



# Characterization of neutralized graphite oxide and its use in electric double layer capacitors <sup>☆</sup>



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## ABSTRACT

Spherical graphite oxide (GO) with high density was synthesized from mesocarbon microbeads (MCMB). The obtained GO was neutralized by various alkaline metal hydroxides and tetraalkylammonium hydroxides. The neutralized GO showed lower water content and much better thermal stability than those of pristine GO. The as-prepared neutralized GOs were investigated as electrode materials for electric double layer capacitor (EDLC) in organic electrolyte. From both the results of galvanostatic charge–discharge and cyclic voltammetry (CV) measurements, it was found that the tetrabutylammonium hydroxide (TBA-OH) together with lithium hydroxide neutralized GO (TBA-Li-GO) displayed a relatively ideal EDLC feature after electrochemical activation at the initial cycle. The positively polarized TBA-Li-GO with small surface area ( $16 \text{ m}^2 \text{ g}^{-1}$ ) exhibited a high volumetric capacitance of  $60 \text{ F cm}^{-3}$  after 1000 cycles, which is much higher than that of commercial activated carbon ( $36 \text{ F cm}^{-3}$ ).

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## 1. Introduction

Electric double layer capacitors (EDLCs) have attracted a considerable attention during the past several decades owing to their extremely high power density and long cycle life. Due to the intrinsic nature of EDLC, it has been considered as a good candidate for high power devices, especially for automotive applications [1–4]. Carbon based materials such as activated carbons [5–7], activated carbon fibers [8,9], carbon aerogels [10,11] and carbon nanotube [12,13] have been studied intensively for the use as electrode materials for EDLCs. Among these carbonaceous materials, porous activated carbons with high surface area ( $1000\text{--}2000 \text{ m}^2 \text{ g}^{-1}$ ) are considered to be the most ideal electrode material for EDLC. It has been proved that the activated carbons show good cycleability and stability in a great variety of electrolytes. However, due to the large surface area and high porosity of activated carbons, the volumetric capacitance of the commercial activated carbon is still in a low level [14,15].

In the past several years, graphene based material has attracted great attention from many researchers because of its exceptional properties and potential applications in energy storage devices [16,17]. Graphene oxide, which is generated from graphite oxide

(GO), has been a promising approach to prepare graphene related materials. Furthermore, the reduced graphene oxide has been studied intensively by many researchers for the use as an electrode material for electrochemical capacitors [18,19]. Although high gravimetric energy density can be obtained in these devices, the volumetric energy density of grapheme based electrode materials is still low because of their porous texture does not allow the dense packing. Only a few works have successfully obtained electrode materials with both high gravimetric and high volumetric capacitance in reduced grapheme oxide [20,21]. Therefore, it is of great necessity to develop high density electrode materials for EDLC.

Herein, we focused on the synthesis of graphite oxide with lamellar structure by selecting mesocarbon microbeads (MCMB) as starting material. MCMB has been recognized as an excellent precursor for the synthesis of high density and high strength carbonaceous material since it was first separated from mesophase pitches by Yamada et al. [22]. The spherical shape of MCMB particles with lamellar graphene sheet would be ideal for approaching dense packing. Zheng et al. have investigated non-porous activated MCMB as the negative electrode for asymmetric electrochemical capacitors with improve energy and power density [23]. Moreover, high content of  $\text{sp}^3$  carbon in MCMB may inhibit the exfoliation of graphene layers during the chemical oxidation so as to retain the high density. It is also well known that various oxygen functional groups are introduced into layers of graphene sheets after oxidation. Due to the existence of some acidic groups, such as COOH and phenolic OH, GO can be neutralized by various alkaline hydroxides as well as tetraalkylammonium hydroxides. In this study, various neutralized GOs with high tap density were

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successfully prepared. Despite of the extremely low surface area, non-porous neutralized GO showed much higher volumetric capacitance than that of activated carbon. Furthermore, compared to the synthetic methods of activated carbons, our method is easy to operate, very fast, low cost and without the need of chemical activation at high temperature.

## 2. Experimental

### 2.1. Preparation of graphite oxide

GO was synthesized from MCMB (average particle size: 15  $\mu\text{m}$ , Hosen Co., Japan) according to the traditional Hummers method [24]. Typically, MCMB (10 g) and  $\text{NaNO}_3$  (5 g) together with  $\text{H}_2\text{SO}_4$  (220 mL) were mixed in a round flask placed into the water ice bath. To avoid vigorous reaction,  $\text{KMnO}_4$  (20 g) was gradually added into the mixture at 0–10  $^\circ\text{C}$ . After the addition of  $\text{KMnO}_4$ , the mixture was kept at 35  $^\circ\text{C}$  for 1 h. Subsequently, the mixture was transferred to 460 mL  $\text{H}_2\text{O}$  and hold strictly at 98  $^\circ\text{C}$  for 30 min. The reaction was terminated by adding 1400 mL  $\text{H}_2\text{O}$  and 10 mL  $\text{H}_2\text{O}_2$ . Then the diluted solution was kept for 1 day followed by filtering and drying at 80  $^\circ\text{C}$  for 12 h.

### 2.2. Preparation of neutralized GO

For the preparation of neutralized GO, the obtained GO (1.0 g) was dispersed in 100 mL  $\text{H}_2\text{O}$ . The dispersion was stirred and then titrated with various alkaline hydroxides solution (0.2 M) and tetraalkylammonium hydroxides solution (0.24 M) until the pH = 11. The whole process was controlled considerably slow to enable the fully neutralization of GO. The reaction was kept at 25  $^\circ\text{C}$  for another 3 h. Then, neutralized GO powder can be obtained after filtering and drying at 80  $^\circ\text{C}$  for 12 h.

### 2.3. Characterization methods

X-ray diffraction (XRD) profiles of the as-prepared GO and neutralized GOs were recorded for two theta value from 3 $^\circ$  to 80 $^\circ$  (Cu K $\alpha$  radiation, XRD-7000, SHIMADZU). Thermo-Gravimetric/Differential Thermal Analysis (TG-DTA) measurement was performed at a heating rate of 5  $^\circ\text{C min}^{-1}$  from room temperature to 500  $^\circ\text{C}$  in air (Thermoflex TG-DTA 8110, Rigaku). Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded on a JASCO 400 FTIR spectrometer (KBr pellets method). Nitrogen adsorption-desorption isotherm were carried out after the samples were outgassed and dehydrated at 180  $^\circ\text{C}$  for 24 h (Micromeritics Gemini 2360, SHIMADZU). The specific surface area of each sample was calculated from the Brunauer-Emment-Teller (BET) method. Mercury intrusion porosimetry measurements were performed on a Micromeritics AutoPore III 9420 mercury porosimeter (SHIMADZU). The tap density is achieved by mechanically tapping a measuring cylinder containing a power sample. After observing the initial volume, the cylinder is mechanically tapped, and volume readings are taken until little further volume change is observed. Generally, replicate measurements were carried out for the determination of tap density.

### 2.4. Electrochemical characterization of GO and neutralized GO

The symmetric capacitors of neutralized GO and commercial activated carbon (AC1, Kuraray Chemical Co., Japan) were examined by using the CR-2032 type coin cell with 1 M triethyl-methylammonium phosphorus hexafluoride ( $\text{TEMAPF}_6$ ) as electrolyte. For the fabrication of electrodes, 10 mg active material together with 4 mg conducting binder (Teflon:Acetylene black = 1:2) was

mixed and pressed on the stainless steel mesh. Then, the electrodes were dehydrated by a vacuum dry at 150  $^\circ\text{C}$  for 12 h. The cell was cycled between 0 and 3 V at a current density of 0.8  $\text{mA cm}^{-2}$ . The specific capacitance of the symmetric capacitors was estimated according to the following equations [25]:

$$C_m = (I \times \Delta t) / (\Delta V \times m) \quad (1)$$

$$C_{sp} = 4C_m \quad (2)$$

where  $C_m$  is the measured capacitance of the electrode ( $\text{F g}^{-1}$ ),  $\Delta t$  is the discharge time (s),  $\Delta V$  is the potential window during the discharge process (V),  $m$  is the total weight of the active material on the two electrodes,  $C_{sp}$  refers to the specific capacitance of a single electrode in two electrodes cell.

The cyclic voltammetry (CV) measurements were conducted under three electrode cells with lithium metal as both reference and counter electrode. The electrolyte used was a mixture of 1 M lithium phosphorus hexafluoride ( $\text{LiPF}_6$ ) and 1 M  $\text{TEMAPF}_6$  in propylene carbonate with volume ration of 1:5. The capacitance estimated from CV ( $C_{cv}$ ) was calculated according to following equation:

$$C_{cv} = \left( \int idV \right) / v\Delta Vm \quad (3)$$

where  $i$  is the response current (A),  $v$  is the scan rate ( $\text{V s}^{-1}$ ),  $\Delta V$  is the potential window (V) and  $m$  is the weight of the electrode material (g).

To investigate the electrochemical activation of TBA-Li-GO electrode, galvanostatic charge-discharge measurement was examined in a half cell with lithium metal as counter and reference electrode. In this case, the electrolyte used was a mixture of 1 M lithium phosphorus hexafluoride ( $\text{LiPF}_6$ ) and 1 M  $\text{TEMAPF}_6$  in propylene carbonate (PC) with volume ration of 1:5. The electrodes were fabricated with the same method as that used in symmetric capacitors. Electrochemical impedance spectroscopy (EIS) was recorded with the potential amplitude of alternative current was 10 mV and the frequency range was from 50 kHz to 10 mHz.

## 3. Results and discussion

### 3.1. Characterization of GO

The XRD patterns of pristine MCMB and GOs are shown in Fig. 1. Pristine MCMB shows a very sharp diffraction peak at  $2\theta = 26^\circ$

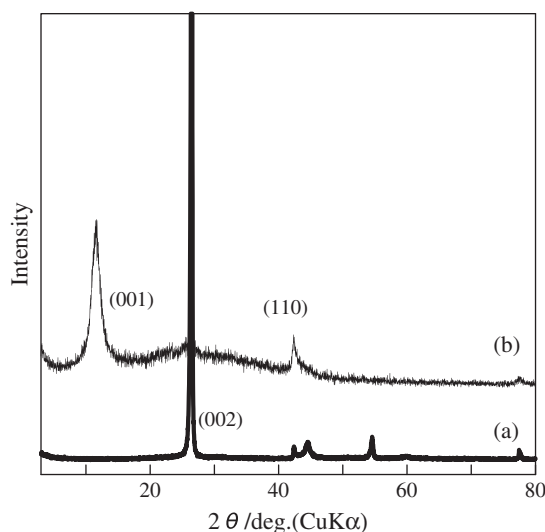


Fig. 1. XRD patterns of pristine MCMB and GO: (a) pristine MCMB, (b) GO.

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