Gaining cycling stability of Si and Ge negative Li-ion high areal capacity electrodes by using carbon nanowall scaffolds


Lomonosov Moscow State University, Leninskie gory, 119991 Moscow, Russia
Dubna University, Universitetskaya str. 19, 141980, Dubna, Russia
L.N. Gumilyov Eurasian National University, Satpayev str. 2, 010000, Astana, Kazakhstan
Engineering Incubator, LLC, Universitetskaya str. 7-2, 141980, Dubna, Russia.

Figure S1. Raman spectra of Si (a) and Ge (b) films on the CNW surface.

Raman spectrum of silicon film on the CNW surface is presented by several wide lines in a region of 300 cm\(^{-1}\), 480 cm\(^{-1}\) in addition to main mode at 510 cm\(^{-1}\) (Figure S1, Supplementary Information). Thus, wide peak at 480 cm\(^{-1}\) as well as broad low-frequency shoulder indicate on amorphous film structure.\(^1\)\(^2\) The same result was obtained for germanium film. The main phonon mode of germanium crystal lattice is located near 300 cm\(^{-1}\) and its amorphization results in appearance of broad lines near 180 and 260 cm\(^{-1}\).
Figure S2. TEM images of Si/CNW (a, b), Ge/CNW (c, d), CNW/Si/CNW (e, f) and CNW/Ge/CNW (g, h) films.

Figure S3. Discharge/charge profiles for the first and second cycles for Ge/CNW (a), Si/CNW (b), 6 layer -Ge/CNW (c) and 7 layer-Si/CNW (d) anodes; CVAs for the first and fifth cycles for Ge/CNW (e) and Si/CNW (f) anodes.
Figure S4. SEM image of damaged Si/CNW anode after 50 cycles at current of 50 µA/cm².

Figure S5. Cycling performance of silicon-based anode covered with additional amorphous carbon layer (α-C/Si/CNW). Si areal mass loading is about 70 µg/cm², thickness of amorphous carbon layer is of 100 nm. Si/CNW anode has been covered with 100 nm amorphous carbon layer by means of magnetron deposition (α-C/Si/CNW) at substrate temperature of 27°C. In order to study influence of carbon film adhesion on cycling performance deposition also has been carried out at substrate temperature of 600°C that as expected stimulated Si-C bonding.
Figure S6. C1s and Si2p photoemission spectra of the CNWs decorated with Si nanoparticles deposited at 250-300°C. Reproduced by permission of the PCCP Owner Societies [3]

No Si-C bonding was observed when Si was deposited by magnetron sputtering onto CNW substrate. Analysis of C1s and Si2p lines (figure S6) revealed no traces of carbide formation. Significant SiOx signal is a result of silicon oxidation during transfer of the sample from magnetron deposition reactor to photoemission spectrometer. In contrast, the growth of CNWs on silicon surface heated in the course of PECVD synthesis to 700 – 800°C leads to carbide formation clearly visible in C 1s spectrum (figure S7).

Figure S7. C 1s X-ray photoelectron spectra for the Si surface with CNWs grown by PECVD. Blue points correspond to the experimental data; red curves show individual components as a result of the fitting procedure. Reprinted from Carbon, 50(4), Krivchenko V.A., Dvorkin V.V., Dzbanovsky N.N., Timofeyev M.A., Stepanov A.S., Rakhimov A.T., Suetin N.V., Vilkov O.Yu., Yashina V.V., “Evolution of carbon film structure during its catalyst-free growth in the plasma of direct current glow discharge”. Copyright 2012, with permission from Elsevier.
Figure S8. SEM images of CNW/Ge/CNW/Ge/CNW/Ge/CNW (a,b) and CNW/Si/CNW/Si/CNW/Si/CNW (c,d) anode surface after 30 cycles.

Table S1. Specific characteristics of different carbon/germanium and carbon/silicon anode materials.

<table>
<thead>
<tr>
<th>Source</th>
<th>C-Ge composite anode material</th>
<th>C-Si composite anode material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mAh/g at 50th cycle</td>
<td>mAh/cm² at 50th cycle</td>
</tr>
<tr>
<td>4</td>
<td>900</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>1300</td>
<td>?</td>
</tr>
<tr>
<td>6</td>
<td>1200</td>
<td>0.96</td>
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<tr>
<td>7</td>
<td>1200</td>
<td>1.8</td>
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<tr>
<td>Current work</td>
<td>580</td>
<td>1.9</td>
</tr>
</tbody>
</table>

References

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