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Electric permittivity of reduced graphite oxide

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ABSTRACT

The through-thickness electric permittivity (real part) of the solid part (53 vol%) of reduced graphite oxide (RGO) paper (100–300 μm thick, prepared by hydrazine reduction of modified-Hummers-method graphite oxide, GO) is 1130 (50 Hz), which is higher than that of the similarly tested parent GO (915, 50 Hz) and other carbons (31–124, 50 Hz). The high permittivity of RGO is attributed to the defects. Due to the conductivity of RGO, an insulating film between the specimen and an electrical contact is necessary during permittivity measurement using an RLC meter. Without the film, the measured capacitance is too high by 10–11 orders of magnitude, thus resulting in incorrectly high values of the permittivity. The relative permittivity 4×10^9 (20 Hz) reported by Sarkar et al. (2016) for similarly prepared RGO is therefore incorrect. The solid part of the RGO paper exhibits at 50 Hz in-plane conductivity 31 S/m, through-thickness conductivity 1.17 S/m, through-thickness relative permittivity (imaginary part) -4.2×10^8, through-thickness dielectric loss angle 90.0°, specific capacitance of the interface with an electrical contact 0.31 $\mu F/m^2$, and areal resistivity of this interface 0.18 $\Omega\ cm^2$. The resistivity and specific capacitance of the RGO-contact interface are lower for RGO than GO.

1. Introduction

The real part of the relative electric permittivity (or relative dielectric constant) is a fundamental material property that describes the dielectric behavior of a material. This behavior relates to the polarizability. The permittivity is one of the key parameters that govern the electromagnetic and optical behavior of materials. Materials of high permittivity are needed for capacitors, ferroelectric memory, piezoelectric sensors and actuators, pyroelectric motion detectors and electromagnetic interference (EMI) shields.

Materials of high permittivity are mainly ceramics that are essentially non-conductive electrically. For example, $CaCu_3Ti_4O_{12}$ exhibits relative permittivity up to 3×10^5 at 1 kHz [1]. Carbon materials typically exhibit relatively low values of the relative permittivity (Table 1). Among the carbons listed, graphite oxide (GO) exhibits the highest relative permittivity of 915 at 50 Hz [2], with the polarizability stemming primarily from the functional groups. The relative permittivity of graphene is low, e.g., ~3 and ~1.8 in the through-thickness and in-plane directions respectively [3].

It has been recently reported that reduced graphite oxide (RGO) obtained by the reduction of GO using hydrazine exhibits relative permittivity 4×10^9 at 20 Hz [4]. This huge value (marking a phenomenon referred to as colossal dielectricity) is attributed to interfaces and defects [4]. This huge value calls for further research. Moreover, the prior work [4] reports the dielectric loss angle (δ) only for the frequency range (above 300 Hz) in which the relative permittivity approaches zero. In other words, the value of δ at the frequencies where the reported permittivity is high was not reported. Therefore, more complete characterization of the dielectric behavior of RGO is needed.

The dielectric behavior of polymer-matrix composites containing RGO as a filler is the subject of other prior work [5,6], which reports for the composites the permittivity values of 2080 at 1 kHz (12.5 vol% RGO) [5] and 350 at 1 kHz (3 wt% RGO) [6]. For epoxy containing 2 wt% exfoliated graphite, the relative permittivity has been reported to be 10^4 at 100 Hz [7]. For carbon fabric, the relative permittivity has been reported to be 4×10^6 at 10 Hz [8]. The values of 2080 [5], 10^4 [7] and 4×10^6 [8] are questionable also, as explained below.

The technique of permittivity measurement is critical to the reliability of the measured values. The technique commonly involves a precision RLC meter (for measuring the resistance R,

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Table 1
Relative permittivity of carbon materials at 50 Hz, all tested with the same method.

Material	Relative permittivity	Source
RGO	1130	This work
GO	915	[2]
Exfoliated graphite, not washed	360	[10]
Exfoliated graphite, washed with water	38	[9]
Natural graphite	53	[9]
Carbon black	31	[9]
Activated carbon	124	[9]
Activated graphite nanoplatelet	121	[9]

inductance L, and capacitance C), as is the case in the above-mentioned questionable prior work [4,5,7,8]. The meter works reliably in measuring the capacitance of electrically non-conductive materials. For conductive materials, the capacitance measurement provided by the meter can be severely inaccurate, e.g., higher than the true value by orders of magnitude, because the meter is not meant for measuring the capacitance of electrically conductive materials.

For measuring the capacitance of an electrically conductive material, a modified method has been developed [9,10]. In this method, the reliable measurement of the relative permittivity (real part) of a conductive material is made possible by (i) the presence of an electrically insulating polymer film at the interface between the specimen and each of the two electrical contacts, and (ii) the performance of the measurement at three (or more) specimen thicknesses and analyzing the data in terms of the slope of the plot of the reciprocal of the capacitance vs. the thickness. Step (ii) enables the decoupling of the contribution of the specimen-contact interface (with the contact including the film) to the measured capacitance from the contribution of the volume of the specimen, as the slope is inversely related to the relative permittivity (a volumetric property), while the intercept of the curve with the vertical axis at zero thickness relates to the interfacial capacitance (Fig. 1(a)). On the other hand, the film is obviously absent for the measurement of the conductivity. Similar conductivity measurement conducted at three (or more) specimen thicknesses enables the decoupling of the contribution of the specimen-contact interface to the measured resistance from the contribution of the volume of the specimen (Fig. 1(b)).

For the testing of RGO, as reported in this work, the removal of the insulating film in the capacitance measurement using an RLC meter increases the measured capacitance by orders of magnitude. Prior work on RGO [4], RGO composite [5], exfoliated graphite composite [7] and carbon fabric [8] uses the conventional method, which does not involve the insulating film.

This paper is aimed at (i) clarifying the previously reported huge value of the relative permittivity of RGO, (ii) establishing the technique of permittivity measurement of a conductive material using an RLC meter, (iii) providing a thorough characterization of the dielectric behavior of RGO, and (iv) providing a comparison of the dielectric behavior of RGO and the parent GO.

2. Experimental methods

2.1. Materials

The GO paper is prepared using the modified Hummers method [11], as in prior work on GO by these authors [2]. The RGO paper is obtained by the reduction of the GO paper. The reduction is performed at 105 °C for 6 h. The GO paper is supported by alumina such that it is above the top surface of the liquid, which is 2.0 g hydrazine hydrate in 100 mL de-ionized water. After reduction, the

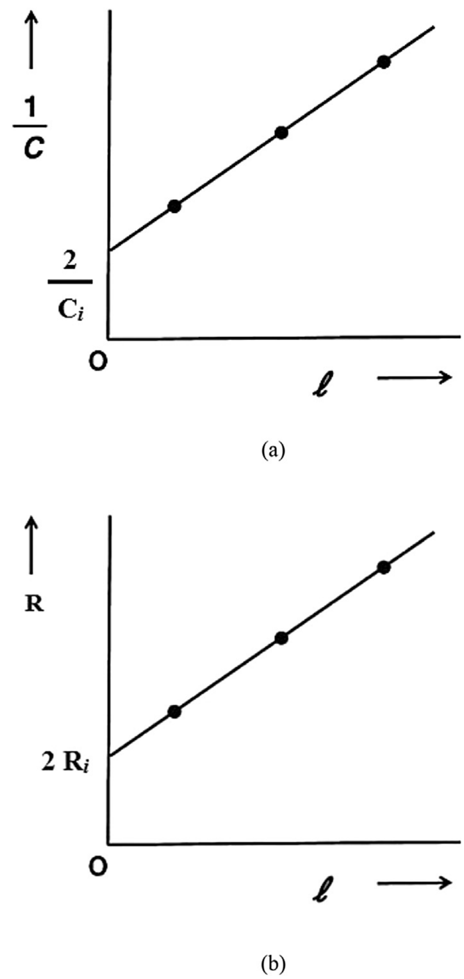

Fig. 1. (a) Schematic plot of $1/C$ vs. l, for the determination of C_i and κ based on Eq. (1). The slope equals $1/(\varepsilon_0 \kappa A)$, where κ is the relative permittivity of the specimen, ε_o is the permittivity of free space, l is the thickness of the specimen and A is the area of the specimen. The intercept on the vertical axis at $l = 0$ equals $2/C_i$. (b) Schematic plot of R vs. l for the determination of R_v and R_i based on Eq. (3). The slope equals the specimen resistance R_v per unit thickness. The intercept on the vertical axis equals two times R_i.

RGO paper is washed with de-ionized water and the excess water is removed by sandwiching the RGO paper with aluminum foils and squeezing out the water by manual compression of the sandwich. The process of washing and squeezing is repeated several times until the pH of the water reaches 7. The RGO paper is dried at 60 °C for 3 h immediately before testing. The volume fraction of solid in the RGO paper is (52.68 ± 0.25)%, as calculated based on the true density of RGO (2.200 g/cm^3 [12]).

The RGO that was reported in prior work [4] to exhibit a high permittivity of 4×10^9 at 20 Hz was prepared using essentially the same method as this work. As in this work, the modified Hummers method was used to prepare the GO, which was subsequently reduced to RGO by using hydrazine hydrate [4].

2.2. Testing methods

Unless noted otherwise, the reported results are for the through-thickness direction. For both through-thickness and in-plane electrical measurements, specimens at three thicknesses are tested. For the through-thickness testing, the specimen is a square of dimension 25.00 ± 0.10 mm at each edge of the square, as obtained by cutting, and the three thicknesses are