Three Dimensional Carbon Supported Ultrasmall Fe$_2$O$_3$ Nanoparticles as Anode Material for Lithium Ion Batteries

Wang Jieru$^1$, Xu Junming$^2$, Zhang Linjuan$^2$

$^1$School of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, PR China
$^2$College of Electronic Information, Hangzhou Dianzi University, Hangzhou 310018, PR China

Abstract. In this article, carbon nanotubes were grown on free standing multi-layer graphene sheet to form three dimensional carbon (3D-carbon) materials, and then used as support of Fe$_2$O$_3$ nanoparticles. Ultrasmall Fe$_2$O$_3$ nanoparticles were uniformly deposited on the surface of the 3D-carbon. Due to the synergistic effect of Fe$_2$O$_3$ nanoparticles and 3D-carbon, the electrochemical properties are higher than that of bare Fe$_2$O$_3$ material and multi-layer graphene sheet supported Fe$_2$O$_3$. Reversible capacity 528 mAh g$^{-1}$ is maintained at a high current density of 500 mA g$^{-1}$ after 50 cycles. This composite shows a stable cycling and high rate performance.

Keywords. Fe$_2$O$_3$; 3D-carbon material; Hydrothermal; Lithium ion battery.

1. Introduction

In order to meet the increasing demand of mobile power, researches on the electrode materials of lithium ion batteries (LIBs) for high energy and power density has become a hotspot. As a typical transition metal oxide (TMO), Fe$_2$O$_3$ has been considered as a promising choice for anode material due to its high theoretical specific capacity (~1000 mAh g$^{-1}$), nontoxicity, abundance and low cost. However, similar to other TMO, they undergo the drawbacks such as poor capacity retention and deprived rate capability. The poor cyclability is caused by a massive volume change in the metal oxides, which leads to electrode swelling/contraction and thus loss of electronic conduction pathways.

Compositing Fe$_2$O$_3$ with carbon materials is considered to one effective way to improve the electrical conductivity. Meng et al [1] reported the 3D α-Fe$_2$O$_3$@graphene aerogel composites. The reversible capacity was maintained at 745 mA h$^{-1}$ while cycling 100 times at 100 mA g$^{-1}$. Cheng et al [2] successfully synthesize α-Fe$_2$O$_3$/C composites and exhibited excellent cycling performance. A reversible capacity of 688 mA h g$^{-1}$ after 50 cycles at 0.2 C was obtained. Wu et al [3]fabricated Fe$_2$O$_3$/CNTs composites by hydrothermal method and heat treatment, which provided initial reversible capacity of 847.5 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ and exhibited a reversible capacity of 865.9
mAh g$^{-1}$ after 50 cycles. Up to now, the uses of graphene and carbon nanotube have improved the Fe$_2$O$_3$ cycling and rate performance as LIB.

Here, we synthesized a kind of 3D-carbon material that CNTs were homogeneously grown on multi-layer graphene sheet (MLGS). And then Fe$_2$O$_3$ nanoparticles are densely deposited on the surface of 3D-carbon. This composite shows a more stable cycling and rate performance.

2. Experimental

2.1. Synthesis of 3D-carbon material

The schematic synthesis process of Fe$_2$O$_3$/3D-carbon composite is shown in Figure 1. 20 mg expanded graphite was added into mixed solution of 8 ml DMF and 2 ml distilled water and ultrasonicated 2 h to obtain MLGS. Then, 100 mg Co (CH$_3$COO)$_2$·4H$_2$O was added into the above suspension and stirred 5 min to obtain uniform solution. Subsequently, the suspension was put into a 30 ml Teflon-lined autoclave and sealed. Then the stainless steel autoclave was heated at 100 °C for 2 h. The autoclave was subsequently cooled to ambient temperature. The precipitate was collected and washed repeatedly with ethanol and distilled water by centrifugation (9000 r min$^{-1}$, 5 min), and then dried in an oven at 60 °C. MLGS with homogeneous Co$_3$O$_4$ nanoparticles on its surface were obtained.

![Figure 1. Schematic synthesis process of Fe$_2$O$_3$/3D-carbon composite](image1)

A CVD reactor was heated to 630 °C. After oxygen was cleaned up with N$_2$ (99.999%) at a flow rate of 200 sccm, the sample was loaded into the reactor. Then acetylene (99.95%) was introduced in with a flow rate of 40 sccm and kept flowing for 10 min. The reactor was cooled to room temperature in an N$_2$ atmosphere. Then the black powders were put in hydrochloric acid (36.5%) and stirred at 80 °C for 24 h to remove the catalysts. After cooling down to room temperature, the powder was washed with distilled water until the pH value of the filtrate was 7. Finally, the 3D-carbon was obtained after dried at 60 °C for 12 h.

2.2. Synthesis of Fe$_2$O$_3$/3D-carbon composites
20 mg 3D-carbon, 96 mg FeCl₂·4H₂O and 200 mg CH₃COONa was added into mixed solution of 8 ml DMF and 2 ml distilled water, then the mixed solution was stirred 5 min to obtain uniform solution. Subsequently, the suspension was put into a Teflon-lined autoclave and sealed at room temperature. Then the stainless steel autoclave was heated at 100 °C for 2 h. After the autoclave was cooled to ambient temperature, the precipitate was collected by centrifugation (9000 r min⁻¹, 5 min) and washed repeatedly with water and ethanol. Finally, Fe₂O₃/3D-carbon composite was collected after dried at 60 °C for 24 h.

For comparison, bare Fe₂O₃ (b-Fe₂O₃) was synthesized in the same conditions but without addition of 3D-carbon. Fe₂O₃/MLGS was synthesized by replacing 3D-carbon with MLGS.

2.3. Material Characterization

Samples were investigated with X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα radiation, 1.5406 Å). The scan range was from 10 °C to 80 °C. Morphologies of samples were examined by scanning electron microscopy (SEM, Hitachi S-4800) at 5 kV and transmission electron microscopy (TEM, Philips 2130) at 120 kV.

2.4. Electrochemical measurements

Electrochemical tests were carried out using CR2032 coin-type cell with pure lithium foil as the counter electrode. The working electrodes were fabricated by mixing as-prepared sample: active carbon: poly (vinylidifluoride) (PVDF) with a weight ratio of 70:15:15 in N-methylpyrrolidone (NMP) solvent and then pasting onto copper foils. The lithium foil was used as counter/reference electrodes and the electrolyte was a solution of 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge/discharge (GCD) technique in a voltage range of 0.01-3.0V. CHI660e electrochemical working station was employed for cyclic voltammetry (CV) measurement. Electrochemical impedance spectroscopy (EIS) measurement was also carried out on CHI600E chemistry workstation by applying a perturbation voltage of 10 mV in a frequency range from 0.01 to 100 KHz.

3. Results and discussion

3.1. Characterization of materials

To confirm the crystal structures of the obtained composites, the XRD patterns of three samples were performed. The XRD patterns of sample Fe₂O₃/3D-carbon, Fe₂O₃/MLGS and b-Fe₂O₃ are showed in Figure 2. The peaks at 26.602° and 54.715° correspond to the graphitic lattice plane (002) and (004) of the MLGS and CNT. The peaks at 30.3°, 35.7°, 43.3°, 57.3°, 62.9° match well with the characteristic diffraction plane (220), (311), (400), (511), (440) of γ-Fe₂O₃ phase (JCPDS 39-1346). The weak peaks at 33.1, 54.1 belong to the (104), (116) plane of α-Fe₂O₃ (JCPDS 24-0072). Little α-Fe₂O₃ phase is present may due to the faster oxidation of Fe²⁺ [4].
Figure 3. SEM and TEM images of samples, (a, b) Fe$_2$O$_3$/MLGS; (c, d) 3D-carbon; (e, f) Fe$_2$O$_3$/3D-carbon

Figure 4. CV curves of (a) Fe$_2$O$_3$/3D-carbon, (b) Fe$_2$O$_3$/MLGS, (c) b-Fe$_2$O$_3$; GCD curves of (d) Fe$_2$O$_3$/3D-carbon, (e) Fe$_2$O$_3$/MLGS, (f) b-Fe$_2$O$_3$.

The morphologies and microstructures of the products were investigated by SEM and TEM, as shown in Figure 3. It is obvious that the Fe$_2$O$_3$ nanoparticles with the size of about 5 nm uniformly cover the surface of MLGS (Figure 3a and b). Figure 3c and 3d show that CNTs with a diameter of around 50-70 nm are grown on the MGLS and form a continuous electron conducting network structure. Figure 3e and 3f shows that the Fe$_2$O$_3$ nanoparticles are homogeneously dispersed on the CNTs with a size at the rage of 5-10nm after this synthesis process.

3.2. Electrochemical performance

Figure 4 displays the initial three cyclic voltammetry (CV) curves of three electrodes at a scan rate of 0.1 mV s$^{-1}$ in the voltage window of 0.01-3.0 V. The peak at 0.56 V in the first cathodic branch could be ascribed to the reduction of Fe (III) to Fe (0), as well as the formation of solid electrolyte interphase (SEI) layer. In the following discharge cycles, the reduction peak at 0.56 V shifts to 0.70 V. In subsequent cycles, the cathodic peaks tend to stable, confirming good reversibility and high columbic efficiency of the samples. In the charging process, the two anodic peaks are observed at 1.65 V and 1.85 V, which associated with the reversible multistep oxidation of Fe (0) to Fe (II) and further oxidation to Fe (III). The peak below 0.5 V is due to lithium intercalation and de-intercalation in the graphitic layers [5], which are not observed in b-Fe$_2$O$_3$ sample.

The typical GCD curves for Fe$_2$O$_3$/3D-carbon, Fe$_2$O$_3$/MLGS and b-Fe$_2$O$_3$ samples at 50 mA g$^{-1}$ are presented in Figure 4d, 4e and 4f. It can be observed from Figure 4f that the first discharge platform of the Fe$_2$O$_3$/3D-carbon is at 0.56 V and the subsequent discharge platform is changed to near 0.7 V, corresponding to the position of the reduction peak shown in the CV curve Figure 4c. The first discharge
and charge capacity is 2050 mAh g⁻¹ and 1327 mAh g⁻¹ for Fe₂O₃/3D-carbon, which is higher than theoretical capacity. The great capacity loss in the initial cycles of electrode is due to the formation of SEI film, the irreversible storage of lithium storage in carbon defects, and incomplete conversion reactions in the Fe₂O₃[6]. The second and third charge/discharge curves of Fe₂O₃/3D-carbon are close to each other, which indicate the relative good stability of the Fe₂O₃/3D-carbon. The reversible specific capacities of Fe₂O₃/MLGS and b-Fe₂O₃ samples have dropped a lot between the third and second cycles, showing the relative poor stability.

**Figure 5.** (a) Rate performance, (b) Cycle performance at a current density of 500 mA g⁻¹ of Fe₂O₃/3D-carbon, Fe₂O₃/MLGS and b-Fe₂O₃ at different current densities. **Figure 6.** Nyquist plots of Fe₂O₃/3D-carbon, Fe₂O₃/MLGS and b-Fe₂O₃ electrode

Figure 5a shows the rate dependence on the capacity performance of Fe₂O₃/3D-carbon, Fe₂O₃/MLGS and b-Fe₂O₃ electrodes. Under the current densities of 0.1, 0.2, 0.5, 1 and 2 A g⁻¹, the reversible capacities are 1025, 678, 547, 394 and 205 mAh g⁻¹ for Fe₂O₃/3D-carbon, 817, 630, 291, 128 and 60 mAh g⁻¹ for Fe₂O₃/MLGS, and 525, 342, 154, 70 and 23 mAh g⁻¹ for b-Fe₂O₃. Figure 5b shows the cycling performance of three electrodes at high current density of 500 mA g⁻¹. Specific capacity 528 mAh g⁻¹ is maintained after 50 cycles for Fe₂O₃/3D-carbon, while 226 mAh g⁻¹ is for Fe₂O₃/MLGS and only 98 mAh g⁻¹ is for b-Fe₂O₃. The results show the 3D-carbon supported Fe₂O₃ has higher performance than that of MLGS supported and bare Fe₂O₃ nanoparticles. EIS measurements were carried out to study the transport kinetics of electrons and ion ability in the electrodes. The Nyquist plots of Fe₂O₃/3D-carbon, Fe₂O₃/MLGS and b-Fe₂O₃ electrodes are shown in Figure 6. A typical semicircle in the high-medium frequency region can be ascribed to the charge-transfer resistance. The radius for the Fe₂O₃/3D-carbon is smaller than that for both Fe₂O₃/MLGS and b-Fe₂O₃, implying that Fe₂O₃/3D-carbon composite electrode exhibits faster charge-transfer and smaller electrochemical reaction resistance than that of Fe₂O₃/MLGS and Fe₂O₃. At low frequency region, the steeper tail of the Fe₂O₃/3D-carbon electrode indicates lower ion diffusion resistance compared to the Fe₂O₃/MLGS and Fe₂O₃ electrode.

4. Conclusions

In summary, Hydrothermal method was developed to deposit homogeneous Fe₂O₃ nanoparticles in size of about 5-10 nm on 3D-carbon based on π-π interaction. Compared with the Fe₂O₃/MLGS and bare Fe₂O₃, the Fe₂O₃/3D-carbon delivers a higher reversible capacity, and exhibits better cycling
performance. Meanwhile, Fe₃O₄/3D-carbon exhibits faster charge-transfer and smaller electrochemical reaction resistance. The excellent electrochemical performance of Fe₃O₄/3D-carbon can be attributed to their 3D conductive network and porous structure.

5. References

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