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Efficient lithium storage of concave graphitic anode embedded with nanoconfined silicon

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ABSTRACT

This study reports the use of engineering nanocarbon film with confined silicon nanoparticles as an anode material for lithium-ion batteries. The unique "concave" graphitic nanostructure, prepared in porous templates with morphology of interconnected arrays, makes nanocarbon electrodes a good lithium-ion intercalation medium and, more importantly, robust nanocontainers to effectively confine high-capacity silicon nanoparticles for lithium-ion storage. Open structures of the concave nanocarbon increase the accessibility of Li ions, and allow Li ions to diffuse active materials. In addition, the highly textured concave pores allow the volume expansion of the silicon nanoparticles to be confined to the nanospace during lithium-ion insertion/extraction. The specific capacity of the nanoconfined silicon/nanocarbon anode reaches up to 2500 mAh/g at 0.5 A/g. After long cycling, the anode materials becomes even more stable, showing the invariant lithium-ion storage capacity as the charge-discharge rate is increased by 10 times from 2–20 A/g. The capacity is retained constantly after 200 charge-discharge cycles.

1. Introduction

Since launching of lithium-ion batteries (LIB) by Sony Corporation in early 1990 [1], they have been commercially used as one of the most heavily utilized energy sources in a wide variety of electronic devices such as cell phones, laptops, and future electric vehicles [2]. The capacity of the active electrode materials is one of the important parameters that determines the performance of the battery [3,4]. Most commercial Li-ion batteries employ graphite and other carbonaceous materials as anodes, which has excellent stability and low cost, but has a theoretical capacity limit at 372 mAh/g by forming a fully intercalated LiC_6 compound [5,6]. For anode materials, silicon (Si) is known to have the highest theoretical specific capacity (4200 mAh/g) [7–10], and is considered to be the active materials for the next generation lithium ion batteries. However it has the large volume change (>400%) during lithiation and delithiation causes pulverization, resulting in capacity loss in a high number of cycles [11,12]. Therefore, strategies to overcome mechanical failure in anode materials are required for commercial applications.

Recently, extensive researches into silicon based thin film, nanowires, nanoparticles, nanotubes and porous structures have shown very encouraging results when used as an anode material in lithium ion batteries [13–18]. It is known that decreasing the size of silicon materials to submicrometers or nanometers can solve some mechanical destruction problems during repeated insertion and extraction of lithium ions [19]. An ultrathin amorphous silicon film of 50 nm or less can provide the highest capacity of about 3750 mAh/g but the small mass limits the attainable cell capacity [17,20]. As the Si film thickness was increased to 250 nm, reversible capacity was only obtained at 3000 mAh/g for a few tens cycles before declining considerably [21,22]. To enable Si to work at high charge/discharge rates, it is therefore very important to have unique structure and properties such as large surface area (below 10 m^2/g for commercial anode materials), shorter Li-conduction distance, high electrical conductivity and tensile strength make them well suited as a critical component in novel anode material for enhanced lithium storage [19]. Particularly concave nanocarbon structure [23] with low aspect ratio is an ideal candidate to improve the electrochemical performance due to the effective diffusion through open structure, provision of nanospace for Si nanoparticles and complementation of electrical conductivity of silicon.

Here, we report the electrochemical properties of the concave nanocarbon films where structure and morphology are engineered

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through the porous templates and film transfer processes for lithium-ion battery negative electrodes, with the aim to obtain high lithiation capability and better overall performance. These nanocarbon films consists of arrays of periodic and interconnected concave morphologies of few layer graphitic structures and are used as nanospace for the Si nanoparticles. The present work also undertakes in order to understand the influence of morphological features of confined silicon/nanocarbon anode on the electrochemical performance. The unique anode, which is based the concave graphitic film and Si nanoparticles confined in its nanospace, have three notable features for the use as the effective electrode material in a lithium-ion battery. First, Li ion diffusion into the interior of the nanocarbons through the opened structures can shorten the diffusion length of the redox couple and provide rapid charge transport. Second, the exposed Si active materials in the direction of Li ion diffusion increase the accessibility of the electrode interior to the electrolyte, which ensures a high charge/discharge capacity. Finally, the nanoconfined Si system inside the carbon nanospace improves the cycle life by preventing volume expansion during electrochemical Li insertion/extraction. As a result, this novel structure can be a promising anode material for high performance lithium-ion batteries.

2. Methods

2.1. Fabrication of concave nanocarbon films and confined Si nanoparticles

A concave nanostructure with an interconnected thin graphitic texture, high specific surface area, and uniform nanopore was obtained using highly engineered anodic aluminum oxide (AAO) nanochannels as templates. The nanoporous alumina templates were prepared using a standard electrochemical anodization process [23,24]. A two-step anodization process was performed at 45 V in 3% oxalic acid ($C_2H_4O_2$) solution, and the second anodization was carried for 20 s to fabricate short nanochannels with low aspect-ratio nanostructures [23,24]. Then, AAO templates were soaked in a 5% phosphoric acid (H_3PO_4) solution for 1 h at room temperature to widen the pore size to 90 nm. The graphitic nanostructures were synthesized by using a chemical vapor deposition (CVD) process at 650 °C using 10% acetylene (C_2H_2) gas as a carbon source. The concave graphitic films were transferred to polydimethylsiloxane (PDMS) and released by dissolving aluminum in 3.4 g copper chloride and 100 mL hydrochloric acid mixture solution with 100 mL deionized water. Then, the graphitic film on the PDMS, bottom parts of as-synthesized graphitic film, was coated with copper and transferred to a copper film used as a current collector. After that, the PDMS polymer was removed in acetone solution to produce concave graphitic carbon electrodes. Finally, the Si nanoparticle arrays were formed in the concave graphitic nanospace by the solution method. For this, Si nanoparticles were dispersed in an ethanol, and the template with graphite nanopores, in which all air pockets were removed in a vacuum, was dipped in a Si solution. The solvent was slowly evaporated and the template was then heated at 900 °C in an argon atmosphere. This process was repeated several times to increase the amount of the Si loading. The total amount of silicon nanoparticles in the nanospace was about 33 $\mu g/cm^2$ in our experiment.

2.2. Fabrication of lithium ion battery cells

Electrochemical coin cells were assembled using lithium metal foil (99.9%, Alfa Aesar) as the cathode and concave graphitic film/silicon nanoparticles as the anodes. The electrodes were separated by a Celgard 2500 battery membrane soaked in a liquid electrolyte solution consisting of 1.0 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, volume ratio) (Aldrich) solution. CR2032 coin cells were assembled in an argon-filled glove box where the oxygen and moisture content were both maintained below 0.01 ppm.

2.3. Characterization of nanocarbon-Si based devices

Electrochemical properties of the concave nanocarbon/Si-based Li-ion battery were analyzed using cyclic voltammetry (CV), galvanostatic charge-discharge (CD), Impedance spectroscopy (EIS) and cyclic stability. The electrochemical characterizations for the anodic materials were carried out by Potentiostat at room temperature. The CV curves of the devices were measured between 0 and 3 V at scan rates of 1 mVs^{-1}. The cells were galvanostatically charged and discharged with cut-off potentials of 2.8 and 0.2 V. Cycling rates for the concave graphitic active materials were calculated based on the theoretical capacity of graphite, and 1C corresponds to a specific current of 372 mA/g [25]. The cycling rate capability and efficiency for the Si/nanocarbon-based devices were carried at current density of 0.5–20 A/g. Before EIS measurement, the cell was held at the designated potential until the current fell below 0.372 mA/g. The amplitude of the AC signal applied to the electrodes was 5 mV and the frequency was varied from 100 kHz–0.01 Hz.

3. Results and discussion

3.1. Concave nanocarbon films and confined Si nanoparticles

We have fabricated a nanoconfined Si/nanocarbon-based battery device by using highly porous concave nanocarbon system. Fig. 1 shows schematics of the fabrication process of silicon/nanocarbon-based electrode and microscope images of the concave nanocarbon structures. As shown in the schematics of Fig. 1a, the concave nano-structure films are transferred to polydimethylsiloxane (PDMS) and released by dissolving aluminum in copper chloride and hydrochloric acid mixture solution, and then the aluminum oxide was dissolved in the phosphoric acid to expose bottom parts of as-synthesized graphitic film. The surface of the convex bottom parts was transferred onto a copper film that is used as a current collector, and the silicon nanoparticles were aligned inside the open concave nanocarbons, where the PDMS was removed by the acetone solution. Fig. 1b and c show scanning electron microscope (SEM) images of the top and side of the concave nanocarbon structures fabricated by two-step anodization. The pore size was about 90 nm and was formed very uniformly. By connecting the highly dense and ordered arrays of concave nanocarbons with continuous graphitic layer, large area porous nanostructured films ideal for energy storage electrodes are achieved. As shown in the side image of Fig. 1c, the ratio of length to pore is about 1.5 and is regularly arranged. The concave nanocarbons are then utilized as dual functions in battery devices where a graphitic layer exposed to the electrolyte acts as active electrodes and concave morphologies work as containers to inhibit the volume expansion of silicon nanoparticles. As shown in transmission electron microscopy (TEM) image (Fig. 1d), the open nanoscale concave geometry as well as its graphitic nature make short channel nanocarbons robust nanocontainers which prevent the change in volume during battery charge/discharge cycles. In the Raman spectrum by 532 nm wavelength in the Fig. 1e, prominent features at 1333 cm^{-1} indicative of the disorder (D) peak usually assigned to the K-point phonons of A_{1g} symmetry typical in polycrystalline graphite, and at 1605 cm^{-1} (G peak), which is com-