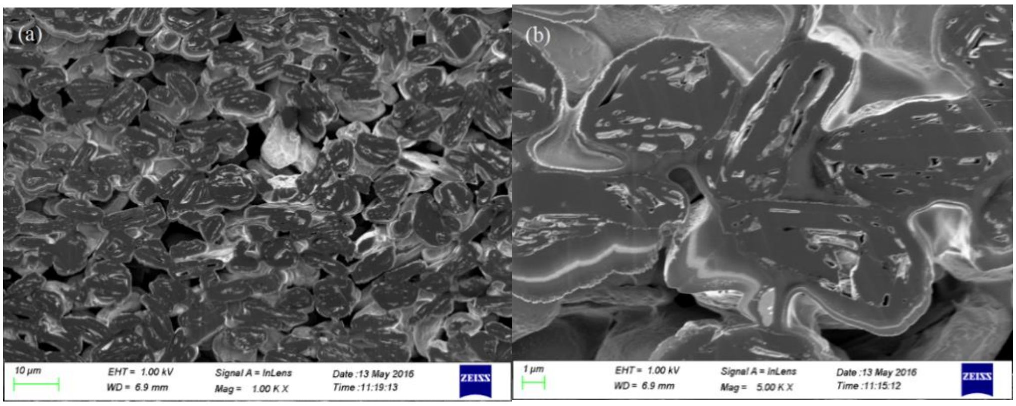


**Figure 4.** SEM images of SMSC (a) Overall face morphology of SMSC (b) Local magnification of the morphology of SMSC

*3.1.3 XRD data*

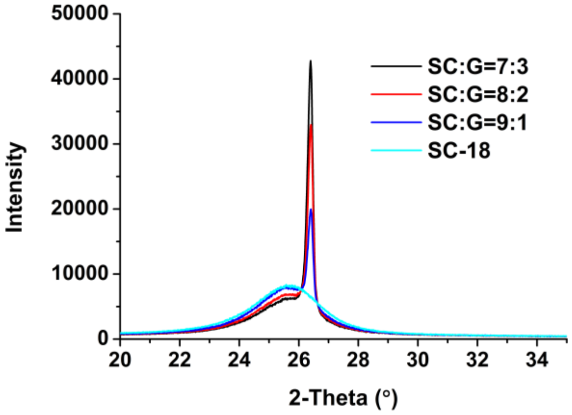


**Figure 5.** XRD diffraction patterns

The broad diffraction peak located at 2θ = 25.7° in Fig. 5 can be ascribed to the characteristic peak of SMSC, which is a material with low crystallinity and disordered internal structure [22], indicating the presence of a large number of amorphous structures in the base carbon compound [23-25]. The sharp characteristic peak at approximately 2θ = 26.5° after adding graphite was ascribed to the characteristic peak of typical graphite material. The diffraction curves of soft carbon: graphite composites with different ratios are similar, and the peak strength increases with increasing doped graphite content. The presence of soft carbon can improve the rate performance and cycle stability of the battery, while the addition of graphite can greatly improve the lithium insertion capacity and first efficiency of the material.

*3.2 Electrochemical characterization of the button cell*

Fig. 6a shows the first charge-discharge curve of the SMSC sample at 0.1C. The discharging capacity and charging capacity are 404.65 mAh/g and 354.07 mAh/g, respectively. The first coulombic efficiency is 87.5%. The electrode material reacts with the electrolyte at the solid-liquid interface to form an SEI, which consumes part of the lithium ions and electrolyte, thus increasing the irreversible capacity of the first charging and discharging cycles.

Cycling stability is a vital evaluation parameter for electrode materials applied in batteries. Better cycling performance means less resource consumption. The experimental results are shown in Fig. 6b. After 50 cycles, the capacity retention of the SMSC samples at 0.5C was 99%; the SMSC material has excellent cycle performance. Therefore, the interface stability of the electrode/electrolyte is enhanced by the soft carbon material being carbonized at low temperature. Furthermore, an SEI can be formed inside the battery. The SEI has a low selectivity for the solvents in the electrolyte and is beneficial to the long-term cycling performance of the battery. After the material is spheroidized, the stacking density increases, which improves the volume energy density of the battery, and the low specific surface area reduces side reactions in the charging and discharging process, thus improving the recycling performance of the battery.

Fig. 6c shows the charge-discharge rate performance of the SMSC sample. The capacity decreases with increasing discharging rate. The charging capacity and discharging capacity at 1C are 337.26 mAh/g and 384.08 mAh/g, respectively, and the charging capacity and discharging capacity at 2C are 286.06 mAh/g and 330.03 mAh/g, respectively. The 2C/1C charging capacity ratio is 84.8%, and the 2C/1C discharging capacity ratio is 85.9%. Therefore, spherical soft carbon materials can provide abundant nano-pore channels through surface modification. These nano-channels are conducive to the rapid diffusion of lithium ions, which can improve the conductivity and large current performance of soft carbon. Soft carbon and organic compounds with pyrolysed carbon can effectively combine the characteristics of smooth soft-carbon voltage platforms with the advantageous high current performance of carbon materials and thus improve the overall performance of soft carbon.

The electrochemical performance of soft carbon (SC), soft carbon annealed at 950 °C (SC-950) and commercial graphite (CG) can be seen from [26]. Discharge capacity of SC is very high up to 1150 mAh/g but the discharge capacity suffered a big loss, the first coulombic efficiency is inefficient. Heat treatment can reduce some irreversible lithium ion storage sites to improve coulombic efficiency [26]. As for SC-950, the discharging capacity and charging capacity are 520.2 mAh/g and 395.0 mAh/g, respectively. The coulombic efficiency for SC-950 was approximately 75.9%. The discharge capacity of SC-950 is a little higher than that of commercial graphite. In conclusion, the charge and discharge capacity of SMSC is lower than that SC, SC-950 and CG but the coulombic efficiency of SMSC is more efficient. The similar conclusion can be drawn by comparing with the CNMCMB in [27]. After 50 cycles, the capacity retention of the SMSC samples at 0.5C was 99%. SMSC has the same cycling performance as SC [26]. In conclusion, SMSC has excellent electrochemical performance and can be assembled into a power battery with excellent performance.

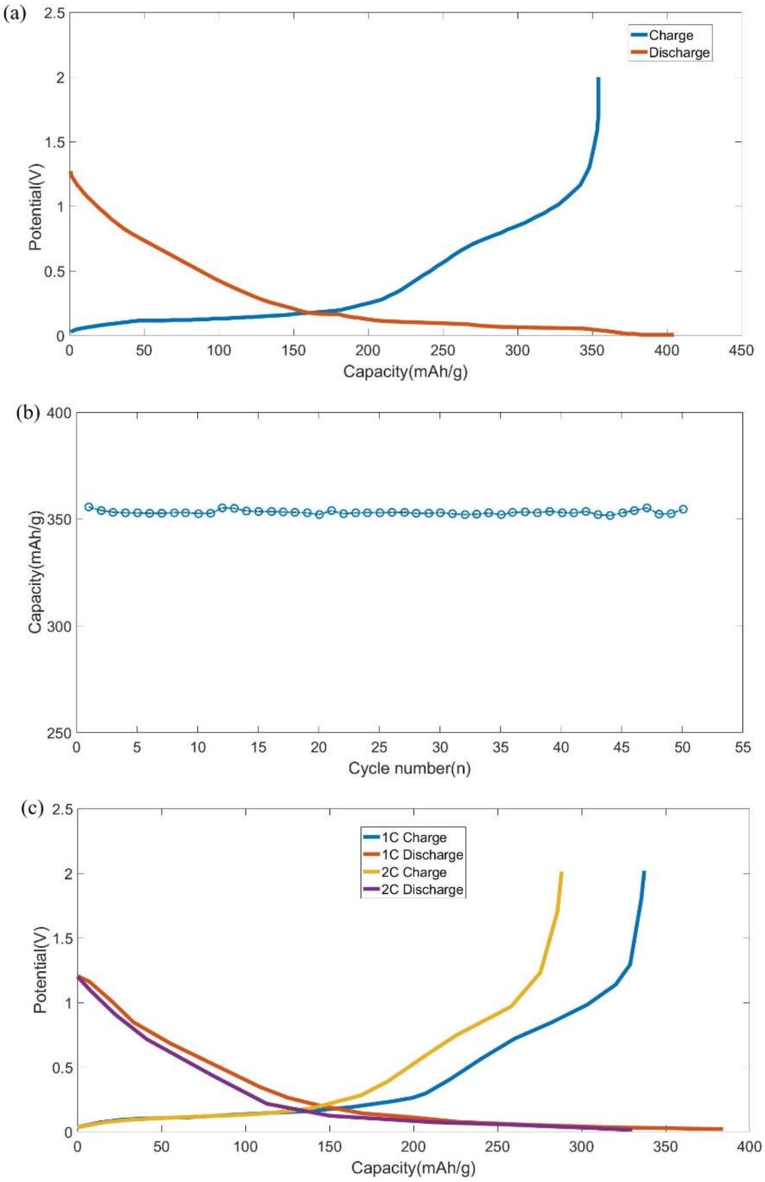


**Figure 6.** Electrochemical performance of SMSC (a) Charge-discharge curves of SMSC at 0.1C rate (b) Cycle curve of SMSC at 0.5C rate (c) SMSC charge-discharge rate

### *3.3 50 Ah full battery performance test*

#### *3.3.1 Rate discharging performance*

The discharge curves of SMSC batteries at different rates are shown in Fig. 7. The voltage generally decreases with increasing discharge current. The voltage of the soft carbon batteries drops rapidly at the beginning of the discharge stage. After the initial dip, the voltage remains nearly constant for more than half of the discharge time, a process known as the discharging platform of the battery; this plateau is wider at smaller discharge rates. With increased discharging rate, the voltage drops at the beginning of discharging increases, and the discharging platform decreases. The voltage has a short increasing trend in the initial stage of discharging at 3C because the polarization phenomenon is more obvious at high rates. The discharging capacities at 0.5C, 1C, 2C, 3C were 48741 mAh, 47497 mAh, 43949 mAh, and 37611 mAh, respectively. Based on the 0.5C discharging results, the 1C, 2C, and 3C discharging ratios were 97.45%, 90.17%, and 77.17%, respectively. The discharge curves of graphite batteries at various rates are depicted in Fig. 8. The discharge trends of the two types of batteries are similar; the discharge platform of the soft carbon battery is lower but still stable. By using low-cost, high-security and long-life micro-nano soft carbon materials as anode materials for lithium-ion batteries in conjunction with the lithium iron phosphate cathode materials widely used in the current market, high-consistency, low-cost, high-rate, long-life and high-security energy storage batteries can be produced.

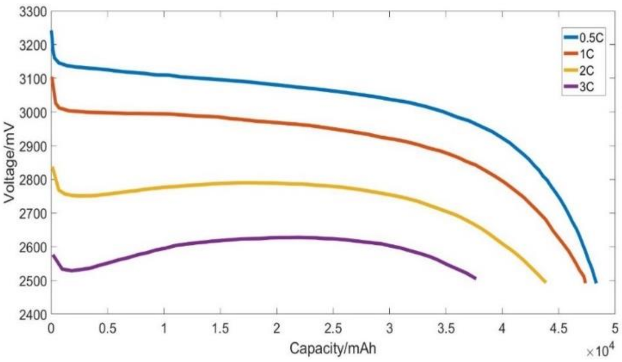


**Figure 7.** Discharge curves of SMSC batteries at different rates

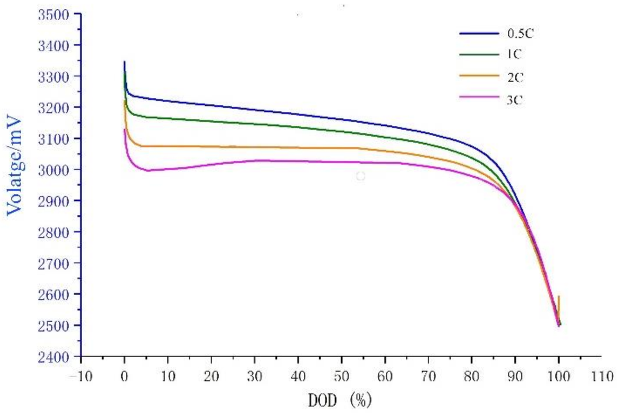


**Figure 8.** Discharge curves of graphite batteries at different rates

### *3.3.2 Cycle performance*

Fig. 9 shows that the initial battery capacity is 46138.5 mAh. As the number of cycles increases, the capacity of the battery shows a significant downward trend. The battery exhibits excellent cycling stability, delivering a stable capacity of 43351 mAh at 0.5C after 500 cycles with a capacity retention of 93.96%. [28] shows the cycling performance of $LiMn_2O_4$ spinel/soft carbon cells. When the uncoated soft carbon was used, the capacity of the cell dropped quickly; more than 10% of the capacity was lost in 50 cycles. The capacity retention of the cell with the TFPTMS coated soft carbon was greatly improved. But after 200 cycles, the maximum capacity still decreases 10 percent. Compared with $LiMn_2O_4$ spinel/soft carbon cell, SMSC batteries has excellent cycle performance. The electrolyte of the new soft carbon battery is highly compatible with the positive and negative materials, leading to good formation of the SEI film and reduced side reactions. The SMSC anode material with a micro-nano composite structure has a stable crystal structure during the cycling process. This material can maintain the lithium intercalation and lithium removal process at the negative electrode of the battery, reduce side reactions in the charging and discharging process, and lead to good battery cycling performance.

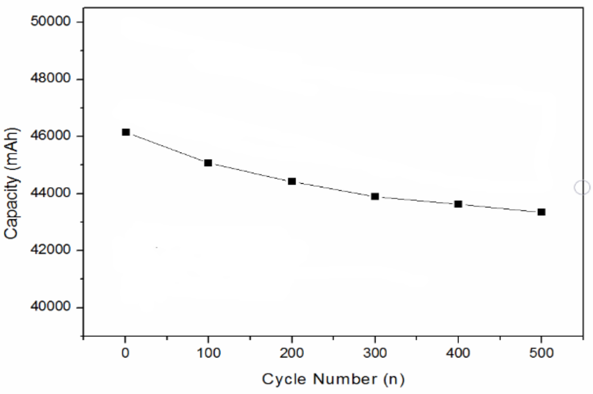


**Figure 9.** Performance of the battery at 0.5C after 500 cycles at room temperature

### *3.3.3 High-temperature performance*

Before the experiment, two soft carbon batteries labelled #1 and #2 were selected to measure the voltage and internal resistance.

**Table 1.** Capacity retention and recovery performance at high temperatures

| | Discharge at 25°C | | Charge and discharge at 25°C after 7 days at 60°C | | | | |
|---|---|---|---|---|---|---|---|
| Battery number | Discharging capacity /mAh | Internal resistance /mΩ | Internal resistance /mΩ | Discharging capacity /mAh | Recovery capacity /mAh | Capacity retention rate % | Capacity recovery rate % |
| #1 | 46238 | 2.15 | 2.274 | 43999 | 44552 | 95.16 | 96.35 |
| #2 | 39627 | 2.13 | 2.207 | 36704 | 37043 | 92.62 | 93.48 |

Table 1 shows that the discharging capacity and internal resistance of battery #1 are 46238 mAh and 2.15 mΩ, respectively. After storage at a high temperature of 60°C for 7 days, the internal resistance was 2.274 mΩ. The recovery capacity and discharging capacity are 44552 mAh and 43999 mAh, so the capacity recovery rate and the capacity retention rate are 96.35% and 95.16%, respectively. Battery #2 has a discharging capacity of 39627 mAh and internal resistance of 2.13 mΩ. After storage at high temperature for 7 days, the internal resistance was 2.207 mΩ. The discharging capacity and recovery capacity are 36704 mAh and 37043 mAh, so the capacity recovery rate and capacity retention rate are 93.48% and 92.62%, respectively. High temperature performance data of NCM cell can be obtained from [29]. The cell showed retention (83.0% after 7 days) and recovery (92.3% after 7 days). The SMSC battery exhibited excellent high temperature retention/recovery capability. From Fig. 10, the change trend of the battery discharging curve at high temperature is essentially consistent with that at room temperature, and the discharging platform is stable and slightly higher than that at room temperature. Therefore, at high temperature, the internal resistance and voltage of the battery increase slightly, and the capacity retention rate and capacity recovery rate are both 93%. The discharging platform is stable, and the discharging curve does not change significantly, so the soft carbon battery has excellent high-temperature performance.

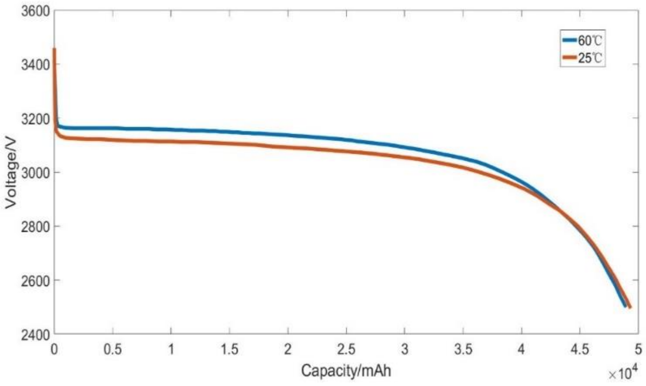
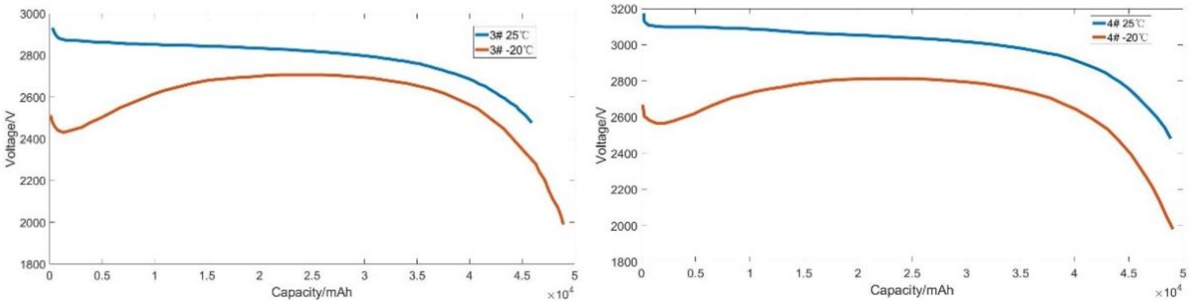


**Figure 10.** Discharging curve at high temperature

### 3.3.4 Low-temperature performance

Experiments were performed to investigate the low-temperature performance of the full cell. Two soft carbon batteries labelled #3 and #4 were used.



(a) (b)

**Figure 11.** (a) Discharging curve of battery #3 at low temperature. (b) Discharging curve of battery #4 at low temperature.

Figure 11 shows the discharging curves of soft carbon batteries #3 and #4 at 25°C and -20°C. This discharge curve is similar to the curve of the ICP 174865 cell in [30] at -40°C. The low-temperature discharging platform is lower than the room temperature discharging platform; to fully discharge, the battery discharges to 2 V. The low-temperature discharging curve is very different from the room-temperature discharging curve. At the initial stage of low-temperature discharging, the voltage decreases slightly and then increases. The electrochemical reaction inside the battery generates heat, so the voltage has a rising trend [30]. The discharging capacity of battery #3 at 25°C and -20°C is 47933 mAh and 4886 mAh, respectively. The discharging capacity of battery #4 at 25°C and -20°C is 49057 mAh and 48738 mAh, respectively. Therefore, the soft carbon battery still has excellent discharging capacity at low temperature. Because soft carbon materials have a large interlayer spacing and amorphous crystalline state, the resistance of lithium ions in the process of embedding is reduced; thus, the trend of concentration polarization is reduced, and the low-temperature discharge performance of the battery is improved.

## 4. CONCLUSION

By using an improved processing technology and adjusting the process parameters, a new type of micro-nano composite structure SMSC material with compact packing, uniform distribution and round shape was prepared. The button cell had a first coulombic efficiency of 87.5%. The 2C/1C charging and discharging capacities were 84.8% and 85.9%, respectively. The capacity retention rate after 50 cycles is 99.9%. Under 1C, 2C and 3C discharging, the discharging ratios of power lithium batteries are 97.45%, 90.17% and 77.17%, respectively. After 500 cycles, 93.96% of the capacity was maintained. At a high temperature of 60°C, the charging retention rate and capacity recovery rate were both 93%. The discharge platform was stable, and the change trend of the discharge curve was similar to that at room temperature. At -20°C, the discharging ratio was 99.3%. SMSC is an excellent anode material for lithium batteries.

ACKNOWLEDGEMENTS
This work was supported by the National Key Research and Development Program of China (No. 2017YFB0102004) and Shandong Province Key Research and Development Program (No. 2017CXGC0502).

## References

1. M. Majima, S. Ujiie, E. Yagasaki, K. Koyama, S. Inazawa, *J. Power Sources*, 101 (2001) 53.
2. A. Antonini, C. Bellitto, M. Pasquali, G. Pistoia, *J. Electrochem Soc.,* 145 (1998) 2726.
3. R. Kiziel, A. Lateef, R. Sabbah, M. M. Farid, J. R. Selman, S. Al-Hallaj, *J. Power Sources*, 183 (2008) 370.
4. G. G. Harding, *J. Power Sources*, 78 (1999) 193.
5. L. Song, X. Li, Z. Wang, X. Xiong, Z. Xiao, F. Zhang, *Int. J. Electrochem Sci*., 7 (2012) 6571.
6. A. Concheso, R. Santamaria, M. Granda, R. Menéndez, J. M. Jiménez-Mateos, R. Alcántara, P. Lavela, J. L. Tirado, *Electrochim Acta*., 50 (2005) 1225.
7. K. T. Lee, YS. Jung, S. M. Oh, *J. Am. Chem. Soc*., 125 (2003) 5652.

8. M. Endo, C. Kim, K. Nishimura, T. Fujino, K. Miyashita, *Carbon*, 38 (2000) 183.
9. Q. Wang, H. Li, L. Q. Chen, X. J. Huang, *Carbon*, 39 (2001) 2211.
10. Y. Wang, F. Su, J. Lee, X. Zhao, *Chem. Mater*., 18 (2006) 1347.
11. A. R. Kamali, D. J. Fray, *J. New Mat. Electrochem. Systems*, 13 (2010) 147.
12. W. J. Zhang, *J. Power Sources*, 196 (2011) 13.
13. W. J. Zhang, *J. Power Sources*, 196 (2011) 877.
14. L. Ji, Z. Lin, M. Alcoutlabi, X. Zhang, *Energy Enviro Sci*., 4 (2011) 2682.
15. M. S. Wu,K. H. Liu, Y. Y. Wang, C. C. Wan, *J. Power Sources*, 109 (2002) 160.
16. Q. Sun, T. Jiang, G. Zhao and J. Shi, *Int. J. Electrochem. Sci.*, 14 (2019) 1.
17. W. Tian, Q. Gao, Y. Tan, K. Yang, L. Zhu, C. Yang, H. Zhang, *J. Mater. Chem. A*., 3 (2015) 5656.
18. B. Cao, H. Liu, B. Xu, Y. Lei, X. Chen and H. Song, *J. Mater. Chem. A*., 4 (2016) 6472.
19. Q. Yao, H. Wang, C. Wang, C. Jin and Q. Sun, *Acs. Sustain Chem Eng.*, 6 (2018) 4695.
20. D. Zeng, Y. Dou, M. Li, M. Zhou, H. Li, K. Jiang, F. Yang and J. Peng, *J. Mater Sci*., 53 (2018) 8372.
21. Y. Shi, L. Zhang, T. B. Schon, H. Li, C. Fan, X. Li, H. Wang, X. Wu, H. Xie, H. Sun, D. S. Seferos and J. Zhang, *Acs. Appl Mater Inter.,* 9 (2017) 42699.
22. F. Huang, Q. Zhao, J. Yang, H. Zhang, W. Huo, F. Xu, *Energy Source. Part. A*., 40 (2018) 1675.
23. J. R. Dahn, A. K. Sleigh, H. Shi, J. N. Reimers, Q. Zhong, B. M. Way, *Electrochim. Acta*, 38 (1993) 1179.
24. B. Genorio,W. Lu, A. M.Dimiev, Y. Zhu, A-R.O. Raji, B. Novosel, L. B. Alemany and J. M. Tour, *ACS. Nano*, 6 (2012) 4231.
25. D. He, K. Cheng, T. Peng, M. Pan, S. Mu, *J. Mater. Chem. A*., 1 (2013) 2126.
26. D. Wang, J. S. Zhou, Z. P. Li, L. Hou, F. M. Gao, *Ionics.*, 8 (2018) 2646.
27. Q. Chen, Y. Nie,T. Li, B. Ren, Y. Liu, *J Mater sci.,*29(2018)14788.
28. Z. Chen, Q. Wang, K. Amine, *Electrochim Acta.,* 51 (2006) 3890.
29. K. S. Kang, S. Choi, J. H. Ho, S. G.Woo, Y. N .Jo, J. Choi, T. Yim, J. S. Yu and Y. J. Kim, *J. Power Sources*, 253 (2014) 48.
30. S. Herreyre, O. Huchet, S. Barusseau, F. Perton, J. M. Bodet and Ph. Biensan, *J. Power Sources*, 97 (2001) 576.