

Application of PANI-Mn Nano-Composite for Corrosion protection

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Abstract: India loses around 5-7% of its Gross Domestic Product (GDP) every year due to corrosion. The International Zinc association (IZA) said that the need for immediate and appropriate measures to control further damage. Corrosion is the biggest problems which affect the economy of the country. Corrosion is the deterioration of materials by chemical interaction with their environment or Corrosion is the degradation or destruction of metals by chemical or electrochemical reaction with the surrounding environment. Conducting polymer such as Polyaniline (ES) salt has a variety of application due its inherent high conductivity. Polyaniline (ES) salt is used in the field of nanotechnology for improvement of Sensor, Electronics, drugs, anti-corrosion materials, photonic device and optoelectric device. It is also used in removal of dyes from wastewater, removal of heavy metals from aqueous solution. When Polyaniline is doped with different metal oxides nano particle there is formation of Polyaniline Nano-composite. The PANI-Mn Nano-composite having great potential to protects the metal from corrosion. In this research the main focus on synthesis and characterization of PANI-Mn Nano-composite and its application in controlling the corrosion.

Keywords: Coating, Electrochemical deposition, SEM, TEM. Nano-composite.

I. INTRODUCTION

Polyaniline (PANI) is one of the best conducting polymers due to its excellent conductivity, thermal stability, enhanced chemical stability and ease of processing for device fabrication. It consist of extended p-p conjugation present along the polymeric backbone hence it shows high conductivity[1]. The synthesis of polyaniline by chemical or electrochemical methods is easy and simple. The primary requirement of the polymers to be conductive it must have conjugation in chain backbone for easy moment of the charge carriers[2]. Once the charge carrier are generated, the band gap is reduced and polymers becomes conductive. The charge carriers introduced in polyaniline called doping. The doping increase the properties like electrical conductivity, stability and process ability of PANI through the choice of perfect dopants[3]. Researchers are interested in improving properties by doping with different metals such as doping of polyaniline with TiO₂[4], ZnO [5], Fe₃O₄[6], MnCl₂[7], MnO₄[8], Al₂O₃[9], HNO₃[10] etc. The corrosion is very costly and has a major impact on economies of industrial nations. The annual cost of corrosion consist of direct cost and indirect costs. One of the consequences of corrosion is the failure of the machine or a system to function according to the specification or prescribed slandered[11]. There are many different types of corrosion, the ten common types of corrosion, including galvanic corrosion and flow-assisted corrosion(**Fig-1**) The main cause of corrosion is too much humidity or condensation of water vapour on metal surface[12]. The corrosive gases such as chlorine, hydrogen, oxides, sulfur oxide, ammonia, corrosion can also be occur due to hydrogen and oxygen exposure. The lot of researchers works on to control the corrosion by using some Nano-composite such as carbon Nano tubes doped with polymers improved the anticorrosion properties[13] as bio-sensing materials[14] solar cell[15] fuel cell [16] nano-composite having application in gas and humidity sensor due to their unique properties of reacting with analytes gases[17-18] super capacitor[19] Ni-W-CF composite coating on P110 steel[20]hybride Nano-composite used for corrosion protection[21] Polymer-based Nano-composite used for anti-corrosion application[22] VOPo₄ Nano-composite used as anti-corrosion application[23] Nano-Composite used as corrosion inhibitor for steel alloys in different corrosive media[24] In this work, we focus on simple method of synthesis of polyaniline and is doping with MnCl₂. The synthesized nano-composite were characterized by SEM, TEM technique. The PANI-Mn Nano-composite used for different coating methods and analyzed its application for anti-corrosion.



Figure 1: Corrosion of Iron Metals

II. MATERIALS AND METHODS

The chemicals used such as Ammonia, aniline, ammonium persulphate, manganese dichloride, ethanol, concentrated HCl, aldehyde, diethyl phosphite are of analytical grade, The Distilled water used for experimental work.

2.1 Synthesis of Polyaniline

The 0.5 M aniline monomer (99%) and 0.5 M ammonium persulphate (APS) was prepared in 0.5M Cons. HCl solution, In a round bottom flask. These are mixed slowly with constant stirring on magnetic stirrer. This mixture was kept in ice bath maintaining the temp below 0-4°C for 8-10 hours. The reaction mixture was poured into 200 ml water to complete the precipitation, washed with distilled water and HCl solution to remove un-reacted monomers[25]. After sometime polymerization take place and the dark suspension becomes green in color. The green colored residue like paste was obtained. The final product was washed 2-3 times with D.W. and ethanol. Finally the dark-green powder is dried at 80°C for 6-8 Hours in Oven The final product was grinded to form a green powder is known as conducting PANI (ES).Fig-2.

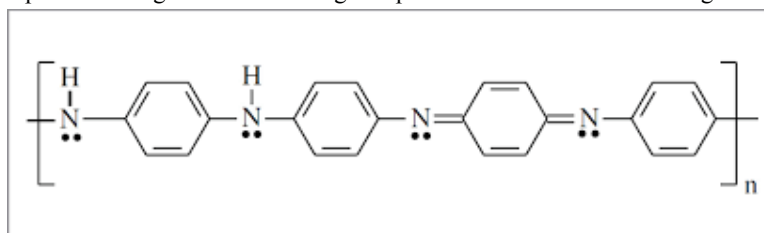


Figure 2: Structure of Polyaniline

2.2 Synthesis of PANI-Mn Nano-Composite

After formation of Polyaniline Emeraldine Salt (ES) the accurate amount of 0.2 M solution of Manganese chloride ($MnCl_2$) slowly and carefully dissolved in polyaniline. The Polyaniline Manganese chloride solution was kept in R. B. flask and kept for vigorous stirring with the help of hot plate with magnetic stirrer (700 RPM) is adjusted, about 3-5 hours. The dark green suspension is formation in the R. B. flask after that this R B flask was kept in Ice bath for 12 Hours. After filtration, The product were washed with 2 times with distilled water and 3 times with ethanol. The prepared Nano catalyst was kept in hot air oven for 7 hours at 70°C. In this method the Nano particle of Mn is uniformly distributed in Polyaniline. There is formation of Nano- catalyst having dark green color, The surface morphology was studied on Scanning Electron Microscopy.

2.3 Transmission Electron Microscopy (TEM 300kV)

The HR-TEM (300kV) was recorded by using FEI, Tacna G2, F30, and Resolution Point: 2.0 Angstrom Line: 1.0 Angstrom, Accelerating potential: 300 kV. F Following fig- 6, 7, 8, 9 shows the TEM images of the synthesized Polyaniline-Mn Nano-catalyst synthesized by oxidative polymerization methods. The TEM analysis were done at 100nm,

200nm, 500nm(Fig-) The TEM can be used to determine the size of Nano-particle and to examine homogeneity and size distribution[26]. It can be seen from the fig: that there is uniform distribution of Mn particle having size 43.16nm(Fig-3-4)

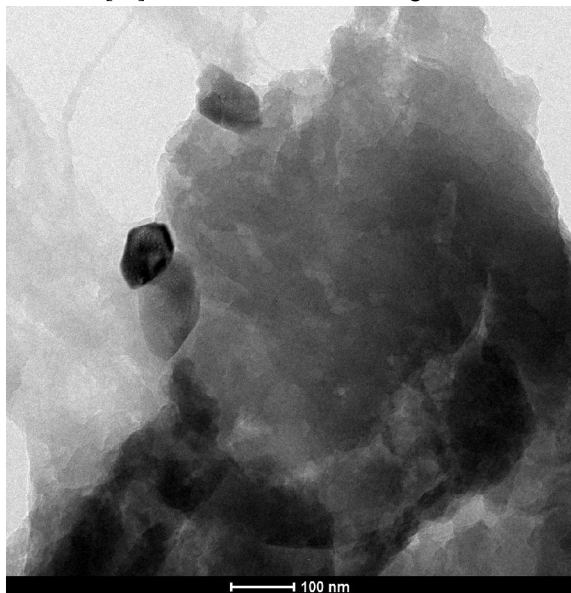


Figure 3: TEM Image at 100nm

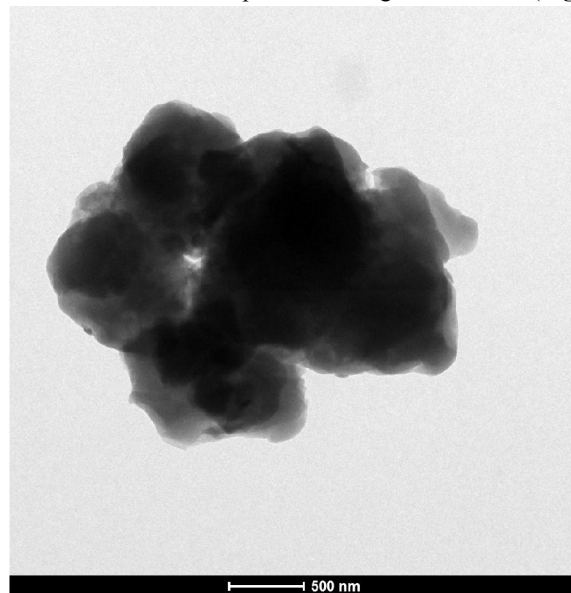


Figure 4: TEM Image at 500nm

2.4 Scanning Electron Microscopy

Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) was taken by using JSM-7600F SEI Resolution: 1.0 nm at 15 Kv. The JEOL JSM – 7600F FEG-SEM combine two proven technology. The main objective of Scanning electron microscopy is to determine morphological features and surface characteristics of the compounds.

The Fig-5-6 show the SEM images of PANI-Mn Nano-catalyst at different magnification. The conducting polymers are highly sensitive towards temperature during recording of SEM. It can be seen from the SEM images that particles are well defined in the size ranging in the nanometers. The high temperature creates a polymerization condition where the interfacial tension decreases with temperature[27],It is seen to form polyaniline-Mn Nano rod morphology. Most of the particles are spherical in shape and slightly agglomerated. The globular particle is produced with high surface.

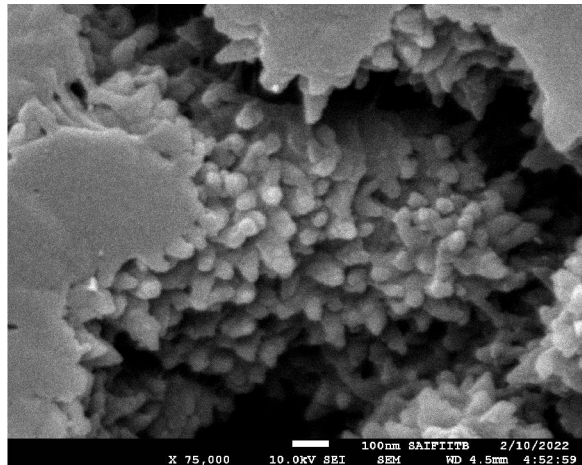


Figure 5: SEM Images at 100nm of PANI-MN

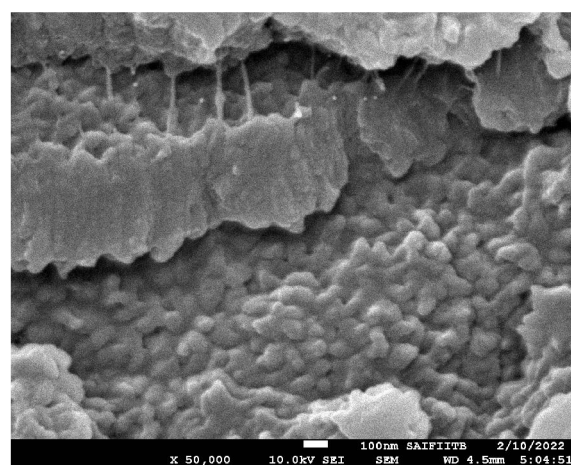


Figure 6: SEM Images at 1nm of PANI-MN

V. MECHANISM OF CORROSION

When oxidation reaction take place on the surface of the metal, when it exposed to moisture. A reduction take place on low energy area of the metal surface. When oxidation and reduction take place at respective anode and cathode simultaneously and hence corrosion is take place.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ electron moves from the anode to the cathode through the iron. The anode and cathode separated by some distance. Insoluble iron (II) hydroxide is formed and the iron (II) ions are further oxidized to produce hydrated iron(III) oxides, or rust .

VI. FACTORS AFFECTING CORROSION OF IRON

Many factors which is responsible for corrosion of iron, such as moisture contain in the environment and the pH of the surrounding area.

6.1 Moisture

The corrosion of iron is limited to availability of the water in the environment. exposure to rains is the most common reason for Corrosion.

6.2 Acid

If the pH of the environment surrounding the metal is low, the rusting process is quickened. The corrosion process is fast when the metal is in contact with Acid rain. Higher pH inhibits the corrosion of iron.

6.3 Salt

Iron tends to rust faster in sea, due to the presence of various salt. Salt water contains many ions that speed up the rusting process via electrochemical process.

6.4 Impurity

Pure iron tends to rust slowly when compare to the iron containing a mixture of metals.

VII. FORMATION AND CORROSION MECHANISM OF PANI-MN COATING

The corrosion process of PANI-Mn in 4.5% NaCl solution. Due to PANI-Mn atomic radius is not large, resulting the formation of coating the gap between the grains and cracks larger, creating the corrosion medium in the Cl. When the coating is done on the surface of the iron metal. Preferentially adsorption at these defects, causing coating surface damage. At this time the destruction of the metal matrix and the undamaged area forms an activation –passivation corrosion primary cell. Thus the material passivation area forms the cathode, activation area forms the anode[28]. The cathode area is much larger than the anode. Causing corrosion to the depth and formation to the corrosion pits. In addition to the rapid dissolution of PANI in pits provide Mn^{2+} which further attract Cl ions. To maintain electro-neutrality. The hydrolysis of high surface coating of metal chlorides produces H^+ , which forms acidification in the pits and thus accelerate the corrosion of the pits coating. When the PANI-Mn coating comes in to contact with corrosive medium, PANI will preferentially dissolve and Mn react easily with H^+ in the corrosive solution. Consuming the large amount of H^+ produce Mn^{2+} , causing the pH of the solution to rises due to lowering of H^+ ions concentration. The Mn eventually converted in to $MnO_2 / Mn(OH)_2$ protective film on the surface of the coating. At the same time the presence of PANI makes the inter atomic bonding force stronger and PANI oxides which hinders the contact of Cl. With the substrate, thus insuring good corrosion resistance of the coating. This two opposite factors makes the corrosion situation significantly lighter in presence of PANI-Mn Nano-composite Coating. (Fig-7)

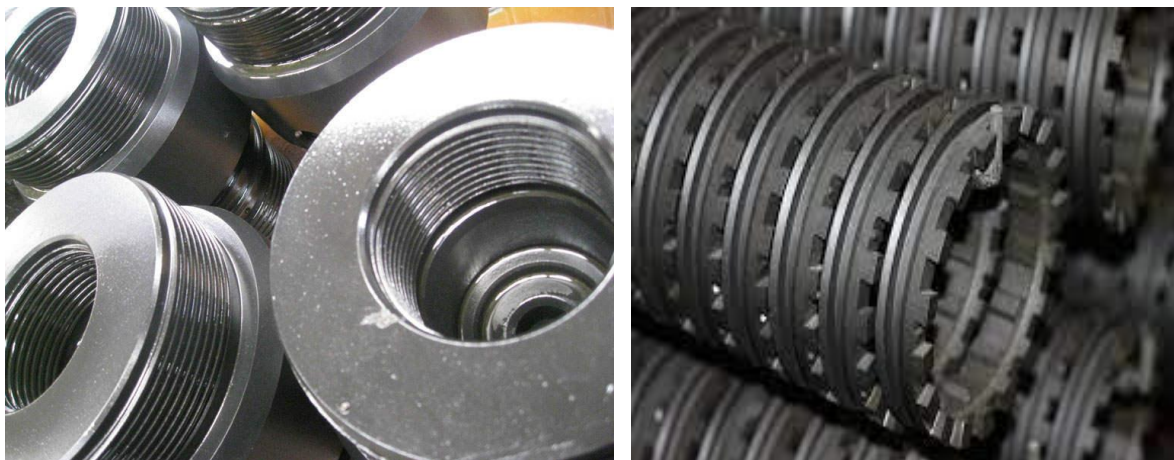


Figure 7: Nano-composite coating on metal surface

VIII. CONCLUSION

The Nano-composite PANI-Mn coating was prepared on the surface of Iron by electrodeposition. The morphology of the nano-composite was studied by SEM, TEM technique. When increase the concentration of Nno-composite which shows good anti corrosion activity on the surface of the metal. The lower concentration does not affect the corrosion. The PANI-Mn Nano-Composite coating having a good potential to protect metal from corrosion.

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