

" Synthesis and Characterization of poly (ANI-co-ANA) for supercapacitor Applications "

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Abstract: In this study, nano structured poly (Aniline-co-Anthranilic acid) (poly (ANI-co-ANA) was synthesized using simple chemical oxidative polymerization. Poly (ANI-co-ANA) was characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM) to investigate both structural and morphological properties. The electrochemical performance of poly (ANI-co-ANA) electrode was investigated using cyclic voltammetry and galvanostatic charge discharge techniques. Poly (ANI-co-ANA) has showed good capacitive behavior with a specific capacitance of 278.07 F/g at scan rate of 10 mV/s indicating that it can be considered as a promising candidate as electrode material for supercapacitors applications.

Keywords: Poly (ANI-co-ANA); Specific capacity; Supercapacitors;

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I. Introduction

Currently, the development of energy storage devices is becoming ever more important [1-2]. Among various energy storage devices, supercapacitors are devices that store a relatively large amount of charge which can be rapidly drained and re-charged [3-4]. The basic construction of supercapacitor is mainly based on two electrodes separated by a dielectric porous film, called a separator, impregnated by an electrolyte. In the fabricating of supercapacitors, the electrode material is considered as the extremely important factor affecting the whole performance of supercapacitors [5,6,7]. Various types of materials such as carbon-based materials, metal oxides and conducting polymers are the most common electrode active materials for supercapacitors [8-9]. Among these materials, conducting polymers especially polyaniline (PANI) are suitable for supercapacitor applications because of their high specific capacitance, low cost and easy of synthesis. However, low processability of PANI due to its low solubility in most aqueous and organic solvents produces some difficulties for practical use. In the recent years, several efforts have tried to overcome these difficulties [10-11].

Copolymerization of aniline (ANI) with other monomers is an efficient approach to get some new properties which are non-existent for homo polymer. Copolymerization of aniline with other monomers such as sulphanilic acid (SA) and anthranilic acid (ANA) offers a possibility to prepare a new PANI based copolymer that not only retains the good properties of PANI itself but also possesses new properties [12,13,14,15,16]. Attaching different functional groups on the aniline ring could modify the properties of PANI. In order to meet the need of industrial demand of new material of specific properties, derivatives of PANI were being studied. Copolymerization of ANI with ANA is considered as one of the best solutions to overcome the low processability of PANI [17,18,19].

The current study is aimed to synthesis of poly (ANI-co-ANA) via chemical oxidative polymerization and study its characteristics focusing on the electrochemical behaviour in an attempt to apply it as a high performance supercapacitor electrode.

II. Experimental

2.1 Materials

Aniline (ANI) (a product of Sigma Aldrich) was distilled under reduced pressure. *o*- Anthranilic acid (ANA) was of chemically pure grade provided by EL-Naser pharmaceutical chemicals company) and used without further purification. Potassium peroxydisulfate (PPS) was provided by Merck-Schuchardt, Germany. Sulfuric acid and Hydrochloric acid were provided by EL-Naser pharmaceutical chemicals company and used as received. All experiments were carried out using bi-distilled water.

2.2 Synthesis of poly(ANI-co-ANA)

Poly (ANI-co-ANA) was chemically synthesized through oxidative co-polymerization with 1:1 molar concentrations of ANA and ANI. 4.656 g of aniline and 6.85g of anthranilic acid were dissolved respectively in aqueous 1.5M HCl. The solution of the two monomers was poured into three neck flask equipped with a thermometer, a mechanical stirrer, and a separating funnel. A solution containing potassium persulfate (0.025 M) in aqueous 1.5M HCl was added drop wise from the separating funnel whilst maintaining the temperature close to 40°C. After the addition is complete, the reaction mixture is then left stirring for approximately 90 min. At the end of reaction a greenish brown colored precipitate of Poly (ANI-co-ANA) was observed. The solid Poly (ANI-co-ANA) was then collected from the reaction mixture by centrifugal separation, evaporated and finally dried in an electric oven at 50°C for 24 hrs.

2.3 Characterization techniques

JASCO- 6100 FT-IR spectrometer was used to record FT-IR spectrum for poly (ANI-co-ANA) sample. The crystal structure was characterized using X-ray diffractometer (Philips PW3050/60) with a Cu-K α X-ray source. TEM images were recorded using JEM-HR-2100-transmission electron microscope operated at an acceleration voltage of 200 kV, National Research Centre in Egypt.

The Electrochemical performance of Poly (ANI-co-ANA) electrode was evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCDC). CV and GCDC measurements were performed using a three-compartment glass cell in which glassy carbon (GC) was used as the working electrode, Pt mesh was employed as the counter-electrode and a saturated calomel electrode (SCE) served as the reference electrode. All experiments were carried out at room temperature (around 25 °C). To investigate the electrochemical behaviour of Poly (ANI-co-ANA), it was dissolved in an organic solvent and then it was drop-casted onto glassy carbon electrode substrate followed by drying gently to evaporate the solvent under atmospheric conditions.

III. Results and discussion

3.1 Polymerization conditions

Copolymer of ANI with ANA was synthesized by in-situ chemical oxidation using PPS as the oxidizing agent and with equimolar quantities of the two monomers. Reasonably good yield of 59.1 % was obtained. The electron-withdrawing carboxylic acid group coupled with the steric factors deactivate the aromatic system retarding the polymerization of anthranilic acid compared to that of aniline. Due to this electronic effect a longer time is need to oxidize anthranilic acid monomer at low temperatures. Raising the temperature close to 40 °C lead to increase the rate of polymerization.

3.2 FTIR

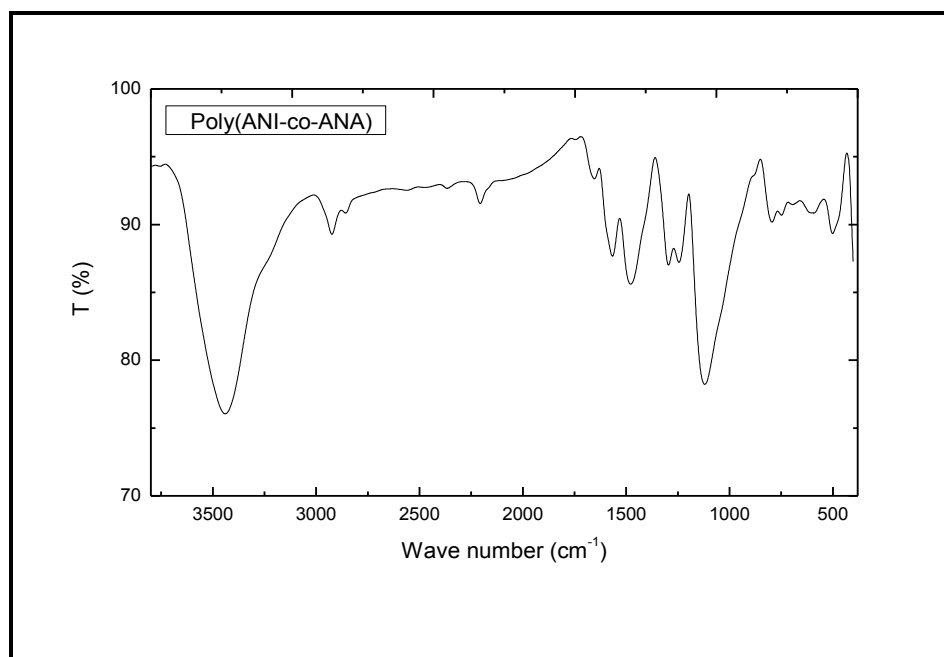
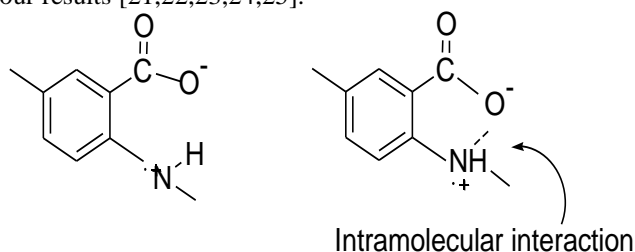


Figure 3.1: IR Spectrum of Poly (ANI-co-ANA).

Figure 3.1 shows the FTIR spectrum of poly (ANI-co-ANA). The spectrum of poly (ANI-co-ANA) showed a band at 3450 cm^{-1} that may be assigned to (NH). FT-IR spectrum showed a small intensity band around 1700 cm^{-1} correspond to the C=O stretch vibration. The small intensity may be due to carboxyl groups along the whole polymer chain form intramolecular hydrogen bonds with amino groups as schematically viewed in scheme 1 [20]. The band at 1580 and 1520 cm^{-1} correspond to the C=C stretching deformation of quinoid and benzenoid rings along the copolymer chain respectively. The appearance of these IR bands confirmed the formation of copolymer. Our results were found in good agreement with the data reported in literature which confirms the reliability of our results [21,22,23,24,25].



Scheme 1: Intramolecular and intermolecular interactions in poly (ANI-co-ANA).

3.3 XRD

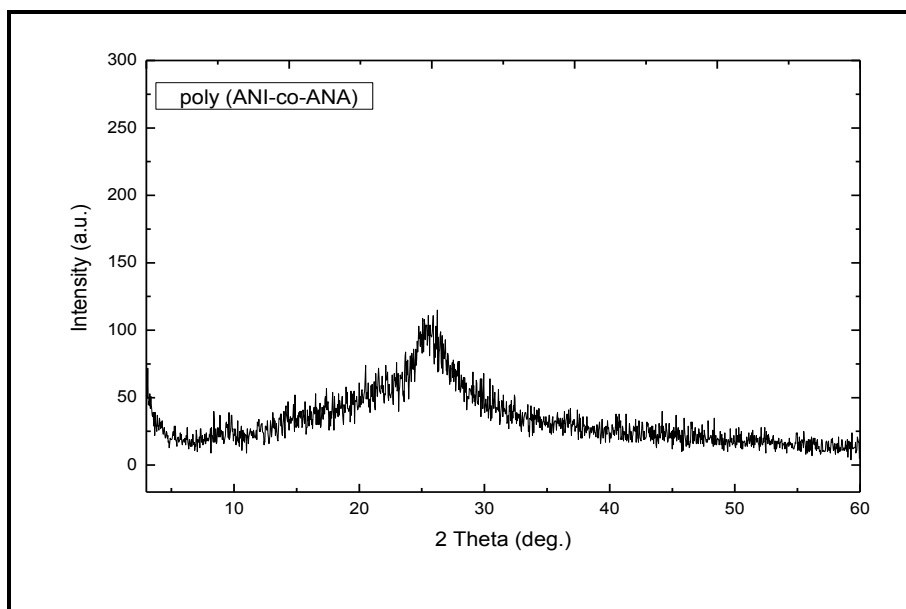


Figure 3.2: XRD patterns of Poly (ANI-co-ANA).

XRD is a common method to discuss the crystallinity orientation and chain backing of conducting polymers [26-27]. The XRD pattern of poly (ANI-co-ANA) was shown in Figure 3.2. Two peaks were observed at $2\theta = 8.5$ and 25.4 values. The data show that, the powder is amorphous in structure and the chains were strongly disordered. As illustrated all peaks are weak and broad, which illustrate an amorphous carbon framework.

3.4 TEM

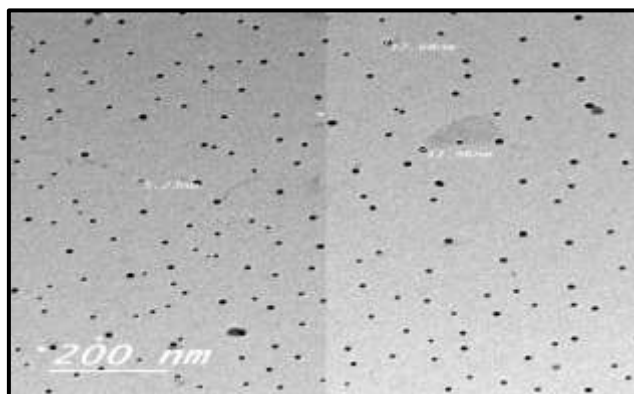


Figure 3.3: TEM image obtained for poly (ANI-co-ANA).

The nano-scale structure of poly (ANI-co-ANA) was examined using transmission electron microscopy. TEM analysis (Figure 3.3 b) revealed that the copolymer particles were almost spherical in shape with a mean diameter of 5–13 nm.

3.5 Electrochemical Characterization

3.5.1 Cyclic voltammetry

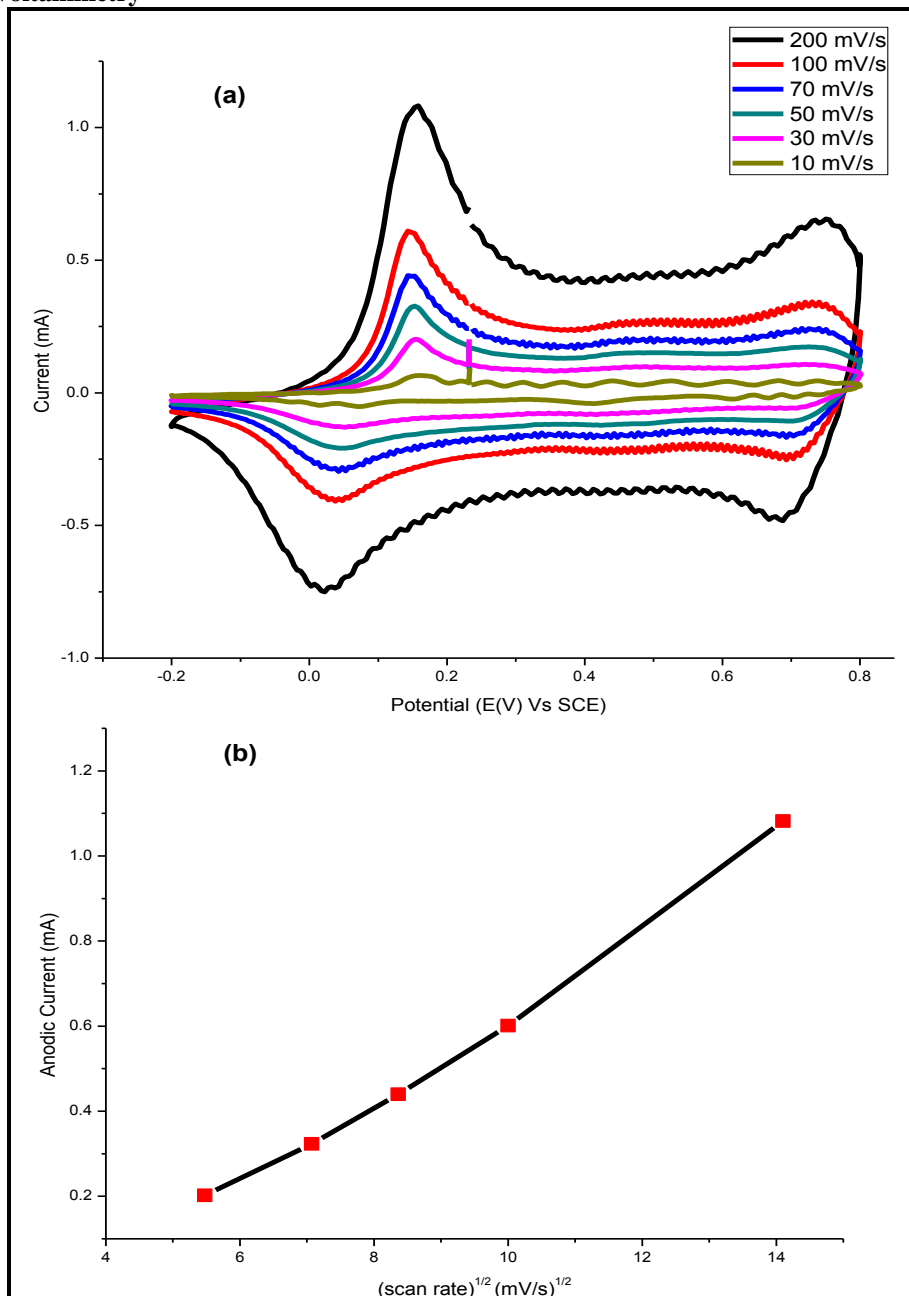


Figure 3.4: (a) Cyclic voltammograms of poly (ANI-co-ANA) at GCE in 1M H₂SO₄ at different scan rates: from inside to outside 10,30,50,70, 100 and 200 mV/s. (b) The linear variation in the anodic peak currents as a function of square root of scan rates for poly (ANI-co-ANA) in 1M H₂SO₄.

The cyclic voltammograms of poly (ANI-co-ANA) onto glassy carbon electrode in 1 M H₂SO₄ over a voltage range from -0.2 to 0.8 V at different scan rates of 10, 30, 50, 70, 100 and 200 mV/s were shown in Figure 3.4(a). The CV profile of poly (ANI-co-ANA) exhibited two pairs of redox peaks at 0.155 V and 0.65 V suggesting the pseudocapacitive behaviour of the electrode.

Anodic currents revealed a linear relationship as a function of square root of scan rate for poly (ANI-co-ANA) electrode, as shown from Figure 3.4(b), when cycling was carried out in 1M H₂SO₄. According to the

Randles-Sevcik equation, the linear relationship as a function of square root of scan rate indicates that the electrochemical process is diffusion controlled [28].

The specific capacitance of poly (ANI-co-ANA)electrode was calculated from CV profile according to the following formula [29]:

$$C_s = \frac{\int I dV}{v m \Delta V}$$

where C_s is the specific capacitance of the electrode (F/g), v is the scan rate (mV/s), m is the mass of poly (ANI-co-ANA)and ΔV is the potential window. The calculated specific capacitance from the CV profile of poly (ANI-co-ANA)electrode at 10 mV/s is 287.07 F/g.

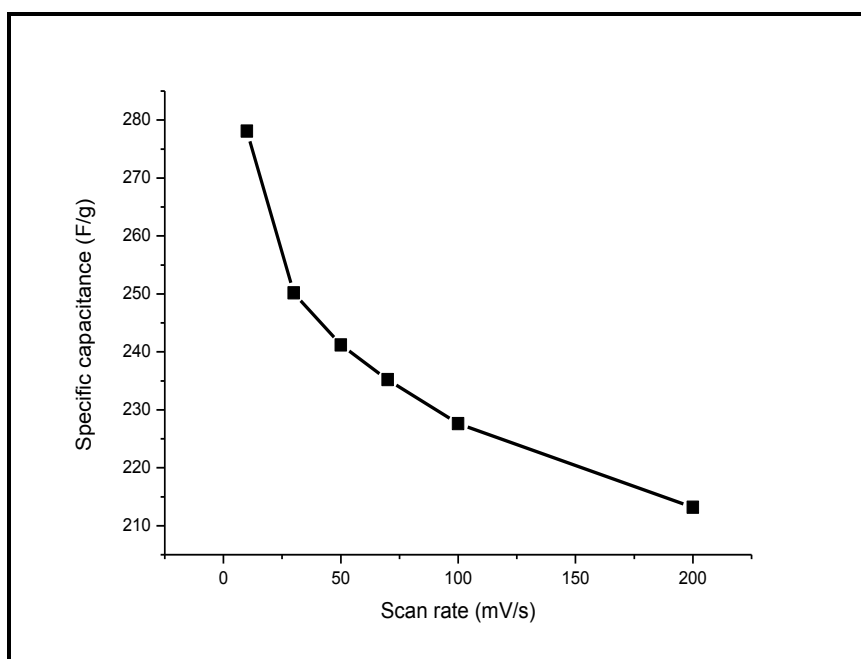


Figure 3.5: Effect of scan rate on the values of specific capacities of Poly (ANI-co-ANA).

As shown from Figure 3.5, the specific capacitances of Poly (ANI-co-ANA) decrease with the increasing scan rates. This may be attributed to the different diffuse rates of electrolyte ions. With high scan rates, electrolyte ions may be limited to contact with only the active materials on the surface due to the time constraint, and thus only the outer active surface can be utilized for charge storage, leading to lower specific capacitance values.

3.5.2 Galvanostatic Charge discharge

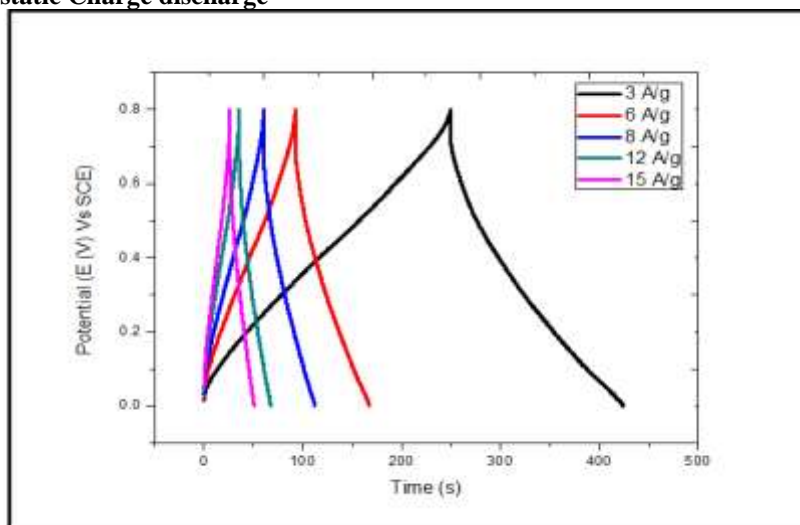


Figure 3.6: a Charge–discharge curves of (a) poly (ANI-co-ANA) electrode at a current density of 3, 6, 8, 12, and 15 A/g in 1 M H₂SO₄.

The charge/discharge curves of Poly (ANI-co-ANA) at different current densities of 3, 6, 8, 12, and 15 A/g, respectively were shown in Figure 3.6. The charge/discharge curves have slightly deviated from linear characteristics and this behavior reveals that the capacitance involves Faradic capacitance due to redox reactions. The large charge/discharge time, as evident in Figure 3.6, suggests that large number of electrons and electrolyte ions are participating in the charge/discharge process.

3.5.3 Cyclic Stability

Study of stability and reversibility of the electrode material is critical in practical applications for supercapacitors [30]. Multiple CV curves for Poly (ANI-co-ANA) was recorded in 1 M H₂SO₄ at 200 mV/s for 1000 cycles as shown in Figure 3.7(a).

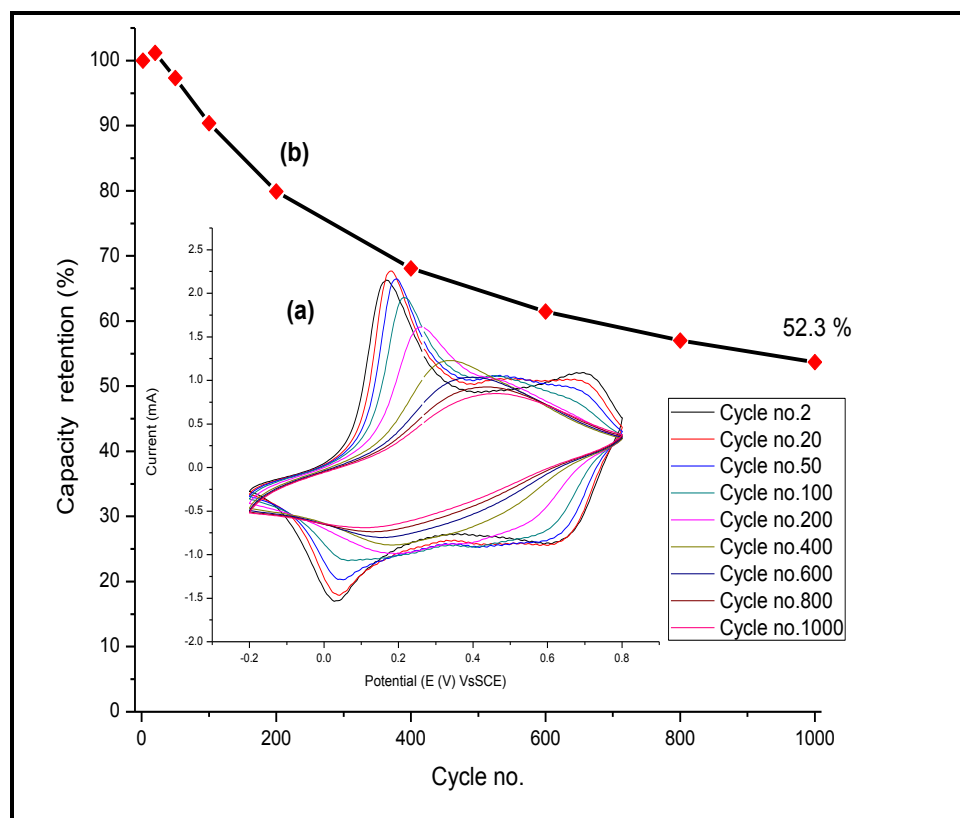


Figure 3.7: (a) Cyclic stability of Poly (ANI-co-ANA) during the multiple CVs process.

(b) Capacity retention of Poly (ANI-co-ANA) as a function of cycle number.

Figure 3.7 (b) shows the specific capacitance retention of Poly (ANI-co-ANA) as a function of cycle number. The retention ability is calculated by taking the ratio of capacitance at a particular cycle to the initial capacitance. At the initial cycles (till cycle no 60), the specific capacitance did not decrease but actually increased dramatically due to electro-activation process. The Poly (ANI-co-ANA) electrode shows 47.7 % loss in specific capacitance after 1000 cycles due to redox reactions. Redox reactions (doping/de-doping of ions) can lead to mechanical changes making the Poly (ANI-co-ANA) electrode swell and shrink, giving rise to poor mechanical stability and low cycle life as all conducting polymers [31]. In our future work we attempt to improve the stability of Poly (ANI-co-ANA) electrode.

3.6 Thermal stability

Thermal stability of Poly (ANI-co-ANA) was analyzed by TGA in He atmosphere. The TGA curve (Figure 3.8) of the copolymer, it exhibited a three-step weight loss. The first minor weight loss step between 50 and 120°C was ascribed to the removal of moisture and physically adsorbed water molecules. The second weight loss step between 150 and 350 °C was attributed to the removal of dopant along with the evolution of carbon dioxide and oligomers from the copolymer. The third major weight loss at around 400 °C was ascribed to the degradation of copolymer.

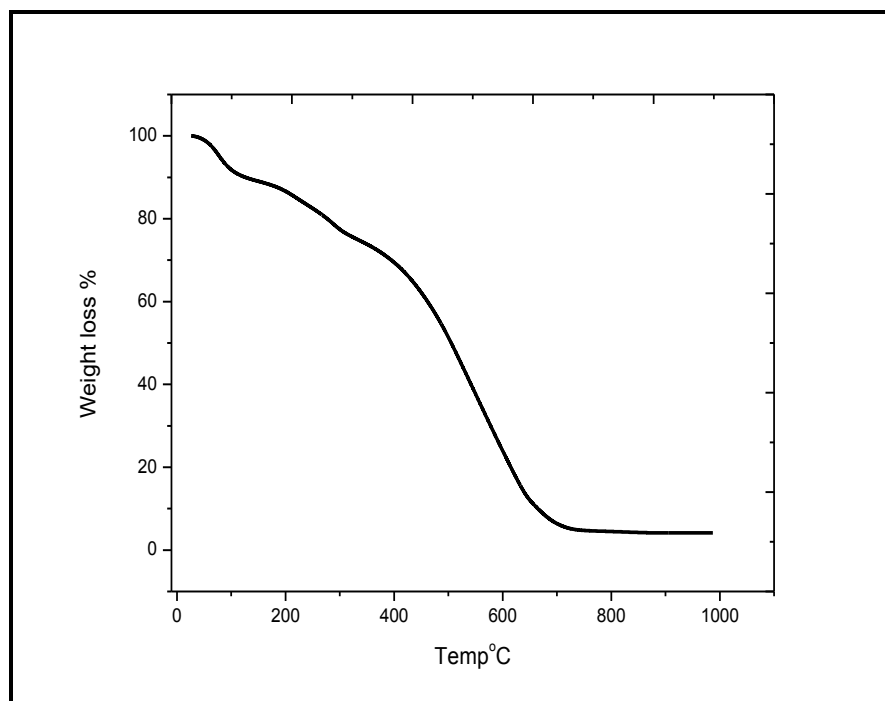


Figure 3.8: TGA thermogram of Poly(ANI-co-ANA).

IV. Conclusion

Poly (ANI-co-ANA) was successfully synthesized as electrode material for supercapacitors via chemical oxidative polymerization. The FT-IR, and XRD characterization tests implied the formation of copolymer composed of ANI and ANA monomers. TEM results showed that chemically synthesized poly (ANI-co-ANA) consisting spherical nanoparticles with mean diameter smaller than 13 nm. The specific capacitance from cyclic voltammetry of copolymer was found to be 278.07 F/g at scan rate of 10 mV/s. Our synthetic approach presents not only an environmentally-friendly option, but also relatively clean and easy processing conditions that would be important for many technological applications. This method can be extended to the fabrication of other PANI-based copolymers.

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