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Solid State Ionics

Facile synthesis of graphene–silicon nanocomposites with an advanced binder for high-performance lithium-ion battery anodes

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A B S T R A C T

In this work, the nanocomposite of silicon nanoparticles dispersed on conducting graphene (Si/graphene) was successfully synthesized using high-energy ball milling followed by thermal treatment, and Xanthan gum was developed for the first time as a novel advanced binder for Si-based lithium-ion battery anodes. Compared to the pristine Si anode, the Si/graphene composite anode showed an enhanced reversible capacity, excellent cyclic performance and rate capability, highlighting the advantages of dispersing Si nanoparticles on graphene sheets. The significant enhancement on electrochemical performance could be ascribed to the fact that the Si/graphene composite anode could maintain excellent electronic contact and accommodate the large volume change of Si during the lithiation/delithiation process. In addition, the Si/graphene anode with the gum binder exhibited improved cycling and rate performances compared to that with the conventional carboxymethyl cellulose (CMC) binder. Such an enhancement was ascribed to the high binder stiffness and the strong adhesion of the binder to Si-based particles due to the binder's specific chemical structure and properties, which helps maintain the integrity of the electrode and accommodate the volume change of Si. This work demonstrates that the Si/graphene nanocomposite with an advanced binder offers great advantages to enhance the lithium storage capacity, cyclic stability, and rate capability, making it a promising candidate as an anode material for high-performance lithium ion batteries (LIBs).

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1. Introduction

Lithium ion batteries (LIBs) have been recognized as an enabling energy storage technology for many emerging applications, including electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) [1–4]. However, such a goal cannot be reached without designing alternative materials both as positive and as negative electrodes to increase the capacity of LIBs. While studies on positive-electrode materials have led to a limited increase of their capacity, the development of silicon-based negative electrodes has already been shown to enhance the capacity of standard graphite electrodes by nearly one order of magnitude [5–7]. Besides the high theoretical capacity (4200 mAh g^{-1}) with a low potential window, silicon-based anode materials are also environment-friendly, easily available and produced in widely distributed areas [8]. Despite all of these advances, silicon-based anodes suffer from severe pulverization triggered by their more than 300% volume change upon lithium insertion and extraction, which, if not addressed, causes serious capacity fading during charge/discharge cycling, especially at high current densities [9,10].

On the one hand, many attempts have been made on tailoring Si to address this issue, including the use of nanostructured silicon compounds

[11,12], alloying with metals [13,14], and dispersing the silicon in a carbon matrix [15–17]. Among these, Si/C composites have attracted particular interest. Different kinds of carbon materials have been demonstrated to accommodate the Si volume change and improve the cycling stability of Si-based materials, including amorphous carbon (pyrolysis [18,19] or hydrothermal [20]), graphite [7,21], carbon nanotubes [22,23] and mesoporous carbon [24]. Graphene, a new kind of carbon material, is an excellent substrate to host active nanomaterials for energy applications due to its high conductivity, large surface area, flexibility, and chemical stability [25–27]. Recently, graphene has been demonstrated as an active matrix for the preparation of Si/graphene nanocomposites to improve the electrochemical performance of Si-based materials [28–40]. The enhanced electrochemical performance can be attributed to the fact that graphene can not only provide a support for dispersing Si nanostructures and work as a highly conductive matrix for enabling good contact between them, but can also effectively prevent the volume expansion/contraction and aggregation of Si nanostructures during Li charge/discharge process. We note that in these earlier reports, Si/graphene nanocomposites were prepared by two approaches: physically blending pre-synthesized Si nanocrystals and graphene [28,30–32,34,35,38–40], and chemical reaction process (such as vapor deposition methods [33], covalent binding via aromatic linkers through diazonium chemistry [36], in situ magnesiothermic reduction of SiO_2/graphene oxide composites [37]). The former physical approach is simple and economical, but difficult to obtain homogeneous and stable

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Si/graphene nanocomposites, which is believed to be a key issue for a composite to exhibit good performances. In spite of the noticeably enhanced homogeneity and stability, the latter chemical approach is complicated, time-consuming and costly. From the viewpoint of industrial application, the former physical approach will be even more promising than the latter chemical approach. Thus, it is crucial to develop a facile physical approach to prepare homogeneous and stable Si/graphene nanocomposites as an advanced anode material for high-performance LIBs with potential industrial applications.

On the other hand, much attention has also been paid to the development of selected binders for anode and cathode electrodes, as they can help to alleviate the structural changes and improve the cycling performance of the electrodes [41]. Poly(vinylidenefluoride) (PVDF), the most conventional binder, is attached to Si particles via weak van der Waals forces only, and fails to accommodate large changes in spacing between the particles [42]. Recently, carboxymethyl cellulose (CMC), one of bio-derived polymers containing carboxy groups, has been demonstrated as an alternative effective binder for Si-based anodes, which typically shows a better battery performance than the PVDF binder [43–46]. However, reasonably stable anode performance could only be achieved when Si volume changes were accommodated by using extra-large binder content [46,47], which lowers the resulting anode capacity. Development of more efficient binders is therefore an important task for the realization of high capacity anodes with stable performance. Recently Kovalenko and coworkers [48] reported that mixing Si nanopowder with sodium alginate (SA), a natural polysaccharide extracted from brown algae, yielded a stable battery anode possessing an enhanced reversible capacity compared to the conventional PVDF binder and the CMC binder.

Herein we demonstrate that the electrochemical performance of Si-based anode can be significantly improved by combining the advantages offered by both design of Si/graphene nanocomposite materials and utilization of a novel binder. Si/graphene nanocomposites are prepared by using high-energy ball milling followed by thermal treatment, and Xanthan gum is employed for the first time as an advanced binder for Si/graphene nanocomposite anodes. The as-prepared Si/graphene composite anode exhibits significantly improved cycling performance compared to the Si anode when CMC is used as binders for both anodes. With the Xanthan gum binder the performance of Si/graphene composite anode has been further improved, comparable to that with the alginate binder.

2. Experimental

Graphene oxide (GO) was prepared by a modified Hummers method [49], and Si nanoparticles was synthesized by the magnesiothermic reduction according to the literature [50]. To prepare the Si/graphene nanocomposites, a mixture of as-prepared Si nanoparticles and GO was blended in a 4 wt.% N-Methyl-2-pyrrolidone (NMP) solution of PVDF. The composition of the resulting mixture was 48 wt.% Si nanoparticles, 28 wt.% GO and 24 wt.% PVDF. The obtained mixture was then ball milled for 10 h with agate balls as the mixing media, and finally vacuum-dried at 100 °C for 6 h. To reduce GO and carbonize PVDF, the dried composite was further calcined at 700 °C in an argon-flowing tube furnace for 3 h with a heating ramp of 5 °C min^{-1}.

Transmission electron microscope (TEM) measurements were conducted on a JEOL 1200 microscope at 200 keV. X-ray diffraction (XRD) patterns of the samples were measured on a Powder X-ray diffractometer (MiniFlex II, Rigaku) using Cu Kα radiation. Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (SDT 2960, TA instruments) with a heating rate of 5 °C min^{-1} in air. The Si-based anodes before and after cycling were characterized by a field-emission scanning electron microscope (FE-SEM, Zeiss LEO 1530). Delithiated Si-based anodes after cycling were taken out of the coin cells inside a glovebox, washed with acetonitrile to remove the residual electrolyte and lithium salts and dried at room temperature before further SEM investigation.

Electrochemical properties of the products were measured using coin cells. The working electrodes were prepared by casting a slurry consisting of 80 wt.% of active material (as-prepared Si nanoparticles, or Si/graphene nanocomposites), 10 wt.% of conductive Super P carbon, and 10 wt.% of a binder (CMC (Alfa Aesar), SA (MP Biomedicals) or Xanthan gum (Tokyo Chem.)) onto copper foil. The electrolyte consisted of a solution of 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v). Lithium foil was used as counter electrodes. The mass loading of active materials was 1.0 mg/cm^2. These cells were assembled in an argon-filled glovebox (MBraunLabstar) and galvanostatically cycled between 0.01 V and 1.5 V on a multi-channel battery cycler (Arbin Instruments). The AC impedance was measured at an Autolab electrochemical workstation (CH Instruments), with the frequency range and voltage amplitude set as 100 kHz to 0.01 Hz and 10 mV, respectively.

3. Results and discussion

Fig. 1 shows the typical TEM images of as-prepared Si nanoparticles, GO and Si/graphene nanocomposites. Si nanoparticles (Fig. 1A) were irregular-shaped particles about 50–150 nm in size and prone to aggregation. For the sample of as-prepared GO (Fig. 1B), it was found that GO was almost transparent, and had one or few layer 2D sheet structure with some obvious wrinkles. These corrugated wrinkles indicated that the 2D sheet structure becomes thermodynamically stable during bending [51]. As for the sample of as-prepared Si/graphene nanocomposite (Fig. 1C), the graphene sheets and Si nanoparticles were distinguished clearly, and Si nanoparticles with the size of about 50–150 nm were well dispersed and attached to the transparent graphene sheets. This indicates that the high-energy ball milling process could prevent Si nanoparticles from agglomerating and enable firm attachment of these nanoparticles to the graphene support.

The XRD patterns obtained from the as-prepared Si nanoparticles and Si/graphene nanocomposites are shown in Fig. 2. All of the peaks of as-prepared Si nanoparticles can be indexed as well-crystallized Si with cubic structure (JCPDS No. 27-1402) indicating that high-purity Si was successfully obtained by magnesiothermic reduction. After mixing with graphene, besides the sharp peaks (2θ = 28.5°, 47.4°, 56.0°, 69.2° and 76.4°) corresponding to the Si crystalline phase, the diffraction peaks at 2θ = 26.0° and 42.8° attributed to the graphite-like (002) and (100) structure from graphene can also be observed [52], which implies that GO was reduced to graphene during the calcination process. In addition, the broad character of the peak at 26.0° proves that graphene was homogeneously distributed in the nanocomposites without significant stacking or agglomeration [32]. Fig. 3 shows the Raman spectrum of the Si/graphene nanocomposite. Two peaks at 1333 and 1614 cm^{-1} can be observed, which correspond to the D (disordered) band and the G (graphite) band of carbon, respectively. These two peaks confirm the presence of graphene in the nanocomposite.

To determine the content of Si in the Si/graphene composites, TGA measurements were performed in air from room temperature to 900 °C and the results are shown in Fig. 4. A small weight loss (10 wt.%) around 120 °C and a major weight loss (33 wt.%) around 200 °C were found in GO due to the loss of adsorbed water and pyrolysis of the labile oxygen-containing functional groups, respectively, while the largest weight loss occurs at around 600 °C due to the complete oxidation reaction of GO. For Si nanoparticles, the weight increases slightly from room-temperature to 600 °C due to the formation of SiO$_x$, indicating that the oxidation of Si powder in air was not significant at 600 °C. Thus, it's reasonable to determine the content of Si in the nanocomposites from the largest weight loss in the TGA curve of Si/graphene nanocomposites. It can be estimated that the largest weight loss in nanocomposites is about 46 wt.% at 600 °C. Correspondingly, the Si content in the