

Enhanced Discharge Energy Density of rGO/PVDF Nanocomposites: The Role of the Heterointerface

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ABSTRACT: 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) nanocomposites as an example to study the energy storage behaviour of high K materials. We show the dielectric behaviour contrasts between weak and strong field. The 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. At 160°C a device with an rGO volume fraction of 1.5 vol.% displayed a discharging energy density of 0.67J/cm³ at 50MV/m. This was 2.9 times greater than pure PVDF. We develop a model to explain this behaviour that proposes a reduced electrical rGO/PVDF heterointerface minimising the recombination of localized charge carriers. Our results indicate, simultaneously, the potential and limitation of high K nanocomposites, and sheds light on the optimisation of the design and fabrication of high discharge energy density flexible capacitors for microelectronic devices.

Light weight, flexible capacitors with high relative dielectric permittivity K and low dissipation factor $\tan \delta$ are in demand in energy applications. In principle, they can possess an enhanced discharging energy density (J_d) over the pure polymer examples. Nanocomposites consisting of poly(vinylidene fluoride) (PVDF) and 2-D conductive fillers have shown the 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 1kHz) with low $\tan \delta$ (<0.5 at 1kHz)^{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 nanocomposites 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 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 . A structural change in the rGO started to emerge at T_r above 140°C. A restoration of the sp^2 bonding networks can be observed resulting in increased conductivity for rGO embedded systems.^{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 figure 1a, 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 1kHz. This is 38 times higher than that of the pure PVDF. This result sets the material as among the most promising currently reported in the literature.^{3,8,15}

The weak field dielectric behaviour indicates a low loss. However, this is not the case at 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 discharging energy density over theoretical energy density, shown in figure 1b. We measure η of 0.025-rGO@200 at 0.04 for an applied field of 1MV/m this decreases to 0.02 at 2MV/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 30MV/m. Hence, we can conclude two major limitations of the high K nanocomposites in energy storage applications, these are (i) weak dielectric strength, and (ii) small energy efficiency. These limitations are attributed to the large conductivity contrast between rGO and PVDF, which are side-effects of the high K.¹⁴ Due to these limitations, the J_d of the nanocomposites, which is plotted in figure 1d, are limited to a values that are too small for practical applications. Reducing the rGO volume fraction does not solve the problem, which means alternative strategy is needed to improve the energy storage performance.

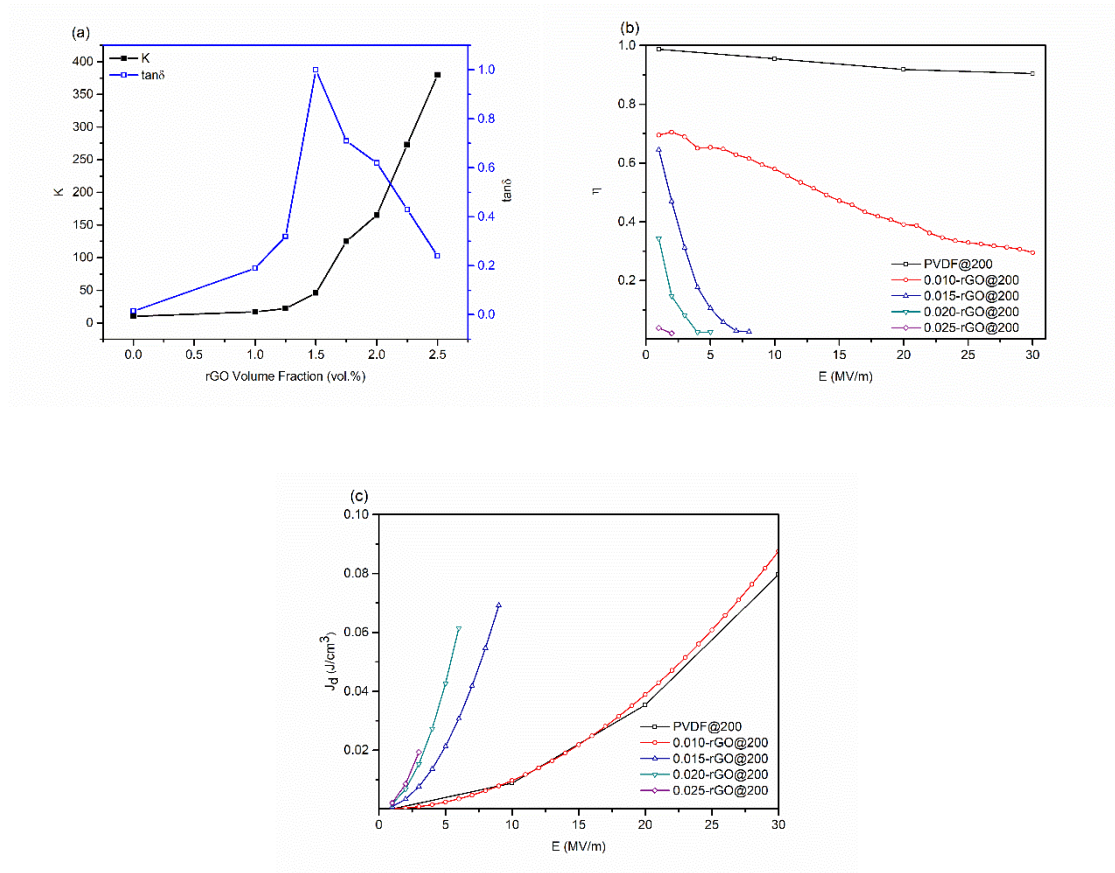


Figure 1 (a) Relative dielectric permittivity K and dissipation factor $\tan\delta$ as a function of rGO volume fraction of 200°C reduced nanocomposites measured at 1kHz, and their corresponding (b) energy efficiency η and (c) discharging energy density J_d measured at 10Hz

Our strategy to improve the energy density was to investigate the impact of atmosphere and processing on performance. We found the in-situ reduction temperature T_r has a direct impact on the strong field loss of the nanocomposites. Figure 2a shows the η vs. T_r of 0.015-rGO. When the T_r is reduced from 200°C to 160°C E_c increases from 8MV/m to 80MV/m. Further reducing T_r to 150°C results in an enhanced E_c of 140MV/m, a 17 times increase over the value at 200°C. These changes means 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 10MV/m, in significant contrast to that of 0.92 and 0.94 for the 0.015-rGO@160 and 0.015-rGO@150 composites. A J_d with $\eta > 0.5$ is shown in figure 2b. The increased E_c and η have led to an increased J_d over pure PVDF at high applied fields. For instance, the J_d of 0.015-rGO@160 is 0.67J/cm³ at 50MV/m ($\eta=0.64$), and that of 0.015-rGO@150 is 0.95J/cm³ at 90MV/m ($\eta=0.55$), corresponding to 3 times and 1.5 times of that of pure PVDF measured under the same conditions. Further increasing 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 2.7J/cm³ is achievable at

150MV/m in 0.015-rGO@150, the η is merely 0.11. Hence, the high J_d at very strong field, i.e. near breakdown, is not practically meaningful because of the decreasing η with increasing E .

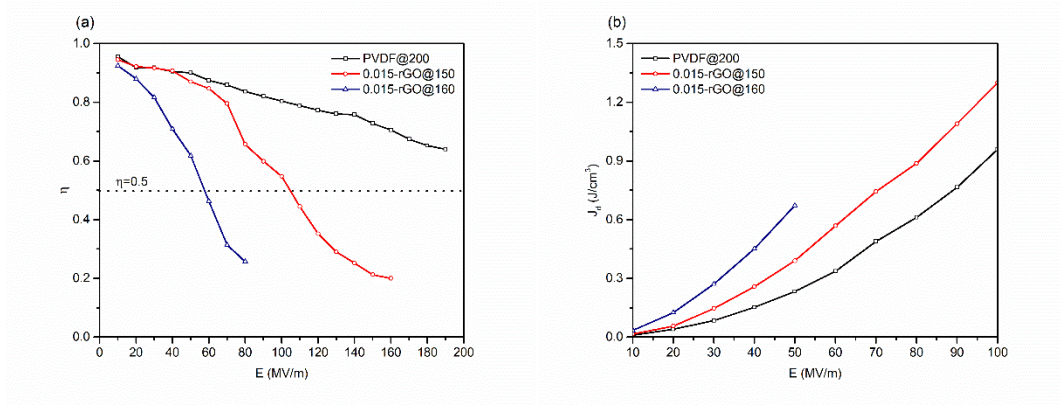


Figure 2 (a) Effect of reduction temperature T_r on the (a) energy efficiency η and (b) discharging energy density J_d of 0.015-rGO nanocomposites measured at 10Hz

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 figure 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, the 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 the charge accumulation with respect to a surface bias:

$$W^2 \propto \phi \quad (1)$$

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

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 plane with in 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 with the external field, hence more charge carriers can be localized under stronger fields. Simultaneously, W also increases under stronger fields, which means the geometrical impact of the space charge layer can become more dominant. Here, we have evidence to show that it is the insufficient free space for extensive expansion of the charge accumulation layer. This then results in a recombination of the localized carriers, and which can thus be attributed as the mechanism of the loss at high fields. The loss is more severe at (i) stronger electric field and (ii) higher filler volume fraction, which are consistent with the experimental evidence we have acquired. Hence, high K

nanocomposites will inevitably become more lossy at 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 thermal removal of oxygen-containing groups on the carbon backbone of GO is a stepwise procedure.¹³ As the electrical structure of rGO is tuneable 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 to 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 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 in 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, higher E_c and η is achievable, both of which can result in a higher J_d .

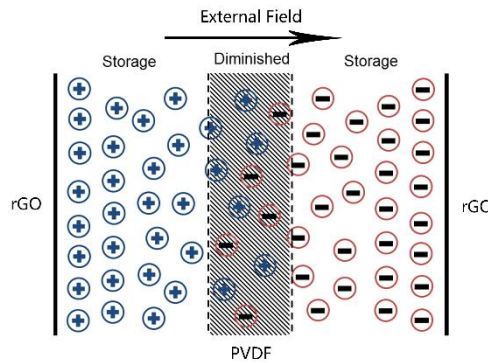


Figure 3 Charge carrier accumulation and recombination at the rGO/PVDF interface area with respect to the external field in the nanocomposites, which is associated to the macroscopic loss behaviour

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 only in very weak field applications. To enhance the strong field energy storage performance there needs to be a compromise between the charge carrier localization and recombination. We demonstrate that this is possible by accessing the thermally tuneable nature of reduced-graphite-oxide (rGO). Compared to the

nanocomposites annealed at 200°C, those at 150°C temperatures can possess much increased dielectric strength and energy efficiency. This is attributed to the decreased interfacial electrical contrast between filler and matrix that reduced the carrier recombination at stronger field, which can simultaneously lead to a higher discharging energy density. The nanocomposites with 1.5 vol.% rGO annealed at 160°C possesses a discharging energy density of 0.67 (at 50MV/m, 10Hz), which is 2.9 times of that of pure PVDF under same conditions. We have highlighted the role of heterointerface in the energy storage performance of the nanocomposites, which can be used to investigate and optimize of a range of composites with variety of conductive fillers.

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Reference

- 1 L. Cui, X. Lu, D. Chao, H. Liu, Y. Li, and C. Wang, *physica status solidi (a)* **208**, 459 (2011).
- 2 A. Javadi, Y. Xiao, W. Xu, and S. Gong, *Journal of Materials Chemistry* **22**, 830 (2012).
- 3 K. Yang, X. Huang, L. Fang, J. He, and P. Jiang, *Nanoscale* **6**, 14740 (2014).
- 4 Q. Zhang, H. Li, M. Poh, F. Xia, Z.-Y. Cheng, H. Xu, and C. Huang, *Nature* **419**, 284 (2002).
- 5 L. Wang and Z.-M. Dang, *Applied Physics Letters* **87**, 042903 (2005).
- 6 F. He, S. Lau, H. L. Chan, and J. Fan, *Advanced Materials* **21**, 710 (2009).
- 7 Q. Chen, P. Du, L. Jin, W. Weng, and G. Han, *Applied Physics Letters* **91**, 022912 (2007).
- 8 H. Tang, G. J. Ehlert, Y. Lin, and H. A. Sodano, *Nano Lett* **12**, 84 (2012).
- 9 A. Miller and E. Abrahams, *Physical Review* **120**, 745 (1960).
- 10 T. J. Lewis, *Dielectrics and Electrical Insulation*, *IEEE Transactions on* **1**, 812 (1994).
- 11 R. Armstrong and B. Horrocks, *Solid State Ionics* **94**, 181 (1997).
- 12 A. Di Bartolomeo, *Physics Reports* **606**, 1 (2016).
- 13 S. H. Huh, *Thermal reduction of graphene oxide* (INTECH Open Access Publisher, 2011).
- 14 J. I. Roscow, C. R. Bowen, and D. P. Almond, *ACS Energy Letters* **2**, 2264 (2017).
- 15 D. Wang, Y. Bao, J. W. Zha, J. Zhao, Z. M. Dang, and G. H. Hu, *ACS Appl Mater Interfaces* **4**, 6273 (2012).
- 16 I. Jung, D. A. Dikin, R. D. Piner, and R. S. Ruoff, *Nano Letters* **8**, 4283 (2008).
- 17 H. F. Liang, C. T. G. Smith, C. A. Mills, and S. R. P. Silva, *J. Mater. Chem. C* **3**, 12484 (2015).