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Electrochemical Performance of Graphene/Activated Carbon Based Electric Double Layer Supercapacitors

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We report a facile and environmental friendly strategy for the fabrication of porous graphene/activated carbon (graphene/AC) composites through chemical activation technique by using Li_2CO_3. The activation process was accomplished by using a pressure dye round by heating mantle at 450 °C for 12 h. The carbonates were considered to decompose under high pressure and temperature in graphene network to produce a porous two-dimensional graphene/activated carbon network. The structures and the properties of graphene/activated carbon composites have been characterized by X-ray diffraction, scanning electron microscopy, cyclic voltammetry, galvanostatic charge-discharge test. Electrochemical test reveals that the graphene/activated carbon composite has stable capacitance performance at charge-discharge current density of 0.3 A g^{-1} and excellent capacity retention.

Keywords: Graphene, Electrochemical measurements, XRD, SEM, Cyclic voltammetry.

INTRODUCTION

The fast growing electronic market of advanced portable electronic devices demands high efficient, low cost environmental friendly energy storage devices. Super capacitor has attracted great attention due to their extraordinary power density, charge discharge, cyclic stability and long life [1-4]. We can classify super capacitor on the basis of their charge storage mechanism. In electric double layer supercapacitors (EDLCs) the charge storage occurs purely from the accumulation of charges on the electrode and electrolyte interface like in carbon based materials. Another one is pseudo capacitance which arises from the reversible redox reaction or faradic charge reaction of the conductive species attached on the surface of the electrode. These conductive may be metal oxide or some conductive polymers.

In recent research trends graphene, a one atom thick single layer of carbon has attracted great interest for super capacitor application because of their astonishing optical, electrical, mechanical and thermal properties. The most desire advantage of graphene is its high surface area which is dependent on growth and synthesis techniques. Graphene has been found as an essential electrode material because of its large surface area which determines its capacitance. The disadvantage of graphene sheet is partial agglomeration which affects its surface area and therefore it is very difficult to utilize the large surface area of graphene. A key issue is how to avoid the aggregation of graphene sheets during the electrode preparation [5-7].

Researcher devoted his work to produce a novel technique to produce a high quality graphene and to overcome the restacking problem of sheet. In this context previous researchers produced graphene using CVD techniques [8-10]. Hydrothermal method was used by Shi *et al*. [11] to produce graphene hydrogel. Wei *et al*. [12] using templating techniques to produce 3D graphene network. However, most of them need a strong oxidizing agent or complicated setup which cannot be considered as facile and simple routes [13].

Here, we describe the design and preparation of two dimensional graphene/activated carbon porous material with facial hydrothermal method using graphene oxide (GO) precursor, ethylene glycol as the reducing agent and Li_2CO_3 as the template. The desire amount of graphene was added to activated carbon under hydrothermal techniques to ensure homogenous mixing of the composites. After drying Li_2CO_3 were added and transfer to a high pressure cylindrical dye round by heating mantle. The temperature was kept at 450 °C for 12 h to ensure the activation through Li_2CO_3. The final compound was then heat treated at 600 °C for 2 h to decompose the residual carbonates in the composites. The composites were labeled as GF1, GF2 and GF3 respectively. This kind of

interconnected two dimensional graphene/activated carbon porous network will facilitate the ions through the internal structure of the graphene sheet to observe a high charge discharge rate. The above technique is desirable to attach some metals or metal oxide for the improvement and performance of graphene based activated carbon super capacitor.

EXPERIMENTAL

Graphene oxide was prepared from graphite according to the Hummers-Offeman method [14]. In brief, graphite powder (10 g) was dispersed in cold concentrated sulphuric acid (230 mL, 98 wt. % and dry ice bath) and potassium permanganate ($KMnO_4$, 30 g) gradually added with continuous vigorous stirring and cooling to prevent the temperature from exceeding 293 K. The dry ice bath was removed and replaced with a water bath by increasing the mixture temperature up to 308 K for 0.5 h under continuous stirring, followed by slow addition of deionized water (460 mL), which produced a rapid increase in solution temperature up to a maximum of 371 K. The reaction was maintained for 40 min in order to increase the oxidation degree of graphite oxide product and then the resultant bright-yellow suspension was terminated by addition of more distilled water (140 mL) followed by hydrogen peroxide solution (H_2O_2, 30 %, 30 mL). The solid product was separated by centrifugation at 3000 rpm and washed initially with 5 % HCl until sulphate ions were no longer detectable with barium chloride and then washed three times with acetone and air dried overnight at 338 K. Resulting graphite oxide was heat treated at 900 °C for 1 h to obtain graphene. Activated carbon was purchased from EAST ASIS Carbon Fibers Co., Ltd, China. The acids, HNO_3, H_2SO_4, which used to modify the activated carbon, were obtained from Duksan Pure Chemical Co., Ltd, Korea.

Fabrication of electrodes: The fabrication of working electrodes and the schematic diagrams are briefly outlined in the Fig. 1. The electrodes were composed of graphene/activated carbon as an active material and carboxymethyl cellulose (CMC) as a binder material. The weight ratio of active material, electric conductor and binder was clearly explained in Table-1. Electrode sheets of commercially available activated carbon powder were prepared by mixing graphene/activated carbon powder with carboxymethyl cellulose binder with appropriate ratios. The mixture was homogenized in isopropyl alcohol for 2 h at 30 rpm and then transferred to cold roller followed by hot roller for fixing the thickness in two steps.

General characterization: The X-ray diffraction was carried out at room temperature using XRD (Shimata XDD1, Japan) with CuK_α radiation (λ = 1.54056 Å) in the range of 2θ = 10-80° at a scan speed of 1.2 degree m^{-1}. Scanning electron microscopy (SEM, JEOL, JEM-2010, Japan) was used to observe the surface state and structure of the graphene/activated carbon

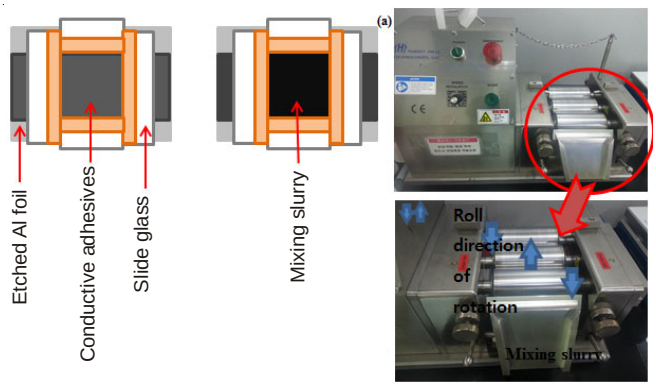

Fig. 1. Electrode preparation block diagram and preparation cell

composites at an acceleration voltage of 200 kV. The electrochemical performance and capacitance measurements of above supercapacitors were studied by cyclic voltammetry (CV), galvanostatic charge/discharge. The CV curves were performed at different scan rates varying from 1 mV to 10 mV s^{-1} at potentials between 0 and 1.0 V with a LK98B II microcomputer-based electrochemical analyzer (LANLIKE). Maccor series 4000 from (Korea thermo-tech Co., Ltd.) were used to study the charge discharge cycle test of the electrodes. The Maccor 4000 has number of test channels from 1 to 192, voltage ratings up to 180 V max, voltage accuracy 0.02 % with voltage resolution of 16 bit. The galvanostatic charge/discharge was carried out with a supercapacitor tester (Arbin MSTAT, USA). All the electrochemical tests were carried out at room temperature. The surface texture and porosity of the materials were examined by N_2 adsorption at 77 K and CO_2 adsorption at 273 K (BET SORP JAPAN). The specific surface area was calculated from the N_2 adsorption isotherm using the BET equation and the micropore volume was calculated from the CO_2 isotherm. Pore size distributions (PSDs) were calculated for N_2 at 77 K in carbon slit pores.

RESULTS AND DISCUSSION

The structure and phase analysis was carried using X-ray diffraction techniques (Fig. 2). The Li_2CO_3 peak around 21.24, 2θ degree has broad reflection and higher intensity therefore it is very difficult to distinguish between graphene and Li peaks. The diffraction occur at (110) (200) (111) (202) (112) (020) (311) (021) (310) (204) corresponds to JCPDS card no: 22-1141. An intense peak centered at 2θ = 21.56 can be observed in the XRD pattern of graphene which corresponds to an average interlayer spacing of 0.84 nm. For the graphene/activated carbon composites the observation of broad peaks indicates poor ordering of the stacking layers of the carbonaceous materials [15].

TABLE-1
SPECIFIC CAPACITANCE AND ELECTRODE DENSITY AFTER 1st AND 5th CYCLE OF GF1, GF2 AND GF3 SAMPLE, RESPECTIVELY

Samples	Electrode density	Capacitance (F)		Sp. capacitance (F/g)		Sp. capacitance (F/cc)	
		1st	5th	1st	5th	1st	5th
GF1	0.1156	0.09	0.08	4.31	4.06	0.74	0.70
GF2	0.0998	0.06	0.06	3.42	3.13	0.64	0.59
GF3	0.0730	0.01	0.01	0.54	0.44	0.10	0.08

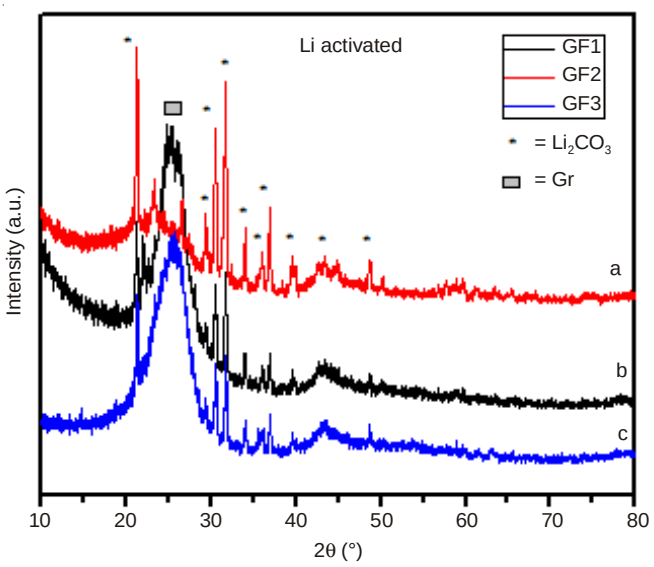

Fig. 2. XRD pattern of graphene/activated carbon composites

The morphology was studied using scanning electron microscopy techniques. Fig. 3 depicts the SEM images of the as prepared GF1, GF2 and GF3 nanocomposites. After heat treatment the 2D morphology was retain by the composites. From the Fig. 3(a-c) it is observed that graphene surface is crumpled with some wrinkles suggesting that some pores of the micrometer range were present. Fig. 3(b) looks like activated carbon staking layer over the whole surface of graphene sheet. This may be beneficial to produce more porous surface to the electrolyte interconnected by graphene layers. Such structure may boost the electrical conductivity by providing more diffusion sites for electrolyte infiltration [16,17].

The nitrogen adsorption/desorption isotherms and BET plot of GF1 sample are shown in Fig. 4(a-b). The BET plot shows the pore size distribution profile of the GF1 sample containing graphene and activated carbon composites after activation. In Fig. 4(b) the slope of the plot depicts the actual values of these pore distribution in their specific range. The samples depict sharp knees at relative lower pressure which are the signature of the microspore system. The slope gradually increase for GF1 samples at higher pressure than > 0.1. This increase in pressure suggest the coexistence of micropores and mesopores [18]. At higher pressure relatively maximum uptake of nitrogen the composites shows that there are some macrospores also present in the samples [19].

The discharge rate at of the GF1, GF2 and GF3 composites were given in Fig. 5(a-b). In Fig. 5(a) the 1st discharge of the three composites were shown. From this figure it is clear that GF1 sample has maximum specific capacitance of 4.31 F/g among the composites. While the specific capacitance of GF2 and GF3 were found to be 3.42 and 0.54 F/g respectively. The enormous increase in the specific capacitance of GF1 sample is attributed to the large pseudo capacitance of carboxymethyl cellulose and the porous structure of GF1 which is quiet clear from the SEM images of GF1. The discharge plot in Fig. 5(b) is almost the same as Fig. 5(a) which indicates that after 5th

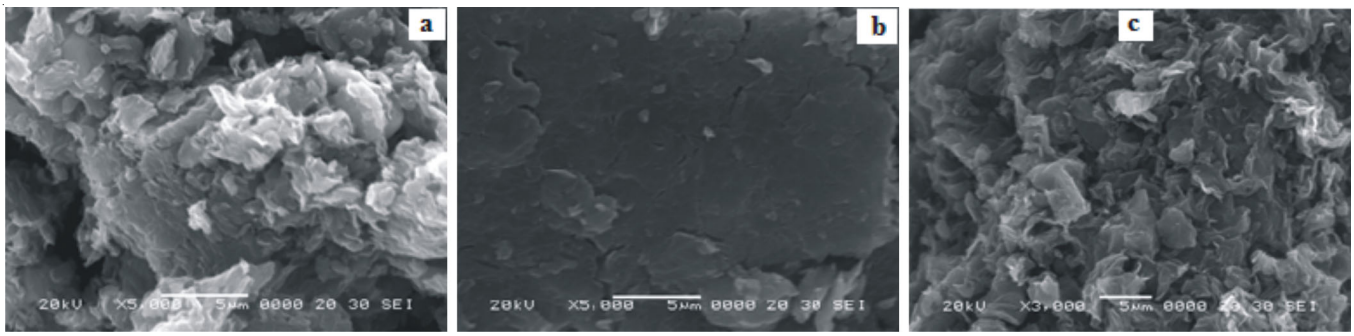

Fig. 3. SEM images of the graphene/activated carbon composites electric double layer supercapacitors

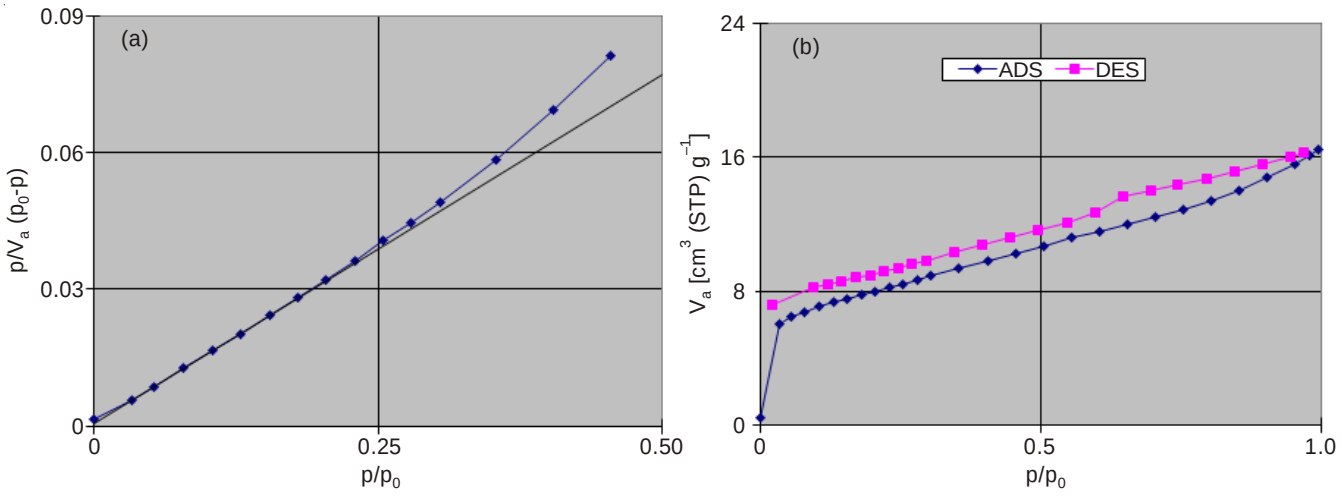

Fig. 4. (a) BET plot and (b) nitrogen absorption/desorption plot of GF1 sample

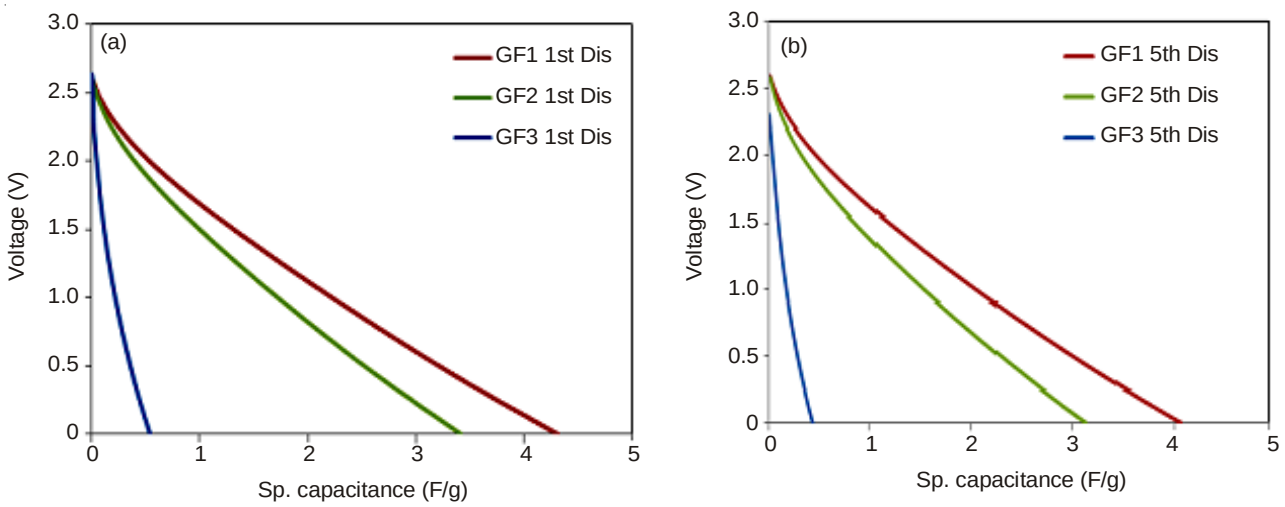

Fig. 5. Discharge profile (a) 1st discharge (b) 5th discharge of the graphene/activated carbon composites

discharge the value of the specific capacitance almost remains the same. The detail of these plots are given in Table-1.

The cyclic charge discharge curve of the GF1, GF2 and GF3 composites were ascribed in Fig. 6(a-c). From Fig. 6, during the cyclic experiments by applying voltage across the capacitor the values of the charge/discharge cycles remains almost the same for all sample. These results further confirm that stability of our prepared EDLCs.

The transport kinetic of the graphene/activated carbon composites supercapacitors were studied by using electrochemical impedance spectroscopy as shown in Fig. 7(a-b). The spectra analyze Nyquist plot of the electrode and electrolyte system along the imaginary part of the impedance against the real part of the impedance. The more vertical the curve the more ideal is the supercapacitor. The Nyquist plot shows a semicircle in the lower frequency region. While, it gives a straight line starting from a little higher frequency region. The equivalent series resistance of the cell can be calculated from the X intercept of the slope of the Nyquist plot. The diameter of the semicircle defines the charge transfer resistance R_{ct}. If there is a large semicircle observed from the plot means there is a large transfer resistance offer by the

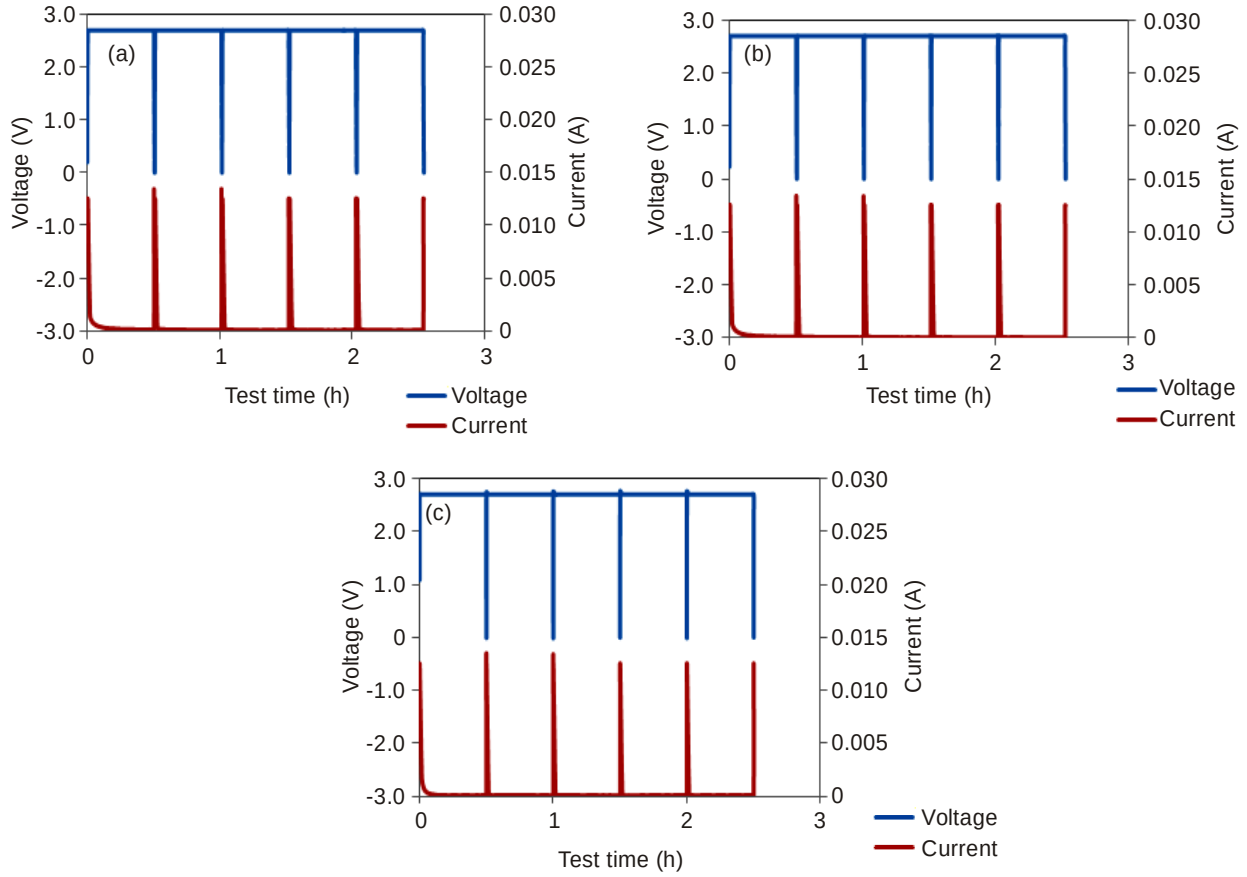

Fig. 6. Charge discharge profile of the GF1, GF2 and GF3 composites at 3 V for 3 h

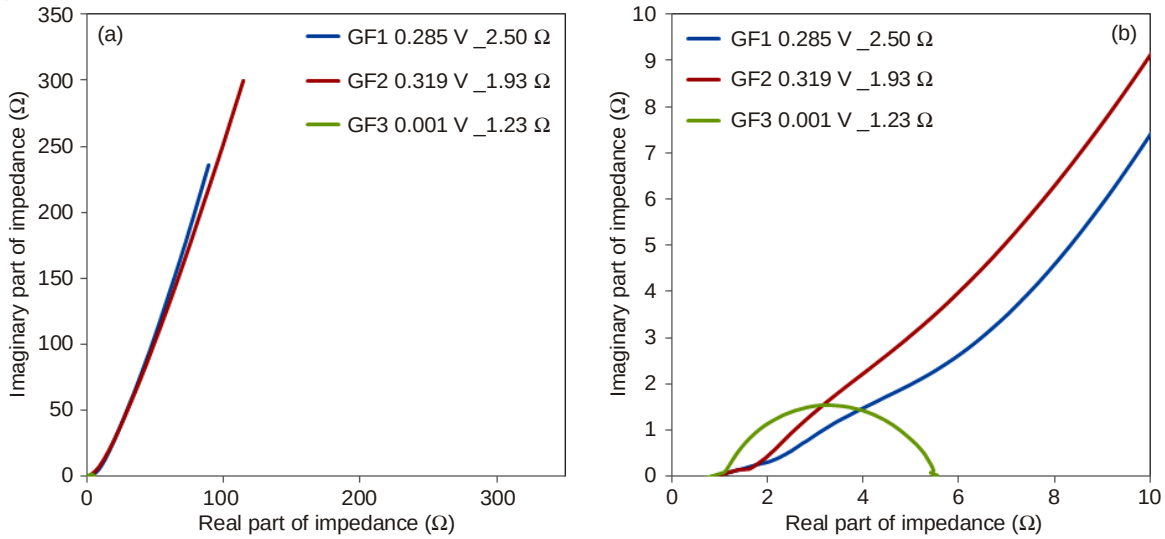

Fig. 7. Nyquist plot of graphene/activated carbon composites (a) large frequency range (b) short frequency range

electrode to the ions at the electrode/electrolyte interfaces. From the figure it can be seen that there is a large semicircle observed for the GF3 sample. This is attributed to the poor conductivity, which may be due to the functional groups present on the surface of the graphene or the partial agglomeration of graphene sheet in the composites. The line in the composites is more vertical for GF1 sample which indicates the low diffusion resistance thus resulting in higher pseudo capacitance. The values of the equivalent series resistance for the composites GF1 and GF2 were found to be 1.8 Ω and 2.0 Ω, respectively. While the diameter of the semicircle for GF3 composites were found higher than other composites in the series. This results for GF3 further confirms the highest charge transfer resistance and high contact resistance between the electrolyte ions and electrode composites [20-25].

Conclusion

In summary, we proposed novel EDLCs consist of graphene and activated carbon composites. We developed a technique to obtain porous graphene/activated carbon composites. The composites have a high specific capacitance of 4.31 F/g and good discharge rate with markedly high retention. From the BET results we can observe the average pore size diameter of around 3.58 nm. The values were found to decrease by increasing amount of activated carbon in the composites. These optimum loading of graphene provide a ridge between the pores which further enhances the specific capacitance of the composites. The Nyquist pot clearly indicates that GF1 has a smaller charge transfer resistance than the other composites. The diameter of the semicircle represent that GF3 offer a higher contact and diffusion resistance to the electrolyte ions which affect the specific capacitance. These results described the importance of graphene in future EDLCs technologies. This cemented a new way to use graphene as electrode material for supercapacitor application.

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