

Surface Analysis of High Capacity Carbon Anode Materials Using Hard X-Ray Photoemission Spectroscopy

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Abstract

Carbon materials are the most widely used anode materials for lithium ion (Li-ion) batteries. However, the small theoretical capacity and poor rate capability limited its application in high energy density and power density Li-ion batteries. While the alternative materials, such as silicon and tin alloys have high capacity, however, have an even more inferior rate capability. We describe here a Graphene-Like-Graphite (GLG) carbon based anode material with oxygen content to be used in Li-ion batteries with higher capacity and good rate capability. As a result, the GLG delivered a capacity of 608 mAh/g and a much better charge/discharge rate capability than the pristine graphite. The HAXPES showed the binding energy of C-O bond shifted with the state of charge (SOC), which indicate the contribution to the large capacity. The GLG material is proposed to use in fast chargeable high capacity anode material of Li-ion batteries for electric vehicles and plug-in hybrid vehicles.

Keyword: HAXPES, anode, lithium ion battery, high capacity, fast charge

1. Introduction

Electrochemical energy storage has become a critical technology for a variety of applications from portable electronics to electric vehicles. The lithium-ion (Li-ion) battery is the most promising energy storage devices because of its relative high energy density, power density and cycle life. However, a further increase of energy density and power presence is very limited in the last two decades since there is little progress in commercializing new electrode materials with significantly higher capacity and fast charging and discharging capability. [1, 2] To meeting the increasing demand for energy storage, novel and practical electrode materials with high capacity, fast chargeable capability, long cycle life, and the ability to be produced at large scale are of great interest.

Silicon (Si) and transition metal oxides have been considered to be used for the anode materials of Li-ion batteries since the high theoretical capacity. [3-5] However, the extreme volume change (~400%) experienced during lithiation/delithiation results in pulverization of the active material and loss of electrical connection leading to rapid capacity loss. [3, 6, 7] In addition, the solid electrolyte interphase (SEI) layer which formed on the first cycle has to bear the same volume expansion and contraction, will also crack and delaminate from the Si, leading to a very thick layer of SEI after several cycles. Although some researcher are tried to use a core-shell structure [8-10], porous [11-14], or hollow silicon sphere [15] to solve this problem, it is still far from real application. At present, carbon is the most popular commercialized anode material for Li-ion battery because of its relative high capacity, long cycle life, low cost and ease of processing. However, the limited theoretical capacity (372 mAh/g) and small interlayer spaces (0.335 nm) made it difficult to be used in the application of Li-ion batteries with higher energy density and fast chargeable Li-ion batteries (Fig.1a).

In this study, we have introduced a novel Graphene-Like-Graphite (GLG) anode material to be used in Li-ion batteries with higher capacity and good rate capability. Graphene, as the parent of all graphitic structures, has been studied as an anode material for high capacity and good rate performance. [16, 17] However, the graphene is hardly to be made into battery electrodes because of this low density and high specific surface area. More than 10wt% of binder need to be used for the graphene based active material and the material density which is much lower than 1g/cc is difficult to be made into a battery with high volumetric energy density. [18, 19] Different from graphene materials with high surface area, the GLG has an unaltered shape and size compared with the conventional natural graphite, which made it compatible with current industrial process and electrodes composition when making slurries for the anode electrodes deposition. Moreover, the GLG has a stacked graphene structure with larger interlayer spaces and defects on the basal plane of graphene which could accommodate lithium ion intercalation/deintercalation at a higher speed than pristine graphite. Most important of all, the capacity can be adjusted by controlling the content of oxygen, that the GLG can deliver a capacity higher than 372 mAh/g. The GLG is showed schematically in Fig.1b.

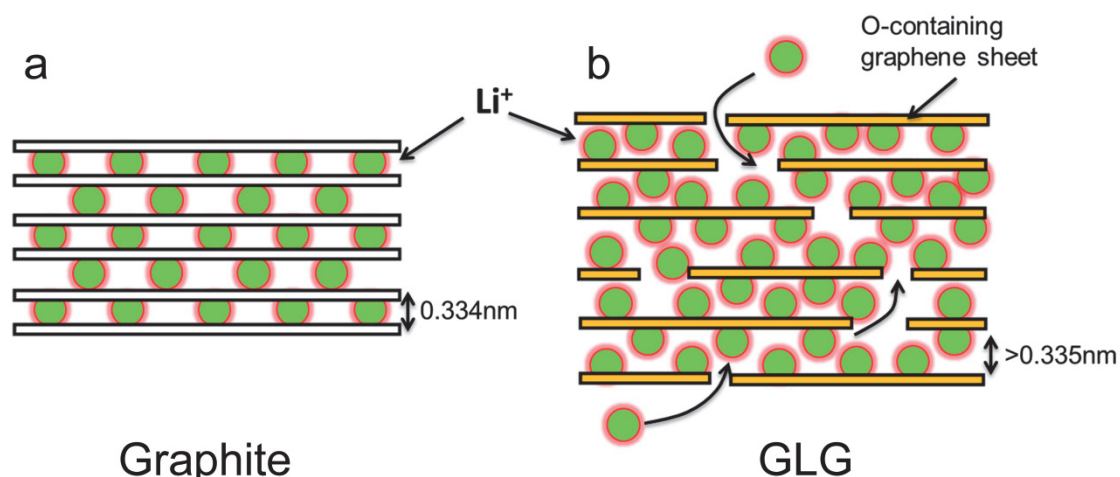


Figure 1. Schematic diagram of a) graphite and b) GLG. a). Graphite have a theoretical capacity of 372 mAh/g in the stage phase of LiC_6 . However, the small interlayer spaces of 0.334nm limited the lithium ion diffusion rate. b). GLG has oxygen content on the surface of graphene sheets which can be used to have reversible reaction with lithium other than Li^+ intercalation, as a result, GLG is possible to have capacity larger than 372 mAh/g. Moreover, the defects on the basal plane of GLG could be used for Li^+ diffusion which may attribute to a better charge and discharge rate capability.

2. Experimental section

2.1 Synthesis of GLG

Graphite oxide is synthesized from natural graphite (Z-5F, Ito Graphite) by oxidation with $\text{HNO}_3/\text{NaClO}_3$, according to the Brodie method. [20] The GO was then heat treated in a step heating process. Specifically, GO was heated to 250°C at a speed of less than 1°C/min, and then heated to 800°C at a speed of 5°C/min and kept in 800°C for 1h. Finally, the sample was used without any further treatment.

2.2 Characterization

The morphology of the products was examined by using field emission scanning electron microscopy (FE-SEM) (Hitachi, SU8000, 5kV). The HAXPES was carried out in BL46XU of Spring-8. The electronic analyzer is R4000 manufactured by VG SIENTA. The measurement is under room temperature, 200eV as pass energy, and curved 0.5mm as the slit size. The take-off angle (TOA) of photoelectrons measured at 80°.

2.3 Cell fabrication

The negative electrode was prepared by coating a mixture of carbon, carbon black, a water-based binder carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) with a weight ratio of 92%: 3%: 2%: 2% on a copper film with a mass loading of 50 g/m² for single side. The density of both the reference graphite and the GLG was controlled to 1.15 g/cc. The size of the anode is 23mm×24mm. 1M LiPF₆ EC/DEC (3:7) with no additive was used as the electrolyte.

3. Results and discussion

The morphologies of the carbon materials are show in Fig. 2. Fig. 2a and 2b are the SEM images of pristine natural graphite in different magnifications. The flake type graphite is used for this experiment. Fig.2c and 2d are the SEM images of GLG materials in the same magnification compare to Fig.1a and 1b. It can be learned that the GLG have almost the same morphology and size with the pristine graphite materials instead of having a large volumetric expansion and graphene sheets exfoliation after the $\text{HNO}_3/\text{NaClO}_3$ oxidation and step heating reduction of the pristine graphite. This property is especially important for the anode materials of current fabrication process. Up to now, there is no solvent that can survive without reduction at an ultra-low potential when charging to 0V vs Li/Li^+ , a solid electrolyte interface (SEI) will be formed on the surface of the anode materials, which consume the Li from either cathode or electrolyte. [1, 21, 22] Currently, the graphite which are used for the anode materials of Li-ion battery are trying to be controlled with a specific surface area under 10 m²/g to have an acceptable initial charge coulombic efficiency and cycleability. Moreover, the required quantity of binder is in proportion to the specific surface area of the electrodes materials. Anode materials with high surface area such as graphene need 15wt% of binder to fabricate the electrode, which is hard to build a battery with high energy

density. [17] As a result, the GLG material with unaltered size made it quite compatible with current process for make a Li-ion battery electrode.

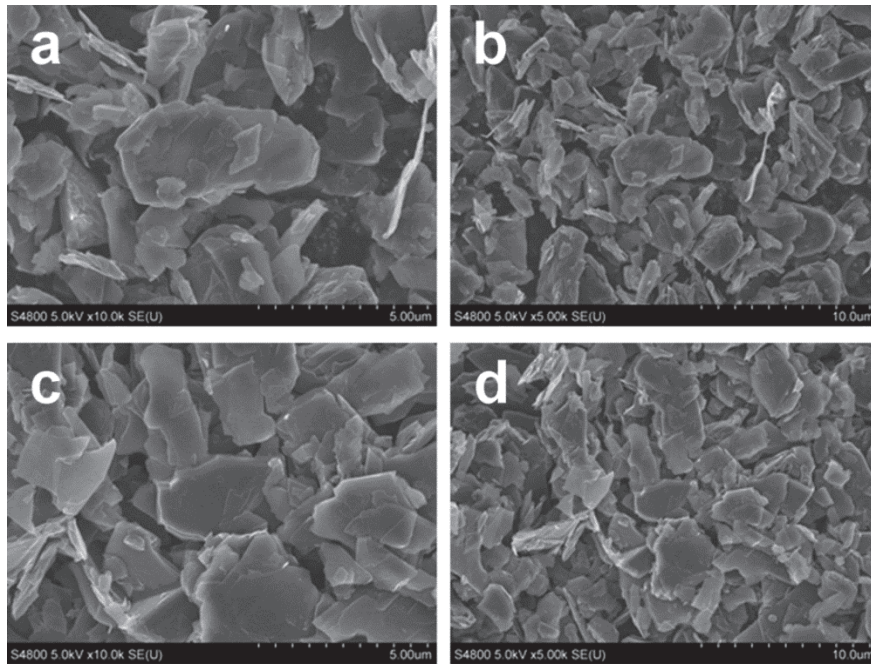


Figure 2. SEM images of carbon materials. a) and b) are pristine natural graphite materials in the magnification of 10k and 5k, respectively. c) and d) are GLG materials in the magnification of 10k and 5k, respectively.

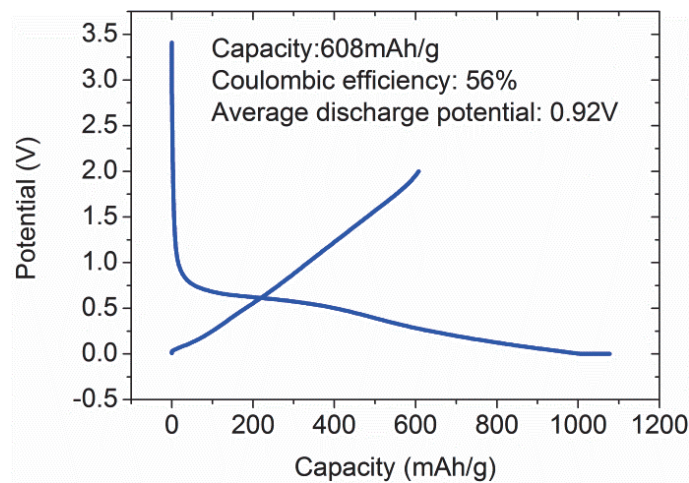


Figure 3. Charge and discharge curves of the pristine graphite and GLG.

Fig. 3 plots the initial charge and discharge curves of GLG. The GLG showed an initial discharge capacity of 608 mAh/g which is much larger than that of graphite. The coulombic efficiency of GLG is 56% which may attribute to the irreversible reaction of oxygen functional groups with lithium ions. An amorphous surface coating technique is considered to increase the coulombic efficiency of GLG. Different from stage phenomena of graphite, GLG showed a under convex discharge curves with an average potential of 0.92V which is higher than graphite (0.2V). The discharge potential could be optimized by tuning the oxygen content GLG material.

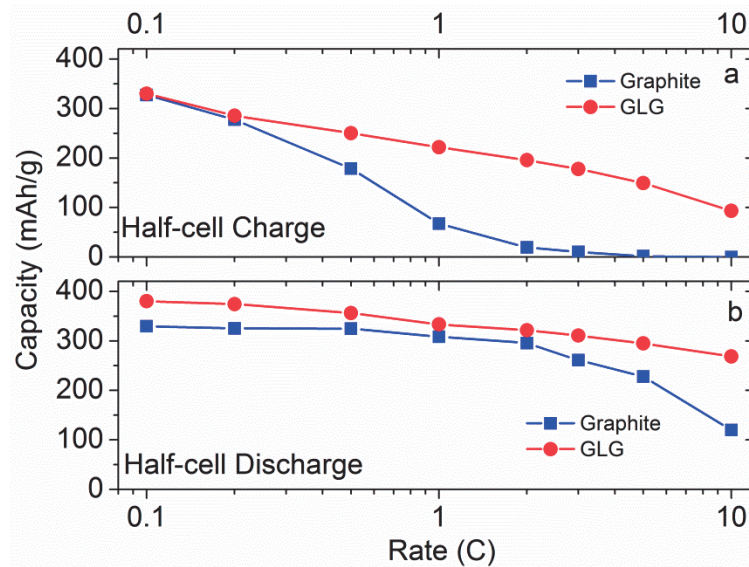


Figure 4. Half-cell a)charge and b)discharge rate capability

The charge and discharge lithiation (Li-input) rate capability of the pristine graphite and the GLG measure in a half cell configuration are shown in Fig. 4. Fig. 4a is the charge (lithiation) rate capability of the graphite and GLG. The cells were charged (Li-ion intercalation) at 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, 5C, 10C, and discharged (Li-ion deintercalation) at 0.1C from 1.5V to 0V versus lithium metal. The capacity at every C-rate is plotted. The GLG showed much higher capacity at 0.5C, 1C, 2C, 3C, and 5C than the pristine graphite, which means the GLG has a better charge rate capability. Fig.4b plots the discharge (delithiation) rate capability of the pristine graphite and GLG. The cells were charged (Li-ion intercalation) at 0.1C and discharged (de-intercalation) at 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, 5C, and 10C from 0V to 1.5V versus lithium metal. The GLG showed higher capacity for any of the discharge rates, which indicate GLG has a better discharge rate capability than pristine graphite. It should be noted that both the pristine graphite and the GLG showed lower capacity than what we calculated from the initial charge and discharge, which showed in Fig. 3. This is because we only use constant current (CC) for both charging and discharging in the rate capability characterization instead of using CC-CV for charging and CC for discharging and the cutting voltage for rate characterization is from 0-1.5V.

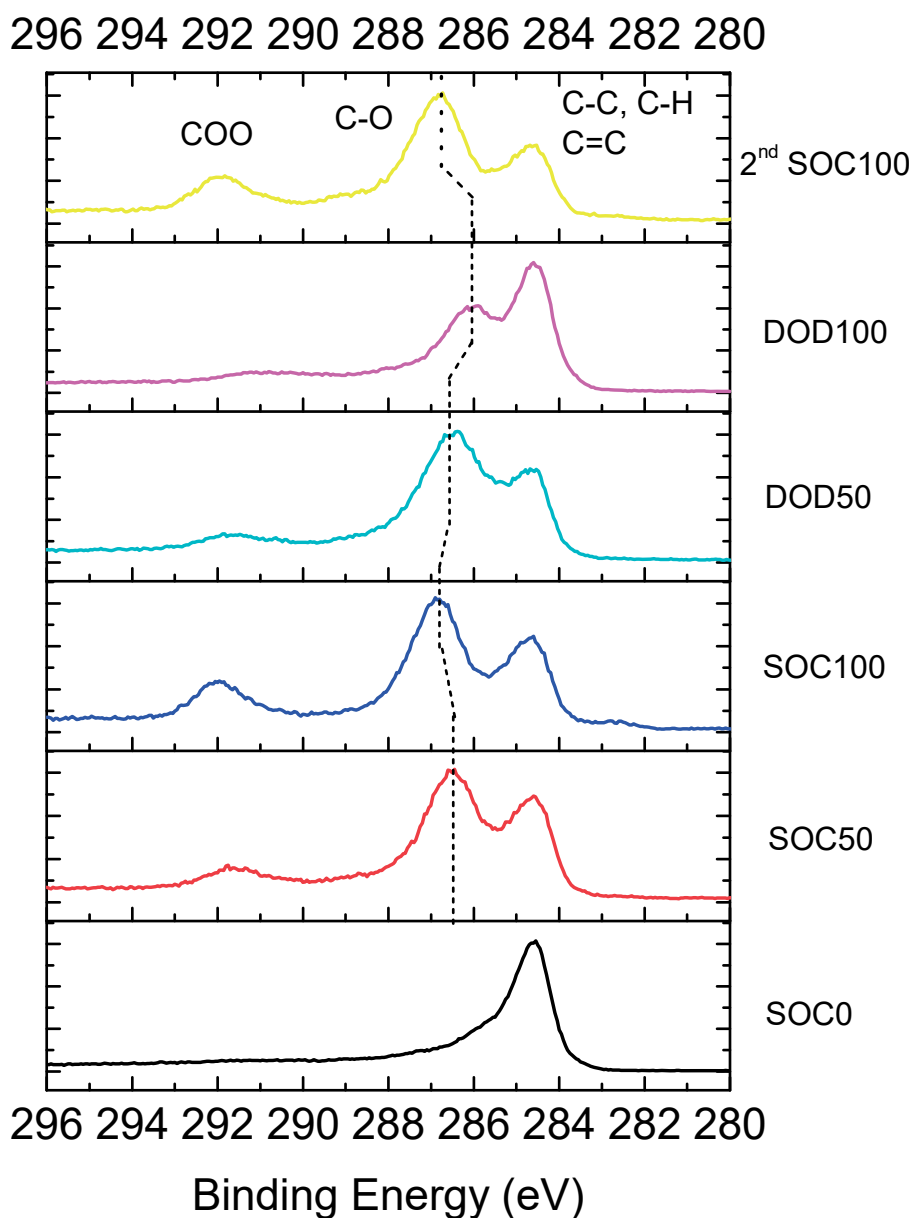


Figure 5 HAXPES result of GLG electrodes with different SOC

The carbon based GLG material has a capacity up to 608mAh/g which is much higher than conventional graphite (372mAh/g). The reason is GLG has some functional groups which are expected to have reversible reactions with lithium ions while charging and discharging that contribute to the capacity. COO, C=O, C-O, C-C, C-H, C=C bonds were detected by the XPS analysis of GLG powder. However, the specific bonds which contribute to the capacity as well as the irrepressible capacity were still unknown. This is because SEI layer will be formed at the surface of anode after the first charge and discharge. The conventional XPS could only give the information of the SEI (less than 10nm). The inner evolutions during charging and discharging are impossible to be learned by XPS. On the other hand, HAXPES has ability for the analysis up to 50nm in depth, which makes it possible to analysis the changes of bonds at different state of charge (SOC). The attached figure showed the C1s at different SOC. All the peaks were normalized by the C-C peak at 286.4eV. The following results can be concluded: 1). The C-O peak shifted along with the SOC reversibly. This may attribute to interaction of lithium ions with C-O bond at different SOC. 2). The intensity ratio of C-O to C-C also changes in different SOC. The charged status showed higher ratio of C-O/C-C. 3). COO bond at around 291.7eV also changed either by intensity and binding energy with

different SOC. The irrepressible capacity is expected as lithium ion trapped by COO functional groups by Li-NMR analysis. The DOD100 have little intensity of COO, but larger intensity of SOC 100 and 2nd SOC100, which is inconsistent with Li-NMR result. The HAXPES of GLG power showed almost the same result of XPS. As a result, we have investigated the HAXPES of the GLG at power status and anode electrodes with different state of charge. The HAXPES of GLG carbon powder showed almost the same result with XPS, while the C-O peak which shifted along with different SOC may contribute to the extra capacity. The COO peak which appear and disappear reversibly may attribute to the irrepressible capacity. Further investigations are still needed to analysis the mechanism of GLG materials. The HAXPES results is showed in figure 5.

4. Conclusion

We have designed and fabricated oxygen rich Graphene-Like-Graphite carbon based anode materials to increase the capacity as well as the charge and discharge rate capability by decorating the carbon with oxygen content. This GLG materials is expected to be a promising carbon based material for next-generation Li-ion batteries anode with both higher capacity and fast chargeable capability for EVs and PHVs. For the next step, we will work on optimizing the model to understand the relationship of the oxygen content and the capacity and boron doping to higher capacity. Moreover, the surface coating technology is also considered to increase the coulombic efficiency.

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