



Graphite Oxide: An Interesting Candidate for Aqueous Supercapacitors



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ABSTRACT

A graphite oxide, obtained on a large scale at low cost as an intermediate in the graphene production, achieves specific capacitances (159 Fg^{-1} in H_2SO_4 and 82 Fg^{-1} in $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ in acetonitrile) that compete with those of activated carbons and largely surpass the values obtained with graphene nanoplatelets. More promising, the high electrode density leads to volumetric capacitances of 177 and 59 F cm^{-3} in the aqueous and the organic electrolytes, respectively, which are above most data reported for carbons. In the aqueous electrolyte, the graphite oxide stands out on energy density when compared to graphene nanoplatelets and on power capability if compared to an activated carbon commercialized for supercapacitors, whereas in the organic electrolyte, the limited interlayer spacing restricts the mobility of the larger ions into the expanded graphitic structure. This study also illustrates that the specific surface of carbons measured by standard gas adsorption may not be a relevant parameter as it does not always match the electrochemically active area involved in the energy storage.

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1. Introduction

Supercapacitors (SC) are under an increasing demand as alternative energy storage devices. Their high rate capability, pulse power supply, long cycle life and low maintenance cost make them highly attractive for powering electric vehicles, portable electronic devices, uninterruptible power supplies, etc. [1].

The electrochemical double layer capacitor (EDLC) is a type of supercapacitor in which the energy is physically stored by means of ion adsorption at the electrode/electrolyte interface [2]. A wide variety of carbons (activated carbons, carbon nanotubes, templated carbons, carbide-derived carbons, carbon gels, carbon blacks, glassy carbons, etc.) have been extensively investigated as electrodes in EDLC [3–10]. The number of candidates has increased with the recently discovered graphene, since its large theoretical surface area and high electrical conductivity result key features for application in SC [11–14].

In spite of the potential of graphene, it still needs to compete with activated carbons in terms of cost/performance [11,12,15] to be used in practice. In this context, up-to-now the most promising approach to obtain graphene for SC involves the chemical

oxidation of graphite followed by an exfoliation process to produce graphene oxide and, finally, a controllable reduction to obtain reduced graphene oxide [11–14]. As lower-cost materials for supercapacitors are a priority, the intermediate graphene oxide will have an advantage over reduced graphene oxide. It has been reported that graphene oxide itself may be promising in EDLC electrodes [16,17] but its application appears to be limited by its low conductivity [11,12,14].

Currently, graphene oxide has not been commercially available in large quantities, normally selling in gram quantities, partly due to the lack of a sustainable production process. However, Abalonyx AS, a Norwegian technology start-up company, has recently developed an improved method for the production of graphene oxide, based on a modified Hummers procedure [18,19], that will now be mass produced. Nitrate is not used in order to avoid noxious fumes, resulting in a more environmentally friendly process now being scaled to tons/year capacity.

Herein, we report that graphite oxide, generated on a large scale at low cost in the early stages of graphene oxide preparation may become competitive for electrodes in aqueous supercapacitors. The systematic comparison of its electrochemical performance with an activated carbon available on the market for SC and commercial graphene nanoplatelets provides reliable information on the relative potential of the graphite oxide for energy storage devices.

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2. Experimental Section

2.1. Material preparation

Graphite oxide S43 was prepared on large scale by a modified Hummers method [16,18] using 100 g Nanocon-1 graphite (NNC Corporation, Japan) as raw material resulting in about 160 g graphite oxide. After oxidation, the material was washed twice with 5% HCl and once with 1% HCl and finally centrifuged, resulting in a thick aqueous paste with about 32 wt% graphite oxide. The material was spread on a plastic sheet and air-dried over night. As a result dry flakes of graphite oxide were obtained.

2.2. Material characterization

A variety of techniques was used to monitor the chemical and structural changes occurring in the different materials. Experimental details are described in the Supporting Information (SI).

The chemical characterization of the sample used (batch S-43) was carried out by elemental microanalysis and by X-ray photoelectron spectroscopy (XPS). It was further studied by Thermal Programmed Desorption (TPD) experiments from room temperature to 1000 °C.

The morphology of the samples was examined by Scanning Electron Microscopy whereas the structural characterization involved X-Ray Diffraction and Raman Spectroscopy.

The textural features were estimated from physisorption isotherm of N₂ at 77 K and CO₂ at 273 K. The density of the sample was determined by He pycnometry.

The electrochemical performance was tested in a sandwich-type capacitor set up with two carbon pellets separated by glassy fibrous paper (300 μm thick) and placed in a Swagelok cell. The dried S43 flakes were mixed with polytetrafluoroethylene to form electrodes consisting of 95 wt.% active material and 5 wt.% binder. The electrode was rolled to a thickness of ~140 μm, punched into a 8 mm diameter and dried in an oven at 100 °C for 24 h. Due to the poor performance, the carbon black Super-P (MMM Carbon) was further added to the composite electrode. The electrolytes were 2 M H₂SO₄ aqueous solution and 1 M (C₂H₅)₄NBF₄ in acetonitrile (TEABF₄/AN). The capacitance was determined by galvanostatic charge-discharge cycles (Autolab-Ecochimie PGSTAT 30) at different current densities, from 1 to 100 mA cm⁻², and cyclic voltammograms at scan rates ranging between 1 and 50 mVs⁻¹. The cell voltage ranged from 0 to 0.8 V for aqueous medium and between 0 and 2 V for the organic electrolyte. The gravimetric capacitance (Fg⁻¹) given in the present study is relative to the graphite oxide mass in a single electrode made of 90%wt. of S43, 5% wt. of PTFE and 5%wt. of Super-P. The experimental values reported correspond to those obtained after 10 charge-discharge cycles for each current intensity.

Electrochemical impedance spectroscopy (EIS) measurements were performed using a sinusoidal signal of ± 15 mV from 2 10⁻⁴ Hz to 60 kHz in a PGSTAT 30 (Autolab B.V., Metrohm) potentiostat equipped with a FRA32 M module.

The electrochemical performance of the graphite oxide was systematically compared with two carbons available on the market: i) the activated carbon Picactif SC (Pica, USA) and ii) graphene nanoplatelets C-750 (XG Sciences, USA) (see Supporting Information). The three samples were tested under the same experimental conditions.

3. Results and Discussion

The procedure developed by Abalonyx results in an extensive oxidation as indicated by the high increase in the oxygen percentage from 0.3 wt.% of the raw graphite to 39.2 wt.% for the

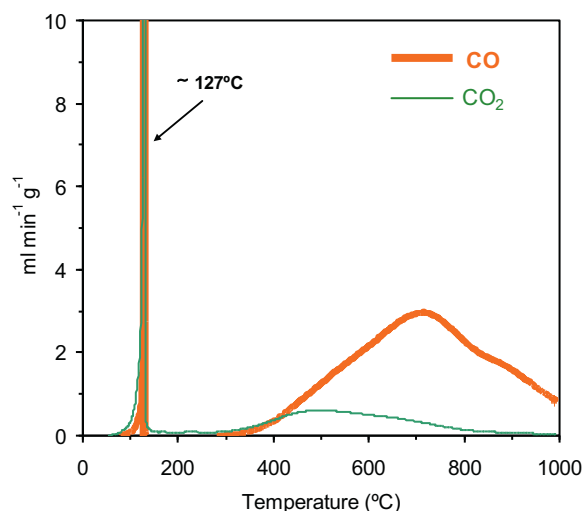


Fig. 1. TPD profile of the graphite oxide showing blasting at 127 °C.

graphite oxide material (labeled as S43). TPD experiments (Fig. 1) reveal the presence of labile oxygen-containing functionalities which start releasing even below 100 °C.

There is an abrupt generation of CO and CO₂ in a very narrow range at around a temperature as low as 127 °C which results in blasting (Fig. 1). Such behavior indicates a high concentration of oxygen functional groups intercalated into the graphene sheets which diminishes the Van der Waals interactions [20,21]. Moreover, there is a continuous and smooth weight loss between 350 and 1000 °C which corresponds mainly to the release of more stable functionalities desorbing as CO. The high concentration of oxygen functional groups is also confirmed by C/O ratio of 2.6, estimated by XPS. The surface oxygen is distributed in 23.2% of C–O (epoxy, hydroxyl) bonds, 14.2% of C=O functionalities and 16.8% of O–C=O carboxyl type-groups.

SEM images illustrate that S43 is composed of flakes with a layered structure (Fig. 2a, see also Figure S1). The analysis by HRTEM (Fig. 2b, see also Figure S2) reveals the presence of both graphene layers and oxidized regions with surface functional groups.

As reported by XRD profiles (Fig. 3a), the oxidation based on Hummers method induces a significant expansion in the graphite structure [21]. The intense (001) peak at 13.64° observed for S43 derives from the incorporation of water and oxygenated-functionalities on the carbon sheets which leads to the widening of the interlayer spacing from the typical 0.34 nm to ~ 0.65 nm on average.

In the Raman spectrum, a wide D-band typical for sp³ hybridation becomes prominent and the relative intensity of D to G band, I_D/I_G, is around 0.9 (Fig. 3b). This indicates the reduction of the in-plane sp² domains induced by the introduction of defective levels (edges, atomic vacancies, functionalities) and disorder [22]. XPS reports 22.2% of C–C in aromatic rings.

The electrochemical performance of the graphite oxide was tested in a sandwich-type capacitor set up with two electrodes separated by glassy fibrous paper. In a first attempt, the electrodes were formed by 95%wt. of S43 and 5%wt. of PTFE as binder. The collapsed cyclic voltammogram at 1 mV s⁻¹ in H₂SO₄ (Fig. 4, left) reveals an extremely low electrical conductivity which prevents electrochemical energy storage. As illustrated by Fig. 4, this shortcoming can be overcome by the addition of a carbon black to the composite electrode.

The steep current change at the switching potentials (Fig. 4, right) reflects quick charge propagation in the electrodes made of

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