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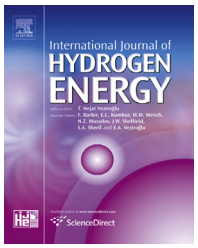

Synthesis of flexible pure graphene papers and utilization as free standing cathodes for lithium-air batteries

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ABSTRACT

In Lithium-air cathode, graphene containing materials have been reported as ideal cathode materials due to their large theoretical specific surface area, chemical stability, high electrical conductivity and charge capacity. In this study; three free-standing flexible graphene cathodes were produced with different thickness by vacuum filtration technique. For preparation of the graphene electrodes, graphene oxide (GO) papers were chemically reduced. Surface morphology of the produced graphene cathodes were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was conducted to understand elemental composition of the GO paper. X-ray diffraction (XRD) technique and Raman spectroscopy were carried out to investigate the structure of the GO paper electrode. Moreover, specific surface area and porosity distribution of the GO paper was performed using Brunauer–Emmett–Teller (BET) method from N_2 adsorption and desorption isotherms and the pore size were calculated using the Barrett–Joyner–Halenda (BJH) algorithm on the desorption branch. Electrochemical performance of the free-standing graphene electrodes were assessed in ECC-Air test cell from 1.5 V to 4.5 V at a constant current density.

Introduction

Graphene is an atomic scale honeycomb lattice made of carbon atoms [1]. It is a 2-dimensional (2D) material, meaning that every atom of graphene can be considered as a surface atom [2]. Because of unique mechanical properties, including high Young's modulus (~1100 GPa) and fracture strength (125 GPa) [3], high electronic and thermal conductivity, high chemical stability and optical properties, graphene is being utilized for various applications [4], including field effect transistors [5], sensors [6], composite materials, energy storage devices [7,8], photovoltaic devices [9] and memory devices.

In 2004, Novoselov et al. [10] produced graphene for the first time by mechanical exfoliation. Since then different methods have been developed to synthesis graphene including exfoliation of graphite, chemical vapor deposition method, electric

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arc discharge, direct sonication of GO, unzipping carbon nanotubes, and chemical or thermal reduction of GO [11]. Chemically reduced GO is the most promising method of obtaining graphene due to large-scale production in low cost [12].

GO is heavily oxidized graphite without any crystalline structure and GO structure imparts a high mechanical stiffness and strength compared to other paper-like membrane materials [13–15]. Reduction of GO by clearing of functional groups improves the electrical conductivity and this material obtained by reducing GOs is generally referred to as reduced graphene oxide (rGO) or simply graphene. rGO has edge and defect sites considered to serve as active sites for chemical reactions. Furthermore, the two-dimensional structure of rGO provides a pathway for access by oxygen gas from both sides of the nanosheet [16].

In this study, it is aimed to produce graphene free standing electrodes via vacuum filtration techniques as an air-breathing cathode material in Li-air batteries without using any binder or additive. The effect of cathode electrode thickness on the electrochemical properties is investigated in detail. The thicknesses of the cathode electrodes were adjusted by weight changes. Graphene free standing papers are produced by chemical reduction of graphene oxide. It is well known that graphene and graphene based air breathing cathodes have been widely used with many catalysts from the literature studies. However, the novelty in this study is to obtain a graphene paper directly reduced from GO paper during vacuum filtration process for Li air batteries.

Experimental details

Graphite oxide was synthesized according to the modified Hummers' method by using pretreated graphite flakes as the starting material. First, 1.0 g of pristine graphite flakes (Alfa Aesar, +100 mesh in size) pretreated with 50 mL of HNO_3/H_2SO_4 (the volume ratio of 1:3) solution under vigorous stirring for 2 h. The obtained product then washed with distilled water until pH become natural and then dried in air at 70 °C for 12 h. After then the product thermally treated at 850 °C for 120 s. For producing of graphitic oxide, 1.0 g of pre-treated graphite flakes and 0.5 g $NaNO_3$ were added into 23 mL of H_2SO_4 and stirred for 2 h. The mixture cooled to 0 °C in an ice bath and 3.0 g $KMnO_4$ was added slowly to keep the reaction temperature below 20 °C. The ice bath was then removed, and the reaction warmed up 35 °C for 0.5 h. Then, 46 mL H_2O was slowly added into the mixture caused an exotherm and increased the temperature to 98 °C and the reaction maintained at this temperature for 15 min. After 15 min, 46 mL of hot water and 10 mL H_2O_2 aqueous solution were added into the mixture, which caused color changing to greenish yellow, and then stirred for 2 h. The resulting suspension was filtered and washed with 25% HCl aqueous solution for three times. Further, the product washed with distilled water and centrifuged until pH become neutral. The product was dried at 60 °C in vacuum oven. The exfoliation of graphite oxide into GO was obtained by ultrasonication.

The free-standing graphene paper cathodes prepared with different amount of GO with their codes are shown in Table 1.

Table 1 – Sample codes of produced graphene paper cathodes.

Weight of GO (mg)	Sample code
10	10G
30	30G
50	50G

The specified amount of GO was dispersed in 50 mL of distilled water and sonicated for 2 h to separate GO layers from the graphite oxide structure and then the solution was filtered on PVDF membrane by vacuum filtration technique to obtain GO paper. In order to produce graphene paper, the as-synthesized GO paper was chemically reduced immediately after filtration by hydrazine solution. 2.0 M, 50 mL hydrazine solution slowly poured on to membrane supported GO paper and filtered. After then the obtained solid was peeled-off from the PVDF membrane and free-standing graphene paper was obtained.

The morphology of produced graphene papers were characterized using environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) was conducted to understand elemental compositions of the graphene oxide and graphene papers. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX 2000 diffractometer (Cu Ka radiation), and Raman spectroscopy was carried out using Kaiser Optical Systems RAMANRXN1 spectrometer to investigate the structure of the graphene oxide papers. The specific surface area and porosity distribution of the graphene oxide paper was performed using Brunauer–Emmett–Teller (BET) method from N_2 adsorption and desorption isotherms and the pore size were calculated using the Barrett–Joyner–Halenda (BJH) algorithm on the desorption branch using Micromeritics ASAP 2000 system.

An ECC-Air test cell (purchased from EL-Cell Company in Germany) was used for electrochemical characterization of the graphene paper cathodes. It is well known that ether based electrolytes are initially stable to reduced O_2 species. However, increasing electrolyte decomposition upon cycling makes these electrolytes unstable and reduces the crystallinity which shows that the ether based electrolytes cannot successfully used due to the unreversible Li_2O_2 formation/decomposition upon cycling [17]. Because of desirable properties such as low viscosity, low flammability and relatively low toxicity, NMP is preferred as an electrolyte in this study. Besides, NMP is also stable in the presence of oxygen reduction species such as O_2 and LiO_2 [18]. 1 M $LiBF_4$ (Sigma Aldrich, 98%) dissolved in N-methyl-2-pyrrolidone solution (NMP) (Sigma Aldrich, 99+%/ Sigma Aldrich, ≥99%) (1:1 by volume) was used as the electrolyte. The as-produced graphene papers were used as the cathode electrode. Anode and cathode was separated using glass fiber separator. Electrochemical characterization of graphene paper cathodes were performed between 1.5 V and 4.5 V at a constant current density of 0.1 mA cm^{-2} using a computer-controlled battery tester (MTI BST8-MA).

Results and discussion

Fig. 1(a) shows the smooth, strong, and flexible nature of the GO paper and Fig. 1(b) shows reduced GO paper which is 32 mm in