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Polyaniline-dodecylbenzenesulfonic acid for corrosion inhibition of stainless steel

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Abstract

Corrosion behavior of stainless steel was investigated by using highly processable polyaniline-dodecylbenzenesulfonic acid (PANI-DBSA) salt. An Electroactivity/redox property of the polymer was investigated by cyclic voltammetry. Conducting salt form of PANI-DBSA was studied by UV-Vis spectroscopy. A solution of PANI-DBSA was drop coated on stainless steel electrode. Corrosion performances of PANI-DBSA coated and un-coated electrodes were investigated in 3% sodium chloride (NaCl) by means of DC corrosion (E Tafel) technique. The results show that PANI coating increased the corrosion resistance of stainless steel in an aggressive sodium chloride medium.

Introduction

Corrosion of metals is a critical problem that the world is facing these days. If not properly manage, it can lead to catastrophic failure of the metal substrates. Millions of dollars of loss throughout the metal industry can be attributed to metal corrosion. The thermodynamic or chemical energy stored in a metal or that is freed by its corrosion varies from metal to metal. It is relatively high for metals such as chromium, zinc, aluminum and iron, and relatively low for metals such as copper, silver and gold. The high reactivity of chromium, zinc, aluminum and iron is paralleled to amount of energy required to transform these metals from their respective ores.

Since metals are produced from their ores by applying vast amount of energy, it is important from the point of view of conservation of energy and resources to prevent metals from being lost by corrosion. The issue looms large on the great scope of National Association of Corrosion Engineer (NACE) International, the corrosion society, which has more than 30,000 individuals and 400 corporate members in 110 countries around the world whose mission is to "protect people, assets and the environment from corrosion". The members of NACE International working in a range of areas related to research and implementation of corrosion control methods. The seriousness of the problem is well reflected in the above scenario.

Although metals like aluminum, chromium, and zinc corrode more readily than iron, their oxides form a coating that protects the metal from further attack but these metals lack in strength. Unlike these metals, iron has enough strength to be used in various potential applications. However, it has a limitation of corrosion. Rust is brittle and flakes off the surface of the iron, continually exposing a fresh surface and thus the corrosion progresses. In order to overcome this limitation, iron is transformed to various alloys known as steel. It retains the strength of iron and can also make it resistant to corrosion. Among various grades of steel, stainless steel is the most resistant to corrosion. It is commonly used in manufacturing machine tools, automobiles, hulls of large ships, machine parts, nuclear power and fossil fuel power plant, transportation, chemical processing, petroleum production & even building parts.

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However, in harsh corroded environments even stainless steel cannot fully serve the purpose.[1] The corrosion of stainless steel substrates is very costly. Therefore, different strategies are developed for its protection. Paint coating and cathodic protection are generally used for protecting metals against corrosion. However, these methods have some advantages such as cost and pollution problems.[2, 3] Replacement of these entire coat layers by less expen-sive, environmentally stable and easy to be synthesized coating is needed for reducing the cost of protection process and increasing the lifetime of steel.

From this point, the important and promising candidates are intrinsically conducting polymers (ICPs). Of all types of ICPs, polyaniline (PANI) has been the most widely studied, due to their environment stability, ease of synthesis, excellent redox reversibility and tunable electrical conductivity.[4] Several reports have demonstrated the effective-ness of PANI in inhibiting corrosion.[5-9] While PANI has been extensively studied for corrosion control, its major drawback is its poor processability. In order to deal with this shortcoming, polyaniline-dodecylbenzene sul-fonic acid salt (PANI-DBSA) was synthesized by a novel pathway.[10] The obtained polymers showed enhance desirable properties. The objective of the present work is to explore its corrosion protection ability of these polymers in saline medium.

Results and Discussion

Electroactivity

The electroactivity/redox property of the polyaniline salt was investigated by cyclic voltammetry. Cyclic voltammogram of the polymer (Figure 1) shows typical redox electrochemistry of PANI. Peak A at ESCE = 0.25 V and peak B at ESCE = 0.89 V corresponding to the transformation of leucoemeraldine (LB) to emeraldine salt (ES) and ES to pernigraniline (PS), respectively. On the reverse scan, peak A' ESCE = 0.68 V and peak B' at ESCE = 0.02V correspond to the conversion of PS to ES and ES to LB, respectively.[11] Generally for polyaniline, a middle redox peak appeared in between the two redox process which is to some degradation products.[12] In the present case the absence of such peak indicates the stability and two well redox processes confirmed the good electroactivity of PANI-DBSA salt.
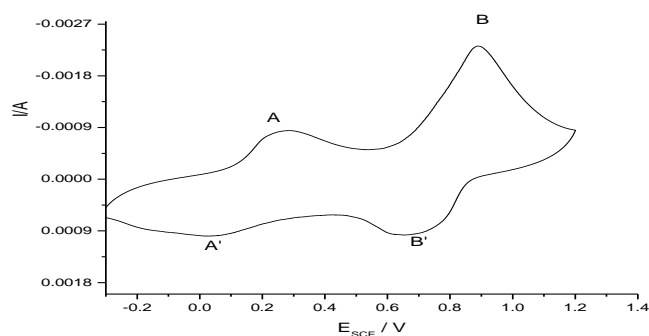

Figure 1: Cyclic voltammetry of PANI-DBSA salt on a gold sheet electrode (vs SCE) in 0.5 M H_2SO_4

UV-Vis Spectroscopy

The UV-Vis spectrum of PANI-DBSA is shown in Figure 2. The spectrum show three characteristic absorptions at 340, 435 and 800 nm wavelength. The first band arises from π-π* electron transition within benzoid (B) ring of the polymer backbone, the second and third absorption bands are assigned to the polaron-π* transition (Quinoid "Q" ring) and π-polaron transition (Exiton), respectively.[13] The second and third peaks are related to the doping level and formation of polaron. The presence of the three characteristic bands support the formation of emeraldine salt form (conducting state) of PANI.[14]
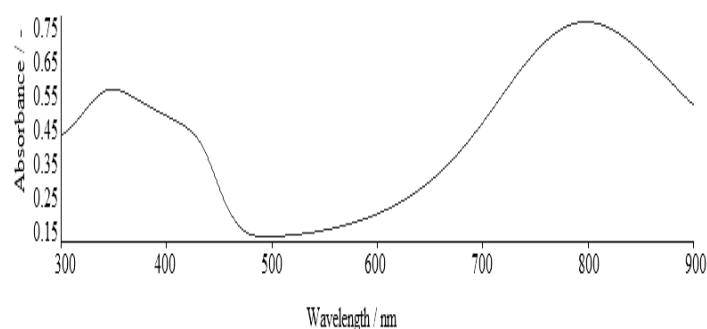

Figure 2: UV–Vis spectrum of PANI-DBSA salt

Corrosion Performance

Figure 3 shows Tafel plots of uncoated and PANI-DBSA coated steel. The values of Ecorr, Icorr and CR are given in Table 1. It demonstrates that the coating caused a remarkable potential shift and reduced Icorr and CR values. The positive shift of corrosion potential and reduction in the Icorr of the coated steel implies that the polymer coatings provide a best protection of steel against corrosion.

The protection efficiency of PANI coated steel was calculated by using the equation;

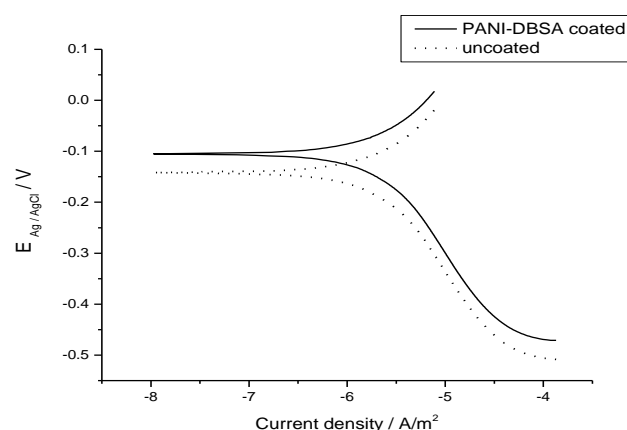$$\%PE = \frac{CRu - CRc}{CRu} \chi\,100$$

Figure 3: Tafel polarization curves of stainless steel electrode in 3% sodium chloride solution

Table 1: Ecorr, Icorr and CR values calculated from Tafel plots

Steel	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	CR (mm/year)
Uncoated	-278	0.937	10.86
PANI-DBSA coated	-105	0.123	1.579

Where CRu is corrosion rate of uncoated steed and CRc is corrosion rate of coated steel.[15] Protection efficiency of PANI-DBSA coated steel is 85%. The results indicate that PANI-DBSA presents a substantial reduction in corro-sion current and corrosion rate, large positive shift in and high corrosion protection efficiency with respect to un-coated steel. The high corrosion protection performance of PANI-DBSA is due to its high processability.[10] The results suggest that PANI-DBSA described in present invention can provide best corrosion protective layer to steel substrates and particularly reducing corrosion to large metallic substrates such as, e.g., bridges, storage tanks, ship-ping industry, as a coating for expose steel structures of road & building construction industries and metallic ma-chines.

Experimental

Materials and Chemicals

Reagent grade Aniline (Acros) was distilled under vacuum, the resulting colorless liquid was stored under nitrogen. Chloroform (Scharlau), Benzoyl Peroxide (Merck), 2-Butanol (Aldrich), DBSA (Acros), 2-Propanol (Merck), To-luene (Scharalau) were used as received.

Synthesis of polyaniline

Polyaniline-dodecylbenzenesulfonic acid (PANI-DBSA) was prepared according to the method reported elsewhere.[10] In a typical experiment 0.29 mol of chloroform was taken in a 100 mL round bottom flask. Then 1.25×10^{-3} mol benzoyl peroxide was added to it under mechanical stirring. To the above solution 0.13 mol of 2-butanol, 3.73×10^{-3} mol DBSA, and 9.66×10^{-4} mol of aniline were added. To the resulting mixture 0.28 mol of deionized water (Millipore) was added to form a milky white emulsion. The mixture turned green in 5 hours and polymerization reaction was allowed to proceed for 24 hours. In the end the organic phase containing Polyaniline salt was separated and washed four times with 50 mL of acetone. After thorough washing, a dark green highly concentrated polyaniline salt was obtained. Then it was dried at room temperature for 24 hours in a Petri dish. On addition of small amount of acetone to the Petri dish the film broke into flakes. Then PANI-DBSA salt was separated by filtration and dried in a desiccator.

Characterizations

Cyclic voltammogram (CV) were recorded with bipotentiostat 2323 (ALS, Japan) in 0.5 M H2SO4 at scan rate of 50 mV/s in a three electrode cell at scan rate of 50 mV/s. PANI-DBSA was dissolved in chloroform and dip coated on gold sheet which was used as a working electrode. The reference electrode was saturated calomel electrode and a gold wire was used as counter electrode. CV was obtained by scanning the potential from ESCE = -0.3V to ESCE = 1.2V. UV-Vis spectrum was collected using Perkin Elmer 650 (UK) Spectrophotometer. A quartz cell of 1cm path length was used for recording spectra of different samples of PANI-DBSA dissolved in different solvents.

Corrosion test

The corrosion protection performance of the chemically synthesized conducting polymers (PANI and POT) was in-vestigated in aqueous 3% NaCl solution in a typical single compartment 3-electrode cell using Gamry Potentios-tat/Galvanostat. Stainless steel disc was used as working electrode. Ag/AgCl and platinum electrodes were used as reference and counter electrodes, respectively. Before coating, steel was polished with abrasive paper and rinsed with mixture of acetone and ethanol and then with distilled water and air dried. The polymer dissolved in tetrahydrofuran (THF) was drop coated on steel electrode. The potentiodynamic scans were acquired by sweeping the potential Ecorr to ±250 mV .the potentiodynamic polarization measurements were performed at the scan rate of 0.002 V/s. The measurements were carried out by using DC corrosion (E Tafel) technique. The values of corrosion potential (Ecorr), corrosion current (Icorr) and corrosion rate (CR mm/year) steel were calculated by using Gamry Echem Analyst softwere.

Conclusions

The polyaniline (PANI-DBSA) coating was applied successfully on stainless steel electrode from a solution of PANI. Inverse emulsion polymerization was carried out for the synthesis of PANI. Cyclic voltammetry and UV-Vis spectroscopy indicated good electro activity and electrical conductivity of the synthesized polymer. The films applied as a top coating was homogenous. The corrosion behavior of PANI coating on stainless steel electrode was investigated using DC corrosion (E Tafel) technique. It was found that the PANI coating led to anodic process and the corrosion rate of steel surface decreased when compared with uncoated steel. In this way, PANI-DBSA coating exhibited an important barrier property against the attack of corrosive environment.

Acknowledgements

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