ANION INTERCALATION TO THE MULTILAYER GRAPHENE

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ABSTRACT

Lithium-ion Batteries (LIBs) are the most dominant electrochemical storage devices among other energy storage devices due to higher columbic efficiency, specific energy and high operating voltage. However, traditional oxygen rich cathode materials of the LIBs cause some safety issues, especially at a charging state. The present study aims to develop a cathode material of multilayer graphene for LIBs applications. First, GO was synthesized according to the modified Hummer’s method using Sri Lankan Natural Graphite (SLNG). The synthesized GO was characterized by using Raman spectroscopy and it shows that the extent of the disorder as intensity ratio (ID/IG) was about 0.43 for GO. Fourier Transform Infrared spectroscopy (FTIR) shows functional groups such as alkoxy (C-O, 1045 cm-1), epoxy (O-C-O, 1222 cm-1), carboxy (C-O, 1370 cm-1), aromatic (C=C, 1625 cm-1), carboxyl or carbonyl (C=O, 1726 cm-1) and Hydroxyl (O-H, 3350 cm-1). X-ray Diffraction (XRD) shows that the interlayer distance (d/2) of GO plates (4.36 Å) are higher than that of graphite. In addition, the Scanning Electron Microscope (SEM) was also used to observe the morphology of synthesized GO and graphene. These results shown, during oxidation of graphite to GO, greater amount of hydrophilic oxidized GO material could be obtained under modified conditions. Then, the synthesized GO was reduced to Graphene by ascorbic acid. Electrochemical studied were then carried out with the synthesized graphene in the voltage range of 3.0-5.0 V Vs Li/Li+, the first charge and discharge capacities of the multi layer graphene cathode were 216.5 and 71.3 mAh g-1, respectively. After 50cycles, the discharge capacity did not fade dramatically. The results indicate that multilayer graphene can be used as cathode material for LIB applications.

INTRODUCTION

Last two decades, rechargeable energy storing devices such as lithium ion batteries (LIBs) and electric double layer capacitors (EDLCs) have been of much interest due to increasing fossil fuel cost and environmental aspects (1). LIBs have high volumetric and gravimetric densities compared with other power storing devices. However, the batteries are bit expensive and have safety issues. At the charge state, short circuits can be happed especially at the cathode of LIBs. In addition, electrolyte can also be reacted with the cathode and oxygen can be released from the cathode material. To avoid those disadvantages, we have introduced graphite as the cathode material (2,3). We have shown that the graphite based cathode materials not only enhance the safety but also increase the energy density of LIBs or the charge storage mechanism of the cathode is principally concerned with adsorption and intercalation of anions in the electrolytes.

To increase the performance of cathode, in this study, we have synthesized multilayer graphene starting from Sri Lankan Natural Graphite (SLNG). The synthesized multilayer graphene was tested as a cathode material for LIBs.

Experimental

Modified Hummer’s method was used to synthesize graphene oxide from SLNG. Then pH of the prepared GO was adjusted to 5.5-6.0 by adding sodium hydroxide (98.8 %, Sigma Aldrich). 5.0 g of L-ascorbic acid (98.5-100%, Sigma Aldrich) was dissolved in 50 cm3 of distilled water and the ascorbic acid solution was prepared. This L-ascorbic acid solution was slowly added to GO suspension up to ~90% by adding hydrochloric acid and the pH was adjusted to 5.5. The suspension was freeze dried. The synthesized GO was characterized by using Raman spectroscopy and it shows that the extent of the disorder as intensity ratio (ID/IG) was about 0.43 for GO. Fourier Transform Infrared spectroscopy (FTIR) shows functional groups such as alkoxy (C-O, 1045 cm-1), epoxy (O-C-O, 1222 cm-1), carboxy (C-O, 1370 cm-1), aromatic (C=C, 1625 cm-1), carboxyl or carbonyl (C=O, 1726 cm-1) and Hydroxyl (O-H, 3350 cm-1). X-ray Diffraction (XRD) reveals that the interlayer distance (d/2) of GO plates (4.36 Å) are higher than that of graphite. In addition, the Scanning Electron Microscope (SEM) was also used to observe the morphology of synthesized GO and graphene. These results shown, during oxidation of graphite to GO, greater amount of hydrophilic oxidized GO material could be obtained under modified conditions. Then, the synthesized GO was reduced to Graphene by ascorbic acid. Electrochemical studied were then carried out with the synthesized graphene in the voltage range of 3.0-5.0 V Vs Li/Li+, the first charge and discharge capacities of the multi layer graphene cathode were 216.5 and 71.3 mAh g-1, respectively. After 50cycles, the discharge capacity did not fade dramatically. The results indicate that multilayer graphene can be used as cathode material for LIB applications.
Charge/discharge tests were carried out using Nagano BST2004W battery tester. Other experimental details can be found in elsewhere (4,5).

RESULTS AND DISCUSSION

Figure 1: FT-IR spectra of graphite, graphene oxide and graphene.

As shown in Figure-1, FT-IR of the graphite samples shows sharp band at 1640 and broad band in the area of 3103–3670 cm\(^{-1}\). Band at 1640 cm\(^{-1}\) due to C=C bond stretching. Broad transmittance band between 3103 and 3670 cm\(^{-1}\) is due to the moisture in the graphite samples. The Synthesized GO shows functional groups belongs to alkoxy (C-O, 1045 cm\(^{-1}\)), epoxy (O-C-O, 1222), carboxy (C-O, 1370 cm\(^{-1}\)), aromatic (C=C, 1625 cm\(^{-1}\)), carboxyl or carbonyl (C=O, 1726 cm\(^{-1}\)) and Hydroxyl (O-H, 3350 cm\(^{-1}\)) in GO. These results indicated successful oxidation of graphite into graphene oxide. However, the functional group cannot be seen in the reduced GO sample.

Figure 2: SEM images of graphite and graphene

As shown in Figure-2(a), graphitic layers cannot be observed due to highly stacking structure of graphite (left). When graphite is oxidized to GO, oxygenized functional groups are attached to graphitic layers and layers are exfoliated while introducing defects to the graphene layers. In addition, wrinkles on graphene surface induced by chemical and mechanical process can be observed. Therefore wrinkles and exfoliated layers can be observed in the synthesized graphene as indicated in Figure- 2(b).

Figure 3: XRD spectra of graphite, graphene oxide and graphene.

As Shown in Figure-3, a sharp peak can be observed at 2\(^\theta\) values 26.6 which belongs to (002) plane. This indicates high crystallinity of graphite samples. The synthesized GO samples shows a relatively broader peak at 2\(^\theta\)= 9.8, which belongs to (001) plane. The inter layer distance of GO can be calculated using Bragg’s low which is 0.905 nm. The peak intensity of the reduced graphene oxide sample is very low. The interlayer space of the sample is 0.374 nm. Debye-Scherrer equation indicated that average number of layers in the reduced graphene oxide sample is ~ 4.

Figure 4: Raman spectra of graphite and graphene.

According to Figure-4, the Raman spectrum of graphite shows D, G and 2D bands at 1355, 1581 and
intercalation processes show the second cycle irreversibility of the intercalated anions. However, from cycles is due to the electrolyte decomposition and partial cycle mAh.g\(^{-1}\) cell is into the graphene layers. The voltage graphene surface This may increase can be seen in the voltage range of 3.25 shown in Figure range of 3.0 charge/discharge cycles of the graphene in the voltage cathode material for LIBs. Figure 5 shows the first five cycles of the charge/discharge of graphene in the voltage range of 3.0-5.0 V Vs Li/Li\(^+\).

After synthesizing graphene, we then test it as a cathode material for LIBs. Figure-5 shows the first five charge/discharge cycles of the graphene in the voltage range of 3.0-5.0 V in 1.0 M LiPF\(_6\) (EC/DMC) solution. As shown in Figure-5, during the first charge a sharp voltage increase can be seen in the voltage range of 3.25-4.25 V. This may be due to the adsorption of PF\(_6\) anion on the graphene surface and edges. Then a slow increment of the voltage can be seen due to the anion intercalation process into the graphene layers. The first charge capacity of the cell is 216.5 mAh.g\(^{-1}\) and the discharge capacity is 71.3 mAh.g\(^{-1}\). Therefore, the coulombic efficiency of the first cycle is 32.9%. The low coulombic efficiency of the first cycles is due to the electrolyte decomposition and partial irreversibility of the intercalated anions. However, from the second cycle onwards the anion intercalation/de-intercalation processes show straight lines.

According to calculations, the synthesized graphene contains less than four layers which is agreed well with the XRD data. The XRD data contains less than four layers which is agreed well with the XRD data.

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\omega_G = 1581.6 + 11/(1 + n^{1.6})
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As shown in Figure-5, the initial discharge capacity is decreasing in the first few cycles. However, after 10 cycles the discharge capacity does not change a lot within the cut-off voltage range. The coulombic efficiency of the cell is also increased with cycle number.

CONCLUSION

Multilayer graphene was successfully synthesized using Sri Lankan Natural Graphite as the starting material. The XRD and Raman spectroscopic data revealed that the number of layers of the synthesized graphene is less than 4. The synthesized multilayer graphene was tested as a cathode material for LIBs. The average discharge capacity of the cathode is ~ 50 mAh.g\(^{-1}\) in the voltage region of 3.0-5.0 V Vs Li/Li\(^+\). The high operating voltage is possible due to non oxidative behavior of the graphene thus the saflty of this cathode is much higher than that of the traditional oxygen rich cathode materials.

REFERENCES


