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Improved electrochemical performance of activated carbon/polyaniline composite electrode

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ABSTRACT

The composite thin films of activated carbon/polyaniline (AC/PANI) have been deposited on stainless steel substrates by a facile dip coating technique. Surface morphology of the films is examined by field emission scanning electron microscopy, which revealed aggregated nanofiber like structure for PANI and well distributed nanofibers with porous structure for AC/PANI films. The highest specific capacitance of 534 F g^{-1} at 5 mV s^{-1} and energy density of 78.49 Wh kg^{-1} at 1 mA cm^{-2} is observed for the AC/PANI electrode, indicating positive synergistic effect of AC and PANI.

1. Introduction

Polyaniline (PANI) is one of the most promising materials due to its reasonably high conductivity and chemical stability in the conducting state, good environmental stability, unique doping/dedoping behavior and mechanical flexibility [1–4]. It is frequently used electrode material for pseudocapacitors owing to its high electronic conductivity (10^3–10^4 Sc cm^{-1}) and high specific capacitance contributed from four oxidation states (leucoemeraldine, emeraldine base, emeraldine salt and pernigraniline) [5,6].

Moreover, activated carbon (AC) has attracted much attention because of its low cost, abundance, good mechanical strength and high surface area. Electric double layer capacitance is directly proportional to the available surface area and hence AC is extensively recognized as the electrode material for electric double layer capacitors (EDLCs).

It is interesting to combine the properties of both the materials to form a promising material possessing long cycle life and high specific capacitance. Recently few reports are published on the chemically and electrochemically synthesized AC/PANI composites. Quin et al. have studied the electrochemical properties of AC coated with PANI [7]. Huo et al. have studied the chemical deposition of PANI onto the surface of AC powder using V_2O_5 as oxidant and their electrochemical capacitor behavior [8]. Hu et al. have reported the supercapacitor behavior of AC fabric and PANI composite in neutral $NaNO_3$ electrolyte [9]. Electro-polymerization of PANI onto the high surface area using different methods has been reported by Martinez et al. for supercapacitor application [10]. Zengin et al. have prepared AC/PANI composite films by chemical polymerization and have studied their optical properties [11].

The present work demonstrates the in-situ polymerization method for AC/PANI composite material preparation and their electrochemical performance. The presence of AC in PANI substantially modifies the surface of the electrode, leading to the enhancement in the electrochemical performance of the composite electrode.

2. Experimental

The AC was prepared from a dry coconut shell. The coconut shell was crushed into small pieces. Then it was washed with double distilled water and dried in an oven at 383 K for 24 h. This dried sample (25 g) was taken in a glass container, to which 50 mL conc. H_2SO_4 was added as an impregnating reagent and then the solution was kept for 24 h. When the solution leaches out the acid, then it is washed off with distilled water till neutral pH. For the complete formation of it as a carbaneous material, the powder was kept in muffle furnace for 1 h at 573 K. Thus dried activated carbon powder was then sieved through BSS-25.

AC/PANI composite was prepared by using a chemical bath consisting of ammonium persulphate (APS), hydrochloric acid (HCl), aniline, AC and distilled water. In-situ polymerization method

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is employed for preparation of AC/PANI composite. In a typical synthesis the aniline monomer was first mixed with AC in 1 M HCl by ultrasonication to form a homogeneous suspension. Then the oxidant was added to this mixture to obtain the homogeneous composite of AC/PANI nanofibers. Uniform deposition of the AC/PANI films are obtained on stainless steel substrates by dip coating technique. This solution was kept under constant stirring throughout the deposition process. For comparison purposes, pure PANI electrode was also prepared via similar polymerization method as described above without any addition of AC.

The electrochemical measurements were performed in an electrolyte of 1 M H_2SO_4 with a conventional three electrode arrangement comprising graphite as a counter electrode and saturated calomel electrode (SCE) serving as the reference electrode. Scanning potentiostat (model- CHI-400A, CH Instrument, USA) was employed for the measurements.

3. Results and discussion

Fig. 1 shows the FTIR spectra of the powder collected from AC, PANI and AC/PANI samples over 450–2000 cm^{-1}. The FTIR spectrum for AC is as shown in Fig. 1(a). It gives four peaks at 1612, 1163, 1120 and 1021 cm^{-1}. The PANI (Fig. 1(b)) spectrum consists of four distinct peaks at 1560, 1492, 1304 and 1131 cm^{-1}. The bands are assigned to the N=Q=N stretching, N–B–N stretching (where Q and B denote the quinoid and benzenoid), N–H bending and –N=vibration which are similar to those obtained by Li et al. [12]. The sample AC/PANI composite exhibits all peaks of PANI sample. The peaks corresponding to wavenumbers 1560, 1492, 1304 and 1131 cm^{-1} for PANI showed shift towards the higher wavenumber corresponding to 1586, 1498, 1305 and 1140 cm^{-1} for AC/PANI composite respectively. This shift in the wavenumber is observed due to the presence of AC in PANI. The peak at 1021 cm^{-1} for AC also reflects in AC/PANI which confirms the formation of AC/PANI composite.

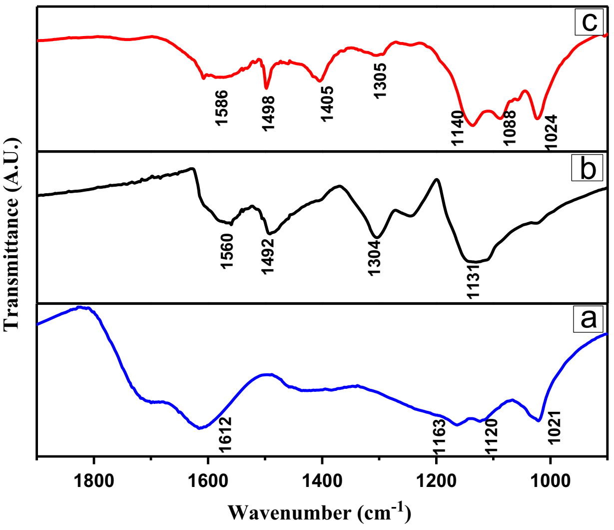

Fig. 1. FTIR transmittance spectra of the (a) AC, (b) PANI and (c) AC/PANI samples recorded in the wavenumber range of 500–1650 cm^{-1}.

Fig. 2(a and b) shows surface morphologies of PANI and AC/PANI samples at 50,000 × magnification. The aggregated nanofibers like structure is observed for PANI sample [Fig. 2(a)]. However, AC/PANI sample revealed the well distributed nanofibers with nanoporous structure. The average diameter of the nanofibers observed is about 30–50 nm for PANI sample whereas it is 20–40 nm for AC/PANI sample. The nanofiber structure provides large surface area to volume ratio leading to a high charge/discharge rate and specific capacitance. Well distributed nanofibers with nanoporous structure offered relatively larger surface area [Fig. 2(b)]. There was no drastic change observed between PANI and AC/PANI composite. Due to the interaction of monomer with AC before polymerization process prevents the aggregation of PANI nanofibers. This nanofibers and porous structure is favorable for supercapacitor, because it reduces the diffusion resistance of the electrolyte into electrode matrix.

Fig. 3(a and b) represents the Nyquist plots obtained for PANI and AC/PANI samples. It is observed that the electrode resistance of PANI (48.29 Ω) decreases significantly to 14.18 Ω for AC/PANI electrode due to the conducting properties of AC. At very high frequency the intercept of the plot with the real impedance (Z) axis are 0.42 and 0.32 Ω for the cells assembled with PANI and AC/PANI respectively. The intercept actually reports the uncompensated electrical resistance (R_Ω) of the electrolyte (R_e), the electrode active material (R_a) and the electrical leads combined (R_l). A decrease in high frequency resistance for AC/PANI than PANI sample may be due to the decrease in resistance of the active materials [13].

Fig. 4(a) shows a cyclic voltammogram for PANI. The oxidization peak corresponding to the leucoemeraldine to emeraldine salt at about 0.22 V and the reduction peaks corresponding to the leucoemeraldine and emeraldine base at 0.06 V and 0.64 V respectively were observed in PANI sample. The small peaks between 0.3 V and 0.55 V potentials are attributed to transformation of PANI charge carriers consisting of polaron (radical cation) and

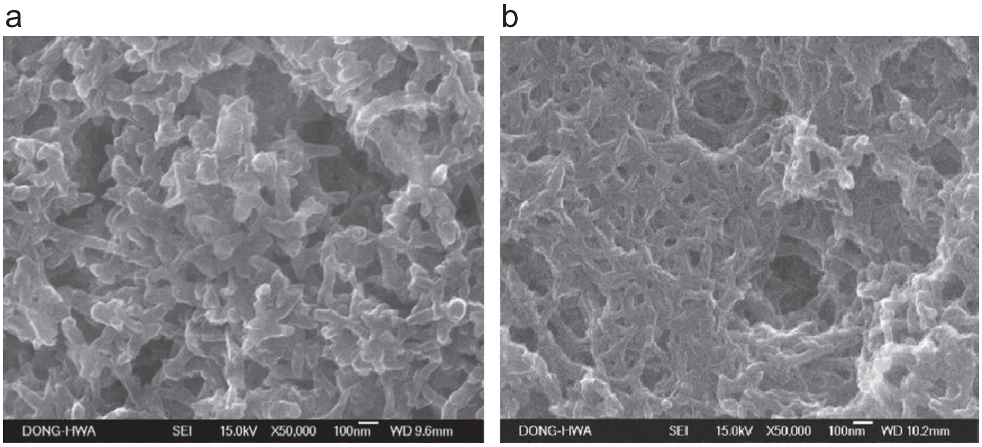

Fig. 2. Field Emission Scanning Electron Micrographs of the (a) PANI (b) AC/PANI samples at 50,000 × magnification.