



Effect of oxygen contents in graphene like graphite anodes on their capacity for lithium ion battery



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HIGHLIGHTS

- The high capacity of GLG was ascribed to the oxygen atoms in introduced in it.
- The capacity of GLG increased with increasing oxygen content.
- A high capacity of 673 mAhg⁻¹ was obtained.
- The coulombic efficiency of GLG was slightly improved by hydrogen gas treatment.

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ABSTRACT

Graphene like graphite (GLG) samples containing various amounts of oxygen are prepared from the thermal reduction of graphite oxide (GO) and are used as anodes of lithium ion battery. The oxygen/carbon (O/C) ratios in GLG varied from 0 to 0.08, depending on the thermal reduction temperature, oxygen gas pressure during heat treatment and degree of oxidation of the starting GO. The cell voltage during discharge almost linearly increases below 1 V independent of the oxygen contents in them. The discharge capacity of GLG above 1 V increases with the increase in the oxygen content with a slope of lithium/oxygen ratio of 3 at lower O/C ratios. Then the slope becomes smaller and the discharge capacity reaches 673 mAhg⁻¹ for GLG with O/C = 0.08. When GLG is treated with hydrogen gas, considerable amounts of oxygen atoms are substituted by hydrogen ones. The discharge capacity of the resulting GLG samples is larger than that expected from their oxygen contents and coulombic efficiency is slightly improved up to 59%. Introduction of oxygen atoms within carbon layers results in the large increase in the interlayer spacing during charging, which leads to accommodation of large amounts of lithium ions.

1. Introduction

Lithium ion batteries (LIBs) with high capacities have been used as a power source for portable electronic devices. Graphite, the commercial anode material, cannot meet the increasing demands of LIBs for electric vehicles due to its low theoretical capacity of 372 mAhg⁻¹ and poor rate performance. Therefore, researchers have continuously focused on the preparation of novel carbon-based anodes with improved capacity and rate performance. Several novel carbon-based anode materials with high capacity, even exceeding 1000 mAhg⁻¹ and high rate performance have been introduced, such as carbon nanotubes, graphene and their

composite materials [1–6]. However, they are suffering from low coulombic efficiency because of their intrinsically high surface area and considerable extent of capacity is achieved above 2 V which is not favorable for the use of them in LIBs. The mechanism of high capacity of these carbons is not well understood yet, though it has been suggested that large interlayer spacing, smaller diameter of graphene sheets, surface area, etc play important roles for it, based on theoretical consideration and experimental data [7–9]. In addition, the density of them is low, which is also not favorable for the volumetric capacity.

In this context, we have recently introduced graphene like graphite (hereafter abbreviated as GLG) as a superior anode for lithium ion

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battery. It shows high capacity of 608 mAhg^{-1} with a cutoff voltage of 2 V, good rate performance and relatively high coulombic efficiency of 56% at the 1 s t cycle [10]. It is prepared from the thermal reduction of graphite oxide (abbreviated as GO) under vacuum, avoiding rapid exfoliation and therefore it possesses low surface area around $30 \text{ m}^2 \text{ g}^{-1}$. The interlayer spacing (ca. 0.34 nm) and morphology are similar to those of graphite ($d = 0.3354 \text{ nm}$). It contains a considerable amount of oxygen within its graphene layers mainly in the form of C-O-C [11] and this functional group seems to play the key role for its superior performance. It has been widely reported that introduction of hetero atoms such as hydrogen, nitrogen, boron, oxygen or defects, etc, into carbon materials enhances the capacity of the resulting ones [11–16]. However, the papers in which the effects of these atoms are quantitatively discussed have been rarely published. This could be because it is very difficult to control the contents of them without changing the structural parameters of carbon materials such as d (002), crystalline sizes along c- or a-axes, compositions, etc or the contents of co-existing elements at the same time, when they are obtained from the heat treatment of their precursors. To the author's best knowledge, only the effect of hydrogen atoms on the capacity of carbon materials has been quantitatively discussed based on the experimental data. It has been pointed out that the capacity linearly increases with the slope of lithium/hydrogen ratio (Li/H) of 1, when the hydrogen contents are low [13,14]. However, even in these reports, the effect of co-existing other elements such as oxygen has not been mentioned. On the other hand, since GLG is obtained from the thermal reduction of GO prepared from highly crystallized graphite and the exfoliation is carefully avoided, the structural parameters such as La and Lc do not change much comparing with carbons obtained from the heat treatment of other precursors at lower temperatures. This makes it possible to know the true effect of hetero atoms introduced in carbon materials on their electrochemical properties.

In this study, in order to know the role of oxygen atoms in GLG samples, those with various oxygen contents were prepared from the thermal reduction of graphite oxide under vacuum at higher temperatures. This is because in our earlier studies, thermal reduction of graphite oxide was performed mainly under hydrogen gas flow or at lower temperatures, and therefore, the resulting samples contained not only oxygen but also hydrogen at the same time [17–19]. The electrochemical properties of the resulting GLG samples were investigated in detail. The effect of hydrogen on the capacity of GLG was also discussed, based on the result of GLG treated with hydrogen gas. The electrochemical properties of the resulting GLG samples were investigated in detail. The effect of hydrogen on the capacity of GLG was also discussed, based on the result of GLG treated with hydrogen gas.

2. Experimental

Graphite oxide (GO) was prepared by the method based on the Brodie's one [21,22] from natural graphite powder (Z-5F; Ito graphite Co. Ltd, ca. 5 μm , C: 99.60%, O: 0.25%). In some cases, the obtained GO was further oxidized in the same manner as above for 1–3 times, in order to obtain GO with different oxidizing levels. Here, the resulting GO samples are denoted as GOn (n; number of oxidation time). The obtained GOn samples were heated at 700–1100 °C and GLGn-T was obtained (The letter “T” denotes the heat treatment temperature). In order to modify the oxygen content in GLG samples, some of them were heated under oxygen or hydrogen atmosphere.

Oxygen treatment of GLG1-800 was performed as follows. The GLG1-800 used in this experiment contained 2.1% of oxygen which was slightly smaller than that obtained above, since a different GO was used as a starting material. Therefore it was denoted as GLG1b-800. It was heated to 800 °C at a temperature increase rate of $1 \text{ }^\circ\text{C min}^{-1}$ under vacuum and was maintained at 800 °C for 20 min. Then, various amounts of oxygen (2–15 kPa) were introduced in the reactor and it was cooled naturally.

The GLG1-T samples were also treated by hydrogen gas. They were placed in the furnace and then it was evacuated. Hydrogen gas of 50 or 150 kPa was introduced at room temperature and the temperature was increased to 700–1100 °C at a temperature increase rate of $1 \text{ }^\circ\text{C min}^{-1}$. They were heated at these temperatures for 5 h. In some cases, this procedure was repeated twice.

The resulting samples were analyzed by XRD (Rigaku Rint-2000) using silicon powder as an internal standard and crystalline sizes along a- and c-axes (La and Lc) were determined. IR measurement was performed by KBr method using Nicolet iS50 (Thermo Fisher Scientific). The compositions of them were determined, based on the elemental analysis data of carbon, hydrogen, nitrogen and oxygen. Note that nitrogen was not detected for all of the GLG samples prepared in this study. Elemental analyses of carbon, hydrogen and nitrogen were carried out using Yanako CHN coder MT-5, MT-6 or J-Science JM10. That of oxygen was performed using J-Science JMO10. Both are made at the Center for Organic Elemental Microanalysis at Kyoto University. The GLG samples were also analyzed by X-ray photoelectron spectroscopy (XPS) using Ulvac PHI-5000.

The GLGn-T samples were mixed with acetylene black (AB), and the resulting mixture was dispersed in the polyvinylidene fluoride (PVDF) solution of N-methyl-2-pyrrolidone. The obtained slurry was pasted onto Cu foil and then dried at 60 °C overnight under vacuum. The weight ratio of GLG-T, AB and PVDF was 8:1:1. In case of the oxygen treated GLG1b-800 samples, carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) were used as binders and the weight ratio of oxygen treated GLG1b-800:carbon black: CMC: SBR was 92: 3: 2: 2. The charge-discharge measurement of GLG samples were performed at a constant current of 40 mA g^{-1} and subsequent constant voltage of 0.01 V for 5 h in 1 M $\text{LiClO}_4\text{-EC} + \text{DMC}$ (1:1) or (3:7) using Li metal as a counter electrode.

3. Results and discussion

3.1. Preparation of GLG with various oxygen contents

Fig. 1(a) shows the X-ray diffraction patterns of GLG1-T samples obtained at various temperatures. The diffraction peak at $2\theta = 12^\circ$ ($d = 0.74 \text{ nm}$) observed for pristine GO (not shown in the figure) greatly shifted to higher angles after heat treatment. At 700 °C the peak appeared at $2\theta = 25.49^\circ$ and d value was 0.349 nm. The diffraction peak gradually shifted to higher angle as the increase in the temperature up to 950 °C and reached $2\theta = 26.7^\circ$ ($d = 0.334 \text{ nm}$). Then it slightly shifted to higher angle and became broader at 1000 °C. It has been already reported that the interlayer spacings of carbons prepared from the thermal reduction of GO around 1000 °C are smaller than those of the carbons obtained from graphitizable precursors [23,24]. As the increase in the thermal reduction temperature, oxygen atoms bonded to the carbon layers are removed, therefore, the interlayer spacing becomes smaller. At the same time, some of them are introduced within the carbon layer in the state of C-O-C as we proposed in the previous paper [10]. In such a case, it is expected that the coulombic attraction between negatively charged oxygen atoms in one layer and positively charged carbon atoms in the other layer can reduce the interlayer spacing. This could result in the smaller d value than that of graphite ($d = 0.3354 \text{ nm}$).

Fig. 1(b) shows the oxygen contents in the above samples, determined based on the elemental analysis data. They almost linearly decreased as the increase in the heat treatment temperature and reached zero at 1000 °C. This result also suggests that the oxygen atoms introduced within carbon layers in GLG play an important role to maintain the stacking regularity of GLG prepared at 900 °C or below and probably because of the above mentioned coulombic interaction between oxygen and carbon atoms existing in different carbon layers. When the oxygen atoms are almost completely removed, the stacking regularity would be lost and the interlayer spacing became similar to

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