

# SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF IRON SULFIDE-EMBEDDED CARBON MICROSPHERES

Bin Wu, Huaihe Song\*, Jisheng Zhou, Xiaohong Chen

State Key Laboratory of Chemical Resource Engineering,  
Beijing University of Chemical Technology, Beijing 100029,  
P.R. China

\* e-mail: songhh@mail.buct.edu.cn

## Introduction

Iron sulfides have attracted much attention for their excellent optical property, catalytic performance, hypotoxicity and electrochemical properties [1-6] in the past decades. Iron sulfides have been investigated as electrode materials in lithium thermal batteries owing to their high capacity of 609 mAhg<sup>-1</sup> for FeS and 894 mAhg<sup>-1</sup> for FeS<sub>2</sub>. The research of pure carbon materials in Li-ion secondary batteries have been widely promoted [7]. Several papers describing the electrochemical behaviours of single samples of sulfides have been published [4-6], but the good electrochemical properties of these electrode materials haven't brought into full play because the intermediate materials during the charge/discharge reaction are easily dissolved in electrolyte.

In view of the high stability of carbon materials and the fact that there have been rarely electrochemical studies concerning iron sulfides/carbon composite as electrodes, a two-step method is developed to obtain new composites as anode materials of Li-ion secondary batteries. The goal of this work is to determine the mechanism of iron sulfide-embedded carbon microspheres (CM) formation, and evaluate the potential of CM application in Li-ion secondary batteries.

## Experimental

In a typical experiment, ferrocene(10 mmol), sublimed sulfur(30 mmol), o-cresol (10 mmol) and benzol (dispersant) were chosen as the raw materials for CM. Firstly the raw materials and benzene were mixed and sealed into a 50ml autoclave. Then the system was heated to 200 °C and maintained at 200 °C for 48 hours. During the process, the system was under autogenous pressure. After the autoclave is cooled to ambient temperature, the products were extracted by pyridine. The pyridine insoluble fraction (PI) was the primary CM (PCM). PCM was annealed at 600 °C for 2 hours under the nitrogen flow and regarded as the desired annealed CM (ACM). Some of the ACM samples are treated by 5 M hydrochloric acid for 24 hours in order to get off iron sulfides.

The investigation of morphology and structure of as-synthesized sample are carried out by Hitachi H-800 transmission electron microscope (TEM) and ZEISS SUPRA<sup>TM</sup>55 field emission scanning electron microscope (FESEM), respectively. The samples for TEM measurement are prepared by dispersing the products in ethanol with an ultrasonic bath for 15 min and then a drop of the suspension is

placed onto a carbon-coated copper grid at room temperature. X-ray diffraction (XRD) measurements are performed with a Rigaku D/max-2500B2+/PCX system using CuK $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) over the range of 5-90 ° (2 $\theta$ ) at room temperature. And the details of electrochemical measurement could be found elsewhere [8].

## Results and Discussion

As shown in Fig.1, the iron sulfide in ACM is pyrrhotite, whose molecular formula is Fe<sub>1-x</sub>S. And the XRD pattern of acidulated ACM demonstrates that pyrrhotite in ACM could be dissolved easily by hydrochloric acid because the pyrrhotite crystals are not encapsulated tightly by carbon layers. The (002) diffraction peak exhibits broad and dispersive character shown in Fig.1, suggesting this low temperature formed carbon possesses disordered structure.

Fig.2a-d compares the SEM images of PCM and ACM. It could be observed that the sphere surface is made up of wrinkles and layers. Many little pyrrhotite crystal platelets are found on the surface of ACM. The diameters of two kinds of spheres are distributed in the range of 800 nm to 2  $\mu\text{m}$  for PCM and 400 nm to 1  $\mu\text{m}$  for ACM, respectively. The spheres shrink and the layers tenuate distinctly after 600 °C treatment. Based on the SEM, TEM and XRD analysis, the formation process of CM could be that the carbon layer be formed by thermal condensation of cyclopentadiene and benzene ring under the iron sulfides catalysis.

Fig.3 shows the cyclic performances and cyclic voltammetry curves of ACM. The charge/discharge cycle is carried out between 2.5 and 0.01 V. ACM electrode shows high specific capacity and well cycle discharge performance during the charge/discharge cycle when used as anode materials for Li-ion secondary battery. Under a relatively low current density (50 mA g<sup>-1</sup>), the initial specific capacity and reversible specific capacities at the first cycle are ca. 1564 and ca. 958 mAhg<sup>-1</sup>, respectively. Therefore, the first coulombic efficiency is up to 61.2%. And, the specific capacity remains ca.736 mAhg<sup>-1</sup> after 50 cycles, which means only ca. 0.5% capacity fading per cycle.

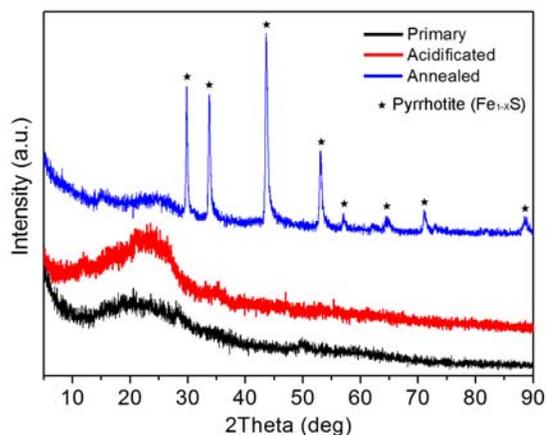
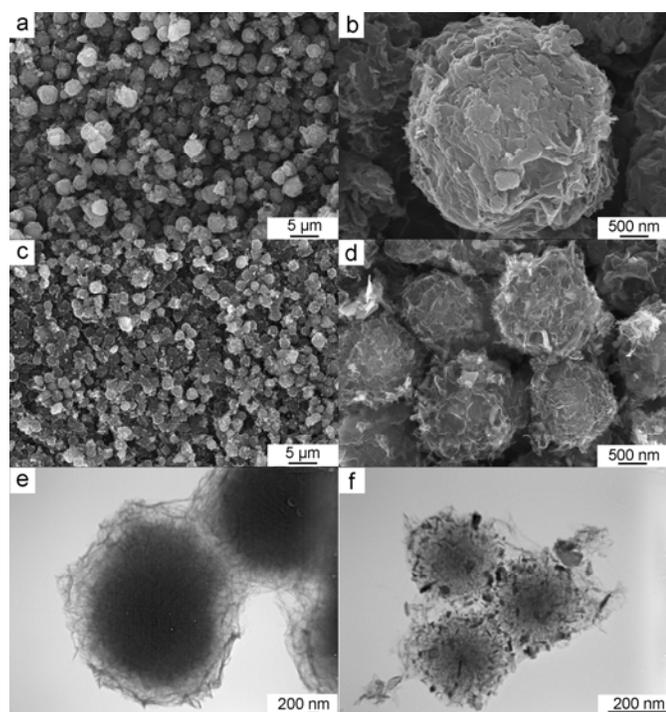
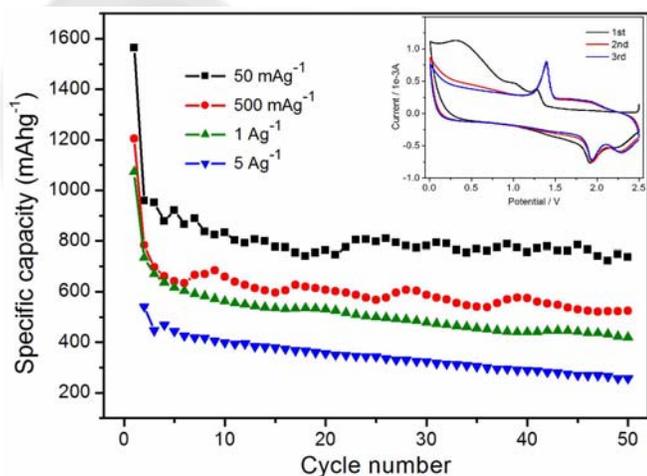


Fig. 1 XRD patterns of primary, acidulated and annealed sample.



**Fig. 2** SEM images of PCM (a and b) and ACM (c and d); TEM images of PCM (e) and ACM (f).



**Fig. 3** Cyclic performances at various current densities and cyclic voltammograms of ACM electrodes at room temperature.

The electrode reaction is deduced from the voltammograms obtained for the first three cycles of the batteries. It is clear that both of the carbon and pyrrhotite should be contributed to the battery capacity. For the first cycle, two mild reduction peaks are seen at 0.3 (solid electrolyte interphase formation) and 1.3 V and two oxidation peaks at 1.9 and 2.3 V. There is a slight change in the position of the peaks from the second cycle, that the reduction peak moves to 1.4 V. That is corresponding to the lithium ions inserting into  $\text{Fe}_{1-x}\text{S}$  to form an intermediate product,  $\text{Li}_x\text{FeS}_2$  ( $0.5 < x < 0.8$ ), and then the final product,  $\text{Li}_2\text{S}$  [9]. The

subsequent two cycle curves coincide well. CM also possesses excellent high-rate performance. The first reversible specific capacities at current densities of 500, 1000 and 5000  $\text{mA}g^{-1}$  are ca. 783, 734 and 541  $\text{mAh}g^{-1}$  respectively, which is obviously higher than those in previous reports [4-6], indicating that ACM should be a promising candidate for anode materials in Li-ion secondary batteries.

## Conclusions

Iron sulfide-embedded carbon microspheres are successfully synthesized by a reaction of ferrocene, o-cresol, sulfide and benzene at about 200 °C. It is found that the pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) is embedded in the amorphous carbon layers. The ACM shows high specific capacity and well cyclic performance during the charge/discharge process. To our knowledge, it is the first time iron sulfides/carbon composite being used as anode materials in Li-ion secondary batteries, which is proved to be a promising candidate for such batteries.

**Acknowledgments.** This work was supported by the National Natural Science Foundation of China (50572003 and 50972004), State Key Basic Research Program of China (2006CB9326022006), Foundation of Excellent Doctoral Dissertation of Beijing City (YB20081001001) and Scientific Research Foundation of Graduate School of Beijing University of Chemical and Technology (09Ma008).

## References

- [1] Liu YH, Meng L, Zhang L. Optical and electrical properties of  $\text{FeS}_2$  thin films with different thickness prepared by sulfurizing evaporated iron. *Thin Solid Films* 2005;479(1-2):83-8.
- [2] Bai LG, Li TC, Wang Y, Ren ZW, Yan YJ. Comparison of effect of ferric sulfide catalyst and nickel sulfide on coliquefaction of coal and biomass. *Fuel. Process. Technol.* 2002;75(3):165-71.
- [3] Takada K, Iwamoto K, Kondo S. Lithium iron sulfide as an electrode material in a solid state lithium battery. *Solid State Ionics* 1999;117(3-4):273-6.
- [4] Huang SY, Liu XY, Li QY, Chen J. Pyrite film synthesized for lithium-ion batteries. *J. Alloy. Compd.* 2009;472(1-2):L9-L12.
- [5] Ritchie A.G., Bowles P.G., Scattergood D.P.. Lithium-ion/iron sulphide rechargeable batteries. *J. Power. Sources.* 2004;136(2):276-80.
- [6] Yufit V, Freedman K, Nathan M, Burstein L, Golodnitsky D, Peled E. Thin-film iron sulfide cathodes for lithium and Li-ion/polymer electrolyte microbatteries. *Electrochim. Acta.* 2004; 50(2-3):417-20.
- [7] Jin YZ, Kim YJ, Gao C, Zhu YQ, Huczko A, Endo M, et al. High temperature annealing effects on carbon spheres and their applications as anode materials in Li-ion secondary battery. *Carbon* 2006;44(4):724-9.
- [8] Zhou JS, Song HH, Chen XH, Zhi LJ, Yang SB, Huo JP, et al. Carbon-Encapsulated Metal Oxide Hollow Nanoparticles and Metal Oxide Hollow Nanoparticles: A General Synthesis Strategy and Its Application to Lithium-Ion Batteries. *Chem. Mater.*2009;21(13): 2935-40.
- [9] Peled E, Golodnitsky D, Strauss E, J. Lang, Lavi Y. Li/CPE/ $\text{FeS}_2$  rechargeable battery. *Electrochim. Acta.* 1998;43(10-11):1593-99.