Electrophoretic Nanocrystalline Graphene Film Electrode for Lithium Ion Battery

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Abstract. Graphene sheets were fabricated by electrophoretic deposition method from water suspension of graphene oxide followed by thermal reduction. The formation of nanocrystalline graphene sheets has been confirmed by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. The electrochemical performance of graphene sheets as anode material for lithium ion batteries was evaluated by cycling voltammetry, galvanostatic charge-discharge cycling, and electrochemical impedance spectroscopy. Fabricated graphene sheets exhibited high discharge capacity of about 1120 mAh·g⁻¹ and demonstrated good reversibility of lithium intercalation and deintercalation in graphene sheet film with capacity retention over 85 % after 50 cycles. Results show that nanocrystalline graphene sheets prepared by EPD demonstrated a high potential for application as anode material in lithium ion batteries.

1. Introduction

Rechargeable lithium ion batteries (LIBs) have attracted much attention as power sources for portable electronic devices, electric vehicles, and energy storage systems due to the high energy density, high operating voltage and low self-discharge rate. To meet the increasing demand for LIBs with high reversible capacity and energy density, as well as more durable cycling performance, an innovative anode material is required. Graphite is commonly used as an anode material for LIBs because of its high columbic efficiency, acceptable specific capacity and cyclic performance by forming intercalation compounds LiC₆ [1-5]. However theoretical specific capacity of graphite is 372 mAh·g⁻¹ because of the limited Li-ion storage sites within the sp² carbon structure [6-8]. One alternative to graphite has recently been reported – graphene nanosheets (GNS) obtained by various fabrication routes [9-15]. Graphene, two-dimensional graphite, is a rapidly rising star in material science. It has extremely low thickness, high aspect ratio (the ratio of lateral size to thickness), excellent electrical conductivity and good mechanical properties, which qualify it a potentially promising anode material for lithium ion batteries [14-16]. To date, various graphene sheet (GS) fabrication methods such as chemical, liquid phase and anodic electrochemical exfoliation have been developed. Unfortunately these “top down” methods have drawbacks such as toxic chemical usage, the generation of graphene defects in sheets and they are also time consuming [17, 18]. While “bottom-up” methods for graphene sheet production, such as epitaxial growth and chemical vapour deposition, enable to produce high quality and large area graphene sheets [19, 20], these methods demand sophisticated equipment and it is complicated to control the fabrication process [18]. Electrophoretic deposition (EPD) is an economical and versatile processing technique that has been applied for deposition of coatings and films. It has many advantages in the preparation of thin films from suspensions, such as high deposition rate and throughput, good uniformity and controlled thickness of the obtained films, no need of binders, and simplicity of scaling up [21]. Fabrication of graphene and CNT/graphene composite nanosheets by electrophoretic deposition technique was...
demonstrated by Seo, Lee et al. [22, 23]. However the specific capacity values of obtained nanosheets by EPD from isopropanol have been dramatically reduced after the first discharge.

In this study direct EPD method is used to prepare free standing porous graphene sheets from water suspension of graphene oxide (GO) and subsequent thermal reduction of as-deposited multilayers. Structure and morphology of graphene sheets were examined by X-ray diffraction analysis (XRD), Raman spectroscopy and scanning electron microscopy (SEM). The electrochemical performance of graphene sheets as LIB anode materials were evaluated by cycling voltammetry (CV), galvanostatic charge-discharge cycling, and electrochemical impedance spectroscopy (EIS).

2. Experimental
2.1. Fabrication of graphene sheets
Water suspension of graphene oxide was used for electrophoretic deposition of films under potentiostatic mode. GO was dispersed in de-ionized water at the concentration 10 mg·mL\(^{-1}\) and diluted to the concentration 1 mg·mL\(^{-1}\) afterwards. Before the EPD process GO suspension was sonicated for 1 h in order to ensure homogenous dispersion. Electrodes used for EPD process were 1 mm thick 316 stainless steel substrates with a size of 1 x 4 cm. The distance between the two electrodes was 10 mm, and the applied electric field was 30 V·cm\(^{-1}\) (DC power supply Agilent Technologies N5772A). Under the applied voltage, the negatively charged graphene oxide particles migrated toward the positive electrode and were subsequently orderly deposited on it. Thermal reduction of as-deposited GO films was performed by heating at 700 °C in argon/hydrogen flow (Ar:H\(_2\) volume ratio – 95:5). The thickness of the graphene films was tuned ranging from several nanometers to a few micrometers by varying the deposition conditions, including the concentration of graphene oxide, the applied voltage, and the deposition time. The thickness of the films was evaluated using a Veeco Dektak 150 profilometer.

2.2. Characterization of graphene sheets
Obtained graphene layers were analyzed by X-ray diffraction (Philips X'Pert Pro MPD diffractometer, Cu K\(_α\) radiation) and Raman spectroscopy (Advantage-785 spectrometer). Morphologies of graphene nanosheets were characterized by scanning electron microscopy (Hitachi S4800). The electrochemical properties of these films as an electrode for lithium ion batteries were tested by various methods such a cyclic voltammetry, galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy (VoltaLab 40). The measurements were performed in Swagelok type two electrode cell with metallic lithium as a reference and a counter electrode, and LiPF\(_6\) in ethylene carbonate and dimethyl carbonate mixture (volume ratio 1:1) as an electrolyte. The cell was assembled in an argon filled glove box. The active area of the GS electrode is 0.8 cm\(^2\), the thickness of graphene film ~ 1.5 μm.

3. Results and discussion
3.1. Structure and morphology of graphene sheets
The structural changes from GO to graphene during the thermal reduction of electrophoretically prepared films were investigated by XRD measurements. The XRD patterns of GO film, stainless steel substrate and graphene sheet obtained at electric field 30 V·cm\(^{-1}\) are shown in Figure 1. The XRD pattern of graphene exhibits a characteristic peak (002) of graphite at 26.5°, which was not observed for GO [5, 12]. The characteristic peak of GO at 11° was not observed for graphene sheets. It means that most of the GO was successfully converted to graphene by thermal reduction of the as-deposited GO films.

Raman spectroscopy was performed to indicate the structures of GO and graphene sheets by analysing carbon D and G bands. The D band at 1350 cm\(^{-1}\) is ascribed to defects and disordered carbon, while G band at 1585 cm\(^{-1}\) arises from the zone centre E\(_{2g}\) mode, corresponding to ordered sp\(^2\) bonded carbon [5, 22]. As seen from the Figure 2 relative intensities of D and G bands are comparable which means that both GO and graphene sheets exhibit the presence of a significant number of defects and high disorder.
Figure 1. XRD pattern for graphene oxide, stainless steel substrate and graphene film obtained at electric field 30 V·cm\(^{-1}\)

Figure 2. Raman spectra of graphene oxide (red) and graphene film (black)

The morphology of graphene sheets obtained by EPD with the electric field 30 V·cm\(^{-1}\) were characterized by SEM and their images are shown in Figure 3. SEM images of graphene sheets exhibit a nanocrystalline structure with the particle size in the range of 200 – 400 nm. Such nanocrystalline structure has been obtained due to the water decomposition during the EPD process at high voltage followed by the intensive evolution of gases on the electrodes. Therefore obtained graphene films possess not only layered but also nanocrystalline structure which is advantageous for enhanced Li-ion transport in films.

3.2. Electrochemical performance of graphene sheets

Electrochemical properties of graphene sheets were first characterized by CV method. Typical cyclic voltammogram of GS electrode at 1 mV·s\(^{-1}\) from 0.01 to 4 V vs. Li/Li\(^+\) is shown in Figure 4. The CV profile is almost similar to the graphitic carbon with two cathodic and two anodic peaks [24, 25]. The wide reductive peak at around 1.2 V can be attributed to the formation of SEI film. The visible cathodic peak observed at around the potential 0.5 V and corresponding anodic peak at around 1.8 V complies to the Li-ion intercalation and deintercalation during the potential scan. This result is consistent with the charge-discharge voltage profiles (Figure 5).
The gravimetric charge capacity dependence on discharge current is shown in Figure 6. At slow discharge rate (I = 0.8 mA) gravimetric charge capacity of obtained GS anode reaches high value ~ 1120 mAh·g⁻¹ which is comparable or even higher than reported by other authors [5, 12, 15, 24-26]. The increasing of discharge rate causes the gradual decrease of capacity. At much higher discharge rate (I = 2 mA) capacity falls to ~ 620 mAh·g⁻¹. The cycling behaviour of obtained GS electrodes at I = 2 mA within the voltage range of 0.01 to 4 V is shown in Figure 7. It was found that after 50 cycles the reversible capacity of GS electrode still maintains ~ 530 mAh·g⁻¹. The Coulombic efficiency for first 50 cycles of GS electrode exceeded over 85 %. The further decrease of capacity during the cycling is negligible.

4. Conclusions
Graphene sheets were fabricated by electrophoretic deposition method followed by thermal reduction. Results of scanning electron microscopy, X-ray diffraction and Raman spectroscopy confirm the formation of nanocrystalline graphene sheet films. The profile of voltammetric curves indicated smooth lithiation and delithiation processes of obtained graphene films. The initial discharge capacity was about 1120 mAh·g⁻¹ at a constant current density of 1 mA·cm⁻². Extended cycling was performed that demonstrated good reversibility of lithium intercalation and deintercalation in graphene sheet film with capacity retention over 85 % after 50 cycles. Results show that nanocrystalline graphene sheets prepared by EPD exhibited a great potential for application as an anode material in lithium ion batteries because of the very nanocrystalline structure of GS, which promotes the Li-ion intercalation through the graphene layers. The use of light-weight graphene and lithium metal provides a high gravimetric...
capacity and energy density. Experimental results indicate that EPD is a highly powerful tool for the deposition of nanocrystalline graphene films from water suspension of graphene oxide.

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