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

Rahmat Agung Susantyoko^{a,b}, Xinghui Wang^b, Leimeng Sun^b, Kin Leong Pey^c, Eugene Fitzgerald^{a,d} and Qing Zhang^{*a,b}

^a Advanced Materials for Micro- and Nano- Systems, Singapore-MIT Alliance, Singapore 637460, Singapore.

^b School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore.

^c Singapore University of Technology and Design (SUTD), 20 Dover Drive, Singapore 138682, Singapore.

^d Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

* Corresponding author. Tel.: +65 6790 5061. Fax: +65 6793 3318. E-mail address: eqzhang@ntu.edu.sg (Q. Zhang).

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 mAhg⁻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 mAhg⁻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.

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 mAhg⁻¹ for Li₂₂Ge₅ phase or 1384 mAhg⁻¹ for Li₁₅Ge₄ phase is higher than that of graphite anode of 372 mAhg⁻¹. [2, 4]

Ge belongs to the alloying-type anode. It has the problems of agglomeration and pulverization during lithiation/delithiation 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 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 minutes in propan-2-ol and then dried inside vacuum oven at 353.15 K for 4 hours. 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 minutes. 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 mgcm^{-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 minutes. 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 mgcm⁻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 mgcm⁻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 mVs $^{-1}$.

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 ~289 cm $^{-1}$ with shoulder at ~265 cm $^{-1}$ were observed for MWCNT/a-Ge that correspond to amorphous form of Ge.[45] The MWCNT peak was not detected in XRD, but detected in the

Raman as the Raman scattering has higher sensitivity to carbon peaks. The peak at about 1350 and 1585 cm^{-1} corresponds to the D and G band of MWCNT.[46, 47] The TEM further evidenced the amorphous Ge coating in MWCNT/a-Ge and polycrystalline Ge coating in MWCNT/c-Ge. Fig. 1c shows the MWCNT/a-Ge has amorphous Ge. The Fast Fourier Transform (FFT) in Fig. 1d only show the spots from the carbon nanotubes that correspond to 0.34 nm lattice spacing. Fig. 1e shows the crystalline nature of the MWCNT/c-Ge. The FFT of MWCNT/c-Ge shows the spots from Ge with lattice spacing of 0.20 nm that correspond to Ge (220) with polycrystalline structure.

Fig. 1 (a) The XRD spectrum and (b) Raman spectrum of MWCNT/a-Ge and MWCNT/c-Ge. (c) The high resolution TEM image of MWCNT/a-Ge (d) The FFT of high resolution TEM image of MWCNT/a-Ge (e) The high resolution TEM image of MWCNT/c-Ge (f) The FFT of high resolution TEM image of MWCNT/c-Ge.

The MWCNT arrays with the average length of 2.5 μm , and average diameter of 179 nm and spacing of 289 nm is shown in **Fig. 2a** and 2b. We deposited similar Ge mass loading for both MWCNT/a-Ge and MWCNT/c-Ge. The MWCNT/a-Ge is shown in Fig. 2c and 2d.

1 The average diameter of the top part of MWCNT/a-Ge was 623 nm. Polycrystalline Ge was
2 deposited as shown in Fig. 2e and 2f. The average diameter MWCNT/c-Ge was 269 nm. Both
3 MWCNT/a-Ge and MWCNT/c-Ge have spacing. Both were directly connected to the
4 MWCNT current collectors. As shown in Fig. 2g, the amorphous Ge mainly coated on the top
5 of MWCNT arrays in the MWCNT/a-Ge sample. MWCNT/a-Ge shows relatively smooth
6 coating, while the MWCNT/c-Ge shows particles of polycrystalline Ge attached to the
7 MWCNT, see Fig. 2g. Although Ni catalyst was not detected in XRD, it was evident in the
8 TEM image of thin-coated MWCNT/a-Ge as shown in Fig. 2h.

9 **Fig. 2** (a) Top-view and (b) tilted-view SEM image of vertically-aligned MWCNT arrays. (c)
10 Top-view and (d) tilted-view SEM image of MWCNT/a-Ge. (e) Top-view and (f) tilted-view

SEM image of MWCNT/c-Ge. (g) The illustration of vertically-aligned MWCNT arrays, MWCNT/a-Ge and MWCNT/c-Ge. (h) Ni catalyst was shown in the TEM image.

The cycle performance of MWCNT/c-Ge and MWCNT/a-Ge is shown in **Fig. 3a** and **3b**, respectively. Fig. 3c and 3d show the voltage profile of the MWCNT/c-Ge and MWCNT/a-Ge, respectively. MWCNT/c-Ge showed first cycle discharge and charge capacity of 955.6 and 710.8 mAhg⁻¹, respectively. It became stable from 2nd to 100th cycle with specific capacity decreasing from 774.3 to 730.2 mAhg⁻¹. The stability could be attributed to MWCNT supporting structures that minimized pulverization of the active Ge.[42] After 100 cycles, the discharge specific capacity of MWCNT/c-Ge was 730.2 mAhg⁻¹ at 0.1 C. MWCNT/a-Ge showed better performance. MWCNT/a-Ge showed first cycle discharge and charge capacity of 1725.8 and 1234 mAhg⁻¹ in Fig. 3b. The specific capacity of MWCNT/a-Ge was 1096.1 mAhg⁻¹ at 0.1 C after 100 cycles. The first cycle's Coulombic efficiency of MWCNT/a-Ge and MWCNT/c-Ge of 73.5 and 71.3 % in average, respectively, were higher than most reports [7, 12, 17, 21, 23, 24, 28-32, 37, 38] but still lower than reference [20]. The irreversible capacity during the first cycle was probably due to the formation of solid electrolyte interphase (SEI) layer at high potential. The MWCNT's contribution was negligible as shown in the Fig. 3a and 3b. The specific capacity of MWCNT normalized to Ge mass was only ~33 mAhg⁻¹ after 100 cycles, less than 5 % contribution to the structure. The areal capacities after 100 cycles of MWCNT/a-Ge and MWCNT/c-Ge were 0.41 and 0.24 mAhcm⁻², respectively. The volumetric capacities after 100 cycles of MWCNT/a-Ge and MWCNT/c-Ge were 1623 and 952 mAhcm⁻³, respectively. The specific and volumetric capacity of both MWCNT/a-Ge and MWCNT/c-Ge were higher than the theoretical specific and volumetric capacity of graphite of 372 mAhg⁻¹ and 830 mAhcm⁻³. [48]

Fig. 3 The cycle performance of (a) MWCNT/c-Ge and (b) MWCNT/a-Ge at the rate of 0.1 C for 100 cycles. The voltage profile of (c) MWCNT/c-Ge and (d) MWCNT/a-Ge.

The morphology of the samples after 1 cycle and 100 cycles were investigated by opening the cells in the delithiated state, followed by washing in propylene carbonate, acetone and isopropyl alcohol, consecutively and then vacuum annealing at 333.15 K. The SEM images of MWCNT/a-Ge and MWCNT/c-Ge in **Fig. 4** confirmed the stability of the structure. Fig. 4a and 4b show the MWCNT arrays in both samples were intact. They formed bundles probably because of the drying effect. Fig. 4c and 4d show that after 100 cycles, both MWCNT/a-Ge and MWCNT/c-Ge have a stable, thick, and conformal SEI. MWCNT/a-Ge and MWCNT/c-Ge showed inter-cracks between the active materials in Fig. 4c and 4d, but remained stable across a large area, as shown in Fig. 4e and 4f. These inter-cracks could originate from strain relaxation of the structures during lithiation/delithiation.[42] Fig. 4e and 4f show that the inter-cracks of MWCNT/a-Ge were lesser in extent than those of MWCNT/c-Ge.

Fig. 4 Top-view SEM images of (a) MWCNT/a-Ge after 1 cycle, (b) MWCNT/c-Ge after 1 cycle, (c) MWCNT/a-Ge after 100 cycles and (d) MWCNT/c-Ge after 100 cycles. Top-view SEM images at lower magnification of (e) MWCNT/a-Ge after 100 cycles and (f) MWCNT/c-Ge after 100 cycles.

The CV of the samples was performed at the scan rate of 0.1 mVs^{-1} and potential window from 0.01 to 1.2 V. A control sample of MWCNT arrays without Ge coating had small/negligible signal compared to **Fig. 5a** and **5b**. MWCNT/a-Ge showed a strong peak at around 0.01 V in the first cathodic scan, as shown in Fig. 5a. In contrast, MWCNT/c-Ge showed strong peaks at around 0.27 and 0.14 V and no peak at 0.01 V, as shown in Fig. 5b. The peaks at 0.27 and 0.14 V could be attributed to lithiation of polycrystalline Ge into amorphous Li_xGe ($0 < x < 3.75$)[35, 49-51] and related to electrochemically-driven solid-state amorphization of polycrystalline Ge.[50] The peak at 0.01 V could be attributed to crystallization of amorphous Li_xGe ($0 < x < 3.75$) to crystalline $\text{Li}_{15}\text{Ge}_4$.[49, 51] The first cycle's cathodic scan of both samples was different, probably because MWCNT/a-Ge did not go through electrochemically-driven solid-state amorphization. Thus, less structural change

was expected during first lithiation of MWCNT/a-Ge. During the first anodic scan, MWCNT/a-Ge showed a broad peak at around 0.44 V and a shoulder at around 0.55 V. In contrast, the MWCNT/c-Ge showed a shoulder at 0.44 V and a sharp peak at 0.55 V. The difference in the first cycle's anodic scan was probably because of different structural ordering and history of lithiation during the previous cathodic scan.[51]

Fig. 5 The CV of (a) MWCNT/a-Ge and (b) MWCNT/c-Ge at first, second and third cycle. (c) The specific capacity of amorphous Ge [2, 6, 11, 12, 33, 34, 36, 41, 52] and crystalline Ge [5, 7-10, 13-15, 17-32, 37-39] from literature. (d) The rate capability of MWCNT/a-Ge. (e) The cycle performance of MWCNT/a-Ge at the rate of 1 C for 100 cycles. (f) The cycle performance of MWCNT/a-Ge at various Ge mass loading.

Fig. 5a shows during the second to third cathodic scan of MWCNT/a-Ge, the peak at about 0.16 and 0.34 V and shoulder at about 0.45 V increased. During the anodic scan of MWCNT/a-Ge, the peak at around 0.42 V and shoulder at around 0.55 and 0.75 V were found. From the second to third cathodic scan, the MWCNT/c-Ge showed the peaks at around 0.14, 0.35 and 0.5 V, as shown in Fig. 5b. The anodic scan of MWCNT/c-Ge showed shoulder at around 0.42 V, peak at around 0.55 V and shoulder at around 0.75 V. The first

cathodic scan of MWCNT/c-Ge was different with its second and third cathodic scan, while the MWCNT/c-Ge first anodic scan remains the same as the second and third anodic scan, suggesting that polycrystalline Ge was amorphized during the first cathodic scan, and did not recover to polycrystalline structure during subsequent anodic scan.[50]

Although MWCNT/c-Ge sample eventually had amorphous Ge, the CV of MWCNT/c-Ge at 2nd and 3rd cycle showed different dominant anodic scan peak than that of MWCNT/a-Ge at 2nd and 3rd cycle. The differences were probably because: 1) The amorphous Ge of MWCNT/c-Ge at 2nd and 3rd cycle had different structures and properties than that of MWCNT/a-Ge due to different fabrication process [53, 54] and different 1st cycle's lithiated state [49]. It is well-known that the properties of amorphous materials are significantly dependent to fabrication process and parameter. [53, 54] For example, in the microelectronics field, amorphous SiO₂ has different values of density and dielectric constant depending on a) the fabrication process such as chemical vapor deposition or thermal oxidation and b) the fabrication parameter such as precursor and temperature.[55] Here, the amorphous Ge of MWCNT/a-Ge was fabricated by sputtering method followed by lithiation/delithiation, while the amorphous Ge of MWCNT/c-Ge was fabricated by LPCVD method followed by lithiation/delithiation. It was also reported that the delithiation peaks are significantly dependent on the lithiated states.[49] 2) The amorphous Ge in MWCNT/c-Ge and MWCNT/a-Ge had different shape and thickness, as illustrated in Fig. 2g, that resulted in different stress that affected the CV peaks. [35]

The specific capacities of MWCNT/c-Ge at 2nd and 3rd cycle were lower than that of MWCNT/a-Ge, despite MWCNT/c-Ge sample had amorphous Ge from 2nd cycle onward. It was probably because 1) MWCNT/c-Ge has amorphous Ge that differs in properties, such as stoichiometry, density, porosity, stress, defect density and resistivity, than those of MWCNT/a-Ge. This might affect the electrochemical performance of the amorphous Ge in

MWCNT/c-Ge. 2) The polycrystalline Ge did not completely reacted with Li-ion, resulted in incomplete conversion to amorphous Ge during delithiated state. Here, we used the initial mass of polycrystalline Ge to calculate the specific capacity of MWCNT/c-Ge of all cycles. From 2nd cycle onwards, since the mass of amorphous Ge in MWCNT/c-Ge was lower than the initial mass of polycrystalline Ge, the calculated specific capacity could be underestimated. 3) The history of electrochemically-driven solid-state amorphization during first lithiation is considered detrimental to the subsequent cycles' specific capacity.[56] This is analogous to the pulverization and/or delamination problems of crystalline Si during first cycle.[49] However, crystalline Ge was reported to have less pulverization than crystalline Si due to weak anisotropy of lithiation front.[4]

The CV peak during cathodic and anodic scan in Fig. 5a and 5b could be translated into potential plateau during lithiation and delithiation, respectively, in Fig. 3c and 3d. Since MWCNT/a-Ge has the lower peak at 0.42 V compared with the peak at 0.55 V of MWCNT/c-Ge during the anodic scan, MWCNT/a-Ge could favor higher energy density than MWCNT/c-Ge when paired with cathode active material such as LiCoO₂. However, this condition only last for about 50 cycles.

Our finding can be summarized as follows: 1) MWCNT/a-Ge has higher specific capacity than MWCNT/c-Ge after 100 cycles; 2) Both MWCNT/a-Ge and MWCNT/c-Ge have a stable SEI film after 100 cycles; 3) the lower peak during initial anodic scan in MWCNT/a-Ge favor higher energy density than MWCNT/c-Ge when paired with cathode materials.

Amorphous Ge has preferable characteristics when designing Ge-based anodes. Amorphous Ge was better than polycrystalline Ge mainly because MWCNT/a-Ge skipped electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation.[50] Also, the synthesis of amorphous Ge generally requires low temperature which

may offer benefit of low processing cost. Our finding was consistent with the majority of reports of Ge based anodes, as shown in Fig. 5c. Most of amorphous Ge based anodes have specific capacity above 1000 mAhg⁻¹. [2, 6, 11, 12, 33, 34, 36, 41, 52] On the contrary, most of the crystalline Ge based anodes have specific capacity below 1000 mAhg⁻¹. [14, 15, 17, 19-23, 25, 26, 29, 30, 32, 38] Crystalline Ge based anodes could only have specific capacities comparable to amorphous Ge based anodes when processed with special treatments, say few-layer graphene coating [27, 28, 31], alkanethiol passivation [8], formation of Ge_{0.95}Sn_{0.05} [39], use of fluoroethylene carbonate based electrolyte [10, 37], deployment of unique structure such as single crystalline Ge nanowires [7, 9, 13], 3D porous Ge assembly [5], and Ge nanoparticles–carbon core–shell nanostructure [18, 24], etc. In comparison, amorphous Ge has more relaxed requirements to achieve a similar high performance.

Fig. 5d and 5e show that MWCNT/a-Ge has a good rate capability. Different charge and discharge rates were programmed each for 5 cycles at the rate of 0.1, 0.5, 1, 2, and 4 C (1 C = 1624 mA g⁻¹) in Fig. 5d. MWCNT/a-Ge sample showed a relatively stable specific capacity of 1315.1, 1158.4, 1120.1, 1049.1 and 906 mAhg⁻¹ at the rate of 0.1, 0.5, 1, 2, and 4 C, respectively. After the rate had returned back to 0.1 C for 5 cycles, MWCNT/a-Ge showed a significant recovery at a specific capacity of 1246.1 mAhg⁻¹. Fig. 5e shows MWCNT/a-Ge specific capacity at the 100th cycle of 957.2 mAhg⁻¹ were achieved at the rate of 1 C.

The performance of MWCNT/a-Ge was dependent to the mass loading. Fig. 5f shows the effect of Ge mass loading to the cycle performance of MWCNT/a-Ge. The specific capacities at the rate of 0.1 C after 30 cycles were 1489.2, 1376.5 and 1177.5 mAhg⁻¹ for Ge mass loading of 0.07, 0.18 and 0.37 mgcm⁻², respectively. MWCNT/a-Ge with lower mass loading had a higher specific capacity because thinner Ge layer and larger Ge spacing allow better ionic and electronic conductance [57] as well as lower stress that reduces the pulverization and/or delamination problems [58]. The MWCNT/a-Ge with 0.37 mgcm⁻² mass

loading had the highest areal capacity of 0.44 mAhcm^{-2} compared to 0.10 and 0.25 mAhcm^{-2} of MWCNT/a-Ge with 0.07 and 0.18 mgcm^{-2} mass loading, respectively. In this case, the mass loading was not optimized. One can find an optimized mass loading with a good balance of specific and areal capacities.

4. Conclusion

We fabricated MWCNT/a-Ge and MWCNT/c-Ge using RF sputtering at room temperature and LPCVD at 803.15 K , respectively. Our MWCNT/a-Ge had a specific capacity of 1096.1 mAhg^{-1} at the rate of 162.4 mAg^{-1} for 100 cycles. In contrast, MWCNT/c-Ge had a specific capacity of 730.2 mAhg^{-1} at the rate of 162.4 mAg^{-1} for 100 cycles. Vertically-aligned MWCNT arrays play a role of minimizing pulverization of Ge coatings in both samples. Our MWCNT/a-Ge had better performances than MWCNT/c-Ge as amorphous Ge coating could skip the electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation. The potential use of amorphous Ge for the design of Ge-based anodes was shown.

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