

Effects of Microwave Annealing of Graphene and its Impact on Structural, Electrochemical Performance for Energy Storage

K. Senthil Kumar
Department of ECE
Kongu Engineering
College

Erode-638060, India
ksenthilkumar@kongu.ac.in

A. Chandrasekaran
Department of ECE
Kongu Engineering
College

Erode-638060, India

K. Kannan
Department of Chemical
Engineering
Kongu Engineering
College
Erode-638060, India

G. Murugesan
Department of ECE
Kongu Engineering
College
Erode-638060, India

Abstract— In this paper, graphene was prepared via modified hummers' method and then with the help of microwave treatment of as prepared graphene, microwave graphene (MG) was prepared. From the electrochemical experiments, graphene and MG exhibited improved electrochemical performance. Electrochemical performance of graphene and MG electrodes were measured by cyclic voltammetry (CV), galvanostatic charge and discharge measurement (GCD) and electrochemical impedance spectroscopy (EIS). The specific capacitance value of 275 Fg^{-1} And 316 Fg^{-1} for graphene and MG, respectively. Equivalent series resistance of MG was 1.78Ω and charge transfer resistance was 1.33Ω , smaller than that of graphene. The fabricated electrodes of supercapacitor show the improved equivalent series resistance and capacitance value. The improved performance of MG electrode was ascribed to the porous nature of graphene after microwave annealing. This work gives the great interest towards the material for high performance high energy and power density application.

Keywords— Annealing, Electrode, Grapheme, Microwave, Supercapacitor

I. INTRODUCTION

Supercapacitors are energy storage devices that store and release energy by electrochemical interaction between electrode and an electrolyte which uses electrochemical double layer capacitance mechanism. Comparing the conventional dielectric capacitors, ultracapacitors have high energy density and when compared to rechargeable batteries, they possess high power density. Low weight, low maintenance, flexibility, long life and high power capability are the important advantages of supercapacitors [1]. The energy density of pseudocapacitance is higher than that of electrochemical double layer capacitance. Even though pseudocapacitance has high energy density, phase changes within the electrode limits the lifetime and power density of supercapacitor. The predominant issue for research on supercapacitor is to enhance the energy density.

Graphene is a two dimensional carbon material and it is considered as an attractive material for electrode in supercapacitor because of its superior electrical conductivity, stable chemical property, high surface area to volume ratio, and high capacitance. Compared with the other carbonaceous materials, graphene based conventional supercapacitor has high energy density. But the power delivery of graphene based supercapacitor has not been effectively improved [2]. The theoretical specific capacitance (C_{sp}) of graphene is 550 Fg^{-1} [3]. However, measured EDLC value is far lower than that of theoretical one, which is due to the stacking

arrangements of graphene sheets during the preparation of graphene and subsequent electrode preparation.

Z.S.Wu et al [4] developed solid state micro supercapacitors through micropatterning of graphene films, which delivers maximum areal capacitance of $80.7 \mu\text{F cm}^{-2}$ and a stack capacitance of 17.9 F cm^{-3} . They showed power density of 495 W cm^{-3} and energy density of 2.5 mWh cm^{-3} , which is considerable to that of Lithium ion battery. Extremely stable capacitive behavior (capacity retention ratio, 98.3 %) was observed even after 1,00,000 electrochemical cycles at a rate of 50 V s^{-1} . Meryl.D.Stoller et al [1] developed chemically modified graphene based supercapacitor cells and tested with three electrolytes such as Potassium hydroxide (KOH), tetra ethyl ammonium tetrafluoroborate (TEABF_4) in acetonitrile, TEABF_4 in propylene carbon solvent. The surface area of CMG is $705 \text{ m}^2\text{g}^{-1}$. Highest specific capacitance value of 107 Fg^{-1} is observed for KOH electrolyte at scan rate of 40 mV s^{-1} .

Weijiang Si et al [5] make reduced graphene oxide aerogel (RGOA) through simultaneous self assembly process and reduction process with the highest surface area of $830 \text{ m}^2\text{g}^{-1}$. The obtained C_{sp} is 278.6 Fg^{-1} for H_2SO_4 electrolyte compared to 211.8 Fg^{-1} for KOH electrolyte. By using 1-ethyl 3-methylimidazolium tetrafluoroborate as an electrolyte, the operating voltage is raised to 3.5 V compared to 1.5 V of an aqueous electrolyte. In this work, graphene has been synthesized through modified hummers' method and then it is treated with microwave oven, serving as an electrode material for supercapacitor. Due to the microwave annealing treatment, porous structure of graphene has been enhanced which will support rapid transfer of ions and improve the diffusion of electrolyte. The prepared material was characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, CV, GCD and EIS.

II. SYNTHESIS

Synthesis of Graphene Oxide and Microwave annealing of graphene oxide

Natural graphite powder was obtained from Aksharchem, sodium nitrate and potassium permanganate were purchased from Merck, hydrogen peroxide and hydrochloric acid were purchased from Nice chemicals private limited and concentrated sulphuric acid was obtained from RFCL limited. All the materials were used as purchased without further purification. Graphene oxide (GO) was obtained from natural graphite flakes through the modified Hummers'

method. Shortly, 15 g of graphite flakes and 3.75 g of sodium nitrate were combined together. Then 172.5 ml of conc. sulphuric acid was added under continuous stirring. After an hour, 11.25 g of potassium permanganate was added to the above prepared solution in gradual manner while maintaining the temperature is approximately less than 5°C to avoid explosion and overheating. The prepared mixture was stirred at a low temperature of 6 °C for 14 h and then the obtained solution was kept diluted by pouring 250 ml of water under constant and forced stirring. To make the reaction to be completed, the solution was once again treated with 30 mL of H₂O₂ solution. The obtained final resulting mixture was continuously washed with diluted HCl, ethanol and distilled water. Then it has to be filtered and dried in hot air oven at 100°C for 24h and the desired graphene oxide sheets were obtained. GO was treated in a microwave oven. The microwave oven had a maximum power of 640 Watts with 4 different power values such as 160, 320, 480 and 640W. The graphene oxide was placed in a petri dish, which was kept in oven (LG/MH3948WB). After microwave irradiation, volume expansion of the graphene nanoparticle observed at 320W for 30 seconds only. Finally, the graphene was treated in microwave oven, named as MG.

III. RESULTS AND DISCUSSION

The vibrational characteristics of graphene and MG were measured using FTIR. FTIR measurements of graphene and MG, shown in Fig (1) were measured by the KBr method recorded on Shimadzu spectrometer over a range from 400 to 4000 cm⁻¹. As for graphene oxide, the following peaks are observed. O-H stretching vibrations (3100 ~ 3600 cm⁻¹), C=C stretching vibrations (approximately, 1634 cm⁻¹) observed after microwave treatment, stretching vibration from epoxy (approximately, 1216 cm⁻¹) [5]. Raman spectra were recorded on EZRaman-N analyzer employing 532 nm frequency stabilized, narrow line width diode Laser beam. Characterization of structural defects in carbon material has been studied by raman spectra. Fig (2) shows the raman spectra of G and MG. The raman spectra of G and MG shows prominent peaks at 1340 cm⁻¹ corresponds to D band arises from the structural defects generated by the oxygen functional groups and 1582 cm⁻¹ corresponding to G band originated from the in phase vibrations. In the electrochemical test, the active electrode was assembled into a three electrode system. The following steps are used for the preparation of the working electrode. To evaluate an electrochemical performance in an aqueous solution, an electrode material was synthesized through the active material, mixed with the rubber solution in the weight ratio (60:40). The mixture was made as slurry and coated on graphite rod with the help of brush. The pasted graphite lead electrodes were dried at room temperature for 30 minutes. The loading amount of active material is approximately 200 µg. The electrolyte used was 0.5 M H₂SO₄ aqueous solution.

The electrochemical behavior was characterized within a maximum potential window of -1.5 to 2 V vs. Ag/AgCl reference electrode. Platinum wire was used as a counter electrode. CV, GCD and EIS were carried out on an electrochemical workstation (metrohm, Netherlands, potentiostat - galvanostat). CV is used to characterize the electrochemical nature and to measure the specific capacitance.

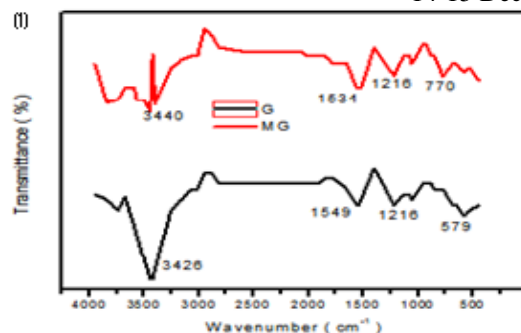


Fig. 1. Fourier transform infrared spectra of G and MG

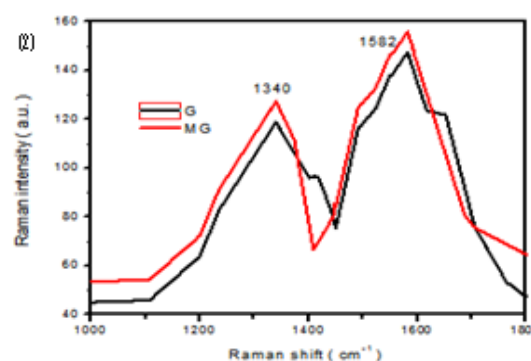


Fig. 2. Fourier transform Raman spectra of G and MG

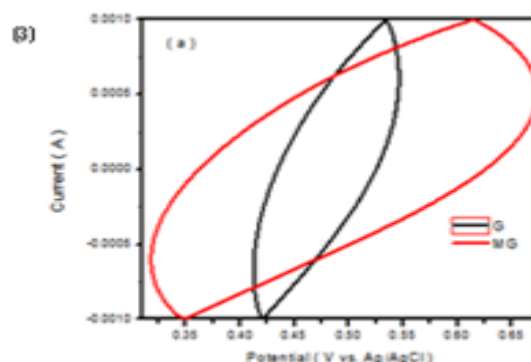


Fig. 3. Cyclic voltammograms of G and MG at scan rate 10 mVs⁻¹ in 0.5 M H₂SO₄ electrolyte

Fig.3. shows the CV spectra of graphene and MG are shown in Fig (3) at a scan rate of 0.005 Vs⁻¹. The CV curves are slightly rectangular ascribed to ideal capacitive behavior based on ion adsorption/desorption. By means of microwave annealing the oxygen functional groups were removed, the effects of pseudocapacitance are negligible. The CV curve suggested ion charge transfer mechanism is fast between an electrode and an electrolyte interface for an efficient supercapacitor. The specific capacitance measured from the CV curves was 266 Fg⁻¹ and 275 Fg⁻¹ for graphene and MG, respectively.

Fig.4. presents GCD curves of graphene and MG in 0.5 M H₂SO₄ at a constant current of 0.05 Ag⁻¹. The shape of the curve is triangular, indicated that there is no pseudocapacitance behavior. From the GCD curves, the

measure specific capacitance value was 292 Fg^{-1} and 316 Fg^{-1} , for graphene and MG, respectively.

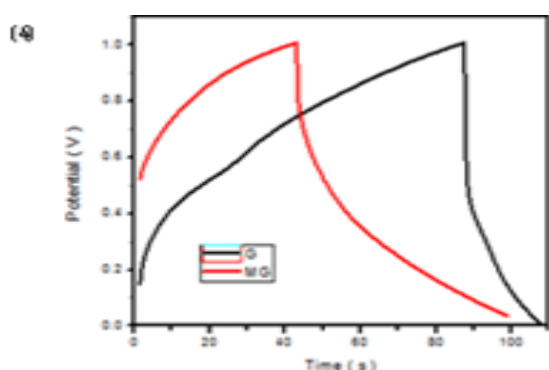


Fig. 4. Galvanostatic charge and discharge curves of G and MG

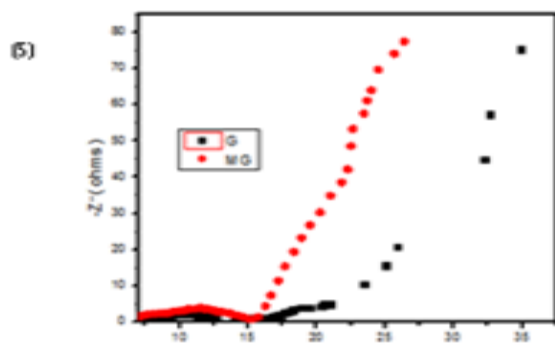


Fig. 5. Nyquist impedance plots of G and MG

The high specific value for MG is due to the porous nature of microwave treated graphene. Microwave annealing suggested the improvement of pores present in graphene. The negligible voltage drop is observed for MG suggested a low equivalent series resistance resulting in a high rate capability [6]. EIS study on the graphene and MG is shown in Fig.5. EIS analysis was performed for the confirmation of the penetration of ions in the electrodes [7]. The nyquist plot shows a semicircle in the low frequency region and vertical line in the high frequency region. The obtained ESR (2.99Ω for graphene and 1.78Ω for MG) value suggested that there is no losses due to the flow of electrons were easily done and also in fast manner in the

electrode and an electrolyte interface. The obtained charge transfer resistance is 1.81Ω for graphene and 1.33Ω for MG. Distribution as well as connection of ions at the boundary was good corresponds to the charge transfer resistance. The 45° slope is known as the Warburg region and is ascribed to ion diffusion takes place between electrolyte and anelectrode.

IV. CONCLUSION

In summary, graphene was prepared via modified hummers' method and MG was prepared via microwave treatment of as prepared graphene. Electrochemical performance of graphene and MG electrodes were measured by CV, GCD and EIS. From the electrochemical experiments, graphene and MG showed improved electrochemical performance. C_{sp} of 275 Fg^{-1} at a 5 mV s^{-1} and 316 Fg^{-1} at 0.05 Ag^{-1} were observed for MG were realized by the porous nature of supercapacitor electrode made by microwave treated graphene. The porous nature of the graphene enhances the ion diffusion and conductivity. This high specific capacitance electrode material is a promising candidate for supercapacitor applications.

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