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Research Article

ELECTROCHEMICAL CHARACTERIZATION AND THE INVESTIGATION OF CORROSION INHIBITION PROPERTY OF PANI-FA MATRIX COMPOSITE

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ABSTRACT

Electrically conducting polymers are novel class of synthetic metals that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semi-conductors. Polyaniline (PANI) is one of the most intensively studied conducting polymers during the last decade. It is highly conducting and easy to synthesize both chemically as well as electrochemically. The chemical method has a great importance since it is very feasible route for the mass production of PANI. The present investigation is dedicated for the synthesis, electrochemical characterization and application of fly ash doped PANI for the anti-corrosive property. The electrochemical behavior study by cyclic voltammetry (CV) revealed the red-ox behavior of PANI composite. The study of mild steel corrosion phenomenon has become important particularly in acid media. The inhibitive properties of PANI-FA 45% composite on the corrosion of mild steel strip in 0.1M HCl were investigated using electrochemical techniques like polarization method and electrochemical impedance spectroscopy (EIS). A good barrier allows very little flow of current thereby showing high resistance impedance measurements for the prepared composite.

INTRODUCTION

Over the past decade, published evidence that (conducting polymers) CPs, specifically polyaniline (PANI) could inhibit corrosion has come from (DeBerry, 1985; Ahmed and MacDiarmid, 1996). These results showed that PANI electrodeposited on passivated steel in a strong acid environment enhanced corrosion protection of the metal. While there is general agreement that PANI performs well in retarding corrosion on carbon steel, the mechanism for this process is still under investigation. Several hypotheses have been suggested for the mechanism of corrosion protection using CPs, specifically PANI:

(a) PANI contributes to the formation of an electric field at the metal surface, restricting the flow of electrons from metal to oxidant.
(b) PANI forms a dense, strong adherent, low-porosity film similar to a barrier coating;
(c) PANI causes the formation of protective layers of metal oxides on a metal surface (McAndrew *et al*., 1996).

In recent years it has been shown that intrinsically conducting polymers such as polyaniline used effectively as pigment due to its environmentally friendly, anticorrosion ability, ease of preparation, excellent environmental stability and interesting red-ox properties associated with the chain of nitrogen. PANI incorporated conventional paint coatings (Acrylic) are able to protect steel due to their passivating ability. Up to now, only little is known about how corrosion protection by conducting polymers might work. Earlier studies by DeBerry (1985), confirmed that stainless steel, in the presence of polyaniline, was passivated considerably under highly acidic conditions. Several strategies have been used to increase the effectiveness of polyaniline as anticorrosive coating on metals.

The corrosion prevention has been enhanced using polyaniline combined with inorganic particles. Recently the PANI-FA composites were synthesized for the first time, by Raghavhendra *et al*.,(2003), and Norden and Krumeirjer (2000), by *in situ* polymerisation of aniline in the presence of fly ash (FA). These composites were prepared with varying weight percentages. The main components of FA are; silica (SiO_2), aluminium (Al_2O_3), Calcium oxide (CaO), Iron oxide (Fe_2O_3), MgO and Titanium oxide (TiO_2) (Petrik *et al*., 2003). These metal oxides have been used in one way or other in the preparation of nanocomposites or nanotubes/rods. (Al_2O_3) and (Fe_2O_3) have been used as catalyst supporter for the production of nanotubes (Albuquerque *et al*., 2000).

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Electrochemical impedance spectroscopy (EIS) seems to be a valuable technique for determining the properties of PANI films and the analysis of data affords information on charge transfer resistance (Rct), double layer capacitance (Cdl) and specific capacitances (Csp) (Popkinov *et al*., 1997). For the oxidized PANI thin film electrodes in acid electrolyte solutions impedance, spectra (IS) measurements were performed at frequencies up to 104 –106 Hz using conventional three-electrode electrochemical cell (Genz *et al*., 1994; Mateeva and Gonales-Tejera, 2000). In this work emeraldine salt of polyaniline oped with flyash in various compositions were prepared by oxidative polymerization. The polymer was electrochemically characterized using Cyclic Voltammetry (CV). The PANI-FA composite films coated on mild steel and to determine the corrosion inhibition applicability by Polarisation Studies (Tafel study) and Electrochemical Impedance Spectroscopy. In our present study the voltammogram of composite exhibited two oxidation peaks and two reduction peaks. This behaviour was associated with the electroactive nature of polyaniline.

Synthesis of PANI-FA Composites

The method used to prepare PANI-FA was by chemical oxidization method (Raghavendra *et al*., 2003). Aniline was prepared in 2 M HCl solution. This aniline solution was stirred and FA was added in the solution with vigorous stirring (0%, 15%, 25%, 35%, 45 and 55% FA to aniline w/w ratio). The mixture was kept in an ice bath with continuous stirring. Then ammonium persulphate (APS) was added slowly to the aniline solution until the reaction mixture turned green. The reaction mixture was then stirred for 8 hrs. The product was collected by filtration and washed with water and acetone until the washing was colorless. The collected samples were dried at room temperature and preserved for further studies.

Corrosion Study

The Mild Steel (MS) coupons with 2×1×0.05 cm dimensions were used. In order to remove any passivated film, the surface of the coupons were polished using emery paper and rinsed with distilled water and acetone prior to coating with composites or pure polyaniline layer. The various PANI/FA composites were mixed with PVA in toluene to get a paste consistency. Then the mixture was coated on the mild steel plate by using glass rod and then labeled. It was dried and then used for polarization and impedance studies.

RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)

The electrochemical analyzer, CHI Electrochemical Workstation model 650C was employed for various electrochemical studies. The cyclic voltammetry was performed in the 0.1 M HCl for PANI, fly ash and PANI-FA 45% composite. A small amount of composite sample was mixed with DMF (dimethyl formamide) to make a paste. It was coated as thin film on the surface of glassy carbon electrode and the cyclic voltammetric behaviour of the composite was studied. The voltammogram was cycled between -200 and 1000 mV in 0.1M HCl at various scan rate like 50, 60, 70, 80, 90, 100 mVs^{-1}. The voltammogram of PANI/FA 45% composite, polyaniline and Fly ash are shown in the Fig.1- 3. The fact that the scan rate increases with current means that, the polymer is conducting. The shifting means that the charge is moving along the polymer backbone (Mathebe *et al*., 2004). For pure PANI pair of oxidation potential peaks centered at 0.3243 V and 0.6357 V respectively. The reduction potential peaks at 0.1664 V and 0.4851 V respectively and their peak height increased with the increase of number of potential scans suggested that the films were electroactive. For PANI-FA 45 % composite also showed two oxidation potentials and two reduction potentials. The oxidation potential peaks centered at 0.3198V and 0.6032V respectively and reduction peaks centered at 0.2003V and 0.4970V respectively. For the composite also, their peak height increased with the increase of number of potential scans and their oxidation peaks shifted towards left and reduction peaks shifted towards right on compared with pure PANI.

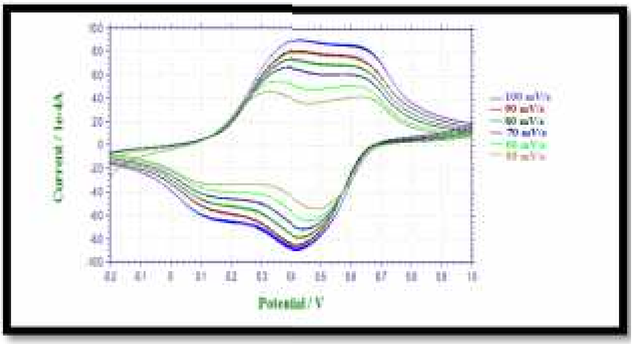

Fig.1 Cyclic Voltammogram of polyaniline in different scan rates

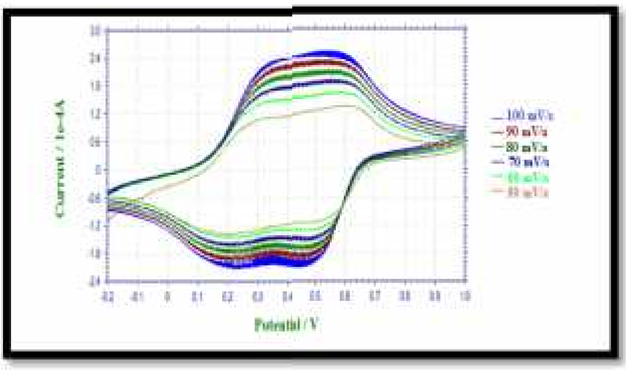

Fig.2 Cyclic Voltammogram of polyaniline PANI-FA 45% composite in different scan rates

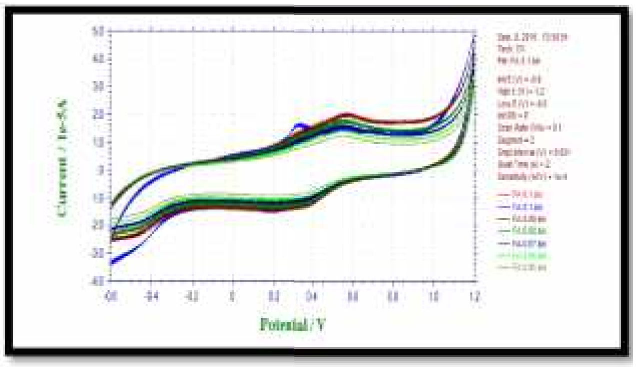

Fig.3 Cyclic voltammogram of Fly ash in different scan rates

Anti-Corrosion behavior on mild steel

Polarisation Studies (Tafel Study)

All electrochemical studies were carried out with CHI 650C electrochemical analyzer under computer control. The polarization was carried out in 0.1M HCl solution by Tafel method. Prior to the experiment the MS plates were cleaned. The plate without any coating, corrosion experiment was done it was considered as bare. The plate was coated with polyvinyl acetate and it was considered as blank. PANI/FA (45%) composite mixed with PVA was coated. The same experiment was repeated for poly aniline and Fly ash coating. Tafel plots are shown in the Fig.4 - 8.

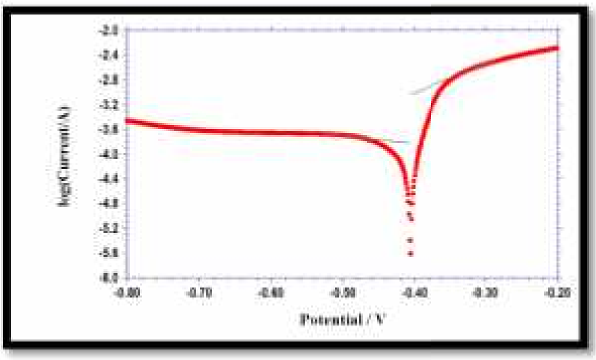

Fig.4 Tafel plot of bare

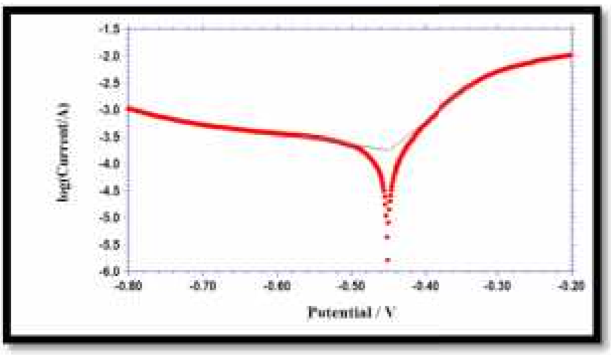

Fig.5 Tafel plot of Blank

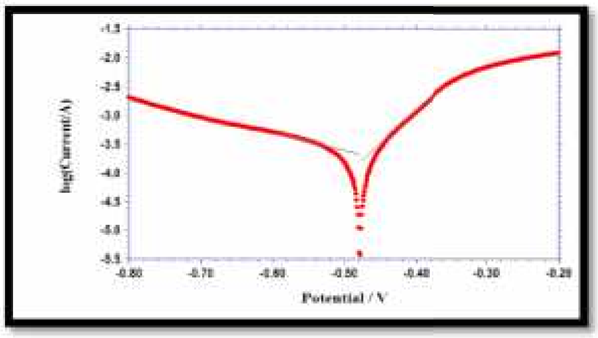

Fig.6 Tafel plot of PANI

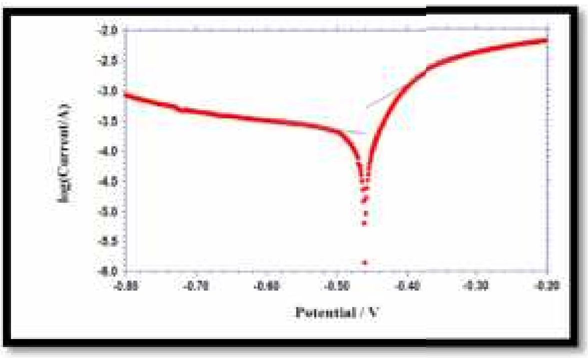

Fig.7 Tafel plot of Fly ash

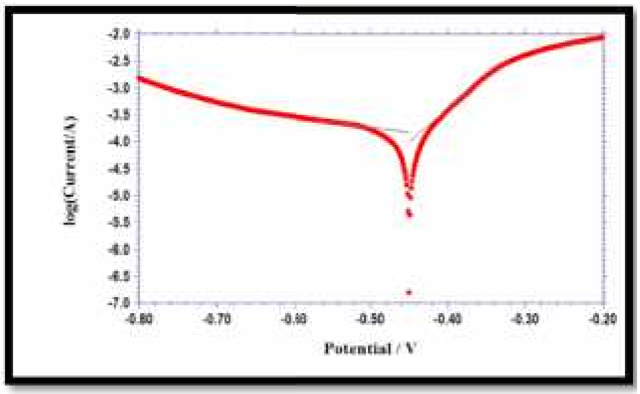

Fig.8 Tafel plot of PANI-FA 45% Composite

Table 1 Charge transfer resistance and double layer capacitance obtained by polarization studies

Parameter	Bare	Blank	Poly aniline	Fly ash	PANI/FA (45%) Composite
Cathodic Tafel Slope	1.298	2.324	3.298	1.614	1.970
Anodic Tafel Slope	4.538	10.759	10.882	6.631	12.005
Cathodic Intercept	3.822	3.742	3.681	3.709	3.829
Anodic Intercept	3.040	3.767	3.794	3.288	3.994
Linear Polarization	143	152	129	122	203
Corrosion Current (A)	5.22×10^{-4}	2.1×10^{-4}	2.37×10^{-4}	4.30×10^{-4}	1.53×10^{-4}
Corrosion Rate (Mil/Year)	43.02	17.97	19.53	35.45	12.64
Corrosion Rate (Angs/mt)	20.79	8.684	9.437	17.13	6.107
Corrosion Rate (g/hour)	9.7×10^{-5}	4.075×10^{-5}	4.428×10^{-5}	8.073×10^{-5}	2.865×10^{-5}

Comparison of polarization resistances for a bare and coated metal allows the calculation of the corrosion inhibitor efficiency (IE), which is used to rate the different surface treatments. Fig. 9-13 shows impedance spectra of PVA coated, PANI-FA 45% composite coated and polyaniline, Fly ash coated MS plates.

The results for the polarization studies are given in the Table 1. From the results it was inferred that the corrosion current of the PANI-FA 45% composite was less compared to poly aniline, Fly ash and PVA coated mild steel plates. PANI-FA 45% composite was showed good anticorrosive property with low corrosion current.

Electrochemical Impedance Spectroscopy (EIS) Impedance Measurements

The EIS method is used to monitor and predict the degradation of the coatings. The durability and performance of protective coatings in typical service environments depend largely on the prevention of the substrate corrosion. As can be seen in Fig. 13 PANI-FA 45% composite coated MS plates show effective anti-corrosive behavior in 0.1M HCl solution compared to PVA coated MS plates. The impedance response can be represented by the capacitance of the interfacial double layer (C_{dl}) in parallel with charge transfer resistance (R_{ct}). R_{ct} and C_{dl} jointly represent the electrochemistry of corrosion. Effective corrosion resistance is associated with high R_{ct} and low C_{dl} values.The interfacial capacitance has been estimated from the impedance value of the frequency (f_{max}) having maximum imaginary component with Nyquist plot by using the following relationship:

$$C_{dl} = \frac{1}{2\Pi f_{max} R_{ct}}$$

R_{ct} is obtained from the measured diameter of depressed semicircle. The inhibition efficiency was evaluated from the measured R_{ct} values as.

$$EI\% = \frac{R'_{ct} - R^0_{ct}}{R'_{ct}} \times 100$$

Where R^0_{ct} and R'_{ct} are the charge transfer resistance values for bare and PANI/FA (45%) composite coated MS plates, respectively. The values of R_{ct}, C_{dl} and are noted in Table 2.

Table 2 listed out the R_{ct} and C_{dl} values of PVA coated, polyaniline , fly ash and PANI-FA 45% composite coated MS plates. PANI-FA 45% composite coated MS plates exhibited high R_{ct} value. Increase in R_{ct} values and decrease in C_{dl} values related to the increased degree of protection of mild steel in corrosive solution. These high R_{ct} and low C_{dl} values show effective resistance of PANI-FA 45% composite against corrosion. Table 3 showing the results of inhibition efficiency calculated by the impedance measurement.

Impedance Plots

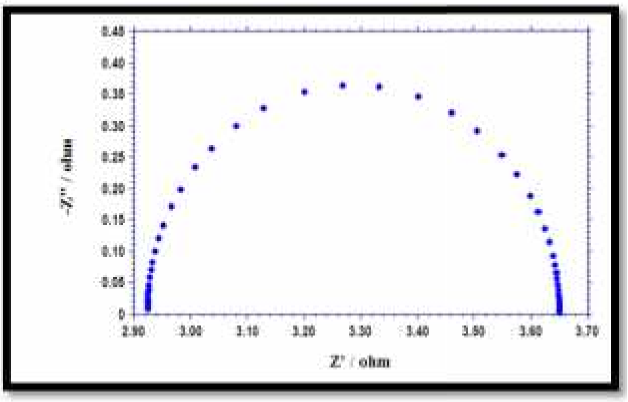

Fig.9 Impedance plot of bare

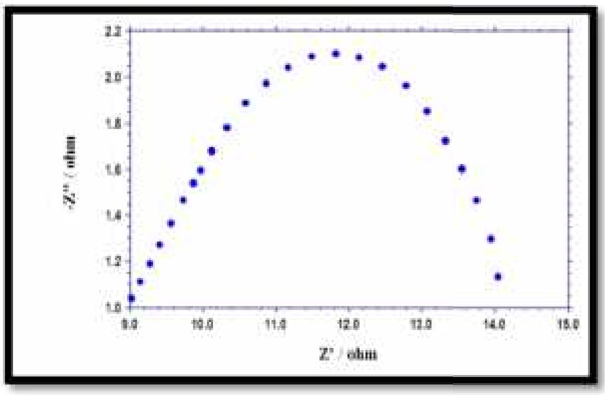

Fig.10 Impedance plot of blank

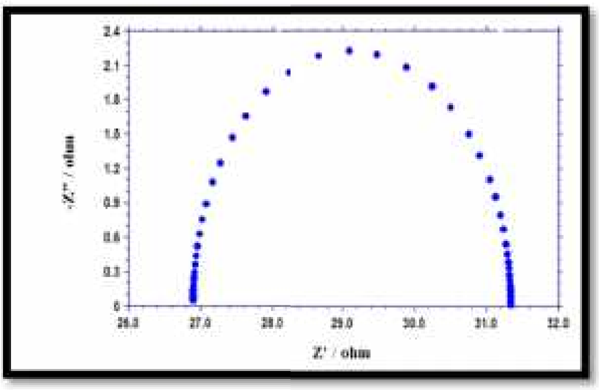

Fig.11 Impedance plot of Polyaniline

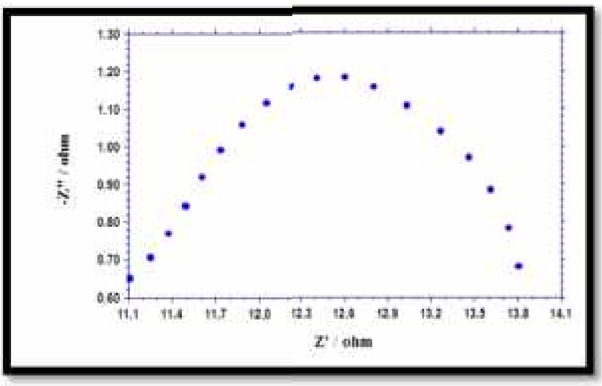

Fig.12 Impedance plot of Fly ash

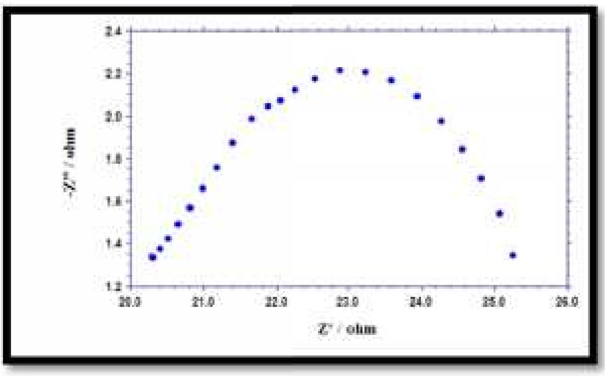

Fig .13 Impedance plot of PANI-FA 45%

Table 2 Impedance measurement of (Mild Steel) MS plates

Specimen	R_i	R_f	R_{ct}	f_{max}	C_{dl}
Bare	2.92	3.66	0.74	0.37	5.81×10^{-1}
Blank	9.0	14.0	5.0	2.1	1.51×10^{-2}
Polyaniline	26.9	31.3	4.4	2.2	1.64×10^{-2}
Fly ash	11.1	13.8	2.7	1.20	4.90×10^{-2}
PANI/FA (45%) Composite	20.2	25.4	5.2	2.2	1.39×10^{-2}

Table 3 Inhibition efficiency measurement of MS plates

Specimen	R'_{ct}	R^0_{ct}	E.I (%)
Blank (PVA coated)	5.0	0.74	85.2
Polyanilne coated	4.4	0.74	83.18
Fly ash coated	2.7	0.74	72.59
PANI-FA 45 % coated	5.2	0.74	85.76

From the Table 2 & 3 it was inferred that PANI-FA 45% composite has good anticorrosive property and it has the highest inhibition efficiency (85.76%). The decrease in C_{dl} is attributed to increase in thickness of electronic double layer. These observation suggested that PANI-FA 45 % composite function by adsorption at metal surface thereby causing the decrease in C_{dl} values and increase in R_{ct} values. A good barrier allows very little flow of current thereby showing high resistance impedance measurements for the prepared composite.

CONCLUSION

The electrochemical behavior study by cyclic voltammetry revealed that the red-ox behavior of PANI and their peak height increased with the increase number of potential scans suggested that the films were electroactive. For PANI-FA 45% composite also showed two oxidation potentials and two reduction potentials. For the composite also their peak height increased with the increase of number of potential scans and their oxidation peaks shifted towards left and reduction peaks shifted towards right on compared with pure PANI. The result of anticorrosive property revealed that the PANI-FA composite was efficient materials to inhibit the corrosion of steel through adsorption mechanism.

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References

1. Ahmed, N., and MacDiarmid, A.G., (1996): Inhibition of corrosion of steels with the exploitation of conducting polymers. *Synth. Met*., 78: 103-110.
2. 2. Albuquerque, J.E., Mattoso, L.H.C., Balogh, D.T., Faria, R.M., Masters, J.G., and Mac Diarmid, A.G., (2000): A Simple way to estimate the oxidation state of polyanilines; *Synthetic metals*, (113), pp.19-22.
3. DeBerry, D.W., (1985): Modification of the Electrochemical and corrosion behavior of stainless steel with an electroactive coating. *J. Electrochem. Soc*., 132: 1022.
4. Genz, O., Lohrengel, M.M., and Schultze, J.W., (1994): Potentiostatic pulse and impedance investigations of the redox process in polyaniline films. *Electrochim. Acta* ., 39: 179.
5. Mathebe, N.G.R., Aoife Morrin, and Emmanuel I. Iwuoha, (2004): Electrochemistry and scanning electron microscopy of polyanilne/peroxidasebased biosensor; *Talanta* 64; pp 115.
6. McAndrew, T.P., Miller, S.A., Gilleinski, A.G., and Robeson, L.M.,1996. Polym. Mater. Sci. Eng.,74: 204.
7. Matveeva, E.S., and Gonzales-Tejera, M.J., (2000): *J. Electrochem. Soc*., 147: 101.
8. Norden, B., and Krumeirjer, E., Noble prize in chemistry, 2000. Conducting polymers; the royal Swedish Academy of science; [online] www.kva.se
9. Petrik, Leslie, F., White, Richard, A., Klink, Michael, J., Somerset, Vernon, S., Burgers, Colleen L., Fey, and Martin, V.,(2003): Paper #61, In: International Ash Utilization Symposium, Centre for Applied Energy Research, University of Kentucky, USA. http://www.flyash.info
10. Popkinov, G.S., Barsokov, E., and Schindler, R.N., (1997): Investigation of conducting polymer electrodes by impedance spectroscopy during electropolymerization under galvanostatic conditions. *J. Electro anal.Chem*., 425: 209.
11. Raghavendra, S.C., Syed Khasim, Revanasiddapp, M., Ambika Prasad, M.V.N., and Kulkarni, A.B., (2003): Synthesis, characterization and low frequency a.c. conduction of polyaniline/fly ash composites. *Bull. Mater. Sci.*, 26(7): 733–739.

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