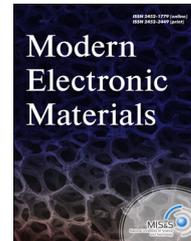




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Carbon nanostructures reduced from graphite oxide as electrode materials for supercapacitors

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Graphene materials;
Composites with conductive polymers

Abstract

In this review we present information about obtaining and properties of carbon nanomaterials (graphite oxide, grapheme oxide, reduced graphene oxide), which are used as electrodes for supercapacitors (SC). This review describes methods of obtaining graphite oxide, followed by separation of graphene oxide and reducing graphene oxide by thermal, photochemical and chemical methods. Information on the composition and concentration of functional groups in graphene oxide and the elemental composition is described in detail. Results of the analysis of epy physical, electrochemical, thermal and optical properties of the graphene oxide and its derivatives are shown. The ratio of oxygen-containing functional groups was estimated by XPS. The presence of partial surface reduction is found. Hydroge-containing functional groups are characterized by IR spectroscopy. Method of estimating the size of graphene crystallites by Raman spectroscopy is shown. Mass loss upon heating is analyzed by thermogravimetry. The gassing of graphene oxide at thermal and photochemical reduction is studied by mass spectrometry. The difference between the abovementioned reduction methods is clearly demonstrated by the difference in the composition of the evolved gases. Also the chemical method of graphene oxide reduction with hydrazine is described. Review considers the literature data which illustrate the most interesting, from the Authors' point of view, aspects of that field of research.

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Introduction

There are predictions in scientific literature that power consumption will grow twofold by 2050 compared with 2002 [1]. It is assumed that this level will only be achievable with the use of nanotechnology which opens new possibilities in the design of materials for power storage and transformation

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devices. Big hopes are placed on carbon nanomaterials having unique properties including low specific weight, high stability against corrosive media and high variability of heat and electrical conductivity.

Below we review questions relating to obtaining and properties of carbon nanomaterials which will be mainly used as electrodes for supercapacitors.

Functionally, a supercapacitor (SC) is a hybrid of a capacitor and a chemical current source. The simplest SC is a capacitor with electrolyte the plates of which are provided by the double dielectric layer (DEL) at the electrolyte/electrode interface. As the DEL thickness is small compared with typical capacitor plate spacing, the energy accumulated by an SC is much greater than that accumulated by a same-sized capacitor. Hence the prefix “super”. The capacity of a capacitor with a DEL will grow with electrode surface area. A DEL forms at the contact between two phases one of which is liquid. Unlike a flat capacitor a DEL has a diffusion structure. In the electrolyte the large thickness of the diffusion layer may impair the charge/discharge parameters of an SC. Electrolyte selection is another important problem, but it is beyond the scope of this review. One should note that a capacitor with a DEL based on porous carbon electrodes was first patented in 1957 by General Electric [2].

Energy accumulation during SC charging may also occur by Red-Ox reactions at the electrode/electrolyte interfaces. During discharge these reactions are inverse. The main difference of these SC from batteries is that the electrochemical processes only occur at the electrode surface leading to their even higher rate due to the absence of diffusion barriers. This capacity type is typically referred to as a pseudocapacity. Pseudocapacity may be considerably higher than the capacity of the DEL, but during cycled operation the pseudocapacity of an SC drops faster than the capacity of the DEL because the reversibility of chemical reactions is usually lower than that of physical charge separation.

The design of an SC can be asymmetrical, i.e. one electrode accumulates energy in a DEL and the other, by electrochemical processes. Theoretically, both energy accumulation methods can be implemented on a single electrode.

A perfect material for SC electrodes could be pure grapheme [3] which has both large specific surface and high conductivity. However, an obstacle to its application is its thermodynamical instability as a two-dimensional object and strong Van-der-Waals attraction between grapheme nano-sheets. Obviously, this application requires a 3D grapheme material, not necessarily on the basis of pure grapheme.

Synthesis of graphite oxide and separation of graphene oxide therefrom

One of the most promising method of producing large quantities of a material similar to grapheme by the presence of a monolayer of carbon atoms is graphene oxide separation from graphite oxide. Graphite oxide has been known since 1859 [4]. Currently graphite oxide is produced using the Hummers method [5]. Details of obtaining graphite oxide using a modified Hummers method used at the

Institute for Chemical Physics of the Russian Academy of Sciences are provided elsewhere [6].

The spacing between carbon atom layers in graphite oxide (0.7-1.2 nm depending on oxidation depth and water exposure duration) is far greater than that in graphite (0.335 nm). This dramatically reduces Van-der-Waals attraction and makes possible producing water suspensions containing sheets called graphene oxide that can be illustrated as graphene sheets covered with oxygen-containing functional groups as hydroxyl ones (–OH) and epoxy ones (C–O–C). The edges of these sheets also have a small quantity of carbonyl (C=O) and carboxyl (COOH) groups.

Graphite oxide is split using the method described elsewhere [6]. An atomic force microscopic study of the residue obtained after drying a drop of graphene oxide water suspension on an atomically smooth substrate (highly-oriented graphite or mica) showed the presence of approx. 0.6 nm thick particles, this thickness corresponding to that of a single-layer graphene oxide particle [7]. One can also obtain dispersions containing 80% single-layer graphene oxide sheets [8].

Properties of graphene oxide

Elemental composition of graphene oxide

Below we present data on the elemental composition of graphene oxide and graphite oxide (without making difference between them). This is based on the assumption that graphite oxide stratification does not change its composition, whereas analysis of graphene oxide does not require its separation from suspension.

Commercially available graphene oxide from Graphene Supermarket, US [8] contains 79% carbon and 20% oxygen. The balance 1% is most probably hydrogen. Brodie [4] characterized graphite oxide composition obtained by him as follows: C:O:H=61.01:37.11:1.85 or in a molecular presentation $C_{2.19}O_{1.00}H_{0.80}$. Graphite oxide samples synthesized using the modified Hummers method contained 50.10% carbon, 44.81% oxygen and 2.69% hydrogen [9]. Summing this up yields less than 100%. The cause is that the samples in fact contain process impurities difficultly removable with distilled water due to their location in closed graphite oxide pores. However, graphene oxide stratification followed by its centrifuging and a sequence of sedimentations produces a more pure material. Analysis of the available data suggests that the composition of graphite and graphene oxides is variable and depends on multiple factors. Therefore one should know the elemental composition of each specific batch to be used in the process route.

XPS spectra of graphene oxide

X-ray photoelectron spectroscopy (XPS) is widely used for the characterization of carbon materials including graphene oxide (see e.g. [10]). XPS spectra bear information on the composition, not of the entire sample, but that of a thin surface layer. Obviously, for single-layer graphene oxide nano-sheets the XPS composition data should be identical to the bulk composition.

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