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# Electroactive graphene nanofluids for fast energy storage

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## LETTER

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**Abstract**

Graphenes have been extensively studied as electrode materials for energy storage in supercapacitors and batteries, but always as solid electrodes. The conception and development of graphene electroactive nanofluids (ENFs) reported here for the first time provides a novel way to ‘form’ graphene electrodes and demonstrates proof of concept for the use of these liquid electrodes for energy storage in novel flow cells. A stabilized dispersion of reduced graphene oxide (rGO) in aqueous sulfuric acid solution was shown to have capacitive energy storage capabilities parallel to those of solid electrode supercapacitors ( $169 \text{ F g}^{-1}(\text{rGO})$ ) but working up to much faster rates (from  $1 \text{ mV s}^{-1}$  to the highest scan rate of  $10 \text{ V s}^{-1}$ ) in nanofluids with 0.025, 0.1 and 0.4 wt% rGO, featuring viscosities very close to that of water, thus being perfectly suitable for scalable flow cells. Our results provide proof of concept for this technology and include preliminary flow cell performance of rGO nanofluids under static and continuous flow conditions. Graphene nanofluids effectively behave as true liquid electrodes with very fast capacitive storage mechanism and herald the application not only of graphenes but also other 2D materials like  $\text{MoS}_2$  in nanofluids for energy storage and beyond.

Energy storage is in the midst of a revolutionary change which will turn it into a key factor within the upcoming sustainable energy model [1]. As a matter of fact, electrochemical energy storage (ECES) has already come a long way from the lead-acid battery to the last generation of rechargeable Lithium-ion batteries, flow cells or hybrid supercapacitors [1, 2]. ECES will predictably be a key player within the framework of distributed energy generation and storage networks. But before that happens, a few major breakthroughs need to take place. In short, ECES systems should be able to store more energy and do it at a much faster rate (i.e. higher power), all of it at a lower cost and topped with environmental friendliness [1–3]. As in the past, these breakthroughs will rest strongly on the development of new materials, among which, graphenes are taking a preeminent place thanks to their perfect suitability to provide eco-friendly high power at ever decreasing cost. And yet, an overwhelming share of the work reported for graphene as an energy material has dealt with solid electrodes.

Totally unrelated to solid electrodes, redox flow batteries (RFBs) are considered the strongest technology to tackle higher-power applications at a low cost [4]. Their feasible design in the kW-MW range could make of them strong players for distributed and smart grid applications [3]. In flow electrochemical cells, energy and power are decoupled by storing electroactive compounds externally to the electrochemical cell. However, these cells have always used solutions of electroactive salts, burdened by a limited solubility (for example 1–2 M Vanadium salts in all-vanadium flow batteries) which limits in turn their energy density. Furthermore, increasing energy density while keeping low cost, could make of flow cells practical systems not only to store intermittent renewable energy but also to feed electric vehicles (EVs) [4].

We present here, for the first time, the novel concept of electroactive nanofluids (ENFs), an alternative type of liquid electrode materials which could be used as improved fluids for fast energy storage in flow electrochemical cells. The work reported here deals with

the first example of such an ENF, in this case based on graphene.

Nanofluids are homogeneous dispersions of nanoparticles in conventional base fluids which constitute an emerging type of unique liquid materials within the field of nanoscience and nanotechnology. They have been proposed and used for a variety of applications with very special emphasis on thermal properties and heat-transfer applications [5]. However, they have never been explored as possible electroactive materials. In our group we are developing a research line on nanofluids for thermal applications and have considered the development of electroactive nanofluids (ENFs), that is, those containing nanoparticles able to store electrical energy, whether through redox or capacitive mechanisms. We present here the first example of the application of ENF materials for the development of fast energy storage in flow cells. In this case we have used a capacitive nanofluid based on graphene which would be the flow-cell analog of solid-electrode graphene supercapacitors.

It should be noted that graphene nanofluids have been reported before, and a comprehensive review has been published recently [5]. That review can help the reader to get an idea of the state of the art on this novel materials, which is beyond the scope of this communication. However, that review, as well as the many relevant recent papers on graphene nanofluids [5] confirm that these materials have been studied and used so far for their rheological and thermal properties, in order to be used for lubricating and heat transfer and storage applications, respectively. But no report on electrochemical energy-storing graphene nanofluids could be found. On the other hand, a few relevant publications can be found in the literature in which carbon slurries (but not graphene nanofluids) have been used as electrodes for energy storage. For instance, Gogotsi *et al* [6] reported an electrochemical flow capacitor (EFC) using a 'flowable' carbon slurry improving upon the concept introduced by Kastening *et al* [7]. However, slurry electrodes are not well-suited for flow cells due precisely to their poor flowing properties. Indeed, suspensions of microparticles have been tried in numerous applications (including heat transfer fluids) but are not up to the task when it comes to the final engineering, due to precipitation and/or clogging. In great contrast, nanofluids are homogeneous liquids incorporating (smaller) nanoparticles which are utterly dispersed and therefore would present no flowing problems.

The electroactive nanofluid reported here is based on reduced graphene oxide (rGO) dispersed in water, forming a nanofluid able to store electricity through a capacitive mechanism, (see figure 1(a)) as supercapacitors do, except that in the present case the electrode is a liquid (figure 1(b)), stored externally and flowing through a flow electrochemical cell. The detailed experimental details are provided in supporting information (S. I. S1).

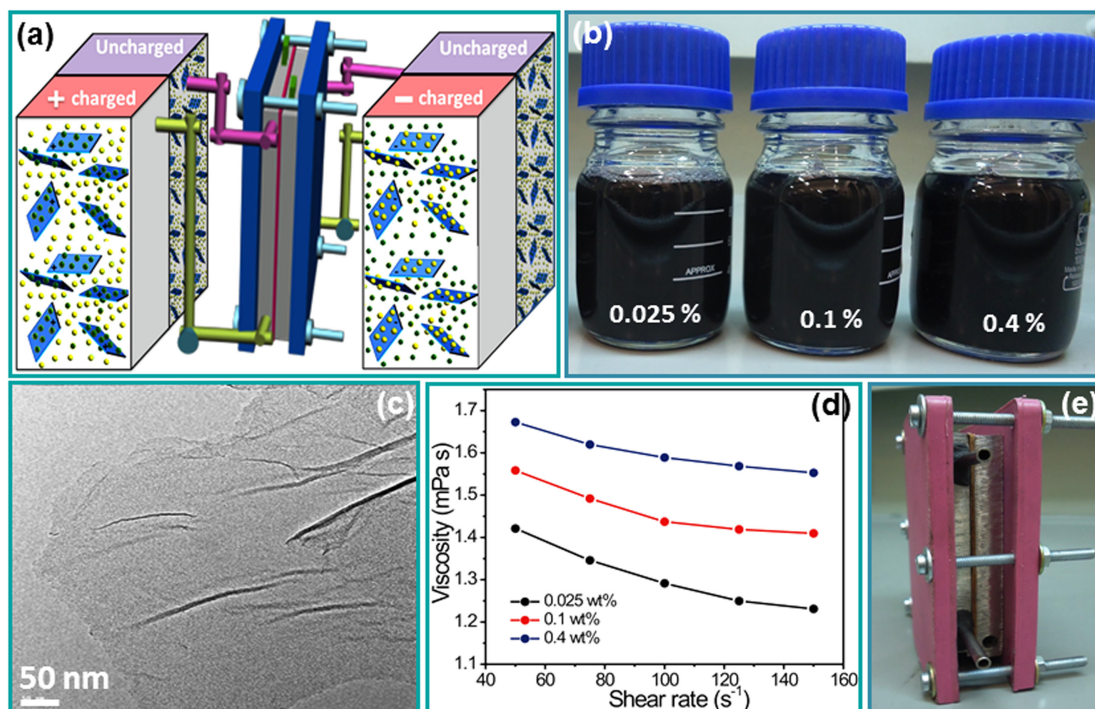
Reduced graphene oxide (rGO) was prepared by a modified Hummer's method. The resulting graphite oxide was thermally reduced at 800 °C under N<sub>2</sub> to yield reduced graphene oxide (rGO) (5.8% oxygen content). The intensity ratio of the Raman D band (at 1348 cm<sup>-1</sup>) to G band (at 1591 cm<sup>-1</sup>) was 1.02, thereby confirming the formation of reduced graphene oxide (see S. I. S2). HRTEM revealed that the rGO sheets are few-layered with completely transparent aspect and adopt a crumpled to a curly, wavy shape. The edges of the sheets are partially folded so that the total surface energy should be reduced (see figure 1(c)).

Nanofluids of rGO in aqueous H<sub>2</sub>SO<sub>4</sub> were prepared with different concentrations (0.025, 0.1 and 0.4 wt%) by dispersing solid rGO (using a 1200 W ultrasonic bath for up to 2 h.) in 1 M aqueous H<sub>2</sub>SO<sub>4</sub> solution containing 0.5 wt% of surfactant (triton X-100), a well-known molecule with no electrochemical activity. With this simple formulation we got stable sols which needed more than 24 h standing still to show any sign of precipitation and were very easily homogenized back by simple shaking (see S. I. 3).

Figure 1(d) shows the rheological behavior of our electroactive rGO nanofluid materials at different concentrations. The viscosities versus shear rate plots show almost Newtonian behavior with an interesting shear-thinning component (the viscosity of rGO nanofluids slightly decreased with increasing shear rate). Most importantly, the viscosities in the range 1.2–1.7 mPa s are very close to that measured for the parent 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution (close to the expected 1 mPa s of water) and one to three orders of magnitude lower than that found for carbon-slurry based pastes (typically around 2000 mPa s) [6]. These data confirm our working hypothesis of the superiority of these novel nanofluid materials for their application in flowing cells.

But the definitive advantage of electroactive nanofluids is related to their electrochemical and energy-storage properties. The electrochemical characterization of these rGO nanofluids was carried out both under static and continuous flow conditions using a specially designed flow cell (S. I. 4) with dual (back and forth) automated flow control of peristaltic pumps for the positive and negative compartments. This simple home-made flow cell, (figure 1(e)) similar to conventional flow battery cells, has allowed for a preliminary but efficient use of our nanofluids in order to show final proof of concept. The choice of aqueous electrolyte naturally limited the cell voltage to <1.2 V but led to high ionic conductivity.

Figure 2(a) shows the CV curves of symmetric rGO nanofluid cells (0.025 wt%) at different scanning rates (from 1 mV s<sup>-1</sup> to the highest scan rate of 10 V s<sup>-1</sup>). Extraordinarily, the ability of our nanofluid electrodes to store energy through their characteristic capacitive mechanism is substantial even at the very high scan rate of 10 000 mV s<sup>-1</sup>. This indicates that



**Figure 1.** (a) Schematic representation of the concept and charge storage mechanism for a flow cell based on electroactive (capacitive) nanofluid. Reduced graphene oxide (rGO) nanofluid is pumped between two polarized current collectors for charging and discharging through a double layer mechanism (yellow spheres represent positive and green negative solvated ions). (b) Actual photograph of rGO nanofluids (rGO dispersions in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution) at three different concentrations showing stable and uniform sols. (c) TEM micrograph of typical rGO nanosheet, (d) Rheological properties of the three nanofluids studied showing low viscosity suitable for efficient pumping, (e) Digital photograph of our home-made flow cell which consists of low-cost polyvinylidene fluoride (PVDF) membrane as a separator and oil paper as a gasket enclosed together using hard plastic plates and screws.

rGO nanofluids possess excellent rate capabilities as needed for high-power supercapacitors and suggests a peculiar and very fast charge transfer mechanism in this type of nanofluids. Similar results are also observed for nanofluids with higher concentration (S. I. 5). To the best of our knowledge this is the fastest scan rate reported to have been successfully used in CV measurements of any flow cell [8–10].

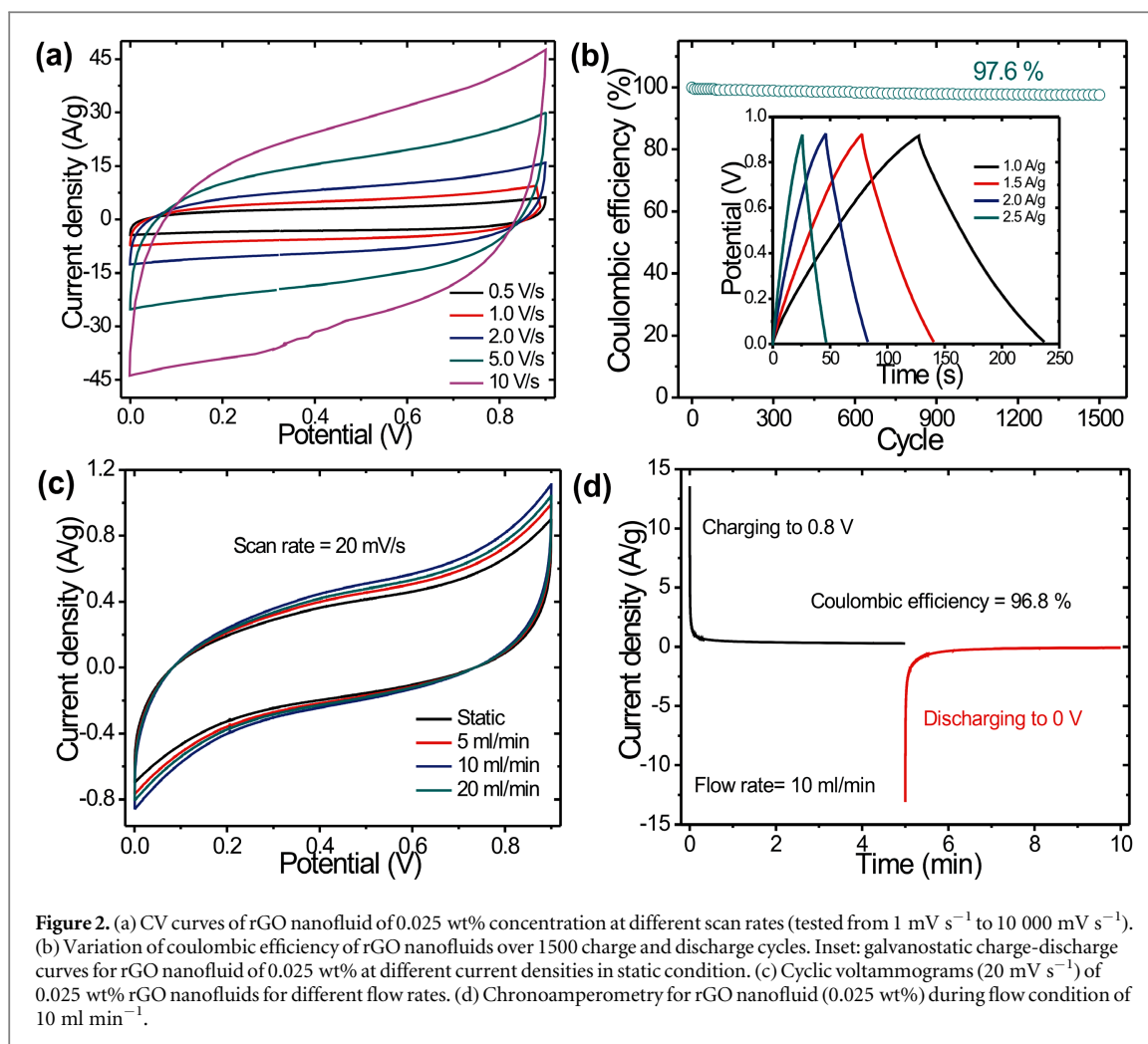
Moreover, what is unique and most remarkable in our case is that this behavior implies the polarization of the bulk electroactive nanofluid. This in turn implies percolative charge transfer through the nanofluid, which could therefore be considered a true liquid electrode.

The values of specific capacitance of the cell for rGO nanofluids were calculated from the CV curves (see S.I. 6). As it could be expected, specific capacitances decrease gradually with increasing scan rate. The maximum specific capacitance value of these series was 169 F g<sup>-1</sup>(rGO) and was obtained for 0.025 wt% rGO nanofluid at a scan rate of 1 mV s<sup>-1</sup>, a value absolutely comparable to bulk solid electrodes (S.I. 7). Here again, in order to store that amount of charge on rGO within the flow cell (at this point under static conditions and without convection), the rGO flakes must be electrically connected to the external load via a conductive pathway derived from fast charge

transfer. Unlike conventional supercapacitors in which solid film electrodes benefit from well-defined fixed conduction paths, our cell utilizes a ‘liquid electrode’ in which charge must percolate through a dynamic network of conductive particles. The values of specific capacitances obtained in this work are also very much comparable or even higher than the values reported for thicker carbon slurries. For instance, Presser *et al* [6] prepared a thick carbon slurry of carbide-derived carbon powder obtained from titanium carbide (TiC: CDC) and 1 M Na<sub>2</sub>SO<sub>4</sub> with compositions of 3:1 and 4:1 (electrolyte: carbon by mass). The highest specific capacitance reported for toothpaste-like TiC:CDC slurry (3:1, electrolyte: carbon) was 109 F g<sup>-1</sup> at the scan rate of 2 mV s<sup>-1</sup>. Furthermore, Zhang *et al* [8] reported a specific capacitance of 154 F g<sup>-1</sup> at 2 mV s<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> for a thick slurry of porous carbon spheres with concentration ranging from 16 wt% to 23 wt%. Thus, our work provides remarkable preliminary data supporting the use of graphene electroactive nanofluids in general and rGO nanofluids in particular for energy storage applications.

Finally, electrochemical impedance spectroscopy data show a low ohmic resistance in the range of ~0.23–0.28 Ω that also agrees with fast ion transport and a highly conductive network facilitating charge





and ion percolation (S.I. 7). These values are even lower than those reported for spherical carbon particles suspension electrodes [9–11].

### Energy storage of rGO electroactive nanofluids (ENFs) in flow cells

The performance of rGO nanofluids in the final flow cell device was studied by galvanostatic charge/discharge cycling in static conditions as shown in figure 2(b) (inset). The shapes of charge-discharge curves are symmetric, triangular and linear for the rGO nanofluids at all different current densities used. The maximum values of specific capacitance for the 0.025 wt% rGO nanofluid were 117 and  $50 \text{ F g}^{-1}(\text{rGO})$  at current densities of  $1 \text{ A g}^{-1}$  and  $2.5 \text{ A g}^{-1}$ , respectively. This corresponds to specific energy values of  $5.7\text{--}13.1 \text{ Wh kg}^{-1}(\text{rGO})$  and specific power of  $0.45\text{--}1.13 \text{ kW kg}^{-1}(\text{rGO})$  (see S.I. 7) The values of specific energy are significantly larger than for previous reports on slurries (for example,  $5.6\text{--}8.2 \text{ Wh kg}^{-1}$  for carbon beads slurry [12]). Moreover, the galvanostatic cycling performance was found to be stable, with cycle efficiencies greater than 97.6% after 1500 charge/discharge cycles (figure 2(b)). A

series of chronoamperometry experiments was carried out for rGO nanofluids under static conditions (see S.I. 8). Specific capacitances calculated for rGO nanofluids at different potentials ( $36\text{--}156 \text{ F g}^{-1}(\text{rGO})$ ) are comparable to the values derived from CVs. The coulombic efficiency of the rGO nanofluid cell was found to be 98.2% (S.I. 8) (a large value considering that we did include the leakage current), which is in very good agreement with the coulombic efficiency derived from galvanostatic charge/discharge experiments (98.9%).

In order to get full insights on the potential of these nanofluids to be applied in flow cells, the performance of rGO nanofluids under continuous flow conditions were also tested. Figure 2(c) shows CV curves (at  $20 \text{ mV s}^{-1}$  scan rate) of 0.025 wt% rGO nanofluid for different flow rates. It is interesting to note that the shape of the CV curves remains unchanged for the different flow rates used, which confirms the uniform and stable nature of the nanofluid. Finally figure 2(d) shows the efficient charge-discharge (CA) process taking place also under flowing conditions with coulombic efficiency values (96.8%) very close to those found in static experiments.

In conclusion, we have demonstrated the first successful example of the possible use of graphene electroactive nanofluids (in particular rGO nanofluid) in a flow cell. Our measurements indicate that, similarly to solid electrodes, these nanofluid electrodes exhibit excellent electrochemical performance, including high capacitance and energy density. Most impressively, our study shows full electrochemical utilization of the rGO active material in the bulk nanofluid (even under static conditions), and even at extremely fast rates, thus showing effective charge transfer percolation in a material that behaves as a true liquid electrode. This discovery supports the application of rGO nanofluids as truly flowing electrodes for flow cells and has led to the recent filing of a patent [13]. It should be stressed however that our home-made flow cell is far from being optimized. Further investigations are already in progress concerning both improved engineering design and improved active materials as those used in hybrid solid supercapacitors [14, 15]. That combination should lead to efficient, low-cost and scalable energy storage in flow cells based on the new family of graphene electroactive nanofluids (ENFs). But in addition to energy storage, these novel graphene ENFs also inaugurate a new way to deliver graphene which could lead to many new and imaginative useful applications, harnessing the many and well-known properties of these extraordinary 2D materials.

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