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Exfoliated graphite with relative dielectric constant reaching 360, obtained by exfoliation of acid-intercalated graphite flakes without subsequent removal of the residual acidity

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ARTICLE INFO

Article history:
Received 23 December 2014
Accepted 13 April 2015
Available online 20 April 2015

ABSTRACT

Exfoliated graphite (obtained by rapid heating of sulfuric-acid intercalated and subsequently deacidified graphite flakes) is optionally subjected to residual acidity removal, which involves repeated washing with water, such that the pH of the wash water increases from 2 to 7. Compared to washed exfoliated graphite, the unwashed material exhibits lower specific surface area (24 vs. 45 m^2/g), a higher value (360 vs. 38 at 50 Hz) of the relative dielectric constant (real part), a similar value of the conductivity (50 S/m), a higher value of the specific carbon–contact interfacial capacitance (1.17 vs. 0.04 $\mu F/m^2$), and a lower value of the carbon–contact interfacial resistivity (0.08 vs. 0.27 $\Omega\,cm^2$). The greater concentration of residual intercalate (containing sulfur and oxygen) present without washing contributes to the polarizability without interfering the conduction. The carbon–contact interface is superior when the exfoliated graphite has not been washed. At 2.0 MHz, the relative dielectric constant (real part) remains high (280) and the carbon–contact interfacial specific capacitance remains high (1.13 $\mu F/m^2$). The imaginary part of the relative dielectric constant and the dielectric loss angle are not affected by the washing. The relative dielectric constant of 360 is even higher than the value of 121 for potassium-hydroxide-activated graphite nanoplatelet.

1. Introduction

High values of the relative dielectric constant (i.e., the real part of the relative permittivity) are attractive for supercapacitor electrodes and electrochemical gas sensor electrodes, due to the associated high polarizability. In particular, for supercapacitors, the polarization of the electrodes promotes the formation of the electric double-layer at the electrode–electrolyte interface. In general, high polarizability in a material is enabled by the availability of mobile ions, polar functional groups or movable molecular segments, which respond to the applied AC electric field.

Carbon materials are widely used for electrochemical electrodes, due to their chemical stability, thermal stability and

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http://dx.doi.org/10.1016/j.carbon.2015.04.042
0008-6223/

electrical conductivity. Mobile ions on the surface or the interior, and polar functional groups on the surface, are mostly responsible for the polarizability of carbon electrode materials, although electronic polarization may play a minor role. There has been much study of the electrical conduction behavior of carbon materials. Much less attention has been given to the dielectric behavior of these materials. In particular, reports of the relative dielectric constant of carbon electrode materials is quite scarce, due to the common use of testing in the electrochemical cell level, using techniques such as electrochemical impedance spectroscopy, cyclic voltammetry and charge/discharge testing. The cell involves multiple electrodes and multiple interfaces, which include the electrode–electrolyte interface and the electrode–contact interface (with the contact referring to the electrical contact). Due to the presence of multiple components in a cell, it is difficult to determine the relative dielectric constant of a particular component by cell-level testing. However, recent material-level testing using carbon materials of different thicknesses and sandwiched by metal electrical contacts has allowed decoupling of the carbon volumetric contribution and the carbon–contact interfacial contribution to the measured capacitance or resistance, thus enabling determination of the relative dielectric constant and AC conductivity of the carbon electrode material [1].

Exfoliated graphite is obtained from intercalated graphite, typically by rapid heating. During the heating, the intercalate vaporizes and/or dissociates, causing the formation of cells that are like expanding balloons and the evolution of gas upon the breaking of the cell wall (balloon wall) [2]. The expansion of a cell (i.e., the stretching of the balloon wall) is enabled by the shear of the graphite layers (e.g., 60 layers in a cell wall) in the cell wall relative to one another [3]. Consistent with the cell formation is the large decrease in *a*-axis conductivity and the large increase in the *c*-axis conductivity upon exfoliation [4].

The specific surface area of exfoliated graphite (washed by water after exfoliation to remove the residual acidity due to the acid intercalate) is 45 m^2/g [1], which is very low compared to those of activated carbons. However, exfoliated graphite provides handleability (mechanical interlocking even in the absence of a binder) and, as previously shown for the washed state, its volumetric and interfacial conductivities are much higher than those of activated carbon [1]. On the other hand, the relative dielectric constant of exfoliated graphite (washed) is low compared to that of activated carbon [1]. This is a drawback of exfoliated graphite (washed) for supercapacitor electrode applications.

Acids such as sulfuric acid and nitric acid are commonly used as intercalates for obtaining exfoliated graphite [5–10], due to the tendency for the exfoliation to be substantially irreversible upon subsequent cooling, in contrast to the relatively high degree of reversibility when bromine is used as the intercalate [2]. The irreversibility is due to the breaking of the cell wall upon the evolution of a significant amount of gas during exfoliation. The amount of gas evolved depends on the intercalate species.

It has been recently reported that the relative dielectric constant is 37.9 ± 0.7 and the conductivity is 52.6 ± 5.6 S/m at 50 Hz for exfoliated graphite that has been washed thoroughly by water after exfoliation. The washing is for the purpose of removing the acidity associated with the residual acid intercalate in the exfoliated graphite (as shown by the pH of the wash water increasing gradually from 2 to 7 as repeated washing is carried out) [1]. This value of the relative dielectric constant is lower than those of natural graphite (53.3 ± 1.3), activated carbon (123.5 ± 6.6) and activated graphite nanoplatelet (activated GNP, 121.1 ± 1.7), but is slightly higher than the value (31.2 ± 1.4) for carbon black, with all these carbons tested using exactly the same method and at the same frequency of 50 Hz [1].

The value (52.6 S/m, 50 Hz [1]) of the electrical conductivity of exfoliated graphite that has been washed is much higher than the values of 8.0 S/m for carbon black, 6.9 S/m for activated GNP, 6.1 S/m for natural graphite, and 0.032 S/m for activated carbon [1]. The high conductivity of exfoliated graphite stems from the electrical connectivity that is made possible by the cellular structure, and is attractive for electrochemical electrode applications, whether in relation to supercapacitors or batteries. Along with the electrical connectivity is the mechanical connectivity, which allows exfoliated graphite to be sheet-like even in the absence of a binder [1].

The value (0.12 $\Omega\,cm^2$ [1]) of the interfacial resistivity of the carbon–copper interface (with the copper serving as an electrical contact) for exfoliated graphite that has been washed is lower than the values of 0.27 $\Omega\,cm^2$ for activated GNP, 1.1 $\Omega\,cm^2$ for carbon black, 1.4 $\Omega\,cm^2$ for natural graphite and 160 $\Omega\,cm^2$ for activated carbon [1]. The low value for exfoliated graphite stems from a degree of electrical connectivity between the exfoliated graphite and the copper contact and is attractive for electrochemical electrode applications, whether in relation to supercapacitors or batteries.

The activated GNP is obtained by the activation of exfoliated graphite using potassium hydroxide (KOH), with sonication followed by washing in water to remove the acidity prior to KOH activation). For the activated GNP, the relative dielectric constant is higher (121.1 ± 1.7 at 50 Hz) and the conductivity is lower (6.96 ± 0.29 S/m at 50 Hz) than the above-mentioned values for exfoliated graphite that has been washed but not activated (37.9 ± 0.7, 52.6 ± 5.6 S/m) [1]. The increase in relative dielectric constant upon KOH activation is largely due to the ions (such as K^+ ions) introduced by the activation. Since KOH activation is an involved high-temperature (850 °C) process, it would be advantageous to increase the relative dielectric constant of exfoliated graphite without activation. Both washing and activation add to the cost of the material processing.

The process of exfoliation is accompanied by extensive desorption of the intercalate, so that only a very small portion of the intercalate in the intercalation compound prior to exfoliation remains after exfoliation [2,11,12]. The residual intercalate is strongly held in the exfoliated graphite. The residual acidity is not desirable for structural applications such as those associated with flexible graphite, which is made by the compression of exfoliated graphite in the absence of a binder and is used industrially as a gasket material and a heat spreader. Furthermore, the residual intercalate is expected to affect the chemistry of the volume (interior) as well as that of the surface. Indeed, an increased concentration of redox active surface functional groups has been reported for exfoliated graphite obtained from graphite intercalated with sulfuric acid, relative to pristine graphite, as shown by cyclic voltammetry in 10 M H_2SO_4 and attributed to an oxidative attack by SO_3 during exfoliation [13].

The residual intercalate, which is partially ionic (due to the charge transfer between the graphite and the intercalate during intercalation), may be useful for enhancing the relative dielectric constant – a hypothesis. The effect of the residual intercalate on the dielectric behavior of exfoliated graphite has not been previously reported. This paper is aimed at testing this hypothesis and quantifying the effect, if any, of the residual intercalate on the relative dielectric constant. This work is thus focused on studying the relative dielectric constant and conductivity of exfoliated graphite that has not been washed or activated after exfoliation.

The relative dielectric constant and AC conductivity of exfoliated graphite are relevant to the applications of exfoliated graphite in electrochemical electrodes [13,14], electromagnetic absorption/shielding [15] and fuel cell biopolar plates [16]. In particular, a high value of the relative dielectric constant is attractive for supercapacitors and electromagnetic absorption/shielding.

2. Experimental methods

The approach [1] used for achieving the decoupling mentioned in Section 1 involves (i) measuring the resistance and capacitance of the exfoliated graphite compact (for determining the quantities pertaining to the carbon solid), and (ii) conducting the measurement for three exfoliated graphite compact thicknesses, thereby decoupling volumetric and compact–contact interfacial quantities. The approach is the same in this paper and Ref. [1].

2.1. *Materials*

As in prior work on exfoliated graphite that has been washed with water [1], exfoliated graphite (worms) is obtained by rapid heating of expandable natural graphite flake (intercalated by using sulfuric acid) from Asbury Graphite Mill (No. 3772) at 900 °C for 2 min with flowing nitrogen. Although sulfuric acid (i.e., bisulfate) is the intercalate, the intercalation process used to obtain the expandable flake is promoted or catalyzed by some oxidizing agent, such as nitric acid and potassium permanganate. The intercalation results in an acceptor-type graphite intercalation compound. The intercalate concentration is typically described in terms of the sulfur content of the expandable graphite. This sulfur content is not well controlled in the manufacturing process, but it may be in the range from 6% to 12%, such that the variation in a given batch may range from 2% to 4%. In this work, the expandable graphite is all from the same batch. After the intercalation process, the expandable flake (not yet exfoliated) is rinsed by the manufacturer to remove the residual surface acid. The rinsed flake is then washed by the manufacturer with an alkaline material in order to deacidify (partially neutralize) the flake. Thus, the expandable graphite supplied by the manufacturer is not high in the intercalate concentration and has little surface residue. Since the intercalate in this case is bisulfate, the surface residue is expected to be composed of some surface sulfur compound(s) and perhaps some potassium permanganate or other residue from the oxidation catalyst.

The worms are of length 2–4 mm. After washing, the specific surface area is 45 m^2/g [1]. The specific surface area before washing has not been previously reported. For the washed material, the specific surface area corresponds to about 60 graphite layers stacked in a cell wall on the average, as obtained by comparison of the measured specific surface area with the calculated value for single-layer graphene. With 60 graphite layers, the cell wall thickness would be about 20 nm.

For the sake of comparison between washed and unwashed exfoliated graphites in terms of the composition and for analyzing the composition of the wash water, this work also conducts washing of exfoliated graphite with water. The washing of 0.05 g of exfoliated graphite is conducted by using deionized water in the amount of 10 ml contained in a glass vial during each wash, which includes manual agitation, such that the pH is measured for the water at the end of each wash. The pH of the water after the first wash is 2. In the complete procedure of washing, the washing is repeated with fresh water each time, until the pH reaches 7.

2.2. *Dielectric and resistance testing methods*

Fig. 1 shows the equivalent circuit used in this work for modeling the conduction and dielectric behavior of a carbon compact. All the quantities shown in the model are decoupled and determined using the method of prior work [1]. For the details of the method, please refer to Ref. [1].

The relative dielectric constant (which describes the volumetric dielectric behavior), the specific interfacial capacitance (which is the capacitance per unit area of the interface between the material and one of the two electrical contacts used to sandwich the material during dielectric testing), the electrical resistivity (which describes the geometry-independent volumetric conduction behavior) and the interfacial electrical resistivity (which is the geometry-independent areal resistivity of the interface between the material and one of the two electrical contacts) are measured in this work, using a precision RLC meter (Quadtech 7600). The frequency is 50 Hz, unless noted otherwise. The capacitance and resistance for the parallel RC circuit configuration are separately obtained from the meter, such that the capacitance is measured with an electrically insulating film (thickness 75 μm) between the specimen and each electrical contact (for the purpose of minimizing the current) and the resistance is measured without this insulating film. The AC electric field is 5.13 V/cm (see Figs. 2 and 3).

In order to decouple the volumetric and interfacial contributions to the capacitance, specimens of three different thicknesses (0.789, 1.747 and 2.032 mm) are tested, as dictated by three frames (with through holes and of these same thicknesses) made of flexible graphite, which is chosen for its chemical inertness and fluid gasketing ability. The electric field is applied between the two copper foils (thickness 62 μm), which are the electrical contacts. The AC voltage is adjusted so that the electric field is fixed while the thickness

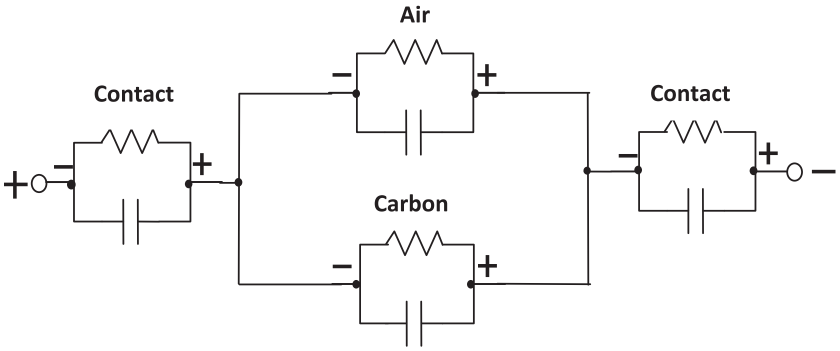

Fig. 1 – Equivalent circuit model for a carbon compact. The contact refers to the interface between the compact and the electrical contact.

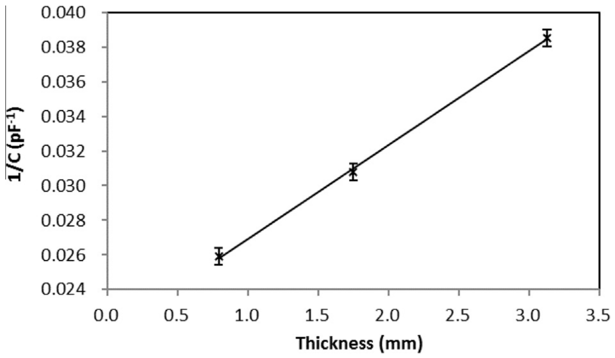

Fig. 2 – Plot of the reciprocal of the measured capacitance (2.0 MHz) vs. the specimen thickness for exfoliated graphite without washing. The slope is inversely related to the relative dielectric constant of the specimen.

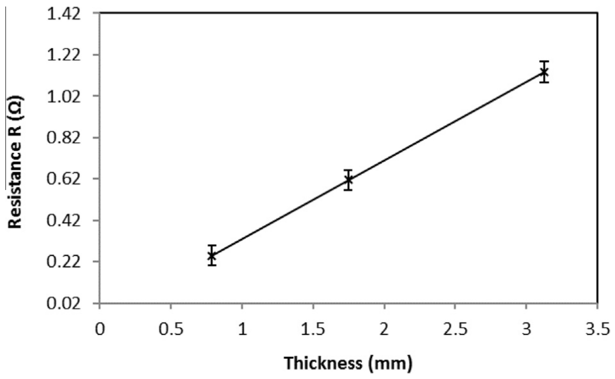

Fig. 3 – Plot of the measured resistance *R* (200 Hz) vs. the specimen thickness for exfoliated graphite without washing. The slope is related to the resistivity of the specimen.

varies. Each specimen fills the entire volume (area 20.0 × 20.0 mm) inside a frame (outer dimensions 25.0 × 25.0 mm). For both dielectric and resistance measurements, the flexible graphite frame is insulated from each of the two copper contacts by using the abovementioned insulating film.

The pressure provided by a copper foil and a steel weight above it on the specimen during testing is 4.3 kPa (0.63 psi). This pressure is much lower than that typically used for the making of flexible graphite. As a result, the worms in the resulting compact are not as well interconnected as those in flexible graphite and the density of the resulting compact is very low (0.295 ± 0.001 g/cm^3) compared to that that of flexible graphite (1.1 g/cm^3) used in prior work [17]. The volume fraction of carbon in the compact of this work is (13.04 ± 0.03)%, as obtained by taking the density of the solid carbon to be 2.260 ± 0.005 g/cm^3 (2.26 g/cm^3 being the value for ideal graphite).

The imaginary part $-\kappa''$ (where κ'' is negative) of the relative dielectric constant of the carbon is related to the conductivity σ of the carbon by the equation

$$-\kappa'' = \sigma/(2\pi\nu\varepsilon_o), \tag{1}$$

where ν is the AC frequency and ε_o is the permittivity of free space. The dielectric loss (tan δ) of the carbon is obtained by using the equation

$$\tan\delta = -\kappa''/\kappa' = \sigma/(2\pi\nu\varepsilon_o\kappa'), \tag{2}$$

where κ' is the real part of the relative dielectric constant of the carbon. For the equations for obtaining κ', σ, the specific capacitance and the interfacial resistivity, please refer to Ref. [1]. In this work, all these quantities are for the carbon solid, such that the contribution by the air part of the specimen has been excluded. The decoupling of the carbon solid and air contributions is performed by using the Rule of Mixtures [1].

2.3. *Microscopy, elemental analysis and specific surface area analysis*

Scanning electron microscopy (SEM) and the associated X-ray spectroscopic elemental analysis are conducted on the exfoliated graphite (both washed and unwashed cases) and on the wash water after the first wash. In relation to the water, the water is contained in an aluminum dish and then subjected to drying in air at 80 °C. The spectroscopy is then conducted on the residue on the aluminum after the drying. Deionized water that has not been used for the washing is similarly analyzed for the sake of comparison with the wash water.

The specific surface area of unwashed exfoliated graphite is measured by nitrogen adsorption, using a Micromeritics ASAP 2010 instrument. The equipment and method are identical to those of prior work [1] that reported the specific surface area of washed exfoliated graphite.

3. Results and discussion

Table 1 shows that the real part of the relative dielectric constant is much higher for exfoliated graphite without washing (this work) than exfoliated graphite with washing [1]. This means that the residual intercalate in the exfoliated graphite without washing contributes much to the polarizability. The real part of the relative dielectric constant of exfoliated graphite without washing is even higher than that of activated GNP [1].

The conductivity is essentially equal for exfoliated graphite with and without washing. Similarly, the imaginary part of the relative dielectric constant is essentially equal for these two materials. This means that the residual intercalate in the exfoliated graphite without washing does not contribute to the conductivity, as expected since the conduction is dominated by hole conduction and the ions associated with the residual intercalate are not dissolved in a liquid. The conductivity of exfoliated graphite with or without washing is much higher than that of activated GNP, due to the greater degree of electrical connectivity for exfoliated graphite compared to activated GNP.

The dielectric loss angle δ is essentially 90° for all of the three carbons in Table 1. However, it is slightly lower for exfoliated graphite without washing than exfoliated graphite with washing. This means that exfoliated graphite with washing is a more perfect conductor than exfoliated graphite without washing. The loss angle for activated GNP is close to that of exfoliated graphite with washing.

The specific capacitance (capacitance per unit area) of the interface between carbon and the electrical contact is much higher for exfoliated graphite without washing than exfoliated graphite with washing. A high interfacial capacitance is less influential to the overall capacitance than a low interfacial capacitance, since the interfacial capacitance and the volumetric capacitance are in series. Thus means that the carbon–contact interface is less influential to the dielectric behavior for exfoliated graphite without washing than exfoliated graphite with washing. This is probably because the washing reduces slightly the degree of fluffiness of the exfoliated graphite (due to the mechanically fragile nature of the fluffy material and the slight mechanical disturbance that accompanied the washing), thereby causing the small gap between the carbon and the electrical contact to be smaller for exfoliated graphite without washing. For the same reason, the interfacial resistivity of the interface between carbon and the electrical contact is lower for exfoliated graphite without washing than exfoliated graphite with washing. Both the high specific capacitance and the low interfacial resistivity provided by exfoliated graphite without washing indicate that the interface between carbon and the electrical contact is more intimate when exfoliated graphite without washing is used in place of exfoliated graphite with washing.

The specific capacitance is higher and the interfacial resistivity is lower for exfoliated graphite without washing than activated GNP. This means that the interface between carbon and the electrical contact is more intimate when exfoliated graphite without washing is used in place of activated GNP. These observations are consistent with the higher degree of fluffiness of exfoliated graphite without washing than activated GNP.

As shown in Table 2, the real part κ' of the relative dielectric constant decreases with increasing frequency for all of the three carbons, as expected. As shown in Fig. 4 for exfoliated graphite without washing, this quantity decreases with increasing frequency quite sharply up to 500 Hz. Above 500 Hz, the decrease is more gradual, with the value remaining high at 280 at the highest frequency of 2.0 MHz.

Fig. 5 shows that the specific capacitance between exfoliated graphite without washing and the electrical contact decreases with increasing frequency, such that the decrease is slight up to 10 kHz and the decrease is significant above 10 kHz. Table 3 shows data up to 1 kHz, so the effect of frequency is negligible in Table 3. This trend in Fig. 5 is expected.

Fig. 6 shows that the conductivity of exfoliated graphite without washing decreases with increasing frequency, such that the decrease is slight up to 0.5 MHz and is significant above 0.5 MHz. The slight decrease up to 1 kHz is shown for all three carbons in Table 4. This trend (with the effect mainly occurring in the high frequency regime) is consistent with the Skin Effect.

Fig. 7 shows that the interfacial resistivity between exfoliated graphite without washing and the copper electrical contact increases with increasing frequency, such that the increase is significant up to 10 kHz and is negligibly small above 10 kHz. Table 5 shows that, for all three carbons, the interfacial resistivity increases slightly with increasing frequency up to 1 kHz. With the effect mainly occurring in the low frequency regime, this trend is not attributed to the Skin Effect. Rather, it is attributed to the decreasing excursion

Table 1 – Dielectric and conduction properties of carbons (air part excluded) at 50 Hz.

Property	Exfoliated graphite		Activated GNP*
	Without washing	With washing*	
κ'	363.9 ± 11.4	37.9 ± 0.7	121.1 ± 1.7
$-\kappa''$ (10^9)	18.27 ± 0. 52	19.60 ± 2.2	2.59 ± 0.11
Conductivity (S/m)	49.4 ± 1.4	52.6 ± 5.6	6.94 ± 0.29
Dielectric loss angle δ (°)	89.99903948 ± 0.00000046	89.99999989 ± 0.00000002	89.99999732 ± 0.00000015
Specific capacitance (μF/m^2)	1.170 ± 0.002	0.036 ± 0.003	0.138 ± 0.006
Interfacial resistivity (Ω cm^2)	0.077 ± 0.005	0.27 ± 0.05	0.12 ± 0.02

* From [1].

Table 2 – Effect of frequency on the real part κ' of the relative dielectric constant of carbons (air part excluded) at 50 Hz.

Frequency (Hz)	Exfoliated graphite		Activated GNP*
	Without washing	With washing*	
50	363.9 ± 11.4	37.9 ± 0.7	121.1 ± 1.7
100	325.7 ± 8.5	33.2 ± 0.9	106.0 ± 2.2
500	304.8 ± 14.0	32.0 ± 1.1	102.3 ± 2.6
1000	303.0 ± 13.1	31.1 ± 0.7	99.5 ± 1.8

* From [1].

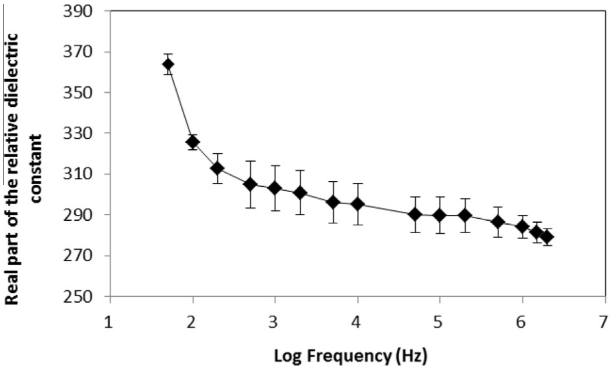

Fig. 4 – Plot of the real part of the relative dielectric constant of the carbon (air part excluded) vs. frequency (log) for exfoliated graphite without washing.

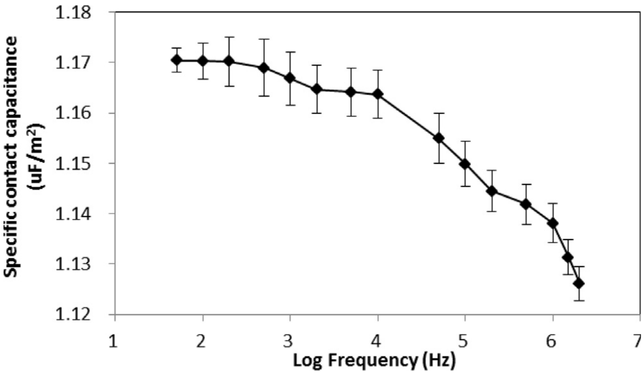

Fig. 5 – Plot of the specific contact capacitance (capacitance per unit area) between carbon (air part excluded) and the copper contact vs. frequency (log) for exfoliated graphite without washing.

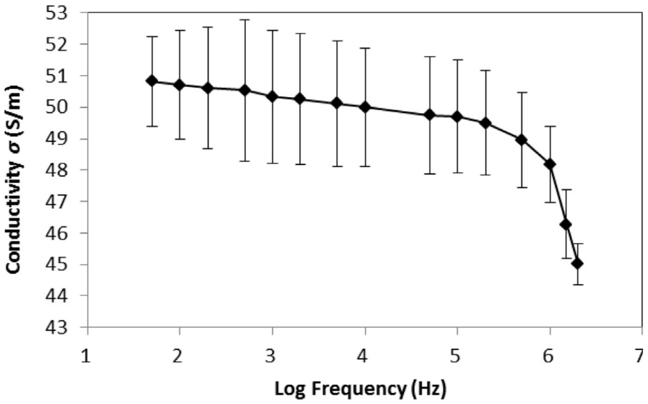

Fig. 6 – Plot of the electrical conductivity of carbon (air part excluded) σ vs. frequency (log) for exfoliated graphite without washing.

of charges that are responsible for the polarization as the frequency increases and the consequent reduced degree of electrical connectivity across the carbon–contact interface.

Fig. 8 shows that the linear relationship between the logarithm of the negative of the imaginary part of the relative dielectric constant and the logarithm of the frequency. This relationship is consistent with Eq. (1) and the fact that the frequency dependence of the conductivity is minor (Fig. 6).

Fig. 9 shows that the dielectric loss angle δ of exfoliated graphite without washing decreases sharply with increasing frequency above 0.1 MHz. This means that the material is an essentially perfect AC conductor up to 0.1 MHz and becomes less perfect as the frequency increases beyond 0.1 MHz. However, even at the highest frequency of 2.0 MHz, δ remains high – nearly 90°. That the material is a nearly perfect conductor is attractive for electromagnetic absorption (shielding).

Table 3 – Effect of frequency on the specific capacitance (capacitance per unit area, $\mu F/m^2$), of the interface between carbon (air part excluded) and a contact.

Frequency (Hz)	Exfoliated graphite		Activated GNP*
	Without washing	With washing*	
50	1.170 ± 0.002	0.036 ± 0.003	0.138 ± 0.006
100	1.170 ± 0.004	0.035 ± 0.001	0.189 ± 0.004
500	1.169 ± 0.006	0.031 ± 0.004	0.153 ± 0.001
1000	1.167 ± 0.005	0.030 ± 0.002	0.136 ± 0.004

* From [1].

Table 4 – Effect of frequency on the electrical conductivity σ (S/m) of carbons (air part excluded).

Frequency (Hz)	Exfoliated graphite		Activated GNP*
	Without washing	With washing*	
50	49.4 ± 1.4	52.6 ± 5.6	6.94 ± 0.29
100	49.0 ± 1.7	52.1 ± 1.0	6.88 ± 0.25
500	48.3 ± 2.2	51.3 ± 0.7	6.79 ± 0.22
1000	48.2 ± 2.1	51.2 ± 1.4	6.77 ± 0.24

* From [1].

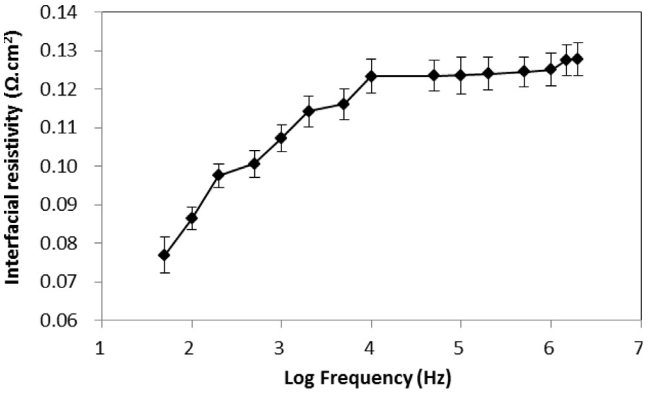

Fig. 7 – Plot of the interfacial resistivity between carbon (air part excluded) and a contact vs. frequency (log) for exfoliated graphite without washing.

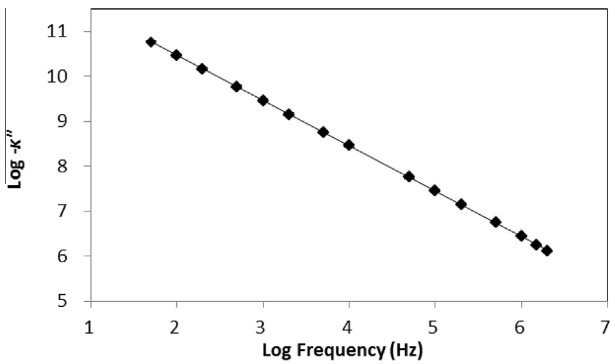

Fig. 8 – Plot of the negative of the imaginary part $-\kappa''$ (log) of the relative dielectric constant of the carbon (air part excluded) vs. frequency (log) for exfoliated graphite without washing.

The residual acidity in exfoliated graphite is not desirable for many applications, such as gasket applications. However, it is not a problem when the material is used in an electrochemical cell with an acid electrolyte.

In spite of the mechanical agitation during washing, the washed material shows the cellular structure that is typical of exfoliated graphite at its surface more clearly than the unwashed material (Fig. 10). The unwashed material shows a blocky appearance (Fig. 10(b) and (d)); nevertheless, cells are visible, as shown in Fig. 10(f). For the washed material, the cells appear empty (Fig. 10(a), (c) and (e)); for the unwashed material, the cells appear filled (Fig. 10(f)). The blocky and somewhat filled cellular structures are attributed to substances that remain on the surface due to the absence of washing.

The specific surface area of the unwashed exfoliated graphite is 24 ± 3 m^2/g, which is lower than the previously reported value of 45 m^2/g for the washed exfoliated graphite [1] tested using the same equipment and method as this work. The lower specific surface area for the unwashed material is consistent with the microscopic observation that the cellular structure at the edge is less sharp for the unwashed material than the washed material (Fig. 10). In spite of the lower specific surface area of the unwashed material, the relative dielectric constant is much higher for the unwashed material than the washed material. This is because the difference in specific surface area is not very large and the high value of the relative dielectric constant of the unwashed material stems from the residual sulfur and oxygen on the surface (as shown by X-ray spectroscopy). The surface residue can be composed of (i) any surface residue remaining from the intercalation process, and (ii) the dissociation product due to both the exfoliation process and the deintercalation process that accompanies exfoliation.

The results of X-ray spectroscopic elemental analysis conducted with the SEM are shown in Table 6. The unwashed material contains more oxygen and slightly more sulfur than the washed material.

Table 5 – Effect of frequency on the interfacial resistivity (Ω cm^2) of the interface between carbon (air part excluded) and a contact.

Frequency (Hz)	Exfoliated graphite		Activated GNP*
	Without washing	With washing*	
50	0.077 ± 0.005	0.27 ± 0.05	0.12 ± 0.02
100	0.086 ± 0.003	0.31 ± 0.06	0.13 ± 0.01
500	0.101 ± 0.003	0.34 ± 0.04	0.15 ± 0.01
1000	0.107 ± 0.004	0.38 ± 0.05	0.17 ± 0.02

* From [1].

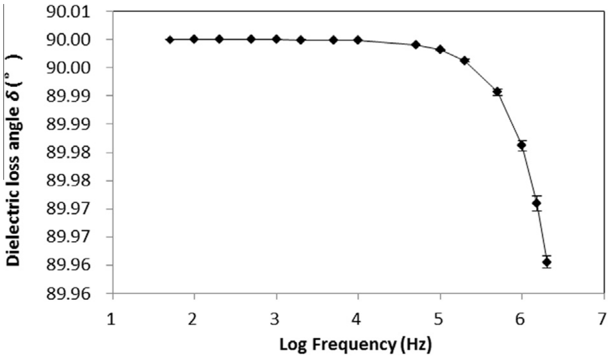

Fig. 9 – Plot of the dielectric loss angle δ vs. frequency (log) for the carbon (air part excluded) in exfoliated graphite without washing.

Table 6 – Elemental composition (at.%) of washed and unwashed exfoliated graphite.

Element	Washed	Unwashed
Carbon	97.2	96.1
Oxygen	2.7	3.8
Sulfur	0.08	0.10

X-ray spectroscopic elemental analysis conducted on the wash water residue obtained by drying the water shows the presence of sulfur and oxygen, which are both absent for pristine deionized water (tested identically). This confirms that the washing removes sulfur and oxygen (associated with the intercalate, which is sulfuric acid) from the exfoliated graphite and is consistent with (i) the gradual pH increase from 2 to 7 during repeated washing and (ii) the decrease of the sulfur and oxygen concentrations in the exfoliated graphite after washing.

4. Conclusions

A high value of the relative dielectric constant (real part) is attractive for supercapacitor electrodes, while a high value of the conductivity is attractive for both supercapacitors and batteries. In addition, high values of both the specific interfacial capacitance and the interfacial resistivity of the carbon–contact interface (with the contact being the electrical contact) are attractive for both supercapacitors and batteries. This work has shown that exfoliated graphite without washing is superior (from a dielectric viewpoint) to exfoliated graphite with washing in that it exhibits a higher value of the

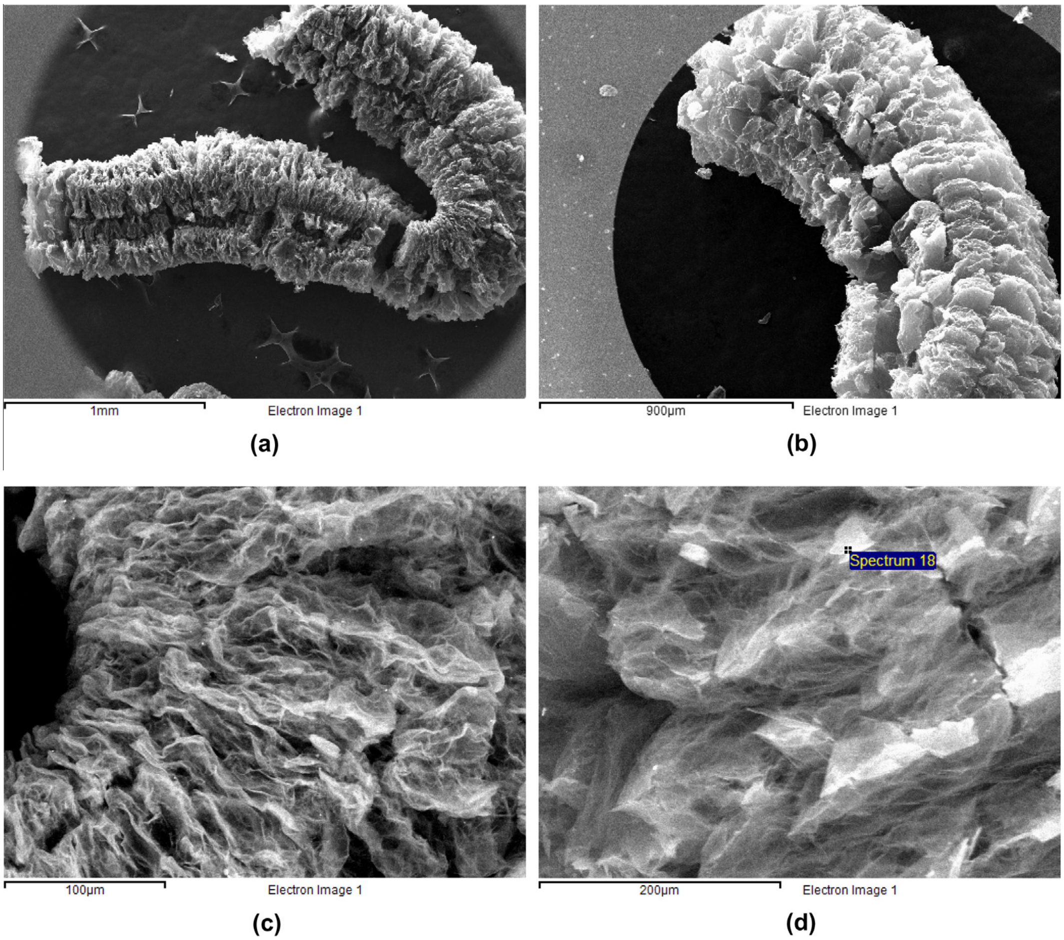

Fig. 10 – SEM photographs of exfoliated graphite. (a) Washed (low magnification). (b) Not washed (low magnification). (c) Washed (high magnification). (d) Not washed (high magnification).

relative dielectric constant (real part), a similar value of the conductivity, a higher value of the specific interfacial capacitance, and a lower value of the interfacial resistivity.

Exfoliated graphite obtained by rapid heating of sulfuric-acid intercalated graphite flakes is studied in terms of the dielectric and conduction behavior. The expandable graphite (prior to exfoliation) is of the type that has been subjected to rinsing and subsequent alkaline treatment for deacidification. Nevertheless, exfoliation of this expandable graphite gives exfoliated graphite that still has substantial residual acidity. Repeated washing of the exfoliated graphite with water to remove the residual acidity was previously conducted in research to study the dielectric and conduction behavior of exfoliated graphite [1]. The repeated washing is accompanied by the pH of the wash water being gradually increased from 2 to 7. The wash water obtained after washing contains sulfur and oxygen.

The high value of the relative dielectric (real part) for the unwashed exfoliated graphite is attributed to the sulfur and oxygen on its surface. The surface morphology of the unwashed material is blocky, with the cells apparently being filled, as viewed at the surface. In contrast, the surface morphology of the washed material is cellular, with the cells being empty, as viewed at the surface. This difference in surface morphology is consistent with the fact that the specific surface area is lower for the unwashed material (24 m^2/g) than the washed material (45 m^2/g [1]). In spite of the lower specific surface area of the unwashed material, the relative dielectric constant is much higher for the unwashed material than the washed material. This is because the difference in specific surface area is not very large and the high value of the relative dielectric constant of the unwashed material stems from the residual sulfur and oxygen on the surface.

Washing with water greatly decreases the real part of the relative dielectric constant from 360 to 38 at 50 Hz, indicating that the residual intercalate in the exfoliated graphite prior to washing contributes much to the polarizability. The value of 360 for exfoliated graphite without washing is even higher than the corresponding value of 121 for KOH-activated GNP. On the other hand, the conductivity (around 50 S/m) of exfoliated graphite is not affected by the washing, due to the dominance of hole conduction and the dry state of the material. Similarly, the imaginary part of the relative dielectric constant (around -19×10^9) and the dielectric loss angle δ (90°) are not affected by the washing. The specific capacitance of the carbon–contact interface is decreased from 1.27 to 0.04 $\mu F/m^2$ by the washing, and the electrical resistivity of the carbon–contact interface is increased from 0.08 to 0.27 $\Omega\,cm^2$ by the washing, both reflecting the reduction of the quality of the interface upon washing the exfoliated graphite.

In spite of the presence of the residual intercalate on the surface, unwashed exfoliated graphite gives a more intimate interface with the contact than washed exfoliated graphite. This is probably due to the slight reduction in the degree of fluffiness of the exfoliated graphite upon washing (which is mechanically disturbing to the worms) and the importance of fluffiness to the intimacy of this interface.

For exfoliated graphite without washing, the real part of the relative dielectric constant decreases with increasing frequency sharply up to 500 Hz; above 500 Hz, the decrease is gradual, with the value remaining high at 280 at 2.0 MHz. The specific capacitance of the carbon–contact interface decreases with increasing frequency, such that the decrease is slight up to 10 kHz and is significant above 10 kHz, such that the value remains high at 1.13 $\mu F/m^2$ at 2.0 MHz. The conductivity decreases with increasing frequency, such that the decrease is slight up to 0.5 MHz and is significant above 0.5 MHz, due to the Skin Effect. The resistivity of the carbon–contact interface increases with increasing frequency, such that the increase is significant up to 10 kHz and is negligibly small above 10 kHz, due to the decreasing excursion of charges that are responsible for the polarization as the frequency increases and the consequent reduced degree of electrical connectivity across the carbon–contact interface. The dielectric loss angle δ decreases sharply with increasing frequency above 0.1 MHz, but the value remains essentially equal to 90° even at 2.0 MHz, indicating that the material is an essentially perfect AC conductor up to at least 2.0 MHz.

This work addresses exfoliated graphite obtained by the rapid heating of a particular type of expandable graphite flake, i.e., a particular intercalate species at a particular intercalate concentration, with the expandable flake subjected to particular rinsing and neutralization processes. Future work should be directed at studying the effects of the intercalate concentration, rinsing process and neutralization process of the expandable graphite on the dielectric and conduction behavior of the resulting unwashed exfoliated graphite. In addition, future work should be directed at increasing the specific surface area of the exfoliated graphite, due to the importance of a high value of the specific surface area for electrochemical electrode applications.

Acknowledgements

The authors thank Mr. Andi Wang of University at Buffalo, State University of New York, for technical assistance. They are also grateful to the China Scholarship Council (Beijing, China) for the 12-month scholarship provided to one of the authors (Hong).

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