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PAPER

Reversible redox reaction on the oxygen-containing functional groups of an electrochemically modified graphite electrode for the pseudo-capacitance

Xinzhuang Fan, Yonghong Lu, Haibo Xu,* Xiangfeng Kong and Jia Wang

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Reversible redox reactions on the oxygen-containing functional groups of an electrochemically modified graphite electrode (GE) by recurrent galvanic pulses in 2.3 M H₂SO₄ solution are investigated. The crystal morphology, surface composition and electrochemical performance of electrochemically modified GE are monitored by scanning electron microscopy, Raman spectroscopy, nitrogen adsorption, Fourier transform infrared spectroscopy, thermogravimetry, Boehm's titration, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy and cyclic voltammetry (CV) tests. After the electrochemical modification, the material shows a turbostratic structure with many small domains consisting of multi-layered graphene sheets in parallel, and presents a high specific capacitance of 179.7 F g⁻¹, as well as a good stability after 10000 CV cycles. The high specific capacitance is mainly attributed to the continuous reversible redox reactions of the active groups among the hydroxyl (reduced state), carbonyl (half-oxidized state) and carboxyl (fully oxidized state) groups; a redox mechanism is obtained consequently. The amount of active groups on the modified GE surface is about 848–875 µmol g⁻¹ by the Boehm titration. Their contribution to the pseudo-capacitance according to the redox mechanism is about 130–140 F g⁻¹, which is consistent with the results of electrochemical measurements.

1. Introduction

Electrochemical capacitors, as new, green, energy storage devices, are widely used in fields requiring high power density.^{1,2} Energy is stored in an electrochemical capacitor either by electrostatic interactions in the electrical double layer at the electrode/electrolyte interface (electrical double layer capacitors) or by fast faradic redox reactions between the electrolyte and electrode (pseudo-capacitors). Distinctively, the former normally uses high-surface area carbon-based materials as the electrode, while the latter resorts to noble metal oxides and electrically conducting polymers.

With the advantages of low cost and high chemical stability, carbon materials such as activated carbon, carbon nanotubes, carbon fibers and xerogels have attracted great interest as the electrode materials of electrical double layer capacitors in recent years.¹⁻³ However, regardless of the high surface area, carbon materials exhibit much lower specific capacitances than expected, which is attributed to the relatively low surface area available to charge storage from poor wettability.⁴ Therefore, considerable efforts have been made to modify the carbon materials (*e.g.*, wet

chemical, ³⁻⁶ dry chemical, ⁶⁻⁸ or electrochemical oxidation^{9–13}), to increase the double layer capacitance, which plays a predominant role in the overall capacitance; or occasionally to increase the pseudo-capacitance whose contribution is only 1-22%.^{1,14,15}

Up to now, the evident pseudo-capacitance of carbon materials has rarely been reported. Sullivan *et al.*^{16,17} once activated glassy carbon electrodes by electrochemical constant potential anodization, generating a high surface area electrode with some pseudo-capacitive characteristic. Recently, an electrochemically modified graphite electrode (GE) has been prepared by recurrent galvanic pulses, producing an active layer directly on the GE surface and showing an excellent specific capacitance with remarkable pseudo-capacitive characteristic.¹⁸

A simplified step-wise progression mechanism of electrochemical modification on carbon materials has been proposed.^{19,20}

$$H_2 O \rightarrow \frac{1}{2} O_2 + H_2 \tag{1}$$

$$> - C - H \xrightarrow{[0]} > - C - OH \xrightarrow{[0]}$$
$$> C = O \xrightarrow{[0]} -COOH \xrightarrow{[0]} CO_2$$
(2)

In this process, the electrolysis of water, as well as the breaking of outer C–C bonds occurs in series; consequently a great

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, 266100, Shandong Province, P.R. China. E-mail: xuwangri@163.com; Fax: +86 532 66782510; Tel: +86 532 66782510

quantity of oxygen-containing functional groups is generated. Conway¹ considered that the quinone or aldehyde groups, which could provide redox activity, might be responsible for the pseudo-capacitive component of the overall capacitance for carbon materials. Additionally, the pseudo-capacitance was mostly connected to the redox reaction involving the quinone and hydroquinone groups by Kinoshita²¹ and Sullivan *et al.*¹⁶ In addition, Frackowiak *et al.*²² considered the redox reactions among the hydroxyl, carbonyl, carboxyl and lactone groups might be attributed to the pseudo-capacitance, however, it was thought that such reactions represented only a quasi-reversible character and a gradual decreasing of the pseudo-capacitance region was observed during long cycling.

In this work, pseudo-capacitance was confirmed to play a dominant role in the overall specific capacitance, and a new mechanism of the interaction among the oxygen-containing functional groups for the pseudo-capacitive characteristic of the modified GE was deeply examined by surface morphology, chemical composition analysis and electrochemical tests. It was found that the pseudo-capacitive characteristic of the modified GE was due to the continuous reversible redox reactions among the hydroxyl, carbonyl and carboxyl groups. The contribution of the pseudo-capacitance to the overall capacitance was discussed through theoretical calculation and electrochemical analysis respectively.

2. Experimental

2.1 Preparation of electrode materials

A 0.8 mm-thick GE plate was commercially procured from SHF (Shanghai Hongfeng Graphite Products Co., Ltd., China). After polishing with wet 1000-grit emery paper and rinsing with ethanol and distilled water, the GE plate was assembled as the working electrode (1 cm² surface area) in Flat Cell K0235 (AMETEK Princeton Applied Research, USA), which was a three-electrode cell configuration immersed in 2.3 M H₂SO₄ solution. A 10 cm² platinum sheet and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. All potentials reported here were referred to SCE. No attempt was made to eliminate O₂ from the electrolyte.

Electrochemical modification of GE was performed by recurrent galvanic pulses, cycling 6 times from an anodic current density of 200 mA cm⁻² for 300 s to a cathodic current density of -120 mA cm⁻² for 100 s. Then the modified GE was taken out and pressed at room temperature in order to further improve the structural strength. At last, a modified GE (MGE) was obtained. In order to clarify the intrinsic redox mechanism of the oxygencontaining functional groups on MGE, a constant charge potential of 1.0 V *vs.* SCE was applied to a MGE for 1000 s to obtain the charged MGE (CMGE), and a constant discharge potential of -0.2 V *vs.* SCE was applied to another MGE for 1000 s to obtain the discharged MGE (DMGE).

Additional samples of GE, MGE, CMGE and CMGE were prepared for further measurements and characterization. Some powder was scraped off from the surface of GE, MGE, CMGE and DMGE. The powder was washed with distilled water, and then dried in a vacuum oven for 12 h at 50 °C.

2.2 Characteristics of samples

The micro-domain morphology of MGE was observed by scanning electron microscopy (SEM; S-4800, Hitachi). The crystal structures of GE and MGE were characterized by Raman spectroscopy (Ramar; LabRam Infinity, JY) with a 632 nm He–Ne laser. The specific surface area of the scraped powder of MGE was examined by nitrogen adsorption (ASAP2030, Micromeritics) at -196 °C.

The oxygen-containing functional groups on GE and MGE were analyzed by Fourier transform infrared spectroscopy (FT-IR; Model 8700, NICOLET) in reflection mode using an attenuated total reflectance accessory. The scraped powder composition of GE and MGE was examined by thermogravimetry (TG; HCT-1/2, Henven) at a 10 °C min⁻¹ ramp rate from 25 to 900 °C with a nitrogen flow rate of 80 ml min⁻¹.

Moreover, the acidic groups on scraped powder from GE, CMGE and DMGE were studied by Boehm's titration. In this process, approximately 10 mg powder was immersed into 20 ml NaOH (10 mM), 20 ml Na₂CO₃ (10 mM) and 20 ml NaHCO₃ (10 mM) solutions, respectively. After ultrasonic treatment, mixtures were left to equilibrate under stirring for 6 h with nitrogen flowing to remove the dissolved CO₂. After centrifugation, 20 ml (40 ml for Na₂CO₃) of 10 mM HCl was added, and stirring and nitrogen-flow were continued for 12 h. Finally, the excess HCl was determined by titration with 10 mM NaOH using a pH meter (PHS-3C, Leici). The surface chemical composition and types of heteroatom-carbon bond of the powder of GE, CMGE and DMGE were further studied by X-ray photoelectron spectroscopy (XPS; PHI5300, PE) using Mg-K α radiation (1253 eV, 250 W) under a pressure of *ca.* 10⁻⁷ Pa.

2.3 Electrochemical measurements

All electrochemical measurements were carried out using an EG&G PAR Model 2263 Potentiostat/Galvanostat at ambient temperature.

The electrochemical impedance spectroscopy (EIS) was measured for MGE at an open circuit potential (0.4 V vs. SCE), with ± 5 mV potential amplitude and a frequency range of 10 kHz–10 mHz. The cyclic voltammetry (CV) tests were performed on MGE and MGE with a partly scraped-off active layer within a range of -0.2-1.0 V vs. SCE at 50 mV s⁻¹. A 10000-cycle CV test was applied to MGE to obtain its stable performance. In addition, another CV test was carried out on MGE in 2.3 M HCl solution as a comparison. Here, a pre-polarization was conducted at -0.2 V vs. SCE for 200 s before each CV test.

3 Results and discussion

3.1 Characteristics of physical properties

After the electrochemical modification of GE, the smooth surface with hexagonal crystal structure turned into obviously porous and rough three-dimensional active layers with a microcrystalline flake structure.¹⁸ The broadened (002) peak at $2\theta = 26.38^{\circ}$ and asymmetric (10) line at $2\theta = 43.22^{\circ}$ in XRD pattern of MGE,¹⁸ which indicated the existence of graphite plane segments in small domains and the turbostratic structure.^{23,24} The microdomain flake structure of MGE is shown in Fig. 1. From the



Fig. 1 An SEM image of the micro-domain structure on MGE.

SEM image, it could be clearly seen that a great quantity of graphene sheets were distorted and it was turbostratic graphite in nature. There may be three factors contributing to the produced active layers: (i) the corrosion and oxidation of GE continuously occur; (ii) the mechanical destructive effect by the formation of CO_2 and O_2 exerts; and (iii) the micro-crystallization process happens throughout the electrochemical modification.²⁵

The microstructures of GE and MGE were further revealed by Raman spectroscopy. It is generally accepted that the Raman spectra of carbon materials are composed of first-order (1100-1800 cm⁻¹) and second-order (2500-3100 cm⁻¹) regions.²⁶⁻²⁸ The first-order Raman spectrum presents a main E_{2g2} band for the single hexagonal crystal graphite (space group D_{6h}^4) at 1582 cm⁻¹ (called G mode) and another band for the polycrystalline graphite at ca. 1357 cm⁻¹ (called the "disorder-induced" or D mode). In the second-order region, the peak at *ca*. 2646 cm^{-1} is attributed to the G' peak, normally appearing with strong intensity in perfect graphite crystals.²⁹⁻³¹ Moreover, the integrated intensity ratio I_D/I_G is often used to manifest the extent of microstructural disorder.^{32,33} The Raman spectra of both GE and MGE in Fig. 2 show D mode at 1328 cm⁻¹, G mode at 1580 cm⁻¹, and the $I_{\rm D}/I_{\rm G}$ of GE and MGE is 0.375 and 1.689, respectively. These meant that the graphitization degree of GE was comparatively higher than MGE, and the crystalline structure of MGE exhibited more disordered state than GE. In addition, the G' peak of MGE at ca. 2646 cm⁻¹ is much weaker than that of GE, also indicating a flawed graphite crystal for MGE, which was consistent with the results of XRD and SEM.

In addition, previous work¹⁸ has shown that the electrochemical activation apparently increased the specific surface area of MGE. It is found that the specific surface area of MGE powder calculated from the nitrogen adsorption measurement using the BET method³⁴ was about 6 m² g⁻¹. Generally, the specific capacitance comes from the contributions of double layer capacitance and



Fig. 2 Raman spectra of GE (a) and MGE (b).

pseudo-capacitance, and the double layer capacitance is almost in proportion to the specific surface area. Therefore, the double layer capacitance of MGE seems very limited comparing its specific area (6 m² g⁻¹) with the heat treated activated carbon (1024 m² g⁻¹)³⁵ and petroleum cokes (2280 m² g⁻¹).³⁶ However, a considerable specific capacitance was obtained¹⁸ and such a huge capacitance is definitely attributed to the pseudo-capacitance, which will be discussed in more detail below.

3.2 Characterizations of surface composition

Fig. 3 presents the FT-IR spectra of GE and MGE. There is no other infrared absorption for GE besides CO_2 at 2430 cm⁻¹,³⁷ but two other peaks appear at *ca*. 1720 and 1576 cm⁻¹ for MGE, which were mostly attributed to the carboxyl and quinone groups, respectively.^{21,38-41} In addition, the relative intensity of the two peaks indicated that a large number of >C=O groups (ketone and/or carboxyl groups) were generated during the modification. The broad peak at 1247–986 cm⁻¹ was associated with the stretching vibration of phenol, alcohol and/or ester groups.⁴¹ These meant that a great quantity of oxygen-containing functional groups was produced after the electrochemical activation.

The powder composition of GE and MGE was further estimated by thermogravimetry (TG) in combination with derivative thermogravimetry (DTG) (shown in Fig. 4). In general, the carboxyl and lactone groups begin to decompose at ca. 250 °C, while the phenol and quinone groups almost entirely decompose between 500 and 900 °C.^{14,21} From the DTG curves in Fig. 4, it can be seen that the initial weight loss occurs at ca. 70 °C and the subsequent weight loss happens at ca. 400 °C for both samples. The former was due to the desorption of the moisture, while the latter was ascribed to the decomposition of -COOH, >C=O and -CO₂, agreeing with the literature.²¹ In addition, the TG curves show that the weight loss is inconspicuous between 200 and 400 °C for GE (see Fig. 4), but seems continuous in case of MGE. By contrast, the initial weight loss that occurs before 400 °C is only 5% for GE, but up to 20% for MGE, indicating that the percentage of -COOH, >C=O and -CO₂ in MGE was larger than that in GE. Finally, comparing GE with MGE, the total weight loss at 900 °C has more than doubled from 19% to 45%, also suggesting that lots of oxygen-containing functional groups were newly generated during the electrochemical modification.

According to FT-IR and TG, it is noticed that the surface oxygen-containing functional groups mainly consist of hydroxyl, carbonyl and carboxyl groups. To investigate the surface oxides



Fig. 3 FT-IR spectra of GE (a) and MGE (b).



Fig. 4 TG and DTG curves of GE (a) and MGE (b) recorded at a 10 $^{\circ}$ C min⁻¹ ramp rate from 25 to 900 $^{\circ}$ C with a nitrogen flow rate of 80 ml min⁻¹.

relevant to the redox reactions during the charging/discharging process, the amount of the surface oxides was quantitatively analyzed.

Quantitative analysis of the acidic surface groups was conducted by Boehm's titration.^{21,42,43} As one of the strongest bases, NaOH solution is assumed to neutralize all Brønsted acids (e.g., carboxyl, phenol and lactone groups), and Na₂CO₃ solution could neutralize carboxyl groups and also allow lactone groups to open and form carboxyl groups which are neutralized, while NaHCO₃ solution only neutralizes carboxylic acids.²¹ Table 1 shows the amount of acidic surface groups (carboxyl, phenolic hydroxyl and lactone groups) of GE, CMGE and DMGE. The amount of total acidic groups is very little for GE, which is nearly one-sixth compared with those of CMGE and DMGE, indicating that both CMGE and DMGE had a significant increase in the amount of the carboxyl, hydroxyl and lactone groups. In addition, the amount of lactone groups is so little that it can be negligible. Moreover, the amount of carboxyl groups for CMGE and DMGE (the 2nd sample in Table 1) is 2148 and 1273 µmol g^{-1} , and the corresponding amount of hydroxyl groups is 1259 and 2107 μ mol g⁻¹, these mean that the amount of consumed hydroxyl groups and produced carboxyl groups during the charging process was 875 and 848 μ mol g⁻¹, respectively, and the almost equal amount also suggested that a correlated transition between hydroxyl groups and carboxyl groups must occur and the following reactions among the electroactive surface functional groups could account for these:

$$>$$
C - OH $\xrightarrow{H^++e}$ $>$ C = O $\xrightarrow{H_2O}$ $\xrightarrow{H_2O}$ $>$ COOH (3)

Graphitic carbon surfaces can be regarded as being made up of (at least) two chemically different kinds of sites: basal and edge

Samples	Total acidic groups (μmol g ⁻¹)	Carboxylic groups (µmol g ⁻¹)	Phenolic hydroxyl groups (µmol g ⁻¹)	Lactone groups (µmol g ⁻¹)
GE1	662	369	256	37
GE2	681	360	273	48
CMGE1	3488	2102	1190	196
CMGE2	3614	2148	1259	207
DMGE1	3438	1209	2049	180
DMGE2	3572	1273	2107	192

carbon sites.³ Edge sites are considered to be more reactive than basal sites as they are often associated with unpaired electrons, so the reaction process of eqn (3) could be expressed as Fig. 5. As shown in Fig. 5, the oxygen-containing functional groups at basal sites are electrochemically inert and only those at the edge sites are electroactive. Different from the acknowledged quinonetype redox reactions on carbon materials,^{1,16,17,21} it is more reasonable to assume carboxyl groups as one participant of faradic redox reactions as eqn (3) according to the results of Boehm's titration. That is to say, with the continuous rise of the polarization potential during the charging process, the hydroxyl groups (reduced state) on MGE are oxidized into ketone groups (half-oxidized state), and then further oxidized into carboxyl groups (fully oxidized state), finally CMGE is formed. Contrarily, DMGE is formed during the discharging process of MGE when reversible reactions occur.

According to eqn (3) and Fig. 5, the continuous reversible redox reactions can be regarded as a two-electron reaction between the hydroxyl and carboxyl groups, and the specific pseudo-capacitance attributed to the hydroxyl groups during the charging process and that ascribed to the carboxyl groups during the discharging process were able to calculated by eqn (4) as below:

$$C_{\rm pm} = \frac{Q}{m \times \Delta V} = \frac{\frac{n}{m} \times z \times F}{\Delta V}$$
(4)

where C_{pm} is the mass specific capacitance of pseudo-capacitance; Q is the charge during the oxidation/reduction reactions; ΔV is the potential window; *m* is the mass of the active layer for the electrode; n is the number of moles of the electroactive functionalities involved in the reactions; z is the number of electrons transferred in the reaction, and F is the Faradiac constant. Here, taking the 2nd sample as the example (as shown in Table 1), the potential window is 1.2 V vs. SCE and the number of electrons transferred in the reactions is 2. The number of moles of hydroxyl groups on each gram of active substance during the charging process was 875 μ mol g⁻¹, and that of carboxyl groups during the discharging process was 848 µmol g^{-1} . Thus, the corresponding mass specific capacitance of pseudo-capacitance for the hydroxyl groups during the charging process and the carboxyl groups during the discharging process is 141 and 136 F g⁻¹, respectively. Furthermore, the corresponding contribution of the hydroxyl and carboxyl groups to the pseudocapacitance is 161 and 160 F mmol⁻¹ respectively. The contribution of corresponding groups to the pseudo-capacitance is far greater than that (63 and 6.02 F mmol⁻¹) to the pseudo-capacitance of the electrical double layer capacitor,^{44,45} and this is the essential reason for such a huge pseudo-capacitance.



Fig. 5 A schematic diagram of the continuous reversible redox reactions (as eqn (3)) among the hydroxyl, carbonyl and carboxyl groups at the edge sites of MGE.

Subsequently, XPS was performed on GE, CMGE and DMGE to further investigate the surface composition (Fig. 6). XPS spectra were fitted by a nonlinear least-square curve fitting program with the Gaussian/Lorentzian product function.⁴⁶ Five peaks were fitted by the deconvolution of the C 1s spectra as following:^{19,47} graphitic carbon (peak I, 284.6 eV), carbon presented in phenol, hydroxyl, ether groups (peak II, 286.1–286.3 eV), carbonyl or quinone groups (peak III, 287.3–287.6 eV), carboxyl or ester groups (peak IV, 288.4–288.9 eV) and carbonate groups and/or adsorbed CO₂ and CO (peak V, 290.4–290.8 eV).

From Table 2, it is found that the total content of the hydroxyl, carbonyl and carboxyl groups of GE is 21.1%, and those of CMGE and DMGE are 30.7% and 34.4%, respectively; it is suggested more oxygen-containing groups were generated. The specific area is so little for GE¹⁸ that most of the surface oxide is on the basal sites and inert. Contrarily, the specific area of MGE was significantly increased¹⁸ and the electroactive sites on the edge region were increased as well. Part of the electroactive sites was newly generated, and the other came from the original basal sites, which changed to the electroactive sites as



Fig. 6 XPS spectra of the C 1s region of GE (a), ⁷CMGE (b) and DMGE (c).⁷ Graphitic carbon (peak I, 284.6 eV), carbon presented in phenol, hydroxyl, ether groups (peak II, 286.1–286.3 eV), carbonyl or quinone groups (peak III, 287.3–287.6 eV), carboxyl or ester groups (peak IV, 288.4–288.9 eV) and carbonate groups and/or adsorbed CO₂ and CO (peak V, 290.4–290.8 eV)⁷ The figures of GE and DMGE came from the supplementary materials of the literature.¹⁸

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some basal layer changed to the edge layer during the electrochemical modification. In addition, the change in the amount of carbonyl groups (about 3%) between CMGE and DMGE, was consistent with the difference in the O 1s/C 1s atomic ratio (0.01) between them, and this may be attributed to the difference in the amount of the inherent carbonyl groups for different GE samples used to modify.

Furthermore, from DMGE to CMGE, the amount of hydroxyl groups reduced by 6.51%, and the amount of carboxyl groups increased by 6.49%, probably indicating that some reactions occurred between hydroxyl and carboxyl groups. In addition to almost the same varying values of hydroxyl and carboxyl groups were reversible. Therefore, the reversible redox reactions are believed to occur among the hydroxyl and carboxyl groups in the charging/discharging process according to eqn (3), further confirming the conclusion drawn from the Boehm titration.

3.3 Electrochemical performance of MGE

3.3.1 Pseudo-capacitive characteristic. In order to investigate the capacitance performance of MGE in 2.3 M H_2SO_4 solution, CV and galvanostatic charging/discharging tests were previously carried out and a considerable specific capacitance was obtained.¹⁸ As mentioned above, the pseudo-capacitance attributed to the hydroxyl and carboxyl groups was high, up to 136–141 F g⁻¹, so it was thought that MGE was a promising electrode material for pseudo-capacitor. Here, EIS and CV tests were conducted to quantitatively analyze the contribution of pseudo-capacitance to the overall capacitance.

EIS measurements were performed at an open circuit potential (0.4 V vs. SCE). The Nyquist diagram shows an apparent capacitive behavior of MGE in Fig. 7. It is noticed that a vertical line is observed and an arc of a one-fourth circle is visible at high frequency (see enlarged graph in Fig. 7). The approximately vertical increase in the imaginary part at low frequency demonstrated the typical capacitive characteristic, which was mainly governed by a faradaic process of the electroactive material.⁴⁸ In the meanwhile, the high frequency arc was attributed to the double-layer process, whose response was much faster than that of the faradaic reaction.⁴⁹

A simplified equivalent circuit model^{50,51} shown as the inset in Fig. 7 was constructed to analyze the impedance spectrum. Here $R_{\rm S}$ was the solution resistance; $R_{\rm F}$ corresponded to the charge-transfer resistance through the pseudo-capacitive process; CPE₁ was the double-layer capacitance at the electrode/electrolyte interface; CPE₂ arose from the pseudo-capacitance and the factor *n*, defined as a CPE power, is an adjustable parameter that lies between 0 and 1. The fitting parameters of the experimental data are displayed in Table 3. $R_{\rm F}$ is only 0.0176 Ω cm², indicating a fast charge-transfer process for MGE. Compared with CPE₁ of 521.2 mF cm⁻², CPE₂ of 1367.2 mF cm⁻² is almost 2.6-fold of that. The result indicated that the pseudo-capacitance played a dominant role in the overall specific capacitance for MGE.

The CV response of MGE in 2.3 M H_2SO_4 solution is shown as Fig. 8. A couple of broad and symmetric redox peaks near 0.4 V vs. SCE in the CV curve are obtained and MGE presents a perfect pseudo-capacitive characteristic.

 Table 2
 The O 1s/C 1s atomic ratio and the relative surface concentration of carbon and oxygen species obtained by fitting the C 1s XPS spectra for GE, CMGE and DMGE

Samples	Atomic ratio n(O)/n(C)	Graphitic carbon	Hydroxyl	Carbonyl	Carboxyl	Carbonate groups
GE ^a	0.08	73.48	10.57	5.61	4.88	5.46
CMGE	0.20	67.71	7.27	9.88	13.54	1.60
DMGE ^a	0.21	64.68	13.78	13.59	7.05	0.90

^a All data for GE and DMGE in this table came from the literature.¹⁸



Fig. 7 A Nyquist diagram with an equivalent circuit (inset) of MGE measured at 0.4 V νs . SCE in 2.3 M H₂SO₄ solution.

Table 3 Fitting values of equivalent circuit (the inset in Fig. 7) to impedance data of MGE at 0.4 V $\nu s.~SCE$

Parameters	$R_{\rm S}$ (Ω cm ²)	$\begin{array}{c} CPE_1 \\ (mF \ cm^{-2}) \end{array}$	n_1	$R_{\rm F}$ (Ω cm ²)	CPE ₂ (mF cm ⁻²)	<i>n</i> ₂
MGE	1.401	521.2	0.938	0.0176	1367.2	0.974

The specific capacitance of MGE can be calculated from the voltammetric charge by the CV curve according to eqn (5):⁵²

$$C = \frac{q_{\rm a} + |q_{\rm c}|}{2\Delta V} \tag{5}$$

where C, q_a , q_c and ΔV are the specific capacitance, the anodic and cathodic voltammetric charge during anodic and cathodic scans, and the potential range of CV, respectively. Here Crepresents the specific capacitance with an apparent area of 1 cm², and it was as high as 1.73 F cm⁻² calculated using eqn (5). In addition, the current density response quickly reached 0.03 A cm⁻² (see the dotted line in Fig. 8), which represented a fast double-layer charging process occurring during the scan performance, while the high and broad peaks denoted the faradaic process.⁵³ Compared with the integrating areas of the two processes, the pseudo-capacitance takes up nearly seventy percent of the overall capacitance, well consistent with the results of EIS.

To confirm that the oxygen-containing functional groups on MGE exclusively account for the pseudo-capacitance, CV tests were performed on MGE in 2.3 M H_2SO_4 and HCl solutions, respectively. The CV curves in Fig. 8 indicate nearly no differences in the current response and the position of the redox peaks



Fig. 8 CV curves of MGE at a scan rate of 50 mV s⁻¹ in 2.3 M H₂SO₄ (a) and HCl (b) solutions. The dashed line in the frame corresponds to the double-layer charging/discharging process.



Fig. 9 A) CV curves of MGE from 1 to 10000 cycles at a scan rate of 50 mV s⁻¹ in 2.3 M H₂SO₄ solution. (a) 1 cycle, (b) 2000 cycles, (c) 4000 cycles, (d) 6000 cycles, (e) 8000 cycles (f) 10000 cycles. (B) Relationships of cycle number (from 1 to 10000) with capacitance (- \bullet -) and capacitance holding ratio (- \blacktriangle -) in 2.3 M H₂SO₄ solution.

in two different solutions. In addition, the absence of S element in the XPS in the previous work¹⁸ also excluded the possibility that the graphite intercalation compounds might result in such a high pseudo-capacitance.



Fig. 10 CV curves of MGE before (a) and after (b) active layers partly being scraped at a scan rate of 50 mV s⁻¹ in 2.3 M H_2SO_4 solution.

Table 4 CV parameters for MGE before and after the active layer being scraped within a range of -0.2-1.0 V vs. SCE at 50 mV s⁻¹ in 2.3 M H₂SO₄ solution (Samples 1–4). C'_{m} and SD are the average mass-specific capacitance and standard deviation of the four samples, respectively

Samples	m _{before} (g)	$m_{\rm after}$ (g)	$ q _{before}$ (C)	$ q _{\text{after}}$ (C)	$C_{\mathrm{m}}~(\mathrm{F}~\mathrm{g}^{-1})$	$\begin{array}{c} C_{\mathrm{m}}^{\prime} \ (\mathrm{F}\ \mathrm{g}^{-1}) \end{array}$	SD (F g ⁻¹)
1	0.6684	0.6658	0.1802	0.1218	187.2	179.7	14.38
2	0.6703	0.6653	0.1847	0.06759	196.2		
3	0.6733	0.6699	0.1711	0.1021	169.1		
4	0.6769	0.6711	0.1786	0.06282	166.3		

3.3.2 Performance of cycle life. Moreover, the stable performance of MGE was investigated by CV tests. The integrating area of CV curves with different cycles only changes a little in Fig. 9A, indicative of a long cycle life. In order to quantitatively analyze the cycle performance of MGE, the relationships of cycle number with capacitance and capacitance holding ratio are shown in Fig. 9B. Eighty two percent of the capacitance remains from 1 (1.73 F cm⁻²) to 10000 cycles (1.41 F cm⁻²), revealing the good stable performance and the practical significance for MGE.

3.3.3 The mass-specific capacitance. The volume-specific capacitance of MGE reached 428 F cm⁻³ in our previous report.¹⁸ Here, in order to obtain the mass-specific capacitance (C_m) , CV tests were performed on MGE before and after scraping off a part of the active layer (Fig. 10). It was difficult to directly define the precise mass of the active material on MGE, so we resorted to obtaining C_m indirectly. Firstly, the mass difference of the partly scraped-off active layer ($\Delta m=m_{before}-m_{after}$) was measured through weighing the mass of MGE before and after being scraped. Secondly, the corresponding integrating charges were obtained from CV curves. Finally, in accordance with eqn (6) as follows, the mass-specific capacitance could be given.

$$C_{\rm m} = \frac{|q|_{\rm before} - |q|_{\rm after}}{2\Delta V \times (m_{\rm before} - m_{\rm after})}$$
(6)

where $C_{\rm m}$, $|q|_{\rm before}$, $|q|_{\rm after}$, $m_{\rm before}$, $m_{\rm after}$ and ΔV are the massspecific capacitance, the total voltammetric charge before and after being scraped, the mass of MGE before and after being scraped, and the potential range of CV, respectively.

In order to ensure the accuracy of our data, four parallel samples with different amounts of active layer were prepared (Table 4) and the standard deviation was calculated. As a result, the average mass-specific capacitance of MGE is 179.7 F g^{-1} and the standard deviation is as small as 14.38 F g^{-1} .

Moreover, the corresponding mass specific capacitance during the charging and discharging process could be calculated respectively, they were 143.5 and 131 F g⁻¹ respectively in terms of their seventy percent proportion in the overall capacitance. These results are almost consistent with the theoretic calculation (141 and 136 F g⁻¹) by Boehm titration, further confirming the conclusion that pseudo-capacitance is mainly attributed to the continuous reversible redox reactions between the hydroxyl and carboxyl groups.

4. Conclusions

GE was electrochemically modified by recurrent galvanic pulses. During the modification, a micro-crystallization process occurred, and the material changed into turbostratic carbon with many small domains consisting of multi-layered graphene sheets in parallel.

After the modification, the number of active sites corresponding to oxygen-containing functional groups such as hydroxyl, carbonyl and carboxyl groups significantly increased. A new mechanism of interaction among the oxygen-containing functional groups on MGE for its pseudo-capacitance is proposed and such a high specific capacitance is mainly attributed to the continuous reversible redox reactions among the (reduced state), carbonyl (half-oxidized state) and carboxyl (fully oxidized state) groups. The pseudo-capacitance from a theoretical calculation according to the reversible redox reaction during the charging/discharging process is about 130–140 F g⁻¹, which is consistent with the corresponding results of electrochemical measurements.

The electrochemical measurements indicated that MGE not only exhibits a high mass-specific capacitance of 179.7 F g⁻¹, but also possesses a good stability performance by 10000 CV cycles. The pseudo-capacitance takes up nearly seventy percent of the overall capacitance according to the CV curve. Therefore, MGE is a promising electrode material for advanced pseudo-capacitors.

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