



Graphene modified copper current collector for enhanced electrochemical performance of Li-ion battery

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ABSTRACT

Our work demonstrates Cu current collector modified by graphene film grown by chemical vapor deposition to enhance contact resistance and adhesion with graphite anode electrode. The graphene film turned Cu surface more hydrophobic and improved its adhesion with graphite anode layer. In addition, the electrochemical characterization results showed that the introduction of graphene film not only increased discharge capacity, but also significantly improved cycle stability of the graphite anode electrode. This enhancement in electrochemical performances can be associated to the reduction of charge transfer resistance of the cells by the introduction of graphene on Cu current collector.

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Li-ion batteries as the most promising power source have attracted attention due to their high operating voltage and high energy density. In recent years, the application of Li-ion battery has been extended from electronic mobile devices to electric vehicles, leading to high demand for high-power performance of Li-ion battery. One of the most effective strategies to enhance the current efficiency of battery is by reducing the overall resistance of the electrochemical system. Much attention has been paid to reduce the ionic diffusion resistance and electronic resistance of active materials [1–3]. In a typical electrode structure of battery, the active material is directly coated on the current collector. Additional contact resistance associated with charge transfer exists at the interface between them. However, fewer studies have focused on the reduction of this contact resistance between the active material and the current collector, because it has been considered to be less significant for the low-power Li-ion battery. Thin copper (Cu) foil is as a common current collector used for the anode in Li-ion battery and graphite is widely used as an anode electrode material for industrial use. The graphite active material has about 13% volume change during lithiation and delithiation processes [4]. However, the repeated volume change causes the so-called pulverization of graphite particles and the formation of unstable solid electrolyte interphase (SEI), resulting in severe electrolyte degradation and eventual delamination from the copper current collector. Delamination particularly induces the loss of electric contact with the Cu current collector and massive capacity fading with cycling [5,6]. Such delamination problem is considered as a major cause of battery failure even for other active materials, including silicon and metal oxide [7–9], however, little attention has been devoted to this issue recently. In this regards, different strategies have been

proposed to solve these problems, including using a high adhesive binder [10], carbon coating on current collectors [11–13], and producing rough surface of current collectors by chemical or electrochemical etching [14–16]. However, these approaches involve high production cost, complicated process and ununiformed electrode structure, thus limiting their practical application for Li-ion batteries. Meanwhile, graphene is a promising material consisting of hexagonal lattices of carbon atoms in submicrometer thickness (0.35 nm). Recently, graphene has attracted significant attention in various research fields including electronics, mechanics and electrochemical applications due to its exceptional electrical, mechanical, and thermal properties [17]. To date, large-scale and high quality graphene films have been synthesized successfully on Cu foil using chemical vapor deposition (CVD) and a transfer process, which shows the capability of cost effective mass production [18].

In this work, we demonstrated a simple and efficient method to improve the contact resistance and adhesion between the current collector and the anode layer. We introduced atomically thin graphene film onto the Cu foil (g-Cu) surface using conventional chemical vapor deposition (CVD) growth method and managed the surface properties of the current collector to enhance cycle stability of Li-ion battery. Since graphene and graphite used here are allotropes of carbon atoms in the forms of two- and three-dimensional structures, they have excellent Van der Waals force and Coulombic interaction between each other. Therefore, it can be expected that the graphene film on the Cu foil has superior adhesion with lower contact resistance between the graphite anode material and the current collector compared to the contact of untreated Cu foil (u-Cu). In addition, the graphene film can facilitate free electron transfer from the active material to the current collector and vice versa due to its high electron conductivity. Thus, the g-Cu and u-Cu current collectors were characterized and their electrochemical performances were investigated in this work. Our results showed that the

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contact resistance was significantly reduced and electrochemical performances of the graphite anode were remarkably enhanced by introducing the graphene film onto Cu current collector.

Commercial 25 μm -thick Cu foil (Alfa Aesar Inc.) was used to synthesize graphene film by high temperature thermal CVD method as shown in Fig. 1 [19]. Briefly, Cu foil was first placed into a vacuum quartz chamber. The temperature was increased up to 1000 $^{\circ}\text{C}$ in H_2 atmosphere and the Cu foil was annealed for 2 h at this temperature to remove the native oxide and organic impurities on the Cu surface. Subsequently, the graphene growth step was held at the same temperature as the annealing step with the gas mixture flow of H_2 and CH_4 (20 and 4 sccm) for 30 min. The quartz chamber was then cooled down to room temperature under Ar gas atmosphere. For electrochemical characterization, the g-Cu was used as current collector without further treatment. For the detailed characterization, the as-synthesized graphene film was transferred on Si/SiO₂ wafer by polymethyl methacrylate (PMMA) assisted transfer method as described previously [19]. Raman spectroscopy was performed to investigate the quality of graphene using Raman spectrometer (DXR) with 532 nm-laser source. The morphology of the current collectors was characterized using a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6500F).

For the fabrication of battery cell, the anode electrode slurry was made of 80 wt% graphite (Sodiff Co. Korea) as the active material with 10 wt% carbon black (Super P, TIMCAL) as the conductive agent and 10 wt% polyvinylidene fluorides (PVDF, Sigma-Aldrich) as the binder. To prepare the anode electrode, the slurry of anode electrode mixture was then coated by doctor-blade technique on the g-Cu and u-Cu. These prepared electrodes were vacuum dried at 120 $^{\circ}\text{C}$ for 12 h. The loading density of the anode electrode was approximately 1.5 g cm^{-3} . For electrochemical characterizations, CR2016 coin half-cells were assembled with the prepared graphene modified electrode and a lithium foil as working and counter electrode, respectively. The electrolyte used in this work was 1 M LiPF₆ (Panaxetec Co., Korea) dissolved into a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylene carbonate (EMC) at volumetric ratio of 1:1:1. All cells were assembled in an argon-filled glove box. The anodic performance was characterized using a galvanostatic charge/discharge between 0.005 V and 1.0 V in a cell cycler (PNE solution Co., Korea) with 0.1 C rate for the first 2 cycles and 0.5 C rate for the next 48 cycles. The rate capability of the prepared anodes was tested at various charge/discharge current rates. Electrochemical impedance spectroscopy (EIS) was conducted using a spectroscopy (VSP, BioLogic Science Instruments) at a frequency range of 100 kHz–0.01 Hz. In addition, the sheet resistance of the prepared current collectors was measured by four-point probe method (CMT-100 MP, Advanced Instrument Technology) and the adhesion strength between the anode electrode and current collector were tested using a texture analyzer (TA-PLUS, Lloyd).

Surface morphology of u-Cu and g-Cu were examined by optical microscopy and SEM. The surface morphology of Cu foil was obviously changed after graphene was grown on the Cu foil by high temperature CVD. Optical microscopy images in Fig. 2(a) and (b) show that the g-

Cu has a smooth surface and the formation of Cu crystalline grain boundary by the recrystallization during high temperature CVD process was also observed. However, the u-Cu shows a rough surface with some dimples. SEM images in Fig. 2(c) and (d) show this morphological change of two Cu foils more clearly. In addition, it was clearly observed in Fig. 2(d) that the g-Cu has the wrinkles of graphene film with grain boundary and small portion of dark color region consisting of multilayer graphene, which are typical morphological features of CVD grown graphene film [20]. Furthermore, Raman spectroscopy was used to evaluate the CVD grown graphene film. Raman spectra of u-Cu and g-Cu shown in Fig. 2(e) reveal that the distinct G-peak around 1580 cm^{-1} and 2D-peak around 2700 cm^{-1} are observed for the g-Cu only, confirming the successful synthesis of graphene. The graphene film was then transferred to Si/SiO₂ substrate after etching the Cu foil to evaluate the quality of graphene. Raman spectrum of the graphene film transferred on Si/SiO₂ substrate exhibits high I_{2D}/I_G ratio and narrow 2D-peak characteristics with negligible D-peak around 1350 cm^{-1} . Optical microscopy image of graphene film transferred in Fig. 2(f) also shows a uniform thickness of graphene film over a large area. These morphological and Raman spectroscopy results indicate that high quality graphene was synthesized over whole Cu foil surface with one or two layer thickness via the CVD method.

Surface characteristics of u-Cu and g-Cu were investigated by measuring contact angles as shown in Fig. 3(a) and (b). The contact angle of g-Cu was increased to be 86 $^{\circ}$ with the presence of graphene film. However, the contact angle of u-Cu was measured to be about 75 $^{\circ}$ in the present study. Besides its superior physical and chemical properties, the graphene film also has excellent hydrophobic property due to its inert nature [21,22]. Therefore, although graphene was synthesized as a single layer or bilayer on the Cu surface, the graphene film might impose the hydrophobicity of Cu surface. This can enhance the adhesion between the Cu current collector and the graphite anode electrode by the graphene film. In order to see the effect of graphene film, we measured sheet resistance of u-Cu and g-Cu current collectors coated anode electrode as shown in Fig. 3(c). Before coating the anode electrode, both u-Cu and g-Cu show similar sheet resistance at about 1.0 $\text{m}\Omega/\text{sq}$. However, after coating the anode electrode, the sheet resistance was sharply increased to about 82 $\text{m}\Omega/\text{sq}$ for u-Cu, while it retained sheet resistance of about 1.2 $\text{m}\Omega/\text{sq}$ for the g-Cu current collector. This indicates that the contact resistance between the anode electrode and the current collector is negligible due to the presence of graphene film. The insulating native oxide layer on the surface of Cu foil might impose significant resistance for the conducting path. However, this oxide layer of Cu surface was removed for g-Cu during the annealing step of high temperature CVD process by the addition of H_2 gas [23]. The highly conductive graphene film synthesized on the bare Cu surface without the oxide layer might provide the effective electric contact between the anode layer and the current collector, resulting in enhanced sheet resistance. Furthermore, the effect of graphene film on adhesion between the current collector and the anode electrode was evaluated by peel test. Fig. 3(d) shows that the anode electrode was

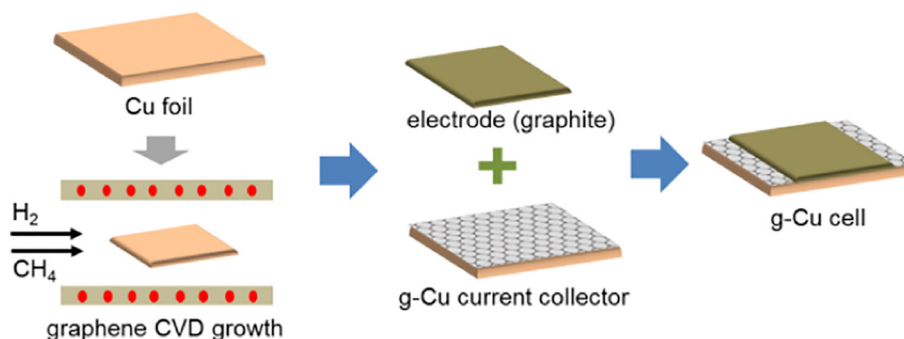


Fig. 1. Schematic diagram for the graphene synthesis on Cu foil by CVD and the preparation of battery cell using g-Cu current collector.

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