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Enhanced discharge energy density of rGO/PVDF nanocomposites: The role of the heterointerface

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Recent reports of conductive-filler/polymer composites with large dielectric permittivity (K) make them potential candidates for flexible capacitors. Hence, an interesting question is how these high K composites behave under a strong electric field strength. In this letter, we use *in-situ*-reduced graphite oxide (rGO)/poly(vinylidene fluoride) (PVDF) nanocomposites as an example to study the energy storage behaviour of high K materials. We show the dielectric behaviour contrasts between weak and strong fields. High K materials inevitably become more lossy with increasing field strength. Simultaneously, we reveal that the *in-situ* reduction temperature can affect the energy storage performance. Improved energy storage performance is achieved for a nanocomposite reduced at a moderate temperature. When reduced at 160 °C, a device with an rGO volume fraction of 1.5 vol. % displayed a discharge energy density of 0.67 J/cm³ at 50 MV/m. This was 2.9 times greater than pure PVDF. We develop a model to explain this behaviour that proposes a reduced electrical contrast of the rGO/PVDF heterointerface minimising the recombination of localized charge carriers. Our results indicate, simultaneously, the potential and limitation of high K nanocomposites and shed light on the optimisation of the design and fabrication of high discharge energy density flexible capacitors for microelectronic devices. *Published by AIP Publishing.*

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Lightweight, flexible capacitors with high relative dielectric permittivity K and low dissipation factor $\tan \delta$ are in demand for energy applications. In principle, they can possess enhanced discharge energy density (J_d) over pure polymer examples. Nanocomposites consisting of poly(vinylidene fluoride) (PVDF) and 2-D conductive fillers have shown potential to fulfil the demands of a high discharge energy capacitor.^{1–7} While these nanocomposites with well-dispersed fillers can possess high K (>100 at 1 kHz) with low $\tan \delta$ (<0.5 at 1 kHz),^{2,3,8} the full potential of their energy storage performances has not been widely investigated. As these systems are non-linear in their dielectric behaviour, the permittivity has been shown to be dependent on the strength of the applied field. Under weak field conditions, the filler-to-filler charge transport can comprise the mobility of free carriers with charge hopping between adjacent sites.⁹ While under stronger fields, charge accumulation at the filler surface due to either polarization^{10,11} or injection¹² can become more dominant. This in turn means that the localized charge carriers can occupy more free space resulting in an increased possibility of carrier recombination between adjacent filler particles. Hence, high K nanocomposites with well-dispersed fillers may still be quite lossy under strong field conditions. This then becomes a major limitation that hinders their potential use in energy applications as capacitors.

To investigate the energy storage performance of high K nanocomposites, we prepared and tested a group of reduced

graphite oxide/poly(vinylidene fluoride) (rGO/PVDF) nanocomposites. We used an *in-situ* thermal reduction method that is reported to be effective in obtaining a homogeneous rGO dispersion in the PVDF matrix.⁸ The electrical conductivity of rGO can be manipulated by the reduction temperature T_r . As is reported, restoration of the sp^2 bonding networks can be observed at T_r above 140 °C resulting in increased conductivity for rGO.^{8,13} The electrically conductive rGO forms a highly contrasting interface with the insulating PVDF. This contributes to the enhancement in K .^{8,14} As can be seen in Fig. 1(a), nanocomposites with 2.5 vol. % rGO reduced at 200 °C (0.025-rGO@200) exhibit a K as high as 380 ($\tan \delta = 0.24$) at 1 kHz. This is 38 times higher than that of the pure PVDF. This result sets the material among the most promising ones currently reported in the literature.^{3,8,15}

The weak field dielectric behaviour indicates a low loss. However, this is not the case under strong applied fields as the nanocomposites exhibit increasing loss with increasing field strength (E). The strong field loss can be expressed by the energy efficiency (η) which is defined as the ratio of discharge energy density over theoretical energy density, shown in Fig. 1(b). We measure η of 0.025-rGO@200 at 0.04 for an applied field of 1 MV/m, which decreases to 0.02 at 2 MV/m, and the material breaks down. This is in significant contrast to the pure PVDF with η above 0.9 for values of E less than 30 MV/m. Hence, we can conclude that there are two major limitations for high K nanocomposites in energy storage applications; they are (i) weak dielectric strength and (ii) small

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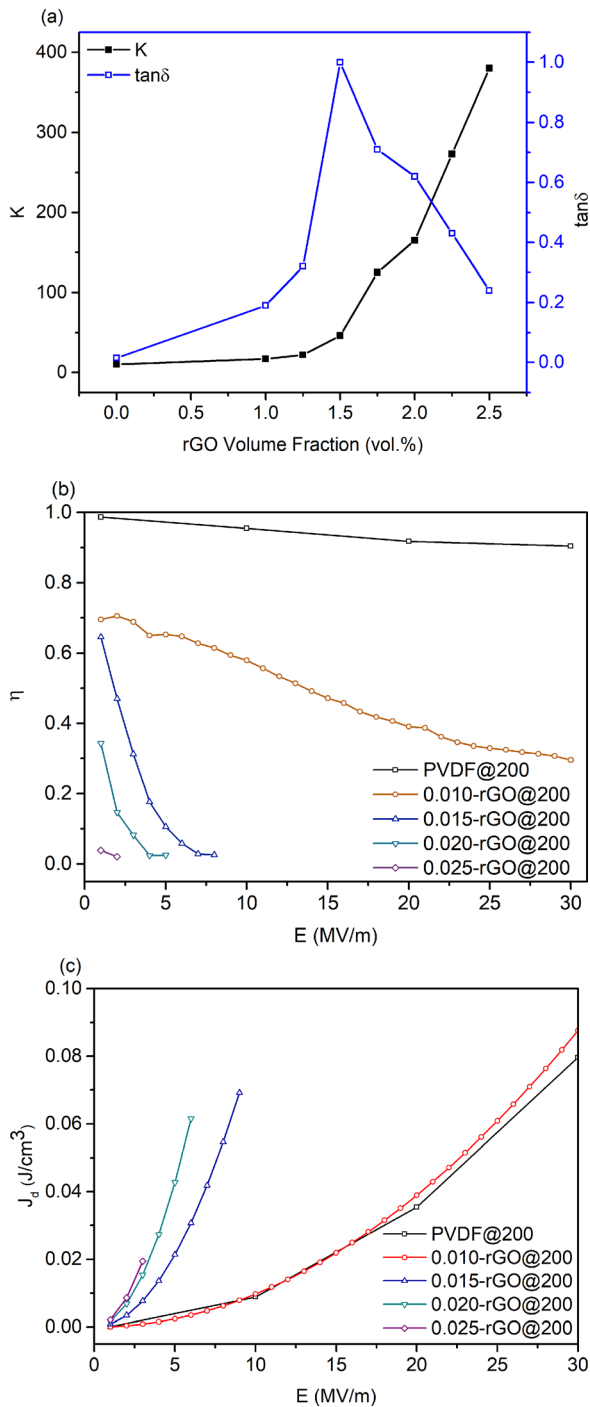


FIG. 1. (a) Relative dielectric permittivity K and dissipation factor $\tan\delta$ as a function of rGO volume fraction of 200°C reduced nanocomposites measured at 1 kHz, and their corresponding (b) energy efficiency η and (c) discharge energy density J_d measured at 10 Hz.

energy efficiency. These limitations are attributed to the large conductivity contrast between rGO and PVDF, which are side-effects of high K .¹⁴ Due to these limitations, the discharge energy density (J_d) of nanocomposites, which is plotted in Fig. 1(c), is limited to values that are too small for practical applications. Reducing the rGO volume fraction does not solve the problem, which means that an alternative strategy is needed to improve the energy storage performance.

Our strategy to improve the energy density was to investigate the impact of processing on performance. We found that the *in-situ* reduction temperature T_r has a direct impact on the

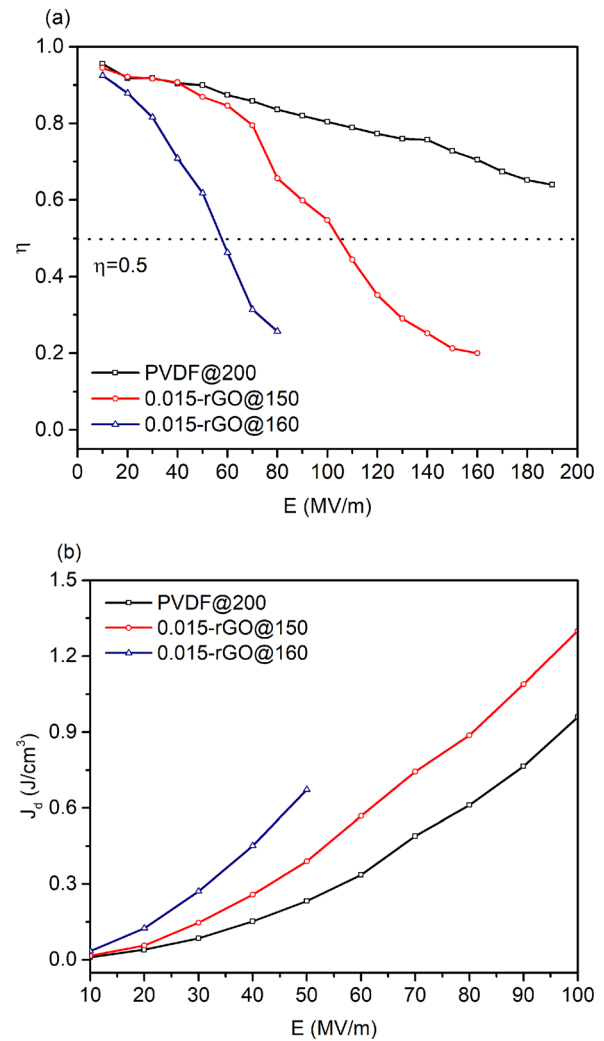


FIG. 2. (a) Effect of reduction temperature T_r on the (a) energy efficiency η and (b) discharge energy density J_d of 0.015-rGO nanocomposites measured at 10 Hz.

strong field loss of the nanocomposites. Figure 2(a) shows the η vs. T_r plot of 0.015-rGO. When T_r is reduced from 200°C to 160°C, E_c increases from 8 MV/m to 80 MV/m. Further reducing T_r to 150°C results in an enhanced E_c of 140 MV/m, a 17 times increase over the value at 200°C. These changes mean that a wider operational electrical field range is available for nanocomposites reduced at moderate T_r , enabling a route to increase J_d . In addition, higher η values were also observed for lower T_r . For instance, the η of 0.010-rGO@200 is 0.60 at 10 MV/m, in significant contrast to that of 0.92 and 0.94 for the 0.015-rGO@160 and 0.015-rGO@150 composites, respectively. A J_d with $\eta > 0.5$ is shown in Fig. 2(b). The increased E_c and η have led to an increased J_d over pure PVDF under high applied fields. For instance, the J_d of 0.015-rGO@160 is 0.67 J/cm³ at 50 MV/m ($\eta = 0.64$) and that of 0.015-rGO@150 is 0.95 J/cm³ at 90 MV/m ($\eta = 0.55$), corresponding to 3 times and 1.5 times of that of pure PVDF measured under the same conditions. A further increase in E can lead to higher J_d , but η will also decrease rapidly and the nanocomposites become vulnerable to breakdown under strong electrical fields. For instance, while a J_d of up to 2.7 J/cm³ is achievable at 150 MV/m in 0.015-rGO@150, η is merely 0.11. Hence, the high J_d under very strong fields, i.e., near breakdown, is not practically meaningful because of the decreasing η with increasing E .

The macroscopic lossy behaviour of the nanocomposites can be associated with the microscopic charge transfer kinetics with respect to the rGO addition. It is well known that charge injection occurs at a metal-solid Schottky junction with respect to a surface bias φ and the charge carriers can occupy the free space to form a charge accumulation layer as illustrated in Fig. 3.¹² It is considered that there is metallic behaviour for rGO, and so it is reasonable to approximate the rGO/PVDF heterointerface to a Schottky junction. Therefore, charge storage and loss can be correlated to the charge transfer kinetics within the interfacial area. Equations (1) and (2) can be used to describe the characteristics of charge accumulation with respect to a surface bias

$$W^2 \propto \varphi, \quad (1)$$

$$N \propto \sum_i \exp\left(\frac{e\varphi}{kT}\right), \quad (2)$$

where W is the width of the accumulation layer, φ is the normalized surface bias, N is the total charge amount, i is the number of crystal planes within the junction area, e is the charge of a single electron, k is the Boltzmann constant, and T is the temperature in Kelvin.¹² φ increases and decreases in the same manner as the external field; hence, more charge carriers can be localized under stronger fields. Simultaneously, W also increases under stronger fields, which means that the geometrical impact of the space charge layer can become more dominant. Here, we have evidence to show that there is insufficient free space for extensive expansion of the charge accumulation layer. This then results in a recombination of the localized carriers, which can thus be attributed to the mechanism of loss under high fields. The loss is more severe under (i) a stronger electric field and (ii) at a higher filler volume fraction, which are consistent with the experimental evidence we have acquired. Hence, high K nanocomposites will inevitably become more lossy under stronger fields. As the charge carriers are localized rather than free, only those in any overlapping volume can recombine. It is, therefore, critical to reduce the overlapping volume to reduce loss. We have found that by reducing T_r , the strong field loss can be effectively reduced. The impact of T_r can be microscopically attributed to that of the electrical contrast of the rGO/PVDF heterointerface. The

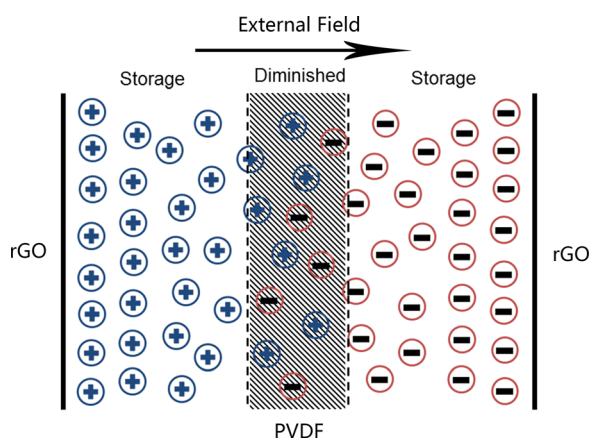


FIG. 3. Charge carrier localization and recombination at the rGO/PVDF interface with respect to the external field in the nanocomposites, which is associated to the macroscopic loss behaviour.

thermal removal of oxygen-containing groups on the carbon backbone of GO is a stepwise procedure.¹³ As the electrical structure of rGO is tunable by manipulating its C/O ratio,^{16,17} a more resistive behaviour is achievable at lower T_r , which effectively increases the lumped resistance R_s of the junction. Practically, the surface bias φ can be described as

$$\varphi = \varphi_0 - IR_s, \quad (3)$$

where φ_0 is the value associated with the field strength, I is the junction current and R_s is the lump resistance.¹² As we have shown, increasing R_s reduces φ , and the resulting microscopic behaviour is (i) to reduce the charge injection and (ii) narrow the accumulation layer width. Due to the uneven carrier distribution within the junction volume, a reduced W will limit recombination only to the “tail” part of the whole layer and the ratio of storage/loss is increased, which directly relates to an increase in η . Hence, we show by engineering the electrical contrast of the heterointerface that higher E_c and η are achievable, both of which can result in a higher J_d .

In summary, we have shown that the contrasting loss behaviour of the nanocomposites between weak and strong fields is due to the greater charge carrier recombination at the rGO/PVDF heterointerface at higher field strength. This shows that high K composites will inevitably become more lossy with increasing field strength, which limits their application to only very weak field applications. To enhance the strong field energy storage performance, there needs to be a compromise between charge carrier localization and recombination. We demonstrate that this is possible by accessing the thermally tunable nature of reduced graphite oxide (rGO). Compared to the nanocomposites reduced at 200 °C, those at 150 °C and 160 °C can possess much increased dielectric strength and energy efficiency. This is attributed to the decreased interfacial electrical contrast between the filler and the matrix that reduced the carrier recombination under a stronger field, which can simultaneously lead to a higher discharge energy density. The nanocomposites with 1.5 vol. % rGO annealed at 160 °C possesses a discharge energy density of 0.67 J/cm³ (at 50 MV/m, 10 Hz), which is 2.9 times that of pure PVDF under the same conditions. We have highlighted the role of the heterointerface in the energy storage performance of the nanocomposites, which can be used to investigate and optimize a range of composites with a variety of conductive fillers.

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