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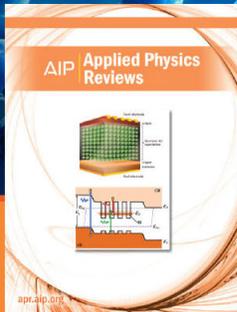
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On the sign of the relaxation activation energy for interfacial polarization in reduced graphene oxide–based nano-composites

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The dielectric relaxation mechanism associated with the interfacial polarization in polyaniline/reduced graphene oxide (PANI/RGO) nano-composites is found to shift towards lower frequencies on increasing temperature. Accordingly, the effective activation energy value is negative. Basic concepts of the Sillars dielectric theory of a heterogeneous medium are revisited for a material consisting of conducting platelets dispersed in a semi-insulating matrix in order to explain the negative sign of the relaxation energy. A plausible explanation to this observation involves a thermally activated de-trapping mechanism through the effective potential barrier at the interfaces between RGO and PANI. This results in an enhancement of the density of charge carriers which contributes to dc conductivity at the expense of the density of charge carriers that relax within RGO inclusions. Subsequently, the intensity of the dielectric peak is suppressed on heating which results in a systematic modification of the shapes of the dc conductivity vs temperature curves. *Published by AIP Publishing.*

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Over the last decade, research on graphene based nano-composites has opened up challenging frontiers in material science due to their numerous potential applications in areas such as reinforced mechanical systems, thermal management equipment, or electronic devices.^{1–3} In recent development of energy conversion and energy storage devices, the nano-composites have attracted tremendous interests owing to their outstanding performance,^{4–6} which relies on the combination of physical properties of the filler and host materials. The characteristics of these hybrid materials are controlled through crucial parameters such as the interactions between the filler and its host, the morphology of their interfacial spacing and/or the quality of the filler dispersion and so on. Of interest to point out are the numerous published articles on the synergistic contribution of the conducting inclusions and its matrix in enhancing thermal, electrical, and mechanical properties of the nano-composites. For example, filler loadings in the nano-composites play an important role in effecting 2D or 3D percolation behavior of electrical and/or thermal behaviors of the materials.^{7,8} Other reports highlight the influence of interface morphology in the control of charge trapping or phonon scattering mechanisms in the hybrid systems.^{8,9}

In the present paper, we report the effect of temperature on interfacial polarization taking place at the (reduced graphene oxide/polyaniline) RGO/PANI interfaces, which, unexpectedly, is characterized by *negative* activation values. While this behavior departs from the conventional picture of molecular dynamics in polymers and polymer nano-composites, it can be understood within the effective dielectric theory of heterogeneous media, modified for semi-insulating matrices.

PANI/RGO nano-composites have been synthesized through in-situ polymerization of aniline monomers in the presence of a graphene suspension. Experimental details on their preparation are reported elsewhere.⁸ Pellets of the as-prepared nano-composites are prepared from ground powder by cold pressing (450 MPa) which provided test samples with a diameter of 12.8 mm and a thickness of $290 \pm 20 \mu\text{m}$. To investigate the dielectric properties, the pellets were placed between aluminium electrodes. Dielectric permittivity measurements were carried out at temperatures ranging from 306 K to 396 K on a Modulab-MTS test system (Solartron Analytical-Amtek) in the frequency (f) range of 1 Hz–1 MHz with an amplitude of the oscillating voltage set at 100 mV. The typical dielectric spectra are fitted with the Grafty software.¹⁰

RGO nano-particles in semi-insulating PANI provide a percolation network that contributes to dc electrical conductivity, while the electrical heterogeneity of the composite, yields capacitance phenomena resulting in the appearance of a dielectric relaxation peak in the frequency range of 1 kHz to 10 kHz. The latter is attributed to electric charge trappings at interfaces separating the conducting RGO flakes from the less conducting PANI matrix.⁹ Room temperature complex permittivity spectra for PANI and PANI/RGO nano-composites of various concentrations were interpreted recently⁹ within the Sillars model for low concentration of conducting oblate spheroid inclusions (which resemble the platelet-like shape of the RGO inclusions in PANI/RGO nano-composites).¹¹

Isotherms of imaginary part (ϵ'') of the complex dielectric permittivity (ϵ^*) of PANI/RGO nano-composites containing different RGO concentration were recorded in the frequency domain ranging from 306 K to 396 K. In a double logarithmic representation [Fig. 1], data points are fitted by: (i) $\sigma_{dc}/(\epsilon_0 f^n)$ (dc conductivity line), where σ_{dc} is the dc conductivity, ϵ_0 is

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^{b)}Deceased.

the relative permittivity of free space and n is a fractional exponent, and (ii) a Kohlrausch-Williams-Watts (KWW) dielectric relaxation peak, which is the Fourier-transform of a time-domain stretched exponential function $\text{Im}(\epsilon^*(t)) = \Delta\epsilon \exp(-(t/\tau_{KWW})^\beta)$, where $\Delta\epsilon$ is the relaxation strength, τ_{KWW} is the apparent KKW-relaxation time, and β is the stretching exponent [inset of Fig. 1]. While the dc component is intense, the quality of the fit is excellent which provides an accurate determination of the position and strength of the relaxation peak. An Arrhenius relation, i.e., $f_{\max} \propto \exp(E/kT)$, where k and E are the Boltzmann's constant and the activation energy, respectively, fits the $\log f_{\max}(1/T)$ data points presented in Fig. 2(a). The activation energies evaluated are: $E = -0.176 \pm 0.02$, -0.1732 ± 0.01 and -0.18 ± 0.06 eV for 0.05, 4.9, and 10 wt.% PANI/RGO, respectively. The result shows negative activation energy values for relaxation process. Although the ultrahigh frequency (transmission-line) peak might affect the accuracy of the beta-parameter evaluation (as it affects the right hand side of the interfacial relaxation), it does not affect the peak maxima (f_{\max}) determination and the subsequent activation energy calculation. They share a common value, confirming that a common microscopic mechanism underlies the relaxation process, such as electric charge relaxation within RGO nanoparticles. Negative activation energy values for relaxation are missing in the literature.

Effective dielectric theories of interfacial polarization in bi-phase heterogeneous structures consisting of conducting inclusions inside an insulating matrix are based on the assumption that the interface is impermeable to electric charge carriers, i.e., the outward transmission coefficient through the interface is null, as different phases do not interact with each other. However, interactions can play a significant role in interfacial polarization phenomena.^{12–15} The Sillars model for low concentrations of conducting oblate spheroid inclusions (such as the RGO “flakes”) predicts a relaxation time τ for interfacial polarization

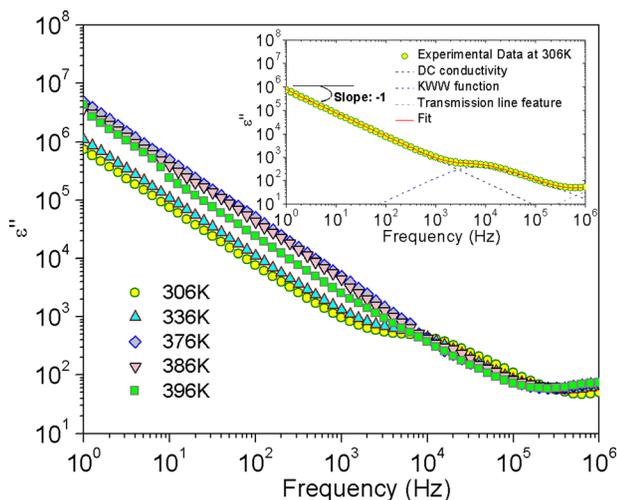


FIG. 1. Isotherms of imaginary part ϵ'' of the complex dielectric permittivity (ϵ^*) vs f for 10 wt. % PANI/RGO nano-composite. Inset: Fitting of a conductivity line with slope -1 and a KWW peak with parameters $\log \tau_{KWW} = -4.692 \pm 0.008$ (τ_{KWW} in s), $\Delta\epsilon = 91 \pm 9$ and fractional exponent $\beta = 0.80 \pm 0.01$ for the 10 wt. % PANI/RGO nano-composite at 306 K.

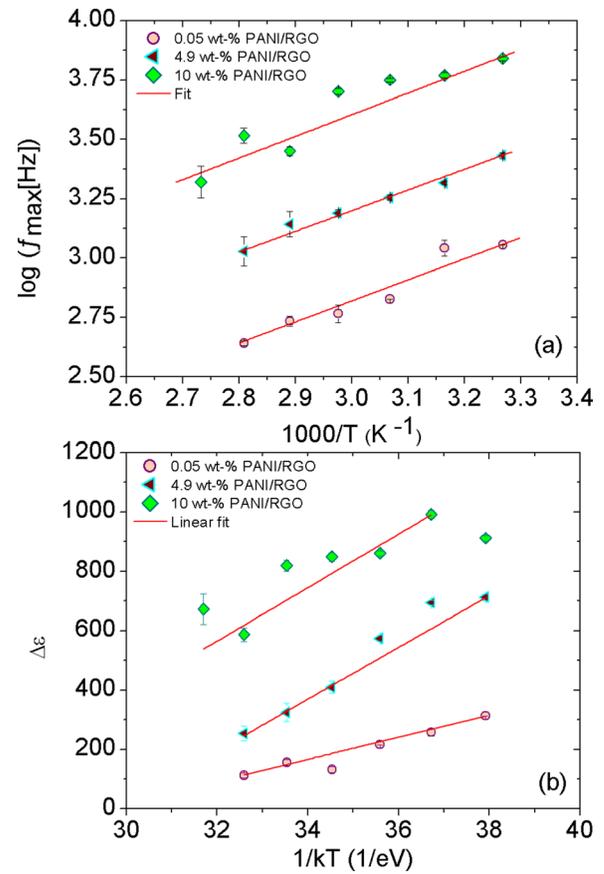


FIG. 2. (a) The logarithm of the peak maximum f_{\max} and (b) the peak intensity $\Delta\epsilon$ for the interfacial relaxation observed against $1/kT$, respectively. The decrease of $\Delta\epsilon$ upon increasing temperature implies a reduction of the density of relaxing electric charges inside the RGO inclusions. Red solid line is linear fit.

$$\tau = \epsilon_0 \frac{\epsilon_2}{\sigma_2}, \quad (1)$$

where ϵ and σ denote the relative static dielectric constant and dc conductivity, respectively, while subscripts 1 and 2 refer to the host (PANI) and the conducting inclusions (RGO), respectively. Since $\tau = 1/f_{\max}$, Eq. (1) implies that both σ_2 and f_{\max} have identical temperature dependencies. For graphene sheets, above roughly 150 K, at the Dirac point, where the Fermi surface is at the intersection of the dispersion relation of two bands in an energy-wave vector diagram, the charge carriers form “puddles” of electrons and holes, probably associated with charged impurities.^{16,17} As a result, at high temperatures, the dc resistance rises (with activation energy equal to 50 meV) in a thermally activated process.^{16,17} Alternatively, a saturation, rather than activated increase, of the dc conductivity vs temperature has also been observed.¹⁸ In any case, the conductivity σ_2 of the RGO phase above room temperature is more or less (depending on the type of defects formed), a decreasing function of temperature, and according to Eq. (1)—under the restriction that the host phase is a perfect insulator— f_{\max} should also increase with rising temperature. However, the opposite behavior is observed, i.e., f_{\max} is lowered on increasing temperature [Fig. 2(a)].

The experimental results can alternatively be interpreted as follows: PANI is a semiconductor, rather than an insulator and in an equivalent circuit representation, the polarized

RGO flakes act as capacitors being short-circuited by a leakage resistance through the semi-conducting PANI environment. Heating supplies thermal energy to the electric charge carriers, relaxing within the RGO, and assists their outward penetration of the effective potential barrier (which resembles that of a Schottky barrier raised at the interface of a metal—semi-conductor junction). Thus, a number of carriers escape and flow through the PANI environment leading to a lowering of the density of charges in the interior of RGO as temperature increases. Subsequently, $d\tau(T)/dT > 0$, or, $df_{\max}(T)/dT = E < 0$. Therefore, the latter prediction is compatible with the negative sign of the activation energy.

The scenario of electric charge de-trapping from the RGO inclusions at elevated temperatures is further supported by the reduction of the intensity $\Delta\varepsilon$ with temperature [Fig. 2(b)], which is a measure of how the relaxing charge population decreases on heating. Note that the values of $\Delta\varepsilon$ increase upon RGO loadings, in agreement with another prediction of the Sillars model: $\Delta\varepsilon = v_2(\varepsilon_1^2/\varepsilon_2)$ ¹¹ (i.e., $\Delta\varepsilon$ is proportional to the volume fraction v_2 of RGO in the host matrix). Note that the latter equation refers to ideally smooth shaped disks; however, the roughness of the interfacial surface are of RGO and RGO cluster is larger in reality, indicating that $\Delta\varepsilon$ is an increasing function of the interfacial area that is subsequently an increasing function of the RGO volume fraction. Charge liberation from the inclusion augments the concentration of free charges participating to the dc conductivity. While $\Delta\varepsilon$ decreases on temperature by a factor of 100, the (total) dc-conductivity increases less (by a factor of 2) because, recalling that $\sigma = n\mu q$, (where n is the concentration of charge participating to conductivity, μ is the charge mobility, and q denotes the net charge) the mobility of the liberated charges is reduced when moving within a semi-conducting environment. The dc conductivity (reduced to the value measured at 306 K) vs temperature plot for PANI reaches a maximum value above room temperature [Fig. 3]. It is noteworthy that the monotony of conductivity-temperature curves in conducting polymers depends strongly on their doping level.¹⁹ Higher RGO concentrations provide more charge-trapping interfaces and more pinned charges are likely to be liberated towards the semi-conducting PANI matrix. The latter mechanism is intensified at higher RGO loading, as can be seen in Fig. 3 in which the right-hand tail of the conductivity curves shifts systematically upward.

In summary, complex permittivity measurements above room temperature on PANI/RGO nano-composites of varying RGO contents reveal an interfacial relaxation mechanism characterized by *negative* activation energy values. This behavior is interpreted by revisiting the basic concepts of the Sillars model for interfacial polarization occurring in an insulator comprising dispersed conducting platelets. The semi-conducting PANI matrix provides a leakage resistance to the polarized RGO inclusions and enhances the dc conductivity of the composites at the expense of the intensity of the relaxation process. This is evidenced by the decrease in intensity of the relaxation peak on increasing temperatures which favors phonon-assisted charge de-trapping in RGO platelets. This phenomenon corroborates with our experimental findings as reflected in the negative values of the relaxation activation energies. The heat-induced charge

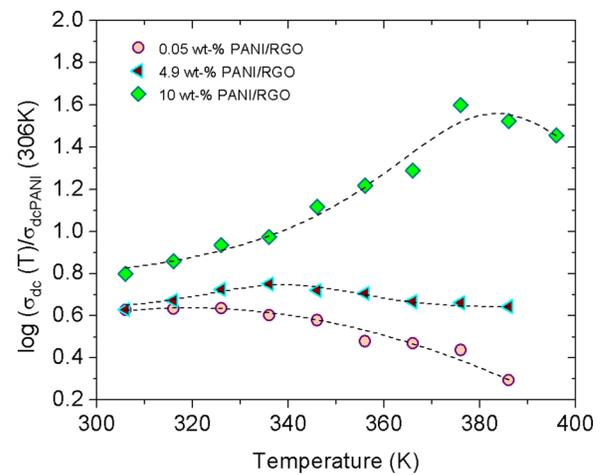


FIG. 3. The logarithm of the dc conductivity reduced to the corresponding one measured at 306 K of PANI vs temperature. On increasing RGO loading, the high temperature tail of the conductivity plots is raised-up, as more electric charge carriers are de-trapped from RGO inclusions and, subsequently, participate to percolation.

liberation contributes to dc conductivity and affects the shape of the dc conductivity - temperature curves for different weight fractions of RGO, which can be explained through the Sillars model.

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