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ScienceDirect

Mendeleev Commun., 2013, **23**, 284–285

Mendeleev
Communications

Graphene-encapsulated silicon nanoparticles as an anode material for lithium-ion batteries

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DOI: 10.1016/j.mencom.2013.09.016

Silicon particles have been embedded into graphene sheets *via* a novel method combining the electrostatic interaction and chemical reduction of graphene oxide, and the electrochemical properties of the composite anode material have been evaluated.

Silicon has attracted great interest as a candidate to replace commercial graphite materials owing to its numerous appealing features: it has the highest theoretical capacity ($\mathrm{Li}_{4.4}\mathrm{Si} \approx 4200$ mAh g^{-1})[1] of all known materials, and it is abundant and inexpensive. A major drawback, however, affects this material, that is, the large volume changes (>300%) upon insertion and extraction of lithium, which results in pulverization and capacity fading.[2–5] Yang *et al.*[6] reported a promising strategy to tackle the aggregation problem of metal oxides in lithium-ion batteries. It consists in encapsulating a metal oxide into a graphene layer by co-assembling between negatively charged graphene oxide and positively charged oxide nanoparticles. The graphene-encapsulated metal oxide leads to remarkable lithium storage performance, including highly reversible capacity and excellent cycle performance.

Here, we extend this encapsulation method to silicon nanoparticles. A silicon particle in air is covered by a fine layer of silica; the covered silicon particle can act as a silica particle with graphene oxide to get encapsulated, but the oxide layer should be then removed to get graphene-encapsulated silicon nanoparticles. We could take advantage of the high lithium storage capacity of silicon nanoparticles and the ability of graphene to confine the nanoparticles, which limits the volume expansion upon lithium insertion and prevents the aggregation of particles, thus improving the overall electrochemical performance of the anode for lithium-ion batteries.

The overall method is illustrated in Figure S1 (see Online Supplementary Materials).[†]

The typical SEM images (Figure 1) of the Si/G composite revealed that the flexible and thin graphene sheets were wrapped around the surface of Si nanoparticles. One can note the random distribution of the particle sizes due to the medium quality of the silicon used for this process. The TEM image [Figure 2(*a*)] indicates that the Si nanoparticles are embedded in graphene sheets. HRTEM [Figure 2(*b*)] reveals that the distances between the neighbouring lattice fringes have an approximate *d*-spacing of 3.16 Å, which is consistent with the lattice spacing of the (111) plane of crystalline silicon.

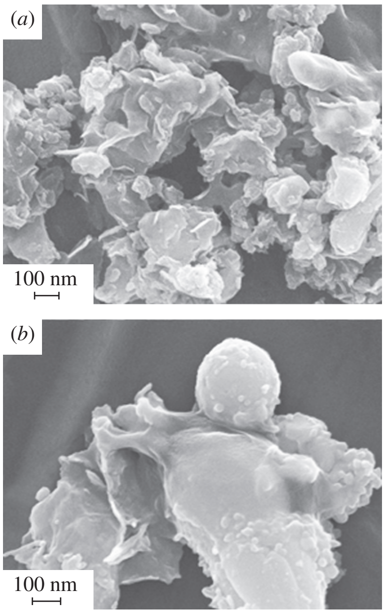

Figure 1 SEM images of the Si/G nanocomposite.

The cycle performance of the Si/G composite electrode has been compared with that of a bare Si electrode. The half cells were cycled at a current density of 100 mA g^{-1} between 0.03 and 1.2 V. The discharge profiles upon cycling are shown in Figure 3. The composite exhibited a first discharge capacity of 1306 mAh g^{-1} and a charge capacity of 1077 mAh g^{-1}, which means a coulombic efficiency of 82.5% and an irreversible capacity of ~130 mAh g^{-1}; it retained 450 mAh g^{-1} after 100 cycles (~34.5% retention). In contrast, the bare Si electrode shows a very fast capacity loss and retains almost 1.2% of its initial capacity of 2014 mAh g^{-1}

[†] Silicon powder was maintained in air for a few minutes in order to coat particles by a fine layer of silica. These silica-coated silicon nanoparticles (0.5 g) were introduced into dry toluene solution (50 ml) and sonicated for 30 min. A 0.5 ml portion of aminopropyltrimethoxysilane (APS) was poured into the above solution and the contents were stirred for 24 h in a closed beaker. APS could render the oxide surface positively charged by grafting onto oxide.[6] The APS-modified Si@SiO$_2$ dispersion (6 ml) was added to 40 ml of an aqueous graphene oxide suspension (0.1 g dm^{-3}). After stirring for 1 h, 0.5 ml of hydrazine (85 wt%) was added to the suspension to reduce graphene oxide to graphene. The resulting graphene encapsulated silica/silicon nanocomposite was washed, centrifuged and treated with an HF solution in ethanol to etch away the layer of silica from the surface of Si nanoparticles. The final product was washed, centrifuged and vacuum dried at 70 °C.

The working electrode was prepared by slurring the Si–graphene composite, carbon black and sodium alginate at a weight ratio of 3 : 1 : 1 with deionized water and pasting the mixture on nickel grid by pressing with a rolling mill. The film was dried in a vacuum oven at 80 °C for 10 h. The electrode disks (1 cm^2) were cut and pressed again before electrochemical tests. The coin cells CR2025 were assembled in an argon-filled glove box. The electrolyte consisted of 1 M LiPF$_6$ solution in EC/DMC (1 : 1 by weight). A porous polypropylene membrane was used as a separator between the composite electrode and a lithium foil used as a counter electrode.

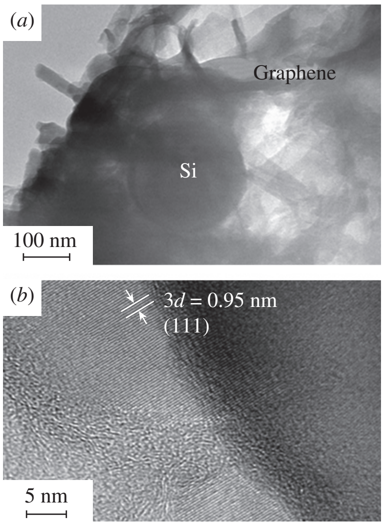

Figure 2 (*a*) TEM and (*b*) HRTEM images of the Si/G nanocomposite.

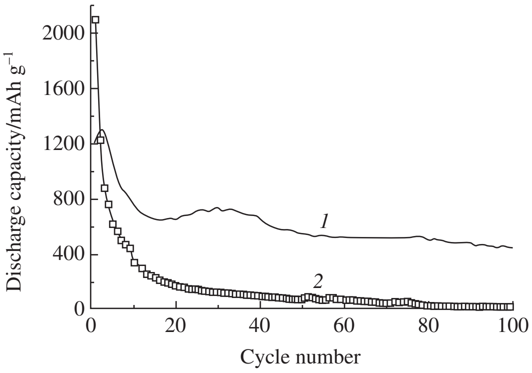

Figure 3 Compared discharge profile of the (*1*) Si/G nanocomposite and (*2*) bare silicon anodes cycled between 0.03 and 1.2 V at a current density of 100 mA g^{-1}.

after 100 cycles. The huge capacity fade of an electrode with bare silicon is due to the severe volume change of silicon during Li insertion/extraction processes, leading to electrode textural disruption, loss of electrical contact and finally poor capacity retention.[7] The Si/G composites exhibit improved cycling performance, which is better than that of bare silicon. The main reason for this improved capacity retention is the buffering effect of the graphene shell, which provides facile strain relaxation during electrode structure changes, accommodates the large Si volume expansion and shrinkage during lithium insertion/extraction. The graphene shell can also act as a barrier to prevent the aggregation of Si particles and thus increase their structure stability during cycling. Moreover, the graphene shell could enhance the conductivity of the entire electrode.

In summary, we have developed a method for the encapsulation of Si nanoparticles in graphene sheets. The composites demonstrate improved lithium storage capacity compared with bare silicon. We believe that such a simple and low-cost assembly protocol presents a promising direction for improving the cycle performance of lithium-ion batteries.

This work was supported by the National Natural Science Foundation of China (grant nos. 50872039 and 51172085).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.09.016.

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Received: 22nd April 2013; Com. 13/4110