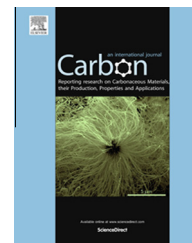


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Germanium coated vertically-aligned multiwall carbon nanotubes as lithium-ion battery anodes

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ABSTRACT

The performance of polycrystalline and amorphous germanium (Ge) as anode active materials for lithium-ion batteries was studied systematically. Polycrystalline Ge on vertically-aligned multiwall carbon nanotube (MWCNT) arrays (MWCNT/c-Ge) and amorphous Ge on the arrays (MWCNT/a-Ge) were fabricated using a low pressure chemical vapor deposition system and a radio frequency sputtering system, respectively. The vertically-aligned MWCNT arrays were used as a platform to minimize pulverization problem. The MWCNT/a-Ge had a specific capacity of 1096.1 mA hg⁻¹ at the rate of 162.4 mA g⁻¹ at the 100th cycle. In comparison, the MWCNT/c-Ge only showed a specific capacity of 730.2 mA hg⁻¹ at the rate of 162.4 mA g⁻¹ at the 100th cycle. The MWCNT/a-Ge sample showed better performances as the MWCNT/a-Ge skipped the electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation.

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1. Introduction

Germanium (Ge) is a promising anode active material for lithium-ion batteries. It has the following merits: (1) High Li-ion diffusion coefficient. It was reported that the diffusivity of Li in Ge might be over 400 times higher than that of Li in silicon (Si) at room temperature [1,2]. (2) High electrical conductivity. The Ge has a band gap of 0.67 eV which is smaller than that of Si of 1.11 eV [3]. (3) High specific capacity. The Ge theoretical specific capacity of 1624 mA hg⁻¹ for Li₂₂Ge₅ phase or 1384 mA hg⁻¹ for Li₁₅Ge₄ phase is higher than that of graphite anode of 372 mA hg⁻¹ [2,4].

Ge belongs to the alloying-type anode. It has the problems of agglomeration and pulverization during lithiation/delithia-

tion that result in cracking and/or delamination that lead to poor cycle performance. Many approaches were used to tackle these problems and improve the performance of Ge anode, such as Ge nanoparticles [5,6], Ge nanowires [7–10], Ge nanotubes [11,12], Ge-carbon composites [13–24], Ge-graphene composites [25–32], Ge thin-film [2,33–35], and other unique structures [36–41]. Notable results were produced by J. Cho group [5,18,27], B.A. Korgel group [10,37], H.Y. Tuan group [8], M.J. Park group [24], etc. However, most studies in the literature used complicated process/treatment. Also, to our knowledge, no one has reported a systematic study of amorphous and polycrystalline Ge on the same platform. Here, we coat Ge active material onto the vertically-aligned multiwall carbon nanotube (MWCNT) arrays to prevent agglomeration

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and minimize pulverization. Vertically-aligned MWCNT arrays had been proved as promising current collectors especially for anode active materials that undergo large volume change during lithiation/delithiation [42,43]. The vertically-aligned MWCNT arrays have several advantages such as: (1) fast electron conduction paths to the coated active material, (2) fast lithium-ion transports due to short lithium-ion diffusion distance of the active material and high coverage of electrolyte to the active material and (3) excellent buffers that minimize the pulverization of active material during lithiation/delithiation.

In this study, amorphous Ge coated vertically-aligned MWCNT arrays (MWCNT/a-Ge) and polycrystalline Ge coated vertically-aligned MWCNT arrays (MWCNT/c-Ge) anodes were fabricated. The performance of the anodes was studied in details.

2. Experimental

2.1. Sample preparation

2.1.1. Fabrication of vertically-aligned MWCNT arrays

The vertically-aligned MWCNT arrays were grown on 16.2 mm diameter stainless steel (SS) disks. Initially, SS disks were cleaned in an ultrasonic bath for 30 min in propan-2-ol and then dried inside vacuum oven at 353.15 K for 4 h. Titanium-titanium nitride barrier layer was deposited using direct-current sputtering system of Elite Sputter. Afterward, 20 nm nickel (Ni) catalyst was deposited using electron-beam (E-beam) evaporation system of Edwards E-Beam Evaporation. After Ni deposition, the samples were placed inside the chamber of a plasma enhanced chemical vapor deposition of Nanoinstruments Ltd system, with the base pressure of typically 3 Pa. The ammonia gas was flowed to maintain a pressure of 8.7×10^2 Pa while the temperature was rapidly increased to 1073.15 K to dewet the Ni thin film become Ni nanoparticles. Subsequently, 120 Watt plasma was switched-on and the acetylene gas was flowed to grow the vertically-aligned MWCNT arrays. The deposition time was 10 min. The mass loading was measured by Mettler Toledo XP26 DeltaRange balance that has readability of 0.002 mg. The average mass of CNTs was 0.12 mg cm^{-2} .

2.1.2. Fabrication of MWCNT/c-Ge

Polycrystalline Ge was deposited on vertically-aligned MWCNT platform using low pressure chemical vapor deposition (LPCVD) system of Semco LPCVD with base pressure of 1.33 Pa. The temperature was increased to 803.15 K with ramping up time of 30 min. The deposition was performed by flowing 88 sccm of 1% GeH₄ in H₂ at deposition pressure of 83.1 Pa. Mass loading of MWCNT/c-Ge was 0.33 mg cm^{-2} . The weight percentage of crystalline Ge in MWCNT/c-Ge was 74%.

2.1.3. Fabrication of MWCNT/a-Ge

Amorphous Ge was deposited on vertically-aligned MWCNT platform using radio frequency (RF) sputtering of Denton sputter system using 99.999% pure Ge target. The base pressure was 8.7×10^{-4} Pa. Then, argon was flowed at 50 sccm

and pressure was maintained at 4.2 Pa. The deposition was performed with 100 watts plasma power and carried out at room temperature. Mass loading of MWCNT/a-Ge was 0.37 mg cm^{-2} . The weight percentage of amorphous Ge in MWCNT/a-Ge was 76%.

2.2. Physical characterization

The MWCNT/c-Ge and MWCNT/a-Ge were characterized using X-ray Diffraction (XRD) of Siemens D5005 XRD with Cu K α of 0.1540 nm and Raman Spectroscopy of WITec with 532 nm excitation wavelength. The morphology of the samples was investigated using Scanning Electron Microscopy (SEM) of LEO-SEM with accelerating voltage of 5.00 kV. Transmission Electron Microscopy (TEM) was performed using JEOL 2010 with accelerating voltage of 200 kV.

2.3. Electrochemical characterization

The MWCNT/c-Ge and MWCNT/a-Ge, Celgard-2300 separators, liquid electrolytes and pure Li metals were assembled in 2032-type coin cells inside an argon glove box that had oxygen and moisture level of less than 5 ppm. The liquid electrolyte used was 1 M lithium hexafluorophosphate dissolved in 1:1 by volume of ethylene carbonate and diethyl carbonate. Since MWCNT/c-Ge and MWCNT/a-Ge were tested in a half-cell configuration where the lithium metal serves as an anode, we refer them as MWCNT/c-Ge and MWCNT/a-Ge samples, respectively. Battery cycle life testing was performed using Neware battery tester at the rate of 0.1 C (1 C = 1624 mA g^{-1}) for both MWCNT/c-Ge and MWCNT/a-Ge. The potential window was 1.2–0.01 V vs. Li/Li⁺. All capacities were normalized with Ge mass. Cyclic voltammetry (CV) was performed using Autolab machine at scan rate of 0.1 mV s^{-1} .

3. Results and discussion

Amorphous and polycrystalline Ge were deposited using RF sputtering at room temperature and LPCVD at 803.15 K, respectively. Ge has a melting temperature (T_m) of 1211.4 K. Ge was deposited by RF sputtering at a relatively low deposition temperature (T_{dep}) of 298.15 K, with $T_{dep}/T_m = 0.25$, in MWCNT/a-Ge sample. At low T_{dep}/T_m ratio, Ge adatoms have low mobility and self-diffusion that promote the formation of amorphous Ge [44]. The LPCVD at relatively high T_{dep} of 803.15 K, with $T_{dep}/T_m = 0.66$, provided enough energy for Ge adatoms' nucleation and self-diffusion to form polycrystalline Ge in MWCNT/c-Ge sample [44]. This was evidenced by using XRD, Raman and TEM analysis. The XRD pattern in Fig. 1a shows MWCNT/c-Ge sample has peaks at 27.23°, 45.28°, and 53.67° that correspond to Ge (111), Ge (220), and Ge (311) with PDF No. 4-545. In contrast, the MWCNT/a-Ge only shows the SS substrate peaks. These indicate amorphous nature of the Ge in MWCNT/a-Ge and higher degree of crystallinity in MWCNT/c-Ge. The Raman data at Fig. 1b shows the sharp peak at about 296.54 cm^{-1} appeared for MWCNT/c-Ge sample that corresponds the crystalline peak of bulk Ge of 300.4 cm^{-1} [45]. In comparison, a broad peak at

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