FABRICATION AND CHARACTERIZATION OF POLYANILINE-GRAPHENE COMPOSITE AS ELECTRODE IN ELECTROCHEMICAL CAPACITOR

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Abstract: In this study, polyaniline-graphene composites with different nano-structures are synthesized and the behaviour of the obtained composites serving as electrode materials in electrochemical capacitors is studied. The morphology, crystal structure, and thermal stability of the composites are examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Thermal gravimetric analysis (TGA). Electrochemical properties are characterized by cyclic voltammetry (CV). According to the results, the obtained composites show different crystal structures and different thermal stabilities, and consequently different electrochemical capacities, when used as electrodes in electrochemical capacitors. A nano-fibre composite is shown to have a good degree of crystallization, 5.17% water content, 637 °C degradation onset temperature, and 379 Fg^{-1} electrochemical capacity.

1. INTRODUCTION

As electrochemical capacitors (EC) are subjected to new power sources, research is being carried out to find suitable materials for them. These different materials — such as activated carbon (carbon nano-tubes), metal oxide and/or hydroxides (MnO_2, $Ni(OH)_2$), conductive polymers (polythiophene, polyacetylene, or polyaniline), and many other composites — have been used in ECs as electrodes. In recent years, Graphene-based composite materials (Graphene/ Conducting Polymer, Graphene/ MnO_2, Graphene/ $Ni(OH)_2$) are becoming promising electrodes for ECs, owing to their unique structure, high surface area, remarkable chemical stability, and electrical conductivity. The performance of an EC is affected by the morphology and crystal structure of the material used for the electrode. It is well recognised that the water content of materials used for electrodes is another key factor in their electrochemical performance as ECs. The hydrous regions in the electrode provide the kinetically facile sites needed for the charge-transfer reaction and cation diffusion [1–8].

In this paper, polyaniline-graphene composites are prepared in different conditions, and are then examined for their suitability as electrode materials for electrochemical supercapacitors. The Specific capacitance of each composite is explained by its morphology, crystalline structure, water content, and thermal stability.

2. EXPERIMENTAL

Homogenous composites of polyaniline and graphene oxide nano-structures were prepared by in situ polymerization of aniline in a suspension of graphene oxide in an acidic solution. The weight feed of aniline to Graphene oxide for the composite samples named PA-G-1, PA-G-2, and PA-G-3 were 90:10, 30:70, and 30:70, respectively. The samples PA-G-1, PA-G-2, and PA-G-3 were prepared by mixing an aqueous solution of aniline and oxidant (ammonium peroxy disulfate) solution in an acidic solution (1, 0.2, and 0.05 M HCl, respectively). The solution was sonicated for at least 30 minutes (min) to produce a stable mixture of Graphene oxide and aniline monomers. For PA-G-1, the mixture was stirred overnight at room temperature to complete polymerization. For PA-G-2 and PA-G-3, polymerization was completed by putting the

29

mixture in an ultrasonic machine at 0 °C for 90 min. The resulting product was isolated by centrifugation and washed several times with de-ionized water.

The resulting polyaniline-graphene oxide composites were reduced by hydrazine. Typically, 0.1g of the composite was heated with 0.1 ml of hydrazine in 50 ml of water at 95 °C for one hour. The reduced composites were filtered and washed repeatedly with de-ionized water to remove excess hydrazine. Finally, the composite products were dried in an oven at 50 °C for one day. The details of polymerization conditions are mentioned in references [9–10].

Morphologies of composites were studied using an AIS 2100 Scanning electron microscope (SEM). X-ray diffraction (XRD) analysis was performed on a Shimadzu X-ray diffractometer with Cu Ka 30 kV radiation to investigate crystal structure. Thermal gravimetric analysis (TGA) of obtained composites was carried out by means of STE 1500 at a ramp rate of 10 °C/min. The specific capacitance was determined by cyclic voltammetry (CV) technique. CV was carried out using the three-electrode system consisting of a Ti plate and a composite material as the counter and working electrodes, respectively. The working electrode was prepared by mixing 70 wt% composite powder, 20 wt% graphite (conducting grade), and 10 wt% acetylene black. The reference electrode was an Ag/AgCl electrode [11].

3. RESULTS AND DISCUSSION

The cyclic voltammograms of samples are shown in Fig. 1. A quasi-perfect rectangular shaped voltammogram with a large current separation, quasi-symmetric in both cathodic and anodic directions, is suitable for electrochemical capacitor applications. The specific capacitance of the polyaniline-graphene composites as a function of scan rate is shown in Fig. 2. The capacities were extracted from CV. The PA-G-1 has the highest specific capacity and PA-G-3 shows the lowest specific capacity at all scan rates. All samples had acceptable capacitance values, and in comparison with other reported results these capacities are good [10]. The dependence of capacity on scan rate can be explained with respect to the mechanism of charge/discharge in an electrochemical supercapacitor, and the effect of samples' structure on this mechanism. At a low scan rate, the electrolyte can completely penetrate the structure of the electrode meaning that all of the
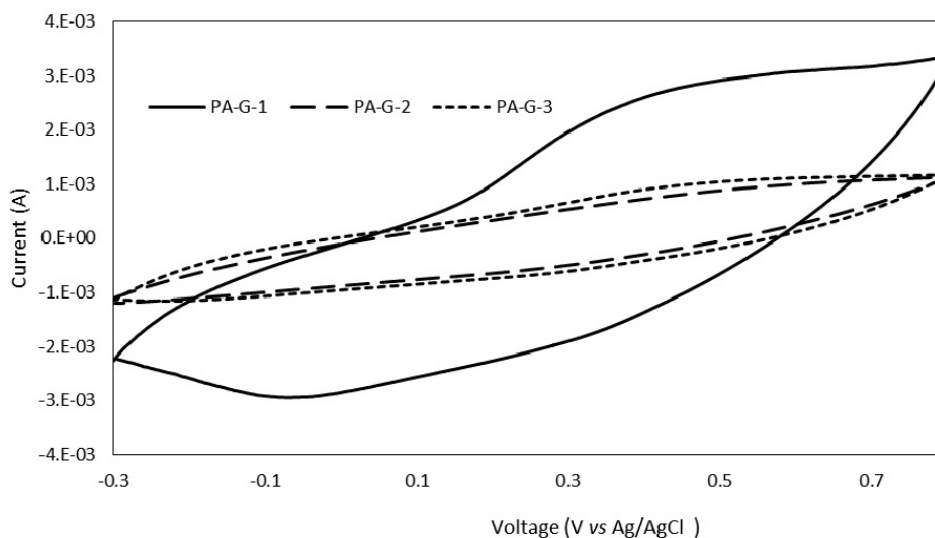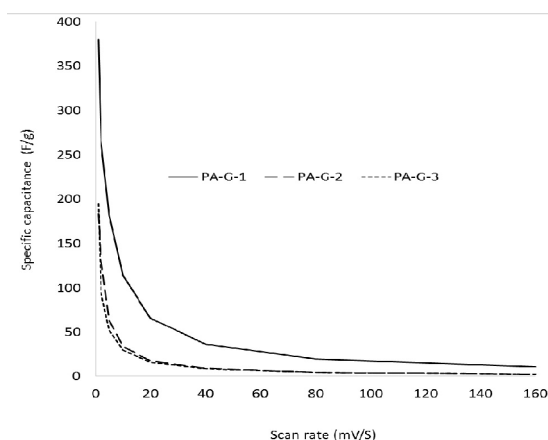

Fig. 1. Cyclic voltammograms

Fig. 2. Specific capacitance of composites against the scan rate

(a)

(b)

(c)

Fig. 3. SEM images of composites (a) PA-G-1, (b) PA-G-2, (c) PA-G-3

electrode's material contributes to electrochemical capacity performance. Consequently, the specific capacity of the samples is high at a low scan rate. At a high scan rate, the limited ionic diffusion in the electrode means that not all of the electrode's material is fully charged or discharged. Consequently only the outer layer of the electrode contributes in the charge/discharge process, and so the specific capacity is low [12].

The structure of the sample plays a key role in this manner. In porous structures, the probability of the diffusion of electrolyte is high and its specific capacity is higher than in a sample with a rigid structure. SEM micrograph of the composites is shown in Fig. 3. As can be seen in Fig. 3-a, there is nano-fibre in the structure of PA-G-1. The length and diameter of the nano-fibre is about 3000nm and 700nm, respectively. Each fibre has a coherent has a coherent, independent, and continued structure. In other words, the condition for nucleation and growth of nano-fibre is suitable. The SEM of PA-G-2 (Fig. 3-b) indicates that the formation of a composite has been stopped in the early stages of nucleation, resulting in an irregular structure because there is not a distinct boundary between the particles. Electrochemical samples with the least capa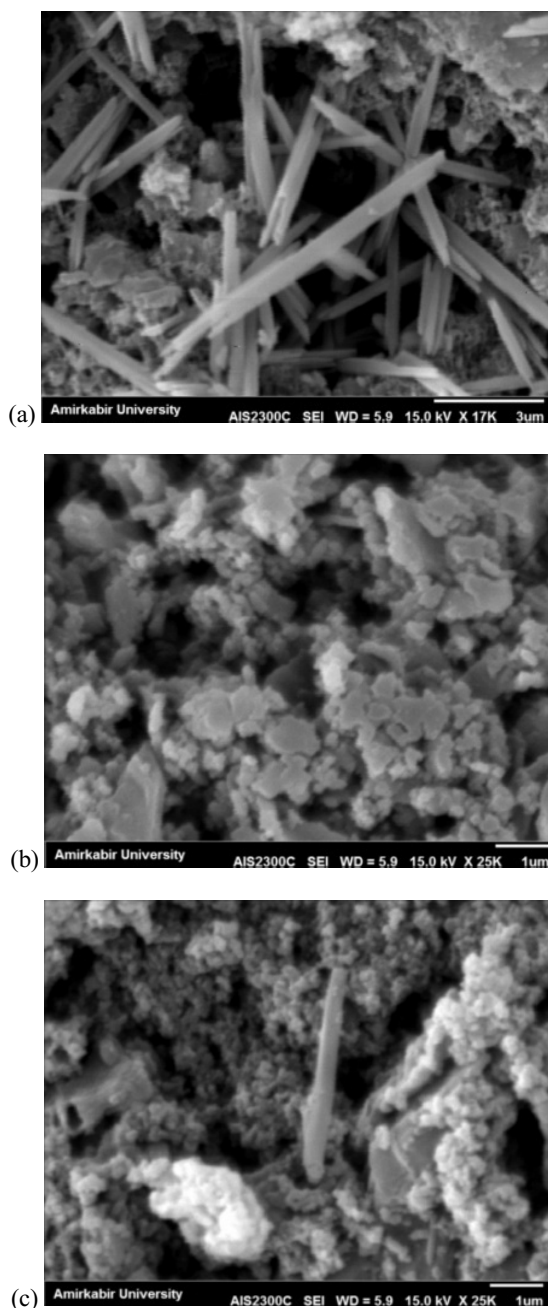city have multiple structures. PA-G-3 (Fig. 3-c) has a puffy background with many rigid rods in it. It seems that continuity of structure in this composite is low. Based on the above, the composite which has a distinct morphology and structure shows good electrochemical behaviour.
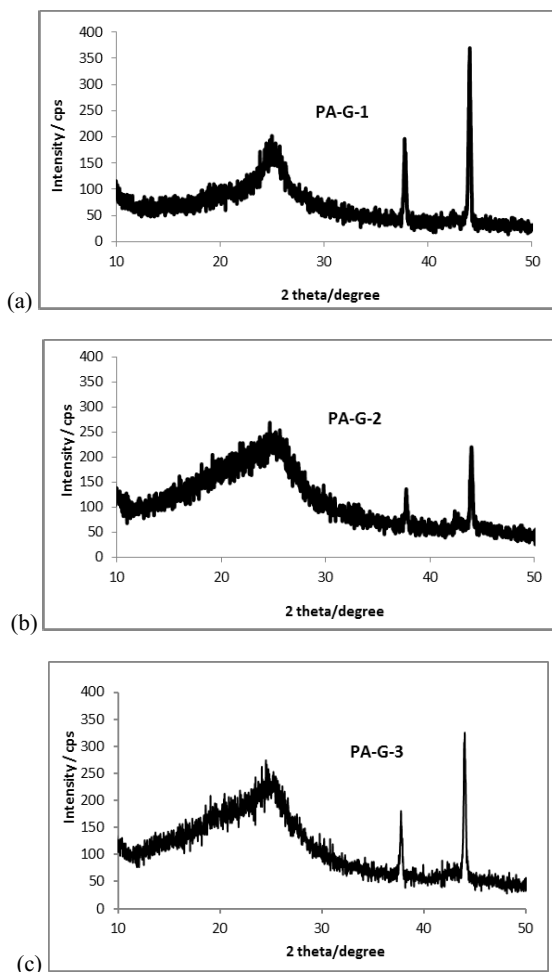
31

Fig. 4. XRD images of composites (a) PA-G-1, (b) PA-G-2, (c) PA-G-3

In other words, independent structures such as PA-G-1 have good electrochemical capacity.

In addition to morphology, the samples' crystal structures is one of the important factors influencing the electrochemical capacity of composites in EC. The powder X-ray diffraction pattern of the composites are shown in Fig. 4. The polyaniline perpendicular chains show band centred at $2\theta \approx 25°$ (110). Also for Graphene, the diffraction peak at $2\theta \approx 24.5°$ can be attributed to its graphite-like structure (002). The broad nature of the diffraction peak at $2\theta \approx 24$–$25°$ indicates that polyaniline and Graphene are simultaneously present in all composites. Furthermore, a sharp peak at $2\theta \approx 44°$ corresponding to the (221) plane

reflections of the polyaniline crystalline phase was also observed. The diffraction peaks at $2\theta \approx 43°$, indicating that Graphene has fully interacted with polyaniline [13]. The XRD results indicate that PA-G-1 and PA-G-2 show better and poorer crystalline structures, respectively. As PA-G-1 shows a sharper peak, it has a more crystalline structure. The superior capacity of PA-G-1 can be attributed to its higher degree of crystallinity of structure and a more consistent morphology.

The water content and thermal stability of the composites were characterized using TGA method. The water content of the composites is reported in Table 1. According to Table 1, PA-G-1 and PA-G-3 have the highest and lowest water contents, respectively. The water content of a composite used as electrode material in an electrochemical supercapacitor is known to affect physicochemical activity because of its effect on electrical conductivity, diffusion, and electrode potential [8, 14]. This means that the higher specific capacity of PA-G-1 can be explained by reference to its higher water content. In other words, compared to PA-G-2 and PA-G-3, the higher specific capacitance of PA-G-1 is attributed to its higher water content and its contribution in the diffusion process.

Thermal stability of the composite was also analysed by monitoring weight loss accompanying increasing temperature using TGA. The degradation onset temperature is the temperature corresponding to 50% mass loss in the composites [15]. A representative degradation onset temperature for each composite is shown in Table 1. In general, the degradation onset temperature of PA-G-1 is approximately ~637°C — higher than other samples. PA-G-2 and PA-G-3 exhibits onset values 572 °C and 586 °C, respectively. It is evident that the PA-G-3 has a higher degradation onset temperature, and so a greater thermal stability, than PA-G-2. The crystal structure has an effect on the degradation onset temperature values; the XRD results confirm that PA-G-1 shows a better crystal structure than the other composites, and that PA-G-3 shows a better crystal structure than PA-G-2.

32

Table 1. The water content and degradation onset temperature of the composites

	Water content at 100 °C (%)	The onset temperature (°C)
PA-G-1	5.17	637
PA-G-2	4.85	572
PA-G-3	4.02	586

4. CONCLUSION

This paper has shown that the characters of polyaniline-graphene composites have significant effects on their electrochemical properties. If the composite has a distinctive structure, a high degree of crystallinity, and a more stable structure, it shows a better electrochemical capacity. It was found that the composite's water content is another effective factor, which also influenced the electrochemical performance of a composite.

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