High specific capacity retention of graphene/silicon nanosized sandwich structure fabricated by continuous electron beam evaporation as anode for lithium-ion batteries

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ABSTRACT

A graphene/silicon (Si) multilayer sandwich structures are fabricated using electron beam (EB) deposition without air exposure. The graphene and Si thin films are formed on Cu current correctors through a continuous process in high-vacuum EB chamber. Synthesized graphene should be suggested to the stacked multilayer structure from Raman analysis. The fabricated multilayer films are used as anodes. In the beginning, the half-cell, which used a seven-layer of each thickness 50-nm graphene and Si film, exhibits good specific capacity retention over 1000 mAh g⁻¹ after 30 charge/discharge cycles. The capacity value changed with the number of graphene and Si layers. In this study, the number of layers that exhibited optimal properties is seven. Morphological investigation showed a fine layer-by-layer structure. The relationship between different thicknesses of graphene and Si is investigated at 7 L. A 100-nm thickness exhibited optimal properties. Finally, the optimal 7 L and 100-nm thick graphene/Si exhibited high discharge capacitance >1600 mAh g⁻¹ at a current density of 100 mA g⁻¹ after 30 cycles. Initial coulombic and reversible efficiencies exceed 84%. The capacity retention (30th/1st discharge value) at 100 nm and 7 L exceeds 90%. Finally, the soft package battery is assembled by combining the fabricated graphene and Si electrode as anode, LiCoO₂ as cathode, separator and liquid electrolyte. It can be used for commercial light-emitting diode (LED) lighting even under bending status.

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1. Introduction

Developing high-performance rechargeable lithium-ion batteries (LIBs) with high energy, power density, and long lifespan for commercial applications, such as portable electronic devices and electric vehicles, has attracted much interest [1–7]. High-capacity LIBs are in-demand. Si-based electrodes for rechargeable LIBs have gained considerable attention. Flexible devices, such as the smartwatch and bendable mobile phone, which employ LIBs, are also gradually released. From these new generation evolution, thin and bendable LIBs are needed. Moreover, the application of elements that electrochemically alloy with Li at room temperature offers an alternative solution to the high-capacity anode demand [8,9]. Si has received particular attention because of its high theoretical specific capacity for Li, which can reach 4200 mAh g⁻¹ in the form of Li₄Si [1–6]. However, its potential in broad commercial applications has been hindered by severe capacity fading and electrical contact loss caused by considerable volume variations. The Li–Si system can expand/contract during alloying/de-alloying by as much as 300% by volume [10]. The cyclical change in volume can generate stress in electrode material, forming cracks, and breaks in electrical conductivity [11,12]. For example, the charge/discharge curves of Si powder with an average size of 10 μm can achieve high capacity on the first lithiation [13]. However, the Si electrode capacity rapidly fades with the increase in cycle number. After only five cycles, the reversible capacity of the Si electrode drops by 70%. In addition, the irreversible capacity loss of Si anode during the first cycle is too high (2650 mAh g⁻¹) for practical application, as demonstrated by the 25% columbic efficiency. In the
present study, we fabricated graphene/Si sandwich structures by electron beam (EB) evaporation method. Graphene films are designed to buffer the structural changes caused by volume expansion and extraction of Si layers during Li alloying/de-alloying processes. A single Si and graphene layer structure was reported by Zhang et al. [14] and Jì et al. [15] reported a graphene and Si multilayer structure on a Cu-foil current collector. In contrast, we used an EB evaporation apparatus for continuous deposition without air exposure. This continuous synthesis process is suitable for the oxygen not to go through into the graphene and Si layer during growth. Moreover, we designed an alternative structure where a graphene top surface is layered onto Si. This structure is expected to prevent Si oxidation to inactive SiOₓ, which does not affect capacitance. Besides, the bottom layer of anode material was also the graphene thin film because the theoretical resistivity of graphene is only 10⁻⁶ ohm cm, which reduces the conductive difference between silicon and current collector (copper foil).

2. Experimental

2.1. Graphene/Si multilayer structures

The E-Beam Evaporation System (Alpha-Plus Co., Ltd.) was used for the graphene/Si multilayer construction. Graphite and Si broken chip (Summit Tech, Taiwan) were used as raw materials for the graphene and Si layers, respectively. The EB fabrication parameters during the deposition were as follows: controlled growth pressure at approximately 10⁻³ Pa; fixed substrate temperature and rotation speed at 200 °C and 60 rpm, respectively; and controlled growth rate at 500 and 1000 nm h⁻¹ for Si and graphene synthases, respectively. The Cu substrate for the graphene and Si deposition was set onto the upper substrate stage, whereas the graphite and Si source targets were set onto the lower stage. Graphite was first heated by EB. Then, graphite vapor was generated, which reached and diffused onto the Cu substrate, forming a graphene layer on top of Cu. The target lower stage was rotated for Si heating by EB. Si vapor similarly formed a Si layer on the surface of the graphene layer. The alternate coating of graphene and Si layers was repeated continuously until the desired graphene/Si multilayer structure was obtained. The substrate temperature was maintained at 200 °C to promote molecule migration.

2.2. Instrumentation and sample analysis

Crystallographic analysis was carried out by powder X-ray diffraction (Bruker D2 PHASER Analyzer) with Cu Kα radiation (λ = 1.54178 Å). Raman spectroscopy (Thermo Fisher Scientific DXR with 532 nm laser) was utilized for elemental and structural analyses. Field-emission scanning electron microscopy (FESEM) (JEOL JSM-6700F) was used for examination of the morphologies for the synthesized material. TEM and high-resolution TEM were conducted using FEI Tecnai G2 F20 (FEI Company) for the structural and compositional investigations.

2.3. Electrochemical measurements

Electrochemical properties of the samples were evaluated under ambient temperature and pressure using (CR2032) with lithium metal role as a counter and reference electrodes. A graphene/Si multilayer structure was used directly as the working electrode (smaller round pieces with coin cell diameter) without any binder and conductive additives. Celgard 2400 was employed for polymer separators. Used the electrolyte was the 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (1:1 by volume). Coin Cell assembly was prepared inside of an argon-filled glove box (moisture and oxygen contents less than 1 ppm). A battery tester (AcuTech Systems Co., Ltd.) was applied for galvanostatic charge/discharge with 0.020 V to 1.2 V voltage window at a constant current density of 100 mA g⁻¹.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD patterns of each layer of the graphene/Si sandwich structure. Two high-intensity peaks at 2θ values of 43.3° and 50.4° corresponded to Cu diffraction planes (1 1 1) and (0 0 2), respectively. In addition, the XRD pattern of graphene showed a weak broad graphite peak at approximately 26° at nine layers (9 L). No peak from Si was observed in the XRD measurement. Scanning
electron microscopy (SEM) and Raman spectroscopy were employed to confirm the presence of graphene and Si.

Fig. 2a shows that the fabricated sample has two different contrast regions, which were assumed as the graphene and Si layers. The top surface morphology indicates that the graphene layer was uniformly coated onto the surface of the Si layer with slight roughness. Fig. 2b shows the Raman spectra of the seven-layer (7L) graphene/Si samples. The characteristic feature of graphene is the presence of a 2D band in the Raman spectra at approximately 2680 cm\(^{-1}\) and a tangential mode G-band at 1580 cm\(^{-1}\). The intensity of the D-band at approximately 1350 cm\(^{-1}\) indicates the presence of defects in the graphene layer, which may be attributed to the effect of the graphene and Si interface because of heteroepitaxial growth. This defects in the graphene reveal some disordered carbon structures which further
enhance Li ions intercalation to improve its electrochemical performance. In addition, Raman spectral peak at approximately 520 cm\(^{-1}\) verified the deposition of Si, confirming the presence of graphene and Si. In general, the Raman spectra of ideal monolayer and bilayer graphene are defined by the higher 2D peak intensity than the G peak. By contrast, the trilayer graphene shows a lower 2D peak than the G peak [16]. From these references, the morphology of our synthesized graphene composes of stacked multiple layer.

Fig. 3 shows a transmission electron microscopy (TEM) image of 7 L graphene/Si sandwich structures, in which two contrast regions in the fabricated sample are found, similar to the SEM image in Fig. 2. One region has bright contrast (graphene), and the other region is dark (Si), thereby indicating that the morphology of the graphene and Si multilayer structure was formed with fine and linearly maintained layer-by-layer structure. This finding is also an indication of good adhesion between Si and graphene. The Si layer has a high density but non-porous configuration. The thickness of each graphene and Si layer was also estimated to be approximately 50 nm (Fig. 3). In addition, the total thickness of the graphene/Si multilayer was estimated to be approximately 750 nm. In this study, each layer of the graphene/Si structure exhibits subnanometer thickness, which is much thinner than those in previous reports. The thickness can be controlled carefully using the EB evaporation method. The Raman, SEM, and TEM images confirm the layer-by-layer fabrication of the graphene/Si multilayer structure.

3.2. Electrochemical performance

Fig. 4 shows the electrochemical performance of the each thickness 50 nm-graphene/Si at 7 L sandwich structures. Fig. 4a shows the charge/discharge profiles of the graphene/Si sandwich structures in the 1st, 2nd, 10th, and 30th cycles at 100 mA g\(^{-1}\) current density. During the first discharge process, the voltage rapidly falls to approximately 0.25 V and exhibits a short plateau, which is attributed to the SEI formation potential on the Si surface. Fig. 4b shows the cyclic performance of the graphene/Si sandwich structures at 100 mA g\(^{-1}\) current density. The obtained sample delivers a considerably high lithium storage capacity of approximately 1720 mA h g\(^{-1}\) during the first discharge process. A charge capacity of 1440 mA h g\(^{-1}\) is achieved, which corresponds to 84.2% coulombic efficiency, and the 2nd discharge capacity exhibited approximately 1440 mA h g\(^{-1}\), which corresponds to a reversible efficiency of 84.2%. Even after 30 cycles, the specific capacity was maintained above 1000 mA h g\(^{-1}\).

For comparison with graphene/Si multilayer, 750-nm thick pure Si and pure carbon (C) layers were also fabricated and characterized (Fig. 5). Although the first discharge shows 1945 mA h g\(^{-1}\), with increasing cycling, the decay rate became a serious problem. At the 30th cycle, the discharge value shows 265 mA h g\(^{-1}\) and the capacity retention, which is defined as the 30th discharge value/1st discharge value, was only 13.6% (Fig. 5a). For the carbon layer, the cyclic performance was also not so high (Fig. 5b). Fig. 5c shows the comparison of graphene/Si multilayer with pure Si and C. The advantage of graphene/Si was confirmed, particularly its good cycling performance. In addition, the benefit of employing both Si and graphene materials are discussed. During cycling, graphene can be considered as a buffer layer, which is useful in suppressing Si volume expansion. Consequently, good adhesion between Si and graphene was also retained, thereby indicating the Si structure was maintained even up to the 30th cycle.

Fig. 6 shows the relationship between electrochemical performance and number of layers of the graphene/Si electrode (Table 1). The first discharge capacity increases with the increase in layer number (Fig. 6a). The discharge capacity values were approximately 552, 1090, 1110, 1660, and 1719 mA h g\(^{-1}\) for 1 L, 3 L, 5 L, 7 L, and 9 L, respectively. The point between 7 L and 9 L shows that the capacity value was saturated. Fig. 6b shows that the corresponding initial coulombic efficiencies were as high as 53.8%, 76.3%, 79.8%, and 82.3% until 7 L and it was 81.0% at 9 L. These results suggest that 7 L may be the approximate critical point. The corresponding reversible efficiencies were as high as 48.3%, 73.3%, 79.8%, and 84.3%. However, the reversible efficiency at 9 L rapidly decreased to approximately 65.4%. The multiple heterostructure of graphene and Si may have been distorted, which indicates that 9 L of the graphene and Si structure is strongly affected by the force from the lattice distortion of the hetero-interface compared with the lower
layer condition. Therefore, damage was assumed in the 9L structure during the charge/discharge process caused by Si volume change. Hence, 7L exhibits the optimal conditions. The coulombic and reversible efficiencies of 7L were 82.3% and 84.3%, respectively.

Fig. 7 shows the soft package battery, which uses LiCoO2 as cathode with 50-nm thick graphene/Si multilayer fixed at 7L as anode and commercial LED lighting. Fig. 7a and 7b shows the LED has function for lighting easily. In addition, even the battery which is under the bent status, thereby indicating the potential use of our fabricated flexible battery device as flexible battery, which can have popularities for the thin film flexible electronics devices.

Fig. 8 shows the relationship between electrochemical performance and layer thickness of the graphene/Si electrode (Table 2). The first discharge capacity also increases up to 200 nm thickness (Fig. 8a). The discharge capacity values were approximately 1660, 1665, 1876, and 1852 mA h g^{-1} for 50, 100, 200, and 300 nm, respectively. The point between 200 and 300 nm shows that the capacity value has been saturated. The corresponding initial coulombic efficiency values exceeded 80%, particularly 82.3%, 84.9%, 86.1%, and 89.7% (Fig. 8b). The corresponding reversible efficiency values were as high as 84.3%, 84.7%, 87.3%, and 110.4%. However, the reversible efficiency at 300 nm showed over 100%, which is a special phenomenon compared with the other thickness condition. Probably, the 300-nm thick sample has large volume. As a result, much more time is needed for this sample to stabilize compared with thinner samples. Therefore, the second discharge capacity is higher than the first discharge value.

Fig. 9 shows cycle performance of each graphene and Si thickness of 50, 100, 200, and 300 nm graphene/Si multilayer at 7L. Thus, the 100 nm thickness is superior up to the 30th discharge value, which exceeded 1600 mA h g^{-1}. For samples with high volume, i.e., with 300-nm thickness, although the first and second capacitance is higher, the fade decay was large with the increase in the number of cycles, which is probably due to the broken structure caused by large Si volume expansion.

Fig. 10 shows the charge/discharge profiles of the graphene/Si sandwich structures in the 1st, 2nd, 10th, and 30th cycles at 100 mA g^{-1} current density. The optimal 7L and 100 nm graphene/Si achieved high discharge capacitance (>1600 mA h g^{-1}) at a current density of 100 mA g^{-1} after 30 cycles. Interestingly, after 10th and 30th still retain the higher discharge capacity than 2nd discharge capacity. It might be thought that during the cycle, the space like a porous or void was generated inside of active region which is suitable space to store the Li^+.

### Table 1
First discharge capacity values, coulombic efficiencies, and reversible efficiencies of each layer number for the graphene/Si sandwich structure.

<table>
<thead>
<tr>
<th>Layer number</th>
<th>First discharge capacity (mA h g^{-1})</th>
<th>Initial coulombic efficiency (%)</th>
<th>Reversible efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>552 ± 45</td>
<td>53.8 ± 3.7</td>
<td>48.3 ± 4.1</td>
</tr>
<tr>
<td>3</td>
<td>1090 ± 136</td>
<td>76.3 ± 2.2</td>
<td>73.3 ± 4.7</td>
</tr>
<tr>
<td>5</td>
<td>1110 ± 105</td>
<td>79.8 ± 1.7</td>
<td>77.7 ± 2.9</td>
</tr>
<tr>
<td>7</td>
<td>1660 ± 65</td>
<td>82.3 ± 1.9</td>
<td>84.3 ± 0.1</td>
</tr>
<tr>
<td>9</td>
<td>1719 ± 29</td>
<td>81.0 ± 0.4</td>
<td>65.4 ± 1.0</td>
</tr>
</tbody>
</table>

### Table 2
First discharge capacity values, coulombic efficiencies, and reversible efficiencies of each layer thickness for the graphene/Si sandwich structure.

<table>
<thead>
<tr>
<th>Each thickness of G and Si (nm)</th>
<th>First discharge capacity (mA h g^{-1})</th>
<th>Initial coulombic efficiency (%)</th>
<th>Reversible efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1660 ± 65</td>
<td>82.3 ± 1.9</td>
<td>84.3 ± 0.1</td>
</tr>
<tr>
<td>100</td>
<td>1665 ± 115</td>
<td>84.9 ± 1.4</td>
<td>84.7 ± 3.1</td>
</tr>
<tr>
<td>200</td>
<td>1876 ± 19</td>
<td>86.1 ± 0.8</td>
<td>87.3 ± 1.6</td>
</tr>
<tr>
<td>300</td>
<td>1852 ± 213</td>
<td>89.7 ± 1.2</td>
<td>110.4 ± 8.5</td>
</tr>
</tbody>
</table>
Fig. 11 shows the relationship between the capacity retention and each graphene and Si thickness (50, 100, 200, and 300 nm) of graphene/Si multilayer at 7 L. Capacity retention is defined as the 30th/1st discharge capacity. From this result, the optimal thickness was determined to be 100 nm. The capacity retention at 100 nm and 7 L was >90%.

4. Conclusions

In summary, a graphene and Si sandwich structure was fabricated via continuous EB evaporation method under low pressure. Synthesized graphene should be categorized to the stacked multiple layer. The fabricated sample maintained fine layer-by-layer structure linearly through the alternate formation of 50 nm graphene and Si layers. In further experiment, the optimal 7 L and 100 nm graphene/Si achieved high discharge capacitance (>1600 mAh g⁻¹) at a current density of 100 mA g⁻¹ after 30 cycles. In addition, the initial coulombic and reversible efficiencies exceeded 84%. The fabricated graphene/Si multilayer exhibits high
capacity, good cyclability, and superior rate capability when used as an anode material for LIBs. Finally, the soft package battery is assembled by combining the fabricated graphene and Si electrode as anode, LiCoO₂ as cathode, separator and liquid electrolyte. It has function for commercial light-emitting diode (LED) lighting even under bending status.

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