



ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF H₂SO₄ DOPED ANILINE

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ABSTRACT

Sulphuric acid doped aniline is synthesized by electrochemical method at 1.7V and characterized by FTIR, UV, NMR, XRD, CV, SEM techniques and conductivity, solubility, impedance measurements and corrosion inhibitor test and the results are analysed. FTIR spectra confirmed the presence of polarons and bipolarons in polymer samples. XRD study showed the microstructure of polyaniline. UV spectra revealed the absorption peaks due to π - π^* transition of polyaniline. The higher wavelength enhanced the intrinsic conductivity. NMR study revealed the fact that polymerization was initiated at 1.7V. The conductivity measurement by four probe method showed the conductivity of 0.83 S/cm. The electrochemical redox activity of PANI is confirmed in the cyclic voltamogram. PANI's solubility in DMSO, NMP, DMF is verified. Polyaniline incorporated with ZnO in 2M NaOH solution confirmed the inhibition to corrosion of commercial aluminum alloys. Impedance plot supports the charge transfer process.

Keywords: Conducting polymer, PANI, electrochemical polymerization, corrosion.

INTRODUCTION

Research in electroactive polymers, particularly in aromatic conducting polymers, has received considerable attention worldwide in the past few years because of their potential Applications in the fields of microelectronics, optics and optoelectronics¹. Among these polymers, polyaniline (PANI) is one of the most widely studied conducting polymers because of its good conductivity that can be influenced both by the charging level and degree of protonation. Its well defined electrochemical (redox) response, easy preparation makes possible applications in rechargeable batteries, corrosion protection, light emitting diodes, molecular sensors, electrochromic devices and microwave screening. Polyaniline is not charge conjugation symmetric i.e. valence and conduction bands are asymmetric to a great extent. A partial oxidation of PANI usually leads to the reorganization of bands, resulting in an increase in electronic conductivity. The physico – chemical properties are strongly related to the proportion of quinone imine units present. PANI possesses two voltametric redox pairs including three stable oxidation states, with the half oxidized state (emeraldine) being highly conductive in its protonated state. Existence of different oxidation states of PANI makes it useful as an electrode material in electrochemical capacitors. In the present study electrochemical synthesis and characterization of H₂SO₄ doped aniline is carried out at 1.7V. FTIR, UV, NMR, XRD, CV, SEM, conductivity, solubility, impedance measurement, corrosion inhibition studies revealed the conducting nature of PANI.

EXPERIMENTAL

Aniline (Merck AR grade) was distilled twice at normal pressure just before use. Triply distilled water obtained from a quartz distillation unit was used for all the dilutions. The aggressive solutions

are made of AR grade H₂SO₄. 0.1M aniline and 1 M H₂SO₄ were prepared using triply distilled water. The working and reference electrodes used were stainless steel. Fourier Infrared spectra were recorded on a FT-IR spectrometer (Perkin-Elmer System 2000) to identify the chemical structure change of the sample. UV-Vis-Spectra of PANI sample was recorded in the Perkin Elmer Spectrophotometer, model Lambda 3B. A nuclear Magnetic resonance spectrum of PANI was obtained using NMR spectrophotometer. X-ray diffraction pattern was measured using MXP 18 diffractometer. Cyclic voltammogram of polyaniline was recorded by using Ag/AgCl electrode as the reference electrode. A four probe system was used to measure the electrical conductivity of the polymer pellet. The solubility of aniline doped with sulphuric acid was investigated with solvents such as DMF, DMSO, NMP. Inhibitive behaviour of ZnO in 2M NaOH with polyaniline was studied using weight loss measurements. A scanning electron microscope was used to examine the surface morphology of 57S aluminum. Impedance analyser was used to analyse the charge transfer process.

RESULTS AND DISCUSSION

The FTIR spectrum of PANI using H₂SO₄ acid is shown in Fig. 1. 3500 – 3100 cm⁻¹ is the N-H stretching region. The absorption of PANI in this region is weak. 3100 – 3800 cm⁻¹ is the C-H stretching region. The absorption of PANI in this region is even weaker. But is observable at 2923.6 cm⁻¹. In the region 1600-1450 cm⁻¹ Aromatic ring breathing, N-H deformation and C=N stretching give absorption. A 1,4 substituted benzene ring may give absorption band at 1600-1580cm⁻¹ and 1510-1500cm⁻¹. The band at 1488.8cm⁻¹ is mainly due to benzoid ring stretching in PANI. We consider the 1572.1 cm⁻¹ band as a characteristic band of nitrogen quinone^{2,3,4}. 1400-1240 cm⁻¹ is the C-N stretching region for aromatic amines. The intrinsic PANI shows peak at 1302 cm⁻¹ which is close to QB_cQ, QBB, BBQ. 1302 cm⁻¹ band is always broad for doped or undoped samples implying that this band may contain more than one vibrational mode. 1220-500 cm⁻¹ is the region of inplane and out plane bending of C-H bonds on aromatic rings. 1118 cm⁻¹ band stands for 1,2,4 substitution. The spectral information is in agreement with NMR results⁵. The band at 1160 cm⁻¹ was referred to by MacDiarmid et al as the electronic like band^{5,6,7} and was considered as a measure of the degree of delocalization of electrons on PANI and this is a characteristic peak of PANI conductivity.

UV-Vis spectra of synthesized PANI is shown in fig. 2. On passing electromagnetic radiation in the UV and visible region through a compound with multiple bands, a portion of radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the compound. The absorption of radiation is due to the subtraction of energy from the radiation beam when electronic orbital of lower energy are excited into orbital of higher energy. This is an electron excitation phenomenon. UV spectra record the wavelength of an absorption maximum λ_{max} . From the fig.2 the absorption peak at 336 nm is due to π - π^* transition of aniline. The higher wavelength of transition enhances the intrinsic conductivity of sample. Nuclear Magnetic resonance spectroscopy study is useful to know the behaviour of certain atomic nuclei, namely those which have magnetic moments arising from their possessing spin in the presence of applied magnetic fields. The applied field is responsible for the splitting up of nuclear energy levels between which transitions may be caused to occur by absorption of suitable electromagnetic radiation. The sensitivity of NMR method^{8,9,10,11} depends primarily upon the strength of nuclear magnet. It is also affected by certain experimental variables. It is observed that only aromatic ring protons around 7-7.5 ppm appeared & NH protons disappeared which are involved in the polymerization as seen in fig.3. Crystallinity and orientation of conducting polymer are of much interest, because the more highly ordered systems could display a metallic- like conductive state¹². Xray powder diffraction measurements reveal the fact that the sample obtained is not purely crystal as seen in fig 4. The nanosize of the particles are confirmed from the data obtained. It indicates that the relative intensity percentage is 100 at $2\theta = 25.472^\circ$. Only one sharp peak exists at this angle of diffraction. The grain size is calculated and it confirmed the nanosize of the particle involved in the reaction. C-V was carried out to determine the electrochemical nature of H₂SO₄ doped aniline. Two main redox couples occur as seen in Fig. 5. The peak to peak separation of H₂SO₄ doped aniline turned small, which means that the

electrochemical activity of the doped PANI has been improved. This is because of the fact that when H₂SO₄ is trapped into the polymer matrix, small cations could move fast back and forth through the H₂SO₄ - PANI chains and the conjugated system of the product is enlarged than before. Therefore we conclude that the electrochemical redox activity of PANI could be improved by doping H₂SO₄ into aniline molecule¹³.

Resistance R of the pellet was measured at room temperature using the four probe technique. The conductivity of the pellet is calculated as 0.83 S/cm^{14,15}. It was also verified that as the polymerization voltage increased, the conductivity also increases. The room temperature solubility of synthesized H₂SO₄ doped aniline was determined in various solvents and summarized in Table 1. It is observed that the dopants with big anions increase the solubility¹⁶. The polyaniline synthesized was incorporated with ZnO in 2 M of NaOH solution to prevent the corrosion of commercial aluminum alloys. The study revealed the formation of very adherent protective layer on the metal surface. Table 2 shows the inhibition efficiency of 57S grade aluminum in 2MNaOH solution + 0.2M ZnO + PANI.

Surface Morphology examination was also carried out using SEM for 57S as seen in fig 6. Corrosion rate is reduced in this process. It is concluded that the PANI can be used as a corrosion inhibitor¹⁷. AC impedance method has been used for the calculation of the corrosion rate, passivation phenomena and mechanism of corrosion inhibition. Nyquist plot of 57s aluminium in 2MNaOH and 0.2 M ZnO and polyaniline is shown in fig 7. A distorted semicircle indicates a charge transfer process occurs at the aluminium electrolyte interface at these potentials, during the corrosion of aluminium in alkaline. The low frequency branch is almost linear and makes 45° angles with the real axis. It indicates Warburg type impedance, corresponding to a mass transfer process involving ionic diffusion¹⁸.

CONCLUSION

In this study, the infrared spectra of soluble polyaniline (PANI) have been studied. It is found that the spectrum of the soluble PANI gives more structural information. λ_{\max} of UV-Vis spectra is derived from polarn / bipolar transition of H₂SO₄ doped aniline. NMR spectra indicated the initialization of electrochemical polymerization and XRD spectrum showed the nano level structure of product. CV study explained the electrochemical activity of doped aniline by its redox behaviour. Electrical conductivity of H₂SO₄ doped aniline is also verified. PANI is soluble in NMP and DMSO. SEM photograph shows an adherent protective layer over 57S aluminum alloy which helps in preventing corrosion.

Table-1: Solubility of PANI in solvents

S. No	Solvent	PANI
1	Acetone	Insoluble
2	Benzene	Insoluble
3	Chloroform	Insoluble
4	NMP	Soluble
5	DMSO	Soluble

Table-2: Inhibition efficiency of PANI

S. No.	Concentration of polyaniline ppm	Corrosion rate Mg/cm ² /min	Inhibition efficiency %
1	0	0.766	18.3
2	100	0.616	34.3
3	200	0.507	45.9
4	300	0.479	48.9
5	400	0.363	61.3

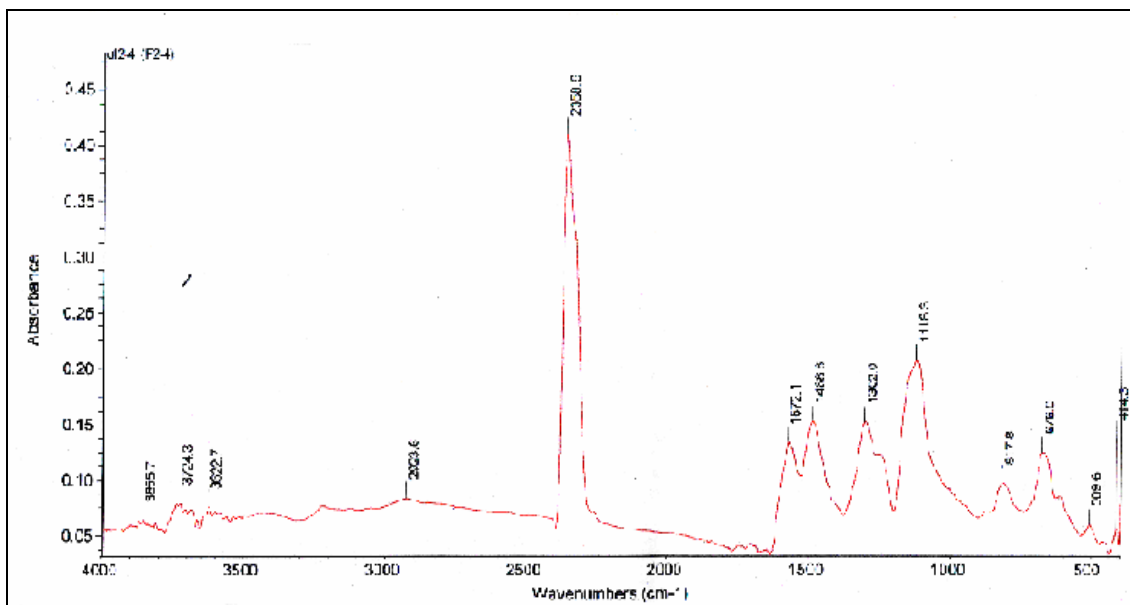


Fig.-1: FTIR Spectrum of Polyaniline

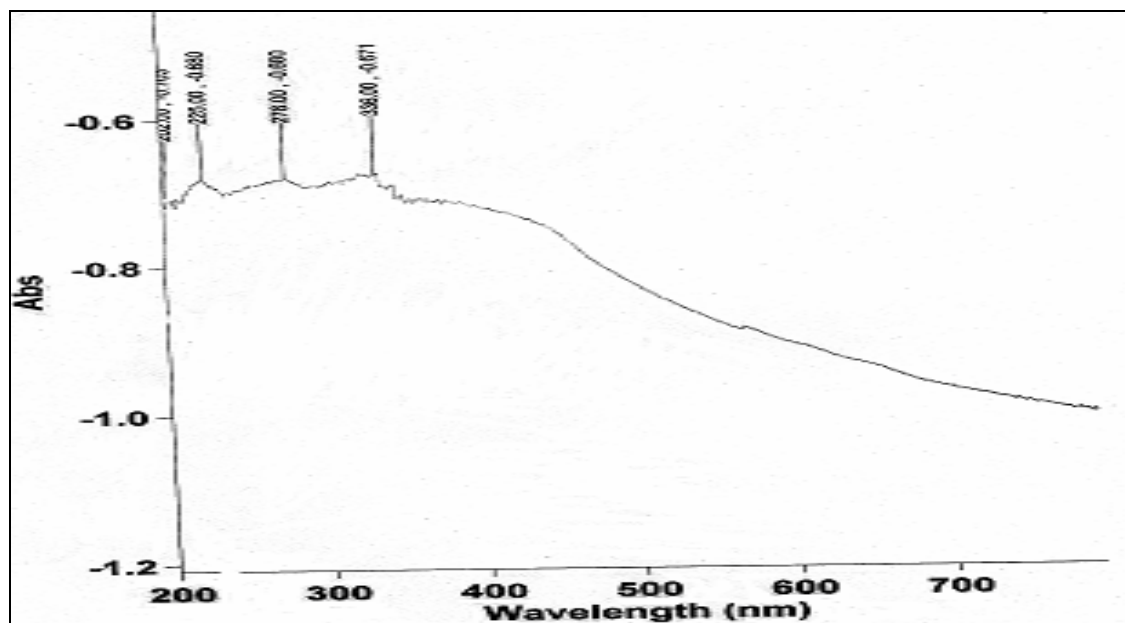


Fig.-2: UV vis spectrum of polyaniline

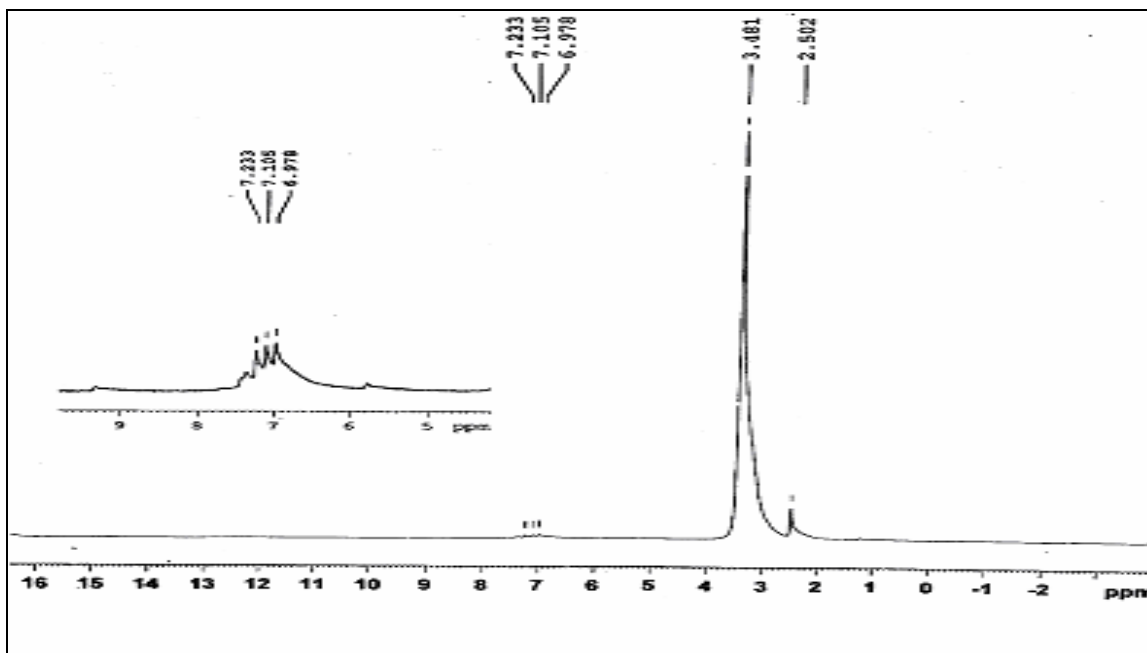


Fig.-3:NMR spectrum of PANI

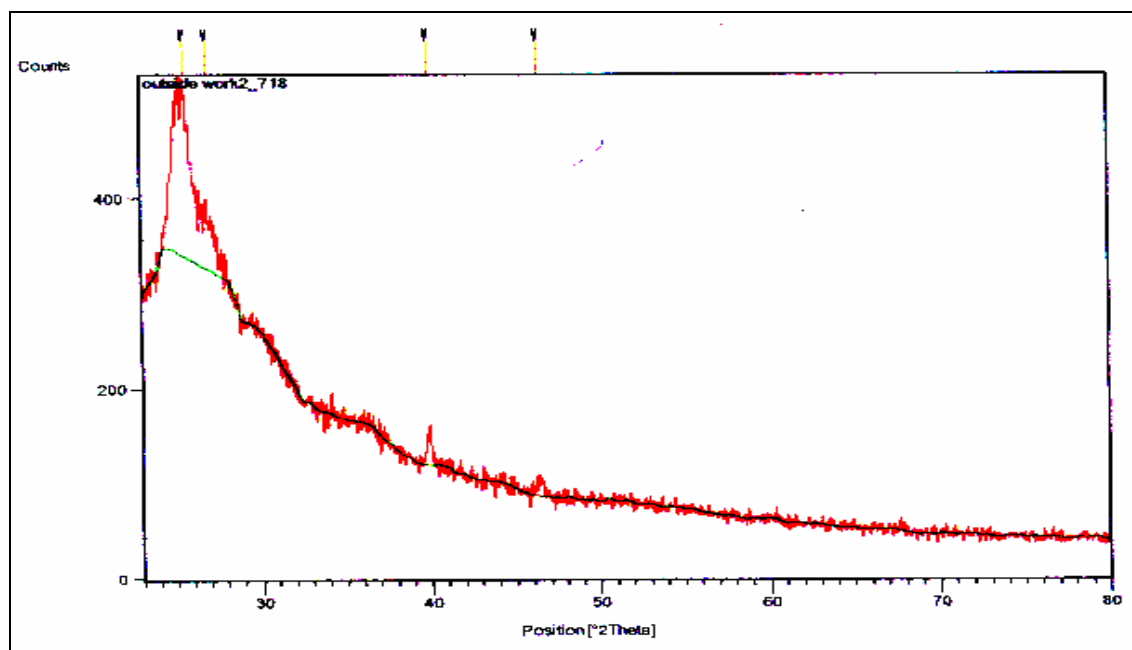


Fig.-4:XRD spectrum

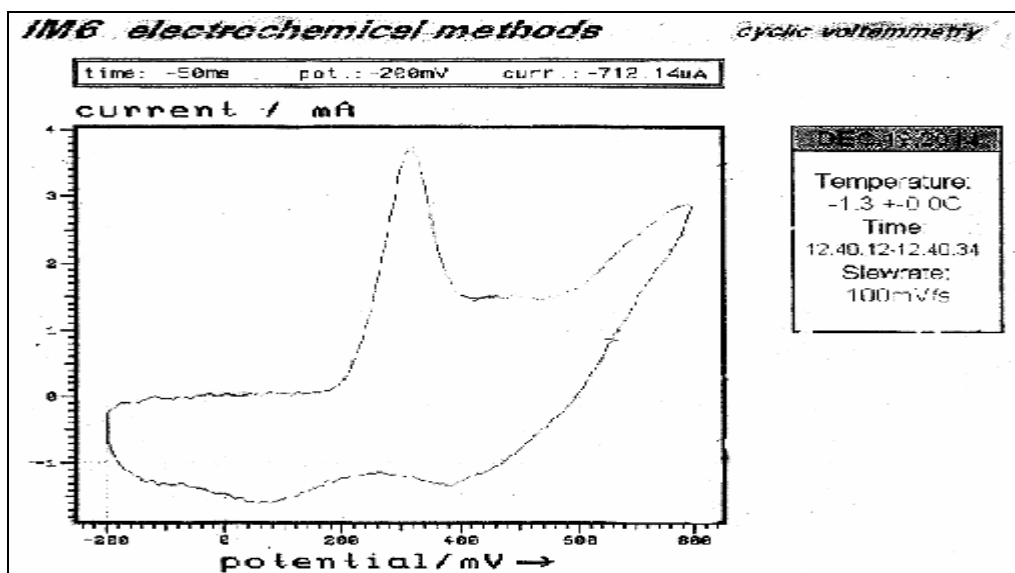
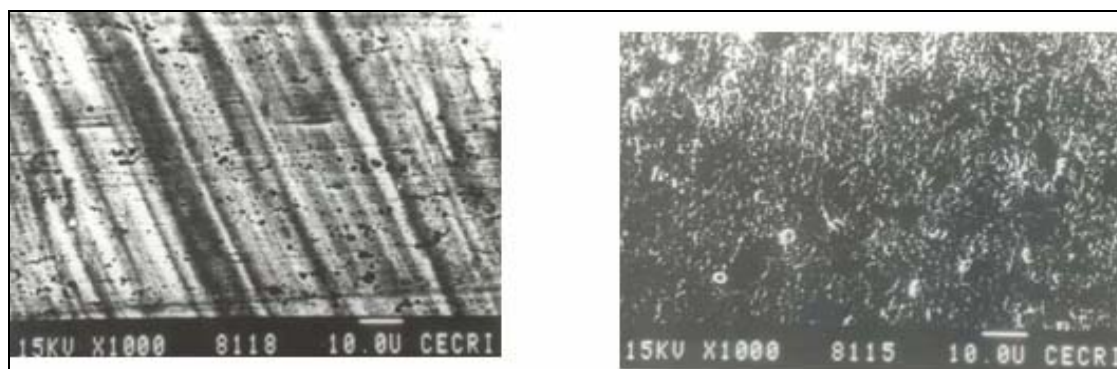


Fig.-5: Cyclic voltamogram



Before inhibition

After inhibition

Fig.-6: SEM photographs of PANI

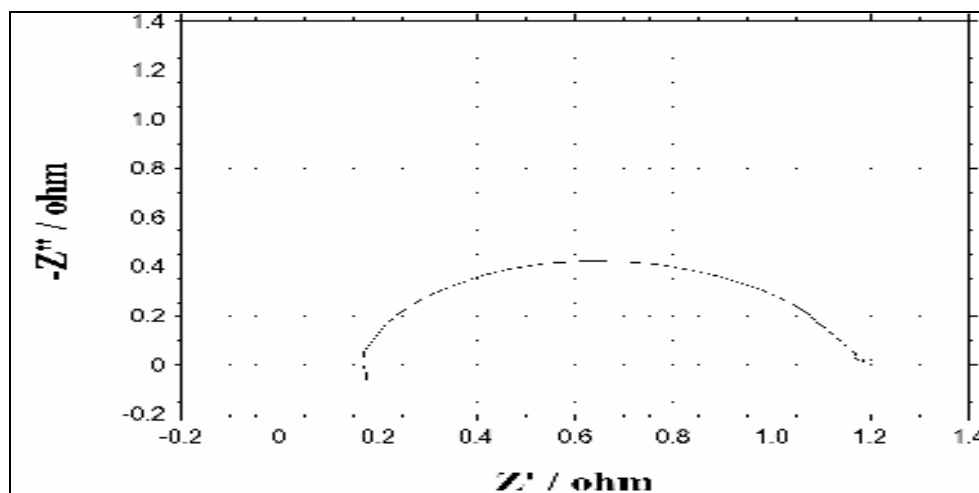


Fig.-7: Nyquist plot of 57S Aluminium

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