

A new synthetic approach of nano-sized polyaniline cathode material for zinc-polyaniline rechargeable battery

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Abstract

The electrochemical performances of electrochemically synthesized polyanilineno (nPANI) material as cathode vs. zinc metal as anode is investigated. The nPANI particle is synthesized by galvanostatic electro-oxidation of aniline from interfacial solution on metal electrode surface and characterized by UV-Visible, FTIR, powder XRD and TEM. The material is crystalline nano spheres with meso pores among them, uniformly distributed and dispersed. The sizes of the particles lie in 50-100 nm region. This nPANI is used as cathode material in $Zn | (NH_4)_2SO_4, ZnSO_4(aq) | nPANI$ battery and its electrochemical performances is investigated by galvanostatic charge-discharge cycling. The electrochemical cell exhibits an open circuit potential of 1.3 volts and a discharge plateau with an average discharge potential of 1.1 volts. The maximum discharge capacity observed is 250 Ah.Kg⁻¹. Copyright © 2017 VBRI Press.

Keywords: Nano polyaniline, biphasial method, TEM image, cathode material, charge-discharge.

Introduction

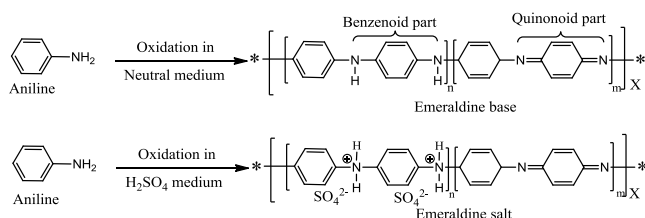
The particle size of different elements or compounds when tends to nanometer in size its physical and chemical properties drastically change from its bulk materials, which is an interesting branch of current research [1, 2]. The cause behind this drastic change of properties stems from the fact that with decrease in particle size, the surface area to volume ratio of the material increases. As a result, most of the atoms/molecules are now exposed to the reaction. In contrast, in case of large particles only the atoms/molecules on the surface are able to take part in the reaction and the atoms/molecules inside the particle are unable to reach in contact with the reactants at the moment. Hence, reaction rates and other physical and chemical properties of small sized particles are varied from the bulk materials [3, 4].

Our research interest in conducting polymer nano particles, particularly polyaniline (PANI), originates from their potential applications in catalysis, sensors and energy storage and conversion [5-10]. This nano particles of PANI (nPANI) exhibit abrupt change in physicochemical behaviour in comparison to its bulk material.

The conventional methods for the preparation of conducting PANI are micro-emulsion, freeze drying, atomizer spraying, and surface spread film patch method [11-14]. Electrochemical methods have been used extensively nowadays due to their simple manipulation and low cost [15]. However, the electrochemical methods employed have different categories such as, cyclic voltammetric, potentiostatic, galvanostatic and pulse potentiostatic. All these techniques mostly produce the coagulate form of PANI not the discrete form [16-19], which do not fulfil our target. Our goal is to synthesize PANI in nano-discrete form which would be utilized as an energy storage material to achieve its high performances.

In this article, we report the synthesis of nPANI employing the straightforward electrochemical deposition technique applying galvanostatic current into a biphasial solvent medium [20-22]. Then the synthesized nPANI has been used as cathode material in $Zn | (NH_4)_2SO_4, ZnSO_4(aq) | nPANI-H_2SO_4$ rechargeable battery and its performances as cathode has been investigated by galvanostatic charge-discharge studies [23-25].

The reaction scheme for the synthesis of PANI from aniline is represented as follows:



Scheme 1: Synthesis of PANI from aniline in neutral and H_2SO_4 medium.

Experimental

Materials used

Aniline (Merck, India, 99%); Dichloromethane (DCM) (Merck, India, 99%); H_2SO_4 (Merck, India, 98%); $(\text{NH}_4)_2\text{SO}_4$ (Merck, India, 99.5%); $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, India, 99.5%).

Synthesis of nano-polyaniline (nPANI)

The nPANI has been synthesized by a typical electrochemical technique applying galvanostatic constant current. 4 ml double distilled aniline is dissolved in 36 ml dichloromethane (DCM) taken in a beaker and stirred with magnetic stirrer for half an hour. 40 ml 1 M sulphuric acid is added into the aniline-DCM mixture and stirred again for another 5 minutes. The solution mixture is then kept intact for few minutes, and the two solutions now get separated and formed two immiscible layers; the DCM layer goes under the aqueous acid layer. Two electrodes; one stainless steel thin plate (5 cm^2 area dipped) serve as working electrode and a platinum foil (2 cm^2 area dipped) as counter & reference electrode, are fixed in the acid layer keeping a distance of 5 cm between them. A constant current of $1 \text{ mA} \cdot \text{cm}^{-2}$ is applied and a film of PANI is noticed to deposit on the surface on the steel plate [26, 27]. However, two different current densities of $1 \text{ mA} \cdot \text{cm}^{-2}$ and $0.5 \text{ mA} \cdot \text{cm}^{-2}$ are used to study the effect of applied current density on particle growth. The deposition is continued for one hour to more than that as required. The deposited PANI is obtained on the steel plate as a uniform layer, is then washed with triple distilled water, collected, vacuum dried with 70°C and stored in desiccators for further use.

Characterization

The synthesized PANI is characterized by using spectroscopic method viz. UV-Visible (Shimadzu, model-UV3101PC, Japan), FTIR (8400S, Shimadzu, Japan), Powder XRD (Ultima III Rigaku, Cu $K\alpha$, $\lambda=1.5406 \text{ \AA}$) etc. UV-Vis spectrum is recorded dissolving PANI in dimethyl sulfoxide (DMSO) as base line solvent. FTIR is carried out with dry solid sample of PANI preparing KBr plate. Powder XRD has recorded with solid dried sample using $\text{CuK}\alpha$ incident beam. Transmission Electron Microscope (TEM, Model no-JEM-100C X 11, JEOL) is employed for investigating particle shape, size and surface morphological distribution. A small amount of dried PANI powder is sonicated for dispersion in benzene before recording the image.

Electrochemical characterization is performed by cyclic voltammetry (CV) and charge-discharge studies, fabricating laboratory model cells with PANI. CV is used to examine the redox properties and charge-discharge studies for electrochemical performances.

CV is carried out constructing three electrode cell as described follows. After deposition of H_2SO_4 doped PANI film at the stainless-steel surface, the electrode is washed with triple distilled water and then dipped into a 1 molar solution of $(\text{NH}_4)_2\text{SO}_4$ and ZnSO_4 mixture. A platinum plate of 2 cm^2 area is also dipped into the same solution. Now, the PANI- H_2SO_4 film electrode is connected with working electrode, platinum plate with counter electrode and saturated calomel electrode with reference electrode. The solution serves as electrolyte and this solution is connected with KCl solution of SCE by a salt bridge. The CV is recorded at the scan rate of $20 \text{ mA} \cdot \text{s}^{-1}$ in the potential range of -0.2 V to 1.0 V vs. SCE using a potentiostat/galvanostat (VersaStatTMII, Princeton Applied Research, USA).

Charge-discharge studies are carried fabricating laboratory model aqueous Zn-PANI cell of the configuration, $[\text{Zn} | (\text{NH}_4)_2\text{SO}_4, \text{ZnSO}_4(\text{aq}) | \text{PANI-H}_2\text{SO}_4]$. The cathode is PANI- H_2SO_4 film electrode, similar to working electrode in CV set up, anode is Zn plate (5 cm^2 are dipped). Both of these electrodes are dipped into the electrolyte of 1 M aqueous solution of $(\text{NH}_4)_2\text{SO}_4$ and ZnSO_4 mixture keeping them 2 cm apart. The charge-discharge studies are carried out applying two different current rates of $25 \mu\text{A} \cdot \text{mg}^{-1}$ & $100 \mu\text{A} \cdot \text{mg}^{-1}$ galvanostatically within the potential windows of 0.7 V to 1.5 V using the same instrument, potentiostat/ galvanostat (VersaStatTMII, Princeton Applied Research, USA).

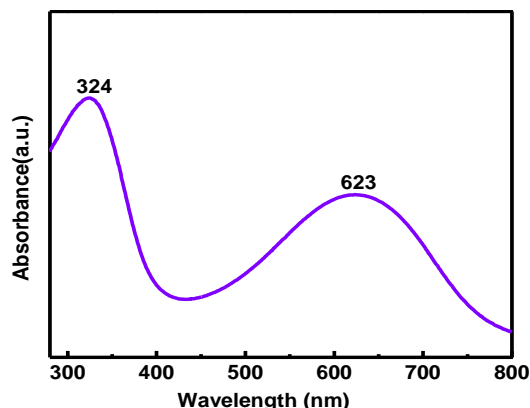


Fig. 1. UV-Vis spectrum of polyaniline film in dimethyl sulfoxide.

Results and discussion

Fig. 1 shows the UV-Visible absorption spectrum of PANI, recorded under the wavelength range of 200-700 nm. A strong sharp absorption peak is observed at 324 nm due to $\pi-\pi^*$ transition in the benzene ring and another strong broad peak at 623 nm attributed to exciton formation in the quinonoid ring of PANI. Thus UV-Visible spectrum reveals the formation of pure PANI film with alternating benzenoid and quinonoid segments, which is responsible for charge storage [28-30].

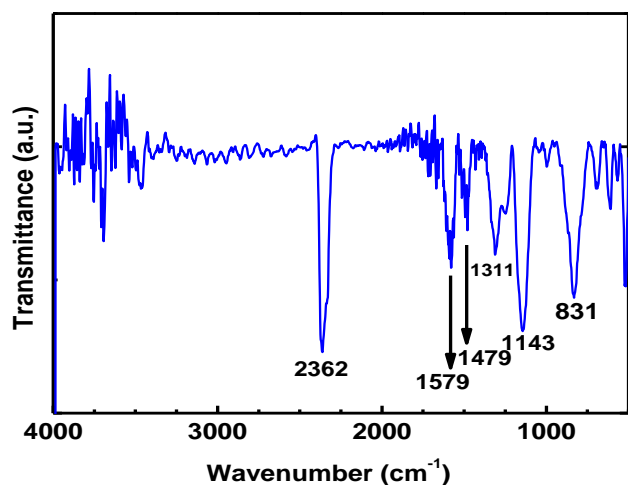


Fig. 2. FTIR spectrum of solid dehydrated polyaniline.

Fig. 2 illustrates the FTIR spectrum of PANI recorded within the frequency range of 500-4000 cm^{-1} . The peaks at 1479 cm^{-1} and 1579 cm^{-1} are the characteristic stretching mode of vibration for benzenoid and quinonoid ring, respectively[31-33]. The presence of benzenoid and quinonoid rings in the PANI chain are responsible for charge transfer process. The vibrational mode at 1143 cm^{-1} is account for the combine mode of benzenoid and quinonoid rings and the vibrational mode at 831 cm^{-1} is for counter ions inserted in the PANI chain. Moreover, the sharp peak at 2362 cm^{-1} is attributed for polaronic C-N stretching and the peak at 1311 cm^{-1} is ascribed for stretching mode of doped sulphate ions from H_2SO_4 . So, FTIR study clearly indicates the formation of pure PANI film over stainless steel surface without any impurities.

Powder X-ray diffraction (XRD) patterns of solid PANI powder, recorded in the range of $2\theta=10-90^\circ$ with scan rate of 5 $\text{deg}\cdot\text{min}^{-1}$ is displayed in Fig. 3. XRD pattern shows two distinct peaks at 20.18° and 25.36°, confirms the formation of phase pure PANI is in good agreement with literature report [34-36]. The broadening nature of the peaks indicates the nano material formation.

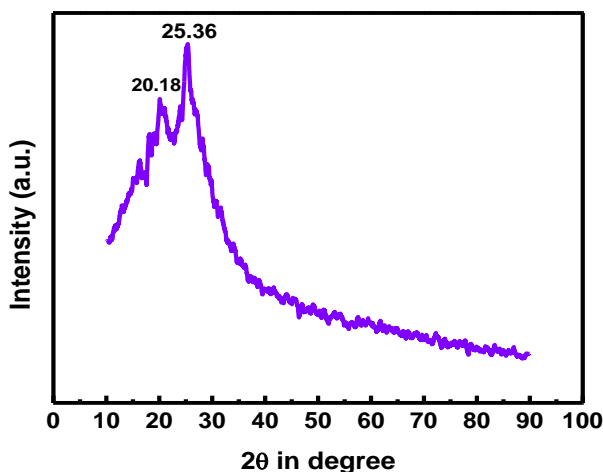


Fig. 3. Powder X-ray diffraction pattern of solid PANI.

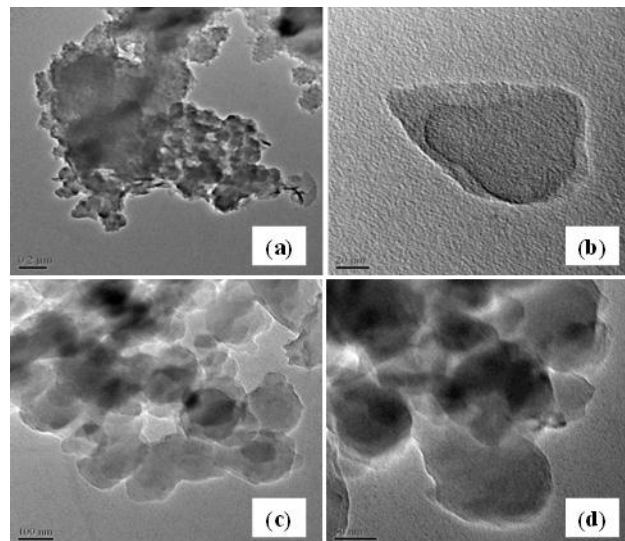


Fig. 4. TEM images of PANI synthesized at 1 $\text{mA}\cdot\text{cm}^{-2}$ (a, b) and 0.5 $\text{mA}\cdot\text{cm}^{-2}$ (c, d) current densities.

Fig. 4 demonstrates the TEM images of PANI powder at different magnification. The polymerization has been carried out at two current densities of 1 $\text{mA}\cdot\text{cm}^{-2}$ and 0.5 $\text{mA}\cdot\text{cm}^{-2}$. This different current flow effects on the particle growth of PANI. TEM images clearly indicates that the particle sizes at current density 1 $\text{mA}\cdot\text{cm}^{-2}$ lie within 100-200 nm ranges (Fig. 4a & 4b), whereas, at current density of 0.5 $\text{mA}\cdot\text{cm}^{-2}$ the size remains between 50-100 nm regions (Fig. 4c & 4d). The particle size decreases with decrease in current-flow, as expected [37-39]. Moreover, mesopores are found among the nano spherical particles. Therefore, TEM investigations reveal that the particles are nano sphere, uniformly distributed, mesoporous and dispersive in nature.

Fig. 5 exhibits the cyclic voltammogram of PANI film vs. saturated calomel electrode. In the cathodic scan, the de-doping of SO_4^{2-} and H^+ occurs at 0.29 and 0.00 volts, respectively and in the anodic scan, the doping of H^+ and SO_4^{2-} occurs at 0.35 and 0.65 volts, respectively. Thus the system is showing reversible behaviour and ability to work as an electrode material. Moreover, the difference between cathodic and anodic peak potential is 35 mV at the scan rate of 20 $\text{mV}\cdot\text{s}^{-1}$, which is good characteristics of an electrode material.

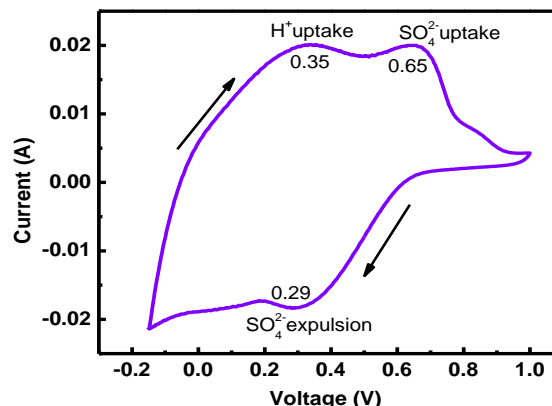


Fig. 5. Cyclic Voltammogram (CV) of PANI vs. SCE at a scan rate of 20 $\text{mV}\cdot\text{s}^{-1}$ in 1 M solution of $(\text{NH}_4)_2\text{SO}_4$ and ZnSO_4 mixture.

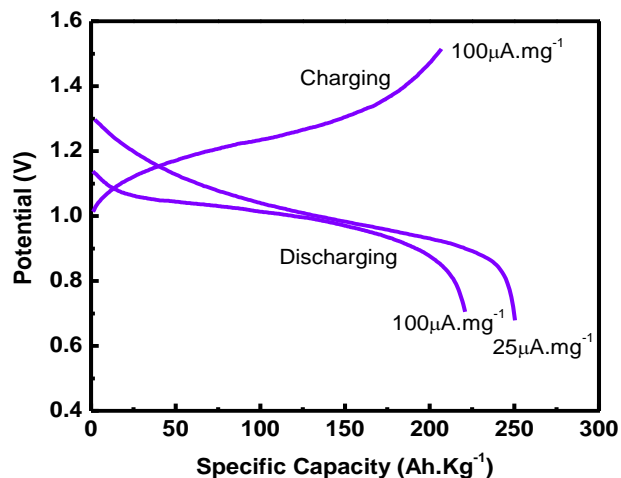


Fig. 6: Charge-discharge curve of nPANI cathode vs. Zn²⁺/Zn anode.

Fig. 6 displays the galvanostatic charge-discharge profile of Zn | (NH₄)₂SO₄.ZnSO₄(aq) | nPANI battery at two different current rates of 25 μA.mg⁻¹ and 100 μA.mg⁻¹ [39-43]. The average discharge and charge potentials are observed at 1.0 V and 1.2 V, respectively with an open circuit potential 1.3 V. A higher specific capacity could have been achieved, if the cell would discharge at very low current density. When the cell is discharged at 25 μA.mg⁻¹ current rate, a discharge capacity of 250 mAh.g⁻¹ is obtained.

Conclusion

Polyaniline in nanometer size range is successfully synthesized by the most popular, cost effective electro-oxidation of aniline. Two immiscible solvents, dichloromethane and dilute sulphuric acid have been used in an interfacial manner, and the reaction is carried out in the dilute sulphuric acid medium to control the particle growth on the electrode. UV-Visible, FTIR and powder XRD confirm the formation of polyaniline in purified form. High broadening in XRD peaks suggests that the particle sizes are in nanometer region. This finding is further confirmed by the TEM investigations, which clearly indicates that the particle sizes reduce to less than 100 nm when galvanostatic applied current is lower than 0.5 mA.cm². Cyclic voltammetry revealed that the material is redox reversible and charge-discharge studies confirm the material's performance as cathode in zinc rechargeable battery. The laboratory model aqueous galvanic cell comprised with nanopolyaniline cathode and zinc anode was cycled in the potential range of 0.7-1.5 volts. The cell exhibits an open circuit potential of 1.3 volts and a discharge capacity of 250 mAh.g⁻¹ at a current rate of 25 μA.mg⁻¹, which is an excellent figure.

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