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# Dielectric and electrical conduction behavior of carbon paste electrochemical electrodes, with decoupling of carbon, electrolyte and interface contributions

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ABSTRACT

The electrical conduction and dielectric (capacitive) properties of electrolyte-filled carbon paste electrochemical electrodes are reported, with the carbon, electrolyte (15% $H_2SO_4$), carbon–electrolyte interface and carbon–contact(metal) interface contributions fully decoupled for the first time. Without full decoupling and with the carbon contributions neglected, the carbon–electrolyte specific interfacial capacitance would be much overestimated and the carbon–electrolyte interfacial resistivity would be much underestimated. The carbons and electrolyte are comparable in both dielectric constant and resistivity. The specific contact capacitance is increased and the contact resistivity is decreased by adding the electrolyte to a carbon. The electrolyte is more effective than water in enhancing carbon–liquid and paste–contact interfaces. Conductivity is attractive for batteries and supercapacitors; strong dielectric properties are attractive for supercapacitors but not batteries. Exfoliated graphite provides handleability and excellent volumetric and interfacial conductivities. It gives low carbon dielectric constant, but contributes to the interfacial capacitances. Activated graphite nanoplatelet (GNP) gives high carbon and paste dielectric constants and high specific contact capacitance. Activated carbon gives poor volumetric and interfacial conductivities. Exfoliated graphite is even better than carbon black for batteries; GNP is even better than activated carbon for supercapacitors; an exfoliated-graphite/GNP mixture is suitable for both; natural graphite is not competitive for either.

## 1. Introduction

Carbon materials are widely used for electrodes in various electrochemical devices, such as batteries, supercapacitors, gas sensors and dye-sensitized solar cells. Battery and supercapacitor applications are dominant.

Carbon electrodes are commonly in the form of a paste [1,2], which commonly comprises carbon particles and a liquid. This is because of the electrical conductivity and chemical stability of carbon materials. In addition, through activation [3], carbon materials can be rendered high in the specific surface area, which is valuable for promoting the

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**List of abbreviations**

| | |
|---|---|
| $C$ | measured capacitance for the composite consisting of the specimen and the frame |
| $C_i$ | capacitance of the interface between the composite (specimen plus frame) and each of the electrical contacts |
| $C_s$ | capacitance of the interface between the specimen (inside the cavity defined by the frame) and each of the electrical contacts |
| $C_r$ | capacitance of the interface between the frame and the electrical contact when the frame material occupies the entire area between the electrical contacts |
| $C_P$ | capacitance of the carbon paste |
| $C_C$ | capacitance of the carbon solid in the carbon paste |
| $C_L$ | capacitance of the liquid |
| $C_f$ | capacitance of the carbon–liquid interface |
| $C_c$ | capacitance of the carbon solid in the dry carbon compact |
| $C_a$ | capacitance of the air in the dry carbon compact |
| $\kappa$ | relative dielectric constant of the composite consisting of the specimen and the frame |
| $\kappa_s$ | relative dielectric constant of the specimen material |
| $\kappa_r$ | relative dielectric constant of the frame material |
| $\kappa_p$ | relative dielectric constant of the carbon paste |
| $\kappa_c$ | relative dielectric constant of the carbon solid |
| $\kappa_L$ | relative dielectric constant of the liquid |
| $\kappa_d$ | relative dielectric constant of the dry carbon compact (i.e., carbon solid plus air) |
| $R$ | resistance between the two electrical contacts that sandwich the specimen |
| $R_s$ | volume resistance of the specimen |
| $R_i$ | resistance of the interface between the specimen and an electrical contact |
| $R_{ic}$ | resistance of the interface between the carbon solid and an electrical contact |
| $R_{ia}$ | resistance of the interface between the air and an electrical contact |
| $R_p$ | volume resistance of the carbon paste |
| $R_c$ | volume resistance of the solid carbon part of the carbon paste |
| $R_L$ | volume resistance of the liquid part (either electrolyte or water) of the carbon paste |
| $R_f$ | resistance of the solid–liquid interface |
| $R_d$ | volume resistance of the dry carbon compact |
| $R_a$ | volume resistance of the air in the dry carbon compact |
| $\rho_f$ | carbon–liquid interfacial resistivity |
| $\sigma_f$ | carbon–liquid interfacial conductivity |
| $V_c$ | volume fraction of the carbon solid in the carbon paste |
| $l$ | carbon paste thickness (the same as the frame thickness) |
| $A$ | specimen area ($25.0 \times 25.0\ \text{mm}^2$) |
| $A_p$ | carbon paste area (the same as the area of the cavity in the frame) |
| $A_f$ | carbon–liquid interface area |
| $v_s$ | area fraction of the specimen relative to the composite (specimen plus frame) |
| $v_r$ | area fraction of the frame relative to the composite (specimen plus frame) |
| $a_c$ | area fraction of the carbon solid in the dry carbon compact |
| $\varepsilon_0$ | the permittivity of free space ($8.85 \times 10^{-12}$ F/m) |

electrochemical reaction that occurs on the electrode surface. Graphite nanoplatelet (GNP) [4] and graphene [5] are particularly attractive for their high specific surface area.

Due to the applications, a carbon electrode is commonly characterized in terms of its effectiveness in the particular electrochemical device where it is intended to function. The device commonly comprises at least two electrodes and an electrolyte among them. The characterization is sometimes conducted as a function of the AC frequency in a technique known as electrochemical impedance spectroscopy [6–11]. Although this method of characterization is meaningful for assessing the overall behavior of the electrochemical cell, it does not allow characterization of the components of the cell in a decoupled manner. Moreover, the method does not allow characterization of the specific interfaces, such as the interface between the electrode and the electrolyte and that between the electrode and the electrical contact that connects the electrode to the outer circuit.

The relevant dielectric and conduction properties of a carbon paste electrode include the properties of (i) the overall paste, (ii) the carbon part of the paste, (iii) the electrolyte part of the paste, and (iv) the interface between the carbon and the electrolyte in the paste, in addition to the relative proportions of the carbon, electrolyte and interface contributions to the overall behavior of the paste. For each of the carbon, the electrolyte and the overall paste, the properties include the volume electrical resistivity and the relative dielectric constant (which relates to the volumetric capacitance). For the carbon–electrolyte interface, the properties include the areal electrical resistivity and the specific interfacial capacitance.

Low values of the volume resistivity of the electrolyte and electrodes and a low value of the electrode–electrolyte interface resistivity are desired for both supercapacitors and batteries in order to minimize the internal resistance of the electrochemical cell. In particular, a low volume resistivity of the electrode helps the transmission of the applied electric potential from the electrical contact to the electrode–electrolyte interface.

For electrical energy storage, a high value of the relative dielectric constant is desired for the electrolyte and the electrodes of a supercapacitor (double-layer capacitor). With the electrode and the electrode–electrolyte interface considered in parallel electrically, a high value of the electrode–electrolyte interface capacitance is also desirable for a supercapacitor. In contrast, for a battery, a low value of the relative dielectric constant is desired for the electrodes and a low value of the electrode–electrolyte interface capacitance is also desired, as electric polarization in an electrode and at the electrode–electrolyte interface is disadvantageous to battery performance.

The dielectric behavior relates to the tendency for capacitance build-up, which commonly involves electric polarization. The associated charge movement can be due to ion movement, polar bond rotation, functional group movement, etc. In case of an electrolyte in the form of an ionic liquid, ion movement is dominant. In case of carbon materials, functional group movement is important. Functional groups are located on the surface of carbon and are tailored by surface treatment [12,13]. The quantity of a type of functional group increases with the surface area. Thus, a larger specific surface area is expected to correlate with a higher polarizability.

Another interface is that between the paste electrode and the electrical contact, which is commonly a metal. For this interface, the properties include the interfacial (areal) electrical resistivity (referred to as the contact resistivity) and the interfacial capacitance. A low value of the contact resistivity is desired for both supercapacitors and batteries. Since the electrode and this interface are in series electrically, a high value of the interfacial capacitance is desired for minimizing the influence of the contact interface on the dielectric behavior of the cell.

The electrode and electrolyte volume resistivities, the carbon–electrolyte interfacial resistivity and the contact resistivity relate to the conduction behavior, whereas the electrode and electrolyte relative dielectric constants, the specific carbon–electrolyte interfacial capacitance (i.e., the interfacial capacitance per unit interface area) and the specific contact capacitance (i.e., the electrode–contact interfacial capacitance per unit interface area) relate to the dielectric behavior. All these quantities contribute to governing the performance of an electrochemical cell.

In relation to the dielectric behavior of an electrochemical cell, prior work has emphasized the dielectric behavior of the electrolyte and the electrode–electrolyte interface, but essentially not the electrode itself. This is because of (i) the common implicit assumption that the electrical conduction behavior of an electrode overshadows the dielectric behavior and (ii) the challenge of decoupling the volumetric (electrode) and interfacial capacitive effects. When the volumetric dielectric effect is assumed to be negligible in the modeling, the interfacial effect resulting from the modeling becomes greater than the actual extent of the effect.

Without understanding how the various volumetric and interfacial quantities contribute to the electrical and dielectric behavior, the development of electrode materials cannot be carried out in a scientifically rigorous manner. An objective of this paper is to decouple and determine these quantities. Full decoupling of these quantities has not been previously accomplished.

Different types of carbon differ in the volume electrical resistivity and the relative dielectric constant. In addition, the type of carbon material affects the carbon–electrolyte interface and the paste–contact interface in terms of both the dielectric and conduction properties. Another objective is to compare different carbon materials in terms of the decoupled quantities. The carbons addressed include natural graphite, carbon black, exfoliated graphite, GNP and activated carbon, which are all important for making paste electrochemical electrodes.

The composition of the electrolyte affects its volume resistivity and relative dielectric constant, in addition to affecting the carbon–electrolyte interface and the paste–contact interface. Yet another objective is to compare electrolytes with different ion concentrations, namely an acidic aqueous solution and water, in terms of the decoupled quantities.

This work is focused on the electrolyte-filled electrode, which is a carbon paste with the liquid being the electrolyte. This uncommon focus has resulted in new information on how the carbon, electrolyte and interfaces contribute to the dielectric and conduction behavior.

Because the carbon materials used for electrochemical electrodes are typically discontinuous, most commonly in the form of particles, a binder (e.g., PTFE, oil and paraffin) is commonly used to form a carbon electrode [14–16]. However, the presence of the binder affects the electrical and dielectric behavior. For characterization of the carbon materials themselves, this work does not use any binder. Instead of including a binder in a carbon paste [15,16], this work uses an electrolyte as the liquid in the paste. This is because the presence of an electrolyte with the electrode solid material (typically porous) is quite common in electrochemical devices.

## 2. Experimental methods

The approach used for achieving the decoupling mentioned in Section 1 involves (i) measuring the resistance and capacitance of the dry carbon compact (for determining the quantities pertaining to the carbon solid), those of an electrolyte-containing paper towel (for determining the quantities pertaining to the electrolyte), and those of the paste (for backing out the quantities pertaining to the carbon–electrolyte interface), and (ii) conducting the measurement for three paste thicknesses, thereby decoupling paste volumetric and paste–contact interfacial quantities.

### 2.1. *Materials*

Five types of carbon particles and one type of carbon particle hybrid are studied. The five types of particles are (i) natural graphite powder, Asbury 2299 (Asbury Graphite Mill, Inc.), with specific surface area 420 ± 42 $m^2/g$, and density 2.26 $g/cm^3$, (ii) carbon black (Ketjenblack EC600JD, a furnace black, Akzo Nobel, Chicago, IL, U.S.A.) with specific surface area 1236 ± 47 $m^2/g$ and density 1.80 $g/cm^3$, (iii) activated carbon, Norit Super 30 (Norit Americas Inc.), with specific surface area 1624 ± 33 $m^2/g$ and density 1.98 $g/cm^3$, (iv) activated GNP prepared in this work, and (v) exfoliated graphite prepared in this work. The types of carbon selected are typical carbons for the various carbon categories. It is recognized that there can be significant differences in properties among carbons of the same category.

The hybrid is a mixture of exfoliated graphite and activated GNP is a 1:3 mass ratio (corresponding to 1:3 volume ratio), as obtained by dry mixing, i.e., manual shaking in a covered container, with the carbon occupying about 30% of the volume of the container and the shaking continued until all the activated GNP clings to the exfoliated graphite. This ratio corresponds to the maximum GNP proportion such that all of GNP clings to the exfoliated graphite.

The exfoliated graphite is prepared by rapid heating of expandable (acid intercalated) graphite flakes (No. 3772, Asbury Graphite Mill, Inc.) in purging nitrogen to 1000 °C. After this, the exfoliated graphite is washed repeatedly in de-ionized water until the pH of the water is around 7. This is followed by drying in air at 110 °C.

The GNP is prepared by mechanical agitation of the above-mentioned exfoliated graphite dispersed in water. The unwashed exfoliated graphite is mixed with water that contains a trace amount of a dispersant (Triton X100, Rohm and Haas, Dow Chemical Co.). Immediately after magnetic stirring, the suspension is sonicated for 48 h. Then the suspension is washed repeatedly with de-ionized water until the pH is around 7, followed by drying in air at 110 °C.

The activation of the GNP is performed by mixing the GNP with potassium hydroxide (88 wt.% KOH) in the mass ratio 1:3 in water. The KOH pellets are dissolved in water, followed by the addition of GNP to the solution and then manual mixing using a stirrer. This is followed by drying at 110 °C to form a KOH coating on the GNP. After this, the GNP is heated to the activation temperature of 850 °C at a rate of 8 °C/min and held at 850 °C for 30 min, followed by cooling. Nitrogen gas purging (flow 80 ml/min) is provided throughout the heating and cooling. After cooling, the suspension is washed by using deionized water and then centrifuged for separating the solid from the liquid. Then the liquid part is decanted and the remaining solid part is dried in air at 110 °C. The weight loss due to the entire treatment is 51%. The density of the resulting activated GNP is 2.03 g/cm$^3$, as determined using the method described in Section 2.5.

The electrolyte is deionized water containing 15 vol.% sulfuric acid ($H_2SO_4$). The density of the solution is 1.08 g/cm$^3$. In case of the natural graphite powder, deionized water (without sulfuric acid) is also used separately for the sake of comparison. Here, “electrolyte” refers to the water containing sulfuric acid, whereas “water” refers to the case of water without sulfuric acid.

### 2.2. *Carbon paste preparation*

A paste consisting of carbon particles and a liquid (either the electrolyte or water) is prepared by mixing of known masses of the solid and liquid using a magnetic stirrer, followed by centrifuging for 1.0 h, which results in a liquid above a paste. This liquid is decanted and weighed. Thus, the mass ratio and hence the volume ratio of the solid and liquid parts of the paste are obtained. The centrifuging step eliminates air from the resulting paste.

### 2.3. *Dielectric testing and analysis method*

The relative dielectric constant is a volumetric geometry-independent material property, whereas the specific interfacial capacitance (interfacial capacitance per unit interface area) is an areal geometry-independent interface property. Because these quantities are geometry independent, they allow calculation of the capacitance for specific geometries and dimensions that are associated with electrodes in practical electrochemical devices.

The measurement of the relative dielectric constant and the specific interfacial capacitance involves a precision RLC meter (Quadtech 7600). The frequency is 50 Hz, unless noted otherwise. The capacitance for the parallel RC circuit configuration is obtained from the meter. The AC electric field is 6.5 V/cm. In order to decouple the volumetric and interfacial contributions to the capacitance, specimens of three different thicknesses (0.42, 1.60 and 3.30 mm) are tested (Fig. S1), as dictated by those of three frames (with through holes) made of flexible graphite (a sheet commercially made by the compression of exfoliated graphite in the absence of a binder), which is chosen for its chemical inertness and fluid gasketing ability. The electric field is applied between the two copper foils (Fig. S2). The AC voltage is adjusted so that the electric field is fixed while the thickness varies. Each specimen fills the entire volume (area 20.0 × 20.0 mm) inside a frame (outer dimensions 25.0 × 25.0 mm, Fig. S2). For both dielectric and resistance measurements, the flexible graphite frame is insulated from each of the two copper contacts (copper foils of thickness 62 μm) by using a glass fiber fabric reinforced Teflon film (CS Hyde Company, Lake Villa, IL) of thickness 75 μm (Fig. S2). 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).

In case of dielectric measurement (Fig. S2(b)), the Teflon film with area 25.0 × 25.0 mm (covering both the specimen and the frame) and relative dielectric constant 2.34 (as measured at 1.000 kHz) is used as an insulating film between the specimen and each of the two copper contacts. In case of resistance measurement, this continuous film is replaced by a frame made by using the same material and positioned between the specimen and the copper (Fig. S2(a)). Thus, the contact is copper in case of conduction testing and Teflon-lined copper in case of dielectric testing. The continuous Teflon lining used in dielectric testing is for minimizing the current.

The measured capacitance $C$ is for the composite of the specimen and the frame in parallel electrically, with inclusion of the effect of the two interfaces between this composite and the two contacts. The two interfaces and this composite are in series electrically. Hence,

$$1/C = 2/C_i + l/(\varepsilon_0 \kappa A), \tag{1}$$

where $C_i$ is the capacitance due to a composite–contact interface, $\varepsilon_0$ is the permittivity of free space (8.85 x 10 $^{-12}$ F/ m), $\kappa$ is the relative dielectric constant of the composite, $A$ is the contact area, which is the same as the specimen area (20.0 × 20.0 mm$^2$), and $l$ is the thickness of the frame. As shown by Eq. (1), $C_i$ should be high in order for it to have little influence.

According to Eq. (1), $1/C$ is plotted against $l$, as illustrated in Fig. S1. The value of $C_i$ is obtained from the intercept of $2/C_i$ at the $1/C$ axis at $l = 0$, and the value of $\kappa$ is obtained from the slope, which is equal to $1/(\varepsilon_0 \kappa A)$. The specific interfacial capacitance is the product of $C_i$ and $A$.

The relative dielectric constant ($\kappa$) of the composite (specimen plus frame) is related to that of the specimen material $\kappa_s$ and that of the frame material $\kappa_r$ by the Rule of Mixtures, as shown by the equation

$$\kappa = \kappa_s v_s + \kappa_r v_r, \tag{2}$$

where $v_s$ is the area fraction of the specimen, and $v_r$ is the area fraction of the frame, with the two area fractions adding up to 1.000.

The contact capacitance ($C_i$) is the capacitance associated with the interface between the composite (specimen plus frame) and each of the contacts (Teflon-lined copper) and is included in the measured capacitance ($C$). The contact capacitance $C_s$ of the interface between the specimen (inside the cavity defined by the frame) and the contact is of more interest and relates to $C_i$ by the Rule of Mixtures for capacitances in parallel, i.e.,

$$C_i = C_s + C_r v_r, \tag{3}$$

where $C_r$ is the contact capacitance of the interface between the frame and the contact when the frame material occupies the entire area between the contacts, and $v_r$ is the area fraction of the frame. Thus, $C_r$ is found to be 55.2, 54.8, 53.1 and 51.9 pF at 50, 100, 500 and 1000 Hz respectively. With the value of $C_r$ known, $C_s$ is obtained from Eq. (3).

In case of the specimen being a dry carbon compact (with air voids), the contact capacitance $C_s$ relates to that of the solid carbon ($C_c$) and that of air ($C_a$) under the assumption of capacitances in parallel, i.e.,

$$C_s = C_c + C_a. \tag{4}$$

The $C_a$ is much less than $C_c$, because of the air gap effectively corresponding to a relatively large thickness. With the second term neglected, Eq. (4) becomes

$$C_c = C_s. \tag{5}$$

Hence, the specific contact capacitance of the carbon solid is given by

$$C_c/(a_c A) = C_s/(a_c A), \tag{6}$$

where $a_c$ is the area fraction of the compact that is carbon solid.

For a carbon paste, the solid part (carbon), the liquid part (either electrolyte or water) and the carbon–liquid interface all contribute to the relative dielectric constant of the paste $\kappa_p$. The capacitance of the paste $C_P$ is the sum of the contributions by the carbon $C_C$, liquid $C_L$ and carbon–liquid interface $C_f$. With consideration of these capacitances in parallel,

$$C_P = C_C + C_L + C_f. \tag{7}$$

Other equivalent circuits involving the three capacitances in series or combinations of the capacitances in series and parallel are not effective. Based on Eq. (7) and the Rule of Mixtures,

$$\kappa_p = \kappa_c V_c + \kappa_L(1 - V_c) + C_f(l/\varepsilon_0 A_p), \tag{8}$$

where $\kappa_c$ is the relative dielectric constant of the carbon solid, $\kappa_L$ is that of the liquid, $V_c$ is the volume fraction of the carbon solid in the paste (natural graphite 37%, activated carbon 40%, activated GNP 35%, exfoliated graphite 41%, hybrid 38%, carbon black 37%), $(1 - V_c)$ is the volume fraction of the liquid part of the paste, $l$ is the paste thickness (the same as the frame thickness) and $A_p$ is the paste area (the same as the area of the cavity in the frame). The quantity $C_f$ $(l/\varepsilon_0 A_p)$ can be considered the effective relative dielectric constant of the carbon–liquid interface. It is valuable for indicating the extent of contribution of the interface to the relative dielectric constant of the paste.

The value of $\kappa_L$ is separately determined by measuring the capacitance of a paper towel soaked with the liquid and that of the corresponding dry paper towel. The details are described in the Supplementary Material section. The obtained values of $\kappa_L$ for water and the electrolyte are shown in Table S1 of the Supplementary Material section. At each frequency, the relative dielectric constant is higher for the electrolyte than water, as expected. Indeed, the addition of an ionic liquid to the liquid binder of a carbon paste improves the electrochemical performance [17]. For water, electrolyte and paper towel, the relative dielectric constant decreases with increasing frequency, as expected.

The relative dielectric constant of the dry material (carbon plus air) $\kappa_d$ is given by

$$\kappa_d = \kappa_c V_c + (1 - V_c). \tag{9}$$

The value of $\kappa_L$ is considered to be unaffected by the proximity of the liquid to the carbon.

By measuring the relative dielectric constant separately for the paste $\kappa_p$ and the dry carbon (with air voids) $\kappa_d$, and using Eq. (8), Eq. (9) and the separately determined value of $\kappa_L$, the quantities $\kappa_c$ and the effective relative dielectric constant of the carbon–liquid interface $C_f$ $(l/\varepsilon_0 A_p)$ are obtained.

The interfacial capacitance $C_f$ is proportional to the area of the interface between carbon and liquid. Thus, in order to describe the area-independent property of the interface, it is meaningful to consider the specific interfacial capacitance. The carbon–liquid interface area ($A_f$) can be estimated as the product of the specific surface area (surface area per unit mass) and the mass of the carbon. This estimation neglects the closed pores, which are not accessible to the liquid anyway.

The three thicknesses used for dielectric testing correspond to three masses, and hence three values of $A_f$. For each thickness, $C_f$ is measured. Thus, a linear plot of $C_f$ vs. $A_f$ is obtained. Its slope is the specific carbon–liquid interfacial capacitance.

### 2.4. *Resistivity testing and analysis method*

The volume electrical resistivity is a volumetric geometry-independent material property, whereas the interfacial resistivity is an areal geometry-independent interface property. Because these quantities are geometrically independent, they allow calculation of the resistance for specific geometries and dimensions that are associated with electrodes in practical devices.

The AC resistance is measured in the absence of an insulating film between the specimen and the copper contact (Fig. S2(a)). Other than this absence, the configuration is the same as that for relative dielectric constant measurement (Fig. S2(b)). The same RLC meter, AC voltage and frequencies are used. The frequency is 50 Hz, unless noted otherwise.

The measured resistance $R$ between the two copper contacts that sandwich the specimen includes the volume resistance $R_s$ of the specimen and the resistance $R_i$ of each of the two interfaces between the specimen and a copper contact, i.e.,

$$R = R_s + 2R_i. \tag{10}$$

By measuring $R$ at three specimen thicknesses, the curve of $R$ versus thickness is obtained (Fig. S1(a)). The intercept of this curve with the vertical axis equals $2R_i$, whereas the slope of this curve equals $R_s/l$, where $R_s$ is the specimen resistance for the specimen thickness of $l$. The specimen resistivity is obtained by multiplying $R_s/l$ by the specimen area $A$. The contact resistivity equals the product of $R_i$ and $A$.

In case of the specimen being a dry carbon compact (with air voids), the contact resistance $R_i$ of the interface between the specimen and the copper contact is contributed by the contact resistance $R_{ic}$ of the interface between the carbon solid and the copper contact and the contact resistance $R_{ia}$ of the interface between the air and the copper contact. Assuming reasonably (based on the geometry) that these contributors are resistances in parallel,

$$1/R_i = 1/R_{ic} + 1/R_{ia}. \tag{11}$$

With $R_{ia}$ being essentially infinity, Eq. (11) becomes

$$1/R_i = 1/R_{ic}. \tag{12}$$

For a paste, the volume resistance $R_c$ of the solid part (carbon), the volume resistance $R_L$ of the liquid part (either electrolyte or water) and the interfacial resistance $R_f$ of the solid–liquid interface all contribute to the volume resistance of the paste $R_p$. Assuming that these contributors are electrically in parallel,

$$1/R_p = 1/R_c + 1/R_L + 1/R_f. \tag{13}$$

The quantity $R_p$ is measured from a paste, using Eq. (10), with $R_p$ substituting $R_s$. The quantity $R_c$ is measured from a dry carbon compact, using Eq. (10), with the resistance of the dry carbon compact $R_d$ substituting $R_s$ in Eq. (10). The quantity $R_d$ is given by

$$1/R_d = 1/R_c + 1/R_a, \tag{14}$$

where $R_a$ is the resistance of the air in the compact, and the carbon and air are considered to be resistances in parallel. Since $R_a$ is essentially infinity, Eq. (14) becomes

$$1/R_d = 1/R_c. \tag{15}$$

The quantity $R_L$ in Eq. (13) equals 981 ± 18 and 5.7 ± 1.2 Ω.cm at 50 Hz for water and the electrolyte respectively, as measured from a paper towel soaked with the liquid (Table S1 of the Supplementary Material section). With $R_p$, $R_c$ and $R_L$ all known, Eq. (13) gives $R_f$.

The carbon–liquid interfacial resistivity $\rho_f$ is given by $A_f$

$$\rho_f = R_f, \tag{16}$$

where $A_f$ is the carbon–liquid interface area. The carbon–liquid interfacial conductivity $\sigma_f$ is

$$\sigma_f = 1/\rho_f. \tag{17}$$

Combination of Eq. (16) and (17) gives

$$1/R_f = \sigma_f A_f, \tag{18}$$

where $1/R_f$ is the conductance of the carbon–liquid interface.

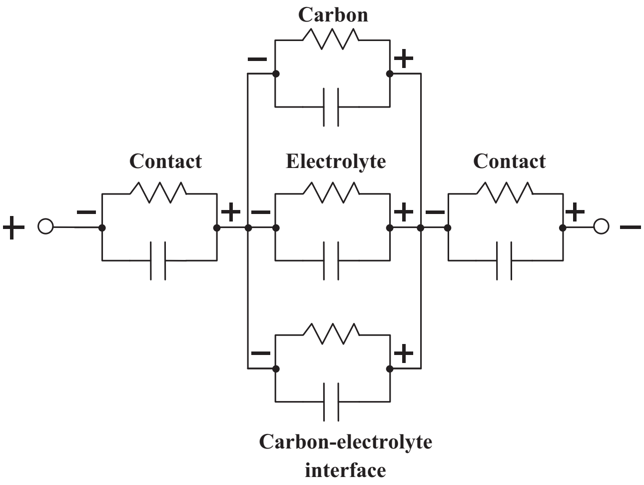

**Fig. 1 – Equivalent circuit model for a carbon paste electrode. The contact refers to the interface between the carbon paste and the electrical contact.**

Conduction testing involves testing specimens at three thicknesses, which correspond to three masses, and hence, based on the specific surface area, three values of $A_f$. For each thickness, $R_f$ is obtained. The plot of $1/R_f$ vs. $A_f$ fit a straight line, the slope of which is $\sigma_f$.

Fig. 1 shows the equivalent circuit used in this work for modeling the conduction and dielectric behavior of an electrolyte-filled carbon paste electrode. All the quantities shown in the model are decoupled and determined using the method described in Sections 2.3 and 2.4.

### 2.5. *Density and specific surface area*

The measured density of the paste is used to obtain the density of the carbon solid in the paste, based on the Rule of Mixtures. The specific surface area of dry carbon particles is measured by nitrogen adsorption, using a Micromeritics ASAP 2010 instrument.

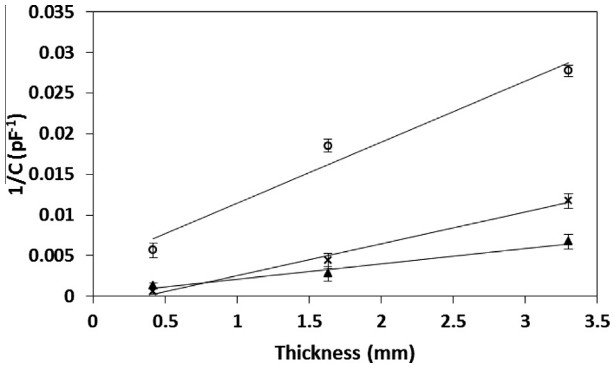

**Fig. 2 – Plot of the reciprocal of the measured capacitance (50 Hz) vs. the specimen thickness. The specimen is carbon particles with an aqueous solution containing 15 vol.% sulfuric acid. ○: natural graphite; ×: activated carbon; ▲: activated GNP.**

## 3. Results and discussion

The absence of a binder is attractive, because a binder hinders the direct contact of the electrode material with the electrolyte. In spite of the absence of a binder, the pastes are coherent and handleable, particularly for those containing exfoliated graphite.

The plot of the reciprocal of the measured capacitance vs. the specimen thickness (Fig. 2) is linear, as expected from Eq. (1). The plot of the measured resistance vs. the thickness (Fig. 3) is linear, as expected from Eq. (10). Different carbons give different slopes and intercepts.

The plot of the carbon–electrolyte interfacial capacitance vs. the carbon–electrolyte interfacial area is linear, as shown in Fig. 4(a) for exfoliated graphite, with the slope giving the specific interfacial capacitance. The plot of the carbon–electrolyte interfacial conductance $1/R_i$ vs. the carbon–electrolyte interfacial area is linear, as shown in Fig. 4(b) for exfoliated graphite, with the slope giving the specific interfacial conductivity (Eq. (18)).

Table 1 shows the relative dielectric constant of natural graphite paste (solid volume fraction = 0.37) with water, along with the values for the carbon solid, water and the carbon–water interface. The interface value is an effective relative dielectric constant, showing that the interface effect is small compared to those of the carbon and water. The addition of water to the carbon solid causes the relative dielectric constant to increase, due to the high value of water.

The specific contact capacitance is much higher for the paste than the carbon solid. This means that the addition of water to the carbon solid improves the electrode–contact interface.

### 3.1. Dielectric behavior

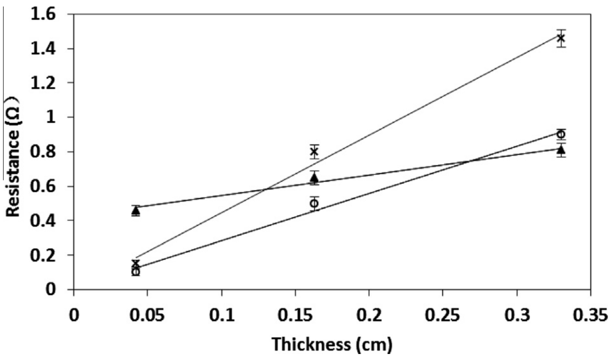

**Fig. 3 – Plot of the measured resistance (50 Hz) vs. the specimen thickness. The specimen is carbon particles with an aqueous solution containing 15 vol.% sulfuric acid. ○: natural graphite; ×: activated carbon; ▲: Activated GNP.**

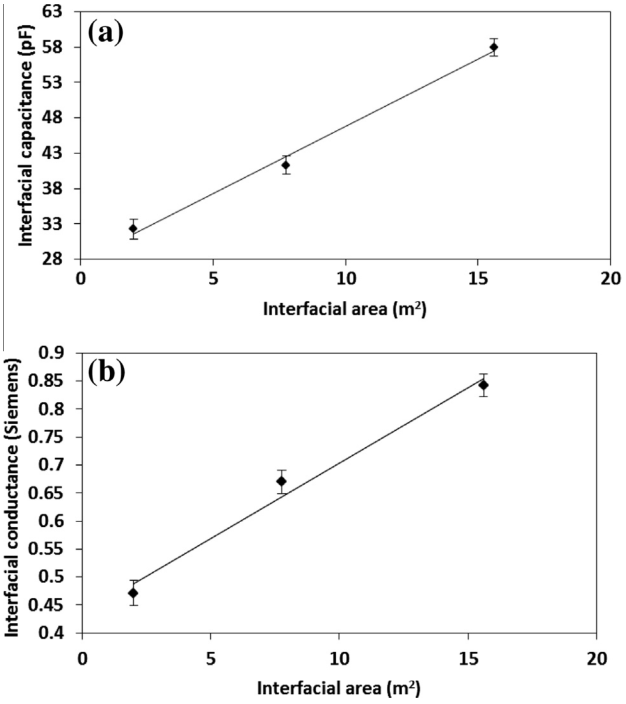

**Fig. 4 – Effect of the carbon–electrolyte interfacial area of the exfoliated graphite paste. (a) Plot of the carbon–electrolyte interfacial capacitance vs. the carbon–electrolyte interfacial area. (b) Plot of the carbon–electrolyte interfacial conductance vs. the carbon–electrolyte interfacial area.**

#### 3.1.1. Volumetric dielectric behavior

Table 2 shows the relative dielectric constant (50 Hz) of carbon pastes (solid volume fraction = 0.37) with either water or the electrolyte (15% $H_2SO_4$) as the liquid in the pastes. The decoupled values for the carbon solid, liquid and the carbon–liquid interface are also shown. The interface value is an effective relative dielectric constant. The value for the liquid is from Table S1 of the Supplementary Material section.

The relative dielectric constant of carbon $\kappa_c$ is less than that of the electrolyte for natural graphite, carbon black and exfoliated graphite, but is higher than that of the electrolyte for activated GNP and activated carbon. Comparison of the carbons in Table 2 shows that the activated carbon and activated GNP exhibit much higher $\kappa_c$ than natural graphite, carbon black or exfoliated graphite, as expected from the relatively large amount of functional groups on the large surface of activated carbon or activated GNP and the slightly polar nature of the functional groups. In spite of the slight decrease in the relative dielectric constant of activated carbon or activated GNP upon addition of the electrolyte to form a paste, and the increase in the relative dielectric constant of natural graphite, carbon black or exfoliated graphite to form a paste, the relative dielectric constant of the paste with the electrolyte $\kappa_p$ is substantially higher for activated carbon or activated GNP than natural graphite, carbon black or exfoliated graphite. Thus, from the viewpoint of the relative dielectric constant, activated carbon or activated GNP is more attractive than natural graphite, carbon black or exfoliated graphite.

The carbon–electrolyte interface contributes to a minor extent to the dielectric behavior of a carbon paste, as shown by the relatively low values of the effective carbon–electrolyte interface relative dielectric constant compared to the values of the relative dielectric constant of the carbon and liquid. Both the carbon and the electrolyte contribute significantly

**Table 1 – Relative dielectric constant of natural graphite paste (solid volume fraction = 0.37) with water, along with the values for the carbon solid, water and the carbon–water interface. The interface value is an effective relative dielectric constant. The values for water are obtained from Table S1. The specific contact capacitance of the specimen–copper interface is also shown. The data are based on two sets of specimen. Each set consists of specimens at three thicknesses.**

| Frequency (Hz) | Relative dielectric constant | | | | Specific carbon–electrolyte interfacial capacitance ($pF/m^2$) | Specific contact capacitance ($\mu F/m^2$) | |
|---|---|---|---|---|---|---|---|
| | Paste | Carbon | Water | Interface[a] | | Paste | Carbon |
| 50 | 71.7 ± 1.4 | 53.3 ± 1.3 | 79.2 ± 1.9 | 2.1 ± 0.6 | 0.27 ± 0.09 | 1.94 ± 0.06 | 0.12 ± 0.01 |
| 100 | 65.9 ± 2.1 | 48.9 ± 3.8 | 74.8 ± 2.3 | 4.7 ± 1.4 | / | 1.80 ± 0.10 | 0.09 ± 0.01 |
| 500 | 61.2 ± 1,5 | 45.2 ± 1.1 | 73.1 ± 2.1 | 4.4 ± 1.3 | / | 1.55 ± 0.08 | 0.07 ± 0.01 |
| 1000 | 55.3 ± 1.8 | 43.5 ± 3.1 | 70.0 ± 3.3 | 3.0 ± 2.0 | / | 1.41 ± 0.12 | 0.04 ± 0.01 |

[a] Effective relative dielectric constant of the carbon–water interface.

to the dielectric behavior of a carbon paste, such that the carbon contribution varies significantly among the different carbons and is particularly significant for activated carbon and activated GNP and least significant for exfoliated graphite and carbon black. Compared to natural graphite, carbon black and exfoliated graphite exhibit lower $\kappa_c$. This means that carbon black and exfoliated graphite are less polarizable than natural graphite from a volumetric viewpoint.

Among the carbons, activated carbon gives the highest values of the relative dielectric constant for both the paste and the carbon, though activated GNP gives values that are almost as high. This is attributed to the abundance of surface functional groups. Carbon black gives the lowest values of the relative dielectric constant for the paste and carbon, probably due to the relatively low density of surface functional groups. Natural graphite gives almost the lowest values of the relative dielectric constant for the paste and carbon and the lowest value of the relative dielectric constant of the carbon–electrolyte interface, probably also due to the relatively low density of surface functional groups.

As shown for natural graphite, the relative dielectric constant $\kappa_c$ (53.3 ± 1.3) is increased by the addition of either water or the electrolyte (Table 2) to form a paste, such that the paste with the electrolyte exhibits a higher value of the relative dielectric constant (85.5 ± 1.8) than the paste with water (71.7 ± 1.4). This is consistent with the expected observation that $\kappa_L$ [electrolyte] (100.9 ± 1.3) is higher than $\kappa_L$ [water] (79.2 ± 1.9). Furthermore, both the volume electrical resistivity and the carbon–liquid interfacial resistivity are higher for water than the electrolyte. This is consistent with the report that the addition of an ionic liquid to the liquid binder of a carbon paste improves the electrochemical performance of the paste [17].

As shown for natural graphite, both $\kappa_L$ [electrolyte] (100.9 ± 1.3) and $\kappa_L$ [water] (79.2 ± 1.9) are higher than $\kappa_c$ (53.3 ± 1.3). This means that both the electrolyte and water are considerably more polarizable than carbon, as expected from the high mobility of the ions in the electrolyte and water and the relatively low mobility of the functional groups (particularly oxygen-containing functional groups [12,13]) on the carbon surface.

For the activated carbon and activated GNP, the relative dielectric constant is decreased from $\kappa_c$ values of 123.5 ± 6.6 and 121.1 ± 1.7 respectively to $\kappa_p$ [electrolyte] values of 116.1 ± 1.5 and 112.6 ± 1.6 respectively by the addition of the electrolyte to form a paste. This means that the abundance of functional groups makes the activated carbon/GNP highly polarizable, such that the polarizability is diminished by the electrolyte addition. This in turn means that there is interaction between the carbon functional groups and the electrolyte. Furthermore, the values are quite close for the paste with the electrolyte (116.1 ± 1.5 and 112.6 ± 1.6 for activated carbon and activated GNP respectively) and for the electrolyte itself (100.9 ± 1.3). This means that the carbon and the electrolyte both contribute substantially to the polarization of the paste.

### 3.1.2. *Interfacial dielectric behavior*

Although the carbon–electrolyte interface contributes to the dielectric behavior of the paste to a minor extent for all the carbons, the contribution varies among the carbons. It is most significant for exfoliated graphite, which gives a high effective interfacial relative dielectric constant (12.0 ± 0.4) and a high carbon–electrolyte specific interfacial capacitance (electrically parallel configuration) of 1.86 ± 0.32 pF/$m^2$. Exfoliated graphite gives an exceptionally high value of the effective relative dielectric constant of the carbon–electrolyte interface, even though its value for the carbon is low (37.9 ± 0.7). As a result of the high value of the interface, the value for the exfoliated graphite paste is quite high (98.9 ± 0.9). The high value for the interface in case of exfoliated graphite is attributed to the residual acidity in the carbon.

The contribution of the carbon–electrolyte interfacial capacitance to the dielectric behavior of the paste is least significant for natural graphite, which gives a low effective interfacial relative dielectric constant of 1.2 ± 0.1. The specific interfacial capacitance is lowest for carbon black (0.037 ± 0.011 pF/$m^2$), compared to a value of 0.27 ± 0.09 pF/$m^2$ for natural graphite. The low specific interfacial capacitance for carbon black relates to the high specific surface area, which is much higher for carbon black (1236 ± 47 $m^2$/g) than natural graphite (420 ± 42 $m^2$/g).

The specific carbon–electrolyte interfacial capacitance is higher for activated GNP than activated carbon, while the effective interfacial relative dielectric constant is higher for activated carbon than activated GNP. This is because the specific surface area is higher for activated carbon (1624 ± 33 $m^2$/g) than activated GNP (26 ± 4 $m^2$/g). The specific interfacial

**Table 2 – Conduction and dielectric properties of carbon pastes (50 Hz) with either water or the electrolyte (15% $H_2SO_4$). The interfacial quantities pertain to the carbon–liquid interface. The contact quantities pertain to the interface with the electrical contact (copper). The conductance is the reciprocal of the resistance.**

| Property | | | | Natural graphite | Carbon black | Exfoliated graphite | Activated GNP | Activated carbon |
|---|---|---|---|---|---|---|---|---|
| Specific surface area of the carbon[c] ($m^2/g$) | | | | 420 ± 42 | 1236 ± 47 | 45 ± 4 | 26 ± 4 | 1624 ± 33 |
| Relative dielectric constant | Carbon | | | 53.3 ± 1.3 | 31.2 ± 1.4 | 37.9 ± 0.7 | 121.1 ± 1.7 | 123.5 ± 6.6 |
| | Liquid | | Water | 79.2 ± 1.9[a] | / | / | / | / |
| | | | Electrolyte | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] |
| | Paste | | Water | 71.7 ± 1.4 | / | / | / | / |
| | | | Electrolyte | 85.5 ± 1.8 | 77.8 ± 3.7 | 98.9 ± 0.9 | 112.6 ± 1.6 | 116.1 ± 1.5 |
| | Carbon–liquid interface[e] | | Water | 2.1 ± 0.6 | / | / | / | / |
| | | | Electrolyte | 1.2 ± 0.1 | 1.8 ± 0.2 | 12.0 ± 0.4 | 4.7 ± 0.9 | 7.3 ± 0.4 |
| Fractional carbon–liquid interface capacitance[f] | | | Water | 0.33 ± 0.04 | / | / | / | / |
| | | | Electrolyte | 0.39 ± 0.08 | 0.36 ± 0.01 | 0.51 ± 0.06 | 0.46 ± 0.01 | 0.50 ± 0.02 |
| Specific capacitance | Carbon–liquid interface ($pF/m^2$) | | Water | 0.16 ± 0.06 | / | / | / | / |
| | | | Electrolyte | 0.27 ± 0.09 | 0.037 ± 0.011 | 1.86 ± 0.32 | 0.98 ± 0.13 | 0.067 ± 0.010 |
| | Contact[d] ($\mu F/m^2$) | Carbon | | 0.119 ± 0.005 | 0.120 ± 0.019 | 0.036 ± 0.003 | 0.138 ± 0.006 | 0.037 ± 0.004 |
| | | Paste | Water | 0.194 ± 0.018 | / | / | / | / |
| | | | Electrolyte | 2.39 ± 0.16 | 3.40 ± 0.14 | 1.44 ± 0.09 | 11.17 ± 1.71 | 8.37 ± 0.56 |
| Volume electrical resistivity (Ω.cm) | Carbon | | | 16.3 ± 0.5 | 12.5 ± 0.3 | 1.9 ± 0.2 | 14.4 ± 0.6 | 3134 ± 39 |
| | Liquid | | Water | 981 ± 18[b] | / | / | / | / |
| | | | Electrolyte | 5.7 ± 1.2[b] | 5.7 ± 1.2[b] | 5.7 ± 1.2[b] | 5.7 ± 1.2[b] | 5.7 ± 1.2[b] |
| | Paste | | Water | 19.3 ± 0.4 | / | / | / | / |
| | | | Electrolyte | 11.0 ± 0.0 | 8.8 ± 0.4 | 3.6 ± 0.2 | 6.7 ± 1.5 | 17.3 ± 1.5 |
| | Carbon–liquid interface[e] | | Water | 35.1 ± 1.6 | / | / | / | / |
| | | | Electrolyte | 17.5 ± 1.8 | 26.5 ± 1.1 | 13.9 ± 1.5 | 8.9 ± 0.9 | 21.4 ± 1.9 |
| Fractional carbon–liquid interface conductance[g] | | | Water | 0.16 ± 0.04 | / | / | / | / |
| | | | Electrolyte | 0.33 ± 0.02 | 0.27 ± 0.02 | 0.21 ± 0.03 | 0.30 ± 0.02 | 0.78 ± 0.02 |
| Areal electrical resistivity | Carbon–liquid interface ($\Omega\ m^2$) | | Water | 1501 ± 28 | / | / | / | / |
| | | | Electrolyte | 308 ± 19 | 192 ± 12 | 15 ± 4 | 63 ± 10 | 1909 ± 28 |
| | Contact[d] ($\Omega.cm^2$) | Carbon | | 1.4 ± 0.1 | 1.1 ± 0.2 | 0.12 ± 0.02 | 0.27 ± 0.05 | 164 ± 13 |
| | | Paste | Water | 0.02 ± 0.00 | / | / | / | / |
| | | | Electrolyte | 0.04 ± 0.01 | 0.04 ± 0.01 | 0.07 ± 0.01 | 0.05 ± 0.00 | 0.19 ± 0.03 |

[a] From Table S1.

[b] From Table S1.

[c] Measured in this work by nitrogen adsorption.

[d] Interface with the electrical contact (copper for conduction testing and Teflon-lined copper for dielectric testing).

[e] Effective volumetric quantity.

[f] Carbon–liquid interface capacitance/(carbon capacitance + carbon–liquid interface capacitance) for the smallest specimen thickness of 0.42 mm.

[g] Carbon–liquid interface conductance/(carbon conductance + carbon–liquid interface conductance) for the smallest specimen thickness of 0.42 mm.

capacitance relates to the surface functional group density, which is thus higher for activated GNP than activated carbon. Among the carbons, carbon black (0.037 ± 0.011 pF/m$^2$) and activated carbon (0.067 ± 0.010 pF/m$^2$) give the lowest values of the specific carbon–electrolyte interfacial capacitance. The low value for carbon black reflects the low density of surface functional groups, whereas the low value for activated carbon reflects the high specific surface area.

For any of the carbons, the specific contact capacitance is much higher than the carbon–electrolyte specific interfacial capacitance. Since the contact and the paste are capacitances in series, this means that the contact is not very influential to the overall dielectric behavior. Nevertheless, the specific contact capacitance varies among the carbons. It is highest for activated GNP (0.138 ± 0.006 μF/m$^2$) and lowest for exfoliated graphite (0.036 ± 0.003 μF/m$^2$). This may be due to the slight residual acidity of the carbon making it more difficult for the $H^+$ ions in the acid electrolyte to penetrate the gap between the carbon and the electrical contact.

As shown for natural graphite, the specific contact capacitance (0.119 ± 0.005 μF/m$^2$) is much increased by the addition of either water (0.194 ± 0.018 μF/m$^2$) or the electrolyte (2.390 ± 0.160 μF/m$^2$) to form a paste (Table 2). This means that the liquid (whether water or the electrolyte) helps improve the specimen–contact interface. The value is higher for the paste with the electrolyte than that with water, indicating that the electrolyte is more effective than water for improving this interface, as expected.

For carbon black and exfoliated graphite, the specific contact capacitance is much increased by the addition of the electrolyte (Table 2). For the activated carbon and the activated GNP, the specific contact capacitance (0.037 ± 0.004 and 0.138 ± 0.006 μF/m$^2$ respectively) is even more greatly increased by the addition of the electrolyte (8.37 ± 0.56 and 11.117 ± 1.710 μF/m$^2$ respectively) to form a paste (Table 2). The positive effect of the electrolyte on the interface is more dramatic for activated carbon or activated GNP than the other three carbons. This probably relates to the interaction between the activated carbon/GNP functional groups and the electrolyte.

Comparison between activated carbon and activated GNP shows that the specific contact capacitance is higher for the latter, whether the electrolyte is present or not. This means that the latter gives a better interface between the electrode and the electrical contact.

Comparison of all five carbons in Table 2 in terms of the specific carbon–contact capacitance shows that natural graphite, carbon black and activated GNP give higher values than activated carbon or exfoliated graphite, but activated carbon/GNP paste (with the electrolyte) gives a higher value of the specific contact capacitance than the other three pastes. This means that the abundance of functional groups on the activated material surface does not help improve the specimen–contact interface unless the electrolyte is present. This probably again relates to the interaction between the activated carbon/GNP functional groups and the electrolyte.

## 3.2. *Electrical conduction behavior*

Table 2 also shows the electrical conduction properties of carbon pastes at 50 Hz with either water or the electrolyte (15% $H_2SO_4$). The quantities shown include the volume resistivities of the carbon solid, liquid and paste, in addition to the contact resistivities of the carbon solid, liquid and paste. The contact resistivity refers to that with the copper (electrical contact) surface.

### 3.2.1. *Volumetric conduction behavior*

The volume electrical resistivity of carbon is higher than that of the electrolyte for activated carbon, but is lower than that of the electrolyte for all the remaining carbons. Among the carbons, exfoliated graphite gives the lowest value of the volume electrical resistivity.

Among the carbons in Table 2, exfoliated graphite gives the lowest value of the carbon volume electrical resistivity $\rho_c$ (1.9 ± 0.2 Ω cm). This reflects the connectivity resulting from the well-known mechanical interlocking among the pieces of exfoliated graphite. For carbon black, the carbon volume electrical resistivity $\rho_c$ (12.5 ± 0.3 Ω cm) is lower than those of natural graphite, activated carbon or activated GNP, probably due to the squishability of carbon black.

As shown for natural graphite, the paste resistivity is higher for water than the electrolyte being the liquid, and the effective interfacial volume resistivity is also higher for water than the electrolyte. Among the various carbons, the paste resistivity (with the electrolyte) is highest for the activated carbon, second highest for the natural graphite, and lowest for the exfoliated graphite. The low value for the exfoliated graphite is consistent with the connectivity in the structure of exfoliated graphite. Among the various carbons in Table 2, the effective carbon–electrolyte interfacial volume resistivity of the paste (with the electrolyte) is highest for carbon black, second highest for activated carbon, and lowest for activated GNP.

The resistivity $\rho_c$ of activated carbon (3134 ± 39 Ω cm) is much higher than that of the electrolyte (5.7 ± 1.2 Ω cm). However, for all the other carbons in Table 2, the resistivity of the carbon is comparable to or lower than that of the electrolyte, so that the electrical conduction is contributed substantially by the carbon part of the paste. In particular, the resistivity $\rho_c$ of exfoliated graphite (1.9 ± 0.2 Ω cm) is substantially lower than that of the electrolyte (5.7 ± 1.2 Ω cm). Thus, the addition of the electrolyte to exfoliated graphite increases the resistivity.

For activated carbon (3134 ± 39 Ω cm), the volume resistivity is dramatically decreased to 17.3 ± 1.5 Ω cm by the addition of the electrolyte to form a paste. This reflects the poor electronic conduction in activated carbon and the strong ionic conduction in the electrolyte, as supported by the low resistivity (5.7 ± 1.2 Ω cm) of the electrolyte. The volume resistivity $\rho_c$ is much higher for activated carbon (3134 ± 39 Ω cm) than natural graphite (16.3 ± 0.5 Ω cm). With the addition of the electrolyte to form a paste, the activated carbon (17.3 ± 1.5 Ω cm) is only slightly more resistive than the natural graphite (11.0 ± 0.0 Ω cm). The volume resistivity $\rho_c$ is much lower for the activated GNP than the activated carbon. This is consistent with the greater crystallinity for activated GNP. The addition of the electrolyte decreases the volume resistivity of both materials, such that activated GNP gives the lower paste resistivity. The electrolyte enhances the conduction more significantly for activated carbon than activated GNP.

As shown for natural graphite, the volume resistivity $\rho_c$ (16.3 ± 0.5 Ω cm) is slightly increased by the addition of water (19.3 ± 0.4 Ω cm), but is decreased by the addition of the electrolyte (11.0 ± 0.0 Ω cm) to form a paste (Table 2). The volume resistivity is much higher for water (981 ± 18 Ω cm) than carbon (16.3 ± 0.5 Ω cm), whereas it is lower for the electrolyte (5.7 ± 1.2 Ω cm) than carbon. This means that ionic conduction in the electrolyte plays a significant role in the paste, whereas that in water is not sufficient to make an impact. Even in the presence of the electrolyte, carbon plays a significant role in the conduction in the paste.

### 3.2.2. *Interfacial conduction behavior*

The carbon–electrolyte interface contributes substantially to the resistance of the paste, as shown by the substantial values of the effective carbon–liquid interface volume resistivity. The carbon–liquid interface areal resistivity is least for exfoliated graphite and highest for activated carbon. As shown for natural graphite, this resistivity is higher for water than the electrolyte as the liquid. This means that the ions in the liquid enable better electrical connectivity between the carbon and the liquid. The carbon–contact interface contributes significantly to the paste–contact interface resistivity. The carbon–contact interfacial areal resistivity is lowest for exfoliated graphite and highest for activated carbon; the paste–contact interfacial areal resistivity is highest for activated GNP and lowest for natural graphite and carbon black.

As shown for natural graphite, the contact electrical resistivity of the interface between the specimen and copper is much reduced by the addition of either water or the electrolyte. This means that the interface is improved by the addition of either water or the electrolyte. Consistent with this observation is the increase in the specific contact capacitance (series configuration) upon addition of either water or the electrolyte.

For all five carbons in Table 2, the contact resistivity is reduced by the addition of the electrolyte, such that the effect is more dramatic for natural graphite, carbon black and activated carbon than exfoliated graphite or activated GNP. The relatively small effect for exfoliated graphite and activated GNP relates to the low values of the contact resistivity of the carbon itself.

The contact resistivity of the carbon is much higher for the activated carbon (164 ± 13 Ω $\text{cm}^2$) than the other four carbons in Table 2. Exfoliated graphite gives the lowest value (0.12 ± 0.02 Ω $\text{cm}^2$). These reflect the high value of the volume electrical resistivity $\rho_c$ for the activated carbon and the low value of this resistivity for exfoliated graphite. In other words, there is a degree of correlation between the volume resistivity and the contact resistivity.

For the paste containing the electrolyte, the contact resistivity is higher for the activated carbon than the other four carbons in Table 2. Nevertheless, the activated carbon benefits from the electrolyte more than the other four carbons in having the interfacial resistivity reduced.

## 3.3. *Overall consideration of the dielectric and conduction behavior*

Among the carbons, exfoliated graphite gives both the lowest value of the carbon–electrolyte interfacial resistivity (15 ± 4 Ω $\text{m}^2$) and the highest value of the carbon–electrolyte specific interfacial capacitance (1.86 ± 0.32 pF/$\text{m}^2$), whereas activated GNP gives both the second lowest value of the carbon–electrolyte interfacial resistivity (63 ± 10 Ω $\text{m}^2$) and the second highest value of the carbon–electrolyte specific interfacial capacitance (0.98 ± 0.3 pF/$\text{m}^2$). On the other hand, activated carbon gives the highest value of the carbon–electrolyte interfacial resistivity (1909 ± 28 Ω $\text{m}^2$) and almost the lowest value of the carbon–electrolyte specific interfacial capacitance (0.067 ± 0.010 pF/$\text{m}^2$). This means that the carbon–electrolyte interface is most influential for exfoliated graphite, the second most influential for activated GNP, and the least influential for activated carbon. This reflects the lowest volume resistivity of exfoliated graphite, the moderate volume resistivity of activated GNP and the highest resistivity of activated carbon, and the fact that electrical conduction within the carbon enables the applied voltage to be delivered from the contact to the carbon surface, which is the location of the carbon–electrolyte interface.

Among the carbons, exfoliated graphite gives the highest value of the specific carbon–electrolyte interfacial capacitance (obtained by the parallel configuration), but the lowest value of the specific carbon–contact capacitance (obtained by the series configuration). This means that, compared to the other carbons, exfoliated graphite gives a carbon–electrolyte interface that is particularly influential to the dielectric behavior of the paste, and a carbon–contact interface that is particularly influential to the dielectric behavior of the paste–contact interface. On the other hand, exfoliated graphite gives the lowest value of the carbon–electrolyte interfacial resistivity and the lowest value of the contact resistivity (carbon solid), indicating that exfoliated graphite excels in providing electrical connectivity across interfaces.

Table 2 shows the fractional carbon–liquid interface capacitance (i.e., carbon–liquid interface capacitance divided by the sum of the carbon capacitance and the carbon–liquid interface capacitance). This value depends on the specimen thickness. The values shown in Table 2 are for the smallest specimen thickness of 0.42 mm. As shown for natural graphite, the value is smaller for water than the electrolyte, as expected. Among the carbons, exfoliated graphite and activated carbon give the highest values, due to the high values of the carbon–electrolyte interface effective relative dielectric constant; carbon black and natural graphite give the lowest values, due to the low values of this effective relative dielectric constant.

The conductance is the reciprocal of the resistance. Table 2 also shows the fractional carbon–liquid interface conductance (i.e., carbon–liquid interface conductance divided by the sum of the carbon conductance and the carbon–liquid interface conductance). This value depends on the thickness. The values shown in Table 2 are for the smallest thickness of 0.42 mm. As shown for natural graphite, the value is smaller for water than the electrolyte. This suggests that the higher conductivity of the electrolyte helps enhance the interfacial conductance. Among the carbons, activated carbon gives the highest value, because of its highest value of the carbon volume resistivity (i.e., its lowest value of the carbon volume conductivity); exfoliated graphite gives the lowest value, because of its low value of the carbon volume resistivity.

**Table 3 – Effect of specimen thickness on the fractional carbon–electrolyte interface capacitance/conductance. The fraction is relative to the sum of the contributions of carbon and the interface. The conductance is the reciprocal of the resistance.**

| Specimen thickness (mm) | Natural graphite | Carbon black | Exfoliated graphite | Activated GNP | Activated carbon |
|---|---|---|---|---|---|
| | Fractional carbon–electrolyte interface capacitance[c] | | | | |
| 3.30 | 0.52 ± 0.07 | 0.59 ± 0.01 | 0.69 ± 0.08 | 0.67 ± 0.04 | 0.70 ± 0.04 |
| 1.63 | 0.49 ± 0.07 | 0.50 ± 0.04 | 0.64 ± 0.07 | 0.60 ± 0.03 | 0.63 ± 0.03 |
| 0.42 | 0.37 ± 0.08 | 0.36 ± 0.04 | 0.51 ± 0.08 | 0.46 ± 0.01 | 0.50 ± 0.02 |
| 0.20 | 0.27[a] | 0.28[a] | 0.41[a] | 0.36[a] | 0.38[a] |
| 0.10 | 0.21[a] | 0.24[a] | 0.38[a] | 0.31[a] | 0.35[a] |
| | Fractional carbon–electrolyte interface conductance[d] | | | | |
| 3.30 | 0.56 ± 0.02 | 0.41 ± 0.01 | 0.45 ± 0.01 | 0.49 ± 0.01 | 0.83 ± 0.01 |
| 1.63 | 0.49 ± 0.01 | 0.33 ± 0.03 | 0.36 ± 0.03 | 0.40 ± 0.02 | 0.81 ± 0.01 |
| 0.42 | 0.33 ± 0.02 | 0.27 ± 0.02 | 0.21 ± 0.03 | 0.30 ± 0.02 | 0.78 ± 0.02 |
| 0.20 | 0.29[b] | 0.11[b] | 0.14[b] | 0.22[b] | 0.76[b] |
| 0.10 | 0.17[b] | 0.06[b] | 0.10[b] | 0.14[b] | 0.74[b] |

[a] Calculated based on the specific carbon–electrolyte interface capacitance in Table 2.

[b] Calculated based on the carbon–electrolyte interface resistivity in Table 2.

[c] Carbon–electrolyte interface capacitance/(carbon capacitance + carbon–electrolyte interface capacitance).

[d] Carbon–electrolyte interface conductance/(carbon conductance + carbon–electrolyte interface conductance).

**Table 4 – Effect of specimen (paste) thickness on the fractional capacitance/conductance due to the carbon, the electrolyte and the carbon–electrolyte interface for the case of the carbon being activated GNP. The conductance is the reciprocal of the resistance.**

| Specimen thickness (mm) | Fraction due to the carbon | | Fraction due to the electrolyte | | Fraction due to the carbon–electrolyte interface | |
|---|---|---|---|---|---|---|
| | Capacitance | Conductance | Capacitance | Conductance | Capacitance | Conductance |
| 0.42 | 0.14 | 0.31 | 0.55 | 0.62 | 0.31 | 0.07 |
| 1.63 | 0.12 | 0.33 | 0.43 | 0.31 | 0.45 | 0.36 |
| 3.30 | 0.11 | 0.14 | 0.34 | 0.18 | 0.55 | 0.68 |

**Table 5 – Dielectric and conduction properties of carbon electrodes (50 Hz), with comparison of exfoliated graphite, activated GNP and a hybrid consisting of exfoliated graphite and activated GNP in a 1:3 mass ratio, with each in the presence of the electrolyte (15% $H_2SO_4$).**

| Property | | | Exfoliated graphite | Activated GNP | Hybrid | |
|---|---|---|---|---|---|---|
| | | | | | Measured | Calculated[c] |
| Relative dielectric constant | Carbon | | 37.9 ± 0.7 | 121 ± 1 | 94.8 ± 0.9 | 100 |
| | Electrolyte | | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] | 100.9 ± 1.3[a] |
| | Paste with electrolyte | | 98.9 ± 0.9 | 113 ± 1 | 106.5 ± 1.9 | 109 |
| | Carbon–electrolyte interface[e] | | 12.0 ± 0.4 | 4.7 ± 0.9 | 7.7 ± 0.6 | 6.5 |
| Specific capacitance | Carbon–electrolyte interface (pF/m$^2$) | | 1.86 ± 0.32 | 0.98 ± 0. 13 | 1.27 ± 0.22 | 1.20 |
| | Contact[d] (nF/m$^2$) | Carbon | 36 ± 3 | 138 ± 6 | 92 ± 7 | 113 |
| | | Paste | 1440 ± 90 | 11170 ± 1710 | 8450 ± 250 | 8738 |
| Volume electrical resistivity (Ω.cm) | Carbon | | 1.9 ± 0.2 | 14.4 ± 0.6 | 5.3 ± 0.4 | 5.4 |
| | Electrolyte | | 5.7 ± 1.2[b] | 5.7 ± 1.2[b] | 5.7 ± 1.2[b] | 5.74[b] |
| | Paste with electrolyte | | 3.6 ± 0.2 | 6.7 ± 1.5 | 5.4 ± 0.2 | 5.5 |
| | Carbon–liquid interface[e] | | 13.9 ± 1.5 | 8.9 ± 0.9 | 9.6 ± 1.1 | 9.8 |
| Areal electrical resistivity | Carbon–electrolyte interface (Ω.m$^2$) | | 38 ± 4 | 72 ± 10 | 49 ± 8 | 58 |
| | Contact[d] resistivity (Ω.cm$^2$) | Carbon | 0.12 ± 0.02 | 0.27 ± 0.05 | 0.18 ± 0.04 | 0.21 |
| | | Paste with electrolyte | 0.07 ± 0.01 | 0.05 ± 0.00 | 0.04 ± 0.01 | 0.05 |

[a] From Table S3.

[b] From Table S1.

[c] Based on the Rule of Mixtures.

[d] Interface with the electrical contact (copper for conduction testing and Teflon-lined copper for dielectric testing).

[e] Effective volumetric quantity.

Table 3 shows that a decrease in thickness decreases the fractional carbon–electrolyte interface capacitance (due to an increase in the volumetric capacitance) and decreases the fractional carbon–electrolyte interface conductance (due to a decrease in the volumetric resistance, i.e., an increase in the volumetric conductance). These fractional quantities are relative to the sum of the contributions from the interface and the carbon. A smaller thickness causes this interface to be less influential to the capacitance but more influential to the resistance.

Table 4 shows the fractional contributions of the carbon, electrolyte and the carbon–electrolyte interface to the measured capacitance and the measured conductance (the reciprocal of the measured resistance) of the specimen (paste) for three specimen thicknesses, with the carbon being activated GNP. For any of the three thicknesses, the fractional capacitance due to the interface and that due to the electrolyte dominate over the fraction due to the carbon. This points to the importance of the interfacial contribution to the capacitance. The fractional capacitance due to the interface increases with increasing specimen thickness, due to the decreasing total capacitance and the increasing interfacial area as the thickness increases. In contrast, the fractional capacitance due to the electrolyte and that due to the carbon decrease with increasing thickness, because of the increase in the interface contribution. On the other hand, the interface contributes little to the conductance at the smallest thickness, whereas it contributes greatly to the conductance at the largest thickness. The increase of the fractional contribution of the interface with increasing thickness is attributed to the increase in interface area with the specimen thickness. The trends in Table 4 also apply to the other types of carbon studied.

### 3.4. *Hybrid carbon*

Among the carbons in Table 2, exfoliated graphite and activated GNP give the best overall performance. From the viewpoint of the volumetric behavior, as indicated by the relative dielectric constant and the volume resistivity, exfoliated graphite and activated GNP excel in different ways, with exfoliated graphite being strong in the conduction behavior and activated GNP being strong in the dielectric behavior. Therefore, exfoliated graphite and activated GNP are mixed to form a hybrid material. The mixing is conducted at the mass ratio of 3:1 (volume ratio essentially 3:1). The hybrid gives resistivity and relative dielectric constant that are intermediate between those for activated GNP and exfoliated graphite, such that both values are close to the values calculated by using the Rule of Mixtures (Table 5). This mixture route is simple and effective for providing a hybrid material that exhibits both relatively low resistivity and relatively high dielectric constant. Furthermore, due to the exfoliated graphite, which forms a framework for the activated GNP particles to rest on, the mixture is coherent and handleable, even in the dry state prior to compression (Fig. 5). In contrast, the activated GNP in the absence of exfoliated graphite does not exhibit

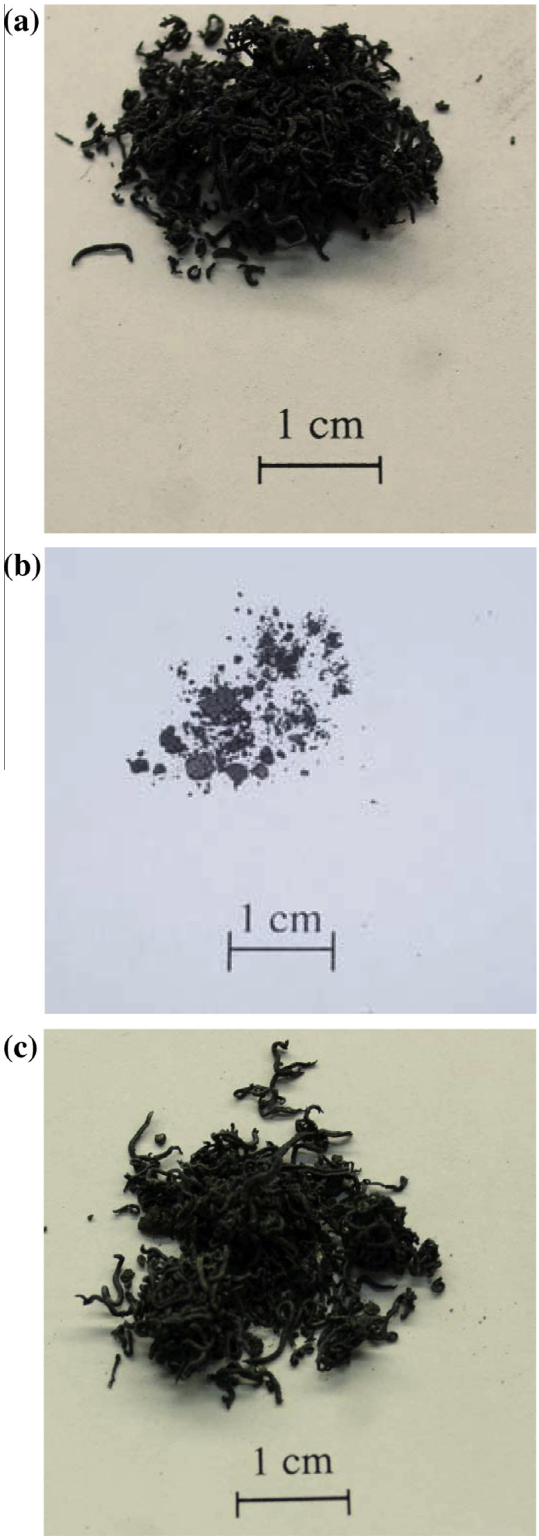

**Fig. 5 – Optical photographs of carbon particles in dry powder form prior to compression. (a) Exfoliated graphite. (b) Activated GNP. (c) Hybrid of GNP and exfoliated graphite (3:1 ratio). (A colour version of this figure can be viewed online.)**

**Table 6 – Effect of frequency on the relative dielectric constants of the carbon solid and the electrolyte.**

| Frequency (Hz) | Carbon | | | Electrolyte |
|---|---|---|---|---|
| | Natural graphite | Activated carbon | Activated GNP | |
| 50 | 53.3 ± 1.3 | 123.5 ± 6.6 | 121.1 ± 1.7 | 100.9 ± 1.3 |
| 100 | 48.9 ± 3.8 | 111.2 ± 0.8 | 106.0 ± 2.2 | 95.0 ± 1.4 |
| 500 | 45.2 ± 1.1 | 103.2 ± 3.5 | 102.3 ± 2.6 | 92.8 ± 2.0 |
| 1000 | 43.5 ± 3.1 | 99.8 ± 2.7 | 99.5 ± 1.8 | 89.9 ± 1.6 |

**Table 7 – Effect of frequency on the specific contact capacitance (μF/m$^2$).**

| Frequency (Hz) | Natural graphite | | | Activated carbon | | Activated GNP | |
|---|---|---|---|---|---|---|---|
| | Carbon | Paste with electrolyte | Paste with water | Carbon | Paste with electrolyte | Carbon | Paste with electrolyte |
| 50 | 0.119 ± 0.005 | 2.39 ± 0.16 | 0.194 ± 0.018 | 0.037 ± 0.004 | 8.37 ± 0.56 | 0.138 ± 0.006 | 11.17 ± 1.71 |
| 100 | 0.150 ± 0.004 | 2.99 ± 0.08 | 0.173 ± 0.004 | 0.047 ± 0.001 | 8.07 ± 0.10 | 0.189 ± 0.004 | 8.16 ± 0.17 |
| 500 | 0.137 ± 0.009 | 1.83 ± 0. 06 | 0.142 ± 0.005 | 0.044 ± 0.002 | 6.48 ± 0.07 | 0.153 ± 0.001 | 7.40 ± 0.19 |
| 1000 | 0.099 ± 0.001 | 1.72 ± 0.05 | 0.115 ± 0.006 | 0.036 ± 0.004 | 5.84 ± 0.14 | 0.136 ± 0. 004 | 6.48 ± 0.10 |

**Table 8 – Effect of the decoupling on the interfacial properties obtained.**

| Property at 50 Hz | | Exfoliated graphite | Activated GNP |
|---|---|---|---|
| Carbon–electrolyte specific interfacial capacitance (pF/m$^2$) | Full decoupling | 1.86 | 0.98 |
| | Partial decoupling[a] | 102 | 161 |
| | No decoupling[b] | 90 | 157 |
| Carbon–electrolyte interfacial electrical resistivity (Ω.m$^2$) | Full decoupling | 43 | 152 |
| | Partial decoupling[a] | 0.63 | 0.51 |
| | No decoupling[b] | 0.62 | 0.53 |

[a] With the contact contribution excluded by decoupling and with the carbon contribution neglected.

[b] With both the contact contribution and the carbon contribution neglected.

such coherence (Fig. 5(b)). The coherence means that a binder is not necessary, thereby simplifying the electrode fabrication and installation and avoiding the loss in electrical behavior due to the presence of the binder, which is typically a polymeric material that is poor in the conduction behavior. The properties of the hybrid agree well with the calculated values based on the Rule of Mixtures (Table 5).

### 3.5. *Effect of frequency*

Tables 6 and 7 show that the effect of frequency from 50 to 1000 Hz on the dielectric behavior is not large. All values of the relative dielectric constants of the carbon solid and the electrolyte decrease with increasing frequency, as expected. The highest values above 100 for the relative dielectric constant obtained in this work at 50 Hz are lower than the value of 180 previously reported for an exfoliated graphite epoxy-matrix composite at 50 Hz [13].

Table 7 shows the effect of frequency on the specific contact capacitance. For all three types of carbon, whether the paste is based on water or the electrolyte, this capacitance decreases monotonically with increasing frequency, as expected. This means that the contact capacitance becomes more influential as the frequency increases.

### 3.6. *Serious discrepancy if the decoupling is not performed*

This work involves the decoupling of the volumetric and interfacial quantities and the distinction between the quantities associated with the carbon–electrolyte interface and with the contact interface (Table 2). This is referred to as “full decoupling”. If the full decoupling is not performed and the carbon volumetric contributions are neglected, serious discrepancy results for the carbon–electrolyte interfacial quantities. The absence of full decoupling can involve either partial decoupling or no decoupling at all. In partial decoupling, the contact contributions are excluded by decoupling, but the carbon volumetric contributions are neglected while the carbon volumetric and interfacial quantities are lumped together. In case of no decoupling at all, the contact interfacial quantities and the carbon volumetric contributions are all neglected, while the carbon volumetric and interfacial quantities and the contact interfacial quantities are all lumped.

Table 8 shows a comparison of the interfacial quantities obtained with full decoupling, partial decoupling and no decoupling. With partial decoupling or no decoupling, the specific interfacial capacitance of the carbon–electrolyte interface is too high by 2 orders of magnitude and the carbon–electrolyte interfacial resistivity is too low by 2 orders of magnitude. Thus, partial decoupling is almost as bad as no decoupling. The discrepancy resulting from inadequate decoupling is partly responsible for the high values of the specific electrode–electrolyte interfacial capacitance [18–23] and the low values of the electrode–electrolyte interfacial resistivity [24,25] that have been previously reported by various workers based on testing using electrochemical cells, which are not conducive to decoupling.

## 4. Conclusions

This work provides characterization of the electrical and dielectric properties of electrolyte-filled carbon pastes for electrochemical electrodes. In addition, the contributions of the carbon, the electrolyte (15% $H_2SO_4$), the carbon–electrolyte interface (modeled as resistance/capacitance in parallel with those of the carbon and the electrolyte) and the carbon–contact interface (modeled as resistance/capacitance in series with that of the paste) to these properties have been decoupled and determined. In the parallel configuration, a high capacitance is influential; in the series configuration, a low capacitance is influential. The contact is copper in case of electrical conduction study and Teflon-coated copper is case of dielectric study. The decoupled characterization enabled by the new methodology of this work is in contrast to the coupled characterization in prior work involving electrochemical impedance spectroscopy [6–12] or electrochemical cell testing [18–25]. The prior work probes the overall electrochemical cell rather than the electrode per se. Moreover, in this work, comparison is provided among natural graphite, carbon black, exfoliated graphite, activated carbon and activated GNP. Comparison is also made between water and the electrolyte in case of natural graphite.

Without the decoupling and with the carbon contribution neglected, the carbon–electrolyte specific interfacial capacitance would be over-estimated by orders of magnitude and the carbon–electrolyte interfacial resistivity would be underestimated by orders of magnitude. A smaller paste thickness causes the carbon–electrolyte interface to contribute less to the capacitance but more to the resistance (i.e., less to the conductance).

Exfoliated graphite is attractive for the low values of the carbon volume electrical resistivity (1.9 ± 0.2 Ω cm), paste volume electrical resistivity (3.6 ± 0.2 Ω cm), carbon–electrolyte interface resistivity (15 ± 4 Ω $m^2$) and carbon–contact interface resistivity (0.12 ± 0.02 Ω $m^2$). Thus, exfoliated graphite excels in providing good electrical conduction within the carbon, across the interface between the carbon and the electrolyte, and across the interface between the carbon and the contact. This reflects the electrical connectivity of exfoliated graphite. Exfoliated graphite contributes to the capacitance of the paste–electrolyte interface (with the high specific carbon–electrolyte interface capacitance of 1.86 ± 0.32 pF/$m^2$ in the parallel configuration, and the high effective carbon–electrolyte interface relative dielectric constant of 12.0 ± 0.4) and to the capacitance of the paste–contact interface (with the low specific carbon–contact interface capacitance of 0.036 ± 0.003 μF/$m^2$ in the series configuration). On the other hand, exfoliated graphite gives low values of the carbon relative dielectric constant (37.9 ± 0.7), and the specific paste–contact interface capacitance in the series configuration (1.440 ± 0.090 μF/$m^2$). Therefore, exfoliated graphite is highly suitable for battery electrodes.

Activated GNP gives high values of the carbon relative dielectric constant (121.1 ± 1.7), the paste relative dielectric constant (112.6 ± 1.6), the specific carbon–contact interface capacitance (the high value of 0.138 ± 0.006 μF/$m^2$ in the series configuration) and the specific paste–contact interface capacitance (the high value of 11.170 ± 1.710 μF/$m^2$ in the series configuration). However, compared to exfoliated graphite, activated GNP is disadvantageous in the higher values of the carbon volume electrical resistivity (14.4 ± 0.6 Ω cm), the paste volume electrical resistivity (6.7 ± 1.5 Ω cm), and the carbon–electrolyte interface resistivity (63 ± 10 Ω $m^2$). Therefore, activated GNP is highly suitable for supercapacitor electrodes.

Activated carbon gives high values of the carbon relative dielectric constant (123.5 ± 6.6), the paste relative dielectric constant (116.1 ± 1.5), and the specific paste–contact interface capacitance (the high value of 8.370 ± 0.560 μF/$m^2$ in the series configuration). However, it is highly disadvantageous in the high values of the carbon volume electrical resistivity (3134 ± 39 Ω cm), the paste volume electrical resistivity (17.3 ± 1.5 Ω cm), the carbon–electrolyte interface resistivity (1909 ± 28 Ω $m^2$), the carbon–contact interface resistivity (164 ± 13 Ω $m^2$), and the paste–contact interface resistivity (0.19 ± 0.03 Ω $m^2$). Therefore, activated carbon is suitable for supercapacitor electrodes, though it is less suitable than activated GNP.

Carbon black is advantageous in the relatively low value of the carbon volume electrical resistivity (12.5 ± 0.3 Ω cm). It is disadvantageous in the high value of the carbon–electrolyte interface effective volume resistivity (26.5 ± 1.1 Ω cm). It gives a low value of the carbon relative dielectric constant (31.2 ± 1.4), and a low value of the paste relative dielectric constant (77.8 ± 3.7). It contributes relatively little to the capacitance of the paste–electrolyte interface (with the low specific carbon–electrolyte interface capacitance of 0.037 ± 0.011 pF/$m^2$ in the parallel configuration, and the low effective carbon–electrolyte interface relative dielectric constant of 1.8 ± 0.2) or to the capacitance of the paste–contact interface (with the high specific carbon–contact interface capacitance of 0.120 ± 0.019 μF/$m^2$ in the series configuration). Therefore, carbon black is moderately suitable for battery electrodes.

Natural graphite is disadvantageous in a relatively high carbon volume resistivity (16.3 ± 0.5 Ω cm), a relatively high paste volume electrical resistivity (11.0 ± 0.0 Ω cm), a relatively high carbon–electrolyte interface resistivity (308 ± 19 Ω $m^2$) and a relatively high carbon–contact interface resistivity (1.4 ± 0.1 Ω $m^2$). It gives a relatively low carbon relative dielectric constant (53.3 ± 1.3), and a relatively low paste relative dielectric constant (85.5 ± 1.8 with the electrolyte). It contributes little to the paste–electrolyte interface capacitance, with the relatively low specific interface capacitance of 0.27 ± 0.09 pF/$m^2$ in the parallel configuration and the low effective interface relative dielectric constant of 1.2 ± 0.1. However, it contributes substantially to the paste–contact interface capacitance, with the relatively low specific paste–contact interface capacitance of 2.39 ± 0.16 μF/$m^2$ in the series configuration. Therefore, compared to the other carbons, natural graphite is not suitable for battery or supercapacitor electrodes.

With exfoliated graphite being strong in the electrical conduction behavior and activated GNP being strong in the dielectric (polarization) behavior (such that the conduction behavior is good), a hybrid of exfoliated graphite and activated GNP in a 1:3 mass ratio (equal to 1:3 volume ratio) gives an electrode material that is suitable for both batteries and supercapacitors, although it is inferior to exfoliated graphite for battery electrodes and is inferior to activated GNP for supercapacitor electrodes. The exfoliated graphite also provides good handleability, even in the presence of activated GNP. The measured property values of the hybrid are in agreement with the calculated values based on the Rule of Mixtures.

The relative dielectric constant of the carbon is much lower than that of the electrolyte for natural graphite, exfoliated graphite and carbon black pastes, but is higher than that of the electrolyte for activated carbon and activated GNP pastes. The resistivity of the carbon is higher than that of the electrolyte for natural graphite, activated carbon and activated GNP pastes, but is lower than that of the electrolyte for exfoliated graphite and carbon black pastes. This means that carbon plays a significant role in the electrical conduction behavior of the paste.

The specific contact capacitance is much increased and the contact resistivity is much decreased by the addition of the electrolyte (15% $H_2SO_4$) to any of the carbons. The electrolyte (15% $H_2SO_4$) exhibits a low volume electrical resistivity and a higher relative dielectric constant than water. The electrolyte-based paste exhibits a low volume electrical resistivity and a higher relative dielectric constant than the corresponding water-based paste. The carbon–liquid interface exhibits a higher specific capacitance (in the parallel configuration) and a lower interface resistivity in case of the liquid being the electrolyte than the case of the liquid being water. The paste–contact interface exhibits a higher specific capacitance (in the series configuration) in case of the liquid being the electrolyte than the case of the liquid being water. This means that the electrolyte is more effective than water in providing an intimate carbon–liquid interface and an intimate paste–contact interface.

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## Appendix A. Supplementary data

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