

# Synthesis of Graphene-Metal Nanocomposite Anode Materials for Lithium Ion Batteries

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## Abstract

Graphene-based nanocomposites have been demonstrated to be promising high-capacity anodes for lithium ion batteries to satisfy the ever growing demands for higher capacity, longer cycle life and better high-rate performance. In this study, graphene-metal based anode materials which have high mechanical, electrochemical, electrical and thermal properties were synthesized. To synthesize graphene-based composite anode materials, primarily bulk graphite was oxidized by using modified Hummers method and then graphite oxide was reduced to nano graphene material through thermal exfoliation method. By virtue of this technique, from bulk graphite good quality graphene in high quantities were obtained. Finally, nano metal particles Tin (Sn) and Molybdenum disulfide (MoS<sub>2</sub>) were added into the graphene nano structure to produce graphene-metal hybrid material. Structural characterization of the obtained samples was characterized by surface electron microscope (SEM), X-Ray Diffraction (XRD) and Raman Spectroscopy. Also electrochemical performances of the prepared composite samples were analyzed in coin cell.

## Introduction

As portable consumer and wearable electronics continue to be increasingly ubiquitous in the modern society, the demand for better lithium ion batteries powering these devices have risen exponentially [1]. Lithium ion batteries have so far been regarded as an ideal candidate due to the ability to deliver high capacities repeatedly over thousands of cycles of operation at reasonable charge/discharge rates. However, as the aforementioned devices become more integral in the consumer's daily routine, the need for long-lasting batteries has become critical. Further, with an increase in feature-intensive next-generation electronics, the need for higher power density batteries has also drawn significant attention [2]. In general, traditional lithium ion batteries comprising of a graphitic anode and a lithium cobalt oxide or lithium iron phosphate cathode are known for relatively high energy densities but low power densities.

Conventionally, graphite is used as an anode material for commercial lithium ion batteries. However, graphite suffers from an inherently low theoretical charge storage capacity (372 mA h/ g) and often operates at significantly lower rates that in turn limit the achievable power densities. For the purpose of improving the energy density and power density of batteries, scientists have made great efforts to explore alternative anode materials with higher capacity, such as Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and Mn<sub>2</sub>O<sub>3</sub> [3-6].

Unfortunately, a large specific volume change commonly occurs in the host matrix of these materials during the cycling process. The resulting partial pulverization of the electrodes leads to a decrease in electrical conductivity and reversible capacity, thereby limiting their commercial viability.

Graphene, a single 2-D carbon sheet with the same structure as the individual layers in graphite, has recently spurred a great interest as lithium ion battery anodes, owing to its high intrinsic surface area and outstanding electrical conductivity [7-10]. Yoo et al. first demonstrated the feasibility of incorporating graphene anodes as the host for lithium storage, delivering capacities of 540 mA h/g [11]. The early results with graphene anodes generally suffered from poor coulombic efficiencies and low cycle life [12], attributed to the use of non-conductive polymer binders, high surface area and aggregation of graphene nano-platelets.

This hypothesis was proved to be true as subsequent studies revealed that binder-free graphene anodes delivered improved performance characteristics as compared to the traditional slurry-based approach. Another approach commonly employed in improving the coulombic efficiency in graphene-based electrodes have been through the incorporation of a nano metal particles (Sn and MoS<sub>2</sub>) to compensate for the irreversible capacity loss during the formation of the solid electrolyte interphase (SEI) in the first

few cycles. While graphene anodes have shown tremendous promise as a potential alternative to graphite for high-performance lithium ion batteries, there are certain fundamental constraints to its incorporation.

In this study, graphene-metal based anode materials which have high mechanical, electrochemical, electrical and thermal properties were synthesized. To synthesize graphene-based composite anode materials, primarily bulk graphite was oxidized by using modified Hummers method and then graphite oxide was reduced to nano graphene material through thermal exfoliation method. By virtue of this technique, from bulk graphite good quality graphene in high quantities were obtained. Finally, nano metal particles of Tin (Sn) and Molybdenum disulfide ( $\text{MoS}_2$ ) were added into the graphene nano structure to produce graphene-metal hybrid material. Structural characterizations of the obtained samples were characterized by surface electron microscope (SEM) and thermogravimetric analysis (TGA) and X-Ray Diffraction (XRD). Also electrochemical performances of the prepared composite samples were analyzed in coin cell.

## Experimentation

### Synthesis of Anode Material & Synthesis of Graphite Oxide from Graphite

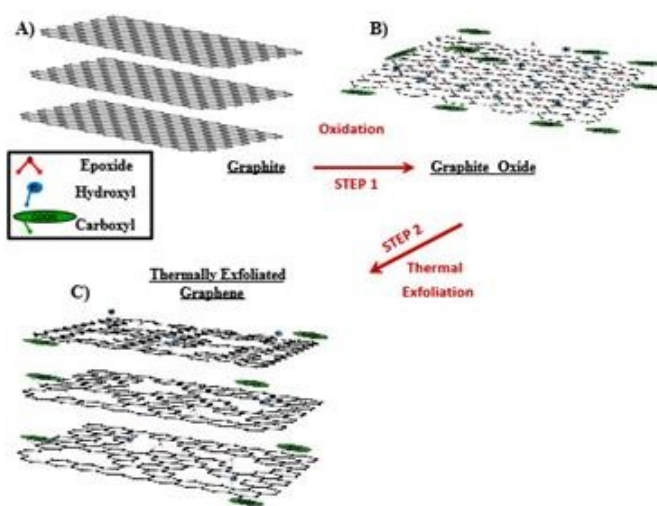
Graphite oxide was prepared by modified Hummers method: Graphite powder (1.5 g, 325 mesh) was put into a mixture of 12 ml concentrated  $\text{H}_2\text{SO}_4$ , 2.5 g  $\text{K}_2\text{S}_2\text{O}_8$  and 2.5 g  $\text{P}_2\text{O}_5$ . The solution was heated to  $80^\circ\text{C}$  and kept stirring for 5 h by using oil-bath. In a next step, the mixture was cooled to room temperature and diluted with deionized water (500 ml) overnight.

Then, the product was obtained by filtering using 0.2 micron nylon film and dried naturally. The pre-oxidized graphite was then re-oxidized by Hummers method. Pretreated graphite powder was put into  $0^\circ\text{C}$  concentrated  $\text{H}_2\text{SO}_4$  (120 ml), soon after, 15 g  $\text{KMnO}_4$  was added gradually under stirring, the temperature of the mixture was kept to be below  $20^\circ\text{C}$  by ice-bath. Successively, the mixture was stirred at  $35^\circ\text{C}$  for 4 hrs, and then diluted with 250 ml deionized water by keeping the temperature less than  $50^\circ\text{C}$ .

700 ml deionized water was then injected into the mixture followed by adding 20 ml 30%  $\text{H}_2\text{O}_2$  drop by drop. The mixture was filtered and washed with 1:10 HCl aqueous solution (1 L) to remove metal ions followed by 1 L of deionized water to remove the acid. Obtained graphite oxide and graphene were characterized by XRD and Raman spectroscopy.

### Synthesis of Graphene

Thermal exfoliation method were used for the reduction of the GO. In this method graphite oxide powder were exposed to high temperatures ( $700^\circ\text{C}$ ) in an air environment for short periods of time ranging from 10 seconds to 20 seconds in order to produce open pore structure graphene. The basic schematic of the fabrication of the entire thermally exfoliated graphene fabrication is shown in Figure 1.



**Figure 1:** Schematic of the thermally exfoliated graphene fabrication showing the various steps involved starting from graphite raw material.

### Graphene-Metal Nanocomposite

Metal-nano particles of Tin (Sn) and Molybdenum disulfide ( $\text{MoS}_2$ ) were added into the graphene by mixing physically via using agate mortar for 30 minutes.

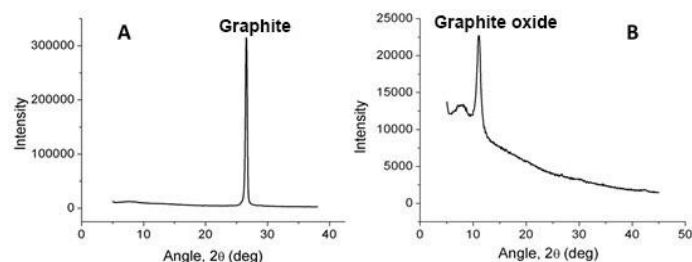
### Lithium Ion Battery Cell Assembly

Thermally exfoliated graphene and graphene-metal nanocomposites were tested as an anode in LIBs. For this 2032 coin cells were assembled inside a glove box (MBraun Labstar) with oxygen and moisture content  $< 1$  ppm. Lithium foil was used as the counter electrode and polypropylene membrane was used as the separator. The electrolyte was 1M LiPF<sub>6</sub> in 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). MTI Battery Testing equipment was used to run the charge/discharge cycles.

## Results

### XRD Characterization of Graphite Oxide

Powder X-ray diffraction studies were done using a PANalytical X'PERT Pro X-ray diffractometer which has a nickel-filtered  $\text{Cu K}\alpha$  radiation as the X-ray source. The scanning was done in the  $2\theta$  range of  $0^\circ$  to  $40^\circ$  with a step size of  $0.2^\circ$ .



**Figure 2:** XRD patterns of the graphite (a), Graphite oxide (b).

XRD pattern of graphite shows its characteristic peak around  $25-26^\circ$  (Figure 2a). This gives an interlayer spacing of approximately  $3.7-3.8 \text{ \AA}$ . After oxidizing the graphite by Hummers method,

GO shows peak  $2\theta = 11^\circ$  (Figure 2b). This peak corresponds to the interlayer spacing  $8.3 \text{ \AA}$ . The presence of the peak around  $11^\circ$  indicated that oxygenated groups have been inserted in the interlayer of graphite which causes increase in the interlayer spacing.

### Raman Characterization of Graphene

The Raman spectroscopic measurements were carried out. A WITec alpha 300 Confocal Raman system equipped with a Nd:YAG laser was used for 532 nm (2.33 Typical Raman spectra of the graphene showing the Raman G ( $\sim 1584 \text{ cm}^{-1}$ ) and 2D ( $\sim 2685 \text{ cm}^{-1}$ ) band peaks that are characteristic of few layer graphene Figure 3. Strong defect concentration D peak ( $\sim 1350 \text{ cm}^{-1}$ ) which indicate highly defective graphene. Thermal exfoliation of graphite oxide produce graphene which contains defects and lacks the perfect honeycomb structure. We found that defects band can have significant impact on the shape of the 2D band of graphene. Figure 3 shows the Raman spectra of graphene. At high defect concentration, the hexagonal network of graphene is disturbed which causes the suppression of the smaller two peak form of 2D band.

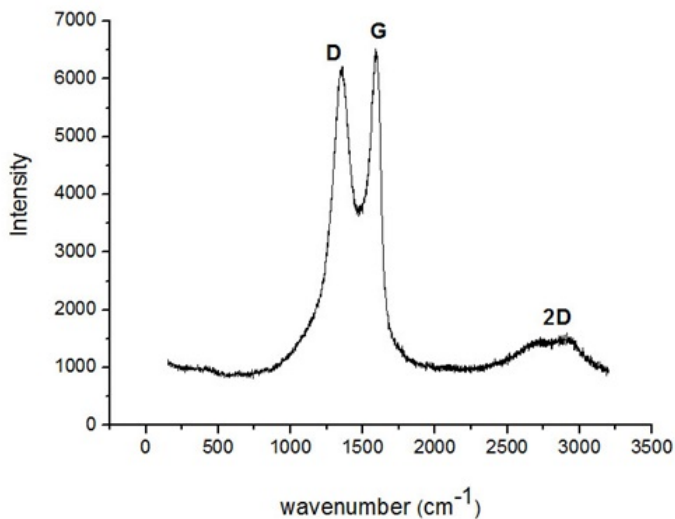


Figure 3: Raman spectra of the graphene.

### Characterization of Anode Materials

#### Results of Pure Graphene as Anode Material

Figure 4 shows SEM images of graphene slurry layer. Mean thickness of the layer is measured as  $106,5 \mu\text{m}$ . As showed in figure 4, graphene layer has heterogen surface.

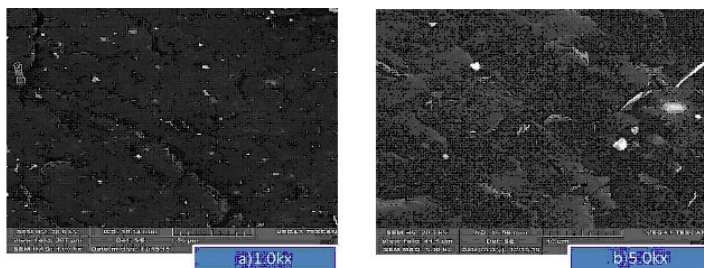


Figure 4: SEM images of Graphene layer a) 1.0kx, b) 5.0kx.

### Results of Graphene-Sn Mixture as Anode Material

Figure 5 and Figure 6 exhibit SEM images of Sn/graphene slurry layers with mixing ratios 30:70 and 50:50, respectively. SEM images show that tin, graphene and were evenly mixed.

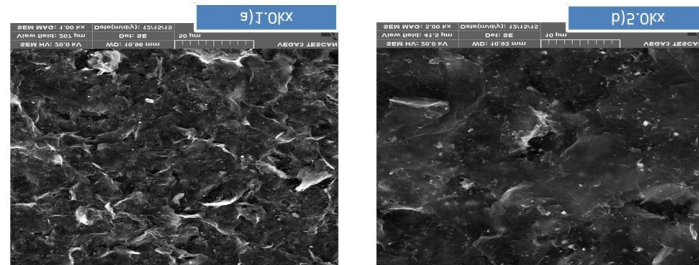


Figure 5: SEM images of Sn-Graphene 30:70 layer a) 1.0kx, b) 5.0kx.

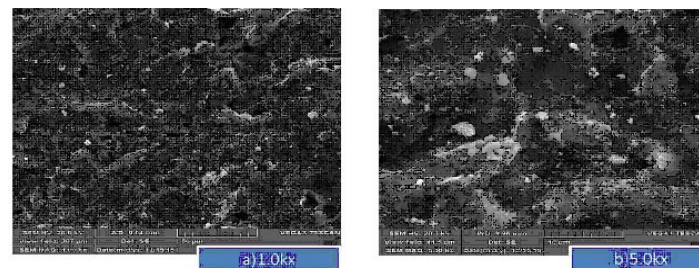


Figure 6: SEM images of Sn-Graphene 50:50 layer. a) 1.0kx, b) 5.0kx.

### Results of Graphene-MoS<sub>2</sub> Mixture as Anode Material

Figures 7 and 8 exhibit SEM images of MoS<sub>2</sub>/graphene slurry layers with mixing ratios of 30:70 and 50:50 SEM images show that materials were good mixed, but not evenly completely.

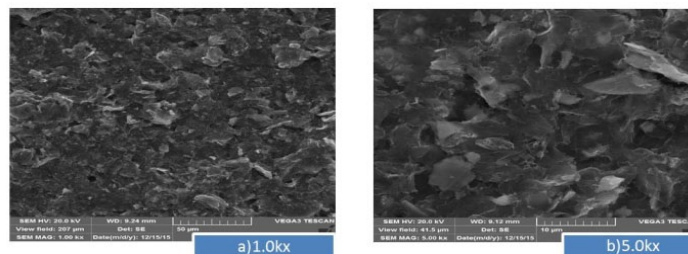


Figure 7: SEM images of Graphene-MoS<sub>2</sub> 30:70 layer a) 1.0kx, b) 5.0kx.

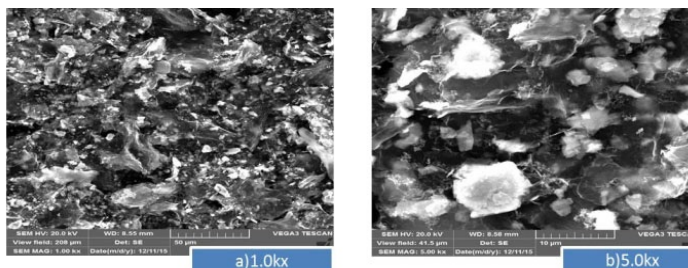


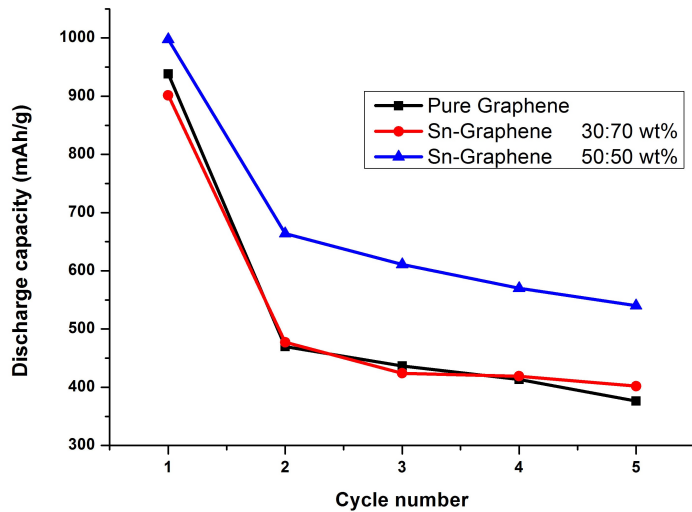
Figure 8: SEM images of Graphene-MoS<sub>2</sub> 50:50 layer a) 1.0kx, b) 5.0kx.

### Results of coin battery performances

Thermally exfoliated graphene and graphene-metal nanocomposites were tested as an anode in LIBs. For this 2032 coin cells were assembled inside a glove box (MBraun Labstar) with oxygen and moisture content  $<1 \text{ ppm}$ .

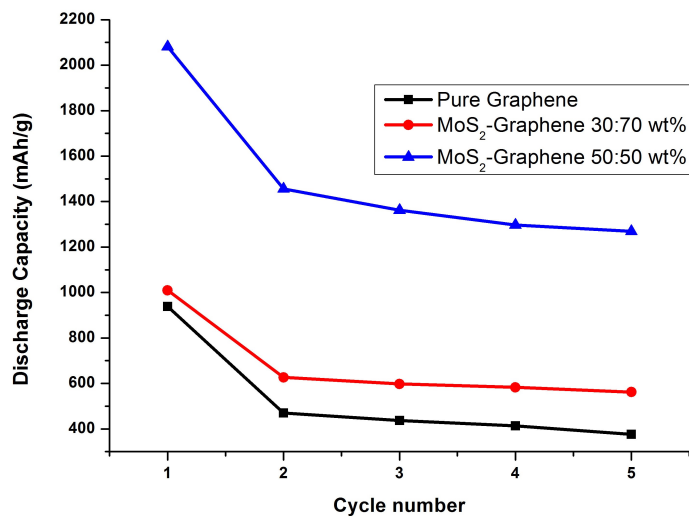


Figure 9 shows discharge capacities of 50 wt% and 30 wt% Sn mixed with graphene samples and pure graphene for the first 5 cycles. Initial discharge capacities of samples are 997 mAh/g and 901 mAh/g for 50 wt% and 30 wt% Sn mixed with graphene, respectively. In agreement with literature data, 50 wt% Sn mixed with graphene's discharge capacity stabilized around ~540 mAh/g which is greater than that of the pure graphene.

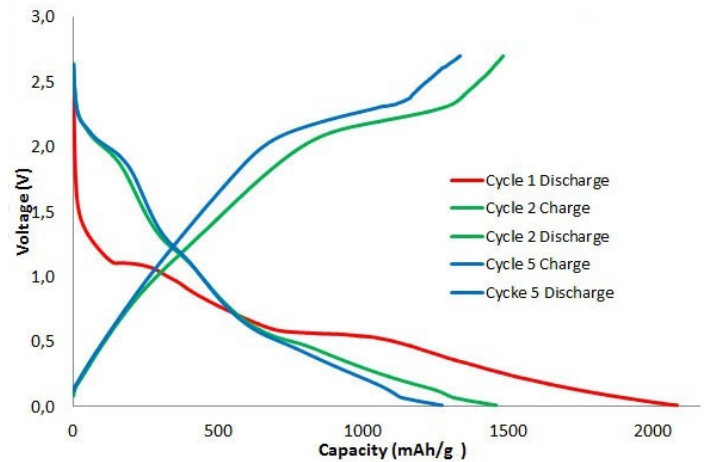


**Figure 9:** Discharge capacity curves of graphene-Sn samples and pure graphene.

Figure 10 shows discharge capacities of 50 wt% and 30 wt% MoS<sub>2</sub> mixed with graphene samples and pure graphene for the first 5 cycles. Initial discharge capacities of samples are 2080 mAh/g and 1009 mAh/g wt% MoS<sub>2</sub> mixed graphene, respectively. The 50 wt% MoS<sub>2</sub> mixed with graphene sample seemed to work the best. After first cycle, its discharge capacity stabilized around 1269 mAh/g. Figure 11 also represents the voltage vs. capacity curves of 50 wt% MoS<sub>2</sub> mixed with graphene sample at first, second and fifth cycle.



**Figure 10:** Discharge capacity curves of graphene-MoS<sub>2</sub> samples and pure graphene.



**Figure 11:** Electrochemical performances of 50:50 wt% MoS<sub>2</sub>-graphene. Charge discharge profile between 2.7V - 0.01V.

## Conclusion

In this work, graphene is synthesized by thermal reduction of graphite oxide, properties and battery performances of metal mixed graphene anode for lithium ion batteries have been investigated. Tin, molybdenum disulfide were used as additives. Samples were prepared by mixing mechanically. No other treatment has been applied to get graphene mixture. Obtained samples are characterized by surface electron microscope (SEM). Graphite oxide and graphene samples were characterized by X-ray diffraction (XRD), Raman spectroscopy.

For electrochemical characterization, galvanostatic measurements have been conducted after the fabrication of coin lithium ion batteries. At the galvanostatic measurement of tin mixed graphene, 50wt% results has come better than graphene for discharge capacity. On the other hand MoS<sub>2</sub> mixed graphene 50 wt% cell showed promising electrode performance for lithium ion batteries with large discharge capacity of ~2080 mAh/g and stabilized around 1270 mAh/g.

In summary, this study confirms that discharge capacities can be improved by preparing the anode as composites, which consists of metals and graphene, as long as the size of the used particles is in nm-region.

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