

Electrochemical Characteristics of GeO_x -Coated Graphitic Carbon as Anode Material in Lithium-Ion Batteries

Xiaoxiong Zhou, Jing Xu*, Dezhan Li, Shuangke Liu, Yufang Chen, Chunman Zheng, Wei Xie

College of Aerospace Science and Engineering, National University of Defense Technology, Changsha 410073, China

*Corresponding author e-mail: xujin503@hotmail.com

Abstract. In the present study, GeO_x -coated graphitic carbon composites were synthesized by coating graphitic carbon with GeO_x through chemical reduction method. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to characterize the structure and morphology of the composites, while galvanostatic charge/discharge and cyclic voltammetry (CV) were carried out to measure their electrochemical performance as an anode material for Li-ion batteries. The experimental results indicated that the GeO_x -coated graphitic carbon composites show initial reversible capacity of 465.6 mAh g^{-1} . After 30 cycles, the electrode capacity was still maintained at 437.6 mAh g^{-1} , and the capacity retention is 93.98%.

1. Introduction

With the continuous development of social development, excessive consumption of fossil fuels and environmental pollution seriously affect people's pursuit of a better life [1]. Therefore, all countries vigorously develop and research new energy technologies [2, 3]. Lithium-ion batteries have been widely used in mobile phones, electric vehicles and other fields because of the advantages of high voltage, high energy density, long cycle life, no memory effect and no pollution [4, 5]. The theoretical capacity of graphitic carbon on Lithium-ion batteries is still only 372 mAh g^{-1} , which cannot meet the needs of the current society. In recent years, researcher have fastened attention on germanium-based anode materials. Germanium has a high theoretical capacity of 1600 mAh g^{-1} , a higher electrical conductivity and a high lithium ion diffusion rate [6, 7]. However, germanium anode material suffers a large volume change during insertion/deintercalation process, which has large negative affection on its cycling stability [8]. Several strategies have been used to alleviate the pulverization by reducing the particle size of germanium material and buffering the volume expansion in carbon matrixes [9]. In this work, GeO_x nanoparticles were coated on the surface of graphitic carbon by chemical reduction method. The synthesized GeO_x -coated graphitic carbon composites have a higher capacity than pure graphitic carbon, which exhibit great potential as an anode material for Li-ion batteries.



2. Experimental

2.1. Preparation of the GeO_x-coated graphitic carbon

0.8 g GeO₂ powders and 0.02 g PVP (K-30) were dissolved completely in 80 mL 0.5 M NaOH solution under stirring for 30 min at constant temperature. And then the pH of the solution was adjusted to 7 by 0.5 M HCl solution, named as a solution. Then, 5 g graphitic carbon powders (CMS, Shanshan Co. Ltd., Shanghai, China) were added into a solution. And 1.59 M NaBH₄ solution was quickly added into the above solution. A green-yellow solution was formed, which was transferred to a water bath at 60°C for 3 h. After that, the sample was washed by deionized water, filtered and dried under vacuum at 60°C for 12 h. the sample was calcined at 700°C for 1 h in N₂ atmosphere. GeO_x-coated CMS composites were obtained.

2.2. Material characteristics

The phase of the composites was analysed by D8 Advance X ray diffractometer operated at 40 kV and 40 mA with Cu K α radiation. The morphology of the composites was observed by HitachiS-4800 field emission scanning electron microscope.

2.3. Electrochemical measurements

Electrodes were fabricated by mixing 80 wt.% active materials (CMS or GeO_x-coated CMS composites) with 10 wt.% Super P and 10 wt.% aqueous LA133 binder using water. The mixed slurry was coated on copper foil and dried at 100 °C for 12 h under vacuum. The 2016 coin cells were assembled in an argon glove box with metallic lithium as the counter electrode, 1M LiPF₆/ (EC+DMC) (1:1, v/v) as the electrolyte solution and Cellgard 2400 as the separator. The cyclic voltammetry was tested using an electrochemical workstation (VersaSTST MC, Princeton, America) at a scan rate of 0.1mV s⁻¹ and the voltage range between 0.01 and 1.5V. The charge/discharge test was performed using a battery tester (CT2001A, Wuhan, China) at 0.2C for galvanostatic measurements in a potential range of 0.01-1.5 V.

3. Results and discussion

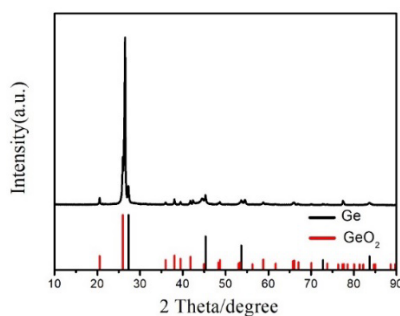


Figure 1. XRD patterns of GeO_x-coated CMS composites

Fig.1 shows the x ray diffraction pattern of GeO_x-coated CMS composites. In addition to the diffraction peak of the graphitic carbon, the composites have several strong diffraction peaks at 20.54°, 25.95°, 36.00°, 38.04°, 39.48° indexed to crystalline hexagonal GeO₂ (JCPDS card 36-1463). And the strong diffraction peaks at 27.28°, 45.30°, 53.68°, 72.80° and 83.69° are attributed to the characteristic peaks of crystalline diamond Ge (JCPDS card 04-0545). It is indicated that the formation of both Ge and GeO₂ (GeO_x) in the composites.

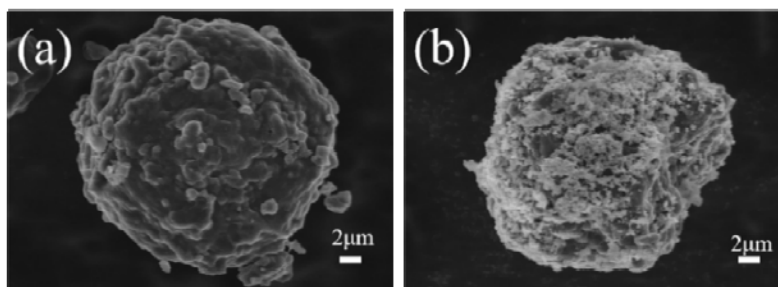


Figure 2. SEM image of (a) pure CMS (b) GeO_x -coated CMS composites

From SEM images of pure CMS and GeO_x -coated CMS composites shown in Fig.2. We can observe small white particles of GeO_x nanoparticles coated on the surface of CMS homogeneously. The SEM results confirmed the formation of GeO_x in CMS matrix, which is consistent with the XRD measurement.

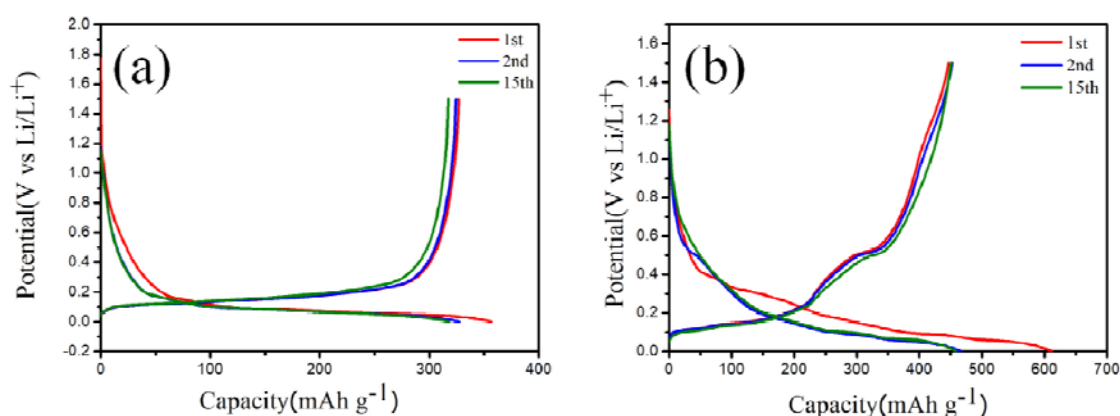


Figure 3. Discharge/charge curves of (a) CMS and (b) GeO_x -coated CMS composites at 0.2C

Fig.3 exhibits the 1st, 2nd and 15th cycle charge/discharge curves of CMS (Fig.3a) and GeO_x -coated CMS (Fig.3b) electrodes. The first discharge and charge capacities of GeO_x -coated CMS are 612.1 and 465.6 mAh g^{-1} respectively. The initial coulomb efficiency was 76.01%, which was caused by the formation of a SEI film. After 15 cycles, the GeO_x -coated CMS electrode shows a high reversible capacity and retains good cycling stability, which is comparable to pure CMS electrode.

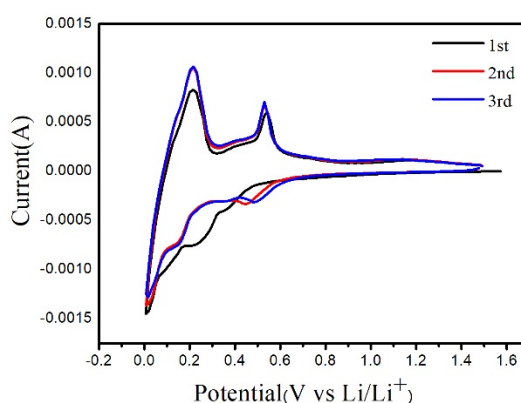


Figure 4. The CV curves of GeO_x -coated CMS composites

Fig.4 shows the first three circles of the cyclic voltammetry of the GeO_x -coated CMS composites. At the first cathodic curve, the irreversible feature at 0.25 V can be attributed to reduction of GeO_2 into Ge and Li_2O . The broad peaks observed at voltages of 0.2 V and 0.01 V are attributed to Li-Ge alloys formation and the CMS lithium intercalation process [10, 11]. From the second cycle onward, two reduction peaks at 0.47V and 0.14V related to the formation of Li_9Ge_4 and $\text{Li}_{15}\text{Ge}_4$ appeared. During the charging process, the peak at 0.2V corresponds to the lithium deintercalation of CMS, and the peak at 0.54V is attributed to the dealloying of Li_xGe into Ge. The results indicated that the lithium insertion reaction in the composites was reversible and stable.

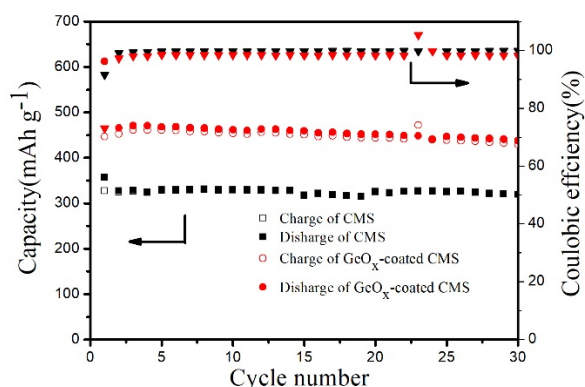


Figure 5. Cycling performance of CMS and GeO_x -coated CMS composites

Fig.5 exhibits the cycling performance of the CMS and the GeO_x -coated CMS composites electrodes at 0.2C. The GeO_x -coated CMS electrode has the first discharge specific capacity of 612.1 mAh g^{-1} , the reversible discharge specific capacity of 446.8 mAh g^{-1} , and the specific capacity of 429.6 mAh g^{-1} after 30 cycles. The capacity retention rate is 93.98%, which has a higher capacity than the CMS electrode of 319.5 mAh g^{-1} .

4. Conclusion

In this study, GeO_x -coated CMS composites were prepared by simple chemical reduction method and their electrochemical properties were investigated. The result showed the GeO_x -coated CMS anode materials exhibit good electrochemical performance with an initial columbic efficiency of 76.01%, and the capacity was 429.6 mAh g^{-1} after 30 cycles. The capacity retention rate is 93.98%. Loading GeO_x nanoparticles on the surface of CMS can buffer the volume expansion of GeO_x and increase the specific capacity of pure carbon materials. The synthesized composite materials can be used as a new anode material for lithium ion batteries.

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