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Non-aqueous energy storage devices using graphene nanosheets synthesized by green route

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In this paper we report the use of triethylene glycol reduced graphene oxide (TRGO) as an electrode material for non-aqueous energy storage devices such as supercapacitors and Li-ion batteries. TRGO based non-aqueous symmetric supercapacitor is constructed and shown to deliver maximum energy and power densities of 60.4 Wh kg\(^{-1}\) and 0.15 kW kg\(^{-1}\), respectively. More importantly, symmetric supercapacitor shows an extraordinary cycleability (5000 cycles) with over 80% of capacitance retention. In addition, Li-storage properties of TRGO are also evaluated in half-cell configuration (Li/TRGO) and shown to deliver a reversible capacity of \(\sim 705\) mAh g\(^{-1}\) with good cycleability at constant current density of 37 mA g\(^{-1}\). This result clearly suggests that green-synthesized graphene can be effectively used as a prospective electrode material for non-aqueous energy storage systems such as Li-ion batteries and supercapacitors.

I. INTRODUCTION

Supercapacitors (SC) and Lithium-ion batteries (LIB) are the key solutions for today’s huge energy storage demands and expected to power hybrid electric vehicles (HEV) and electric vehicles (EV) in near future.1–6 SC or electric double layer capacitors (EDLC) are important high performance electrochemical energy storage devices with long cycleability and high power density in aqueous media which predominantly contain carbonaceous electrodes.7, 8 However, energy density is highly limited due to the restricted (due to water splitting issue) operating potential (\(\sim 1.23\) V) of such aqueous electrolyte solutions.\(^9,10\) Hence, the concept of making asymmetric SC has emerged to suppress the negative and positive polarization and thereby widening the operating potential in an aqueous medium up to \(\sim 2\) V.\(^11\) However, still the energy density of such asymmetric SC system is far below than the desired level to power HEV and EV, poor cycleability being another important concern. Another approach to enhance the energy density is employing non-aqueous electrolytes without compromising power density according to the equation, \(E = 1/2 CV^2\). Since the electrochemical stability window for organic solutes is wider (\(\sim 3\) V) than that of aqueous solutions (\(\sim 1.23\) V), higher voltages can be accessed and thus higher energy density can be realized. While
employing such non-aqueous electrolyte solutions, cycleability of SC is severely affected as compared to aqueous solutions.\textsuperscript{10,12–16} Poor cycleability in non-aqueous media results in the case of EDLC capacitors irrespective of carbon allotropes used.\textsuperscript{7,8} Among the various forms of carbon, graphene is found to be a more attractive candidate to study the supercapacitive behaviour in non-aqueous media, however no extensive work has yet been carried out in such medium.\textsuperscript{17–19} Taking the overwhelming advantages of graphene-like unique two-dimensional structure made up of honeycomb lattice of \textit{sp}^2 hybridized carbon atoms, superior electrical conductivity, high specific surface area and high thermal and chemical stability, we made an attempt to employ it as an electrode material for non-aqueous SC applications.\textsuperscript{20,21} Previously, Ruoff and co-workers\textsuperscript{17,18,22} have reported the utilization of such graphene-based materials as electrode material for non-aqueous SC applications by employing ionic liquids as electrolyte solutions. Unfortunately, no cycleability study has been reported, hence we set out to investigate the electrochemical performance of such graphene-based symmetric SC using conventional Li-ion battery electrolytes up to 5000 galvanostatic cycles.

In addition to the supercapacitive properties of graphene, the possibility of using the same as anode material for LIBs has also been explored in half-cell configurations.\textsuperscript{23–25} Generally, high energy density LIB requires good performance anodes with capacity more than commercially available graphitic anodes (\textasciitilde 372 mAh g\textsuperscript{−1}). Due to the unique two dimensional structures of graphene nanosheets capable of adsorbing Li\textsuperscript{+} ions on both sides turbostatically, it provides a maximum reversible capacity of \textasciitilde 744 mAh g\textsuperscript{−1}.\textsuperscript{17,24} Further, graphitic anodes are involved in Li-insertion/extraction reaction, and under high current operations such anodes endure the problem of Li-plating issues and poor cycleability, which in turn provide a poor power density of Li-ion power packs. Whereas in graphene nanosheets pseudocapacitive storage mechanism certainly increases the power density as well without compromising energy density and this makes graphene nanosheets as an attractive anode material for LIB applications.\textsuperscript{26–28}

From the applications standpoint scalable synthesis of graphene nanosheets is very crucial for high performance SC and LIB applications.\textsuperscript{9} Most solution processed graphene nanosheet preparations involve the usage of environmentally hazardous reagents such as hydrazine hydrate, NaBH\textsubscript{4}, hydroquinone, sodium azide, dimethyl hydrazine etc., to reduce graphite oxide (GO) in water medium, since it is heavily loaded with oxygen containing functionalities such as (-COOH, -OH, -C=O etc.).\textsuperscript{20,29} Hence, cost-effective and eco-friendly approach is warranted for the synthesis graphene nanosheets. At the same time, it is important to evaluate whether the quality of such green-synthesized graphene nanosheets is adequate for realistic charge storage applications. In this work we have evaluated the performance of triethylene glycol reduced graphene oxide (TRGO) nanosheets\textsuperscript{29} for non-aqueous energy storage applications and show that such sheets exhibit excellent performance in these application domains.

II. EXPERIMENTAL

High purity 99.8\% graphite powder was purchased from Alfa Aeser. For GO and TRGO synthesis KMnO\textsubscript{4}, NaNO\textsubscript{3}, Conc. H\textsubscript{2}SO\textsubscript{4}, Conc. HCl, NH\textsubscript{3}, 30\% H\textsubscript{2}O\textsubscript{2}, and trigol were purchased from Merck and used as such. Modified Hummers method was used for the synthesis of GO.\textsuperscript{29} It mainly involves concentrated H\textsubscript{2}SO\textsubscript{4} mediated oxidation of graphite powder in the presence of strong oxidizing agent KMnO\textsubscript{4}. Briefly, in an ice-water bath 5 g of graphite powder was mixed with 3.75 g of NaNO\textsubscript{3}. To this 375 mL of Conc. H\textsubscript{2}SO\textsubscript{4} was added slowly. The solution was stirred for getting homogeneous mixture and subsequently 22.5 g of KMnO\textsubscript{4} was added slowly. The slurry thus obtained was cooled for additional 2 h in the same ice-water bath. At this stage the ice bath was removed and the slurry was further stirred at room temperature for \textasciitilde 5 days yielding a brownish slurry. This slurry was then diluted with 700 ml 5\% H\textsubscript{2}SO\textsubscript{4} solution at 98 °C. Finally, 15 ml 30\% H\textsubscript{2}O\textsubscript{2} was added to the above solution. The GO solution was then subjected for purification to remove inorganic impurities. Reduction of GO was then carried out in non-aqueous medium and is described in details elsewhere.\textsuperscript{29} Briefly, sufficient quantity i.e. 100 mg of purified GO was subjected to exfoliation in 100 ml trigol for 1 h in sonicator bath followed by reduction by heating in argon atmosphere at \textasciitilde 278 °C. The obtained product was kept for drying after washing several times with deionised water and methanol.
Powder XRD pattern was recorded using Philips X’Pert PRO. Raman spectroscopy was carried out using confocal micro-Raman spectrometer LabRAM ARAMIS Horiba Jobin-Yvon apparatus with laser excitation wavelength of 532 nm. Brunauer-Emmett-Teller (BET) surface area measurements were conducted using Quantachrome (Nova 3200 e) Surface area & Pore size analyzer. Morphological features of TRGO were analyzed by FE-SEM (Hitachi S-4200) and HR-TEM (HR-TEM, FEI Tecnai 300). All the electrochemical measurements were conducted in two electrode coin-cell (CR2016) assembly. For the fabrication of LIB anode, composite electrode was made up of 5 mg of TRGO, 1 mg of Super-p and 1 mg of conductive binder (Teflonized acetylene black, TAB-2). Then, it was pressed on a 200 mm² stainless steel mesh, which served as the current collector, and dried at 60 °C for 4 h under vacuum before conducting cell assembly under Ar filled glove box. The test cells (half-cell) were composed of TRGO as an anode and metallic lithium as cathode, separated by microporous glass fiber separator (Whatman, Cat. No. 1825 047, UK). One molar (1 M) LiPF₆ was dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) 1:1 wt.% mixture (obtained from DAN VEC) which was used as electrolyte. In the text it is referred to as EC:DEC. For the supercapacitor assembly, composite electrodes were made consisting of 4 mg of TRGO, 2 mg of Super-p and 1 mg of TAB-2 loading. SC were assembled with two symmetric electrodes and separated by Whatman paper and filled with the above electrolyte solution. Pictorial presentation of cells under study is shown in electronic supplementary information (ESI) FIG S1. Cyclic voltammetric (CV) studies were carried out using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat. Galvanostatic cycling profiles were recorded using Arbin battery tester (BT 2000) at ambient temperature conditions.

III. RESULTS AND DISCUSSION

Fine synthesis of GO from graphite (oxidation) and its conversion in the presence of trigol to TRGO (reduction) was characterized by XRD, UV-vis absorption spectroscopy, Raman spectroscopy, XPS, thermo gravimetric analysis (TGA) as partly discussed in our previous work. The key XRD and Raman data for three samples (graphite powder, GO and TRGO) are shown in Figure 1(a) and 1(b) respectively. The substantial elimination of oxygen containing functionalities from GO was further confirmed by FTIR spectroscopy. Figure 1(c) shows the FT-IR spectra for GO and TRGO. Three main stretching frequencies of GO at ∼1616 cm⁻¹ (O-H bending, epoxide group or ring vibrations), 1722 cm⁻¹ (C=O) and ∼3350 cm⁻¹ (O−H) are completely eliminated and new band in olefinic (i.e. C≡C) region is clearly observed. The HR-TEM analysis was carried out for thin and sheets-like morphological features of TRGO. Figure 1(d) (i) and (ii) show representative FE-SEM and HR-TEM image for TRGO respectively. Additional HR-TEM images are shown in the (ESI) FIG S2. The thickness of the as-prepared TRGO was observed by atomic force microscopy (AFM). The images (FIG S3, ESI) confirm presence of few layers of graphene nanosheets; the average measured height for TRGO being ∼8-10 nm. The BET surface area of TRGO is found to be 62 m² g⁻¹.

Cyclic voltammetry (CV) was used to study the supercapacitive behaviour of TRGO nanosheets in symmetric two electrode configuration between 0-3 V. Figure 2(a) represents the CV traces of symmetric supercapacitor cycled at different scan rates from 1 to 50 mV s⁻¹. Rectangular shape with mirror like CV signatures indicates a purely capacitive behaviour of TRGO nanosheets. It is obvious to notice that increasing sweep rate leads to a decrease in net charge under the curve. At higher scan rates the surface of the active material (TRGO) is only involved in the electrochemical reaction rather than bulk which results in a decrease in specific capacitance. As per the energy storage mechanism, during charging process both anions (PF₆⁻) and cations (Li⁺) are adsorbed on the graphene nanosheets, whereas the process is reversed during discharge. Further, the electrochemical performance of hydrazine reduced graphene is also given in figure 2(b) for comparison under the same testing conditions. A small variation in the electrochemical performance of such systems is known to occur due to the specifics of the synthetic procedures employed for the preparation of such graphene nanosheets. It is worth noticing that the observed current responses for both graphene based systems are found to be comparable to each other, which clearly indicates that trigol
reduction is beneficial for the synthesis of high performance supercapacitor electrode component with environmental friendliness.

Galvanostatic charge-discharge studies were conducted for the symmetric configuration and typical charge-discharge curves at various current densities are obtained as given in Figure 3.

The specific capacitance ($C_s$) values are calculated according to the following equation,

$$C_s = 2 \times \frac{I}{m \cdot \frac{dv}{dt}}$$

where, $C_s$ is the specific capacitance (F g$^{-1}$), $I$ is current applied, $m$ is the mass of single TRGO electrode pressed on stainless steel mesh, $dv/dt$ is the value of slope obtained from the discharge curve. The $C_s$ of 97, 80, 67, 52 and 25 F g$^{-1}$ are noted for current density values of 0.1, 0.5, 1, 2 and 5 A g$^{-1}$, respectively. The observed values are highly comparable to the previous reports by Ruoff and co-workers,$^{17,18}$ in which the authors used ionic liquids (1 M tetraethylammonium tetrafluoroborate...
FIG. 2. Cyclic voltammetric traces of (a) triethylene glycol reduced graphene oxide (TRGO) and (b) hydrazine reduced graphene in symmetric supercapacitor configuration with 1 M LiPF$_6$ in EC:DEC electrolyte solution recorded between 0-3 V at various scan rates.

(TEA BF$_4$) in acetonitrile or propylene carbonate) as electrolytes in single electrode configuration and such a system delivered a specific capacitance of $\sim 112$ F g$^{-1}$. Further, the cycleability of symmetric supercapacitor was evaluated between the 0-3 V at a current density of 2 A g$^{-1}$ up to 5000 cycles and the data are shown in Figure 4.

It is clear that symmetric supercapacitor delivers a good cycleability with capacitance retention of over $\sim 80\%$ even after 5000 cycles. Generally, Li-ion containing organic electrolytes are reactive with the carbonaceous electrodes via side reactions. As a result, unwanted mass (inorganic by-products) builds up over the surface of the electrode, reducing the active area for the electrochemical reaction and increasing the cell resistance. Therefore, specific capacitance value decreases somewhat under the prolonged cycling.

Unfortunately, there is no extended cycleability of non-aqueous symmetric supercapacitors to be able to compare with the present values. However, recently Kim et al. have reported 67% capacitance retention in the ionic liquid medium after 2000 cycles in the case of vertically aligned carbon nanotube (CNT) based non-aqueous supercapacitor. Further, such an excellent performance
FIG. 3. Typical galvanostatic cycling profiles of triethylene glycol reduced graphene oxide (TRGO) in symmetric supercapacitor assembly with 1 M LiPF₆ in EC:DEC electrolyte solution recorded between 0-3 V at various current densities.

FIG. 4. Cycling profiles of triethylene glycol reduced graphene oxide (TRGO) in symmetric supercapacitor assembly with 1 M LiPF₆ in EC:DEC electrolyte solution recorded between 0-3 V at current density of 2 A g⁻¹. Inset: Ragone plot of non-aqueous symmetric supercapacitor. The energy and power densities were calculated by the data obtained from figure 3.

is mainly due to the usage of conventional Li-ion battery electrolytes, wherein the anionic size is also close to BF₄⁻ anions.¹⁶ Figure 4 inset shows the plot of specific energy vs. specific power densities and the values are calculated based on the equation given in our previous reports.³², ³⁵ TRGO based supercapacitor is capable of delivering maximum energy and power densities of 60.4 Wh kg⁻¹ and 0.15 kW kg⁻¹, respectively. The observed energy density values are higher than the aqueous system comprising graphene based electrodes and other carbon based systems as well.⁶–⁹, ¹⁴

Li-storage properties of TRGO nanosheets as anode were evaluated in half-cell configurations (Li/TRGO) by both potentiostatic and galvanostatic measurements. First, cyclic voltammetric traces were recorded between 0.005-3 V vs. Li at scan rate of 0.1 mV s⁻¹ and the result is given in Figure 5. In the first cathodic sweep, decomposition of electrolyte is apparently evident at lower potentials (<∼0.7 V vs. Li), which consume excess lithium ions and it is not reversible.³⁶ The decomposed solvent molecules form the solid electrolyte interphase (SEI) over the surface of the

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FIG. 5. Cyclic voltammogram of triethylene glycol reduced graphene oxide (TRGO) in half-cell configuration (Li/TRGO) and cycled between 0.005-3 V vs. Li, in which metallic lithium serves as both counter and reference, electrodes.

to graphene nanosheets, which mainly comprises of polyethylene oxide, polycarbonates and some insoluble inorganic by-products. However, in the subsequent anodic sweep and rest of the cycles, no noticeable reduction/oxidation curves are apparent. In addition, almost rectangular shape of CV traces clearly indicates that the Li-ions are adsorbed on the both sides of the graphene nanosheets or in other words pseudocapacitive storage. Reduction of area under the curve during the cycling up to 10 cycles corresponds to the decrease in the specific capacity values.

Galvanostatic charge-discharge profiles were conducted between 0.005-3 V vs. Li at current density of 37 mA g⁻¹ in ambient temperature conditions. The cell showed the initial discharge capacity of ~1178 mAh g⁻¹ (Figure 6(a)) with reversible capacity of ~704 mAh g⁻¹. Irreversible capacity is found ~474 mAh g⁻¹ (40%) and this huge irreversible capacity loss is common in the case of all carbonaceous materials during first cycle except graphite. In the second cycle, TRGO half-cell displayed the discharge capacity of 600 mAh g⁻¹ with columbic efficiency of ~95%.

As mentioned earlier, huge irreversible capacity loss is expected for all the cases of anode materials except insertion type which is mainly attributed to the decomposition of solvent molecules and subsequent formation polymeric films. The polymeric films are the main components in the solid electrolyte interphase (SEI) formed over the surface of the electrode. The plot of discharge capacity vs. cycle number is given for 30 cycles in figure 6(b). Capacity fading is observed during the cycling and capacity of 365 mAh g⁻¹ is noted after 30 cycles, which is 52% of reversible capacity. Yoo et al. reported that chemically synthesized graphene nanosheets show reversible capacity of 540 mAh g⁻¹ and retains 54% of its capacity after 20 cycles. In their work on graphene nanoribbons Bhardwaj et al. showed a reversible capacity of ~820 and ~520 mAh g⁻¹ for first and 14th cycles, respectively.

Very recently, Vargas et al. have summarized the Li-storage properties of graphene nanosheets and concluded that, “The quality and structure of the graphene nanosheets can differ from batch to batch, which can make devices behave inconsistently.” Further, it is apparent to notice that graphene nanosheets exhibited capacity fading in half-cell configurations, irrespective of the synthesis conditions employed with different reversible capacity values. However, further studies are in progress to suppress the capacity fade during cycling. Such pseudocapacitive storage mechanism in graphene nanosheets certainly improves the power density of Li-ion power packs and thereby enabling and ability to power the HEV and EV. Rate capability study was conducted for TRGO nanosheets with various current densities and presented in figure 6(c). The cell delivered the reversible capacities of ~677, 282, 152, 92 and 54 mAh g⁻¹ for current density of 0.037, 0.5, 1, 2 and 4 A g⁻¹, respectively.
FIG. 6. (a) Galvanostatic discharge-charge profiles of triethylene glycol reduced graphene oxide (TRGO) in half-cell configuration (Li/TRGO) at current density of 37 mA g$^{-1}$ between 0.005-3 V vs. Li (integer number represents cycle number) (b) Plot of discharge capacity vs. number of cycles and (c) Rate capability studies of Li/TRGO cell at various current densities.

It is apparent to notice that the test cells are capable of delivering stable capacities at relatively high current rates. Such high current performance of TRGO nanosheets is also noticed in the symmetric supercapacitor studies as well. This clearly indicates that the TRGO nanosheets can be effectively used for high power applications irrespective of the non-aqueous storage devices used.

IV. CONCLUSIONS

To summarize, graphene nanosheets prepared by eco-friendly trigol assisted reduction process are evaluated for charge storage applications in non-aqueous media. Excellent cycleability was noted for TRGO in non-aqueous symmetric supercapacitor assembly with over $\sim$80% capacity retention.
after 5000 cycles. The symmetric supercapacitor delivered the maximum energy and power densities of 60.4 Wh kg$^{-1}$ and 0.15 kW kg$^{-1}$, respectively. The Li-storage properties of TRGO nanosheets were also evaluated in half-cell configuration (Li|TRGO). The cell delivered the reversible capacity of $\sim 705$ mAh g$^{-1}$ at current density of 37 mA g$^{-1}$ with noticeable amount of capacity fade. At high current rates, stable cycling profiles were noted at ambient temperature conditions.

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30 See supplementary material at http://dx.doi.org/10.1063/1.4802243 (Pictorial presentation for test cells under study. HR-TEM and AFM images for trigol reduced graphene oxide).