Carbon 116 (2017) 154–166

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

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

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ARTICLE INFO

Article history:
Received 17 December 2016
Received in revised form
1 February 2017
Accepted 2 February 2017
Available online 3 February 2017

ABSTRACT

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 $LiPF_6$/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 $LiClO_4$/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 H_2O_2 [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 MnO_2/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.

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http://dx.doi.org/10.1016/j.carbon.2017.02.005
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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 O_2 cathode composed of a MnO_2/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, O_2 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 H_2SO_4 electrolyte exhibited a superior performance compared to an analogous supercapacitor which utilized two unmodified carbon fabric 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 sulfonyl) 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/cm^2.

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 $LiClO_4$ in PC and 1M $LiPF_6$ 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 multi-channel 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 active 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 (^{1}H 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 α-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 ($\lambda = 1.54056$ Å). The diffraction data was collected in the range of 3°–80° with a step size of 0.02 (2θ).

The atomic contents of the graphite, GO, RGO, and RGO- AQ samples were evaluated by XPS analysis. XPS studies were carried on a Thermo Scientific K-Alpha X-ray Photoelectron spectrometer