Ultrafast/stable lithium-storage electrochemical performance of Fe/Fe₃O₄/carbon nanocomposites as lithium-ion battery anode

Man Zhang, Mengdi Cao, Yongming Fu, Lili Xing, Qiang Wang* and Xinyu Xue*

College of Sciences, Northeastern University, Shenyang 110004, China.

Abstract

Fe/Fe₃O₄/carbon nanocomposites are synthesized by a facile two-step solvothermal method. Some (Fe₃O₄, Fe) nanoparticles are embedded in carbon nanosheets, and some other (Fe₃O₄, Fe) nanoparticles form core-shell structure (Fe₃O₄/C, Fe/C) on the surface of carbon nanosheets. As anode of lithium-ion battery, the nanocomposites exhibit ultrafast/stable cycling performance. Their charging time can be shortened to merely ~4 min with reversible capacity of 330 mAh/g and maintains 108 mAh/g after 3500 cycles. At 0.2C rate, the reversible capacity is up to 690 mAh/g and it increases to 755 mAh/g after 100 cycles. The present results demonstrate a right way to produce metal-oxide/carbon nanocomposites in mass production for realizing ultrafast-charging lithium-ion battery.

Keywords: nanocomposites; lithium-ion battery; energy storage and conversion

1. Introduction

In recent years, lithium-ion batteries (LIBs) have received more attention because of their promising applications in electric vehicles and renewable energy

---

* Corresponding author. Tel: (+86) 24-83687658
E-mail address: neuphysics@163.com (Q. Wang).

* Corresponding author. Tel: (+86) 24-83687658
E-mail address: xuexinyu@mail.neu.edu.cn (X. Y. Xue).

conversion/storage. The charging speed is a very important parameter, many research efforts are being made to explore alternative materials for anode to achieve fast-charging lithium-storage performance [1-5]. Among these anode materials, the nanocomposites composed from metal oxides and nano-carbon families are promising candidates, such as carbon-coated Fe_3O_4 nanocomposites [2, 3]. The nano-carbon membranes can tightly pack Fe_3O_4 nanostructures, so that it can effectively restrain their volume expansion and increase electron transfer velocity and electrolyte diffusion efficiency, resulting in fast charging process [3]. Another way for shortening the charging time is doping metallic nanoparticles as additives in the composites, such as Sn and Fe [4, 5]. The metallic nanoparticles can enhance the conductivity of the system and fasten the charging speed [4, 5]. Thus, developing a new synthesis method can facilitate controlling the nanocomposites, realizing the high ion/electron transportation mobility and enhancing the electrochemical performances of LIBs.

In this work, Fe/ Fe_3O_4 /carbon nanocomposites are synthesized via a facile two-step solvothermal route. As anode of LIBs, Fe/ Fe_3O_4 /carbon nanocomposites exhibit ultrafast/stable cycling performance.

2. Experimental

Fe/ Fe_3O_4 /carbon nanocomposites were synthesized by two-step solvothermal method, as shown in Fig .1a. Firstly, 0.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 15 mL of ethanol. Then, 2 g sodium was added, sealed in a 50 mL Teflon line stainless steel autoclave and kept at 220°C for 72 h. After cooling down to room temperature, the solid was collected, grounded and rapidly pyrolyzed at 1000°C . Finally, the products

were washed and dried. During the solvothermal process, sodium reacts with ethanol, forming sodium ethoxide. The initial crude carbon product can be obtained from the pyrolysis process, and Na_2O can be removed with distilled water [1].

The working electrodes were prepared by mixing Fe/ Fe_3O_4 /carbon, acetylene black and carboxymethyl cellulose with a mass ratio of 8:1:1. The mixture was painted onto copper foils and dried at 100°C in vacuum. The CR2016-coin cells were assembled in an argon filled glove box, and pure Li foils were used as the counter electrodes. The electrolyte was composed of 1 M of LiPF_6 dissolved in the mixture of EC and DEC. The galvanostatic discharge/charge tests were carried out in the voltage range of 0.001 to 3.000 V versus Li^+/Li under room temperature at various current rates (the current density of $1\text{C} = 760\text{ mA/g}$). The specific capacity is calculated based on the total weight of Fe/ Fe_3O_4 /carbon nanocomposites (including carbon sheets).

3. Results and Discussion

Fig. 1b shows the XRD pattern of Fe/ Fe_3O_4 /carbon. The diffraction peak at 26.6° corresponds to (002) plane of carbon (JCPDS card No. 26-1080). The peaks at 18.31° , 30.12° , 35.48° , 57.03° and 62.62° can be indexed to (111), (220), (311), (511) and (440) planes of Fe_3O_4 (JCPDS card No. 88-0866). The peaks at 44.67° , 65.02° and 82.33° can be indexed to (110), (200) and (211) planes of $\alpha\text{-Fe}$ (JCPDS card No. 06-0696). The Fe phase is accidentally obtained in the solvothermal and pyrolysis processes. And Fe/ Fe_3O_4 /carbon nanocomposites compose of 33.6 wt% Fe, 36.5 wt% Fe_3O_4 and 29.9 wt% carbon (provided in Supplementary Information).

Typical SEM images of Fe/ Fe_3O_4 /carbon nanocomposites are shown in Fig. 2a-b

and Fig. S1. Some (Fe_3O_4 , Fe) nanoparticles are embedded in carbon nanosheets, and some other (Fe_3O_4 , Fe) nanoparticles form core-shell structure ($\text{Fe}_3\text{O}_4/\text{C}$, Fe/C) on the surface of carbon nanosheets. Fig. 2c and Fig. 2d are the elemental mapping and EDS pattern results of the nanocomposites. The elements C, O and Fe can be observed on the nanocomposites. Fig. 2e-h and Fig. S2 are TEM and high resolution TEM images of the nanocomposites, it can be seen that Fe_3O_4 and Fe nanoparticles randomly distribute in carbon matrix. The crystal lattice fringes of 0.25, 0.48 and 0.20 nm are consistent with Fe_3O_4 (311), Fe_3O_4 (111) and $\alpha\text{-Fe}$ (110).

Fig. 3a is the discharge/charge capacity versus the voltage of Fe/ Fe_3O_4 /carbon at 0.2C rate (the current density of 0.2C = 150 mA/g). The 1st, 2nd, 10th, 30th, 50th and 100th discharge/charge capacity is 1166/717, 690/664, 590/585, 645/637, 705/691 and 755/746 mAh/g, respectively. The initial capacity loss can be attributed to the formation of solid electrolyte interphase (SEI) layer and irreversible lithiation reactions [6]. Fig. S4 shows the typical TEM images of Fe/ Fe_3O_4 /carbon nanocomposites after first discharge process at 0.5 C rate, confirming the formation of SEI layer. After 100 cycles (Fig. 3b), the discharge capacity maintains at 755 mAh/g, higher than the theoretical capacity of Fe/ Fe_3O_4 /carbon composites (448 mAh/g, provided in Supplementary Information). After 200 cycles (Fig. 3c), the discharge capacity is 762, 592, 500, 311, 295 and 262 mAh/g at 0.3C, 1C, 1.5C, 3C, 4C and 6C rate, respectively. The capacity increase from the beginning instead of a conventional decrease, which can be attributed to the increasing defects in the

nanocarbon and the growth of a polymeric gel-like film on Fe_3O_4 particles [7, 8]. Fig. 3d is the rate capability of the nanocomposites. The discharge capacity is 467, 324, 290, 243, 209, 179 and 156 mAh/g at 1C, 2C, 3C, 6C, 8C, 10C and 15C rate, respectively. When the rate recovers to 1C, the discharge capacity recovers to 449 mAh/g. At rate of 15C (Fig. 3e), the discharge capacity is up to 200 mAh/g in the first 500 cycles. After 3500 cycles, the discharge capacity can still maintain at 108 mAh/g. The comparison of the electrochemical performances between Fe/ Fe_3O_4 /carbon composites and other results on Fe_3O_4 -based composites are shown in Table S1.

Fig. 4a is the differential capacity curves (dC/dV vs. potential) of Fe/ Fe_3O_4 /carbon for different cycles at 0.2C rate. In the 1st cycle, the discharge peak at 0.02 V corresponds to the reaction between Li^+ and C [10]. The peak at 0.71 V correspond to the reaction between Fe_3O_4 and Li^+ with the formation of Fe and Li_2O [6, 9]. After the 1st discharge/charge process, both the charge and discharge peaks in the range of 0~0.3 V can be related to the reversible reaction between Li_xC and Li^+ [10]. During the followed cycles, the anodic peak around 1.0 V can be attributed to the reversible reaction between Li^+ and Fe_3O_4 [6, 9], the peaks at 0.16 V and 0.02 V can be ascribed to the reversible reaction between Li^+ and C [10]. The charge peak at 0.24 V can be attributed to the reversible reaction of Li-C, the charge peaks around 1.5~2.0 V correspond to the conversion reaction of metallic Fe^0 to Fe^{2+} and Fe^{3+} [6, 9]. The lithiation and delithiation processes are schematically illustrated in Fig. 4b.

The high electrochemical performance can be attributed to the following factors:

(1) The carbon sheet have high electronic conductivity and Fe nanoparticles in the

composites can further improve the electron conductivity [2-5]. (2) The core-shell structure can accommodate the strain of volume change during cycles [9]. (3) Fe nanoparticles can participate in the reduction process of Li_2O (from Fe_3O_4 nanoparticles). More Li_2O can be reduced to Li^+ , leading to high capacity [11].

4. Conclusions

In summary, Fe/ Fe_3O_4 /carbon nanocomposites have been synthesized by a facile two-step solvothermal route. As LIBs anode, the nanocomposites exhibit ultrafast/stable cycling performance. Such excellent performance can be attributed to the good electronic conductivity, unique structure and synergistic effect.

Acknowledgments

This work was supported by the National Science Foundation of China (51102041) and Program for New Century Excellent Talents in University (NCET-13-0112).

References

- [1] M. Choucair, P. Thordarson, J. A. Stride, *Nat. Nanotechnol.*, 4 (2009) 30.
- [2] X. Y. Fan, S. H. Li, H. H. Zhou, L. Lu, *Electrochim. Acta* 180 (2015) 1041.
- [3] W. Wan, C. Wang, W. D. Zhang, J. T. Chen, H. H. Zhou, X. X. Zhang, *Funct. Mater. Lett.* 7 (2014) 1450005.
- [4] N. Zhang, Q. Zhao, X. P. Han, J. G. Yang, J. Chen, *Nanoscale* 6 (2014) 2827.
- [5] D. H. Lee, S. D. Seo, G. H. Lee, H. S. Hong, D. W. Kim, *J. Alloy. Compd.* 606 (2014) 204.
- [6] M. Sathish, T. Tomai, I. Honma, *J. Power Sources* 217 (2012) 85.
- [7] Y. G. Zhu, J. Xie, G. S. Cao, T. J. Zhu, X. B. Zhao, *RSC Adv.* 3 (2013) 6787.

[8] P. C. Wang, H. P. Ding, T. Bark, C. H. Chen, *Electrochim. Acta* 52 (2007) 6650.

[9] Y. He, L. Huang, X. M. Zheng, S. G. Sun, *Electrochim. Acta* 55 (2010) 1140.

[10] M. D. Levi, D. Aurbach, *J. Electroanal. Chem.* 421 (1997) 79.

[11] D. Y. Park, S. T. Myung, *ACS Appl. Mater. Interfaces* 6 (2014) 11749.

Figure Captions

Fig. 1. (a) Two-step solvothermal method for synthesizing Fe/Fe₃O₄/carbon nanocomposites. (b) The XRD pattern of Fe/Fe₃O₄/carbon nanocomposites.

Fig. 2. (a, b) SEM, (c) Elemental mapping, (d) EDS pattern, (e, f) TEM and (g, h) HRTEM images of Fe/Fe₃O₄/carbon nanocomposites.

Fig. 3. (a) The discharge/charge voltage profiles and (b) The cycling performance of Fe/Fe₃O₄/carbon at 0.2C rate. (c) The cycling performances of Fe/Fe₃O₄/carbon at different current rates. (d) The rate capability of Fe/Fe₃O₄/carbon at various current rates and (e) The cycling performance of Fe/Fe₃O₄/carbon at 15C rate.

Fig. 4. (a) The differential capacity curves (dC/dV vs. potential) of Fe/Fe₃O₄/carbon for different cycles. (b) Schematic illustration of the Li insertion/extraction mechanism for Fe/Fe₃O₄/carbon.

Fig. 1

Fig. 2

Fig. 3

Fig. 4