CorrosionProtection By Conducting Polymer

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Abstract

New modern of CPs in protective coatings (dopants, composites, blends) technologies require new innovative materials. Corrosion control of metals is an important activity of technical, economical, environmental, and aesthetic importance. The use of oxides, such as chromates, is highly effective in corrosion protection. Scientists are looking at alternative materials to replace environmentally hazardous materials, e.g., chromates. One of the group of materials identified as corrosion inhibiting are conducting polymers (CPs). CPs have acquired more attentions in the last decades due to their environmentally benign nature and high effectiveness to protect steels against corrosion. The conducting polymer such as Polyaniline, Polypyrrole, Polythiophene, Polycarbazole, Polyindole etc. work as a strong oxidant to the steel, inducing the potential shift to the noble direction. The strongly oxidative conducting polymer facilitates the steel to be passivated. The review paper presented below attempts to summarize extensive studies of Polyaniline, Polypyrrole and Polythiophene polymer and their anticorrosive properties. Several researchers have reported diverse views about corrosion protection by CPs and hence various mechanisms have been suggested to explain their anticorrosion properties. These include anodic protection, controlled inhibitor release as well as barrier protection mechanisms. Different approaches have been developed for the use

Introduction: -

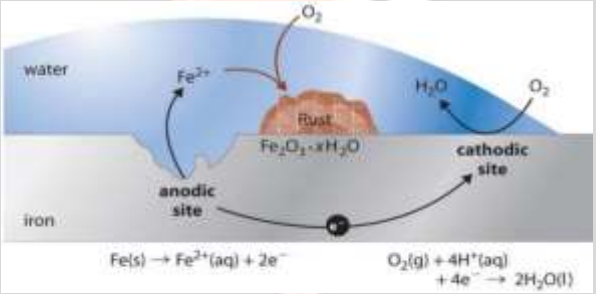
Metals and their alloys are thermodynamically favored to undergo corrosion events. Corrosion can be defined as the destruction or deterioration of a material because of reaction with its environment.1 The inhibition of corrosion of metals is a subject of theoretical research but, more importantly, is of practical interest to multiple industries. The most common corrosion prevention technique is, perhaps, the application of paint or an organic coating on a metal substrate. Ideally, organic coatings would provide long-lasting corrosion protection. However, this property depends on the coating's ability to protect an exposed metal surface when defects appear during their service lifetime. In recent years, the design and development of alternative organic coatings with self-healing abilities [i.e., shape memory materials and intrinsically conductive polymers (CPs)] have been considered useful materials in the protection of metals against corrosion.

The interest in CPs stems from the possibility of formulating CP-based ‘‘smart’’ coatings, which can prevent metallic corrosion even in defect areas where bare metal surface is exposed to the corrosive environment. CPs may exist in different states (oxidation conductive state/reduction-nonconductive state) and can easily interchange between them under appropriate conditions. The CPs undergo redox processes and thereby allow for the binding and expelling counter ions (dopants) in response to the variation of the metal surface potential triggered by local electrochemical reactions due to the corrosion. The dopants, which may be inserted or expelled by the CP depending on the local corrosive conditions, are often inhibitors preventing the local corrosion process upon release. This is one of the strategies that is suggested in exploiting theadvantages provided when a CP is used as a key constituent of a corrosion-resistant coating.

The use of CPs for the corrosion protection of metals has attracted great interest over the last 30 years. DeBerry2 has indicated the Polyaniline (PANI) induced stabilization of the passive state for 400 series stainless steels in sulfuric acid solutions since 1985. The key feature of this process is that CPs are able to maintain the surface potential of the substrate into the passive state where a protective oxide film is formed on the metal substrates. This is due to the fact that CPs-based coatings are pinhole and defect tolerant in a manner similar to that of the coatings based on the environmentally hazardous hexavalent chromium. This is explained by the fact that oxygen reduction within the CP layer replenishes the CP charge consumed by metal oxidation. Along with the switching of the CP into the oxidation state, the potential turns into the passive state of the metal preventing the corrosion process. Despite the extended work devoted to the anticorrosive properties of CPs there are still many issues to be resolved for CP- based coatings to fulfill physio- electrochemical and mechanical requirements of high-performance anticorrosive coatings under widely varying practical conditions. Limitations of CPs as anticorrosive coatings include: (i) irreversible consumption of the charge stored in the CP which is capable of oxidizing the base metal and resulting in the formation of a passive oxide layer, (ii) porous structure and poor barrier effect, (iii) anionexchange properties, (iv) poor adhesion to the metal substrate. All the above-mentioned disadvantages are especially magnified under severe corrosion conditions as in the presence of chlorides, which may reach the metal- substrate surface either due to the CPlayer permeability or to its anion-exchange properties if chlorides replace CP doping anions. Then, chlorides may induce extended localized corrosion and the storedcharge might be irreversibly consumed during the redox reactions of the metal |metal oxide |CP system.

One of the efficient strategies to eliminate the above disadvantages is to consider CP-based composite systems usually comprising a CP in which different inorganic fillers such as metal oxides have been encapsulated. These CP-based composite materials combine the redox properties and hence the self-healing feature of CP with qualities of inorganic materials. Thus, CP-based composites have shown better mechanical and physicochemical properties improving the barrier effect, adhesion and perhaps hydrophobicity. The more these properties are improved the better the metal is protected against corrosion. Furthermore, the design and development of CP-based coating systems with commercial viability is expected to be advanced by applyingnanotechnology,17 which has received substantial attention recently.

Nanocomposite CP-based coatings seem to combine more efficiently the properties of CPs and organic polymers to that of inorganic materials.



Literature Survey: -

Since the discovery of intrinsically conducting polymers (ICPs) in the late **1970s by Heeger, MacDiarmid, and Shirakawa**, for which they were awarded with the Nobel prize [1 – 3], the unique combination of physical and chemical properties of ICPs has drawn the attention of scientists and engineers from many different fields of research and they were studied for various application possibilities. ICPs were investigated for use as light emitting diodes [4, 5], bio-sensors [6, 7], gas sensors [8], bio-membranes, actuators [9 – 11], batteries [12, 13]. The major feature which made the ICPs so promising is that they possess both electronic properties of semiconductors and the processing advantages of conventional polymers. The first reports on the corrosion protection of metals by ICPs were presented by **Mengoli et al. [14]** and **Deberry [15]** in the **early 80s of the last century**, who studied the behavior of polyaniline (PANI) electrodeposited on steel. Their results suggested that their might be a considerable potential behind using ICPs for corrosion control coatings. This fueled an intense research on that topicover the last three decades, because new ways for an efficient corrosion protectionare urgently needed.

Methodology: -

a) From barrier effect to passivation: the classically suggested mechanisms for corrosion protection by conductingpolymers

As nearly all studies on the application of conducting polymers focus on redox-active conducting polymers, such as polyaniline, polypyrrole, or polythiophene, in the following ICP refers to redox-active polymers only and the discussion will also only focus on such redox polymers. As pointed out since the early work by Mengoli and DE Berry a large number of studies on this topic were performed. Up to now, only little is known about how corrosion protection by conducting polymers might work. A number of different mechanisms are proposed, such as the so-called “ennobling mechanism”, that is based on the assumption that conductive redox polymers such as polyaniline or polypyrrole, applied in their oxidized state, may act as an oxidizer, improving the oxide layer at the polymer/metal interface or even maintain the metal in small defects in the passive domain (anodic protection).

b) Intelligent release of inhibitor anions stored in the conducting polymer: -

Maybe the most promising corrosion protection mechanism of ICP coatings is the so-called intelligent release of corrosion inhibiting dopant anions. For the first time it has been pointed out by Barisci et al. that as a result of a galvanic coupling between the corroding metal and an ICP th polymer could be reduced and consequently dopants could be set free. If dopants with corrosion-inhibiting properties are chosen, the release from the ICP might result in the inhibition of the corrosion in the defect or at least in a slowdown of the coating delamination. Kinlen et al. and Kendig et al. showed that in the case of polyaniline anions can be released, most likely by a corrosion- induced increase in pH caused by oxygen reduction at the conducting polymer. Dopant release as a definitive consequence of electrochemical ICP reduction induced by decrease in potential, which always accompanies delamination originating at a defect, was shown by Paliwoda et al. [49].

c) Corrosion protection by ICPs as partof a pretreatment: -

In ICP-based pre-treatments the ICP is fully reduced during application of the pre-treatment leading to an improved conversion layer, such as reported by Sathiyanarayanan et al. [73]. In this study, a wash primer based on polyaniline powder and phosphate was formulated and applied on galvanized iron (GI) and its corrosion protection ability on GI has been compared with that of traditional chromate-based wash primer by salt spray and EIS test. They found that the polyaniline based wash primer is able to protect GI and that its corrosion protection performance is similar to chromate-based wash primer coating. The high impedance they measured on the conversion layer formed from the PANI powder containing formulation indicates that the PANI was reduced (i. e. no longer conductive). It is reasonable to assume that the oxidation power of the PANI had a beneficial effect on the formation of a highly protective phosphate conversion layer. As all ICP is deactivated upon application, this concept goes without the dangers that accompany the use of active ICPs in a corrosion protection coating. However, for the same reason no active function of the ICP is left. Hence, such usage of ICP does not lead to a coating with active anti-corrosion properties. Another proposed mechanism is that conductive polymers might shift the reaction site of oxygen reduction, the key reaction during delamination (as products and side products, such as the OH· -radical, of this reaction are responsible for the degradation of the interfacial bonds, from the metal/polymer interface into the polymer and thus smear out the produced radicals over the full coating, which would significantly lower their concentration at the interface. However, we could show that this would just shift the site of oxygen reduction from the metal/ICP coating interface to the ICP coating/top coat interface.

Coatings basics: -

While the variety in pretreatments and coating formation is nearly limitless, examples of common techniques employed in corrosion control for steel substrates by paint coatings are detailed below.

a) Zinc-rich coatings: -

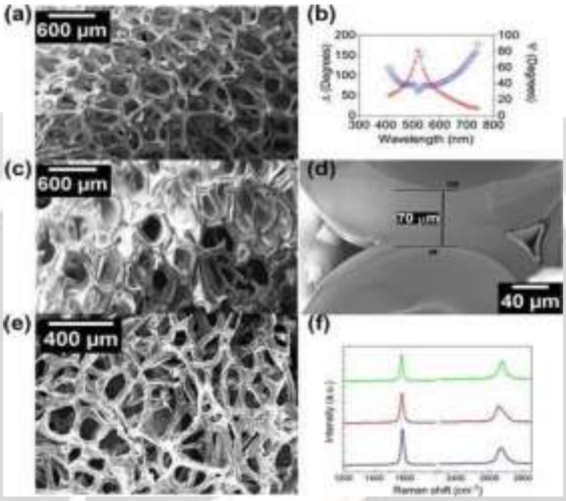
Zinc-rich coatings contain zinc particles and, hence protect the steel by a sacrificial mechanism or by cathodic protection. To have sufficient electrical contact with the steel, the coating must contain 85– 95% w/ w of zinc. In addition, the resulting zinc corrosion products, which preferentially form upon exposure to the environment, tend to block the pores in the coating and improve the barrier properties of the coating. Therefore, there are two modes of corrosion protection via this technique: sacrificial followed by increased barrier properties as the zinc is consumed.

b) Impervious or barrier: -

coatings Impermeable barrier coatings tend to reduce both water and oxygen permeation to a sufficient extent so that corrosion is precluded. The prevention of oxygen access to the metal stops the cathode reaction and current transfer between the anodic and cathodic areas is prevented due to ionic transfer resistance.

c) Inhibitive coatings: -

Inhibitive coatings, generally used as primers, are obtained by adding pigments that release corrosion inhibiting substances. The pigments react with the moisture absorbed in the coating and passivate the steel. However, all effective inhibitors such as strontium chromates have harmful effects on the environment. As the release of inhibitors is based on leaching, coatings need to be highly pigmented in order to insure sufficient leaching. Toxic inhibitors, therefore, are constantly released into the environment even when they are not needed. To sum up, paint coatings are essential in one way or another to protect steel products from corrosion and there is a need to replace conventional paint contents by environmental friendly and nontoxic formulations.



APPLICATIONS OF CPs: -

Including more process able materials with improved physical and electrical properties and cheaper costs, conducting polymers are attracting considerable interest in potential approaches.

I. Super capacitors/ ultra-capacitors (SCs): - SC is attractive because of its high power capacitive energy density, long life, and environmental friendly compared to batteries. The electrode materials for SCs are generally transition metal oxides, high surface carbons, and CPs. Double layer electrical capacitors (EDLC), hybrid capacitors, and pseudo capacitors are the three types of ultra-capacitors based on charge storage. EDLC type uses a non- faradic mechanism while pseudo capacitors use a faradic mechanism. Carbon-based composites coated with CPs are excessively used for SCs, because of their high power capacities. By using a CP and copolymer as additives to fabricate conductive hydrogels, natural polysaccharides can be used in the electrodes due to their lightweight and flexibility. Polythiophene and its derivatives like PEDOT, PFPT, PMeT, PDTT are highly used for SCs applications

II. Light emitting diode (LED): -

Polymer LEDs and polymer light- emitting electrochemical cells (LECs) have excellent capability to function next- generation displays and illuminants. PLED are usually made from multilayered organic materials, sandwiched between a transparent anode and an air unstable cathode, which is frequently coupled with an electron injection layer. Both the indium-tin oxide and thin aluminum films can be used as the transparent electrode. Poly (p-phenylene vinylene), polyfluorene, poly(p-phenylene), and polycarbazole and their derivatives have been intensively researched to produce superior deviceperformances.

III. Solar cells: -

The solar cell is one of the most efficient methods of utilizing solar energy. Different types of solar cells are generated following preferences, like crystalline silicon solar cells, thin-film solar cells, desensitized solar cells, perovskite solar cells. DSSC cells are fabricated using natural dyes. Zhang et al., [28] synthesized PBDTT-4S-TT and PBDTT-4SBDD using benzo dithiophene unit with 4- methylthio substituted thiophene side chains and found that 4-methylthio substitution on the thiophene side chain of two-dimensional polymers is an effective strategy to enhance the Voc of polymer solar cells.

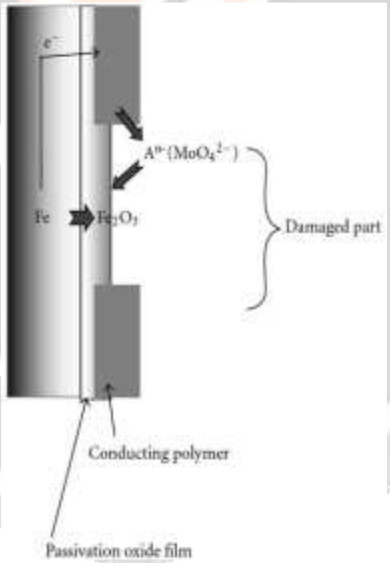
IV. Field effect transistors (FET) andDiodes: -

CP field-effect transistor (CPFET) platform is a promising technology due to its established applications in electronics as field-effect transistors and for charge storage purposes. Hirose et al., [31] investigated the electrical characteristics of OFET with a short channel length from 1 µm to 30 nm using polymer semiconductors, and these impacts can be minimized by regulating the ionization capacity of organic semiconductors.

V. Batteries: - Conducting polymer has a high commercial impact. CP electrodes in battery components have greater importance due to better cyclability and stability. Lee et al., [58] investigated the modified sulfur PEDOT: PSS material used as a cathode in Li-S batteries. PEDOT: PSS coated sulfur electrode exhibits improved electrochemical performances compared to pure sulfur electrode [58]. Nanoscale porous carbon fibers (CNFs) have a highercapacity even at a high charge or dischargecurrent density.

Mechanism: -

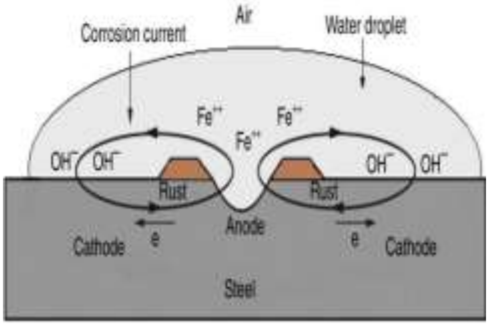
a) **Anodic protection mechanism: -** Secures embedded reinforcement against present and potential corrosion utilizing anodes that are embedded in fix patches, and no requirement for wiring or external device.



b) **Controlled inhibitor release mechanism (CIR): -**
The CIR model recommends that the oxidized and doped type of specific ICPs, like Polyaniline(PANI), when applied to a base metal substrate, delivers the anion dopant upon reduction due tocoupling to the base metal through defects in the coating.

c) **An active electronic barrier at themetallic surface: -**
whenever metallic comes into contact with a doped semiconductor or an electronically carrying out polymer, an electric field is expected to be formed, limiting the flow of electrons from the metallic to an oxidizing speciesand subsequently avoiding or reducing corrosion.

d) **Barrier protection mechanism: -** CPs coatings form a solid, adhesive, low porosity barrier on a base metal that maintains a basic environment, reducing oxidant access and avoiding oxidation of the metal compactness. Surface. CPs coatings serve active protection in preference to a simple barrier, and the barrier impact improves with an increase in adherence, lesser porosity, and higher compactness.



Conclusions: -

CPs can be used in various forms for corrosion protection of metals and metal alloys. They can be used as pigments, multilayers, and composites. Corrosion- inhibitive dopants can be incorporated on the backbone of CPs which can be released when CPs are reduced under particular conditions. Bulk synthesis of CPs is possible by chemical oxidative polymerization method. Electrochemical deposition of CP layers directly on the oxidizable surfaces of metals and alloys using appropriate electrolytes in polymerization solutions is also possible. Anodic protection occurs as far as the OCP of the M|CP system is kept within the passivation state of the metal substrate. However, a simple CP coating seems unable to provide protection for a long period in aggressive environments where localized breakdown of the CP coating usually occurs. Using suitable doping ions and an optimized amount of CP in protective coatings, a self-healing process operates as far as the CP is in its electroactive state. The morphology of CPs influences the anticorrosion properties of the CP-based coatings. Future investigations exerting more control over the synthetic paths of nanostructured CPs are expected to lead to improved. protective CP-based materials with a better performance. Numerous studies in recent times show the tremendous potential of CPs for the corrosion protection of metals and their alloys, which is yet to be fully explored.

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