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Role of conducting polymers in corrosion protection

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Abstract

Corrosion is an environmental evil related to metal and their alloys. Researchers trying their best to overcome it with traditional and new techniques. Recently Conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPy) etc. are used for the corrosion protection of metals and metal alloys. Various mechanisms have been suggested to explain anticorrosion properties of CPs. These include anodic protection, controlled inhibitor release as well as barrier protection mechanisms. The presenting review is mainly focused on Different approaches that have been developed for the use of CPs in protective coatings.

Key words: Conducting polymers; PANI; Polypyrrole; Metals

1. Introduction

Corrosion is the destruction/deterioration of a material due to adverse environment and other related factors. Due to high material cost factors and limited availability of metals, corrosion control is at high priority important subject of the modern metallic, electrical and electronic finishing industry. Surface modification of metallic substrates by polymeric coatings is an essential and alternative approach for enhancing surface properties. In the similar way, a variety of other methods have been used to protect the precious metals from corrosion. The technique of application of conducting polymer coatings is of great scientific importance as old techniques and methods like coatings, such as paints contain toxic and hazards constituents while conducting polymers do not contain toxic and hazardous constituents for the environment. Secondly Conducting Polymers (CPs) provide both physical and electronic barrier effects and electromagnetic interference (EMI) shielding which enhances the protection behavior [1], compared to traditional coatings that only provide physical barriers against corrosive environments. According to available literature, coating a metal with a conducting polymer places the potential of the electrode in the passive zone in the absence of redox reactions [2].

CPs have been applied on the surface of metals [2-3] and it is one of the most studied alternatives for corrosion protection i.e., the use of conducting polymers [4]. Conducting polymers such as polyaniline, polypyrrole etc. are used for coating metal substrates [5-11]. This review paper has a literature overview of composite conducting polymers coated on various metal substrates. Generally, these polymers are not thermoplastics and thereby they are not thermoformable, behaving like insulating polymers in their intrinsic forms. But, conducting polymers are not similar to other commercial polymers as they exhibit high electrical conductivity with backbone modification [8]. Using organic synthesis process methods and with advanced dispersion techniques, the electrical properties of these polymers can be fine-tuned as per requirements [9]. To synthesize conducting polymers (CPs), electrochemical or chemical oxidation methods are generally used. Polyaniline (PANI) and its derivatives are extensively utilized for anticorrosion coatings due to facile synthesis, enhanced environmental stability. As localized/delocalized polarons and bipolarons present in the polyaniline prepared structure, PANI is practically applied to protect concrete steel bar reinforcement [8]. Also, we can consider Polypyrrole (PPy) as promising material due to its high conductivity, flexible preparation, good mechanical

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properties, and stability factors. Great scientific potential technological application of PPy include electronic and electrochromic devices, light-weight batteries, sensors and counter electrode in electrolytic capacitors [7,].

In recent researches, it has been reported that PPy have corrosion protection properties and it can protect metals and their alloys from corrosion [7]. However, the corrosion protection mechanisms of CPs are complex and affected by various parameters. Some researchers have proposed that a passive oxide film is formed on the metal surface by oxidation-reduction processes, while others have predicted that the barrier mechanism is responsible for provided protection [12]. We can technically design CP-based coatings to inhibit corrosion of metals and under appropriate conditions, conducting polymers can easily switch between reduction-nonconductive state or oxidation conductive state states, useful for corrosion control. Due to Redox processes of these polymers, the expelling/binding of dopants (counterions) is conducted in response to the metal surface potential variation. This potential variation is initiated by local electrochemical reactions resulting from the corrosion. So, depending on corrosive conditions, the dopants can be expelled or inserted by the CPs, which often act as inhibitors that prevent the corrosion reactions. This is considered as a strategy suggested for taking advantage of conducting polymer-based corrosion-resistant coatings [13]. Considering Ppy as a leading candidate for corrosion control, several reports on the corrosion protection of metals and their alloys by PPy have been published. PPy has been added to epoxy polyamide coatings in 1% w/w. An improvement in corrosion protection was found as compared to the control sample, but higher proportions did not improve the performance. It was observed that the efficacy of CPs depends on the method of application and the conditions under which the experiments were performed. In this study, authors claim that the conducting polymers have a similar electrochemical mechanism of protection as that of hexavalent chromium [13-14]. Corrosion protective effect of PPy coatings on mild steel by producing a shift of corrosion potential to positive direction and reducing the reduction oxidation current have been also reported [14]. It was found that the mechanical and chemical treatments of the electrode surface allow improving this effect by creating an additional positive shift of corrosion potential. Composite coatings composed of PANI and nano-TiO2 prepared by in-situ polymerization on steel plates showed superior corrosion resistance than did PANI coatings in aggressive environments. It was proposed that the improvement is the result of the high surface area accessible for the dopant release due to nano-size additive, redox properties of PANI, charge transport prevention by the TiO2 nanoparticles and an increase in diffusion barrier. The PPy/TiO2 composite coating also exhibited a remarkable improvement in corrosion protection [15]. Researchers added poly-o-anisidine (POA) and PANI nanoparticles to alkyd paint formulation for protecting the steel and reported corrosion protection of the PANI/Alkyd coatings was good. Also Epoxy/graphene composite coatings with hydrophobic surfaces were prepared and improvement of the corrosion resistance by applying the composite coating was reported to be due to the physical barrier effect, a decrease in the adsorption of water/corrosive media resulting from the coating hydrophobicity, and high aspect ratio of graphene nanosheets leading to enhancement of the oxygen barrier property [16-17].

There have been several studies regarding the deposition of conducting polymer-based coatings on Aluminum (Al) based substrates to enhance their corrosion resistance. Kunal et al. [18] coated Al-2024-T3 substrate with PPy, PANI, and PPy/PANI composites via potentiostatic and galvanostatic techniques, results showed that the corrosion rate reduction in the presence of CPs was about three orders of magnitude. Copper and its alloys are used in industrial and technological applications on a large scale because of its outstanding processability, thermal, electrical conductivity and ductility. Copper (Cu) is the best selection for integrates circuits, especially microprocessors due to its improved electromigration performance as well as low resistivity [19]. In oxidative environments, the mechanism of corrosion for copper involves the electrochemical reduction of water and oxygen at local cathodic zones and the dissolution of Cu at local anodic zones. The rates of reactions are slowed down by the conductive polymers protective film formation. However, the diffusion and reduction of oxygen, the influential candidate cannot be prohibited by the hydroxide and oxides layers [20]. In research literature we can find many reports regarding applications of conducting polymers on copper, copper alloys and their corrosion related behaviors. Many researchers reported recent polymerization techniques to protect copper from corrosion. Annibaldi et al. [21] reported reproducible electrodeposition of adherent and homogeneous polypyrrole on copper from a salicylate solution. The process was facilitated by the formation of a passive layer which inhibited further dissolution of copper but was sufficiently conducting to allow electro-polymerization. The corrosion protection properties of the coating wire assessed using polarization plots, Tafel analysis, OCP measurements and electrochemical impedance spectroscopy. The polymer coating was effective in protecting copper and was stable for periods exceeding 2 weeks. Many researchers report the PPy/PANI bilayer coating was much effective than for inhibiting the penetration of corrosive species in parent metal.

2. Conclusions

Conducting polymers are extremely useful and widely investigated for the protection of metals such as Copper, Aluminum, Steel, Mild steel, Iron etc. Polyaniline, Polypyrrole etc. are common conducting polymers that have been developed as protective coatings for metals. Composite conducting polymers have been prepared with the incorporation of different components with different preparation techniques. Scientifically, corrosion inhibiting and anodic protection is the most important contributing mechanisms for the reduction of the corrosion rate of metals. It has been demonstrated and analyzed that CPs have excellent corrosion protection properties with coatings. It is expected that in future research investigations, a variety of new scientific valuable prevention coatings or techniques will be at the center of attention to protect valuable metals.

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