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Short communication

Silicon oxide-on-graphite planar composite synthesized using a microwave-assisted coating method for use as a fast-charging lithium-ion battery anode

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HIGHLIGHTS

- Si oxide-coated graphite flake (SGF) is synthesized by a microwave-heating method.
- Synthesis uses nonexplosive liquid polysiloxanes as the Si-containing precursor.
- Nanometer Si-containing conformal coating is formed on graphite flakes.
- SGF electrode shows a specific capacity of ~480 mAh g⁻¹ and 97% capacity at 5C-rate.
- SGF electrode retains 94% capacity after 500 cycles with Coulombic efficiency >99.9%.

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ABSTRACT

A high-performance Si oxide-coated graphite flake (SGF) composite anode for Li-ion batteries (LIBs) is synthesized using a microwave-assisted coating method. In this synthesis, a solution comprising liquid polysiloxanes is used as the Si-containing precursor. Heating the graphite flakes (GFs) with microwave induces the deposition of a Si-containing conformal layer on the GF surfaces, which is subsequently calcined to produce SGFs. When tested as a LIB anode, the resulting SGF exhibits a reversible specific capacity of nearly 480 mAh g⁻¹, 97% capacity retention at a current density of 2.5 A g⁻¹ (approximately 5 C-rate), and 94% capacity retention after 500 cycles with an average Coulombic efficiency > 99.9%. The results suggest new strategies for both designing and synthesizing high-performance anode materials for LIB applications.

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1. Introduction

In the development of advanced Li-ion batteries (LIBs), high capacity density, high-rate performance, and long cycle life are emphasized. Graphite is the predominant anode for commercial LIBs and is expected to continue to play a crucial role in the process of manufacturing advanced LIBs because of its low cost, low charge–discharge plateau potential, satisfactory specific capacity (372 mAh g⁻¹), and high dimensional stability. The state-of-the-art

commercial graphite anodes include primarily micron-sized particles, and these nearly spherical particles typically possess specific capacities in the range of 350–360 mAh g⁻¹ but suffer from poor rate performance. Planar type of graphite materials, such as plates and flakes, offer the opportunity of superior rate performance but exhibit substantially lower specific capacities.

Various high-capacity anode materials have been extensively investigated as potential alternatives to graphite for achieving high energy density. Although Si has a substantially higher capacity (3579 mAh g⁻¹, corresponding to the formation of Li₁₅Si₄ at room temperature) than that of graphite, it is susceptible to considerable volume expansion (>300% when fully lithiated) when subjected to

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lithiation [1–3]. This volume variation results in the pulverization of Si particles and cracking and crumbling of the electrode structure, leading to fast capacity fade and poor cycle life. Composite anodes comprising a limited amount of Si or Si oxides to enhance the capacities of the graphite anodes with minimum volume expansion problem may be attractive transient products for advanced high-energy LIBs before realization of viable Si-dominant anodes. Moreover, the rate capability of Si-based anodes must be improved to meet the power requirements of various applications [4–6].

In previous studies, various forms of Si, such as surface coatings [7,8] and nano- or macroparticles [9,10], have been combined with graphite or other carbon materials to form composite anode materials for capacity enhancement. Surface-coating composites have the potential to achieve high lithiation–delithiation kinetics because of the short diffusion length along the thickness of the coating. Furthermore, coating thicknesses within the nanometer range can facilitate reducing the mechanical strain induced by volume variations, thereby preventing active materials from cracking and pulverizing [11]. Saito et al. [12] synthesized a layered Si/Ni planar composite by using physical vapor deposition, and Holzapfel et al. [8] synthesized planar Si-coated graphite by using chemical vapor deposition. Both studies have reported that the Si components exhibited enhanced cycle stability compared with a bulk Si anode; however, the problem associated with rate performance was not addressed. Si coatings have typically been synthesized using chemical vapor deposition [7–9], which entails using toxic and explosive Si-containing vapor precursors, such as Si_nH_m or SiH_xCl_y . By contrast, in the current study, a fast-charging high-capacity Si oxide-coated graphite flake (SGF) anode was synthesized using a novel low-temperature microwave-heating method. In this method, a nonexplosive liquid Si-containing precursor was used. The resulting SGF anode exhibited excellent rate and cycle performance. This study proposes new strategies for designing and synthesizing high-performance anode materials for LIB applications.

2. Experimental

2.1. Synthesis of the SGF powder

To prepare the Si-containing liquid precursor, 19 g of poly-methylhydrosiloxane (Aldrich) was mixed with 1 g of divinyl polydimethylsiloxane (Aldrich) and 0.25 g of a catalyst solution (1 wt.% hydrogen hexachloroplatinate in isopropyl alcohol), and the resulting mixture was heated at 70 °C for 2 h. Graphitic flake (GF; KS6, Timcal) powder, which consisted of flakes having an average particle size of 3 μm (vender's value) and thicknesses ranging from 50 to 100 nm, was added into the liquid precursor and stirred for 1 h. The suspension was then filtered to collect solution-coated GFs. The wet GF powder was placed in an evacuated glass vessel and heated in a commercial microwave oven (Panasonic, NN-ST651; power setting: low-300 W) for 15 min. After the heating process, the powder was washed with hexane to remove residual precursors and then finally calcined at 1000 °C under vacuum for 1 h in a quartz tube furnace to obtain the SGFs.

2.2. Materials and electrochemical characterizations

The particle size and morphology were analyzed using a scanning electron microscope (SEM; Nova™ NanoSEM 230) operated at 5 kV and equipped with an energy-dispersive X-ray spectrometer (EDS) and a transmission electron microscope (TEM; Philips Technai G2) operated at 200 kV. Thermogravimetric (TG) analysis was conducted using a Thermoanalyzer (Rigaku, TG 8120) with an air

flow rate of 100 ml min^{-1} and a heating rate of 5 °C min^{-1} .

Electrochemical characterizations were performed using 2032-type coin cells with Li foil serving as the counter and reference electrode. The working electrodes were prepared by casting a slurry consisting of 91 wt.% of the active material, 2 wt.% of Super P (Timcal) carbon black, and 7 wt.% of polyvinylidene difluoride (PVdF; Kureha) binder. The slurry was uniformly coated onto a Cu foil (Sambo, 99.9%) and air-dried at 90 °C. To fabricate the coin cells, the electrodes were punched into disks measuring 13 mm in diameter and further dried at 150 °C under vacuum for 8 h before the cell assembly. The mass loading of the active material was approximately 2.4 mg cm^{-2} . The electrolyte was 1 M LiPF_6 in ethylene carbonate:ethyl methyl carbonate (volume ratio of 1:2) with 2% vinylene carbonate and 10% fluoroethylene carbonate (FEC; >98%, TCI) serving as an additive. The cell assembly was carried out in an argon-filled glove box. When the assembly was completed, the cells were stored at room temperature for 24 h before test. The electrochemical measurements were conducted on a battery tester (Maccor, series 4000) at room temperature in the voltage range of 1.2–0.01 V versus Li^+/Li . The current density and specific capacity were calculated according to the total mass of the active material. Coulombic efficiency is defined as the ratio of the charge (de-lithiation) capacity to the discharge (lithiation) capacity.

3. Results and discussion

In this study, microwave was employed to heat rapidly and selectively the GFs that were immersed in the Si-containing liquid precursor. Because of their strong microwave absorbing properties, the GFs reached sufficiently high temperature levels within a few seconds of heating, and this induced the precursor molecules near the GF surfaces to be cross-linked and/or decomposed, resulting in material deposition on the surfaces. Because the deposited thin film is a poor heat conductor as well as a poor microwave-absorber, the surface reactions automatically ceased when this film grew to a certain thickness. This self-limiting deposition process enabled depositing a conformal Si-containing layer onto the surfaces of the GFs despite their extremely high aspect ratios. Furthermore, because the unreacted portion of the liquid precursor maintained a low temperature throughout the reaction process and retained its chemical properties, the excess Si-containing precursors were recovered by washing the GF powder with an appropriate solvent.

The GFs exhibited high aspect ratios and smooth surfaces (Fig. 1a). After the coating process, the flake morphology was maintained, but the coating could not clearly be distinguished (Fig. 1b). To examine the microstructures of the coating, the SGF powder was heated in air at 1000 °C to burn off the carbon while converting the coating into SiO_2 . The leftover SiO_2 accurately replicated the morphology of the GFs (Fig. 1c), indicating that the coating process produced conformal Si-containing layers covering the surfaces and even the edges of the GFs. When the precursor-impregnated GF powder was dried without microwave heating, no conformal layer was produced; instead, aggregates of particles were obtained.

TEM analysis showed that the coating thickness was approximately 8 nm (Fig. 2a). The EDS analysis indicated that the SGF powder contained O and Si at a weight ratio of 1 (± 0.23):1 (± 0.29). Both O and Si primarily existed within the deposited layer. TG analysis in air (Fig. 2b) showed that pristine GF was completely burned off at 800 °C, but the SGF sample retained 19% of its weight, which was due to the SiO_2 residue. Considering the EDS and TG data, the Si content within the coating layer was estimated to be 8.9 wt.%.

Fig. 3a illustrates a comparison of the first-cycle voltage plots of the GF and SGF electrodes. The first-cycle reversible charge capacity

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