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Surface modification of vertically aligned graphene nanosheets by microwave assisted etching for application as anode of lithium ion battery

Monalisa Ghosh, G. Venkatesh, G. Mohan Rao

Instrumentation and Applied Physics, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Vertically aligned graphene nanosheets (VAGNS) are grown by plasma enhanced chemical vapor deposition (PECVD) using electron cyclotron resonance (ECR) plasma system for application as an anode material in lithium ion battery (LIB). Microwave assisted etching, in presence and absence of substrate bias, is carried out on as grown VAGNS films to modify the morphology of the film. Scanning electron microscopy (SEM) is used for characterizing the surface features of the VAGNS films. The VAGNS sample which is microwave plasma treated (power 400 W) with substrate bias of 100 V, showed an initial charging specific capacity of 223 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$, while as deposited VAGNS showed specific capacity of 124.4 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$. After 5 cycles, while the former showed a specific capacity of 68.1 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$ (760.7 mAh g^{-1}), while the later showed a specific capacity of 43.9 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$(458.7 mAh $\cdot g^{-1}$). During discharge initially while surface modified VAGNS showed a capacity of 100.1 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$, the as deposited VAGNS showed a capacity of 38.2 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$. The specific capacity after five cycles, during discharge for modified VAGNS is 68 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$ (725.9 mAh g^{-1}), and for as deposited VAGNS it is 34 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$(380.6 mAh $\cdot g^{-1}$). The specific capacity remains fairly constant after this initial capacity loss up to 50 cycles. The results indicate that surface modification of VAGNS improves the performance of the material as anode for lithium ion battery.

1. Introduction

Lithium ion battery (LIB) is one of the most important topics of study in the fields of energy research in recent times and most widely used type of secondary battery in portable electronic devices. Any battery consists of many electrochemical cell connected in series while each electrochemical cell consists of an anode and a cathode (both sites of electrochemical reaction) separated by an electrolytic solution (enables ion transfer from one electrode to other). [1–2] Many research groups are working to improve the performance of LIB by studying different possible electrodes and electrolyte combination as well as by trying to find new and better working electrode or electrolyte. The ideal anode material for lithium-ion battery (LIB) should have a high lithium storage capability and a structure that remains intact after repeated lithiation and delithiation on cycling of the cell. Graphite is the most commonly used anode material for lithium ion battery. Graphite anode has the disadvantage of low gravimetric (372 mAh g^{-1}) and volumetric specific capacity (833 mAh cm^{-3}) [2–5]. So the research is focused on alternative anode materials which are new carbon based materials like graphene, carbon nanotubes or alloys of lithium with metal like Sn [6–7].

Vertically aligned graphene nanosheets (VAGNS), also known as carbon or graphene nanowalls, carbon/graphene nanosheets, and carbon nanoflowers, are a class of graphitic carbon in which networks of graphene sheets are oriented perpendicular to the surface of the substrate. Due to unique orientation of the graphene sheets and non-stacking morphology of the graphene sheets in GNS, it has a porous structure which results in a large exposed surface area to volume ratio [8]. VAGNS is highly suitable for application as anode for lithium ion battery, as due to its large effective surface area and exposed edges, it is easier for lithium ions to find a favorable site for attachment to the anode material. As the planes of graphene sheets have a very good contact with the current collector, as well as there are interconnected channels between graphene sheets, the diffusion of lithium ions to the current collector will have lower transport resistance [9–10].

Though there numerous reports using graphene as anode [11–12], there are a few reports existing in literature where VAGNS is used as an anode material for lithium ion battery. Tanaike et al. [10] first used VAGNS synthesized by dc plasma enhanced chemical vapor deposition (DC-PECVD), as the anode of lithium ion battery (LIB) and reported reversible capacity of 200 mAh g^{-1}. Since the material had brittle structure, electrodes was prepared by slurry method after peeling off the

E-mail address: monalisa.ind10@gmail.com (M. Ghosh).

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film from the substrate. The insulating polymer binder and inactive conductive additives used in the slurry method decreased the performance of the VAGNS for the aforementioned study. Xiao et al. [13] deposited VAGNS by microwave plasma enhanced chemical vapor deposition (MW-PECVD) on nickel substrate and studied its performance directly as anode of LIB. Reported capacity for this anode is 380 mAh g^{-1} at C/3 rate when cycled between 0.01 V to 1.2 V. Kim et al. [9] cycled highly branched graphene nanosheets (HBGN) which is structurally similar to VAGNS between 0.01 V to 2 V and reported a capacity of 461 mAh g^{-1}. Performance study of VAGNS deposited on Copper substrate by electron cyclotron resonance (ECR) PECVD by our research group was also done and reported to have reversible capacity of 520 mAh g^{-1} on cycling between 0.01 V to 2 V after 50 cycles.[14] Other studies in literature has used VAGNS in composite state with materials like tin[15,16], tin oxide[17], zinc oxide[18], germanium [19] etc.

In the present study the effect of etching on the surface morphology of the VAGNS, by plasma created by electron cyclotron resonance (ECR) system is done initially. Henceforth the effect of the surface modification on the performance as an anode material for LIB has been done. Further, to improve the plasma treatment effect, the etchant ions are imparted extra energy by providing a DC bias to the substrate. The motivation for this work is to increase the surface area of the anode in order to increase the capacity and better life for the battery. The novelty of the study is that, all experiments have been carried out only with VAGNS, without forming composite with any other material.

2. Experimental

2.1. Materials and methods

Vertically aligned graphene nanosheets (VAGNS) are synthesized by plasma enhanced chemical vapor deposition (PECVD) process in a homemade ECR PECVD setup, as shown in Fig. 1. The details of the ECR system and its working principle have been described in group's previous study [20]. The substrate is kept at a distance of 10 cm from the ECR source. The substrate stage has mechanism for heating the substrate up to 800 °C. The GNS synthesis is done on copper substrate which is cleaned in dilute HCl and DI water before loading in ECR system. The substrate is heated at 500 °C for 15 min prior deposition, which is followed by etching in hydrogen plasma at a microwave power of 500 W for 10 min at the same temperature. The deposition of GNS is then done at a temperature of 750 °C for 15 min at a microwave power of 500 W. A mixture of acetylene (C_2H_2) and hydrogen (H_2) at a ratio of 1:2 is used as the reactive gases for the PECVD process. A pressure of 7×10^{-4} mbar is maintained in the chamber during the deposition of VAGNS.

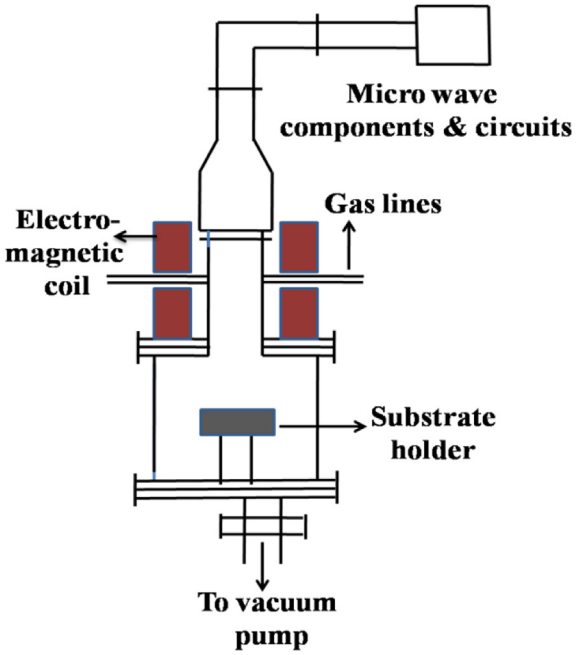

Fig. 1. Schematic diagram of Electron cyclotron Resonance (ECR) PECVD setup.

For surface modification, the as deposited GNS thin films are etched in ECR plasma for 10 min at a pressure of 6×10^{-4} mbar. Hydrogen or argon gas is used as the etchant gas. Different microwave powers, in range 300 W to 500 W, are used in order to see the effect of plasma on the surface morphology of the films. Substrate bias is applied for some etching experiments. Three different dc voltages, 50 V, 100 V and 150 V respectively, are used for the biasing purpose. Substrate was biased negative with respect to ground. While applying the bias voltage 15 mA current was kept constant in the power supply.

2.2. Characterizations

The surface morphology of the VAGNS films is studied by field emission scanning electron microscopy (ULTRA 55 FESEM, Carl Zeiss). The electrochemical performance of the VAGNS is studied using cyclic voltammetry and galvanostatic charge discharge cycling in electrochemical workstation from Solatron Analytical.

The electrochemical performance study of VAGNS thin films, deposited on circular copper substrates of diameter 12 mm, is done by assembling half cells (Swagelok type) in Argon filled glove box. Lithium metal foil of thickness 0.38 mm from Sigma Aldrich is used as reference and counter electrode. 1 mol $LiPF_6$ salt dissolved in 2:1:2 (v/v) mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) is used as the electrolyte with absorbed glass mat (AGM) of thickness 3 mm acting as separator.

3. Results and discussion

The surface morphological features of the as deposited VAGNS as well as surface modified VAGNS are studied by FESEM. The VAGNS shows a highly porous structure with interconnected network of graphene nanosheets grown about 1 μm in height perpendicular to the surface of the substrate (as shown in Fig. 2a and a inset). The pores are approximately 50 nm in diameter with graphene walls about 10–20 nm thick. The details of growth mechanism and characterizations of the VAGNS sample using Raman spectroscopy, X-Ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are reported in our group's previous study [21].

The surface modification of the VAGNS was initially tried with hydrogen plasma keeping the pressure and time (10 min) constant and varying the microwave power. It is seen that for both the samples which are treated with hydrogen plasma at 300 W and 400 W, the VAGNS structure is lost and a kind of agglomerated structure has formed. The thickness of the sample has also decreased to about 500 nm and 350 nm respectively. We have decided not to go for higher microwave powers for hydrogen plasma because of too much material loss and undesirable surface characteristics. Lower microwave power is also not an option as plasma does not strike at power below 250 W. So it was decided to try modification with Argon plasma.

Fig. 3 shows the comparison between surface modification of VAGNS with argon plasma at different microwave powers at same pressure of argon gas (5×10^{-4} mbar) and same time (10 min). Fig. 3b, c and d shows the surface morphology and cross section (inset) of VAGNS (Fig. 3a) after plasma treatment at 300 W, 400 W and 500 W respectively in argon atmosphere. Sample treated with argon plasma at microwave 300 W shows very nominal change in surface features with only loss of thickness (approximately 10% to 15%) and cleaner, more uniform surface with bit thicker graphene walls (Fig. 2b). When treated with argon plasma of 400 W microwave power the surface morphology shows change in features with approximately 50% loss in thickness