

The Effects of Polyacrylic Acid/Polypyrrole Composite Coating on Photocorrosion and Photoactivity of Pyrite Electrodes

A. Sezai SARAÇ, Belkıs USTAMEHMETOĞLU, Esmâ SEZER, Candan ERBİL
*Department of Chemistry, Istanbul Technical University,
80626 Maslak, İstanbul-TURKEY*

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Electrically conducting polyacrylic acid (PAA)/Polypyrrole (PPy) composite films were prepared by electrochemical polymerization of pyrrole on PAA which was electrochemically adsorbed on natural and synthetic pyrite (FeS_2) electrodes. The application of such polymer coating on pyrite, which is one of the semiconducting materials for solar applications, shows almost total protection against corrosion and can improve the photoactive character of the electrode. Addition of Ce(IV) ammonium nitrate into this system improved the photoactivity of the PAA/PPy composite. The composite polymer has higher photoconductivity than the pure PPy, because of the doping effect of anions on the PPA/PPy composite.

Key words: Polyacrylic acid, Polyacrylic acid/Polypyrrole composite, Synthetic and natural pyrite.

Introduction

Modification of the electrode surface by means of layers of conducting polymers has constituted an area of major interest in recent years. One of the reasons for such interest is that the catalytic activity of the electrodes changes with the polymer coatings. Another source of attention is the use of conducting polymers as coating for unstable semiconductors in order to prevent photodegradation of the semiconductive materials^{1,2}. In spite of the great importance of the stability aspects, not much is known about the mechanism of degradation or corrosion³. A few conductivity measurements are known, with respect to the exposure time to the air^{4,5} but these results cannot be evaluated in terms of corrosion. Photocorrosion is probably the most significant limitation in the use of semiconductors in photochemical solar cells and is an area where conducting polymers may successfully find an application. One of these materials could be polypyrrole films for coating the electrodes of photochemical devices⁶. Because of its conductive properties, polypyrrole has been shown to work as a protective layer against photocorrosion for photoelectrodes⁷. Studies relevant to the use of polypyrrole film as electrode coatings for photochemical devices were recently included in a review by Frank⁸.

We have recently reported oxidative polymerization of pyrrole in PAA⁹ by the matrix polymerization of pyrrole to form stable interpolymer complexes. These results support the conclusion that PPy can interact with PAA, which has been adsorbed on the pyrite electrode, by interpolymer complex formation.

The preparation of such composites by electrochemical polymerization of pyrrole on polymer (matrix) coated working electrodes is one of the best methods used to improve some properties of PPy¹⁰. PPy/Polyester amid¹¹, PPy/Polystyrene¹², PPy/Polyethylene¹³, PPy/Polyurethane¹⁴ systems are some successful examples.

There are several reasons for the current interest in the electrochemical behaviour of PPA/PPy coated pyrite electrodes, e.g, suitability of this semiconducting material for solar energy applications due to its environmental compatibility and its very high light absorption coefficient^{15–20}, effectiveness of PAA in inhibiting the corrosion of ferrous materials when adsorbed on metal surfaces²¹, and the possibility of polycomplex formation between PAA and PPy⁹.

The aim of this paper is to show that pyrrole can be polymerized in a polymer matrix of conventional insulating polymer by electrochemical method. The basic idea is to prevent the pyrite corrosion almost completely by composite coating without a significant decrease in photoactivity. In this study a PPA/PPy composite film obtained for the first time by the electrochemical polymerization of pyrrole on PAA coated electrode and the effect of this composite film on the photocorrosion and photoactivity of pyrite electrode were discussed.

Experimental

Electrolytes

Polyacrylic acid (PAA) was obtained by radical polymerization using dibenzoylperoxide as the initiator. The molecular weight of PAA obtained by viscometric measurement was 140.000, PAA concentration was 3 g. dm⁻³. Ceric(IV) ammonium nitrate (CAN), pyrrole, H₂SO₄, KI, I₂, HF, CH₃COOH, HNO₃ were all Merck reagent grade chemicals of the highest purity and were used without further purification. The redox electrolyte concentration was 0.05 M I₂+4M KI and the $n_{CAN}/n_{pyrrole}$ molar ratio was between 0.037-0.800.

Preparation of pyrite electrodes

Natural pyrite crystals were obtained from Black Sea Murgul Mine Company (KBI, Turkey) and the synthetic pyrite samples were obtained from Hahn Meitner Institut (Bereich Strahlenchemier, Berlin). Impurities in the FeS₂ (natural and synthetic) are given in Table 1.

Table 1. Impurities in natural and synthetic FeS₂ compared with literature values¹⁹

Element ($\mu\text{g/g}$)	FeS ₂ (nat). Turkey ($\mu\text{g/g}$)	FeS ₂ (synth.) ($\mu\text{g/g}$)
S/Fe ratio	1.89	1.98
Na	n.m.	570
Mg	257	6
Al	8850	n.m
Si	18800	n.m
Ca	55	n.m
Co	82	< 1
Ni	4	< 1
Cu	3344	< 1
Zn	4886	2000
Ga	1.0	6
Pb	982	< 1
Ba	609	7
W	2	< 1

n.m.:Not Measured

The electrodes were made by cutting the pyrite samples into small disk-shaped pieces. Electrodes were then prepared by coating the back side of the samples with silver paste (Scotchcast 3M), making a contact with the copper rod by using an electrical resin (Scotchcast 3M). Polishing was performed using a diamond paste (0.5 μm) followed by rinsing with deionized water and methanol in an ultrasonic bath for 10 s. Pyrite surface oxidizes spontaneously in humid air¹⁵⁻¹⁶. Surface mechanical damage of FeS_2 produced by polishing and this oxide surface was removed by etching for 30 s in concentrated $\text{HF} : \text{CH}_3\text{COOH} : \text{HNO}_3$ (1:1:2 by volume) followed by rinsing with deionized water. This chemical etching procedure was used by Tributsch *et al.*¹⁵ who demonstrated by XPS measurements that this treatment produces an oxide-free clean pyrite surface.

Photopotential of electrodes (in I^-/I_3^- vs Pt) increased from about 10-20 mV up to 90 mV by chemical etching.

Electrochemical Measurements

A Wenking POS 73 Model Potentiostat and Kipp and Zonen X-Y Recorder were used for electrochemical measurements. The conventional three-electrode system consisting of a pyrite working electrode and platinum electrode as a counter electrode was used. The reference electrode was a saturated calomel electrode (SCE) connected with measuring solution by a Luggin capillary via a salt bridge. Sweep rate was 50 mVs⁻¹ and 5m Vs⁻¹ for cyclic voltammetry (CV) and corrosion measurements respectively.

Photoelectrochemical Measurements

A standard three electrode photoelectrochemical cell was used for obtaining cyclic voltammograms.

Illumination was carried out by a tungsten lamp (20 W). The cell had one compartment containing the working electrode, the reference electrode (SCE), and a platinum wire as the counter electrode.

Photopotential changes with time for bare and coated electrodes in KI/I_2 redox electrolyte were measured against Pt.

Coating Procedure

Polypyrrole can be synthesized at the surface of PAA film. PAA adsorbed natural and synthetic pyrite electrodes by this method were used as substrate for the polymerization reaction. First, PAA (3g.dm⁻³) was adsorbed on the electrode surface electrochemically by cycling in the range of 0-1200mV (scan speed 50mV.s⁻¹). First cycle values without having supporting electrolyte are $E_a \cong 550$ mV, 470 mV and $E_c \cong 250$ mV, 160 mV for natural and synthetic pyrite respectively. When anodic and cathodic peaks had almost disappeared we assumed that PAA has been coated on the electrode surface (Figure 1, a, b). Then, two procedures were successively applied for coating of PPy on the PAA adsorbed electrode:

Procedure I- A certain amount of pyrrole was added to electrolyte solution and polymerized electrochemically onto the PAA coated electrode surface.

Procedure II- Excess of pyrrole (unpolymerized portion in procedure I) was chemically polymerized by adding CAN, which was used as an oxidant for matrix polymerization of pyrrole in PAA⁹, into the PAA solution and electrodes were held in this solution for several hours with the aim of increasing the photoactivity.

Results and Discussion

Pt as working electrode

For 3 g.dm³ PAA, PAA+Ce(IV) mixture and PAA-Py-Ce(IV) ternary complex (as explained in the previous study⁹) solutions in the range of 0-1200 mV no detectable peaks for the anodic scan were obtained (Figure 2, a, b, c) which means none of the components show an characteristic oxidation peak in this range as expected due to absence of free pyrrole or PPy in this ternary complex.

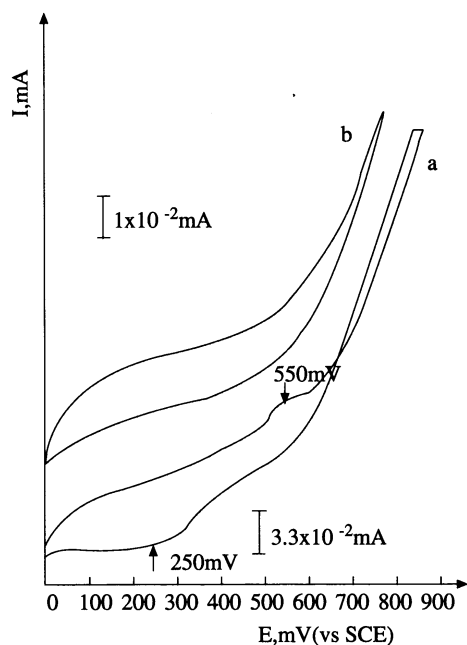


Figure 1. Cyclic voltammograms of natural pyrite 1 in PAA (a) first cycle, (b) after multiple cycles for 10 min. [PAA]=3 g. dm⁻³

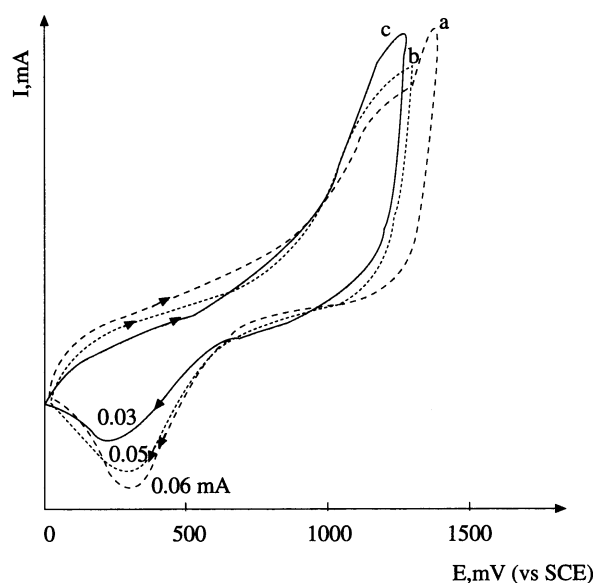
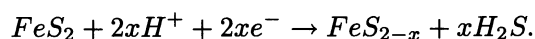


Figure 2. Cyclic voltammograms of Pt electrode in PAA (a), PAA+Ce(IV) (b) and PAA-Py-Ce(IV) ternary complex (c). [PAA]=3 g. dm⁻³, [Ce(IV)]=0.00167 mol dm⁻³, [Py]=0.0127 mol dm⁻³

Natural pyrite as working electrode, comparison with synthetic pyrite

When natural pyrites (NP_1, NP_2) were used as working electrodes in PAA solution, depending on pyrite composition and the surface properties, different anodic and cathodic peaks were observed. For both of the two different natural pyrite electrodes peak potentials were higher than of synthetic pyrite. The anodic peaks of NP_1 and NP_2 correspond to the oxidation of Fe^{2+} to Fe^{3+} and the first cathodic peak corresponds to its reductions⁹ (Figure 1 and Figure 3). As mentioned by Biegler²², in acidic solution the second cathodic peak at about 140-200 mV probably arises from the reduction of pyrite according to the following reaction:



Since composition of pyrite differs from one mineral to another (Table 1), the second cathodic peak which corresponds to the equation above at 140 mV for NP_2 was not observed in the case of NP_1 .

If multiple scanning in PAA continues for 10 minutes, all peaks previously present disappear due to adsorption of PAA on the electrode surface (Figure 1 curve b).

For a longer period of waiting (i.e. electrode was held in PAA solution for 4.5 hours), although the anodic peaks were the same, two peaks were observed again at the cathodic direction. This might be due to the diffusion of the soluble complexes of PAA-Fe from the electrode surface to the solution (Figure 4). These results support the idea of soluble complexes of PAA-Fe reported in literature²¹.

As a qualitative measure of polymerization of pyrrole on the PAA adsorbed electrode surface, cyclic voltammograms in the range of 0-1200 mV were recorded after pyrrole was added to the PAA solution without having any supporting electrolyte present in medium (Figure 5). Increase in current and shift in peak potentials in anodic and cathodic directions is probably due to the growing of PPy on the surface.

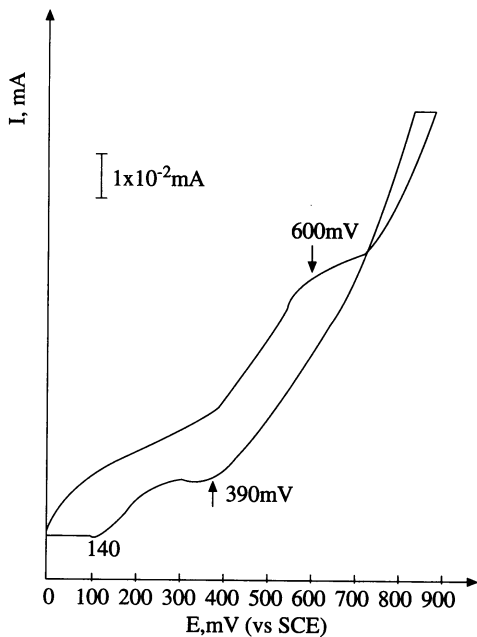


Figure 3. Cyclic voltammogram of natural pyrite 2 in PAA. [PAA]=3 g.dm⁻³

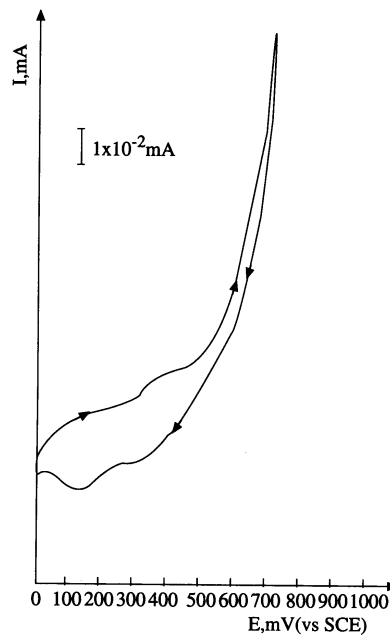


Figure 4. Cyclic voltammogram of PAA adsorbed pyrite electrode after holding the electrode in PAA for 4.5 hour. [PAA]=3 g.dm⁻³

Investigation of Coated Electrode

Corrosion Measurements

Photocorrosion currents of natural and synthetic pyrite in KI/I_2 redox electrolyte and another corrosive medium (0.5 M H_2SO_4) were collected in Table 2. While the PPy coating of pyrite electrodes for NP and SP case inhibited the corrosion by about 30 % and 66 % respectively, composite coatings exhibit almost

Table 2. Photocorrosion current (PCC) of bare, PPy coated and PAA/PPy (composite) coated natural (NP) and synthetic (SP) pyrite electrode

Electrode	PCC, A/cm ² in KI/I_2		PCC, A/cm ² in H_2O_4	
	NP	SP	NP	SP
Bare	$1,0 \times 10^{-3}$	$0,6 \times 10^{-3}$	$3,2 \times 10^{-4}$	$3,0 \times 10^{-3}$
PPy coated	$0,7 \times 10^{-3}$	$2,0 \times 10^{-3}$	$2,5 \times 10^{-4}$	$1,0 \times 10^{-3}$
PPy/PAA coated	$8,0 \times 10^{-5}$	$9,0 \times 10^{-5}$	$4,0 \times 10^{-5}$	$5,0 \times 10^{-5}$

total inhibition in KI/I_2 electrolyte in both cases. Similarly, in 0.5 M H_2SO_4 electrolyte higher photo-corrosion inhibition effects were observed for PAA/PPy composite coating electrodes than for PPy coating alone.

Photovoltage measurements

a) Natural pyrite as the working electrode

Open circuit photopotentials (OCP) of bare and coated natural pyrite electrodes are collected in Table 3. The dark potentials of all bare electrodes were about zero. Since each sample was prepared from different minerals, each bare electrode showed different photopotentials (90, 37, 130 mV). These photopotentials (ΔE) were given as follows: $E = E_{light} - E_{dark}$. (E_{light} = Open circuit potential under illumination, E_{dark} = Open circuit potential without illumination). Due to the instability of pyrite, these photopotentials decrease with immersion time in KI/I_2 electrolyte. As it can be seen from Table 3, then $n_{CAN}/n_{pyrrole}$ ratio effects the photopotentials of the coated electrodes. If this ratio is low, (0.073), the effect is small (Sample 1). Use of the highest $n_{CAN}/n_{pyrrole}$ ratio shows better photovoltage stability (Sample 3).

Table 3. Potentials of Bare and Coated Natural Pyrite Electrode vs Pt in KI/I_2 (According to procedure I+II)

Sample Number	Immersion time in KI/I_2 (min.)	Bare	Coated	
		OCP $\Delta E(mV)$	n_{CAN}/n_{py}	OCP $\Delta E(mV)$
1	0	90	0.073	$70^1, 87^2$
	22	10		44^2
2	0	37	0.400	62^2
	10	5		46^2
3	0	130	0.800	200^1
	5	60		150^1
	12	30		190^1

1 Reaction time is about 12 h. (According to procedure II)

2 Reaction time is 5 days (procedure II).

Each sample was prepared from different minerals.

b) Synthetic pyrite as the working electrode

Similar to the case of natural pyrite, dark potentials of bare synthetic pyrite electrodes were about zero and open circuit photopotentials (OCP) were about 90 mV (in KI/I_2 vs Pt):

Since the higher voltage difference between the bare and coated electrodes was obtained with $n_{CAN}/n_{pyrrole} = 0.4$ ratio in the case of natural pyrite (Table 3), coated synthetic pyrite electrodes were investigated in this solution (Table 4).

The longer the immersion time in the solution which was prepared according to Procedure II, the higher the OCP in KI/I_2 electrolyte. This increase continued if the time of immersion in KI/I_2 redox solution was quite long.

Table 4. Potentials of coated synthetic pyrite electrode vs Pt in KI/I_2 (According to procedure I and II)

Immersion time in PAA+Py-CAN Solution (h)	Immersion time in KI/I_2 (min)	OCP ΔE , (mV)
24	0	30
	12	30
	16	53
48	0	20
	3	50
96	0	10
	20	20
	35	50
	50	100

Photoactivities of both natural and synthetic pyrite were in the range of previous findings of the literature¹⁵. As can be seen from Table 3 and Table 4, some photoelectrochemical effects were observed after using composite polymer coating on the electrode surface.

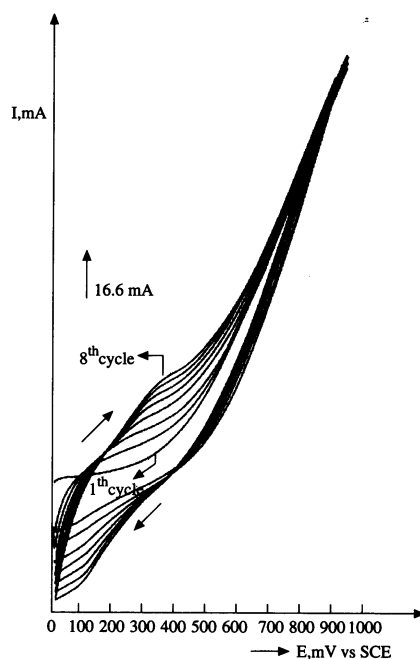


Figure 5. Cyclic voltammograms of pyrrole grown on PAA absorbed pyrite electrode after the process shown in Figure 1b. $[PAA]=3 \text{ g.dm}^{-3}$, $[Py]=0.0127 \text{ mol dm}^{-3}$.

Conclusion

The higher photopotentials of the coated natural pyrite electrodes relative to that of the coated synthetic pyrite electrodes, suggests that the impurities might be a reason for the higher photoactivity for natural pyrite. The higher the $n_{CAN}/n_{pyrrole}$ ratio, the better the photopotential stabilities of coated electrodes in KI/I_2 electrolyte. These observations might be due to the diffusion of anions of cerium salt into the PPy chain which is consistent with our previous conclusion that the differences in conductivities are explained in terms of the mobility of doping ions⁴.

As mentioned before, a PAA coating alone is not stable because of the solubility of PAA-Fe complex. The final composite PPy not only has a more transparent coating but also becomes more stable in KI/I_2 electrolyte than pure PPy. This composite polymer has a corrosion inhibition property about three times higher than PPy alone. PAA protects PPy against corrosion as an insulator and the composite polymer shows a more stable photopotential than the pure PPy.

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References

1. A. F. Diaz, J. I. Castillo, **J. Chem. Soc. Chem. Comm.**, 397, (1980).
2. O. Inganas, I. Lundstrom, **J. Electrochem. Soc.**, **131**, 1129, (1984).
3. S. B. Lalvani, B. A. DeNeve and A. Weston, *Cor.*, **47**, 1, (1991).
4. A. S. Saraç, C. Erbil, B. Ustamehmetoğlu, **Polymer Bulletin**, **33**, 535-540, (1994).
5. L. A. Samuelson and M. A. Drvy, *Macromolecules*, **19**, 824, (1986).
6. A. S. N. Murthy and K. S. Reddy, **Electrochim. Acta** **28**, 4, 473- 476, (1983).
7. M. G. Kanatzidis, **Chem. eng. News** **68**, 36, (1990).
8. A. J. Frank, **Electrically Conductive Polymer Layers on Semiconductor Electrodes In: Energy Resources Through Photochemistry and Catalysis** (1982).
9. A. S. Saraç, B. Ustamehmetoğlu, M. I. Mustafaev, C. Erbil and G. Uzelli, **J. Polymer Sci.**, **33**, 1581-1587, (1995).
10. V. Bocci and G. P. Gardini, **J. Chem. Soc., Chem. Commun**, 148, (1986).
11. G. P. Zhang, G. R. Peng, and X. T. BI. **Syn. Met.**, 55-57, 1123-1128, (1993).
12. E. Ruckenstein, J. H. Chen, **J. Appl. Polym. Sci.**, **43**, 1209-1218, (1991).
13. B. Zinger and D. Kijel, **Syn. Met.**, 41-43, 1013-1023, (1991).
14. E. Ruckenstein, J. H. Chen, **Polymer**, **32**, 7, 1230-1235, (1991).
15. A. Ennaoui, S. Fiechter, W. Jaegermann and H. Tributsch, **J. Electrochem. Soc.**, **133**, 97, (1986).
16. K. K. Mishra and K. Osseo Asae, **J. Electrochem. Soc.**, **135**, 8, 1898-1901 (1988) and references there in.
17. Xue-Ping Li, N. A. Vante and H. Tributsch, **J. Electroanal. Chem.**, **242**, 255-264, (1988).
18. N. Alonso-Vante, G. Chatzitheodorav, S. Fiechter, N. Mgoduka, I. Poullos and H. Tributsch, **Solar Energy Materials**, **18**, 9-21, (1988).
19. A. Ennaoui, S. Fiechter, Ch Pettenkofer, N. Alonso-Vante, K. Büker, M. Bronold, Ch Höpfner and H. Tributsch, **Solar energy Materials and solar Cells**, **29**, 289-370, (1993).
20. S. B. Lalvani and M. Shami, **J. Electrochem., Soc.**, **133**, 1364, (1986).
21. T. Grchey, M. Cvetkovska and J. W. Schultze, **Corrosion Sci.**, **32**, 1, 103-112, (1991).
22. T. Biegler, **J. Electroanal. Chem.**, **70**, 265, (1976).