An anthraquinone-functionalized reduced graphene oxide as electrode material for rechargeable batteries

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The use of electro-active organic compounds as electrode materials in rechargeable batteries has been a very active research topic due to their high theoretical capacity, availability of various redox potentials depending on the electro-active group, ease of modification of properties, and improved safety. However, the issue of solubility in electrolytes limits their applications in batteries. The most common solutions for this problem involve incorporation of these organic molecules into the insoluble polymeric structures and trapping of these inside porous carbon materials. Here, we have demonstrated the covalent attachment of anthraquinone (AQ) derivatives via nitrene chemistry onto reduced graphene oxide (RGO) as another alternative. The successful synthesis of the RGO functionalized with anthraquinone groups (RGO-AQ), and its utilization as cathode materials in Li-batteries have also been demonstrated. The cells with RGO-AQ used as cathode materials initially discharged 126 mA h/g when cycled between 1.8 and 3.2 V at the rate of 5.35 mA/g in LiPF6/EC:DEC (1:1) electrolyte, and discharged 185.7 mA h/g when cycled between 1.3 and 3.6 V against Li metal at the rate of 6.0 mA/g in LiClO4/PC electrolyte.

1. Introduction

Quinones and their derivatives have found applications in a wide range of areas due to their reversible electrochemical redox behavior [1]. These areas include the industrial production of H2O2 [2], biochemistry [3] and medicine [4–6]. Quinone derivatives have attracted considerable interest as electroactive groups in rechargeable lithium and Li-ion batteries due to their properties allowing for the development of high energy density materials [7–11]. These properties include high theoretical charge capacities, relatively high redox potentials against Li, a high degree of reversibility of their electrochemical reactions, and their propensity for manipulation of their redox potential through the introduction of various functional groups. Anthraquinone (AQ) which belong to the quinone family also shows electrochemical activity [1,12,13].

Organic rechargeable batteries based on redox polymers bearing AQ as the electro-active group have been reported in the literature [8,14–19]. A prototype air cell constructed with a poly(2-vinylanthraquinone) anode and MnO2/C cathode exhibited a discharging capacity of 214 mA h/g (93% of its theoretical capacity) and a working voltage of 0.63 V at 34 A/g discharge rate for 500 cycles [15]. The first relatively successful example of utilization of an AQ-functionalized polymer as cathode material in a lithium battery was demonstrated by Song et al. [20]. Despite its high initial discharge capacity of 251 mA h/g at 2.15 V average working potential, this battery with a poly(anthraquinonyl sulfide) (PAQS) cathode-active material lost more than half of its capacity after 50 charge-discharge cycles between 1.4 and 3.5 V at 50 mA/g. In another recent study, a redox polymer bearing four AQ units per monomer was also incorporated into a lithium battery. It provided an initial discharge capacity of 84 mA h/g at 14 mA/g which faded only very little over 50 cycles in 1.4–3.5 V range [14]. Most of these AQ-based materials exhibited good rate performance retaining 50–70% of their capacities at high current rates.
An interesting example of a photo rechargeable battery is the one employing a photo anode made of poly(2-vinyl AQ) sandwiched between indium titanium oxide (ITO) and a boron-dipyrromethene (BODIPY) dye, and an O₂ cathode composed of a MnO₂/Carbon composite in an aqueous KOH electrolyte [21]. The battery can be photo charged to a capacity of 166 mA h/g and can discharge 143 mA h/g at 0.63 V at the rate of 0.25 mA. Interestingly, O₂ supply for the cathode comes from two sources: air and oxidation of hydroxide ions at the anode.

The covalent attachment of electro-active molecules to conductive carbon substrates has been proven to be a viable means of increasing electron transfer rates and preventing the dissolution of redox-active material leading to a good cycle life. Many different strategies have been reported for functionalization of various forms of carbon with molecules, such as insertion of aryl free radicals obtained via aryldiazonium salts [22–28] and Bingel reaction [29]. Graphene has also been covalently functionalized with organic molecules via two general routes: (a) reactions between reactive species such as free radicals or dienophiles and C=C bonds on graphene and (b) reactions between organic functional groups and the oxygenated groups in graphene oxide (GO) [27,30–32]. The functionalization of graphene by nitrene chemistry is also used for the preparation of graphene-based materials for different applications [32–37].

There are numerous examples of functionalization of carbon materials with AQ for different purposes [12.38–42]. An aqueous supercapacitor employing AQ-modified carbon fabric as the negative electrode together with an unmodified carbon fiber electrode, a Nafion separator, and 1M H₂SO₄ electrolyte exhibited a superior performance compared to an analogous supercapacitor which utilized two unmodified carbon fiber electrodes. Incorporation of AQ-modified carbon fiber caused an increase in capacitance by 42% and in energy density by 86% [38]. In a more recent study, high surface area Ketjenblack (KB) was modified with some quinone groups including AQ using diazonium chemistry [40]. The battery using AQ-modified KB cathode and Li metal anode in 1M lithium bis(trifluoromethane sulfonil) imide (LiTFSI) in propylene carbonate (PC) provided a charge capacity of 89 mA h/g at the current rate of 5 mA/g in 1.5–3.1 V potential range. The more impressive feature of these batteries was their high rate capabilities, maintaining a capacity of 58 mA h/g even at 1500 mA/g current rate.

In this article, we have described, for the first time, the synthesis of an azide functionalized AQ derivative (AQ-EA), and its use in one-step functionalization of reduced graphene oxide (RGO) by nitrene chemistry (simple thermal degradation of the azide group to yield nitrene), with varying amounts of AQ-EA to yield AQ-modified RGOs (RGO-AQ). We have also reported the utilization of RGO-AQ as a cathode material in rechargeable Li-batteries. The rechargeable lithium batteries constructed with these cathode materials exhibited quite high charge capacities and good rate capabilities.

2. Experimental

2.1. The synthesis

In this study, RGO is synthesized by hydrazine reduction of GO which was prepared by oxidation of natural graphite flakes by Tour’s method [43]. GO obtained was reduced to RGO by hydrazine induced reduction method. RGO was utilized as a conductive substrate for direct covalent functionalization with electro-active molecules. It is modified by an azide-functionalized anthraquinone derivative (AQ-EA) in various ratios via a simple approach based on nitrene chemistry. These AQ-functionalized RGO samples are referred to as RGO-AQ 50%, RGO-AQ 200% and RGO-AQ 500% indicating the weight ratio of AQ to RGO used during modification. The synthesized GO, RGO, and RGO-AQ materials are characterized by using various techniques to evaluate the effects of modification in physical, chemical and electrochemical properties. Please see the Supplementary Data for all details.

2.2. Methods of characterization

The electrochemical properties of RGO and AQ functionalized RGO samples were investigated by preparing their composites with addition of 15% teflonized acetylene black (TAB) in N-methyl-2-pyrrolidone (NMP) solvent. Obtained slurry of composites was uniformly loaded on Al or Ni current collector and dried in vacuum oven at 80 °C for 24 h, then roll-pressed. The amounts of composites loaded on the current collector varied between 0.7 and 1.3 mg/cm².

Split cells (supplied by MTI Co.) were used for battery construction, and cells were assembled in an Argon-filled glove box. RGO or AQ functionalized RGO electrodes were used as cathode and Li metal as the anode in two electrode configuration. 1M LiClO₄ in PC and 1M LiPF₆ in EC: DMC (1:1) were used as the electrolyte and the Whatman Glass microfiber filter (Grade GF/A) separator soaked with electrolyte was placed between RGO and Li electrodes. Electrochemical profiles were first investigated by cyclic voltammetry (Gamry Reference 3000 Potentiostat) with a scan rate of 0.05 mV/s at different potential ranges. Then galvanostatic charge-discharge tests were carried out at various current densities using multichannel battery analyzer (MTI 8 Channels Battery Analyzer with a current range of 0.1–10 mA and a potential range of 0.0–5.0 V). The specific charge capacities were calculated by taking the entire electrode material weight into consideration, rather than the actual material mass which constituted 85% by mass of the electrode material.

The weight percent of the AQ moieties present in the electrode material was calculated from the cyclic voltammetry (CV) data as follows. The quantity of the charge delivered by the AQ moieties was obtained by the integration of the Faradic peak in each cyclic voltammogram. Then the amount of substance was calculated by using the correlation between the charge that must be delivered theoretically per gram of the AQ moiety (182.8 mA h/g = theoretical specific charge capacity for the structure of the electro-active group) whose calculation is shown in Supp. Data. The weight percentage of the substance in the electrode material was calculated by dividing this calculated amount by the active compound weight present in the electrode material.

The proton nuclear magnetic resonance (¹H NMR) was recorded using Bruker Ultra Shield Plus, Ultra long hold time 400 MHz NMR Spectrometer for the characterization of synthesized azide functionalized AQ derivative (AQ-EA).

The Raman spectra of the samples were recorded with Thermo Scientific DXR Raman microscope by applying 532 nm (2.33eV) laser excitation with 0.5 mW power. The measurements were carried out directly on powdered samples.

Fourier transform infrared (FT-IR) analysis by the attenuated total reflection (ATR) technique was recorded on a Bruker alpha-P in transmission mode in the range of 4000–400 cm⁻¹ to investigate changes in structural modification of samples.

The crystal sizes of graphite, GO, RGO and RGO-AQ samples were determined by X-ray diffraction (XRD) measurements on a Rigaku D/Max—IIIC using Cu Kα radiation (λ = 1.54056 Å). The diffraction data was collected in the range of 3°–80° with a step size of 0.02°/step.

The atomic contents of the graphite, GO, RGO, and RGO-AQ samples were evaluated by XPS analysis. XPS studies were carried out on a Thermo Scientific K-Alpha X-ray Photoelectron spectrometer
using Al-Kα micro-focused monochromator by excitation at a spot size of 400 μm with a pass energy of 50eV (Energy Step Size:0.100eV). The peak area concentrations of C, O, S and N elements at the surface of each sample were obtained from survey data. Types of each functional group and their respective percentages were analyzed by using the CASAXPS fit program by a nonlinear least-squares fitting the areas according to some ratio of Lorentzian and Gaussian mathematical functions after Shirley background removal.

Thermogravimetric analysis (TGA) of samples was conducted on a STA 6000 model Perkin Elmer Instruments. The TGA thermographs were recorded for ca. 3–4 mg of powder sample at a heating rate of 10 °C/min in the temperature range of 30 °C–750 °C under the nitrogen atmosphere.

Scanning electron microscope (SEM) images were recorded using a Philips XL30 SFEG scanning electron microscope that was operated at an accelerating voltage of 15 kV, and the samples were placed directly on the surface of conductive carbon adhesive tape on copper sample plate during measurement.

The electrical properties (I–V curve) of samples were measured by the four-probe method using Keithley 2400 model source meter. Samples were produced by compression of about 23.5–24 mg powdered sample into pellets with 11 mm radius using 6-ton pressure.

3. Results and discussion

The synthesis scheme for anthraquinone functionalized RGO (RGO-AQ) is shown in Fig. 1. The synthetic sequence leading to RGO-AQ started with the synthesis of GO from natural graphite according to the Tour method. Then, GO was reduced to RGO with hydrazine hydrate and ammonia. According to this scheme, 2-azido-ethanol (2), obtained from 2-chloroethanol (1) as shown in Fig. 1, was reacted with 9,10-dioxo-9,10-dihydroanthracene-2-carboxylic acid (AQ-2-COOH) to yield the anthraquinone derivative with alkyl azide functionality (AQ-EA). The RGO obtained as described above was mixed with different weight ratios of AQ-EA in DMAc (1/0.5; 1/2; 1/5 w/w of RGO:AQ-EA). The reaction mixture was vigorously stirred and refluxed at 165 °C under Ar(g) for 24 h. The RGO derivatives functionalized with AQ at different w/w ratios (termed as RGO-AQ50%, RGO-AQ200%, RGO-AQ500% according to the weight ratio of AQ-EA to RGO) were obtained after filtration and repeated washings with acetone, CH2Cl2, and ethanol. For a complete description of the synthesis and characterizations, please refer to the Supp. Data.

One evidence for the successful syntheses of RGO-AQ by the reaction between the azido compound the AQ group (AQ-EA) and RGO came from FT-IR analysis (Fig. 2). The disappearance of the azide peak at ~2100 cm⁻¹ due to the stretching vibration of azido group in AQ-EA, the increase in the intensities of the Ar C—H dop peak at 692 cm⁻¹ and carbonyl stretching peak at 1660 cm⁻¹ with
the increased degree of functionalization of RGO with AQ group reflected the incremental degree of AQ-functionalization in the series RGO-AQ 50%, RGO-AQ 200% and RGO-AQ 500%.

The Raman analysis of powdered samples was performed using a 532-nm laser beam with very low power (0.5 mW). The data collected from at least three different regions of each sample were well overlapped, ensuring the homogeneity of powdered samples (Table S1 in Supp. Data summarizes the Raman analysis results).

The typical defect activated D band (at \( \sim 1350 \text{ cm}^{-1} \)) and the G band (at \( \sim 1580 \text{ cm}^{-1} \)) arising due to sp\(^2\) bond vibrational modes were observed in all Raman spectra (Fig. 3). 2D bands (at \( \sim 2700 \text{ cm}^{-1} \)) were also observed in the second order-two phonon region of all Raman spectra. A broad and low-intensity band composed of three peaks (2D, D + G and 2D\(^0\)) is also eminent in the Raman spectra of RGO and RGO-AQ samples between 2000 and 3400 \text{ cm}^{-1}.

Compared to that of graphite, the Raman spectrum of GO showed a more broadened G band blue shifted to 1599 \text{ cm}^{-1}. Also, the D band at 1350 \text{ cm}^{-1} became more intense, leading to a higher \( I_D/I_G \) ratio which indicates a reduction in the size of the in-plane sp\(^2\) carbon domains, possibly due to the extensive oxidation. The \( I_D/I_C \) ratio in the Raman spectrum of the RGO sample was increased compared to that in GO. This is generally contradictory to what is expected since the reduction should entail a healing of the defected sites, leading to a lowering of the D band intensity accompanied by an increase in the G band intensity. This may be explained by the creation of the smaller sized new graphitic domains which are more numerous in number [44]. This may mean that the reduction caused disintegration of the graphitic sheets and formation of a high number of smaller sized platelets in RGO. This was supported by the SEM images of the GO and RGO samples which showed that RGO and RGO-AQ appeared as aggregations of wrinkled graphene sheets which are smaller in size compared to GO (Fig. S2 in Supp. Data). Additionally, the \( I_D/I_C \) ratio of RGO which had nitrogen atom incorporated into the graphitic layers during reduction process with hydrazine, exhibited resembled that of the nitrogen-doped graphene (N-graphene). The results seen in the literature confirm the much larger values of \( I_D/I_C \) ratios in N-graphene compared to those in C-graphene, (0.59 in C-graphene vs. 1.33 in N-graphene) [45]. This larger \( I_D/I_C \) ratio is ascribed to the structural defects and edge plane exposure caused by nitrogen atom incorporation into the graphene layers [46]. The XPS and elemental analysis results discussed below (also presented in Supp. Data) validated incorporation of nitrogen into RGO and RGO-AQ structures which was absent in graphite and GO samples. Also, The \( I_D/I_C \) ratio, which is generally taken as a measure of inter-defect distance in graphene, is considered to be unreliable when applied to the highly defected and amorphous samples such as our GO, RGO and RGO-AQ samples. In amorphous carbon, the \( I_D/I_C \) ratio is proportional to the square of the crystallite size (still containing sp\(^2\) hybridized domains) and it would decrease with the addition of defects [47].

Both physically and chemically induced defects are expected to affect the intensity of 2D band [48]. In RGO-AQ samples, the \( I_D/I_C \) ratio was observed to go higher as the feed ratio of AQ-EA introduced into the reaction was increased, indicating a higher level of modification of RGO with increasing AQ-EA feed.

In the Raman spectra of RGO-AQ samples, another band at \( \sim 1660 \text{ cm}^{-1} \) observed as a side-band next to the G band was intensified as the degree of AQ-functionalization increased. This band is known as the D\(^0\) band. Since this band cannot be seen at crystalline graphite, it has most probably emerged due to the destruction of finite sized crystallites, and thus it can be classified as a defect induced Raman feature [49].

The chemical analyses of powder samples of GO, RGO, and RGO-AQ samples were conducted by X-ray photoelectron spectroscopy (XPS) and by elemental analysis (EA) (Figs. 4 and 5, Tables S2 and S3).
The enormous increase in O% in GO sample (25.97%) with AQ moieties. The area under the C, N and O peaks in the XPS version of this figure can be viewed online.)

The deconvolution of the experimentally obtained C 1s, O 1s and N 1s peaks were performed by using the XPS Peak 4.0 software. Determination of the functional groups and their respective percentages were done via a curve fitting procedure performed on the experimental data utilizing a mixture of Lorentzian and Gaussian functions (see Figs. S3 and S4, Tables S4–S6 in Supp. Data). The structural variations among the samples are expected to produce discrepancies in the electronic environments experienced by the elements analyzed. These discrepancies can cause sample-to-sample variations in the bonding energies for each element in a specific functional group. Thus, making comparisons among different samples for the same element in a specific functional group became quite complicated, especially for C and O elements which are possibly present in a larger variety of functional groups compared to N. Therefore, the deconvoluted data were not fully interpreted, except for the N 1s data which seemed to be less affected by the electronic environments present in different samples.

Fig. 4. The XPS analysis results for graphite, GO, RGO and RGO-AQ samples. (A colour version of this figure can be viewed online.)

in Supp. Data) to elucidate the level of surface modification of RGO with AQ moieties. The area under the C, N and O peaks in the XPS survey scan data (Fig. 5) was calculated to yield the atomic percentages of C, N and O elements in the samples (Table S2 in Supp. Data). The enormous increase in 0% in GO sample (25.97%) with respect to that of graphite (8.69%) and its significant decrease in RGO (8.49%) with respect to that in GO indicated a vigorous oxidation of graphite to GO and a successful reduction of GO to RGO, respectively. The variations of C and O percentages seemed uncorrelated with the degree of AQ-functionalization. This may be attributed to the removal of some oxygenated functional groups and defects during the high-temperature functionalization reaction.

The atomic percentage of N was observed to increase steadily, although in very small quantities, as the RGO was reacted with higher amounts of AQ-EA (Fig. 5). Similar trends were observed in the atomic weight percentages of N obtained by elemental analysis (Table S3 in Supp. Data) and in the C/N ratios obtained through XPS and elemental analyses (Fig. 6). These results possibly reflected an increasing degree of functionalization of RGO with AQ-moieties, but the degree of functionalization did not seem to closely follow the AQ-EA feed ratio in the functionalization reaction. This may be attributed to a change in the composition of RGO when it was subjected to reflux at 165 °C for 24 h during the functionalization reaction leading to the removal of some oxygen-containing groups from RGO surface [36]. Also, the nitrogen atom constitutes only a small percentage (3.03% by number and 4.78% by weight) of the AQ nitrene derivative inserted onto the RGO surface. Another reason may be the total elimination of nitrogen atoms from some of the AQ-EA molecules due to thermal degradations occurring during the diazotization of the AQ-EA, which can produce reactive radical species which can be inserted into the RGO surface [50–52]. The other reason is the possible side reactions of azido compounds which may occur during this thermal reaction, yielding unreactive products that cannot insert into the RGO surface, thus causing a reduction in the functionalization yield [50–52].

The appearance of an intense broad peaks centered about 286.3 eV in C1s XPS spectrum of GO (Fig. 5) which is associated with C–O bond of hydroxy/epoxy, C=O bond of ketone/carboxyl functionalities [53] also indicates a rigorous oxidation of graphite, whereas its disappearance in C1s spectrum of RGO is indicative of a successful reduction involving the elimination of these oxygenated groups which will restore the sp2 carbon network.

The deconvolution of the N1s spectra of RGO, RGO-AQ 200% and RGO-AQ 500% yielded a peak at 398.7 ± 0.2 eV ascribed to pyridine-like structures, a peak at 400.3 ± 0.3 eV attributed to the nitrogen atoms in pyrrolic or amine type moieties, and a peak at 402.4 ± 0.5 eV contains a contribution from quaternary or protonated nitrogen [54]. The presence of such peaks in RGO samples proved incorporation of different types of nitrogen atoms, including those inserted into aromatic rings in the graphene layers during reduction of GO with hydrazine. The reaction with a higher feed of AQ-EA mostly produced pyrrolic nitrogen incorporation evidenced by the increase in the contribution from the peak at 400.3 ± 0.3 eV (the values for RGO, RGO-AQ 200% and RGO-AQ 500% are 32.7%, 67.1%, and 78.5%, respectively).

The thermal gravimetric analysis (TGA) under nitrogen environment measured up to 750 °C provided interesting thermal property information about RGO and RGO-AQ samples (Fig. 7). The azido functionalized molecule (AQ-EA) showed a higher thermal stability than expected up to 345 °C losing 49.3% of its weight which was comparable that of GO (49.5%). Probably, the weight loss of GO was largely due to the presence of some thermally labile oxygenated functional groups on its surface and the absorbed water. GO lost about 69.4% of its initial weight at 750 °C, whereas AQ-EA lost 80.4% of its weight at this temperature. The success of the reduction of GO to RGO which involved elimination of thermally labile surface groups and restoration of conjugated carbon network was also evidenced by the much higher stability of RGO (weight loss of 31.2%) at 750 °C compared to GO, as well as its high electrical conductivity of 2016 S/m as can be seen in Fig. S5 in Supp. Data. The same figure also shows a decline in conductivities and increase in the sheet resistance values as the degree of AQ-functionalization increased in the sample series of RGO-AQ (RGO- AQ 50%, RGO-AQ 200% and RGO-AQ 500%).

Interestingly, the thermal stabilities of all AQ-functionalized samples remained higher than that of RGO below 575 °C (Table S7 in Supp. Data). RGO-AQ 200% and RGO-AQ 500% samples lost slightly more weight than RGO, but RGO-AQ 50% lost slightly less weight than RGO at 750 °C.

The AQ-EA, RGO, RGO-AQ 50%, RGO-AQ 200% and RGO-AQ 500% lost only very small amount from their initial weights at 225 °C (5%,
5.2%, 3%, 1% and 1% respectively, as shown in Table S7 of Supp. Data). AQ-EA seemed to lose a large portion of its weight (57.6%) between 225 and 400 °C whereas RGO lost only 10.5% of its weight (Table S8 in Supp. Data). Based on this result, the largest portion of weight loss in RGO-AQ samples may be expected in this temperature interval to be due to thermal fragmentation of the AQ-based functional moiety, accompanied by some minor contribution from oxygenated functional groups and other defects. However, in the 225–400 °C interval, RGO lost about the same amount of its weight as all RGO-AQ samples did and the differences in weight loss for all these samples were small regardless of the degree of AQ-functionalization. So, the amount of weight loss occurred in all samples must be the weighted average of different kinds of fragmentations associated with the thermal degradations of all kinds of surface groups and defects including the oxygenated groups, the AQ derivative and the others, each contributing to a different extent.

Fig. 5. The C1s, O1s and N1s XPS peaks of graphite, GO, RGO and RGO-AQ samples. (A colour version of this figure can be viewed online.)
depending on the sample. Also, there should be some structural differences other than the levels of AQ-functionalization among the RGO and RGO-AQ samples, possibly due to the dissimilarities of thermal defect healing in carbon network which may have occurred during the reaction between RGO and AQ-EA which involved rather a high temperature. All these factors must be taken into account when interpreting the TGA results, rendering it to be a very complex task.

Fig. 8 shows the X-ray diffraction (XRD) analyses of the graphite, RGO, RGO-AQ 50%, RGO-AQ 200% and RGO-AQ 500% powder samples. Structural analysis was performed by the FullProf program, employing profile matching with a constant scale factor (see Table 1).

The interlayer distances (d), the number of graphene layers (N), crystallite sizes (L002—the volume average of the crystal thickness in the direction normal to the reflecting planes) were determined from the Scherrer equation; \( L = \frac{k \cdot \lambda}{b \cdot (2 \theta)} \cos \theta \) [55,56], where the geometric factor k is 0.94, \( \lambda = 1.54056 \text{ Å} \) (the wavelength of Cu-K\( \alpha \) radiation), \( \beta(2 \theta) \) is the full width at half maximum (FWHM), \( \theta \) is the angle between the incident ray and the scattering planes. The number of graphene layers (N) is calculated from the equation \( L_{002} = \frac{(N - 1) \cdot d_{002}}{C_{01}} \) [57,58].

After fitting the raw data, the results of XRD analysis of graphite

Fig. 6. The atomic percentages of C, N, and O obtained from XPS surface scan (top), and a comparison of C/N ratio obtained (bottom) by XPS and EA techniques. (A colour version of this figure can be viewed online.)
showed a pattern having the main $P6_{3}mc$ crystal symmetry (space group no:186) without any impurity. Lattice parameters were found as $a = b = 2.478058\ Å$, $c = 6.714006\ Å$, and the d-spacing was obtained from (002) Bragg reflection as 3.358 Å which were consistent with the literature [59]. The basal diffraction peak from (002) plane which appeared at 26.52° (2θ) for graphite shifted to 10.28° in the GO sample with a larger d-spacing of 8.598 Å. This is due to the oxygen-containing groups formed upon oxidation, which also causes the intercalation of $H_{2}O$ molecules between carbon sheets, resulting in an enlargement of the interlayer distance. After the reduction of RGO and its functionalization with AQ-EA, the diffraction peak appeared at about 25.2° (accompanied by a decrease in d-spacing to about 3.5 Å) in the RGO and RGO-AQ samples, while that of pristine graphene nanosheets has been reported to be observed at 26° [36,60]. The shallow and rather broad peak at ~43° (observable in graphite, RGO and RGO-AQs' XRD patterns) corresponds to the (100) in-plane hexagonal atom arrangement. 

The (002) reflections of RGO and all RGO-AQ samples are quite broad, which indicates that the nanosheets have poor ordering along the stacking direction, many being in the free form or in the form of few-layer nanosheets (N value is being around 1.5) with low crystallite size due to the rather highly defected structure [61] as also can be seen in the SEM images (Fig. S2 in Supp. Data).

Interestingly, the crystallite size and number of stacked layers (N) were calculated to be slightly bigger for all RGO-AQ samples compared to the those calculated for RGO. This may be partially due to both the healing of some of the defects present on RGO surface during its high-temperature thermal treatment with AQ-EA and the contribution from some possible π-π stacking between AQ groups introduced onto RGO surface. Among RGO-AQ samples, these values were observed to be the largest for the least AQ-functionalized RGO-AQ 50% and decreased as the degree of functionalization increased which may be related to an increase in the number of defects introduced with the insertion of AQ groups on the surface.

The peculiar higher thermal stability of RGO-AQ 50% as compared to RGO and the other more AQ-functionalized may also be attributed to the above mentioned higher crystallinity of RGO-AQ 50% due to a smaller number of defects. The lower thermal stability of RGO-AQ 200% and RGO-AQ 500% at 750 °C compared to RGO was probably due to the high degree of functionalization with thermally labile groups. The reason for the RGO-AQ 500% to be slightly more stable than RGO-AQ 200% at 750 °C is difficult to explain and may be due to a complex set of factors mentioned before related to the differences in the relative proportions of functional groups and defects with varying thermal stabilities present in these materials.

The AQs are known to undergo a two-electron reversible electrochemical reduction process. This reduction of AQ derivatives is a two-step process in which the first step involves the reduction of AQ to anion radical (AQ$^{-}$) and the second involves the reduction of AQ$^{-}$ to dianion (AQ$^{2-}$). The two processes can appear as two separate peaks or as a single broad peak in a CV analysis depending on the structure of the AQ derivative, and the electrolyte system used [1,62,63]. The merging of these two peaks into a single broad peak is quite common in the case of polymers bearing AQ moieties and of AQ moieties that are attached to a surface, because a variety of electronic environments may be experienced by the electroactive groups located in different positions in the bulk of the material, thus leading them to have a range of reduction potentials [16,17,40,64,65]. Typically, a single and rather broad two-electron reduction peak in the 2.0–2.5 V region is expected from such materials [66,67].

In our CV studies, the electrochemical properties of electrode materials were investigated against Li metal in two electrode cell systems containing either 1M LiClO$_4$ in propylene carbonate (PC) or 1M LiPF$_6$ in an equal volume mixture of ethylene carbonate: dimethyl carbonate (EC: DMC) (1:1) as the electrolytes (Figs. 9 and 10). The electrode materials were prepared by mixing RGO-AQ (85% by weight) with teflonized acetylene black (TAB) (15% by weight) to attain high enough electronic conductivity. The reversible faradic redox peak of the AQ group observable at ~2.4 V (Fig. 9) which was absent in CV of RGO itself (shown in the inset of Fig. 9) verified the presence of AQ groups on RGO surface. The RGO itself only showed a totally capacitive behavior as reflected by its rectangularly shaped CV curve. For the RGO-AQ 500% sample, the cathodic and anodic peaks were observed at ~2.34 V and ~2.49 V respectively vs Li electrode in 1M LiPF$_6$ in EC: DMC (1:1). In 1M LiClO$_4$ in PC electrolytic solution, the corresponding values were found to be ~2.28 V and ~2.57 V, respectively.

The weight percentages of the redox active AQ moieties present in RGO-AQ samples were calculated from the areas under the peaks of CV results for each sample, as shown in Table 1. The weight percentages of the redox active AQ moieties present in RGO-AQ samples were calculated from the areas under the peaks of CV results for each sample, as shown in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>X-ray diffraction parameters</th>
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<tbody>
<tr>
<td></td>
<td>2θ (°)</td>
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<tr>
<td>Graphite</td>
<td>26.51(8)</td>
</tr>
<tr>
<td>GO</td>
<td>10.28(1)</td>
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<tr>
<td>RGO</td>
<td>25.25(9)</td>
</tr>
<tr>
<td>RGO AQ 50%</td>
<td>25.18(2)</td>
</tr>
<tr>
<td>RGO AQ 200%</td>
<td>25.30(1)</td>
</tr>
<tr>
<td>RGO AQ 500%</td>
<td>25.27(1)</td>
</tr>
</tbody>
</table>

Fig. 9. Cyclic voltammetry analysis results of AQ functionalized RGO (RGO-AQ) electrodes vs. Li metal in 1M LiClO$_4$/PC. Scan rate = 0.07 mV/s, scan range = 1.4–3.2 V. Inlay: Cyclic voltammetry of RGO under the same conditions. (A colour version of this figure can be viewed online.)
anodic peaks obtained in CV studies according to the procedure described in the methods of characterization section above (Section 2.2, an example of calculation is also shown in Supp. Data), as 5.14%, 7.81%, and 25.80% for the RGO AQ-50%, 200% and 500% samples, respectively. These results confirm the deductions made previously from the XPS and EA data about the relative degrees of functionalization in RGO-AQ samples which implied an increasing degree of functionalization obtained with the higher ratio of AQ-EA feed in the functionalization reaction. However, a direct comparison of the results obtained by each analysis method will possibly exhibit the presence of discrepancies among them since each method uses a different variable amenable to different kinds of error. For example, in CV analysis the sample-to-sample variations in the contribution to the charge measured made by other groups present in the electrode material which are redox active in the same voltage region as the AQ moiety cannot be calculated. Likewise, in XPS and EA data, there is no way to account for the variations in the relative amounts and the types of surface groups which may have occurred to different extents in each sample during the thermal conversion of RGO to RGO-AQ. So, it is not possible to determine the error associated with the change in the weight and atomic percentage of nitrogen due to degradation of the oxygenated surface groups during the thermal treatment.

Cells prepared using electrode materials mentioned above were subjected to charge-discharge cycles. Fig. 11 below shows the charge-discharge behavior at comparable discharge rates for the cells employing 1M LiPF₆ in EC: DMC as the electrolyte. Although no redox activity in the CV study of unmodified RGO electrodes was detected, the cell with RGO cathode displayed a low initial discharge capacity of about 51.1 mA h/g capacity when cycled between 1.8 and 3.2 V at 4.0 mA/g rate. This may be attributed to the remnant carbonyl groups which could not be chemically reduced by the action of hydrazine hydrate [68]. A direct subtraction of this amount from charge capacities obtained from RGO-AQ samples cannot be performed since the relative quantities of these groups present in RGO, and each of the RGO-AQ samples should be different. The RGO-AQ50%, RGO-AQ200% and RGO-AQ500% discharged 126.0, 104.8 and 99.3 mA h/g at 5.0, 3.5 and 5.35 mA/g rate, respectively. Their sloping discharge curves may be attributed to the varying local chemical and electronic environments available for the AQ functional groups in the bulk of the material, leading to a range of redox potentials [68]. The cell with RGO-AQ500% also showed a high degree of cyclic stability as depicted in Fig. 12. When this cell was subjected to deeper charge-discharge cycles between 1.3 V and 3.6 V after being cycled 170 times, the first discharge provided 610.6 mA h/g which degraded quickly down to 76.8 mA h/g in the following 11 cycles (Fig. 13). This indicates the importance of the voltage range chosen for battery operation and shows that discharging below a certain voltage limit causes the deterioration of cell’s capacity to hold the electrical charge. This may be primarily due to the disintegration of the cathode material during Li insertion or removal of redox active groups from the RGO surface via electrochemical reduction below 1.5 V in this electrolyte system.

Another cell employing the RGO AQ 500% as the cathode material showed a high charge capacity of 185.7 mA h/g in 1M LiClO₄/PC electrolyte when cycled in the potential range of 1.2–3.6 V at 5.9 mA h/g current density (Fig. 14). The energy capacity discharged by this cell reached to 330.6 mWh/g in its third cycle. However, both charge and energy capacities declined to 130.6 mA h/g and 236.5 mWh/g after ten cycles, respectively.

The same cell when continued to be cycled at 4.8 mA/g between...
1.2 and 3. V yielded the maximum specific charge and energy capacities of 142.3 mA h/g and 230.8 mWh/g which decreased to 99.8 mA h/g and 164.9 mWh/g respectively in the consecutive cycles (Fig. 15).

Also, we observed a large difference between the discharge potential and the charge potential, suggesting the presence of a large electrochemical polarization in these battery systems. This can be explained as follows. Once the AQ is reduced to the dianion, it forms a stable lithium salt in the non-aqueous electrolyte containing Li⁺ ions. The strength of the association between small positively charged lithium ions and the AQ dianion should presumably be quite high. The process of oxidation of AQ dianions back to AQ during charging which involves the breaking of these strong associations should require a high amount of energy. Thus the oxidation reaction occurs at a high potential, leading to a large electrochemical polarization.

4. Conclusion

We successfully managed to functionalize RGO with AQ.

1.3. Specific charge-discharge profiles of RGO AQ 500% in 1M LiPF₆/EC: DMCP (1:1), the following 12 cycles after the 170 cycle, potential range – 1.3–3.6 V, current density of 10 mA/g. (A colour version of this figure can be viewed online.)

Fig. 14. Specific charge-discharge (A), charge and energy capacities vs number of cycles (B, C) graphics for RGO AQ 500% in 1M LiClO₄/PC, potential range – 1.2–3.6 V, current density = 5.9 mA/g. (A colour version of this figure can be viewed online.)
moieties via a simple thermal reaction involving nitrene chemistry utilizing a novel azide-functionalized AQ derivative. We proved that this method of anchoring the electro-active species directly onto the conductive carbon is an effective method which can directly give the desired electrode material and can eliminate the need for a laborious and costly synthesis of a redox polymer that needed to be blended subsequently with a conductive carbon to obtain the electrode material. We also showed the effect of the feed ratio of the azide derivative employed in the functionalization reaction. These AQ-functionalized RGO derivatives were successfully incorporated in Li-batteries as cathode materials which demonstrated differences in performance and capacity based on the electrolyte and the potential range used in cycling. Further studies are planned to find the right electrolyte for their optimal performance. One possibility may be the use of aqueous electrolytes in which AQ groups are known to exhibit good performance. Therefore, we believe that RGO-AQ is a good candidate as the electrode material to obtain high capacity rechargeable batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.02.005.

References


