

Preparation and Characterization of Polyaniline (PANI)-Platinum Nanocomposite

Kumar Neeraj, Ranjan Haldar

Abstract—Polyaniline is an indispensable component in light-emitting devices (LEDs), televisions, cellular telephones, automotive, corrosion-resistant coatings, actuators etc. The electrical conductivity properties was found be increased by introduction of metal nano particles. In the present study, an attempt has been made to utilize platinum nano particles to achieve the improved electrical properties. Polyaniline and Pt-polyaniline composite are synthesized by electrochemical routes. X-ray diffractometer confirms the amorphous nature of polyaniline. The Bragg's diffraction peaks correspond to platinum nanoparticles in Pt-polyaniline composite and thermogravimetric analyzer indicates its decomposition at certain temperature. The Scanning Electron Micrographs of colloidal platinum nanoparticles were spherical, uniform shape in the composite. The current-voltage (I-V) characteristics of the PANI and composites were also studied which indicate a significant decreasing resistivity than PANI-Platinum after introduction of pt nanoparticles in the matrix of polyaniline (PANI).

Keywords—Polyaniline, XRD and Platinum Nanoparticles.

I. INTRODUCTION

CONDUCTING polymers exhibit semiconductor or metal-like electrical and optical properties while at the same time they are lightweight, flexible, inexpensive, and easy to synthesize [1]. Although these materials are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteenth century. At that time 'aniline black' was obtained as the product of oxidation of aniline, however, its electronic properties were not established [2] the Conductivity of Polyaniline (PANI) is about 8 S cm^{-1} , exists in four main oxidation states; leucoemeraldine base, emeraldine, emeraldine salt and pernigraniline [3]. The conduction mechanism in such polymers is very complex since such a material exhibits conductivity across a range of about fifteen orders of magnitude and many involve different mechanisms within different regimes. Conducting polymers show enhanced electrical conductivity by several orders of magnitude after doping. The concept of solitons, polarons and bipolarons has been used to explain the electronic phenomena in these systems. Conductivity in conducting polymers is influenced by a variety of factors including polaron length, the conjugation length, the overall chain length, and by the charge transfer to adjacent molecules. These phenomena can be

explained by large number of models based on intersoliton hopping, hopping between localized states assisted by lattice vibrations, intra-chain hopping of bipolarons, variable range hopping in 3-dimensions and tunneling between conducting domains [4]. Conducting polymers usually can be synthesized by chemical or electrochemical to form a cation radical followed by coupling to form dications and leads to polymer [5]. The most intensively studied among the conducting polymers due to its unique properties, and this focus has resulted in significant development. Polyaniline shows reversible insulator-to-metal transitions and electrochromic behavior (yellow-green-blue-violet), depending on its oxidation state and pH. It has good stability in the presence of air and humidity. The combination of these characteristics makes polyaniline useful for various applications including rechargeable batteries [6] light emitting diodes [7], transistors [8], molecular sensors [9], nonlinear optical devices [10], corrosion protection [11], electromagnetic interference shielding [12], and electrochromic displays [13] Conducting polymer composites are typically a physical mixture of a nonconductive polymer and a conducting material such as a metal or carbon powder distributed throughout the material. Conductive carbon blacks, short graphite fibers, and metal coated glass fibers, as well as metal particles or flakes, were used in early experiments for the preparation of such composites. Their conductivity is governed by percolation theory, which describes the movement of electrons between metallic phases and exhibits a sudden drop in conductivity (percolation threshold) at the point where the dispersed conductive phase no longer provides a continuous path for the transport of electrons through the material [14]. These composites have the ability to enhance their material properties with desirable mechanical and physical characteristics [15], [16].

The incorporation of metal nanoparticles in the matrix of conductive polymer offers enhanced the properties [17]. They have diverse potential in electronics because merge of metal clusters to increase the conductivity of composite [18]. The aim of this work is to synthesize polyaniline and Platinum-polyaniline composite samples and to study their electric characteristics

II. EXPERIMENTAL

A. Synthesis of Polyaniline

Polyaniline was synthesized using commercially available aniline monomer by various methods [19]. For this, 2 ml of aniline monomer was taken in a beaker and ice cooled by

Neeraj Kumar is Asst. Professor with the Center of Excellence, Material Science and Engineering, Department of Metallurgy, OP Jindal Institute of Technology, Raigarh, Chhattisgarh, 496001, India (phone: +91-7869832398; Fax: 7762 304040; e-mail: thapar.neerajkuverma@gmail.com).

putting it in a refrigerator. After it 100 ml solution of 2 M HCl was prepared. Then the ice-cooled aniline monomer was added in the 100 ml 2M HCl with continuous shaking. This mixture of solution was put in the refrigerator at zero degree. In separate beaker, 10 gm of ammonium peroxisulphate (APS) was added in 50 ml water. This solution is called APS solution and it oxidizes the monomer of aniline. The mixture of monomer and HCl was put in ice cubes so that the temperature would maintained at zero degree. After that APS solution was added drop wise to the monomer mixture with constant stirring using a magnetic stir. Due to this a greenish black precipitate started to appear which indicated the polymerization of the monomer unit. After mixing the solution was kept overnight so that polymerization may be completed. Next day the solution was filtered and washed with distilled water several times. The prepared powder was dried at 60°C this greenish black powder was the poly aniline polymer powder.

B. Synthesis of Platinum Nanoparticles

For the synthesis of Pt nanoparticles a 0.2 M stock solution of platinum hexachloride ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$) was prepared. The 2 ml of this stock solution was mixed with 10 ml ethylene glycol. Here the ethylene glycol acts as a reductant. The resulting solution was stirred for 30 minutes. After this the solution was heated at 120°C in an oven to reduce platinum compound into platinum nanoparticles. The colour of solution changed from yellowish to brown and finally into black. The heating was continued for further 5 minutes. This synthesized solution of Pt nanoparticles was kept as such for further use.

C. Synthesis of Platinum-Polyaniline Nanocomposite

The synthesized polyaniline was dissolved in appropriate concentration in the synthesized solution of Pt nanoparticles. This mixture was refluxed at 100°C for 2 hours. Finally the precipitate was washed several times with water and then dried under vacuum. In final product the ratio Pt/polyaniline was about 20 wt %.

III. RESULT AND DISCUSSION

A. XRD Analysis

X-ray diffraction pattern of synthesized sample of polyaniline are shown in Fig. 1. It is clear from the pattern that the product obtained is an amorphous nature of polyaniline.

X-ray diffraction pattern of synthesized sample of pt-polyaniline is shown in Fig. 2. This pattern clearly shows for crystalline in nature due to three peaks at 39.68°, 45.86° and 67.28° with respect to (111), (200), (220) reflection. The characteristic peaks at diffraction angles correspond to Miller indices, indicating the formation of platinum particle with FCC structure in the polyaniline matrix.

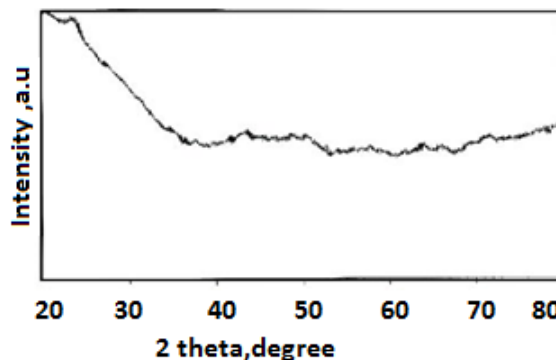


Fig. 1 Room temperature X-ray diffraction pattern of Polyaniline

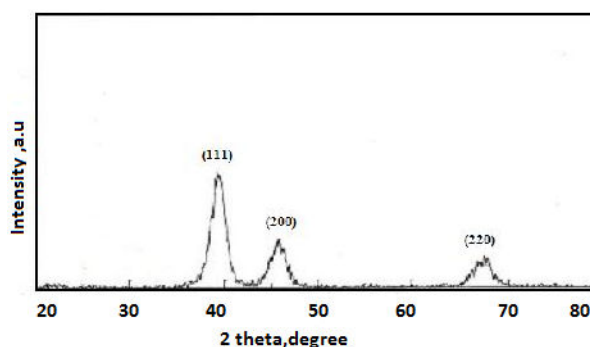


Fig. 2 Room temperature X-ray diffraction pattern of pt-Polyaniline

This pattern shows diffraction peaks for platinum. These peaks are also found to be broadened. This indicates that the platinum in the composite material is in nanocrystalline form. The average crystallite size d of the nanoparticles is calculated using the modified Scherrer formula

$$t = 0.9 \lambda / \cos \theta_B (B_M - B_S) \quad (1)$$

Here λ = wavelength of x-ray used, θ_B = Bragg's angle, B_M = Full width at half maximum of the peak, B_S = Full width half maximum of the same peak from a standard material. The average crystalline size of as synthesized composite turns out to be about 25 nm.

B. Thermal Analysis

Many compounds are not stable at higher temperatures and decompose into other compounds on heating. Keeping this thing in mind the prepared samples are characterized with help of a thermogravimetric analyzer. In thermogravimetric analysis the mass of a given material is measured as a function of temperature by keeping the material at a constant heating rate. The prepared sample of polyaniline is heated at a rate of 10°C per minute for this analysis. The thermal graph for polyaniline is shown in the Fig. 3. This indicates the mass of the sample decreases with increasing temperature continuously up to 650°C. After this weight loss becomes almost zero. In other words the decomposition of the polyaniline is almost complete at about 650°C.

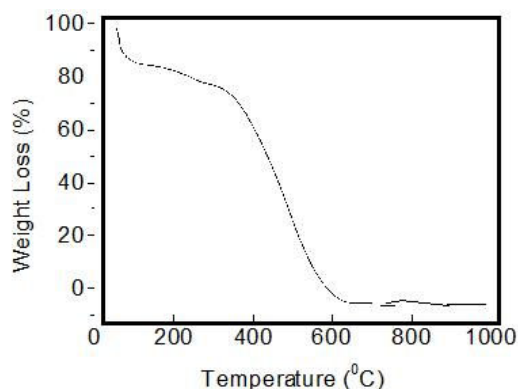


Fig. 3 Weight loss as a function of temperature for the polyaniline

The weight loss as a function of temperature for the Pt-polyaniline composite is shown in Fig. 4. From this figure it is clear that the decomposition of the polyaniline in the composite is over it relatively lower temperature compared to that shown in Fig. 3 and from Fig. 4 it is also clear that the mass of the composed material, the Platinum in this case, is about 20% of the initial mass of the composite. In other words the concentration of pt in the sample is about 20%.

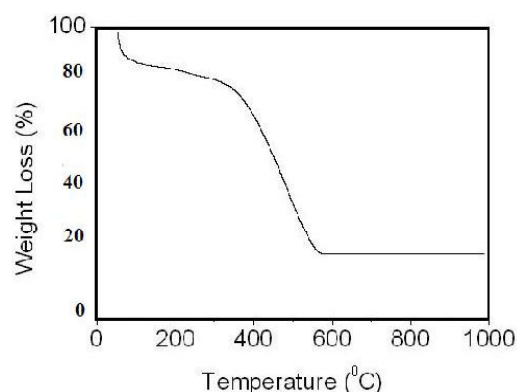


Fig. 4 Weight loss as a function of temperature for the Pt-polyaniline

C. Scanning Electron Micrograph Analysis

Scanning Electron Micrographs of colloidal platinum nanoparticles was prepared by spreading it on the carbon tape. The conducting stub (Au, Ag, Al) is used for scanning purpose. The analysis shows that the platinum nanoparticle in the chain of conductive polyaniline are nearly monodispersed and spherical in shape which is shown in Fig. 5.

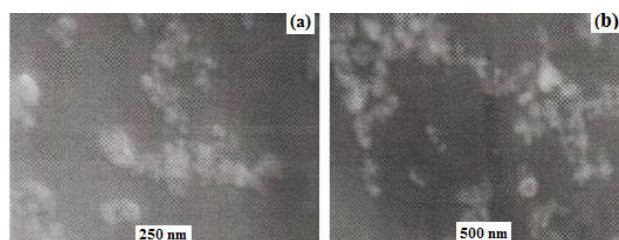


Fig. 5 Scanning Electron Micrographs of Pt-Polyaniline

D. Electrical Characteristics of Polyaniline (PANI) and Pt-Polyaniline

Fig. 6 shows typical Current-Potential plots of the polyaniline and composite which clearly shows the resistance of Polyaniline is one order higher than nanoparticle based composite. The enhancement of the conductivity in the composite is possible due to attach of metallic nanoparticles in the matrix of polyaniline.

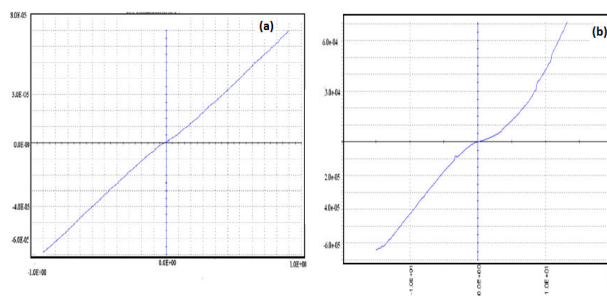


Fig. 6 I-V Characteristics of Films of (a) Polyaniline (b) Platinum – polyaniline composite

Fig. 6 (b) shows that the current increases nonlinearly with increasing voltage across the composite due to trapped charged near to nanoparticle which leads random charge disorder, in a real system, it is possible some energetically favorable paths that consumed most of the Current in the platinum based composite

TABLE I
CONDUCTIVITY OF POLYANILINE AND PT-POLYANILINE COMPOSITE

| Sample | Length (cm) | Cross Section (Cm ²) | R (Ω) | σ (S/cm) |
|-----------------|-------------|----------------------------------|-----------------------|------------------------|
| Polyaniline | 1.4 | 1.204 | 1.4 X 10 ³ | 7.1 X 10 ⁻⁴ |
| Pt- Polyaniline | 1.4 | 1.204 | 2.5X10 ⁴ | 4.0X10 ⁻⁵ |

IV. CONCLUSION

In the present study, polyaniline and Pt-polyaniline composites are prepared through chemical routes

1. X-ray diffraction confirms the amorphous nature of the Polyaniline.
2. X- ray diffraction of Pt-polyaniline composite shows Bragg's diffraction peaks corresponding to platinum.
3. Thermogravimetric analysis on the polyaniline sample shows that its decomposition almost is complete at about 650°C.
4. Concentration of Pt in the Pt-polyaniline Composite sample is about 20 wt % from thermogravimetric analysis.
5. The SEM analysis predicts the shape and distribution of nanoparticles matrix of polymer.
6. Current-potential (I-V) characteristics established that conductivity of pt-polyaniline composite increases by about one order of magnitude compared to polyaniline

ACKNOWLEDGMENT

The Authors appreciate the support of Director, OPJIT.

REFERENCES

- [1] Yuvraj Singh Negi and P. V. Adhyapak, Polymer Research and Development Division, Centre for Materials for Electronics Technology, 42, 35-53.
- [2] H. Letheby, Journal of the Chemical Society 15(1862)
- [3] Di Wei and Ari Ivaska "Electrochemical Biosensors Based on Polyaniline" Chem. Anal: (Warsaw), 51, (2006), 839.
- [4] Rosa Vera, Hugo Romero, Eduardo Ahumada, J. Chil. Chem. Soc.v.48 (2003).
- [5] Shi, G. Q., Jin, S. Xue, G. Li, C. A conducting polymer film stronger than Aluminum Science 1995, 267, 994-996.
- [6] A. F. Diaz, K. K. Kanazawa, G. P. Gardini Chemical Communications 14 (1979) 635.
- [7] A. G. Mac Diarmid, Angewandte Chemie –International Edition 40 (2001) 2581.
- [8] E. Menefee, Y. H. Pao, Journal of Chemical Physics 36 (1962) 3472.
- [9] V. V. J. Walatka, M. M. Labes, J. H. Perlstein, Physical Review Letters 31.
- [10] W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, G. B. Street, Physical Review Letters 38 (1977) 1305.
- [11] G. Natta, G. Mazzanti, P. Corradini, Stereospecific polymerization of acetylene, Attiaccad. Nazi Lincei Rend. 25 (1958) 3.
- [12] C. K. Chiang, S. C. Gau, C. R. J. Fincher Y. W. Park, A. G. MacDiarmid, A. J. Heeger, Applied Physics Letters 33 (1978) 18.
- [13] R. B. Seymour, Conductive Polymers; Polymer Science and Technology, 1st Plenum Press, New York, 1981.
- [14] Self doped conducting polymers by Michael. S. Fruend and Bhavana Deore (2007) 20-25.
- [15] Z. Kurmaev et al 2001 J. Phys: Cond1. R. Gangopadhaya, A. De, Chem. Mater. 12, 608 (2000).
- [16] Z. Peng, L. Guo, Z. Zhang, B. Tesche, T. Wike, D. Ogermann, S. Hu, K. Kleinermmans, Langmuir 22,10915 (2006).
- [17] R McNeill, DE Weiss and D. Willis Australian Journal of Chemistry 47718 (1965).
- [18] J. Stejskal, R. G. Gilbert Pure Appl. Chem., Vol.74, No.5, pp.857–867, (2002).
- [19] K. Gupta, P. C. Jana, A. K. Meikap Synthetic Metals Vol. 160, pp 1566–1573(2010).