

# Electrochemical performance of modified artificial graphite as anode material for lithium ion batteries

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**Abstract** Artificial graphite anode material was modified by coating an amorphous carbon layer on the particle surface via a sol-gel and pyrolysis route. The electrochemical measurements demonstrate that appropriate carbon coating can increase the specific capacity and the initial coulombic efficiency of the graphite material, while excessive carbon coating leads to the decrease in specific capacity. Thick coating layer is obviously unfavorable for the lithium ion diffusion due to the increased diffusion distance, but the decreased specific surface area caused by carbon coating is beneficial to the decrease of initial irreversible capacity loss. The sample coated with 5 wt.% glucose exhibits a stable specific capacity of  $340 \text{ mAhg}^{-1}$ . Carbon coating can remarkably enhance the rate capability of the graphite anode material, which is mainly attributed to the increased diffusion coefficient of lithium ion.

**Keywords** Li ion batteries · Electrodes · Anodes · Electrochemical characterizations

## Introduction

Artificial graphite (noted as AGP) has been widely used as an anode material for lithium ion batteries due to its

desirable charge potential profile, excellent cyclability, and good safety feature since the invention of lithium ion rechargeable batteries in the early 1990s. However, its low theoretical capacity ( $372 \text{ mAhg}^{-1}$ ) cannot satisfy the increasing requirements of the electronic devices and electric vehicles to the batteries. Besides, the drawbacks related to graphite, such as cointercalation phenomenon of solvent molecules and anisotropic structure feature, limit its electrochemical performance. The former can result in exfoliation of graphite and thereby cause the consequent destruction of the graphite structure. This prevents the use of small molecule solvent with high ionic conductivity. The latter restricts the random diffusion of lithium ions into the graphite structure. Both of them limit the rate capability of graphite anode. Moreover, large initial irreversible capacity loss is another serious problem for graphite anode, which is mainly caused by the complex and imperfect surface structure, such as  $\text{sp}^3$ -hybridized carbon, carbon chains, and edge carbon [1]. Many works have been carried out to improve the electrochemical performance of graphite anode, such as employing smaller particles [2], preparing graphite/nanopowder composite [3–5], and oxidizing or purifying the graphite [6–9]. Recently, a lot of research findings have confirmed that cycling performance and rate capability can be improved by surface coating with amorphous carbon [10–13].

Compared with graphite, amorphous carbon has an isotropic feature, which enables lithium ions to transport inside randomly and thereby exhibits a good rate capability. Besides, amorphous carbon shows minor volume change during charge/discharge process [14, 15] and thus has a good cyclic performance. Therefore, surface modification by coating amorphous carbon is as an effective approach to improve the electrochemical performance of graphite. Recently, many works have been reported, which focused mainly on the effect of carbon precursor [16, 17], coating

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processes [18, 19], and the following heat treatment conditions [20, 21]. However, little attention was paid to the effect of the amount of amorphous carbon on the electrochemical performance of artificial graphite. Actually, a proper coating layer is essential to the surface structure and the electrochemical properties of graphite. Incomplete coating layer will lead to the exposure of part of the graphite surface, while excessive coating can cause a thick layer, which will increase the diffusion distance of lithium ions and thus affect the rate capability. In this work, commercially available AGP sample was modified by amorphous carbon coating derived from glucose. The effect of the coating amount of glucose on the surface structure and the electrochemical properties, especially the rate capability, of AGP was investigated. The coated sample shows improved initial coulombic efficiency than uncoated graphite, and the sample coated with 5 wt.% glucose exhibits the highest reversible specific capacity, excellent rate capability, and good cyclic performance. The role of the carbon layer on the graphite particle is discussed.

## Experimental

### Preparation of materials

AGP materials were obtained directly from suppliers and used as received. Glucose (A.R. grade) was used as a carbon source. Firstly, glucose was dissolved in deionized water to form 2.5, 5, and 7.5 wt.% solutions. The AGP powder was then added into the glucose aqueous solution, and this was followed by vigorous stirring at room temperature to obtain a homogeneous solution. The solution was transferred into an evaporator and dried at 80 °C under refluxing condition to form a viscous slurry. The slurry was coked at 180 °C for 5 h in an oven and then heated in a tube furnace with flowing argon at 1,000 °C for 2 h at a heating rate of 5 °C/min. The carbon-coated samples were noted as GAG2.5, GAG5, and GAG7.5.

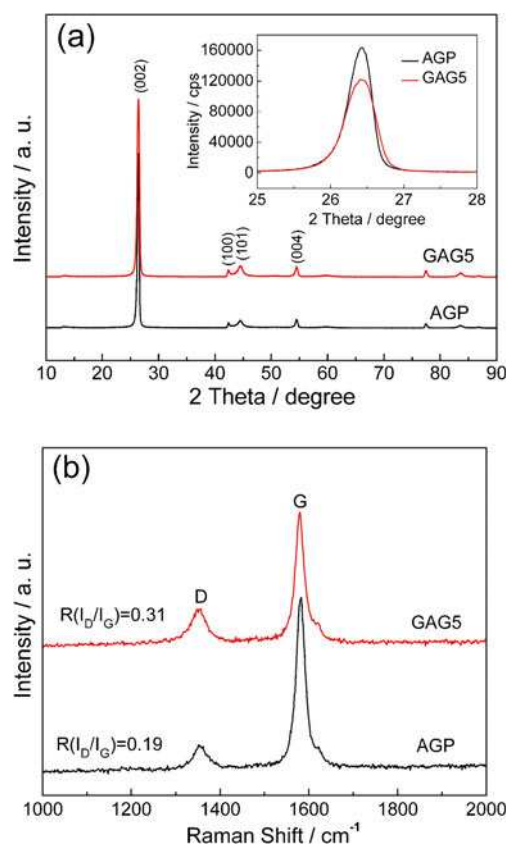
### Characterization

The coated samples were characterized by X-ray diffraction (XRD, Rigaku D/max-A X-ray diffractometer) using Cu K $\alpha$  radiation ( $\lambda=1.5406$  Å) at a scan rate of 1° min<sup>-1</sup> from 10° to 90°. The morphology of the coated GAG was observed by a scanning electron microscope (SEM, LEO-1450) with an accelerating voltage of 20 kV. The specific surface area of each sample was measured by the Brunauer–Emmett–Teller (BET) method from N<sub>2</sub> adsorption with a surface area analyzer (Micromeritics, model ASAP2010). Surface structure ordering degree of graphite coated with and without glucose was examined by Raman spectrometer (microscopic

confocal Raman spectrometer, Renishaw, RM2000 with Ar ion laser of 514.5 nm).

### Electrochemical measurement

The electrochemical properties of the carbon-coated AGP were evaluated with a half cell. The working electrode was prepared by coating a slurry of an active material (85 wt.%), acetylene black (5 wt.%), and polyvinylidene fluoride binder (10 wt.%) dissolved in *N*-methyl pyrrolidine (NMP) onto a copper foil. After NMP evaporation, the copper foil with electrode materials was punched into circular disks with a diameter of 8 mm and dried at 120 °C in vacuum for 24 h. Half cells were assembled in an Ar-filled glove box with a working electrode, a lithium foil counter electrode, and a porous separator (Celgard 2400); 1 M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate (1:1:1 in volume) was used as electrolyte. The cell was galvanostatically cycled at different constant current densities between 0.01 and 2.0 V vs. Li/Li<sup>+</sup> with a Land CT2100 battery test system. Cyclic voltammetry (CV) test was performed at 0.1 mV s<sup>-1</sup> within the range of 0.01–1.0 V using an electrochemistry working station (CHI660A). Electrochemical impedance spectroscopy was recorded for different electrodes with an amplitude of 5 mV



**Fig. 1** XRD patterns (a) and Raman spectra (b) of pristine AGP and GAG5 samples

over the frequency range of  $10^{-2}$  to  $10^5$  Hz using a Solartron 1260 FRA coupled with 1287 interface. The impedance data were analyzed by using ZsimpWin software.

## Results and discussion

### Structure and morphology characterization

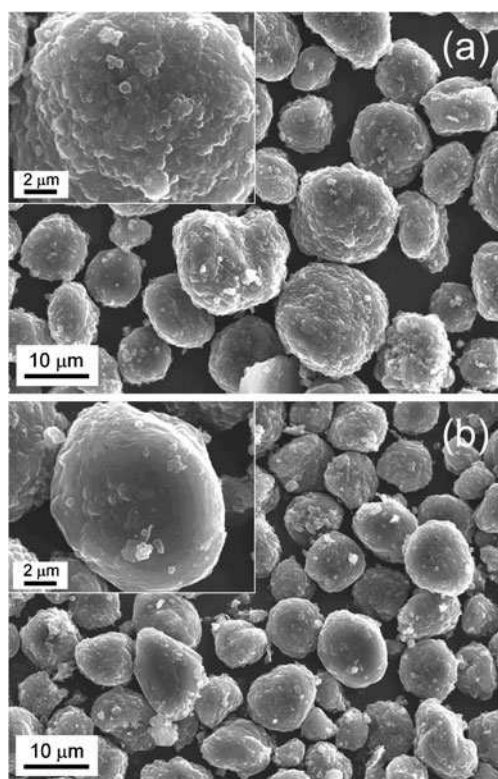
In order to evaluate the coating effect of pyrolysis carbon on the structure of graphite powders, pristine (AGP) and coated samples (GAG5) were subjected to XRD and Raman examination. The results are shown in Fig. 1. Two samples exhibit similar XRD patterns (Fig. 1a), which can be indexed to a typical hexagonal graphite structure (JCPDF no. 41-1487), as evidenced by the main peaks of  $2\theta$  at  $26.42^\circ$ ,  $44.52^\circ$ , and  $54.52^\circ$ . This indicates that the modifying process of coating on AGP did not destroy the typical structure of graphite. However, the diffraction intensity of GAG5 decreases lightly after carbon coating, suggesting the lowered crystallinity. The decrease in crystallinity might imply that a small change on the surface morphology of AGP takes place, i.e., the amorphous surface layer is formed [7]. This feature can also be identified from the Raman spectra of the two samples (Fig. 1b), where the value of  $R$  (the intensity ratio of  $D$  band to  $G$  band), which represents

the ratio of amorphous structure to graphitic structure [22], also increases from 0.19 of the original AGP to 0.31 of GAG5.

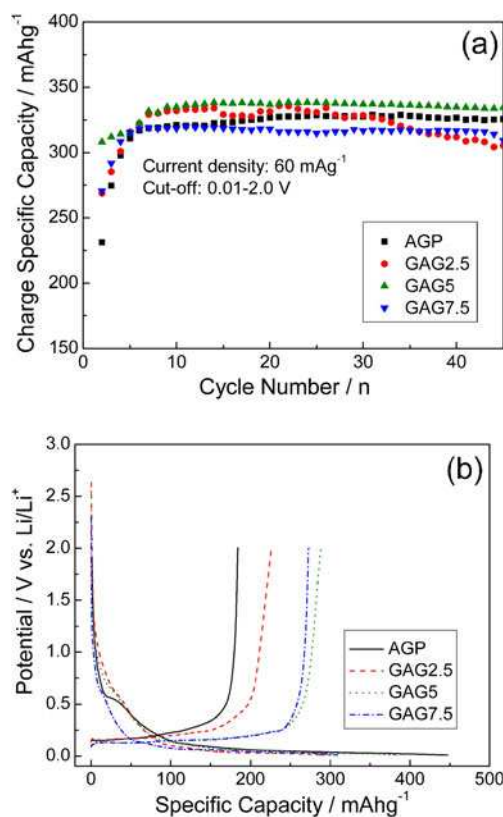
SEM observation reveals that carbon coating does not change the spherical morphology of AGP particles, as illustrated in Fig. 2. However, some changes on the particle surface take place. There are some bulgings on the surface of AGP particles (Fig. 2a), while the particle surface of the GAG5 sample becomes relatively smooth and tidy (Fig. 2b), suggesting that amorphous carbon is formed on the particle surface after carbon coating, forming core-shell structured particles.

### Electrochemical characterization

The electrodes of pristine and carbon-coated AGP were cycled at a current density of  $60 \text{ mA g}^{-1}$  to evaluate the effect of carbon coating on the specific capacity and initial coulombic efficiency of AGP materials. Figure 3a presents the comparison of charge capacity and cyclic performance of the pristine and coated samples. Herein, the charge capacity means the lithium ions were extracted from the graphite electrode and discharge capacity corresponds to



**Fig. 2** SEM images of pristine AGP (a) and carbon-coated GAG5 (b) samples. Insets are the magnified images of the corresponding sample



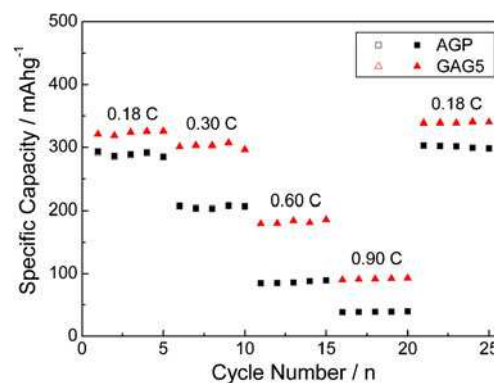
**Fig. 3** Electrochemical performance of pristine AGP and carbon-coated AGP samples cycled at a current density of  $60 \text{ mA g}^{-1}$ . **a** Charge capacity vs. cycle number (from the second cycle). **b** Initial charge/discharge voltage profiles

the insertion of lithium ion into the graphite electrode, as the examined electrode was assembled as positive electrode with metal lithium as negative electrode in this work. During the first five cycles, the charge-specific capacity increases with increasing cycle, indicating that the graphite is slowly being “conditioned” and hence there is an increased utilization of the active material [2]. It is noted that an appropriate amount of amorphous carbon coating can enhance the specific capacity of the AGP electrode. The sample GAG5 coated with 5 wt.% glucose exhibits the highest reversible specific capacity of about 340 mAh g<sup>-1</sup>, much better than that of the sample coated with 2.5 or 7.5 wt.% glucose, as depicted in Fig. 3a. Less or excessive carbon coating results in the decrease in reversible capacity.

The isotropic structure characteristics of amorphous carbon film on the AGP particle surface increase the diffusion channels of lithium ions and thus facilitate the electrode reaction process, which is favorable for the improvement in specific capacity. However, less carbon coating may form an incomplete coating film and the naked surface of AGP particles may be destroyed during the calcination for carbon pyrolysis (e.g., GAG2.5). As a result, the solvated lithium ions can intercalate into the deteriorated surface of AGP particle, which will cause the exfoliation of the graphite during cycling and thus eventually result in the degradation of the cycling performance. On the other hand, the excessive coating with amorphous carbon increases the thickness of the coating film and therefore elongates the distance traveled by lithium ions in graphite particles during the intercalation process, which will lead to the increase in both electronic and ionic resistances [2]. This will retard the electrode reaction process and thereby cause the decrease in reversible capacity, as reflected by the sample GAG7.5.

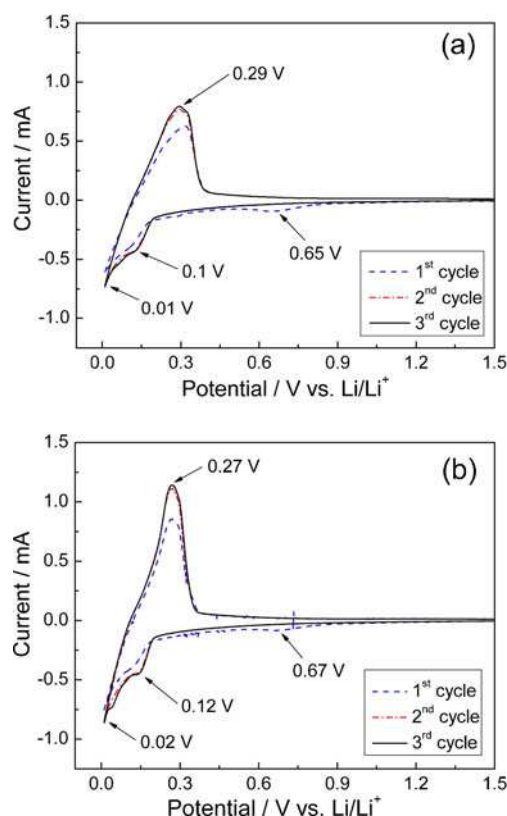
With respect to the initial coulombic efficiency (ICE), the amorphous carbon coating decreases the initial capacity loss and thus increases the ICE remarkably. The ICE increases from 41.1 to 88.2 % when the AGP was coated by 7.5 wt.% glucose (GAG7.5). The improvement can be attributed to the decrease in BET-specific surface area and the special structure and performance of amorphous carbon on the particle surface structure [23]. The BET-specific surface area for AGP and GAG5 is 2.056 and 0.799 m<sup>2</sup>g<sup>-1</sup>, respectively. The decreased specific surface area of the coated sample makes the initial irreversible capacity from the contribution of solid electrolyte interphase (SEI) film notably reduced, as demonstrated by the voltage profiles in Fig. 3b. At about 0.65 V, a plateau corresponding to the formation of SEI film is distinguishable in the first discharge process curve of the pristine AGP, whereas no plateau is found for the coated samples.

The crystallite of graphite is markedly anisotropic because the bonding in the layer is covalent but that between



**Fig. 4** Charge/discharge capacity of AGP and GAG5 electrodes at different C rates

the layers is van der Waals-like [8, 24]. The diffusion of lithium ion along the carbon layer is much easier than that along vertical plane during the charge/discharge process. This strongly limits the rate capability of graphite electrode. Considering the isotropic structure characteristics of amorphous carbon, which can provide more equivalent channels for lithium ion diffusion compared to graphite, a good rate capability is thereby expected for amorphous carbon-coated samples. The lithium ions that reached at the surface of the active particles can be easily guided by the amorphous



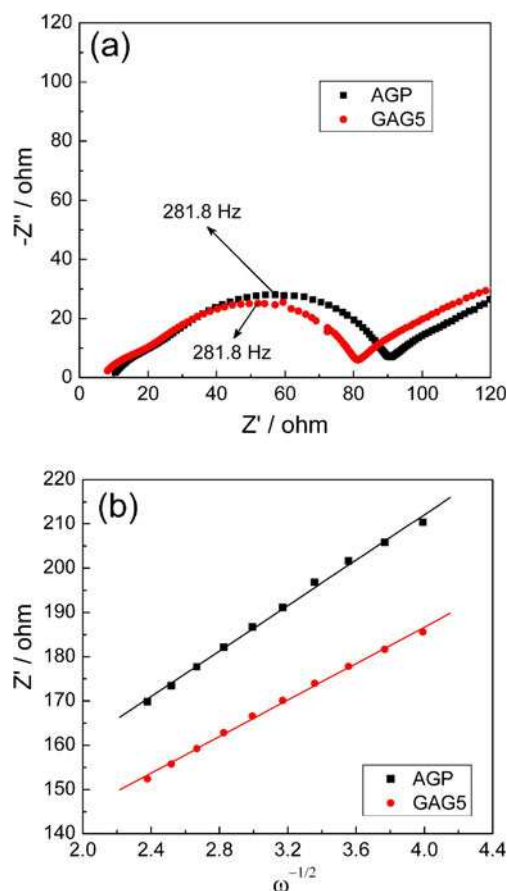
**Fig. 5** Cyclic voltammetric curves of AGP (a) and GAG5 (b) electrodes recorded at a scan rate of 0.1 mVs<sup>-1</sup>



carbon to the preferable (002) direction of the graphite particle and thus promoting the diffusion of lithium ion into the graphite particles. Samples of pristine AGP and carbon-coated GAG5 were selected to evaluate the effect of amorphous carbon coating on the rate capability. Two samples were charged/discharged at 0.18 C for the first five cycles and then followed by 0.30, 0.60, 0.90, and 0.18 C for the second, third, fourth, and fifth five cycles, respectively. The results are displayed in Fig. 4. As expected, the sample GAG5 shows much better rate capability than AGP.

In order to gain insight into the electrode reactions, the two electrodes AGP and GAG5 were subjected to the CV examination. Figure 5 illustrates the results. The increase in redox currents with successive cycling indicates that there is an activation stage during the lithiation/delithiation process which is consistent with the results shown in Fig. 3a. Three stages of lithium ion intercalation/deintercalation occurring below 1.0 V with distinct intercalation steps at about 0.01, 0.1, and 0.65 V were observed. During the first cathodic scan, before the intercalation of lithium ions into the graphite, a reductive decomposition of the electrolyte occurs on the graphite surface and the decomposition products form the so-called SEI film on the graphite at 0.65 V, which protects the electrolyte from continuous decomposition during subsequent cycling. This peak is difficult to observe for sample GAG5 and disappears in the following cycles. The peaks observed at around 0.1 and 0.01 V are assignable to the lithiation process of graphite [25, 26]. The anodic peak at ca. 0.29 V is ascribed to the delithiation process of graphite. The comparison between the CV curves of the two samples reveals that the potential difference of redox peaks decreases after amorphous carbon coating, indicating the reduced electrode polarization, which should be responsible for the improved rate capability of the sample GAG5.

To further investigate the electrode reaction kinetic process, AC impedance measurements were performed on the half-discharged AGP and GAG5 electrodes to estimate the diffusion coefficient of lithium ion in the electrode. Herein, three samples were used to get the average value of the lithium ion diffusion coefficient in AGP and GAG5 electrodes. The representative Nyquist plots and Randles plots for these two electrodes are shown in Fig. 6. The impedance of the electrode is decreased after amorphous carbon coating, indicating the improved electrode reaction process. Based on the slope of fitted lines in Fig. 6b, the diffusion coefficient of lithium ions ( $D_{Li}$ ) in the two electrodes can be derived according to the reported formula [27]. The calculated average  $D_{Li}$  with errors for AGP and GAG5 electrodes is shown in Table 1. The GAG5 electrode presents higher  $D_{Li}$  than the pristine AGP electrode, demonstrating that amorphous carbon coating can indeed enhance the lithium ion diffusivity of graphite electrode materials. This is also reflected in the improved rate capability of GAG5 electrode (Fig. 4).



**Fig. 6** Nyquist plots (a) and Randles plots (b) for half-discharged AGP and GAG5 electrodes

## Conclusions

Amorphous carbon-coated artificial graphite anode materials with a core-shell structure were prepared using glucose as the carbon source. Appropriate carbon coating can increase the reversible specific capacity and initial coulombic efficiency, while excessive carbon coating will increase the diffusion distance of lithium ions into the active particle, which is unfavorable for the improvement of the specific capacity. The sample coated with 5 wt.% glucose exhibits a stable specific capacity of 340 mAh g<sup>-1</sup>. The rate capability of the graphite anode material can be remarkably enhanced by carbon coating, which is mainly attributed to the increased diffusion coefficient of lithium ion.

**Table 1** Calculated diffusion coefficient of lithium ions ( $D_{Li}$ ) for AGP and GAG5 electrodes at the depth of half discharge

Sample	$D_{Li}/\text{cm}^2\text{S}^{-1}$
AGP	$(9.598 \pm 0.008) \times 10^{-14}$
GAG5	$(1.192 \pm 0.009) \times 10^{-13}$

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