

Short Communication

Impact of C-S-TiO₂ Composite Material Coated by Graphene on the Conductive Properties of Sulfur Cathode Material

Xing Hua LIANG*, Chao Chao YE*, Lin SHI, Qing Qing SONG

Guangxi University of Science and Technology, Guangxi Key Laboratory of Automobile Components and Vehicle Technology, liuzhou 5450006 china

*E-mail: lxh304@aliyun.com; jia8327196@126.com

Received: 3 July 2014 / Accepted: 7 August 2014 / Published: 25 August 2014

The way to solve the sulfur conductive problem is the key to improve the performance of lithium sulfur battery. Nano oxides can not only improve sulfur electrode porosity, but also adsorb more sulphur, in addition play a catalytic role to oxidation reduction reaction of cells, the graphene has a unique two-dimensional structure and excellent physical and chemical properties, very suitable for coating composite containing sulfur materials. This paper was studied on electrical properties of sulfur cathode materials on lithium sulfur batteries, and the influence on sulfur electrochemical performance of C/S composite material, C-S-TiO₂ composite material, C-S-TiO₂ composite material coated by grapheme. Three composite materials were characterized by used XRD, SEM. The results showed that the specific capacity of C-S-TiO₂ composite material coated by grapheme reach to 1366 mAh/g, C/S composite material was 400 mAh/g, while the C-S-TiO₂ composite material, the specific capacity up to 966mAh/g. After 20 cycles of charge and discharge, C-S-TiO₂ composite material coated by graphene retention rate was 78.9%, while C/S composite material was lower to 62.6%.

Keywords: lithium sulfur battery; composite material; grapheme ; coated

1. INTRODUCTION

Lithium ion battery is a new generation of power supply which has broad development prospects. Elemental sulfur theoretical specific capacity is 1675mAh/g, is the highest of all known as cathode materials for lithium ion batteries[1], and sulfur based material is a kind of the most potential cathode materials in lithium ion battery[2].

As is all known that electrical conductivity of the elemental sulfur in general is very low (5×10^{-30} S/cm) [3], the electrical conductivity must be improved to be as the cathode material. At the same time, in the process of lithium-sulfur battery charging and discharging generating lithium polysulfide

[4], the compound is easy to dissolve in the electrolyte leads to decrease cycle performance[5]. This is the main obstacle of lithium sulfur batteries for commercial application. In addition, polysulfide electrolyte dissolved easily [6], and is easy to react with Li electrode form discharge products of Li_2S and Li_2S_2 . The products deposited on the Li electrode, forming a solid electrolyte interface (SEI) film [7], to decrease utilization of sulfur and the cycle performance. Due to the insulativity of elemental sulfur, the conductive material is mixed with sulfur are inevitable, conductive materials including MWCNTs[8, 9], Carbon nanotube [10-14], graphene coated, etc.

In order to solve sulfur conductive problem, using different ether modified or compound with electrolyte additive LiNO_3 [15], anode material compound with polymer or coated by graphene[16]. To study sulfur anode material conductivity, C/S composite material, C-S- TiO_2 composite material, C-S- TiO_2 composite material coated by graphene were prepared, study the first charge discharge capacity and cycle capacity retention rate influence were careful studied, the related mechanism was discussed.

2 EXPERIMENT

2.1. Preparation Material

2.1.1 Preparation of graphene

Mixed expandable graphite with 150ml concentrated H_2SO_4 (95.5% -96.5%) and placed them in a three-neck flask, stirred until uniformly mixed thoroughly. Then mixed liquid was added potassium permanganate KMnO_4 , until discoloration reaction mixture, followed by heating to 60 °C for 24h. The deionized water into a three-necked flask, after five minutes, H_2O_2 was poured into three-necked flask slowly, and until the colour changed to orange, the preparation of graphene oxide completed, reduction using hydroiodic graphene oxide.

2.1.2 cathode material preparation

The elemental sulfur and active carbon at the mass ratio of 2:1 into the ball milling tank, the composite was milled by ball for 10h, and then the mixture was placed in a mortar, after mechanical grinding evenly, composite material was placed into a drying box. High-purity argon was added in the drying box, inert gas must be in the flow state to prevent the oxidation of sulfur, the drying temperature at 155 °C for 10h. Let the sulfur into the activated carbon in the melting state, and then the temperature of the heating to 300 °C to burn the sulfur that did not enter the carbon hole. Then the temperature was increased to 250 °C for 3h, got black product, this product was labeled as A. Press the activated carbon, elemental sulfur and pure TiO_2 , according to the 1:2:1.2 quality with the same method to get the black product B. A part of the B products was coated by graphene with the ratio of 4% , to obtain the product C.

2.2 battery assembly

Take N- methyl pyrrolidone (NMP) as solvent, grinding evenly the anode composite materials and polyvinylidene fluoride (PVDF) according to the mass ratio of 8: 1 ratio by mortar, modulation into uniform slurry, after coating, drying at 50°C for 6h, then the lithium as negative electrode, used 1mol/L LiPF₆ DME/DOL (volume 1:1) as the electrolyte, the vacuum glove box into the argon, assembled into a button battery, three battery cathode materials of different were respectively A, B, C.

2.3 test method and characterization

X ray diffraction test, test method used step measurements as a starting point and ending point of view, respectively 10-90°, strafing speed 0.030/s. tube voltage of 40kV. Other analysis of TG, SEM and the performance of the battery test.

3. RESULTS AND DISCUSSION

Figure 1 is the TG curve of C/S composite materials, with the rise of the temperature, the quality of elemental sulfur content changes. At 300°C, TG curve began to decline significantly, which indicated that sublimation of sulfur in the carbon pore outside began with the rise of temperature, sulfur quality ratio decreases. At 470°C, TG curve began to flat, which shows that sulfur can enter the carbon hole, dispersed into the porous structure of activated carbon under the high surface force of activated carbon and strong adsorption properties. In addition, compared with some carbon/sulfur composites[17,18], the sulfur component in the composite evaporates at a much higher temperature, which suggests that the C-S-TiO₂ composite has a nice encapsulation capability [19].

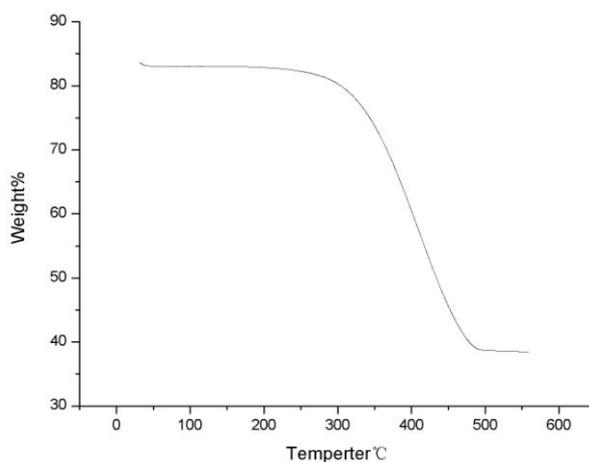


Figure 1. TG curve of C/S composite materials

Figure 2 is XRD of C/S composite material(A), C-S-TiO₂ composite material(B), C-S-TiO₂ composite material coated by graphene(C), elemental sulfur(D), activated carbon (E). Elemental sulfur is crystal structure exists, and in complex with activated carbon exists as amorphous structure, an amorphous state. Compared with A, E and D at 23° ,the peak of A declined, also appeared in a wide, it is due to the sulfur highly dispersed into the activated carbon pore. In the heating process, sulfur melting state into the pores, the elemental sulfur has strong capacity of adsorption and surface force. This result indicates that sulfur becomes amorphous and homogeneously distributed in the carbon matrix [20].Compared with A and B, a diffraction peaks of TiO₂ was appeared among B, because the TiO₂ and the composite material is a kind of mixed state. XRD of C is C-S-TiO₂ composite material coated by graphene, a enhanced diffraction peaks of TiO₂ was appeared among C, it is indicated that more TiO₂ was doped into C composite material.

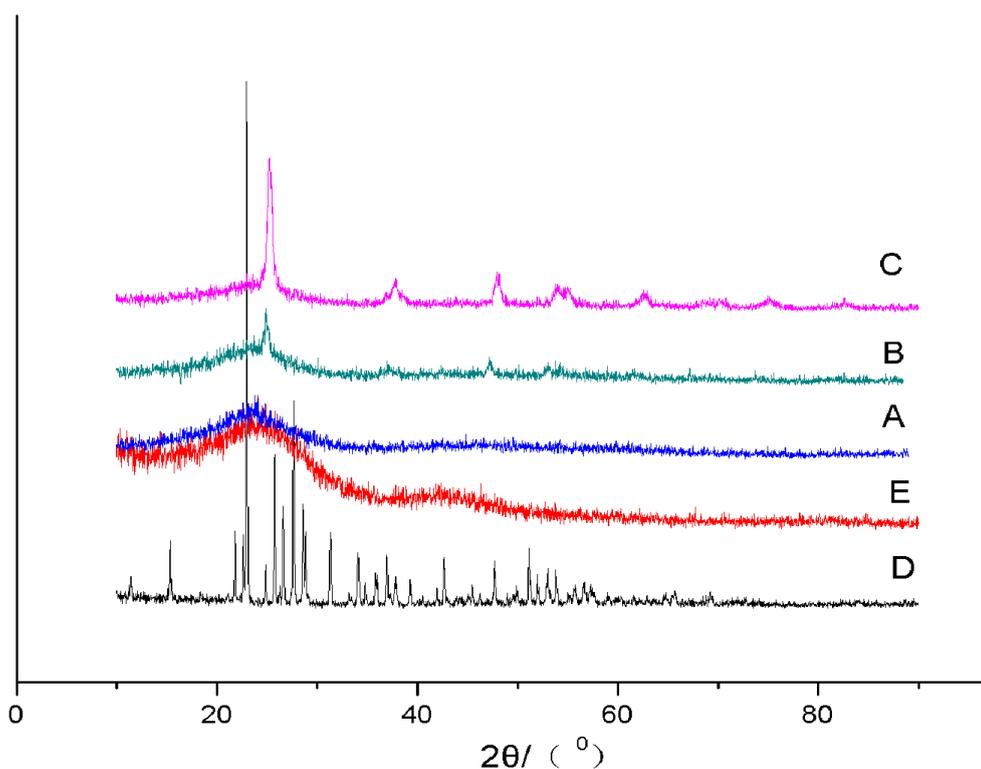


Figure 2. A is C/S composite material, B is C-S-TiO₂ composite material, C is C-S-TiO₂ composite material coated by graphene, D is elemental sulfur, E is activated carbon

Figure 3 is SEM photographs of three composite materials. Diameter range of three composite materials is 100-200 μm, showing a rhombic multilayer structure. Figure 3-1 C/S composite material, sulfur into the carbon hole, no agglomeration, thus reducing the contact opportunity elemental sulfur and electrolyte. Figure 3-2 C-S-TiO₂ composite material, TiO₂ attached to the carbon surface, so to protect the sulfur positive role. Figure 3-3 C-S-TiO₂ composite material coated by graphene, it can clearly see the graphene coated composite material, coating thickness uniformity.

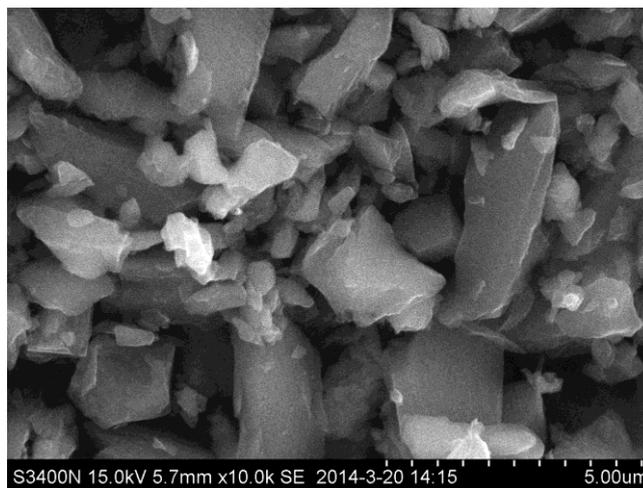


Figure3-1
C/S composite material

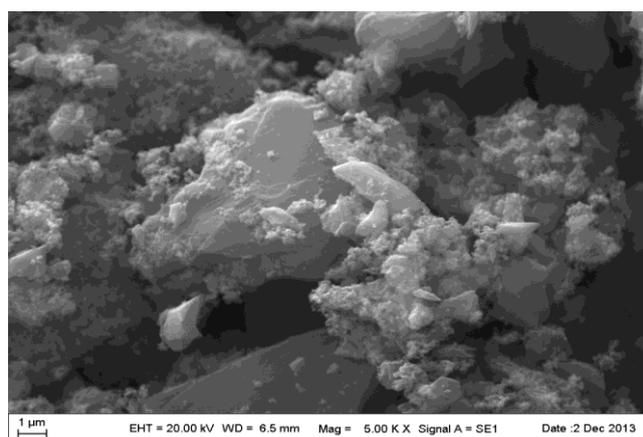


Figure 3-2
C-S-TiO₂ composite material

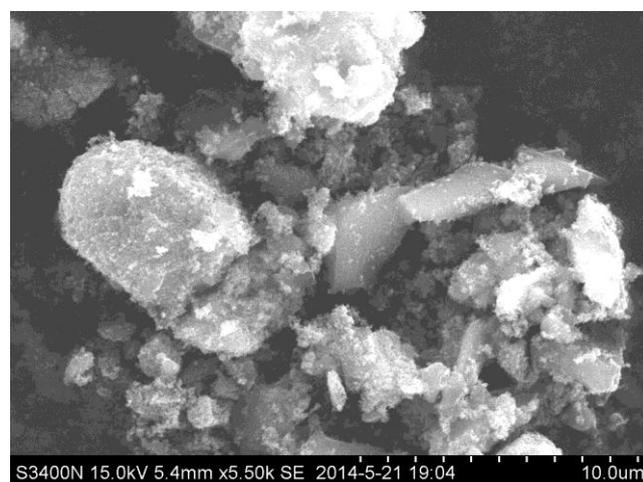


Figure 3-3
C-S-TiO₂ composite material coated by graphene

Figure 3. SEM image of three different materials

3.1 discharge characteristics

Figure 4,4-1, 4-2 and 4-3 respectively for the initial discharge curves of C/S composite material, C-S-TiO₂ composite material and C-S-TiO₂ composite material coated by graphene. From the initial discharge curve, C/S composite material was 400 mAh/g(Figure 4-1), while the C-S-TiO₂ composite material, the specific capacity up to 966mAh/g(Figure 4-2), far higher than C/S composite material. C/S composites has only a discharge plateaus in 1.2 -1.5V, and the discharge platform C-S-TiO₂ composite material between 1.8V-2.0V, the discharge platform is higher than that of the former. The specific capacity of C-S-TiO₂ composite material coated by graphene(Figure 4-3) can reach as high as 1366 mAh/g, there are 2 discharge plateaus, one in 2.2V-2.5 V, another is between 1.5V-1.8V. The first discharge plateau is relatively shorter, while the second one extends longer and contributes to the majority of the discharge capacity [21] . The second discharge stages present a long horizontal plateau, which implies a highly complete reduction process from polysulfides to sulfides [22]. It is indicated that the TiO₂ can improve the discharge platform and specific capacity, and graphene coated C-S-TiO₂ composite material can lower polysulfides. The C-S-TiO₂ composite material coated by graphene have the characteristics of the 2 discharge platform of lithium sulfur, specific capacity is the highest, the most close to the theoretical capacity.

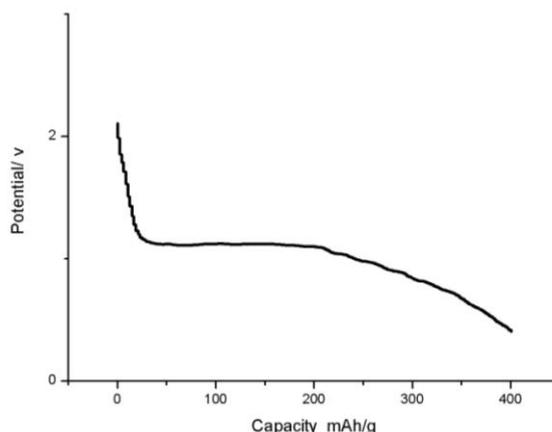


Figure4-1. initial discharge curves of C/S composite material

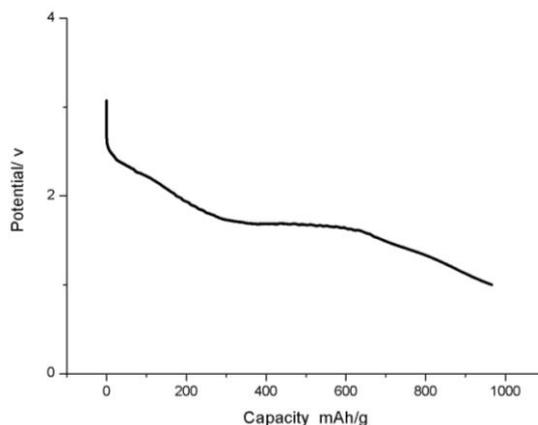


Figure 4-2. initial discharge curves of C-S-TiO₂ composite material

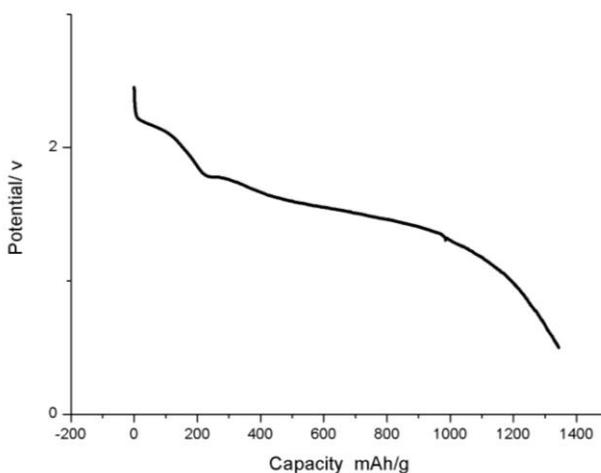


Figure 4-3. initial discharge curves of C-S-TiO₂ composite material coated by graphene

Figure initial discharge curves of three different materials

As shown in Figure 5, the cyclic stability and observe the different charge and discharge capacity in the case of the same number of cycles. The B(C-S-TiO₂ composite material) specific capacity retention rate of about 72.8%. C(C-S-TiO₂ composite material coated by graphene) retention rate was 78.9%, and the retention rate of A(C/S composite material) capacity was lower to 62.6%. Because the battery charge and discharge caused a reversible reaction, bring about more polysulfide. And the lower plateau at 2.0V corresponds to the reduction of sulfur in lithium polysulfides to Li₂S₂ and eventually to Li₂S [23]. And metal oxides (TiO₂) can adsorb poly-sulfides, graphene can reducing the contact with the electrolyte, also can lower the opportunity of the sulfur in contact with electrolyte.

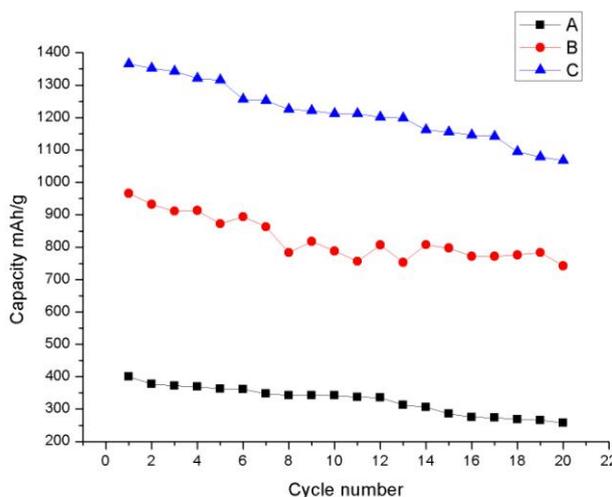


Figure 5. A is C/S composite material, B is C-S-TiO₂ composite material, C is C-S-TiO₂ composite material coated by graphene

4 ANALYSIS OF POSSIBLE MECHANISMS

Due to TiO_2 has good chemical stability, can suppress the surface oxidation activity, reduce the reaction between the electrode and electrolyte, and thus improve the cycle stability of the charge and discharge process of lithium battery material and the specific capacity of battery. At the same time, it can improve the electrochemical performance of lithium battery, prolong life. Composites of activated carbon and sulfur, sulfur particles smaller, exists in the porous structure of activated carbon, dissolution reaction in the electrolyte can be suppressed. The discharge process of C-S- TiO_2 composite material coated by graphene, reducing irreversible reaction, so the graphene coated composites can exhibit the electrochemical properties and good cycle performance.

5. CONCLUSION

The innovation of this paper lies in the coated composite of three materials. General lithium sulfur battery cathode materials are using composite cathode materials by adding transition metal oxides and coating, can greatly improve the cycle stability of the battery[24,25]. After the graphene coated composite, obviously appeared 2 discharge platform, and the discharge platform is improved, the cycle performance became more stable than the former. C/S composites material had only one discharge platform which was in 1.2 -1.5V, the discharging platform of C-S- TiO_2 composite material coated by graphene was in 2.2V-2.5 V, another between 1.5V-1.8V, capacity retention rate of C/S composites was 62.6%, while the graphene coated C-S- TiO_2 composite material capacity retention rate reached to 78.9%, the latter cycle remains rate also increased significantly. Based on the previous study. This is higher than that of the counterpart without graphene coating. A reversible discharge capacity of about 734 mAh/g at 0.5C was obtained[26]. C/S composite material was 400 mAh/g, while the C-S- TiO_2 composite material, the specific capacity up to 966mAh/g. The specific capacity of C-S- TiO_2 composite material coated by graphene reach to 1366 mAh/g, it is highest.

ACKNOWLEDGEMENTS

This project was funded by the Building Fund (No.13-051-38) and Opening Project (No.2012KFMS04,2013KFM01) of Guangxi Key Laboratory of Automobile Components and Vehicle Technology. And it was financially supported by The innovation project of Guangxi Education(YCSZ2014201).

References

1. L.C. Yin, J.L. W, F.J. Lin, J. Yang, Y.N. Nuli, *Energ Environ Sci.*, 5 (2012) 6966-6972.
2. J. Nelson, S. Misra, Y. Yang, A. Jackson, Y. Liu, H. Wang, H. Dai, J.C. Andrews, Y. Cui, M.F. Toney, *J Am Chem Soc.*, 134 (2012) 6337-6343.
3. Young-Jin Choi, Young-Dong Chung, Chang-Yong Baek, Ki-Won Kim, Hyo-Jun Ahn, *J Power Sources*, 184(2008)548.

4. D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, *J Power Sources*, 89(2000)219.
5. D. Marmorstein, Th. Yu, K.A.Striebel, *J Power Sources*, 89(2000)219.
6. C. Lai, X.P.Gao, B.Zhang, *ChemPhysChem.*, 113 (2009)4 712.
7. S.E. Cheon, K. S. Ko, J. H. Cho, *J Electrochem soc.*, 150(6) (2003) A800.
8. B. Zhang, C.Lai, Z.Zhou, X.P.Gao, *Electrochim Acta.*, 54 (2009) 3708.
9. L.Zhao, L.Gao, *Carbon.*, 42 (2004)858–1861 .
10. E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, *Carbon*, 37(1999)619.
11. J. Chen, A.I. Minett, Y. Liu, *Adv Mater.*, 20(2008)566–70.
12. A. Claye, J. Fischer, C. Huffman, A. Rinzler, R.E. Smalley, *J Electrochem Soc.*, 147(2000)2845–2852.
13. P. Liu, G.L. Hornyak, A.C. Dillon, T. Gennett, M.J. Heben, J.A.Turner, *J Electrochem Soc.*, 31(1999)9.
14. H.M. Hsoeh, N.H. Tai, C.Y. Lee, J.M. Chen, F.T. Wang, *Rev Adv Mater Sci.*5(2003)67–71.
15. L. Noerochim, J.Z. Wang, S.L. Chou, D.Wexler, H.K. Liu, *Carbon*, 50(2012)1289–1297.
16. Li Duan, Jiachun Lu, Wenyuan Liu, Ping Huang, Wushang Wang, Zhichao Liu, *Colloid Surface A.*, 414(2012)98.
17. S.R. Chen, Y.P. Zhai, G.L. Xu, Y.X. Jiang, D.Y. Zhao, J.T. Li, L. Huang, S.G. Sun, *Electrochim. Acta*, 56 (2011) 9549-9555.
18. G. He, X.L. Ji, L. Nazar, *Energy Environ Sci.*, 4 (2011) 2878.
19. B. Ding, C.Z. Yuan, L.F. Shen, G.Y. Xu, P. Nie, X.G. Zhang, *Chem Eur J.*, 19 (2013)1013-1019.
20. X. Ji, K.T. Lee, L.F. Nazar, *Nat. Mater.*, 8 (2009) 500.
21. K.F. Li, B. Wang, D.W. Su, J. Park, H. Ahn, G.X. Wang, *J Power Sources*, 202(2012) 389-393 .
22. E. Peled, A. Gorenshtein, M. Segal, Y. Sternberg, *J Power Sources*, 26 (1989)269-271.
23. C.F. Zhang, H.B. Wu, C.Z. Yuan, Z.P. Guo, X.W. David Lou, *Angew. Chem. Int. Ed.*51 (2012) 9592-9595.
24. X.Y. Zhao, J.P. Tu, Y. Lu, J.B. Cai, Y.J. Zhang, X.L. Wang, C.D. Gu, *Electrochim Acta*, 113 (2013) 256–262.
25. Xiwen Wang, Zhian Zhang, Yaohui Qu, Yanqing Lai, Jie Li, *J Power Sources*, 256 (2014) 361-368.
26. Xiangyang Zhou, Jing Xie, Juan Yang, Youlan Zou, Jingjing Tang, Songcan Wang, Lulu Ma, Qunchao Liao, *J Power Sources*, 234(2013)993-1000.