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Protective properties of redox polymer film deposited on stainless steel

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Abstract We propose a novel composite organic-inorganic coating in the form of a redox polymer film for protection of stainless steel against general corrosion in strong acid medium (2 M H_2SO_4). We utilize an anion exchange polymer, protonated poly(4-vinylpyridine), into which hexacyanoferrate anions have been introduced. Owing to the presence of $Fe(CN)_6{}^{3-/4-}$ at the interface formed by the film and the steel, a sparingly soluble metal hexacyanoferrate (mostly Prussian blue, PB) is formed as an overcoating on the steel's surface, presumably on the passive (metal oxide) layer. The redox polymer film on the steel seems to act as a composite three-dimensional bilayer-type coating in which hexacyanoferrate(III,II) anions (that are capable of effective charge storage) exist in the outer portions of the film, whereas the inner PB layer improves the system's overall adherence and stability. By analogy to a conducting polymer (e.g. polyaniline, polypyrrole), introduction of the redox polymer composite film leads to stabilization of the steel substrate's potential within the passive range.

Keywords Corrosion protection · Hexacyanoferrate · Poly(4-vinylpyridine) · Prussian blue · Stainless steel

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Dedicated to the memory of Harry B. Mark, Jr. (28 February 1934–3 March 2003)

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Introduction

During recent years, there has been a growing interest in conducting polymers, particularly polyaniline (PANI) and polypyrrole (PPy), and their composites for the fabrication of anticorrosive protective coatings [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. An important feature of such polymer coatings is their ability to store large quantities of charge that can be effectively used to oxidize base metal to form a passive layer. In other words, the conducting polymer films are, in principle, capable of maintaining a stationary potential of protected metal in the passive range.

Electrochemical behavior of organic conductive polymers resembles the characteristics of so-called redox polymers which, for example, can be formed by introduction of anionic inorganic redox centers into thin microporous anion exchange membrane films on electrodes [17, 18, 19, 20]. Protonated or quaternized poly(4-vinylpyridine), 4PVP, is a prominent example of such a membrane film. This polymer (4PVP) has also been considered as a matrix for immobilization of metallic (e.g. Pt [21]), molecular (e.g. cobalt phthalocyanine [22]) or anionic (e.g. ruthenate [23]) microcenters with catalytic properties.

Exposure of 4PVP to aqueous acid solution results in protonation of the polymer and formation of the polyelectrolyte membrane [24]. The presence of weakly basic nitrogen atoms in pyridine units of the polymer chains permits reactions such as protonation, quaternization or coordination of metal cations. The actual polymerization of vinylpyridine was also studied [25]. It is noteworthy that partially protonated 4PVP can be used together with poly(styrene-4-sulfonate) to fabricate self-assembled films for light-emitting diodes (LEDs) [26]. Recently, formation, conductivity and electrochemical properties of a PANI/4PVP copolymer have been described [27]. It has been demonstrated that thin films of this copolymer adhere well to carbon steel surfaces and show promise for corrosion protection.

Our and other studies [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 28, 29, 30] have demonstrated that conducting polymer (PANI, PPy) based composite films can be used for the corrosion protection of steels. In order to assure the long-term ability of the system to hold potential within the passive range, an effective catalyst for oxygen reduction (e.g. Pt) has been introduced [10, 31]. As far as pitting corrosion is concerned, incorporation of large inorganic anions into the polymer film tends to block the access of pitting (e.g. Cl^-) anions to the steel surface [11, 32].

In the present work, we consider a redox conducting polymer, namely protonated 4PVP containing hexacyanoferrates, $4PVP/Fe(CN)_6^{3-/4-}$, as an alternative material to conductive polymers for the formation of well-adhering and stable protective films on steel substrates. Historically, protonated or quaternized 4PVP was found to act as a useful anion-exchange film for such anions as hexacyanoferrates [33], hexachloroiridates [34] or chromates [35] in acid media. For corrosion protection, we explore such features as: (1) the ability of hexacyanoferrates to interact with iron and chromium ions from steel to form sparingly soluble products stabilizing a film on the substrate [11]; (2) very good overall stability of the polymer (4PVP) matrix [35]; (3) conducting polymer-like capability of $4PVP/Fe(CN)_6^{3-/4-}$ film to propagate and store charge efficiently [33, 34]; and (4) the possibility of forming well-adhering protective coatings. We demonstrate here the useful protective properties of $4PVP/Fe(CN)_6^{3-/4-}$ film against general corrosion of stainless steel in strong acid media.

Experimental

Electrochemical measurements were performed using an electrochemical workstation from CH Instruments (Austin, Tx., USA), model CHI 620, and a computer-controlled EP-20 potentiostat from Elpan (Poland). Experiments were done in conventional three-electrode mode, where a platinum wire served as the counter electrode and a glassy carbon (GC) disk of 5 mm diameter or a stainless steel (C, 0.17%; Cr, 12.61%; Si, 0.34%; Ni, 0.25%; Mn, 0.30%; V, 0.04%; P, 0.024%; S, <0.005%) disk of 9 mm diameter (embedded in epoxy resin) acted as the working electrode. The potentials are expressed versus a saturated calomel electrode (SCE).

Unless otherwise stated, all chemicals were reagent grade, and they were used as received. 4PVP, 2% cross-linked, was from Aldrich. Solutions of 4PVP were obtained by dissolving the polymer in methanol. The actual modification procedure was by dip-coating, and it involved multiple (typically three) dipping (in the modification solution) and consecutive air-drying cycles. Incorporation of hexacyanoferrates to form a redox conducting polymer (composite film) was achieved voltammetrically by potential cycling (30–50 cycles) from 0 to 0.8 V at 50 mV s^{-1} scan rate in the solution 0.2 M H_2SO_4 + 0.01 M $K_3Fe(CN)_6$. Although introduction of hexacyanoferrates into 4PVP film is mostly driven by electrostatics (and they can be alternatively incorporated by simple dipping of the modified electrode in the above-mentioned solution for 1 h), the application of potential cycling is expected to accelerate the flux of charge (e^-, H^+) and anions (HSO_4^-, $Fe(CN)_6^{3-/4-}$) and to facilitate ion exchange and, certainly, interaction of hexacyanoferates with the steel substrate. Loadings (in mol cm^{-2}) of the resulting $4PVP/Fe(CN)_6^{3-/4-}$ films on steel were assessed upon estimation of charges under the system's oxidation voltammetric peaks recorded in 1 M H_2SO_4 + 0.5 M KNO_3 at a slow scan rate, 5 mV s^{-1}, in the potential range 0.3–0.7 V. Film thicknesses were determined ex situ using a profilometer (Talysurf 2, Taylor Hobson, UK). Typical $4PVP/Fe(CN)_6^{3-/4-}$ films on stainless steel were characterized by thicknesses ranging from 150 to 250 nm and loadings from 1.5 to 2.5×10^{-8} mol cm^{-2}. Using the fabrication procedure described above, and provided that the number of voltammetric potential cycles employed was the same (e.g. 40), the sample-to-sample variability was, in terms of the film thickness (loading), on the order of 20%.

Potentiodynamic curves were recorded at a fairly low (10 mV s^{-1}) scan rate, in 1 M H_2SO_4 + 0.5 M KNO_3 supporting electrolyte. Measurements were done in aerated solutions at 20 ± 2 °C.

Results and discussion

It has been demonstrated [33, 34, 35] that, despite the excess of other monovalent anions (HSO_4^-) in the supporting electrolyte, $Fe(CN)_6^{3-/4-}$ anions bear a sufficiently large negative charge to be preferentially attracted (electrostatically) by a positively charged polymer (protonated 4PVP). The hexacyanoferrate anions are known to be permanently trapped in the polymer matrix and cannot be exchanged during their redox reactions, where, for the sake of electroneutrality, sorption/desorption of electrolyte ions is operative. The system's electrochemical behavior is somewhat dependent on the molecular weight of 4PVP, the choice of solvent used for its dissolution, dipping and exposure (to the solution containing hexacyanoferrate) times.

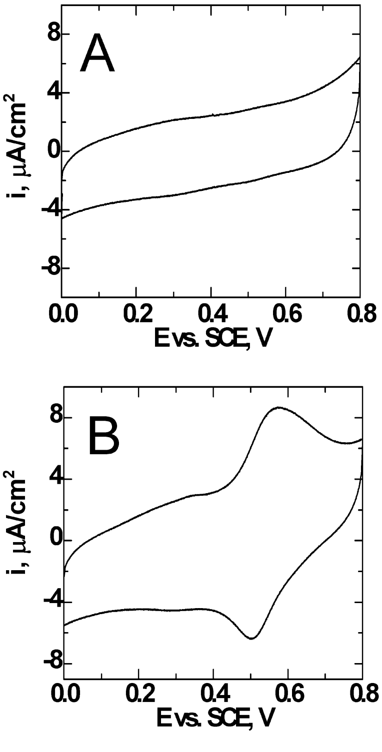

Fig. 1 Cyclic voltammetric responses of a glassy carbon electrode modified with (**A**) protonated 4PVP and (**B**) protonated 4PVP containing hexacyanoferrates(III,II). Electrolyte: 1 M H_2SO_4 + 0.5 M KNO_3. Scan rate: 50 mV s^{-1}

To characterize our redox polymer (composite) 4PVP/$Fe(CN)_6^{3-/4-}$ film in strong acid media, we have first performed diagnostic experiments with the use of an inert glassy carbon substrate. Figure 1 shows cyclic voltammetric responses of (A) a glassy carbon substrate covered with a thin film of 4PVP only and (B) following introduction of hexacyanoferrate anions into the protonated 4PVP film. The presence of hexacyanoferrates is evident from the appearance of a pair of voltammetric peaks at about 0.55 V. Although their shape is far from being ideal for either solution or surface- type behavior of such a one-electron reversible system as $Fe(CN)_6^{3-/4-}$, the results of Fig. 1B are consistent with the formation and electroactivity of a composite redox polymer film in strong acid medium (1 M $H_2SO_4 + 0.5$ M KNO_3). From a mechanistic point of view, charge propagation involves electron hopping (self-exchange) [36, 37] between three-dimensionally immobilized hexacyanoferrate redox sites. Apparently, their concentration within the polymer films is sufficiently high to make the above mechanism operative. The presence of hexacyanoferrate has also been confirmed by taking ex situ Fourier transform infrared (FTIR) spectra of the film: the appearance of a band at 2050 cm^{-1} is related to $C \equiv N$ stretching.

It is apparent from Fig. 2 that, upon formation of a redox polymer film on stainless steel, hexacyanoferrate peaks become much more poorly defined and drawn out when compared to the behavior of the film deposited on an inert substrate (Fig. 1B). Hexacyanoferrate ions from the film are expected to interact in the presence of K^+ ions (from KNO_3) with iron(II), and probably with chromium(III) as well, to form Prussian blue (PB) [38, 39, 40, 41] type and sparingly soluble metal hexacyanoferrate microdeposits at the interface formed with stainless steel [11]. Indeed, formation of PB, or PB-containing, blue-colored microdeposits, has been observed visually using optical microscopy. Also, microscopic examination of the mechanically scratched films (from the steel surfaces) is consistent with the existence of blue-colored species as powders. Therefore, we believe that our protective films on steel are in a sense three-component and consist of a 4PVP matrix, hexacyanoferrate anions and Prussian blue [4PVP/PB/$Fe(CN)_6^{3-/4-}$]. The inner (i.e. in the vicinity of the stainless steel substrate) portion of the composite film that is likely to contain PB within the 4PVP polymer matrix should act as a stabilizing overcoating on the passive (metal oxide) film on stainless steel. On the other hand, the unreacted (namely with iron ions from stainless steel) hexacyanoferrate redox centers are expected to exist in the outer portion of the film. During voltammetric potential cycling, electron transfers from the electrode (steel) substrate to hexacyanoferrate are presumably mediated by PB microcenters in the inner portion of the film. It should be remembered that PB ($KFe^{III}[Fe^{II}(CN)_6]$) undergoes reduction to Prussian white or Everitt's salt ($K_2Fe^{II}[Fe^{II}(CN)_6]$) at about 0.1–0.2 V, and it is oxidized to Prussian yellow ($Fe^{III}[Fe^{III}(CN)_6]$) at potentials more positive than 0.7 V [38, 39, 40, 41]. The redox mediation role of PB (in the inner portion of the composite film) is most pronounced during reduction of hexacyanoferrate(III): no reduction currents are observed until PB starts to be reduced to Prussian white. On the other hand, the mediation process is less evident during oxidation of hexacyanoferrate(II); in the latter case, the partially oxidized mixed-valent PB presumably acts as a good electronic conductor and no redox mediation is operative.

Figure 3 illustrates potentiodynamic curves recorded for bare stainless steel (A), and stainless steel substrates covered with 4PVP/PB/$Fe(CN)_6^{3-/4-}$ following 30 (B) and 50 (C) voltammetric potential cycles in the hexacyanoferrate containing solution for modification. As is seen from Fig. 3, the presence of a composite 4PVP/PB/$Fe(CN)_6^{3-/4-}$ film on stainless steel has led to a significant decrease of current densities, particularly in the cathodic range. By comparison to our previous studies [11, 32], typical conducting polymers (PANI, PPy) seem to behave in a different way: they tend to accelerate somewhat cathodic processes and shift the corrosion

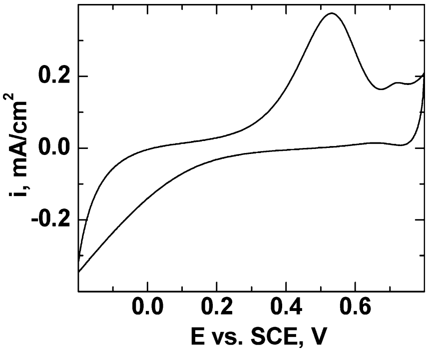

Fig. 2 Cyclic voltammogram of 4PVP/$Fe(CN)_6^{3-/4-}$ film deposited on stainless steel. Scan rate: 50 mV s^{-1}. Electrolyte: 1 M $H_2SO_4 + 0.5$ M KNO_3

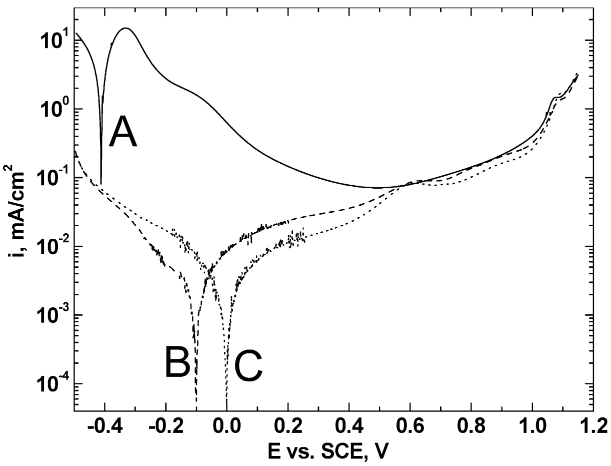

Fig. 3 Potentiodynamic curves recorded for stainless steel: (**A**) bare, and covered with a composite 4PVP/PB/$Fe(CN)_6^{3-/4-}$ film following (**B**) 30 and (**C**) 50 modification cycles, respectively. Electrolyte: 2 M H_2SO_4. Scan rate: 10 mV s^{-1}

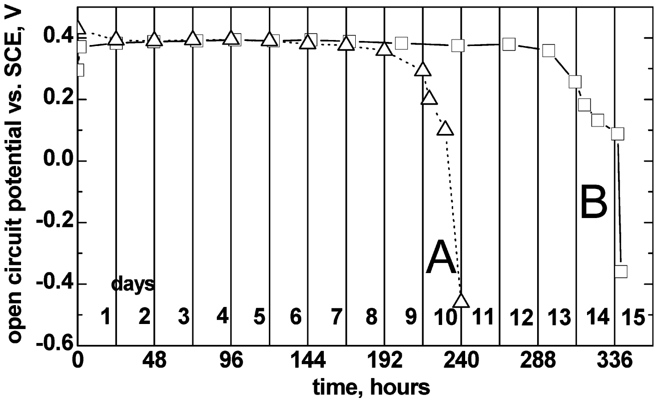

Fig. 4 Time-dependent monitoring of the open circuit potentials of stainless steel samples covered with 4PVP/PB/$Fe(CN)_6^{3-/4-}$ films fabricated following (**A**) 30 and (**B**) 50 modification cycles

potential towards more negative values relative to uncovered steel. Further, it comes from the data of Fig. 3 that the corrosion current estimated by usual means has decreased by ca. three orders of magnitude upon introduction of the composite film. It is also noteworthy that the corrosion potential has shifted from −0.4 V (curve A) to −0.1 V (curve B) and 0 V (curve C), respectively. These results imply good protective properties of the 4PVP/PB/$Fe(CN)_6^{3-/4-}$ film against general corrosion in strong acid media. Here, an important feature is the stability and very low solubility of PB in acid media. In the present work, we have added potassium ions to the H_2SO_4 electrolyte in order to accelerate PB formation and to facilitate electroactivity of PB during voltammetric diagnostic experiments.

We have also addressed (Fig. 4) changes of the open circuit corrosion potential of stainless steel substrates modified with 4PVP/PB/$Fe(CN)_6^{3-/4-}$ films, as for Fig. 2B and Fig. 2C. Figure 4 illustrates the respective data obtained in 2 M H_2SO_4 corrosion medium. Under such conditions, the general corrosion of bare steel proceeded at a fast rate immediately after its immersion in 2 M H_2SO_4 [10]. Modification of the steel substrate with our composite film resulted in the development of the open circuit corrosion potential equal to ca. 0.4 V for long periods of time (10–14 days). The latter potential value implies the overall stabilization of the system and the existence of the stainless steel substrate in the passive range.

Conclusions

Thin films of such a redox polymer as hexacyanoferrate containing protonated poly(4-vinylpyridine) exhibit similar, or even superior, protective properties against general corrosion of stainless steel in strong acid media when compared to conducting polymers (e.g. polyaniline [10] and their composites, polyaniline/Prussian blue/hexacyanoferrates [11]).

It can be expected that a composite organic-inorganic redox polymer acts as a charge-storage film and stabilizes the system's potential in the passive range. Judging from comparison of film thicknesses and loadings, hexacyanoferrate anions are expected to be trapped within the film at fairly high concentration of ca. 1×10^{-3} mol cm^{-3}. Although the charge propagation mechanism is different, when compared to an organic conducting polymer, because it involves fast electron hopping [36, 37] between mixed-valence hexacyanoferrate redox centers, rather than propagation of polaron or bipolaron carriers, accumulation of charge is effective in the redox polymer because it has persisted for relatively long periods of time (more than 10 days). Hexacyanoferrates are also likely to form a sparingly soluble interfacial overlayer that adheres well to and stabilizes the metal oxide passive layer on steel. Important issues are the simplicity of the fabrication procedure and the system's overall stability. Further research is in progress and aims at further structural derivatization and functionalization of the redox polymer film to make the system's open circuit potential stable (within passive range) indefinitely and to modify its membrane properties in a such a way as to minimize access of the pitting causing (chloride) anions. This work has much in common with recent concepts of the derivatization of protective conducting polymer films [11, 12] and the stabilization of the metal/polymer interface with precursor [14] or sparingly soluble interlayers [6].

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