A METHOD FOR PRODUCING AN ELECTRODE OF A CAPACITOR, IN PARTICULAR A SUPER-CAPACITOR

Title:

Abstract:

Partially reduced graphite oxide (GOpr) prepared from natural as well as synthetic graphite was used as electrode material for supercapacitors in e.g. 1 M Et$_2$NBF$_4$ in acetonitrile electrolyte. As a function of the degree of reduction of graphite oxide (GO) the graphite layer distance was varied between 0.46 and 0.33 nm. The initial specific capacitance of all samples was negligibly small around the open circuit potential, which was in agreement with the small BET surface area of the reduced GO powder of around 15 m$^2$/g. During the first potential cycle, however, electrochemical activation resulted in a specific capacitance of up to 220 F/g for samples with a graphene layer distance of 0.44 nm using 1 M Et$_2$NBF$_4$ in acetonitrile. For lithium containing electrolytes, e.g. 1 M LiPF$_6$ in EC/DMC, the measured specific capacitance after activation was found to be approximately 600 F/g. The potential for anodic and cathodic electrochemical activation was found to be a function of the GO layer distance. Dilatometric investigations showed a significant swelling and shrinking of the samples.
— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))
A method for producing an electrode of a capacitor, in particular a super-capacitor

The present invention relates to a method for producing an electrode of a capacitor, in particular a super-capacitor.

Electrochemical activation of carbons for supercapacitor electrodes was first described for mesophase coal tar pitch derived coke (MPC) as precursor material. The preparation of the material and some characterization is described in the US patent application US 2002/0039275 A1 by Takeuchi et al. Some years later this material and the electrochemical activation process were rediscovered in conjunction with the so called Nanogate Capacitor utilizing patented Nanogate Carbon®. The Nanogate Capacitor was expected to work at cell voltages of 3.5 V and above and to provide a specific energy of 27 Wh/kg with a specific power of 8 kW/kg.

During electrochemical activation the original carbon precursor material with a small surface area of below 100 m²/g and a rather small capacitance develops a significant capacitance if the potential is driven beyond the critical value for activation. This effect can be irreversible. The resulting material was assumed to be electrochemically more stable than activated carbon and to allow to build a capacitor which works at a cell voltage of 3.5 V or higher. In an early paper by Takeuchi et al. the effect of layer spacing on the performance of the activated carbon was also studied and the resulting effect was ascribed to ion and solvent intercalation (see US 2002/0039275 A1).

The electrochemical activation effect was further investigated for mesophase pitch-derived activated carbon using in situ SAXS and in situ dilatometry. The KOH activated carbon showed a specific capacitance of around 150 F/g after electrochemical activation and exhibited an irreversible volume expansion during activation of
24%. The increased capacitance after activation was primarily attributed to pores between the graphitic units which were not accessible before activation. Starting from needle coke a graphite oxide was produced with an interlayer distance of 0.36 nm, which exhibited electrochemical activation at a cell voltage of 1.0 V. Further, expanded MCMB (mesocarbon microbeads) was investigated with an interlayer distance of 0.404 nm using dilatometrie and impedance spectroscopy and described the electrochemical activation in a special electrolyte, which was a mixture of tetraethyl ammonium tetrafluoroborate (Et4NBF4, 0.95 M) and lithium tetrafluoroborate (LiBF4, 0.05 M) that was dissolved in propylene carbonate (PC). The specific capacitance of these electrodes was around 100 F/cm3. It is therefore an object of the present invention to provide a method for producing an electrode of a capacitor, in particular a super-capacitor, that can deliver an electrode material having a high capacitance and being rather simple in terms of the production process.

These objectives are achieved according to the present invention by a method for producing an electrode of a capacitor, in particular an electrode for a super-capacitor, using partially reduced graphite oxide (GOpr), equal to partially oxidized graphite, as active or additive material for the capacitor electrode.

Typically, the partially reduced graphite oxide has an interlayer distance bigger than graphite, typically in the range 0.34 - 0.47 nm wherein graphitic or graphite oxidic structures with interlayer distance above 0.55 nm could remain within the partially reduced graphite oxide.

The capacitive behavior of GOpr is achieved by the activation of the GOpr in order to give the electrolyte ions access to the
layered structure of the GOpr; said activation is done electrochemically by either an anodic or cathodic current sweep or chemical or physical treatment.

The activated form of GOpr has a changed crystalline structure and is distinguishable from the non activated GOpr by X-ray defraction (XRD), said activated form of GOpr showing a bigger interlayer distance than the equivalent form of non activated GOpr, preferably typically between 0.5 to 1.0 nm.

Typically, the activated GOpr applied as electrode material shows after the first formation cycle a specific capacitance above the capacitance of activated carbon based electrodes, e.g. 220 F/g when using aprotic electrolytes, for example 1 M Et4NBF4 in acetonitrile , or e.g. up to 600 F/g when using 1M LiPF6 in EC/DMC.

With respect to preferred compositions, the electrolytes are either aqueous or aprotic organic or ionic liquid, preferably aprotic organic electrolytes or ionic liquids such as:

i) examples for the salt are TEABF4, TEMABF4, LiClO4, LiPF6;
ii) examples for the solvent are acetonitrile (AN), propylene carbonate (PC), ethylene carbonate dimethylcarbonate (EC/DMC)
iii) ionic liquids, wherein the salt concentration is variable and also salt and/or solvent mixtures are possible.

Preferred electrode compositions are activated partially reduced graphite oxide powder, the active material (GOpr) bound with e.g. a polymer (e.g. PTFE, PVDF), active material (GOpr) combined with a conductive agent (e.g. Super P) bound with e.g. a polymer (e.g. PTFE, PVDF) and/or mixtures thereof.

Typically, the composition of the electrode varies between 50 to 100 wt.% activated partially reduced graphite oxide , 0 to 25 wt.%
conducting agent (e.g. Super P) and 0 to 25 wt.% polymer binder (e.g. PTFE or PVDF).

Advantageous electrode design are achieved when the electrode is formed as self standing bound electrode or is directly coated onto a current collector; the electrode thickness varies between 1 to 1000 µm, preferably in the range of 10 to 300 µm.

As for a preferred example, the electrode can be manufactured according to the following steps:

a) preparing graphite oxide from natural graphite or from synthetic graphite according to the well known method by Brodie:

10g graphite were mixed with 85g sodium perchlorate powder. The mixture was cooled to approx. -20°C using an ice sodium chloride mixture and then slowly stirred. Then 60ml fuming nitric acid were very slowly added. The green mass was stirred for additional 3 hours at room temperature. The mixture was left over night without agitation and then heated to 60°C for 12 hours. Then 2 liters of water were added to the reaction product, the mixture was filtered and once washed with diluted hydrochloric acid and at least twice, each time with 2 liters of water. After filtration, the obtained mass was freeze dried yielding about 14g of graphite oxide as a very fluffy ivory powder.

Based on the elemental analysis of the graphite oxide the chemical formula C₈O₄H₁.₇ results. Using x-ray diffraction it could be shown that the interlayer distance of 0.335 nm in graphite was enlarged to 0.61 nm in the dry graphite oxide.

b) preparing partially reduced graphite oxide, equal to partially oxidized graphite:
Preparation of GOpr in the demonstrated quality and the conditioning of the layer distance can e.g. be done by thermal reduction of graphite oxide.

2g graphite oxide were heated up in a glassy carbon crucible under an argon atmosphere. After the desired temperature was set the furnace was switched off cooling down to room temperature. The GOpr was obtained as a fine black powder of low bulk density.

c1) assembling the obtained partially reduced graphite oxide as a powder electrode; or

c2) assembling the obtained partially reduced graphite oxide to a polymer-bound electrode.

This method yields in result a partially reduced graphite oxide, equal to partially oxidized graphite, that has a rather high capacitance above the capacitance of activated carbon based electrodes, e.g. 220 F/g as shown using aprotic electrolytes for example 1M Et₄NBF₄ in acetonitrile (Fig. 4), or e.g. up to 600 F/g as shown using 1M LiPF₆ in EC/DMC (Fig. 5). The method is rather too simple to be accomplished and the electrochemical activation reproducible for different lots of graphite oxides.

A suitable way to produce a PTFE-bound electrode can be achieved e.g. when the PTFE-bound electrode is prepared from a suspension, containing 80 wt.% partially reduced graphite oxide, 10 wt.% conductive agent and 10 wt.% PTFE binder, such as 60 wt.% PTFE solution dispersed in ethanol, by evaporating the solvent, preferably under constant stirring, and rolling the obtained compound to an electrode with a thickness of 1 to 1000 µm, and finally drying the rolled electrode for 1 to 24 h at 80 to 180 °C under vacuum at about 10 to 1000 Pa. The electrode thickness could vary between 1 - 1000 µm, but is preferable in the range of 10-300 µm.
Experimental data have shown that the capacitance of the electrode reaches the desired level when the thickness of the electrode is in the range of 10 to 300 µm. Suitable reaction conditions can be chosen to be for the drying of the rolled electrode to be carried out for 1 to 5 hours at temperature in the range of 100 to 150°C and under vacuum in the range of 50 to 200 Pa. The method for producing a capacitor assembly is preferably preformed when filling of an electrolyte is performed under a noble gas atmosphere and by using e.g. 1 M Et4NBF4 in acetonitrile as electrolyte. Generally, the capacitive properties can be also achieved with other electrolytes, as for example known from the battery electrolytes, regardless an aqueous or an aprotic or a Li-electrolyte.

The capacitance in the range of 220 F/g has been identified (Fig. 4) to depend largely of the interlayer distance of the partially reduced graphite oxide used for the electrode assembly A capacitance in the range of 600 F/g has been identified for GOpr43 using 1M LiPF6 in EC/DMC (Fig. 5). According to a preferred embodiment of the present invention, the partially reduced graphite oxide to be used for the assembly of an electrode is chosen to have an interlayer distance in the range of 0.3 to 0.6 nm, preferably in the range of 0.4 to 0.5 nm whereas this interlayer distance has been identified prior to the activation of the so-generated supercapacitor electrodes. GOpr has an interlayer distance bigger than graphite, typically 0.34 - 0.47 nm. It is possible that graphitic or graphite oxidic structures with interlayer distance above 0.55 nm remain within the GOpr.

Preferred embodiments of the present invention are hereinafter described with more detail and with reference to the following drawings which depict in:
In the present application it is shown that graphite oxide (GO) from natural as well as from synthetic graphite is an excellent precursor for partially reduced graphite oxide (GOpr) and that the GOpr shows electrochemical activation similar to the mesophase coal tar pitch-derived coke (MPC). Thus, a well-characterized and controllable precursor (synthetic graphite) is available to investigate and utilize the electrochemical activation of graphitic materials to the full. Contaminations of the resulting GOpr
electrode material, by unwanted components such as amorphous or activated carbon, which may cause a stability problem for the capacitor, can be widely controlled. In addition, oxidation and subsequent partial reduction of the graphite precursor allow to investigate the effect of the initial lattice expansion on the electrochemical activation and on the resulting capacitance (Fig. 2). Within the context of the present invention, it will be shown that the activation potential for the anode as well as for the cathode depends directly on the degree of reduction of the GO (equal to oxidation of graphite). It will be also demonstrate that a specific electrode capacitance beyond 200 F/g can be e.g. achieved in standard organic IM Et₄NBF₄ in acetonitrile electrolyte.

Graphite oxide (GO) was prepared from natural graphite (Alfa Aeser; 200 mesh, 99,9995 metal basis) as well as from synthetic graphite (TIMCAL; Timrex SFG44) according to a modified Brodie method. In deviation from the original method NaC103 (Sigma-Aldrich, puriss. p.a.) was used instead of KC103. The interlayer distance of the thus prepared GO was 6.1 Å. The dried GO (2 g) was thermally reduced in an argon atmosphere by heating GO between 200 and 1000 °C depending on the final layer distance, between 0.46 and 0.33 nm. GOpr was obtained as a fine black powder of low bulk density. The layer distance of the GOpr was determined by XRD (STOE STADI P2, transmission-mode, CuKa) and the surface area by BET (Autosorb-1 from Quantachrome Instruments, USA). GOpr materials were assembled to PTFE-bound electrodes as well as directly used as powder electrodes. Each bound electrode was prepared from a suspension, containing 80 wt.% active material (GOpr as received), 10 wt.% conductive agent (Super P; TIMCAL) and 10 wt.% PTFE binder (60 wt.% PTFE solution; Alfa Aeser) dispersed in ethanol (analytic grade). The solvent was then evaporated under constant stirring and the obtained compound was rolled to an electrode with a thickness of
Finally the electrode was dried for 12 h at 120 °C under vacuum at 10³ Pa.

For the electrochemical characterization a three electrode setup was used, employing an in-house designed and manufactured electrochemical cell. The setup was always consisting of an oversized counter electrode, PTFE-bound activated carbon (YP17; Kuraray Chemical Co., Japan), as well as a carbon quasi-reference from the same material. The potential of the quasi-reference was measured to be 3.01±0.05 V vs. Li/Li⁺ in the used electrolyte of 1M Et₄NBF₄ in acetonitrile.

A glass fiber separator was sandwiched between the electrodes which were contacted by Ti pistons. After assembling, the cell was dried for 12 h at 120 °C under vacuum at 10³ Pa. The electrolyte filling with 1M Et₄NBF₄ in acetonitrile took place in an argon-filled glove box containing less than 1 ppm H₂O and O₂. The electrochemical characterization was done by using an IM6e potentiostat (Zahner-Elektrik GmbH & Co. KG, Germany). During cyclic voltammetry a sweep rate of 1 mV/s was routinely used. The investigated electrode was either cathodically (negative sweep to -2.0 V vs. carbon) or anodically (positive sweep to 1.6 V vs. carbon) activated. After the activation full cycle experiments were performed with increasing potential range, starting with a potential window close to 0 V vs. carbon and rising stepwise up to 3.6 V.

The expansion behavior of the investigated GOpr during electrochemistry was measured with an in-house constructed dilatometer. Apart from the different cell design the setup of the measurements was kept unchanged compared to the electrochemical characterization. Electrochemical activation of partially reduced graphite oxides (GOpr) with a layer distance of 4.4 Å is shown in Fig. 1 for cathodic and anodic activation together with the cyclic voltammograms of the starting material SFG44 (Fig. 1, top).
the beginning of the cycle around 0 V vs. the carbon reference the capacitance is almost negligible at the beginning of the scan until a large negative or positive current peak is observed for both, the cathodic and anodic scan, respectively. This current maximum represents the activation process. After activation the capacitance is significantly increased and remains large for the subsequent cycles.

As described earlier in the US patent application US 2002/0039275 Al for pitch-derived mesophase carbon the activation step is accompanied by a rather significant expansion of the electrode material generating internal stress. The dimensional changes of a GOpr with a layer distance of 4.4 Å are reproduced in Fig. 2. Dimensional changes are measured in the order of 28% and 17% for cathodic and anodic activation, respectively, and are comparable to the earlier results on activated pitch-derived mesoporous carbon. For the negative activation the irreversible swelling is followed by a reversible swelling of about 12% during successive cycling. For the positive activation the reversible swelling amounts to about 10%. The overlay of an irreversible expansion with a smaller reversible thickness change was already observed earlier although in a different electrolyte. For various GOpr with different degree of reduction and consequently with different layer distance the electrochemical activation process was investigated by means of CV and determined the corresponding activation potentials.

Fig. 3 shows the anodic as well as cathodic activation potential as a function of the layer distance of the investigated GOpr, of the starting materials and as a function of electrode preparation with and without binder. The activation potential clearly decreases with increasing layer distance for negative as well as for positive activation. However, the slope of negative and positive activation is different. The results are obviously independent of the kind of graphite – natural or synthetic – used as precursor material.
Takeuchi et al. presented a similar investigation of the activation voltage of a petroleum based needle coke as a function of the lattice spacing. However, these authors varied the interlayer distance between 0.36 and 0.38 nm only and determined the activation voltage of a complete capacitor cell. The observed trend of a decreasing activation voltage with an increased layer distance is in accord with the present investigations of the applicants. In order to demonstrate that the electrochemical activation is irreversible and useful for supercapacitor electrodes, the full CV after activation was recorded for the different samples. The full CV for the GOpr sample, which exhibited the highest specific capacitance with a lattice spacing of 4.4 Å, is reproduced in Fig. 4 for a potential window of 3.6 V. The achieved specific capacitance of 220 F/g at 0 V vs. the carbon reference is rather large. This value is the highest specific capacitance ever reported for an activated carbon material in organic aprotic electrolyte.

Assuming pure double layer charging (no pseudo capacitance) and a specific double layer capacitance (DLC) of 8 µF/cm² the above GOpr sample has a surface area of 2687 m²/g, which is close to the theoretical surface area of graphene of 2630 m²/g when exposed on both sides. Therefore, it has to be concluded that both sides of the graphene like layers in our GOpr are utilized for double layer charging and provide the respective capacitance. GOpr contains a certain amount of oxygen containing functional groups and the assumption of a lack of pseudo capacitive contributions has to be verified. It has been demonstrated, however, that the contribution to the specific capacitance of such groups can be neglected in organic electrolyte. In addition, the assumption of a specific double layer capacitance of 8 µF/cm² is based on results obtained on the basal planes of graphite. The specific DLC of graphene like materials has to be determined yet and might be very different like other properties of graphene are exceptional.
The clear dependence of the activation potential of GOpr on the lattice spacing indicates that the electrochemical activation is — at least in part — related to ion and/or solvent intercalation. GOpr with an interlayer distance of 4.4 Å is an excellent material for electrochemical double layer capacitors with a specific low frequency capacitance of 220 F/g and a potential window well beyond 3.0 V. Natural as well as synthetic graphite are good precursors for the preparation of GO based electrodes.
Patent Claims

1. A method for producing an electrode of a capacitor, in particular a super-capacitor electrode, using partially reduced graphite oxide (GOpr), equal to partially oxidized graphite, as active or additive material for the capacitor electrode.

2. The method according to claim 1, wherein the partially reduced graphite oxide has an interlayer distance bigger than graphite, typically in the range 0.34 - 0.47 nm wherein graphitic or graphite oxidic structures with interlayer distance above 0.55 nm optionally remain within the partially reduced graphite oxide.

3. The method according to claim 1 or 2 wherein the capacitive behavior of GOpr is achieved by the activation of the GOpr in order to give the electrolyte ions access to the layered structure of the GOpr; said activation is done electrochemically by either an anodic or cathodic current sweep or by chemical or physical treatment.

4. The method according to any of the preceding claims, wherein the activated form of GOpr has a changed crystalline structure and is distinguishable from the non activated GOpr by X-ray diffraction (XRD), said activated form of GOpr showing a bigger interlayer distance than the equivalent form of non activated GOpr, preferably typically between 0.5 to 1.0 nm.

5. The method according to any of the preceding claims, wherein the activated GOpr applied as electrode material shows after the first formation cycle a specific capacitance above the capacitance of activated carbon based electrodes, e.g. 220 F/g when using aprotic electrolytes, for example 1M Et₄NBF₄ in acetonitrile , or e.g. up to 600 F/g when using 1M LiPF₆ in EC/DMC.
6. The method according to any of the preceding claims, wherein the electrolytes are either aqueous or aprotic organic or ionic liquid, preferably aprotic organic electrolytes or ionic liquids such as:
   i) examples for the salt are TEABF₄, TEMABF₄, LiClO₄, LiPF₆,
   LiBF₄;
   ii) examples for the solvent are acetonitrile (AN), propylene carbonate (PC), ethylene carbonate dimethylcarbonate (EC/DMC)
   iii) ionic liquids, wherein the salt concentration is variable and also salt and/or solvent mixtures are possible.

7. The method according to any of the preceding claims, wherein electrode compositions are activated partially reduced graphite oxide powder, active material (GOpr) bound with e.g. a polymer (e.g. PTFE, PVDF), active material (GOpr) combined with a conductive agent (e.g. Super P) bound with e.g. a polymer (e.g. PTFE, PVDF) and mixtures thereof.

8. The method according to claim 7, wherein the composition of the electrode varies between 50 to 100 wt.% activated partially reduced graphite oxide, 0 to 25 wt.% conducting agent (e.g. Super P) and 0 to 25 wt.% polymer binder (e.g. PTFE or PVDF).

9. The method according to any of the preceding claims wherein the electrode is formed as self standing bound electrode or is directly coated onto a current collector; the electrode thickness varies between 1 to 1000 µm, preferably in the range of 10 to 300 µm.
Figure 1

Figure 2
Figure 6
### A. CLASSIFICATION OF SUBJECT MATTER

**INV.** H01G9/058

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)

- EPO-Internal
- WPI Data
- COMPENDEX
- INSPEC

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 2009/134707 A2 (UNIV TEXAS [US]; RUOFF RODNEY S [US]; STOLLER MERYL [US]) 5 November 2009 (2009-11-05) paragraphs [0031], [0045], [0050], [0052]; cl aim 8</td>
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**X** Further documents are listed in the continuation of Box C.  
**X** See patent family annex.

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