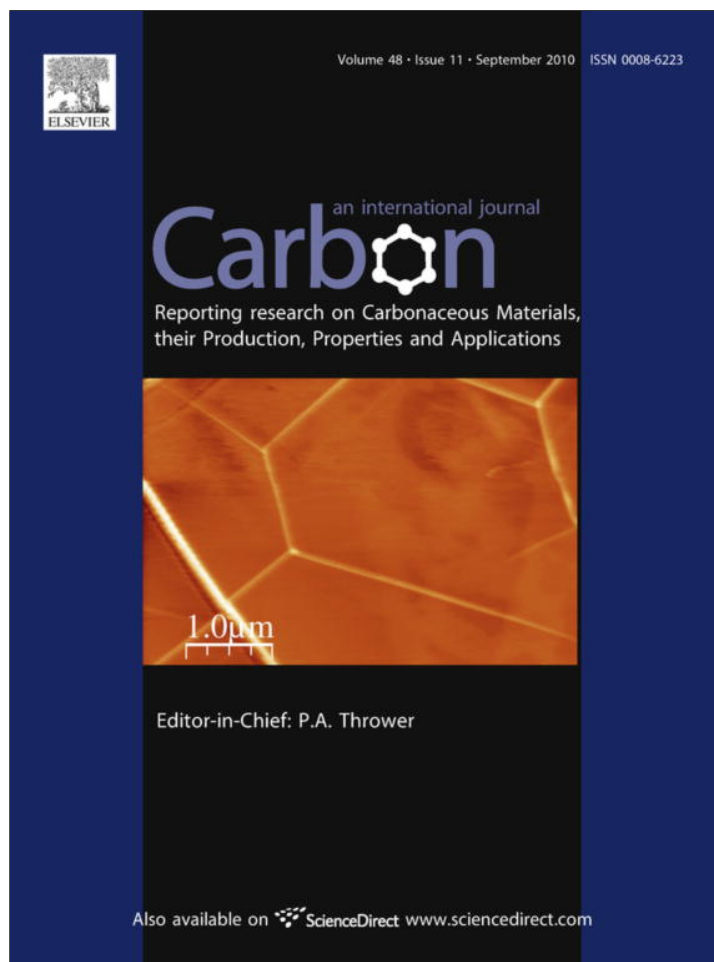




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Preparation of an electrochemically modified graphite electrode and its electrochemical performance for pseudo-capacitors in a sulfuric acid electrolyte

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ARTICLE INFO

Article history:

Received 1 March 2010

Accepted 28 April 2010

Available online 6 May 2010

ABSTRACT

A graphite electrode was activated using recurrent electrochemical galvanic pulses. After activation, the original smooth surface was changed into an obviously porous, rough surface with microcrystalline flake structures with a larger number of O-containing functional groups. The material had a high capacitance and a satisfactory high-rate performance. The superior volumetric capacitance in active layer was ca. 428 F cm^{-3} . Eighty-eight percentage of the capacitance remained after the discharge current increased from 2 mA (1.71 F cm^{-2}) to 100 mA (1.50 F cm^{-2}) in 2.3 M H_2SO_4 .

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Electrochemical capacitor (EC) has attracted worldwide interest because of its potential applications in energy storage devices [1]. Graphite has been widely used as a conductive agent for an EC electrode [2]. Recently, it was often chosen as the positive electrode material for hybrid capacitors [3]. Nano-structured graphite showed high specific capacitance when used for an electrochemical double layer capacitor [4]. However, as far as we know, graphite electrode (GE) was seldom really used for pseudo-capacitors, even though the activated carbon material could produce some O-containing surface functional groups with pseudo-capacitive characteristics. Only Sullivan et al. [5,6] ever tried to use an activated glassy carbon electrode as the pseudo-capacitor. And results showed that the carbon material was promising for pseudo-capacitor electrode in spite of the high material cost and long activation time. In this paper, a GE was activated using recurrent galvanic pulses and evaluated for EC applications.

A 0.8 mm thick graphite plate, a typical bipolar plate material in proton exchange membrane fuel cell (PEMFC), purchased from SHF (Shanghai Hongfeng Graphite Products Co., Ltd., China), was used as a GE. After sanding and cleaning, the plate was assembled in the Flat Cell K0235 (AMETEK Princeton Applied Research, USA), a standard three-electrode cell with 1 cm^2 working area. A platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Using recurrent galvanic pulses, the activation involved the oxidation and subsequent reduction processes repeated six times in 2.3 M H_2SO_4 , from the applied anodic current of 200 mA (holding for 300 s), to the cathodic current of -120 mA (holding for 100 s). After that,

the electrolyte was replaced by fresh 2.3 M H_2SO_4 to remove the gas bubbles absorbed on electrode surface. Cyclic voltammetry (CV) was conducted by an EG&G PAR Model 2263 Potentiostat/Galvanostat, sweeping from -0.2 to 1.0 V vs. SCE with different scan rates. The crystal structures of the non-activated and activated GE were determined by X-ray diffraction (XRD; D8 ADVANCE, Bruker). Surface morphology of the activated GE was observed with a color CCD camera (JT-2182II, JETET) and a scanning electron microscope (SEM; KYKY-2800B, KYKY). Surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS; PHI5300, PE).

The surface morphology of the activated GE was shown in Fig. 1. In Fig. 1A, the activated surface corresponding to the central protuberance bulged, indicating of a distinct volume increase during film growth. Moreover, as shown in Fig. 1B, the microstructure of the activated GE was rough and porous, with numerous flakes in micron scale.

The XRD patterns were shown in Fig. 2. Before activation, it was the standard hexagonal crystal graphite (see Fig. 2a). However, after activation, two broad XRD bands appeared (see Fig. 2b), which could be attributed to a microcrystalline carbon structure [7], in agreement with the SEM result. The detailed results from XPS spectra were shown in Table 1. After activation, the relative peak intensity of O 1s/C 1s was considerably increased from 0.08 up to 0.21, indicating of the formation of more O-containing functional groups [8].

The typical CV capacitance responses were shown in Fig. 3. Before activation, there seemed no visible redox peak between -0.2 and 1.0 V vs. SCE. However, after activation, the

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CV capacitance was considerably increased and a redox peak at ca. 0.4 V vs. SCE appeared, which could be attributed to the active quinoidal functional groups [5,9]. Moreover, the CV capacitance in Fig. 3 seemed symmetric and little changed in the different scan rates, indicating that the activated GE might be fit for EC electrode.

The typical galvanostatic charge–discharge behaviors at different currents were shown in Fig. 4(A). The symmetry of curves indicated a good capacitive characteristic again. Moreover, the capacitances at different applied currents were showed in Fig. 4(B). The activated GE suggested a superior capacitance and a satisfactory high-rate performance. Eighty-eight percentage of the capacitance re-

mained after the discharge current increased from 2 mA (1.71 F cm^{-2}) to 100 mA (1.50 F cm^{-2}).

The active layer was carefully scraped off with a blade from the activated GE, and its thickness was about $40 \mu\text{m}$. The volumetric capacitance in active layer was about 428 F cm^{-3} under 2 mA discharge current. Hence, this thin modified GE was a suitable material for an EC electrode with the excellent specific energy and power density.

In our experiments, GE could be easily exfoliated solely by galvanostatic anodization, whereas this was seldom occurred using recurrent galvanostatic pulses. The formation of the thick porous layer with certain intensity seemed capable of explaining this phenomenon. Besenhard and Fritz [10] ever

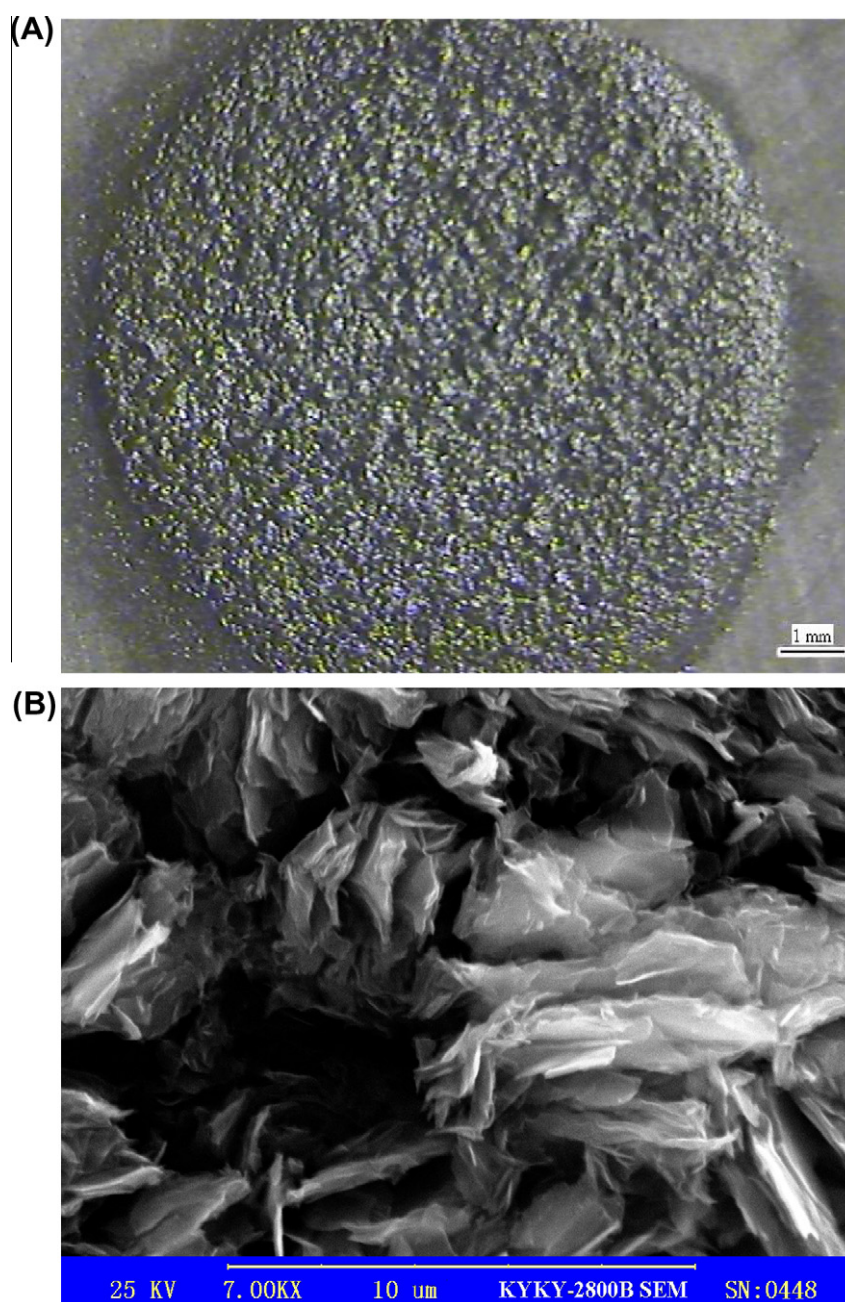


Fig. 1 – Surface morphology of the activated GE. (A) Optical photograph and (B) SEM image.

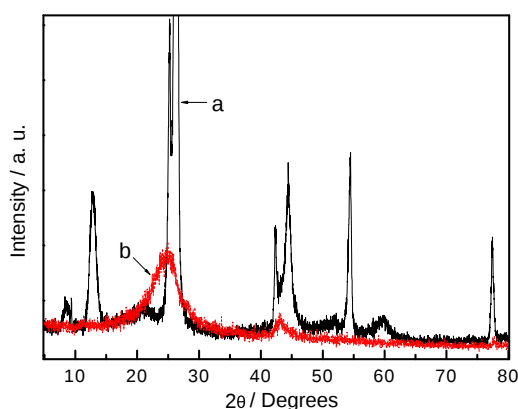


Fig. 2 – XRD patterns of (a) the non-activated and (b) the activated GE.

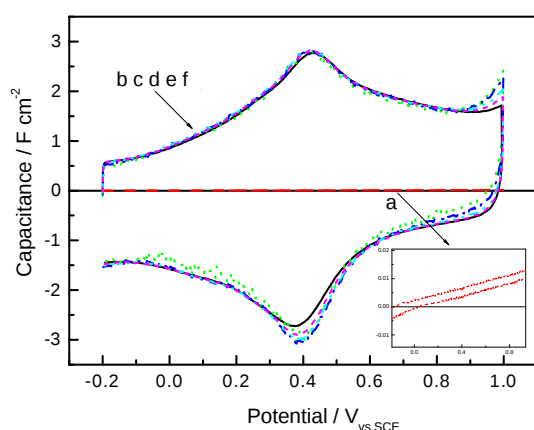


Fig. 3 – CV capacitance of (a) the non-activated GE at 50 mV s^{-1} and the activated GE at (b) 3 mV s^{-1} , (c) 5 mV s^{-1} , (d) 10 mV s^{-1} , (e) 20 mV s^{-1} and (f) 50 mV s^{-1} in $2.3 \text{ M H}_2\text{SO}_4$.

reported that an electrochemical graphite oxide (EGO) was formed on the GE surface by anodic overoxidation, and the EGO could be reduced back to graphite again with nearly 100% current efficiency by cathodic current. Therefore, limited by a drastic decrease in electric conductivity of the anodic products EGO on the GE surface [10], the electrochemical reaction front would likely move into the bulk only in depth by galvanostatic anodization, and the exfoliation of oxidation layers were easily occurred after longer activated time. Contrarily, electrochemical reaction was promoted in three-dimensional direction by recurrent galvanostatic pulses. After the EGO was reduced by cathodic current, one part of applied

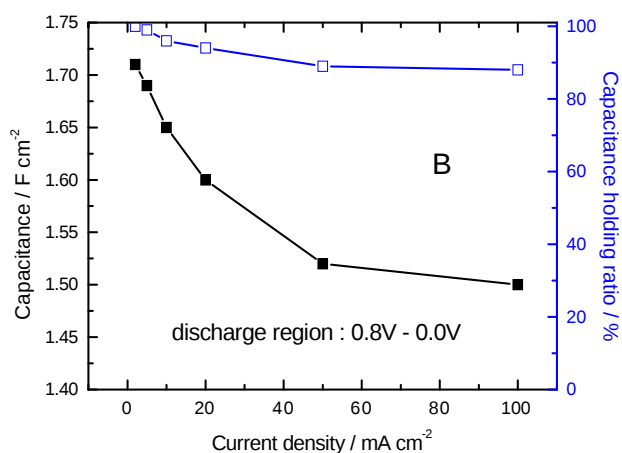
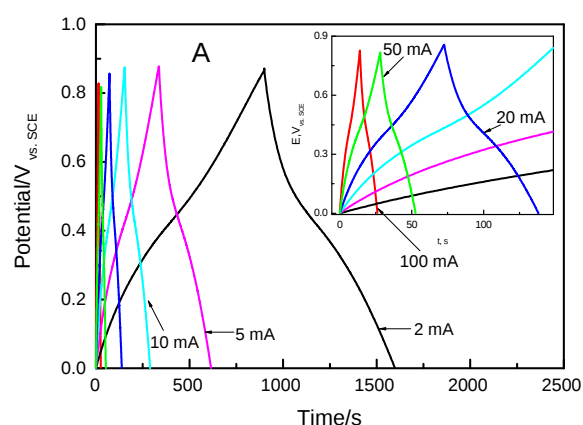


Fig. 4 – (A) Galvanostatic charge–discharge curves at different currents in $2.3 \text{ M H}_2\text{SO}_4$ (including an enlarged graph). (B) Relationships of discharge current density with capacitance ($\blacksquare$) and capacitance holding ratio ($\blacksquare$) in $2.3 \text{ M H}_2\text{SO}_4$.

anodic current thickened the active layer by overoxidizing the bulk, while the other part encouraged the active layer forming fine microcrystalline flakes by overoxidizing the reduced EGO again. After longer activated time, not only more O-containing surface functional groups were produced, but also the exfoliation of oxidation layers was little occurred.

Additionally, several other advantages were expected from the modified GE when used for pseudo-capacitors, such as minimizing the resistance between the active layer and the current collector [11], easily constructing a scalable bipolar plate/electrode assembly (similar to PEMFC) due to the impermeability of gases and ions, and the high-voltage EC was guaranteed consequently, etc.

Table 1 – O 1s/C 1s atomic ratio and the relative surface concentrations of carbon and oxygen species obtained by fitting the C 1s XPS spectra.

Samples	Atomic ratio O 1s/C 1s	Graphitic carbon	Hydroxy	Carbonyl	Carboxyl	Carbonate
Non-activated GE	0.08	73.48	10.57	5.61	4.88	5.46
Activated GE	0.21	64.68	13.78	13.59	7.05	0.90

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.04.051.

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Preliminary data on processing and characterization of recycled irradiated graphite

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ARTICLE INFO

Article history:

Received 21 April 2010

Accepted 6 May 2010

Available online 13 May 2010

ABSTRACT

Neutron irradiated graphite was recycled as the “filler” material in reconstituted graphite. The work, performed in a radiological facility at the Oak Ridge National Laboratory, is believed to be the first ever demonstration of the feasibility of recycling irradiated graphite. The recycled graphite was lower in selected properties than commercially available nuclear graphite, but it is believed that similar property values could have been achieved with an impregnation step and a refined particle size distribution. The irradiation temperature and fluence of the graphites that were recycled had no discernable impact on the properties of the graphites made from them.

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One of the US DOE reactor concepts is a graphite moderated, helium cooled, high temperature reactor. A number of designs exist for such a reactor, including a prismatic block or pebble bed unit, but regardless of design, the reactor will utilize graphite as the moderator. Over the life of the reactor significant quantities of nuclear graphite components will need to be replaced, creating a radioactive materials management issue: storage, transportation, and burial, all with associated costs and environmental implications. One method for

addressing the irradiated graphite management issue is to re-use/recycle the graphite. Reuse of irradiated graphite could be as straightforward as shuffling the graphite components within the reactor to maximize the useful life of that material, or to use an expended block as the raw material for making a fresh component. This latter option is essentially the production of a new graphite component through a true recycle process. This letter reports the first experimental study into the viability of recycling irradiated nuclear graphite.

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0008-6223/\$ - see front matter Published by Elsevier Ltd.

doi:10.1016/j.carbon.2010.05.012