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Ionic liquid electrodeposition of germanium/carbon nanotube composite anode material for lithium ion batteries

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ABSTRACT

Germanium nanoparticles (Ge-NPs) are combined with carbon nanotubes (CNTs) to fabricate anodes for Li-ion batteries through the electrodeposition of Ge from ionic liquids on the surface of the CNTs. The latter are electrophoretically deposited on a copper collector at room temperature without any binders, with a good electrical contact achieved nonetheless between the active material and the collector. In the composite, the CNTs readily accommodate the large volume changes of the Ge particles during cycling. The composite exhibits better reversible lithiation–delithiation behavior, an improved rate performance, and also has better electrochemical properties than Ge-NPs. The nanocomposite anode developed here delivers a reversible capacity of 810 mA h/g after 100 cycles at 0.2 C.

1. Introduction

Si and Ge based materials due to their high theoretical capacities of 4200 [1] and 1600 [2] mA h/g, have emerged as alternative high-energy and high-power anode candidates for replacement of currently employed graphite electrodes in advanced Li ion batteries (LIB). Although Ge has gained increased attention because of its faster lithium ion diffusivity and higher electrical conductivity [3], it is subject to large volume expansion, which results in the electrode materials becoming detached from the current collector, leading to conductivity losses during cycling [4]. To avoid this problem many nanoscale materials have been made for example, nanoparticles [5], nanorods [6] and lines [7], nanosprings [8], nanotubes [9], and nanostructure arrays [10]. A buffer phase can also be introduced to cushion the tremendous volume changes. CNTs are particularly attractive in this context, as their linear structure facilitates electron migration [11] and they can buffer the volume expansion of active particles [12]. Indeed, Si [13], Fe_2O_3 [14], and SnO_2 [15] CNTs, and Ge MWCNTs [16] have been investigated as anode materials. A number of approaches are possible for the preparation of Ge-based materials, notably chemical vapor deposition [17], electron beam evaporation [18], and magnetron sputtering [19]. Although anodes prepared in those methods have shown impressive electrochemical performances, the preparation routes mentioned above are too complicated or require too high reaction temperatures. An efficient, low-temperature, and environmentally friendly synthesis route for composite anode materials is therefore of substantial interest.

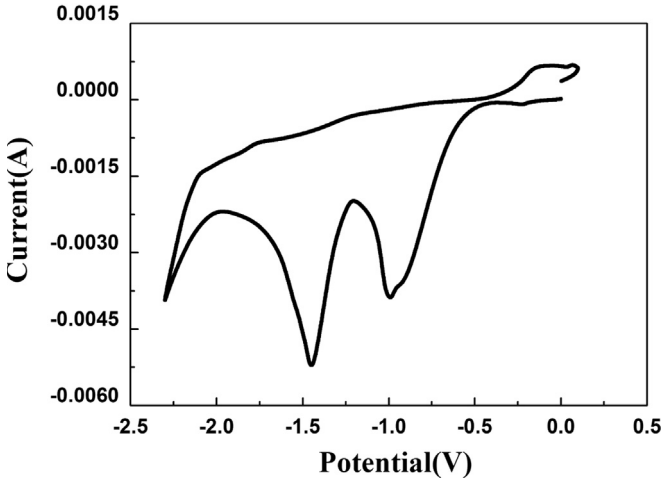

Fig. 1. Cyclic voltammogram for the electrodeposition of Ge on CNTs surface. Scan rate: 10 mV/s.

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In this study, a Ge-NP/CNTs composite was carefully designed as an anode material for LIB. The composite electrode was coated with Ge NPs using ionic liquid electrodeposition, a process that can be conducted at room temperature [20] and that allows the thickness of the semiconductor layer to be controlled simply by varying the current intensity and the duration of the deposition process.

2. Experimental

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide, ($EmimTf_2N$, 99%) was purchased from IOLITEC and used after drying under vacuum at 100 °C for 24 h. $GeCl_4$ (99.998%) was purchased from Alfa Aesar. The CNTs were functionalized by dissolution in a mixed acid of concentrated H_2SO_4 and HNO_3 for 3 h. For the formation of CNTs films on copper foil, 20 mg of CNTs and 4 mg of $Ni(NO_3)_2 \cdot 5H_2O$ were added to 50 mL of isopropyl alcohol. Cathodic electrophoretic deposition of the well-dispersed CNTs suspension was then performed under a constant voltage of 100 V for 2 min. Electrochemical experiments were performed in an argon-filled glove box with water and oxygen contents below 2 ppm (Vigor Glove Box, Suzhou, China). A three-electrode system was assembled with a CNTs-covered copper-foil working electrode, a Pt ring counter electrode, and an Ag quasi-reference electrode. After the experiments, the deposit was rinsed with isopropanol. Morphological characterization was performed with a Hitachi S-4800 scanning electron microscope operating at 20 kV. Raman spectra were measured on a Renishaw inVia micro-Raman spectrometer with the 633 nm laser. The electrochemical properties of the composite electrodes were tested in 2016 coin-type half-cells prepared in a glove box as mentioned before. The half-cells were assembled using a Ge-NP/CNTs cathode, a Li metal-foil anode, separator film (Celgard

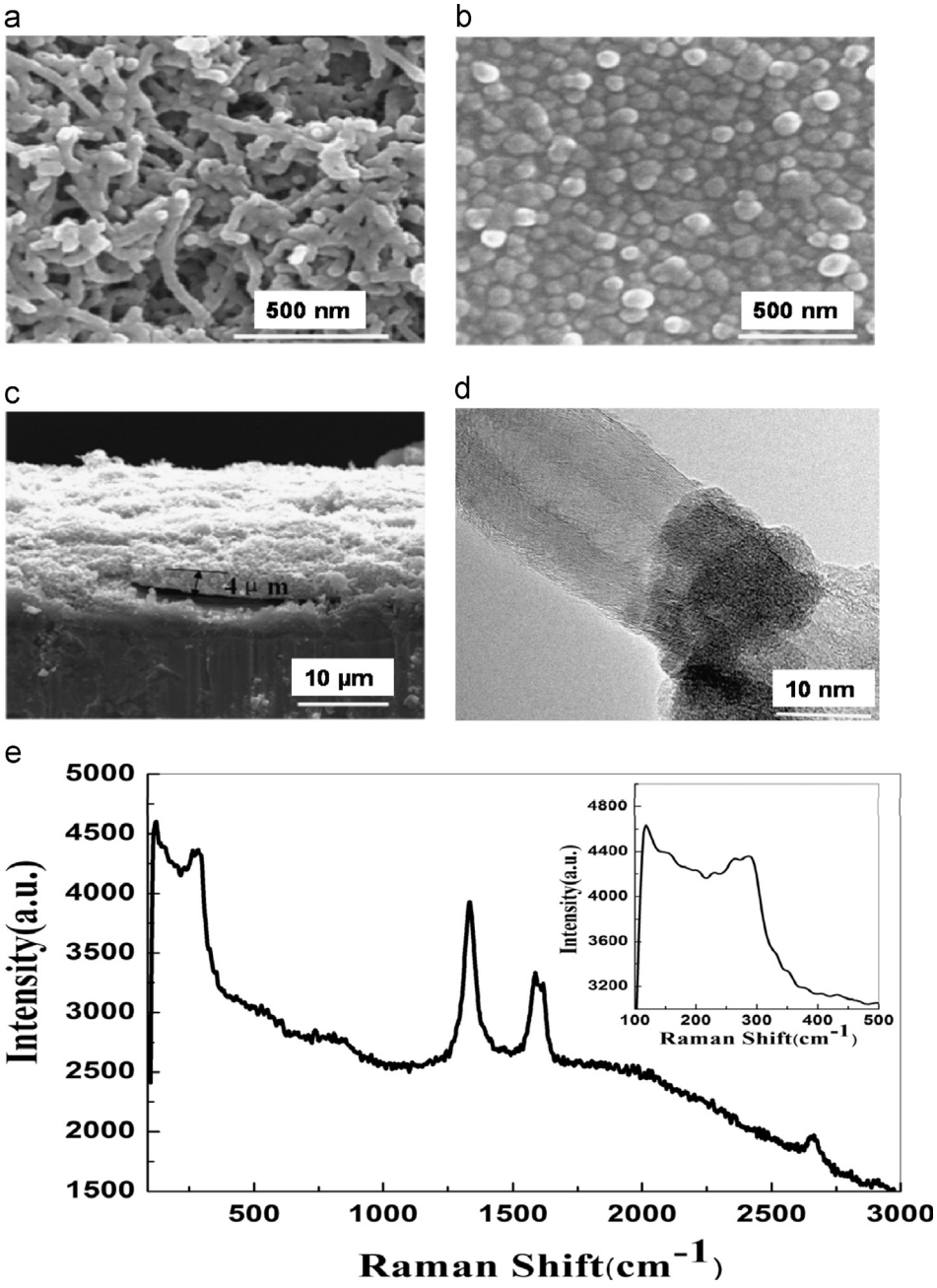

Fig. 2. SEM images of (a) a CNTs layer and (b) the surface and (c) the cross-section of the Ge-NP/CNTs composite. (d) The HRTEM image of Ge-NP/CNTs composite. (e) Raman spectrum of the Ge-NP/CNTs composite.