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Synthesis and Characterization of Polyaniline Film by $K_2Cr_2O_7$, K_2CrO_4 and $FeCl_3$ a Comparative Study

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***Abstract* -** Aniline was electrochemically synthesized with $K_2Cr_2O_7$, K_2CrO_4, and $FeCl_3$ as oxidants and Polyaniline (PANI) films is prepared. Electrochemical cell was used for deposition of monomer, oxidants and dopant in galvanostatic technique. ITO coated glass plate has been used as a working electrode, platinum foil as a counter electrode and Ag/AgCl as a reference electrode. The electrolyte solution was prepared in deionized water with optimum parameter viz. pH, potential, conductivity. After synthesis of composite films by galvanostatic electrochemical technique it was focused to various characterizations such as FTIR, UV-vis. spectroscopy and SEM etc. For comparative study it has been finding that $FeCl_3$ is best supporting electrolyte for PANI.

***Keywords* –** *Polyaniline, Electrochemical, Synthesis, Electrolyte, Conductivity*

I. INTRODUCTION

In the earlier days, there are so many new materials coming up for several technological oriented applications. The conducting polymer is one of the most capable classes of materials being used for several applications [1]. PANI is one of most conducting organic polymer which shows many interesting properties such as electrochemical redox performance, electro chromic catalytic activities [2]. Due to conductive performance, PANI is used to develop a various sensors using composite thin film by enzymes such as biosensor [3].

The demand for new polymeric materials that can be used as a matrix for the immobilization of biomaterials has been recently intensified. Among the various polymeric materials, the porous polymer matrix has been projected to have innumerable applications in biosensors and presently at the centre stage of research and development. Conducting polymers have attracted a lot of interest as a suitable matrix for the setup of enzymes. Conducting polymers are used to enhance the speed, sensitivity and versatility of biosensors. Electrically conducting polymers have excellent flexibility in its chemical structure, which can be modified as per the requirement of specific application. Therefore, conducting polymers are being used as biosensor applications such as detection of various Pesticides in fruits and vegetables [4].

In the present work, we report the performance of a PANI film made by galvanostatic electrochemical polymerization method with supporting electrolyte and $K_2Cr_2O_7$, K_2CrO_4, and $FeCl_3$. The ITO coated glass plate was used as a working electrode, platinum foil as a counter electrode and Ag/AgCl as a reference electrode. The electrolyte solution was prepared in deionized water with optimum parameter i.e. pH and potential. Synthesized composite films are subjected to various characterizations such as FTIR, UV-vis. spectroscopy, SEM and conductivity by four probe methods. Then comparative study has been done amongst three supporting electrolyte.

II. EXPERIMENTAL

The aniline was electrochemically synthesized with various oxidants like potassium dichromate ($K_2Cr_2O_7$), potassium

chromate (K_2CrO_4) and ferrous chloride ($FeCl_3$) .We were freshly prepared 0.1N an aqueous solution aniline (99%) in double distilled water , Also we prepared an aqueous solution of 0.1N potassium dichromate ($K_2Cr_2O_7$), 0.1N potassium chromate (K_2CrO_4) And 0.1 N ferrous chloride ($FeCl_3$) in double distilled water. The pH of mixture are maintain by using buffer solution. The electrochemical polymerization of PANI was carried out by galvanastatic method in one compartment electrochemical cell [5-7]. Platinum foil was used as a counter electrode (cathode) and Indium Tin Oxide glass (20mm x 0.5mm) was used as a working electrode (anode). The reference electrode was silver/silver chloride (Ag/AgCl). All three electrodes were placed vertically in an electrochemical cell. A 50 ml solution was used for each reaction. The pH of the electrolyte was measured by calibrated ELICO LI120 pH meter. The electrochemical characterization was carried out by galvanostatic technique, which maintains a constant current throughout reaction. The optical absorption study was carried out in Analytic Jena specord 210 plus (Wavelength 200nm-800nm) UV- visible spectrophotometer. The conductivity was measured by using four-probe technique (S.E.S. Instrument Pvt. Ltd. Roorkee). The JEOL JSM-7500F is an ultra-high resolution field emission scanning electron microscope.

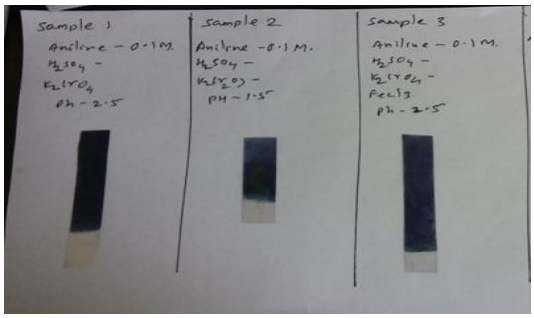

Figure-1 Electrochemical synthesis of Polymer films (PANI) using K_2CrO_4, $K_2Cr_2O_7$ and FeCl3

III. RESULTS AND DISCUSSION

Electrochemically synthesis of PANI established that the different supporting oxidants nature and concentration used to synthesize a conducting polymer affecting its morphology and some of its properties. The previous reported work electrochemical synthesis of PANI on Platinum substrate [8-9]. However, once the PANI oxidation was initiated, this process is much faster for increased polyelectrolyte concentration that was investigates the effects of various synthesis parameters such as Electro-synthesis method, monomer concentration, and electrolyte on electro polymerization of PANI [10-11].

3.1 SEM study-

The scanning electron microscopy of synthesized Polyaniline and poly O-Anisidine polymer films with optimized process parameters for H_2SO_4 are shown in figures 2. Scanning Electron micrographs were recorded using JEOL JSM-6360 an analytical SEM. It shows very good uniformity and porosity. It can be seen that the surface morphology is more porous and uniform like structure [12].

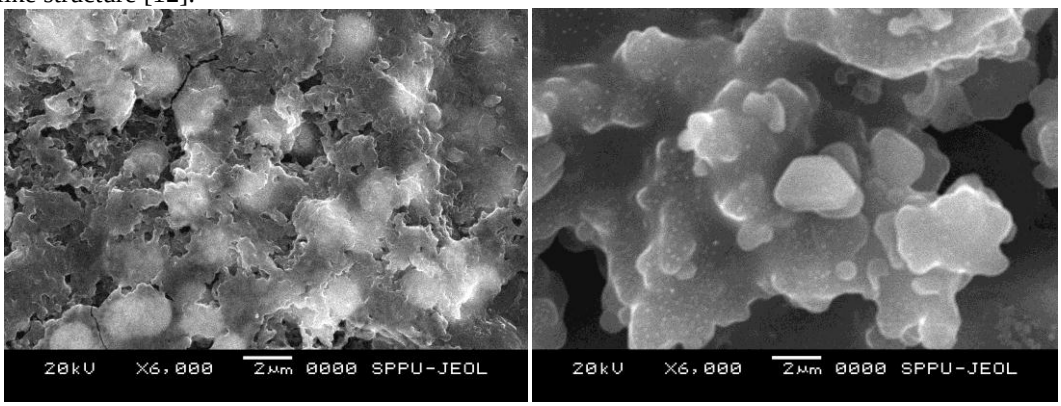

Figure- 2 SEM of PANI and POA (Mag.25KX)

3.2 UV-vis. study-

The optical absorption spectrum of synthesized PANI with oxidants $K_2Cr_2O_7$, K_2CrO_4, and $FeCl_3$ films with optimized parameters are as shown in fig.3, 4 and 5 respectively. It is recorded that the wavelength range is 200-800nm. For measurement

of UV-visible Spectrophotoscopey of thin films Lab India spectrometer (V-600) was used. All spectra were recorded in the wavelength range of 350-800 nm & the peak is appearing at 600, 620 and 580 nm for PANI for $K_2Cr_2O_7$, K_2CrO_4, and $FeCl_3$ respectively. It shows very good resemblance with earlier work.

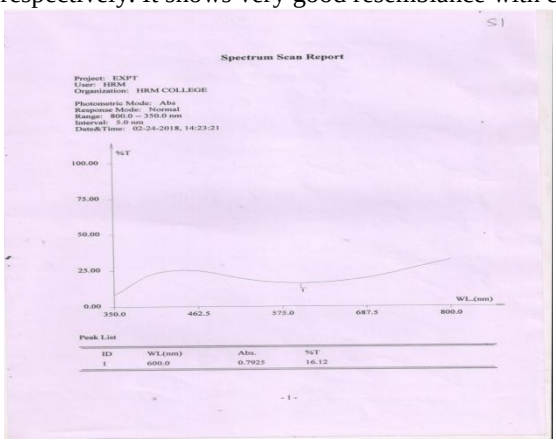

Fig-3 UV PANI/ $K_2Cr_2O_7$

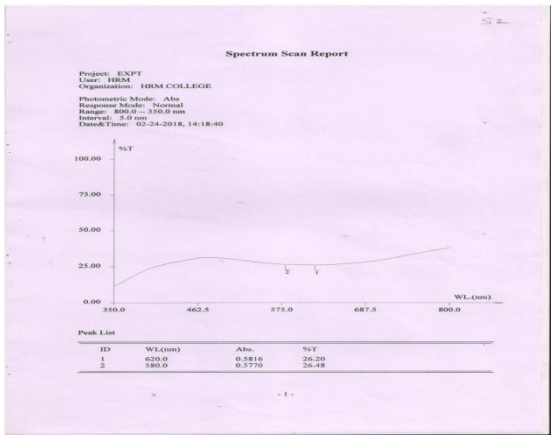

Fig-4 UV PANI/ K_2CrO_4

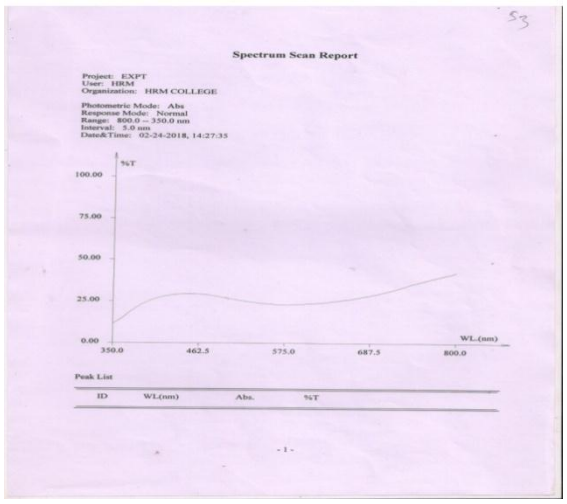

Fig-5 UV PANI/ $FeCl_3$

3.3 FTIR study-

The FTIR spectroscopy was used for structural characterization of synthesized Poly- Aniline with supporting oxidants $K_2Cr_2O_7$, K_2CrO_4, and $FeCl_3$ films with optimized parameters for as shown in fig.6, 7and 8 respectively it was recorded that the wave number range is 400 to

4000 cm^{-1}on the ALPHA BRUKER

Photo-1 ALPHA (Bruker) FTIR

An FTIR spectrum shows molecular structure of synthesized samples PANI of various dopants and its recorded range is 400 - 4000cm^{-1}. The bonds 1463 cm^{-1} and 1597 cm^{-1} corresponds to C=C stretching vibrations of the benzoid and quinoid rings respectively. The peak at 1259 cm^{-1} is the characteristic band of aromatic C-N stretching vibration and a weak peak at 3462 cm^{-1} is assigned to stretching mode of N-H. The absorption band appears at 1101 cm^{-1} has been explained as vibration band of Nitrogen quinine (N=Q=N). In addition the band at 860 cm^{-1} can be ascribed to C-H out of plane bending vibrations for the aromatic ring which clearly supports the formation of PANI. The polymer shows the absorption bands at 2968 are due to asymmetric C-H stretching and symmetric C-H stretching vibrations. These bands corresponds to the characteristics bands of Aniline, it shows Very good agreement. Thus the FTIR spectral lines results confirm the formation of Polyaniline [13].

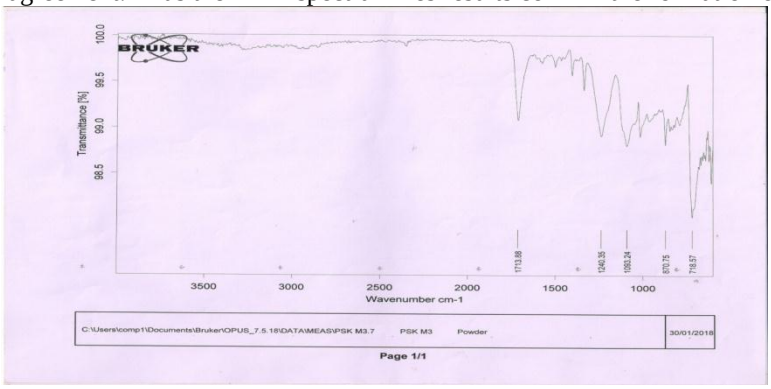

Fig - 6 FTIR study of PANI film with K_2CrO_4

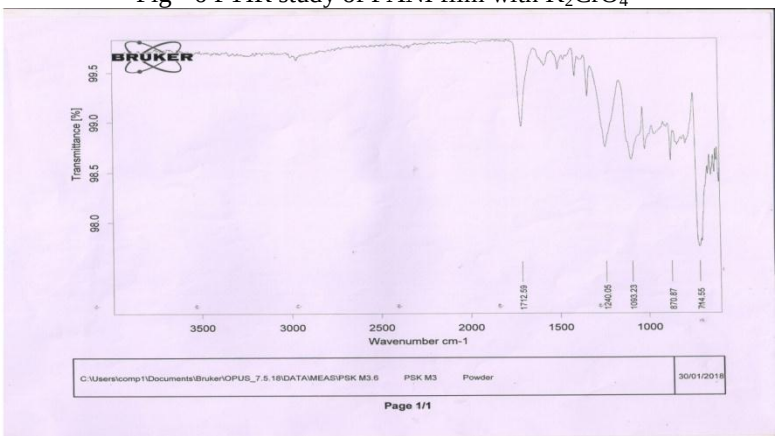

Fig- 7 FTIR study of PANI film with $K_2Cr_2O_7$

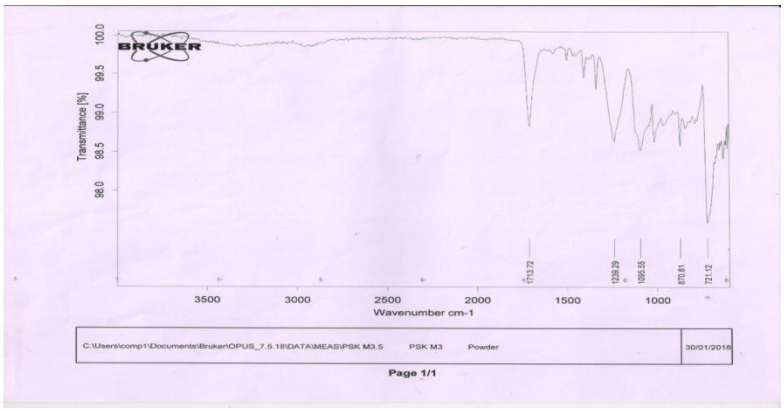

Fig- 8 FTIR study of PANI film with $FeCl_3$

3.4 Conductivity Measurement-

The four-probe set up (S.E.S. Instrument Pvt. Ltd. Roorkee) was used for the measurement of electrical conductivity of synthesized PANI films. The Four Probe Method is one of the standard and most widely used methods for the measurement of resistivity of semiconductors. The experimental arrangement is illustrated. In its useful form, the probes are collinear the error due to contact resistance, which is especially serious in the electrical measurement on semiconductors, is avoided by the use of two extra contacts (probes) between the current contacts. In this arrangement the contact resistance may all be high compare to the sample resistance, but as long as the resistance of the sample and contact resistances are small compared with the effective resistance of the voltage measuring device (potentiometer, electrometer or electronic voltmeter),the measured value will remain unaffected. Because of pressure contacts, the arrangement is also especially useful for quick measurement on different samples or sampling different parts of the same sample. Table.1 shows conductivity of PANI films with different oxidants $K_2Cr_2O_7$, K_2CrO_4, and $FeCl_3$, along which $FeCl_3$ shows highest conductivity 1.62 S/cm at potential 670 mV for current density $0.5A/2cm^2$ at pH 6.

Table-1

Sr. No.	PANI film with	Polymerization potential (mV)	Conductivity (S/cm)
1	FeCl3	670	1.62
2	$K_2Cr_2O_7$	676	1.54
3	K_2CrO_4	700	1.2

IV. GALVANOSTATIC STUDY

A computer controlled Potentiostat/Galvanostat, indigenously considered and fabricated in the Materials Research Laboratory, Department of physics, Shri Anand College, Pathardi, and Dist. Ahmednagar. (MS) India was working for the electrochemical synthesis of PANI film by using potentiometric (Galvanostatic) method. Arrangement is also mainly useful for quick measurement on different samples. Above figure.1 shows thin films of 50ml solution of 0.1N aniline and 50ml solution of 0.1 N $K_2Cr_2O_7$, $FeCl_3$, K_2CrO_4 respectively on an ITO substrate electrode in the presence of dispersed in electrolyte solution. Table.1 shows the comparative study of polymerization voltage and conductivity of (PANI/$K_2Cr_2O_7$), (PANI/K_2CrO_4) and (PANI/$FeCl_3$) during the formation on ITO substrate along which $FeCl_3$ shows highest conductivity 1.62 S/cm at potential 670 mV for current density $0.5mA/2cm^2$ at pH 6 it can be concluded that electro polymerization on the PANI/$FeCl_3$ composite initial layers is easier than the PANI/K_2CrO_4 and PANI/$K_2Cr_2O_7$ initial layers. So, the film can be presents a large surface area. As is well known, properties of a broad range of materials and performance of different devices depend strongly on their surface characteristics. It clearly shows porous morphology of PANI Film. By immobilization of various enzymes these films are used as a sensor for detection of pesticide in fruits and vegetables [14].

V. CONCLUSION

The influence of electrochemical process parameter on the surface morphology and the conductivity of PANI/ $FeCl_3$ film were successfully studied. As compare to PANI/$K_2Cr_2O_7$, PANI/K_2CrO_4 and PANI/$FeCl_3$ we have seen that 1:1 concentration ratio

of PANI and FeCl3 is good combination for deposition on ITO film. This film shows good conductivity for current density 0.5mA/2cm^2 at pH 6. The PANI/$FeCl_3$ film provides a polymer matrix having a good porosity, high conductivity, uniform surface morphology and good mechanical and environmental stability.

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