Self-supporting Si/Reduced Graphene Oxide nanocomposite films as anode for lithium ion batteries

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ABSTRACT

Self-supporting Si/Reduced Graphene Oxide (RGO) nanocomposite films have been prepared by thermal reduction of Si/graphene oxide nanocomposite, which is fabricated by dispersing silicon nanoparticles into an aqueous suspension of graphene oxide nanosheets. The Si nanoparticles are well encapsulated in a RGO matrix and the Si/RGO composite has much higher reversible discharge capacity and a better cycle stability than pure nanosized Si particles as well as the RGO. Such enhancement can be attributed to the RGO matrix, which offers an efficient electrically conductive channel and a flexible mechanical support for strain release.

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1. Introduction

Rechargeable lithium ion batteries with high energy capacity and long cycle life are indispensable for portable electronic devices. Silicon has a low discharge potential and the highest theoretical capacity (4200 mAh g^{-1}) and it is considered as an ideal anode material for next-generation lithium ion batteries. However, this material suffers from a seriously irreversible capacity and a poor cycling stability, which results from a large volume change (about 300%) during the lithium ion insertion/extraction process. The huge volume expansion could lead to cracks of particles, and thus losing electronic contacts between them and also with current collectors. In addition, silicon has a low electronic conductivity, which could also cause the polarization of the electrode. Various efforts have been made to enhance the capacity retention, such as decreasing the silicon particle size [1], using silicon nanowires [2], silicon nanotubes [3], silicon nanoarrays [4], porous silicon [5], or dispersing silicon into a carbon matrix. Various carbon materials have been investigated to improve the cycling stability of Si-based materials, such as amorphous carbon [6], graphene [7–9], carbon nanotubes [10], graphite [11], mesoporous carbon [12] and Fullerene [13]. It is believed that these approaches buffer the volume changes and improve the electronic and ionic conductivities.

Graphene has excellent electronic conductivity, mechanical properties and high surface area (theoretical value of 2630 m^2/g) and it can be used as an ideal conductive additive for electrodes. Recently, Si/graphene papers have been prepared by reduction of Si/graphene oxide composite using H$_2$[8] or hydrazine monohydrate [9]. These methods are environmentally unfriendly when flammable H$_2$ or toxic hydrazine monohydrate is involved. In this communication, self-supporting Si/Reduced Graphene Oxide (RGO) nanocomposite films with high strength have been prepared by using a simple filtration method together with a thermal reduction. The films exhibit a high capacity and a good cycling stability when they are used as anode materials for lithium ion batteries.

2. Experimental

The self-supporting Si/RGO nanocomposite film was prepared by filtration method and a subsequent thermal reduction (Fig. 1a). Firstly, graphite oxide was synthesized from graphite (Aldrich) by Hummers method [14]. The graphite oxide was re-dispersed into deionized water and exfoliated to generate graphene oxide nanosheets by ultrasonication. Then, 100 mg silicon nanoparticles (50–100 nm in diameter) were dispersed into a 200 mL graphene oxide (0.5 mg/mL) aqueous suspension by sonication. After that, the Si/graphene oxide (1:1 in weight) composite suspension was filtrated with a filter membrane (0.22 μm) to produce a self-supporting Si-graphene oxide nanocomposite film. Subsequently, the Si/graphene oxide film was dried in air and thermally reduced in a flow of Ar for 1 h at 700 °C to form a self-supporting Si/RGO nanocomposite film. The weight ratio of Si to RGO is 2:1 as estimated from thermogravimetry and differential thermal analysis (TG-DTA, Seiko Instruments TG/DTA 6200) at a heating rate of 10 °C/min in air flow. To compare the electrochemical performance, the control sample was

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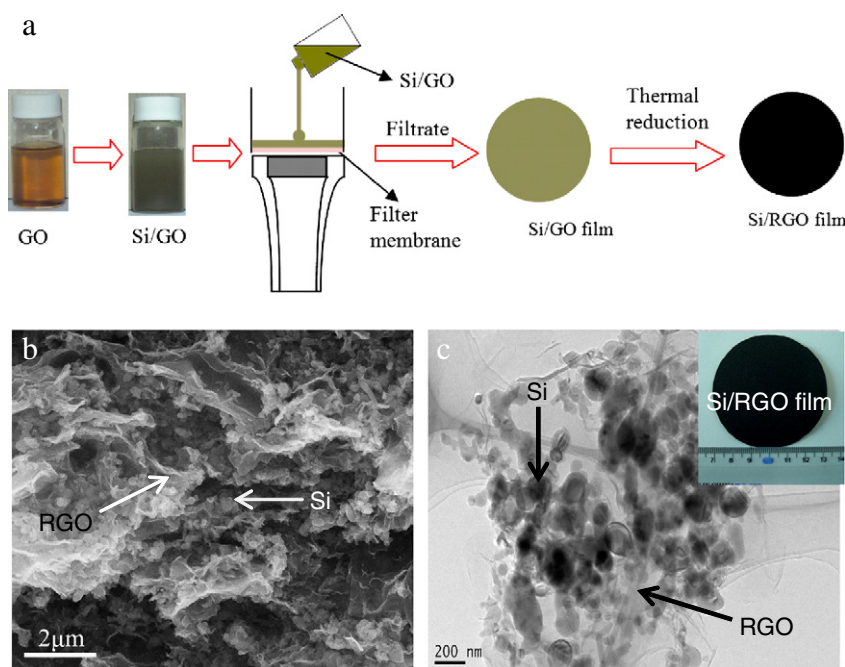 E-mail address: fanlizhen@ustb.edu.cn (L.-Z. Fan).

Fig. 1. A schematic diagram of the fabrication of Si/RGO film (a), FE-SEM image (b), and TEM image (c) of the self-supporting Si/RGO composite, inset is the photo of the self-supporting Si/RGO composite film.

prepared by thermal reduction of graphene oxide film at the same condition without the dispersion of Si nanoparticles.

The structure of as-prepared samples was characterized by powder X-ray diffraction (XRD, Rigaku/mac250) using Cu Ka radiation and Raman spectroscopy (514.5 nm, Ar-Ion laser on LabRAM Aramis). Field emission scanning electron microscopy (FE-SEM, JSM-6330) and transmission electron microscopy (TEM, JEM-2100F) were used to study the morphology and microstructure of the samples.

Electrochemical performances were measured using two-electrode 2032 coin-type cells. The RGO and Si/RGO self-supporting films were used as working electrode directly without any further treatments. Si electrodes were prepared by mixing Si nanoparticles, carbon black (Super-P), and polyvinylidene fluoride (PVDF) at a weight ratio of 4:4:2 and pasted on pure copper foil. Pure Li foil was used as the counter electrode. The electrolyte is a solution of 1 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume). The cell assembly was operated in a glove box filled with pure argon (99.999%). The cells were charged and discharged galvanostatically in the fixed voltage window from 10 mV to 1.5 V on a LAND battery tester at 25 °C .

3. Results and discussion

Fig. 1 illustrates the schematic diagram of the fabrication procedure and the morphology of the prepared Si/RGO film. Here, we employed a simple filtration method to fabricate self-supporting Si-graphene oxide film, and then the film was directly heated in argon atmosphere to remove oxygen functional group. The prepared Si/RGO film (Fig. 1c inset) is self-supporting, high strength, flexible and smooth. It can be prepared into different sizes (diameter and thickness) by controlling the amount of solution and the size of filter papers. From both the FE-SEM (Fig. 1b, cross section of the film) and TEM images (Fig. 1c) of Si/RGO nanocomposite film, it can be seen that Si nanoparticles and RGO sheets are distributed uniformly into the whole film and Si nanoparticles are well embedded into RGO nanosheets.

Fig. 2 presents XRD patterns and Raman spectra of pure RGO film and Si/RGO nanocomposite film, along with those of Si nanoparticles, pristine graphite and graphite oxide. For graphite oxide, the appearance of a broad diffraction peak at $2\theta = 10.3°$ and the disappearance of peak at 26.4° for graphite indicate the oxidation of graphite to graphite oxide [15]. For the RGO film, the reappearance of the peaks at 25° and 42.7° corresponding to the (002) and (100) of graphite respectively indicates the successful reduction of graphite oxide to graphite. The diffraction peaks of the Si-RGO film appear at 26.5°, 28.4°, 47.3° and 56.1°, suggesting the presence of both RGO and Si nanoparticles. The successful oxidization from graphite to graphite oxide can also be proved from Raman spectra (Fig. 2b). The ratio of the intensities (I_D/I_G) for the graphite oxide is markedly increased in contrast with graphite, indicating the formation of some sp^3 carbon by functionalization. For Si/RGO composite film, the peak at about 517 cm^{-1} is in agreement with the data in the spectrum of Si nanoparticles, while the peaks at 1359 cm^{-1} and 1596 cm^{-1} correspond to the D band and the G band of graphite respectively. Compared with graphite oxide, the I_D/I_G intensity ratios of Si/RGO and RGO have decreased after thermal reduction, which can be attributed to the significant increase of the size of the in-plane sp^2 domain [16].

The first charge (lithium insertion)–discharge (lithium extraction) curves of the Si/RGO nanocomposite film, RGO film and Si nanoparticles at a rate of 50 mA g^{-1} are presented in Fig. 3a. Cycling stabilities determined from charge–discharge curves are presented in Fig. 3b and c. For pure silicon, it exhibits a high discharge capacity only for the initial 5 cycles, and then the capacity degrades rapidly to below 500 mAh g^{-1}. The RGO film displays a capacity of 1921 mAh g^{-1} and 524 mAh g^{-1} for the first charge–discharge cycle respectively with the reversible capacity of only 27%. Fig. 3a inset shows dQ/dV profiles of RGO and Si/RGO films during the first charge–discharge process. The broad peak at 0.8 V for RGO film is due to the formation of a solid electrolyte interphase (SEI) film on the graphene surface, which consumes large amounts of Li ion [17] and thus leading to the huge initial irreversible capacity. In the Si/RGO film, there are two peaks at 0.5 V and 0.05 V during the charge process and one peak at 0.45 V during the discharge process, which comes from the phase transition between Li$_x$Si [18]. In contrast, the Si/RGO nanocomposite film
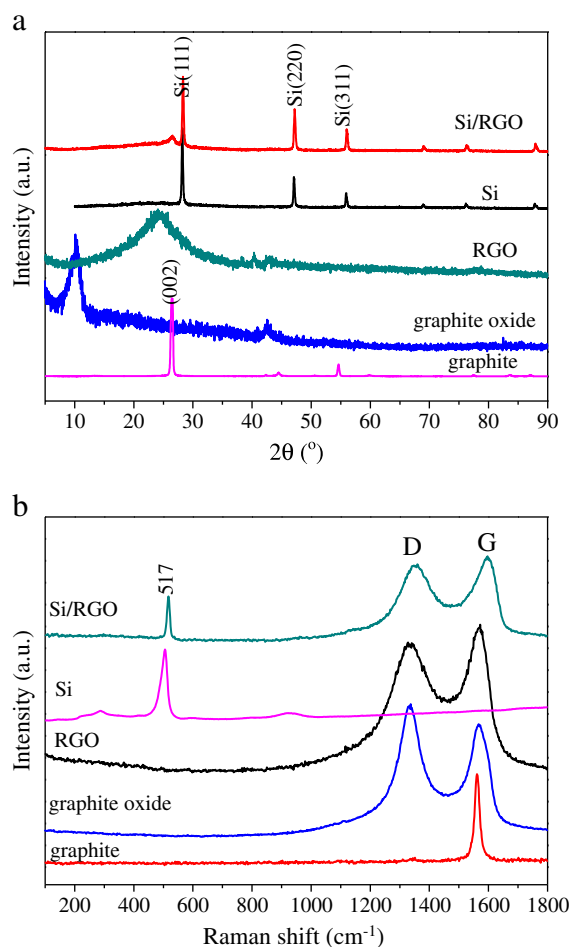
Fig. 2. (a) X-ray diffraction patterns and (b) Raman spectra for graphite, graphite oxide, RGO film, Si and self-supporting Si/RGO film.

delivers a reversible specific capacity of 1040 mAh g^{-1} (the capacity is based on the total composite) in the first cycle, with an initial coulombic efficiency of 63%. Compared with pure Si, the self-supporting Si/RGO composite film reveals a significantly improved cyclic ability. After 30 cycles, the capacity retention ratio for Si/RGO composite film is 94% (about 977 mAh g^{-1}). Good cyclic performance (Fig. 3c) is further confirmed by the fact that a relatively stable capacity was obtained after 300 cycles (about 786 mAh g^{-1} at a current density of 50 mA g^{-1}) even if it went through large current density charge and discharge. The initial coulombic efficiency, discharge specific capacity and also cyclic stability of the film here are all better than Si/graphene composite produced by reduction of Si-graphene oxide using hydrazine monohydrate [9]. The superior electrochemical performance of Si/RGO film is attributed to the unique morphology, that is, Si nanoparticles are homogeneously distributed among the RGO sheets which could prevent Si nanoparticles from aggregating and RGO can provide an efficient elastic matrix to accommodate the mechanical stresses/strains of Si phase, and also uniformly distributed RGO can also contribute to the enhanced electrical conductivity of the film. In addition, the good performance may also be due to oxygen functionalities (e.g., –O- and –OH) left attached to carbon because of the relatively mild reduction condition and these agents might interact with the surface of Si nanoparticles. Furthermore, our specially designed self-supporting film without the current collector can prevent loss of the electrical contact between active materials and substrates, which normally occurs for the conventional electrode.
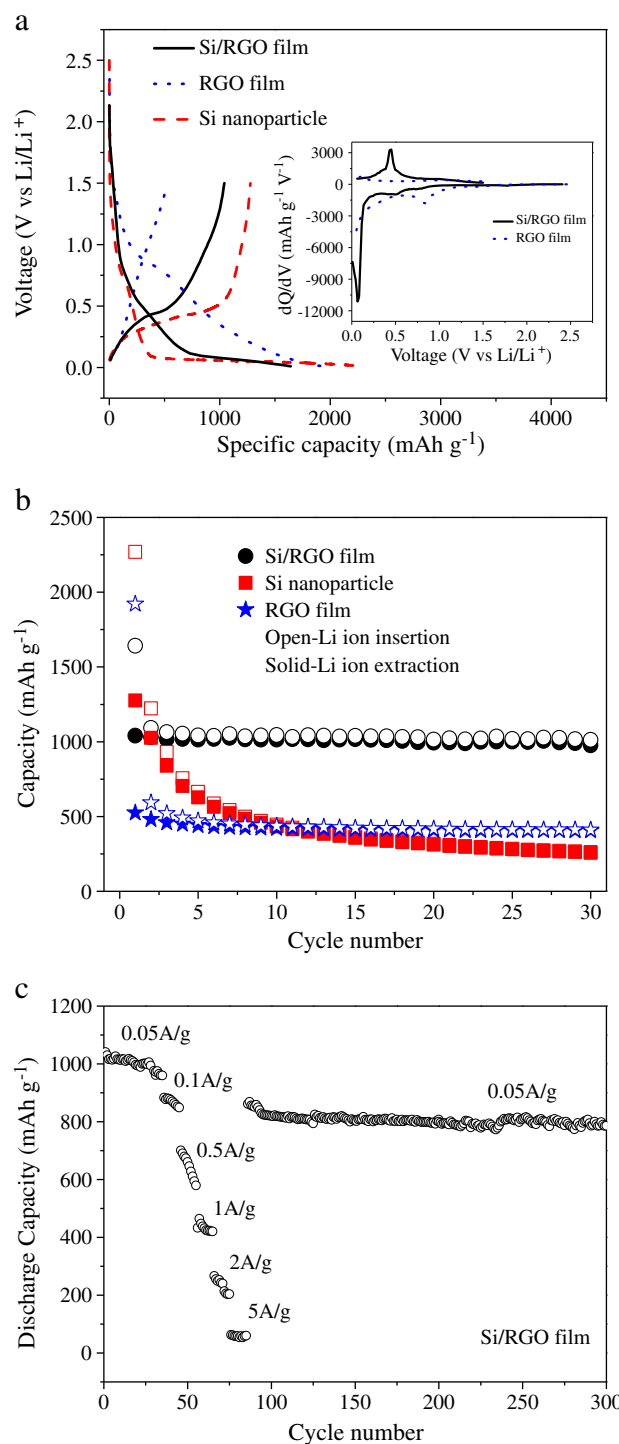

Fig. 3. Comparison of the electrochemical properties: (a) The first charge–discharge curves of the self-supporting Si/RGO film, RGO film and Si nanoparticles at a rate of 50 mA g^{-1}, inset shows differential profiles of RGO and Si/RGO films during the first charge–discharge process; (b) cycling stabilities of Si/RGO film, RGO film and Si nanoparticle electrodes at a rate of 50 mA g^{-1}; and (c) discharge capacities versus the cycle number for the self-supporting Si/RGO film at different current rates of 0.05–5 A g^{-1}. The weight ratio of Si to RGO is 2.

4. Conclusion

A self-supporting Si/RGO nanocomposite film was prepared by a simple filtration method together an environmentally friendly thermal reduction treatment and it exhibits a high storage capacity and a good cyclic stability. The uniform distribution of Si nanoparticles

and RGO sheets in the film could not only make highly utilization of high capacity of Si nanoparticles, but also contribute to the enhanced electronic transportation of the whole film. The flexible RGO sheets can alleviate the large volume changes of silicon nanoparticles effectively, and thus enhancing the cyclic stability of the Si/RGO film. We expect that this facile preparation method could be extended to other RGO-based electrode materials in electrochemical energy storage and conversion.

Acknowledgements

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