Graduate School of Pure and Applied Sciences

Fabrication and Structural Control of Graphene-based Electrode Materials in Lithium-ion Capacitors and Batteries

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数理物質科学研究科　博士論文の要約:

1. Introduction

In the past decades, there has been a dramatic increase in the demand for the energy storage devices due to the rapid development of portable electronics and electric vehicles [1]. Among most commonly used energy storage devices, lithium-ion batteries (Figure 1(a)) can achieve high energy density, thus can be used in hybrid vehicles [2].However, the low power density limits its application. Much efforts have been made in modification of the electrode material in lithium-ion batteries to increase its power density without energy density loss [2]. Besides, extensive research has been performed on the new generation of energy storage devices: a lithium-ion capacitors (Figure 1(c)), which has a hybrid structure of electrochemical double-layer capacitors (Figure 1(b)) and lithium-ion batteries, to combine the advantages of both energy storage devices.

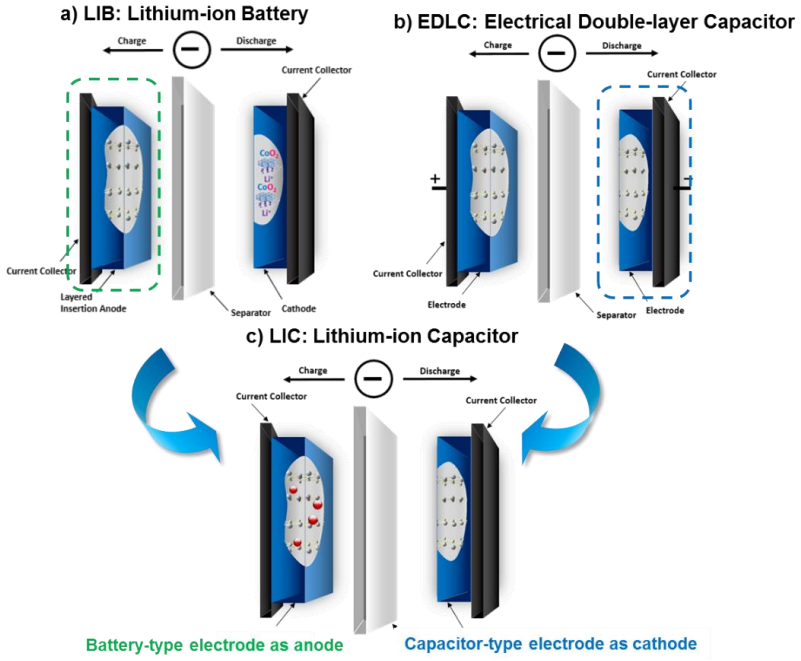

Figure 1. The structure of a) the Lithium-ion batteries, b) electrochemical double-layer capacitor and c) Lithium-ion capacitor.

2. Result and Discussion

2.1 Graphene combine with 1 dimensional single-wall carbon nanotubes as electrodes in lithium-ion capacitor

The dramatically increased demand for electric devices such as electric vehicles and consumer electronics, prompted us to explore new ideas in fabricating novel energy storage devices. In this work, we constructed and tested an asymmetric hybrid lithium-ion capacitors by combining an electrochemical double-layer capacitors (EDLC)-type cathode and a lithium-ion batteries (LIB)-type anode. Both electrodes are made of single-wall carbon nanotubes/graphene nanosheets composites to avoid restacking of the graphene nanosheets, and to maintain the capacity and increase the conductance of the electrodes. One of the electrodes was pre-lithiated through electrochemical method. After pre-lithiation, the 3-dimensional structured Li-SG electrode showed excellent lithium intercalation and de-intercalation capacity and was used as an anode for the lithium-ion capacitors (LIC) (Figure 2) [3].

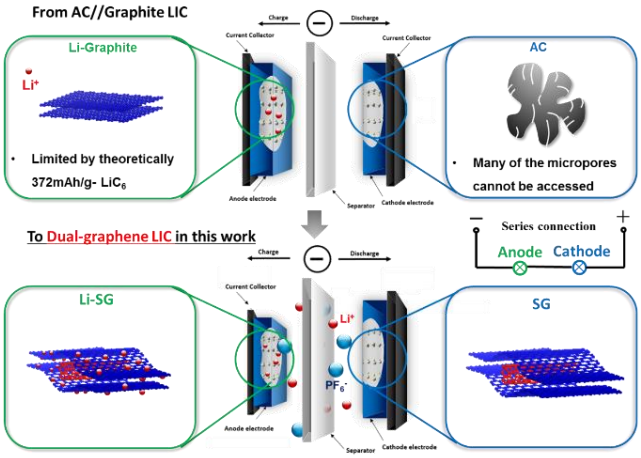

Figure 2. The structure of dual-graphene LIC SG//Li-SG in this work [3].

As LIC is a hybrid system, the combined effect of both electrodes determines the overall performance of the LIC. Therefore, we investigated the electrochemical behavior of each electrode separately as the foundation of overall LIC analysis. A non-faradaic process happens in the cathode of the LIC, which works by a mechanism similar to that of an EDLC. In order to evaluate the electrochemical behavior of the SG electrode as a cathode in the LIC, a symmetric capacitors device SG//SG was fabricated. The voltammetry characteristic curves of SG//SG in the voltage window ranging from 0 to 2.7 V with a near rectangular shape over a wide range of scan rates from 10 to 200 mV s^{-1}. The specific capacitance of SG was up to 145 F g^{-1} under a current density of 50 mA g^{-1}. It was slowly reduced to 101 F g^{-1} when the current density was increased to 1 A g^{-1}. This value is much larger than that of the symmetric capacitors device AC//AC. On the Li-SG electrode material side, the first discharge capacity was up to 1520 mAh g^{-1}, while the first charge capacity was only 562 mAh g^{-1} (37% of the first discharge capacity). The charge and discharge capacity were stable at about 500 mAh g^{-1} in the following cycles. Thus, this value was set as the maximum lithium intercalation and de-intercalation capacity in this work, which is superior to that of graphite (250 mAh g^{-1}).

The electrochemical performance of LIC full-cell SG//Li-SG has been summarized. When the current density is 0.2 A g^{-1}, the capacity of the LIC full- cell under the voltage range from 0 to 4 V is up to 105 mAh g^{-1} (capacitance: 94 F g^{-1}). As can been seen in Figure 3, the energy density of this dual-graphene LIC has reached 222 Wh kg^{-1} when the power density kept 410 W kg^{-1} as the working voltage is 4.1 V. The advantages of asymmetric hybrid dual-graphene LIC are analyzed in detail to show the potential for achieving even better performance.

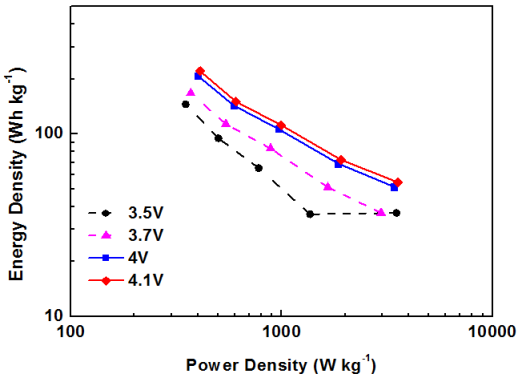

Figure 3. Ragone Plot of a dual-graphene lithium-ion capacitor with increasing voltage window. [3]

2.2 Parallel-oriented graphene as anode in lithium-ion batteries

Despite recent progress and success in exploring new electrode materials, such as Si, for lithium ion batteries (LIBs), carbon-based electrodes, such as CNTs [3], hard carbon [4], soft carbon [5], and graphite [6] remain to be the dominant ones for LIBs and other energy storage devices. Among carbon-based electrode materials, graphite has been the most widely used electrode material for LIBs due to its excellent electrical conductivity, layered crystals and the low cost for mass production [6]. Since its successful isolation in 2004, graphene-single atomic layered graphite sheets has been considered as a more promising electrode material for various types of energy storage devices.

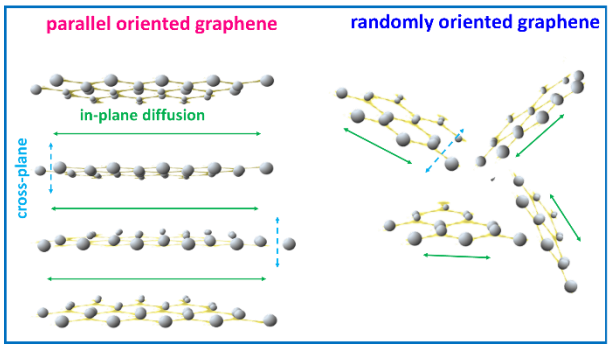

Figure 4. Schematic image of in-plane lithium diffusion and cross-plane diffusion for POG and ROG [7].

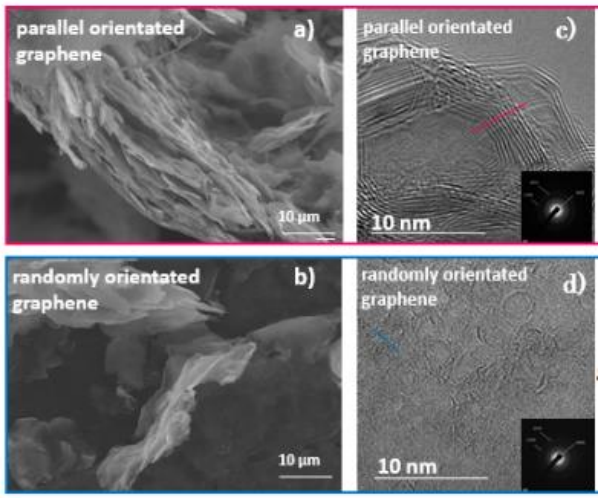

Figure 5. The morphology of parallel-orientated graphene and randomly oriented graphene [7].

In this work, the reduced graphite oxide (noted as parallel oriented graphene: POG in Figure 4) inherits the layer structure of graphite (Figure 5) with an averaged spacing between neighboring layers (d-spacing) of 0.374 nm, as measured exceed that of graphite (0.335 nm) [7]. The larger d-spacing provides wider channels for transporting lithium ions in the material. We show reduced graphite oxide as anode in lithium ion batteries can reach a specific capacity of 917 mAh g^{-1} (Figure 6), which is about three times of 372 mAh g^{-1}, a value expected for LiC_6 structure on the electrode. The lithium ions diffusion coefficient of parallel oriented graphene is 2.12×10^{-11} cm^2s^{-1}, however that of randomly oriented graphene is only 0.55×10^{-11} cm^2s^{-1} (about 25% compared with POG). This is because the lithium-ion diffusion in "the direction parallel to graphene plane" (in-plane diffusion) is much larger than cross-plane lithium-ion diffusion. Such an increase is consistent with the wider d-spacing which enhances lithium intercalation and de-intercalation on the electrodes. The electrochemical performance of lithium-ion batteries with reduced graphite oxide as anode show a noticeable improvement comparing to that with reduced graphene oxide. Such an improvement indicates that reduced graphite oxide with larger interlayer spacing might has less defects and thus more stable.

In summary, we find reduced graphite oxide might be a more favorable form of graphene in making electrode for lithium-ion type of batteries and other energy storage devices.

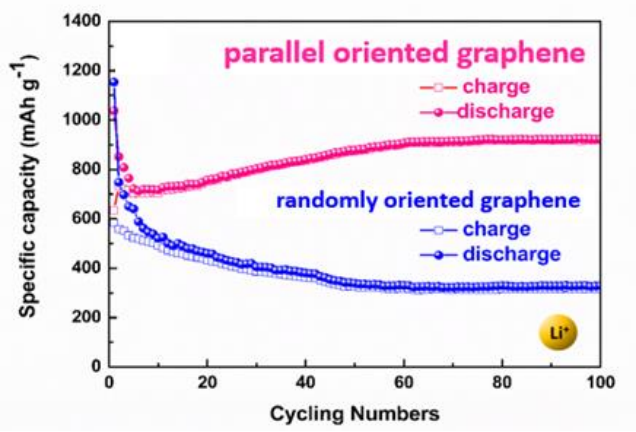

Figure 6. The Cycling performance of parallel oriented graphene and randomly oriented graphene. [7]

2.3 Parallel-oriented graphene combined with 2 dimensional molybdenum disulfide (MoS_2) as anode in lithium-ion batteries

Nowadays, lithium-ion battery (LIB) is one of the most crucial power sources for various electronic devices in human's daily life. To accommodate the increasing demands, the research of lithium-ion battery is focus on higher specific capacity, higher energy density, longer cycling life, and better rate capability. Carbon material, typically graphite, has been widely used an anode in LIB due to its layered structure. This layered structure can achieve the lithium ions intercalation and de-intercalation, which exhibit a specific capacity less than 372 mAh g^{-1} due to the LiC_6 structure. Therefore, to establish an alternative anode with higher specific capacity is a key factor to develop the lithium-ion battery.

Molydbenum sulphide (MoS_2) is a typical graphite-like layered structure. In which each Mo atom and S atoms are covalently bonded to form a two-dimensional (2D) layer structure. These 2D layer are stacked through weak van der Waals attraction, providing a very large interlayer spacing of about 0.61 nm along C-axis. This interlayer spacing is about twice that of graphite (only 0.335 nm), which can accommodate lithium-ions even sodium-ions. Although theoretical specific capacity of MoS_2 (4 mol of lithium ions insertion per formulla) is 670 mAh g^{-1}, there are still some problems need to be conquered, such as low conductive, restacking of 2D structure, low cyclic stability and low rate performance. To solve the problems, in this work, we firstly combine the parallel-oriented graphene (POG) with MoS_2 to form a 3-D structure, which can prevent the restacking of MoS_2 and achieve a specific of 1319 mAh g^{-1}, and good cycling performance as well as excellent rate performance.

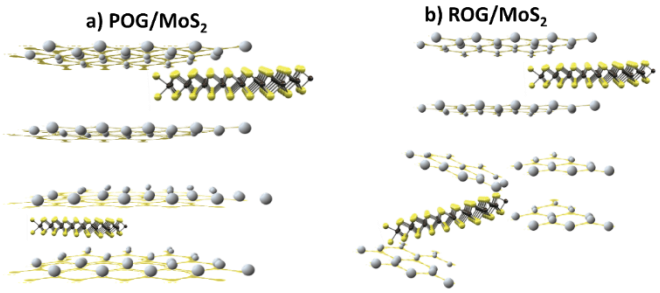

Figure 7. The schematic structure of POG/MoS_2 and ROG/MoS_2.

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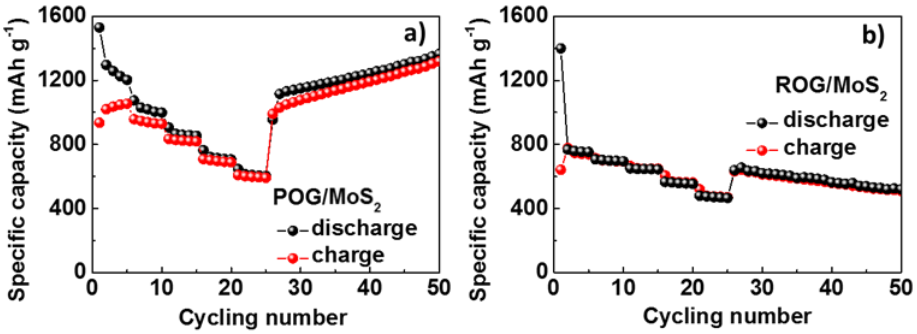

Figure 8. Rate performance of a) POG/MoS_2 and b) ROG/ MoS_2.

Conclusions

- **Graphene combine with 1 dimensional single-wall carbon nanotubes as electrodes in lithium-ion capacitor**

We have designed and fabricated an aymmmetric hybrid dual-graphene lithium-ion capacitor. We have successfully achieved lithium pre-lithiation into the single wall carbon nanotubes/graphene electrode. The maximum reversible capacity of this pre-lithiated Li-SG anode has achieved 500 mAh g^{-1}. Such a capacity resembles significant improvement from that of LICs employed with a graphite anodes (theoretically value for graphite anode is only 372 mAh g^{-1}). The energy density of the fabricated dual-graphene LIC reached 222 Wh kg^{-1}. These results suggest that asymmetric hybrid duel-single wall carbon nanotubes/graphene LIC might be one of the directions in developing high efficient energy storage devices.

- **Parallel-oriented graphene as anode in lithium-ion batteries**

We have synthesized graphene via direct reduction of graphite oxide and via reduction of graphene oxide. We find the graphene produced via direct reduction of graphite oxide maintain certain degree of layer morphology. X-ray deflection measurements show that the d-spacing (d_{002}) in reduced graphite oxide is larger than that in reduced graphene oxide, giving rise to wide transportation channels for ions. Lithium ion batteries with reduced graphite oxide as anode reach an energy density of 917 mAh g^{-1}, which is almost twice that of reduced graphene oxide. The reduced graphite oxide show smaller surface area, less defect compared with those of reduced graphene oxide. Besides of structural and chemical differences between reduced graphite oxide and reduced graphene oxide, the kinetics properties of both electrodes in lithium ions diffusion and sodium ions diffusion were analysed. The results showed that the reduced graphite oxide exhibits a much larger lithium-ion and sodium-ion coefficient compared with reduced graphene oxide. The electrochemical performance of lithium-ion batteries and sodium-ion batteries with reduced graphite oxide anode show a noticeable improvement comparing to those with reduced graphene oxide anode. We find reduced graphite oxide might be a more favourable form of graphene in making electrode for lithium/sodium ion type of batteries and other energy storage devices.

- **Parallel-oriented graphene combined with 2 dimensional molybdenum disulfide (MoS_2) as anode in lithium-ion batteries**

MoS_2 sheet dispersed form MoS_2 bulk have been combined with parallel-oriented graphene (POG) to form a three-dimensional structure. Through a comparative study of POG/MoS_2 and ROG/MoS_2 as anode in lithium-ion batteries, the POG/MoS_2 shows a much higher specific capacity than the ROG/MoS_2 and it exhibits a very good rate and cycling performance. The charge capacity of POG/MoS_2 is 1319 mAh g^{-1} at the current density of 50 mA g^{-1} in the 50^{th} cycle. This is attributed to the POG with stable layer structure as binder and spacer to increase the conductivity and prohibit the restacking of MoS_2. This study indicates that POG/MoS_2 has great potential to lead to a new class of anode material in lithium-ion battery, even sodium-ion battery.

3. Outlook

In order to further increase the energy density of lithium-ion capacitors as well as lithium-ion batteries, one strategy is to design the structure of electrode material with large inter-layer spacing, stable ion diffusion channel, and high tolerance of voltage; one strategy is to achieve the electrolyte which can reduce irreversible capacity and generation of gas during the formation of solid electrolyte interphase and long-term cycling. Lithium-ion batteries and lithium-ion capacitors can play crucial rules in energy storage, combining with energy harvesting, to meet the requirement of the low CO_2 emissions.

4. References

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