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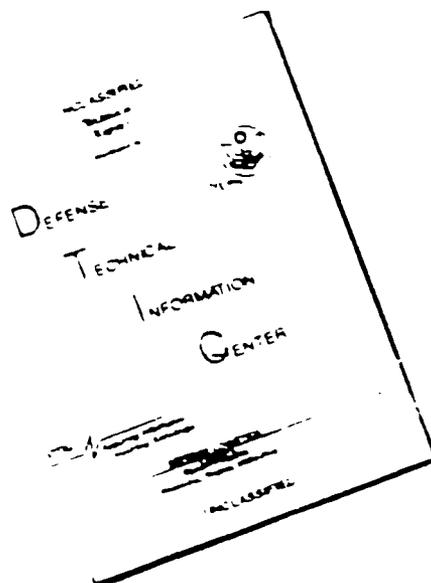
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13. ABSTRACT (Maximum 200 words) Conductive polymer coatings were deposited on steel and titanium substrates by electrooxidative polymerization of poly(3-methylthiophene). The properties of the polymer coatings in acidic, basic and chloride containing solutions were evaluated by electroanalytic means, and the effectiveness of the coatings in providing anodic protection of the substrate were evaluated. The polymer contains a reversible couple with an equilibrium potential near 0.4V positive of Ag/AgCl sat'd KCl. It is effective in passivating 430 stainless steel and titanium in sulfuric acid solution at temperatures below 50C. Excursions of potential negative of -0.3V result in irreversible reduction of the polymer to a nonconductive state. The polymer is also rendered permanently inactive by basic solutions and by chloride.				
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Corrosion Inhibition by Electrodeposited Conductive Polymer Films

Final Report

Dale P. Barkey

October 30, 1993

U.S. Army Research Office

Gr. No. DAAL03-89-K-0138

University of New Hampshire

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Final Report: Corrosion Inhibition by Electrodeposited

Conductive Polymer Films, Gr. No. DAAL03-89-K-0138

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Problem Studied

Some structural metals, including stainless steel and titanium, form passive layers that reduce corrosion rates to very low levels in certain environments. Anodic protection exploits this effect by inducing and maintaining passivation by chemical or electrical means. In this study, passive films were supported electrochemically by conductive polymer coatings electroformed directly on the metal to be protected. Poly(3-methyl thiophene) was chosen because it contains a reversible couple in acidic aqueous solution that lies within the passive region for stainless steels and titanium, and because it is a relatively stable conductive polymer. A principal advantage of this form of protection is that the protected surface need not be completely covered by the coating. If the coating is breached, it still acts to passivate the substrate. As a means of maintaining anodic protection, these coatings have advantages over direct imposition of a potential with a power supply. The most obvious advantage is in energy savings, since the coating is spontaneously regenerated by ambient oxygen. In addition, since the polymer becomes non-conductive at negative potentials, it ceases to drive dissolution if the metal becomes active. It thus has a built in governor that prevents catastrophic loss of material.

Our approach has been to first characterize the dependence of the properties of a coating on the conditions under which it was formed. We also studied pretreatments with the objective of improving adhesion and uniformity. These experiments were performed with platinum, steel and titanium substrates. The electrochemical properties of the coatings were examined by conventional electroanalytical techniques.

The coating were then subjected to a range of tests to evaluate their permanence in corrosive environments and their effectiveness in protecting the metal substrate. We were interested in the steady-state condition of coated samples, the behavior of coatings galvanically coupled with uncoated samples and the dynamic response of the coatings to excursions outside the protected potential range.

What follows is a brief description of results. The original data and details of the experimental work can be found in the references listed under 'Publications'.

Major Results

Dependence of coating properties on deposition conditions: The coatings were formed by electrooxidative polymerization in galvanostatic operation. The metal samples, in the form of disk electrodes one square centimeter in diameter, were immersed in solutions of monomer in propylene carbonate with an organic electrolyte. An anodic current was imposed on the working electrode while it was rotated at a controlled rate. A total charge of one half coulomb was passed in the deposition step, and the coatings varied in thickness between roughly one and ten micrometers.

The coated electrodes were then transferred to sulfuric acid solution and characterized by electroanalytic means. We measured the redox capacity of the coatings by integration of cyclic voltammograms and the exchange current density for oxygen reduction by construction of Tafel plots. The redox capacity and the exchange current density of oxygen reduction at the coated electrodes both increased with increasing deposition current and decreasing rotation rate. The mass of the coating evidently increases under those conditions, probably because one of the steps in the formation process is homogeneous growth of oligomers in the solution. At high rates of convection or low rates of oxidation, more material is convected away from the electrode before it precipitates. We found no evidence of variation in the microstructure of the coatings with deposition conditions. All of the variation in properties could be explained by variation in coating thickness.

Surface pretreatment: Metal substrates were prepared with cleaning and polishing steps. For steel and titanium, it was necessary to further pretreat the substrate to obtain adherent coatings. Stainless steel was first anodized in phosphate solution to produce a microporous surface. Polymerization onto the pretreated surface produced adherent coatings. Formation of adherent coatings on titanium required a two step procedure. First a thin layer was applied by deposition from a dilute monomer solution containing chloride. A full coating was then applied on top of this layer by deposition from concentrated monomer solution. The role of the chloride is to penetrate the passive layer on the titanium and provide points of direct contact between the metal and the polymer.

Coating permanence: In the time frame of our experiments (up to one month), the coatings retained their effectiveness in both air and sulfuric acid solution. There was, however, a measurable degree of irreversible chemical degradation within this time. In base, or in the presence of chloride, the coatings became inactive, and they clearly cannot be used under

these conditions. The mechanism of attack by chloride appears to be permeation of the coating follows by an undermining attack on the substrate. Base solution, on the other hand, attacks the polymer directly and renders it non-conducting. The coatings also became inactive at temperatures above 50 C.

In one normal sulfuric acid, the polymer may be reversibly reduced to potentials of -0.3V vs Ag/AgCl sat'd KCl. After being held at potentials equal to or positive of this limit, the polymer recovers its conductive state and original steady potential (about +0.4V). If the polymer is driven to more negative potentials and held there for a period of minutes, it is irreversibly reduced and will not recover the conductive state.

Effectiveness for corrosion control: In the case of 430 stainless steel, corrosion protection was demonstrated directly. Uncoated samples immersed in sulfuric acid solution became active and corroded rapidly. Coated samples lost no material over comparable time spans (up to one month). In addition, uncoated samples connected galvanically to coated samples by an external circuit remained passive as well. The passive state was also maintained on sections of coated samples that had been scraped free of polymer. The remaining portions of the coating provided galvanic support for passivation of the entire sample.

We found that the coating does not support the entire corrosion current of the passivated metal. Moreover, protection was provided even under nitrogen purge where oxygen reduction at the coating is greatly reduced. Apparently the coating acts to prevent depassivation by healing small gaps in the passive layer before they spread. This mechanism requires only periodic and transient discharge of the polymer.

Protection of 430 SS is treated in detail in publication #1.

In the case of titanium, we did not explore conditions where the metal spontaneously becomes active. However, we did measure the galvanic current between uncoated samples and coated electrodes coupled to them. The galvanic current was approximately six microamperes per square centimeter of exposed metal in sulfuric acid solution.

Publications

1. "Electrochemically Prepared Poly(3-methyl thiophene) Films for Passivation of 430 Stainless Steel." S. Ren and D. Barkey, J. Electrochem. Soc., **139**, 1021 (1992)
2. "Corrosion Inhibition by Electrochemically Prepared Poly(3-methyl thiophene) Films on Phosphated Steel," S. Ren, D. Barkey, J. Knight and S. Tukimin, 178th Electrochemical Society Meeting, Seattle, Washington, October 14-19, 1990. Vol. 90-2, Ab. No. 230.
3. "Passivation of Titanium by Poly(3-methyl thiophene) Coatings," S. Ren and D. Barkey,

182nd Electrochemical Society Meeting, Toronto, Ontario, October 11-16, 1992, Vol. 92-2, Ab. No. 359.

Participating Scientific Personnel

Dale P. Barkey, Associate Professor of Chemical Engineering, PI

Shouxian Ren, Graduate Research Assistant, PhD Chemical Engineering, 12/92.

Inventions

None

Bibliography

1. "Electrochemically Prepared Poly(3-methyl thiophene) Films for Passivation of 430 Stainless Steel," S. Ren and D. Barkey, *J. Electrochem. Soc.*, **139**, 1021 (1992)
2. "Corrosion Inhibition by Electrochemically Prepared Poly(3-methyl thiophene) Films on Phosphated Steel," S. Ren, D. Barkey, J. Knight and S. Tukimin, 178th Electrochemical Society Meeting, Seattle, Washington, October 14-19, 1990. Vol. 90-2, Ab. No. 230.
3. "Passivation of Titanium by Poly(3-methyl thiophene) Coatings," S. Ren and D. Barkey, 182nd Electrochemical Society Meeting, Toronto, Ontario, October 11-16, 1992, Vol. 92-2, Ab. No. 359.
4. "Corrosion Protection of Metals by Poly(3-methylthiophene) Coatings," S. Ren. PhD thesis, University of New Hampshire, (1992).

Appendix A: Publication #2

Corrosion Inhibition by Electrochemically Prepared Poly(3-methyl thiophene) Films on Phosphated Steel

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Electroactive conductive-polymer films on passivating metals may be used to poise the substrate metal in the passive potential range (1,2). Requirements are that the metal normally be passive under the given conditions, that the polymer be moderately conductive, contain a reversible couple at an appropriate potential that can be sustained by an oxidant in the environment and that it form a stable mechanical and electrical bond with the substrate.

We have undertaken studies on poly(3-methyl thiophene), (PMT), films electrodeposited on phosphated 430 stainless steel. Our goals are to determine the effects of film preparation conditions and corrosion environment and to demonstrate protection of clean 430SS test samples galvanically coupled to the composite films. We report the influence of deposition conditions on morphology and electrochemical behavior and present results of galvanic corrosion measurements as they depend on convection conditions at the test surface and film characteristics.

Experimental

PMT films were formed by electrooxidative polymerization onto rotating disk electrodes (RDE) from 1.0M 3-methyl thiophene/0.1M tetrabutyl ammonium tetrafluoroborate (TBATFB) in propylene carbonate at room temperature under air. Because the polymer does not adhere to polished steel, substrates were pre-treated by anodizing them in concentrated phosphoric acid. The resulting composite electrodes were then galvanically coupled to clean steel RDEs. Both electrodes were immersed in air-saturated 1N H₂SO₄ with a Ag/AgCl-sat'd KCl reference electrode. The test electrode was rotated, while the composite electrode was stationary.

Because maintenance of the film potential depends on reversibility of the film to the oxidant, we sought to optimize the exchange current density of oxygen reduction by variation of film-deposition conditions. These experiments were carried out on platinum RDEs with independent variation of current density and rotation rate. Current densities were varied between 7.9 and 980 mA/cm² and rotation rates between 25 and 6400 RPM. Deposition times were adjusted to produce a total charge of 0.06 coul/cm². Oxygen-reduction kinetics were evaluated by scanning between 0.0 and 1.0V at 2mV/s in 1N H₂SO₄. Exchange current densities were then found by construction of Tafel plots. Film capacity, a measure of film mass, was taken as proportional to the peak reduction current as the film was cycled between -0.6V and 1.6V at 120mV/s in TBATFB in propylene carbonate. In propylene carbonate solutions, the reference electrode was a silver wire in a saturated solution of AgCl in propylene carbonate with 0.1M TBATFB.

Results and Discussion

Film Morphology. On platinum, the films are very smooth and uniform and are deep blue or black. On steel, the films are dull black and visibly porous. The microtexture, observed by scanning electron microscopy (SEM), is made up of overlapping hemispheres five to twenty micrometers in diameter. The hemispheres may be the result of growth from nucleation centers or of cellular growth induced by an interfacial instability. A network of fissures is visible in films on phosphated steel (see Figure 1),

but the films adhered well to these surfaces.

Kinetics of oxygen reduction and film capacity
Film-deposition conditions had a marked effect on both exchange current density, i_0 , of oxygen reduction and on peak current density, i_p , in propylene carbonate. Both i_0 and i_p increased with the inverse square root of RDE rotation rate during film preparation (see Figure 2). We believe that both i_0 and i_p increase with film mass, which in turn depends on rotation rate and current density during deposition. The rate of film growth must increase with the concentration of radical cations at the electrode surface. This concentration is highest at high current density and low rotation rate. The variation of i_0 and i_p with deposition current density is shown in Figure 3.

Galvanic Corrosion. The purpose of the films is to bias the substrate into the passive region and protect the metal, including exposed surfaces, from corrosion. We found that the composite films held the potential of the substrate, and of coupled, clean test samples, at a potential near +0.4V, which is in the passive range for 430SS in 1N H₂SO₄. Test samples coupled to clean steel surfaces showed signs of corrosion, including dulling of the surface and loss of material. Those coupled to composite films remained bright in appearance and suffered no measurable loss of material.

References

- 1) D.W. ReBerry, J. Electrochem. Soc., 132, 1022 (1985)
- 2) Z. Deng, W.N. Smyrl, H.S. White, J. Electrochem. Soc., 136, 2152 (1989)

Acknowledgement

This work was supported by the United States Army Research Office under Contract #DAAL03-89-K-0138.



Figure 1. SEM micrograph of a PMT film on phosphated 430SS. The film was deposited on a 11mm dia RDE from 0.5M 3MT/0.1M TBATFB in propylene carbonate at a current of 60mA and a rotation rate of 100 RPM. The total charge passed was 15 mC/cm².

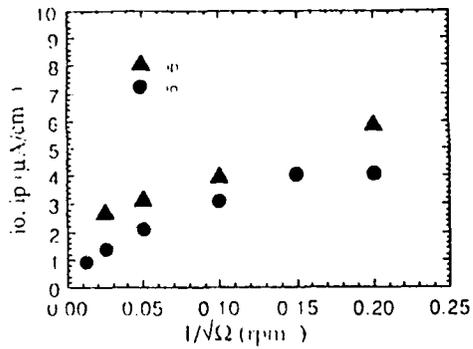


Figure 2. Exchange current density, i_0 , and peak reduction current density, i_p , versus the rotation rate at which the P3MI film was formed. All films were deposited on a 5mm dia platinum RDE from 1.0M $\text{Mn}(\text{OAc})_2$ in 0.1M IPAHEP at a current density of 7.0 mA/cm^2 . i_0 was measured in 1N H_2SO_4 by scanning between 0.0 and 1.0V at 20mV/s . i_p was measured in 0.1M IPAHEP in propylene carbonate by scanning between -0.6 and 0.6V at 120mV/s .

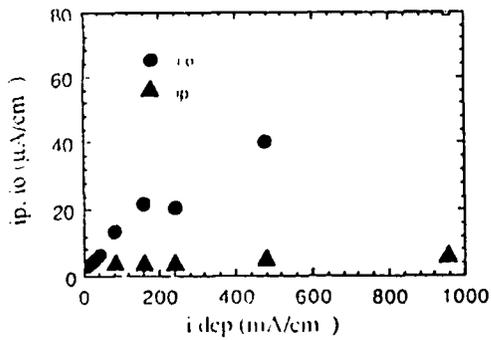


Figure 3. Exchange current density, i_0 , and peak reduction current density, i_p , versus the current density at which the P3MI film was formed. All films were formed at a rotation rate of 100 RPM. Materials and procedures are described in the caption to Figure 2.

Passivation of Titanium by
Poly (3-methylthiophene) Coatings.

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April 29, 1992

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Abstract

Electrochemically prepared poly (3-methylthiophene) (P3MT) coatings on TiGr2 disk were investigated. To adhere a P3MT film onto TiGr2, a strike was deposited by electropolymerization in the presence of chloride ions. A thick film was then deposited on top of it. P3MT coated-TiGr2 disks were tested in acid solutions at several temperatures. P3MT coatings galvanically protected clean Ti samples at temperature up to 50°C.

Electroactive conductive polymer coatings, such as poly (3-methylthiophene) (P3MT) and polyaniline (PA), have a demonstrated capability to poison a metal in its passive potential range [1,2,3]. The mechanism was examined by Deng et al. who coupled titanium samples with P3MT-coated glassy carbon electrodes modified by platinum particles. The P3MT films galvanically stabilized the Ti/TiO₂ interface [2]. The authors presented a study of P3MT coating on stainless steel [3]. Our current study is aimed at the direct electropolymerization of adhesive P3MT coatings on TiGr2 titanium rotating disk electrodes and use of P3MT coatings for corrosion protection of Titanium.

1 Electropolymerization process

TiGr2 RDEs were first polished and then degreased in boiling hexane. Two deposition steps were undertaken to firmly adhere a P3MT film onto the TiGr2 RDE.

Formation of an adhesive P3MT thin film: The TiGr2 RDE was first treated in 0.5 M 3-methylthiophene/0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) propylene carbonate solution containing ZnCl₂. The purpose of the ZnCl₂ was to form pits in the TiGr2 surface during electropolymerization. The pits provided a grip for this P3MT strike. The thin film was formed galvanostatically at 10 mA/cm² and 5 rpm for 40 s.

Formation of a thick P3MT coating on the strike: The P3MT strike had very low charge capacity, and was not capable of protecting the substrate metal. A thicker P3MT film was formed on top of the thin film by electropolymerization in 1.0 M 3-methylthiophene/0.1 M TBATFB propylene carbonate solution. The morphology and thickness of this film can be controlled by changing deposition conditions [3]. In this step, the applied deposition condition was: 200 mA, 500 rpm and 7.5 sec. The formed P3MT film was dull black [3] and had a uniform appearance. The P3MT coatings formed by this process adhered to TiGr2 aqueous acid solutions.

2 Passivation of TiGr2 by P3MT coatings

Self-discharge curves of TiGr2 RDE, the thin film-coated TiGr2 (the pre-coated RDE) and the thick film-coated TiGr2 (the coated RDE), were measured in both 4 N sulfuric and 4 N hydrochloric acid solutions of a rotation rate of 500 rpm. Self-discharge curves of TiGr2 RDEs galvanically coupled with the coated-RDE were also examined.

At 50°C, the potential of the rotating TiGr2 RDE moved negative of 0 V after 2000 s of immersion in the sulfuric or hydrochloric acid solution. With the P3MT coating, the TiGr2 substrate was held positive of 0.2 V within the test period for both acid solutions. The P3MT coating was able to passivate the TiGr2 substrate at the temperature below 50°C.

The self-discharge curves at 70°C showed that the TiGr2 RDE moved to its active potential (about -0.5 V)

after 250 s in 4 N sulfuric acid solution and after 1200 s in 4 N hydrochloric acid solution. In the case of the coated-RDE, the P3MT coating was broken after 1800 s in both acid solutions, following a sharp E_{OC} drop of the RDE into its active range.

The galvanic corrosion test was conducted in 4 N sulfuric acid solution at 45°C. A TiGr2 RDE was first pretreated in 1 N sulfuric acid solution to form a TiO₂ oxide film [2]. The pretreated TiGr2 was then galvanically coupled with the coated-RDE the self-discharge curve of the TiGr2 RDE as well as the galvanic current between these two electrodes were recorded simultaneously. It was shown that the coupled P3MT coating was able to hold the TiGr2 RDE in positive potential range for at least 5 hours. A galvanic current of 8 mA was observed. Without galvanic coupling to a P3MT film, the TiGr2 RDE (with oxide film) began to corrode after about 900 s of immersion in the same acid solution.

References

- [1] D.W. DeBerry, J. Electrochem. Soc., 132, 1022 (1985).
- [2] Z. Deng, W.N. Smyrl and H.S. White, J. Electrochem. Soc., 136, 2152 (1989).
- [3] S. Ren and D. Barkey, J. Electrochem. Soc., 139, 1021 (1992).

3 Acknowledgement

This work was supported by the U. S. Army Research Office under contract #DAAL03-89-K-0138.