

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Conducting Polymers Films Deposited on Carbon Steel and Their Interaction with Crude Oil

Oscar E. Vázquez-Noriega, Javier Guzmán,
Nohra V. Gallardo-Rivas,
Reinaldo David Martínez Orozco,
Ana M. Mendoza-Martínez,
María Yolanda Chávez Cinco,
Luciano Aguilera Vázquez and Ulises Páramo-García

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.70091>

Abstract

The formation of scale/solids deposits inside the pipelines is a frequent problem in the petrochemical industry. These scales can be organic as the asphaltenes and inorganic as the accumulations of salts, which apart from blocking the inside of the pipes can also cause a change in the integrity of the steel. Therefore, it is necessary to avoid the conditions where deposition occurs, together with chemical and mechanical methods of remediation to mitigate the deposition. In this work we intend to use conductive polymers in order to inhibit the deposition of asphaltenes on carbon steel surfaces, by using polypyrrole (PPy) as material capable of conducting electrical current. The electrodeposition of PPy on carbon steel were performed by cyclic voltammetry (CV) and chronoamperometry (CA). The results showed that under certain experimental conditions it is possible to make a PPy film with adequate characteristics. Important factors were the grip and electrochemical stability of the formed film on steel, which depends on the electrosynthesis technique and in some cases favoured by a pre-treatment with a 10% HNO₃ solution applied to the steel prior to electropolymerization. The PPy films deposited with pre-treatment completely covered the steel surface and showed better stability, adherence and generated a hydrophobic material.

Keywords: conducting polymers, corrosion protections, carbon steel, polypyrrole, asphaltenes, crude oil

1. Introduction

The formation of solid deposits is a frequent problem in the hydrocarbons transport due to asphaltenes precipitation where the crude oils flow. The asphaltenes are the fraction of higher molecular weight and polarity of the crude oil and they are responsible for these solid deposits, which usually give rise to several problems in the transport and processing of crude oil, mainly by the obstruction of the pipelines [1–6].

Common oilfield scales are crystalline deposits, resulting from the precipitation of mineral compound such as carbonates and sulfates present in the injected water, as method for enhanced oil recovery. These scale deposits may appear as a thick layer adhered to the inner walls of the pipes, they are often several centimeters thick with particles sizes up to 1 cm or more. One of the primary problems of scale formation in pipes is the reduction in flow rate by increasing the inner surface roughness of the pipe and reducing the flow ability area. This produces an increase in the pressure drop and consequently production decreases. By increasing the growth of deposited minerals, it becomes impossible to access deeper pipe sections, and finally the scale deposits end up blocking the flow of production. On the other hand, organic scales formation results from asphaltenes and waxes deposition. Usually, the localized corrosion can be developed beneath or around these deposits present in the steel surfaces, due to the presence of bacteria or sulfurous gas, which reduces the integrity of the metal.

The petroleum in its natural state is a mixture of organic compounds of varied structures and different molecular weights. In general, it is possible to group the oil constituents into four well-defined organic components: saturated, aromatic, resin, and asphaltenes [7], known as SARA. The study of the heavy oil fraction (asphaltenes) has increased in recent years due to the problems that they represent in the production and conversion processes. In general, the structure of asphaltenes is considered to consist of a condensed aromatic nucleus with side alkyl chains and heteroatoms incorporated into many of the cyclic structures. The condensed aromatic system may contain from 4 to 20 benzene rings [8]. Nowadays, there is a considerable debate about the structure of asphaltenes, particularly in the size of aromatic groups and how they are linked to other groups in the structure. The type and amount of deposits of heavy organic compounds varies depending on the hydrocarbons present, and the relative amount of each organic family involved. In general, asphaltenes deposition can be explained in detail on the basis of four effects or mechanisms: (1) effect of polydispersity, (2) colloidal steric effect, (3) aggregation effect, and (4) electrokinetic effect.

On the other hand, during crude oil transportation through pipes, there may be sludge deposits along the line and these are also called sediments. The deposits at the bottom of the storage tanks or crude transport lines are water, salts, sand, and heavy hydrocarbons, and their average concentration is about 25% water, 5% inorganic compounds, and 70% vol. of hydrocarbons [9]. In general, asphaltenes deposits cause problems in five points: extraction, transportation, processing, economic benefit of crude oil, and environmental pollution. There are several methods to prevent and/or remove asphaltenes deposits: mechanical methods [10], chemical cleaning, pressure [11, 12], temperature and flow rate manipulations [13], additives, and chemical inhibitors [14, 15]. The conductive polymers applications are highly diverse and

several studies have pointed out the different variables that affect the properties and performance of polypyrrole (PPy) electrodeposition on the steel surface such as the conductivity, stability, roughness, adhesion, film thickness, and so on [16–21].

When an electroactive conducting polymer coats a metal surface, it can act as a membrane-like selective permeable layer, allowing the diffusion of certain ions and rejects others, depending on their chemical affinity, electronic structure, and inter- and intra-molecular arrangement. In this context, some works have been reported on the inhibition of corrosion and stability of conductive polymer films on steel substrates [22–24].

1.1. Conductive polymers

Conductive polymers are those synthetic polymers that are capable of conducting electrical current. These polymers may owe their conductivity to intrinsic properties of the material or modifications. Conductive polymers have a wide range of applications due to their physico-chemical characteristics; many of these properties include electrical conductivity, electroactivity, electrochromism, environmental stability, chemical stability, among others [25, 26]. The scientific and technological development has given rise to two types of electronic conductive materials with polymer matrix: the intrinsically conductive polymers and the extrinsically conductive polymers [27].

Several reviews in the literature focus on the corrosion protection by conductive polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh). Although a number of possible protection mechanisms are proposed, the possible passivation of the metal by polymers such as polypyrrole or polyaniline is frequently indicated. In this work, we propose the use of PPy films to inhibit asphaltenes depositions. It is shown that the efficacy of conducting polymers for corrosion protection depends on the application modus and the experimental conditions, that is, depending on the suitable conditions, a conductive polymer may have excellent protection capacity or may lead to negative response of the coating. An important part of the deposition of PPy lies in the surface treatment of the electrode surface.

Intrinsically conductive polymers are organic polymer in which the electrical conductivity originates from the extended electrons conjugation along the polymer chain. The most common conductive polymers (polyacetylene, polyparaphenylene, polypyrrole, polythiophene, and polyaniline) have carbon atoms in the backbone with sp^2 hybridization. This hybridization creates covalent σ bonds between the carbons of the main chain and those of the branched chains. The sp^2 hybridization leaves an unbonded orbital p (usually pz); these orbitals overlap and form a bond, with a distribution of C = C double bonds alternating with single carbon-carbon bonds along the chain.

Extrinsically conductive polymers are those that owe their conductivity to the inclusion of conductive materials such as metals, graphite, or charge transfer complexes in the polymer matrix, generally thermoplastic. In this case, above the percolation concentration, the conductive paths along the material give it electronic conductivity, while the polymer matrix allows the material to be processed in industrial operations to achieve different types of products and finishes [28]. The conductive polymers are formed from suitable monomers, and can be obtained either by chemical synthesis or by electrochemical methods (Table 1).

Conducting polymers	General comments	Refs
Polypyrrole (PPy)	PPy is chemically and thermally stable. The conductivity of PPy strongly depends on the preparation technique.	[19, 20]
Polyaniline (PANi)	PANi is easy to synthesize and used as corrosion inhibitor and relatively inexpensive.	[29, 30]
Polythiophenes (PTh)	PTh poses high charge-carrier mobility due to their relative structural order, is soluble and demonstrates solvatochromism and thermochromism effect.	[31, 32]
Polyacetylene	Despite its discovery started the development of conductive polymers, to date, polyacetylene has no commercial applications.	[33]
Polyphenylenes	Thermally stable up to 500–600°C but is quite insoluble in most solvent, with potential applications as light-emitting diode due to their electroluminescence properties.	[34]

Table 1. Typical conducting polymers and their common applications.

1.2. Electrochemical synthesis of conductive polymers

The electrochemical synthesis of any conductive polymer has its particularities; however, there are a number of common factors in its synthesis that have been exposed and that must be taken into account at the time of its preparation. In principle, it is assumed that, except for the initiation step, the electrochemical polymerization will proceed by a similar mechanism as the thermal polymerization for the same monomer in a comparable environment.

Experimentation usually begins with the evaluation of the potential window in the selected electrolyte medium, which will allow defining the electrochemical parameters for the subsequent electrolysis. In the evaluation stage as in the synthesis itself, strict control of electrochemical variables (electrode potential, electrode nature, current density, solution conductivity, electric field, etc.) and aspects such as medium, presence or not of protonating agents, oxygen, inert atmosphere, and so on [35] are observed.

From a scientific point of view, the flow of an anodic current through an electrochemical system, formed by a monomer, a solvent, and an electrolyte, can initiate reactions such as the formation of an oxide layer on the electrode, oxidation of monomer on the metal, oxidation of the solvent, and oxidation of the electrolyte. But in this process, the polymerization develops an electrode coating the chemical nature of the electrode changes after a few seconds of polymerization from a metal electrode to a polymer electrode. So, the above reactions will

occur at different potentials on the new electrode, and a new metal-polymer interface appears in addition to that of the growth-dissolution polymer and then new reactions will occur, oxidation of the polymer and degradation thereof [27].

1.3. Applications of conducting polymers electrochemically synthesized

Conductive polymers have been widely used in the fields of electrochemistry, electroanalysis, electrocatalysis, batteries and capacitors, and so on [36]. In these applications, the electrochemical activity and the conductivity are two important properties of the conducting polymers, because they play fundamental roles. In addition, small ions and molecules are able to diffuse into matrices of conducting polymers, providing other advantages over conventional electrode materials. This intrinsic property allows electrochemical reactions to take place along the matrices of the conducting polymers and thus increase the active sites for the electrochemical processes by using a 3D electrode. However, in order to efficiently utilize all active sites and improve mass transport during the electrode process, the film thickness of the conductive polymer should be reduced to facilitate diffusion of the ion in the polymeric matrix. Considering these factors, conductive polymer nanomaterials show different characteristics that can provide advantages over other materials. In addition, nanostructures can produce conductive polymers with new surface properties and new functions [36]. Different applications of conducting polymers prepared nanomaterials by electrochemical techniques as been reported: sensors [37–39], electrochemical capacitors [40], fuel cell electrodes [41], batteries [42, 43], electrochromic devices [44], and electrochemical actuators [45–47].

1.4. Inhibitors of asphaltenes deposition by using conducting polymer coatings

Polypyrrole (PPy) and polythiophene (PTh) are conductive polymers, which have been used as corrosion protection and have the characteristic that they can coat the steel [48, 49]. This process can be carried out by electropolymerization in aqueous phase; in addition, PPy exhibits good mechanical properties, thermal stability, and high conductivity [49]. The performance of corrosion protection by bi-layered PPy coatings was investigated by Kowalski et al.; they used an inner PPy layer doped with molybdophosphate ions to protect steels from corrosion. The polymer layer maintained the passive state of the steel in an acid solution and a neutral NaCl solution for several days [22].

Warren et al. [16] reported that anion dopants containing sulfonates, such as dodecylbenzenesulfonic acid (DBSA), can be used to form PPy films with high conductivities, good stability, mechanical properties, and apparent order. However, when there is a chemical-physical mismatch at the metal-polymer interface, the adhesion between the PPy layer and the metal substrate is generally poor [50].

Beck and Michaelis [51] described anodic electrodeposition of black PPy films on steel electrodes from aqueous electrolytes containing the monomers and oxalic acid, with strong adherence and low surface roughness. Su and Iroh [52] investigated the electrodeposition mechanism of PPy coatings on steel substrates from aqueous oxalate solutions. Their results revealed the formation of a passive layer on the steel substrate before reaching the electropolymerization potential of pyrrole.

Tüken et al. [53] prepared multilayer coating of polypyrrole/polyphenol on mild steel by cyclic voltammetry (CV). The corrosion performance of this multilayer coating was investigated by electrochemical impedance in sulfate solution. Another study carried out by the same authors consisted of the coating of copper with a mixture of polymers (PPy/PTh) [31]. They observed that the electrochemical synthesis of stable and homogeneous PTh films could not be achieved on copper electrode by direct oxidation of thiophene in acetonitrile-LiClO₄ due to insufficient surface passivation, and the copper dissolution in monomer oxidation potential region.

On the other hand, Pekmez et al. [32] informed that the electrochemical synthesis of an anti-corrosive polybithiophene (PBTh) on stainless steel is feasible, and the obtained PBTh coatings strongly adhered to the working substrate.

Rocha et al. [14] carried out a study on the inhibition of asphaltenes precipitation in Brazilian crude oils using amphiphiles substances such as low molecular mass ethoxylated nonylphenols, vegetable oils (coconut essential oil, sweet almond, andiroba, and sandalwood oil), and organic acids (linoleic, caprylic, and palmytic). These compounds showed great efficiency in the asphaltenes precipitation inhibition, through a mechanism of asphaltenes stabilization as a function of its surfactant capacity.

Castellano et al. [15] performed a theoretical investigation of σ - π and π - π interactions on benzene, pyridine, and thiophene dimers; they observed the influence of these interactions with asphaltene stability on crude oil and concluded that chemical interactions between species with opposite polarities lead to an intermolecular association in the asphaltenes, which are responsible for the phenomenon of aggregation. This study was aimed to understand why these compounds tend to aggregate and then flocculate in oil operation processes.

The applications of the conducting polymers are highly diverse and rely on the final properties from the synthesis conditions [23, 24]. Therefore, conducting electrochemical studies to understand the effect of the synthesis variables that affect electrodeposition of conductive polymers is necessary, in order to attain the required conditions in each specific application, as it is the case for application in corrosion protection [54]. When the electroactive conducting polymer is coated to the electrode surface, it may work as a selective permeable layer, which allows certain ions and molecules to pass, according to the degree of cross-linking of the films and supported molecules on the monomer. So the study of the surface properties of polymeric materials is justified, and the way in which the species present in the system can cause the material to deteriorate. In this context and considering the studies reported in the literature, the inhibitors of the asphaltenes deposit using PPy and PTh electrodeposited in carbon steel, is a novel application of this type of materials, in the literature there are few reports in this line of research.

1.5. Interfacial interaction (contact angle)

The deposition of a coating on a solid generates new interfaces between dissimilar materials and involves considerations of wettability, spreading, interface evolution, and adhesion. The interaction at solid-liquid interface is determined by a balance between the adhesive and cohesive forces. Adhesive forces between a liquid and a solid cause a liquid drop to spread on

the surface. The cohesive forces within the liquid cause the drop to maintain a stable position and avoid contact with the surface. This solid-liquid interaction at the interphase is called wettability. The wettability of electrochemically deposited conductive polymer films depends to a large extent on several parameters, such as deposition conditions (applied voltage, transferred charge, etc.), dopant, and working electrode roughness [55]. Mecerreyes et al. [56] carried out a study where they obtained a hydrophobic PPy film (water contact angle of $>90^\circ$) using a per-fluorinated dopant anion, and a hydrophilic film using a ClO_4^- doping anion. Controlling the wettability of a solid surface is important in many applications, for example, in self-cleaning surfaces, liquid lenses, smart fabrics, and in biomedicine [57–59].

It has been reported that the roughness of hydrophobic solid increases its hydrophobicity due to two different ways: roughness increases the surface area of the solid, which geometrically enhances hydrophobicity and due to the air that can remain under the drop [60, 61]. It is important to note that a roughness at two or more length scales has been implicated as the cause of imitating the “lotus effect,” which is the characteristic of a lotus leaf to promote water repellency and self-cleaning [62]. One method to surface wettability control is by oxidizing or reducing the polymer film by modifying thereby the surface morphology. Several research groups have produced films of superhydrophobic conductive polymers, creating micro- and nanostructured surfaces by tempering methods [63–66]. However, these methods have a disadvantage due to the complexity of manufacturing processes [67].

For both improved oil recovery and crude oil transport, it is necessary to develop chemical additives that modify the wetting behavior of reservoir rock (also known as a core), in order to facilitate the crude oil extraction, or to prevent it from wetting the pipe’s inner wall and allow crude oil to easily flow through pipelines [68]. The oilfield scale formations are associated to interface activity of polar components of the crude oil. Asphaltenes are the most polar fraction of the crude and contain large amounts of active species [69] and because of this, asphaltenes are reported as the major fractions responsible for altering surface wettability through the interaction of polar functional groups with polar sites of solid surface [70, 71]. A study by Kaminsky and Radke [72] indicates that low solubility asphaltenes can diffuse through water films to arrive at rock surfaces without significant wettability alteration; the rupture of the water film followed by direct deposition of crude oil onto rock allows explaining the wettability reservoir rock.

2. Experimental

2.1. Reagents and chemicals

The electrolytes used were 0.1 M aqueous solutions of KNO_3 and KCl (both from J. T. Baker, reagent grade). Also a 0.1 M¹ of pyrrole (Py, Sigma Aldrich) solution was prepared with previous purification in a bed column packed with silica and activated carbon. All the solutions were prepared with deoxygenated water (Millipore, 18.2 M Ω) for 15 min with an atmosphere of pure nitrogen (Praxair, 99.99%) before each experiment. The film stability was evaluated in a KCl electrolyte according to a procedure reported [73].

The crude oil used in this work originates from the Gulf of Mexico and presents the following features: 15°API, 25% weight of asphaltenes, density 0.9647 g cm^{-3} , and a kinematic viscosity of 1.697 mPa s .

2.2. Materials

A conventional three-electrode cell was used for the electrodeposition of PPy over carbon steel (CS-1018) as the working electrode, graphite electrode as counter-electrode, and aqueous saturated calomel electrode, SCE (Tacussel), as reference electrode. Initially, the CS-1018 electrode was polished with different grain sandpaper to achieve a defined surface and subjected to ultrasonic baths (Branson 2510) for 5 min to remove contaminants from the surface. To improve the adhesion of the polymer to the steel surface, it was necessary to carry out a pre-treatment of the electrode with a mordant layer to increase the roughness. For this purpose, some authors [23, 24] immerse the metal electrode in acidic solutions of HCl or HNO_3 . In this work, the electrode was treated with acid solutions of 10% HNO_3 with an immersion time of 2 min. The treated surfaces were designated as treated in HNO_3 (T) and only polished surfaces without acidic treatment were designated as untreated in HNO_3 (NT).

2.3. Equipment

The polypyrrole electrosynthesis was performed by cyclic voltammetry and chronoamperometry (CA) techniques by using a Gamry Reference-600 potentiostat, in a three-electrode cell at room temperature ($20 \pm 3^\circ\text{C}$). The electrodeposition by cyclic voltammetry was carried out at a scan rate of 100 mVs^{-1} , in a potential window of -0.8 to 1.0 V/SCE for 40 cycles of polymerization. The conditions for the chronoamperometry were at constant potential of 1.0 V/SCE , for 300 s. For the characterization of the polymeric films, a scanning electron microscope, SEM (Jeol, JSM-6390LV) coupled with energy dispersive spectroscopy (EDS) analysis (Oxford Instruments, INCAx-sight), an atomic force microscope, AFM (Veeco, Innova Scanning Probe Microscope), and an equipment to measure contact angle (Chem Instruments, CAM-plus) were used. The contact angle measurements of polymer surfaces were conducted with deionized water and crude oil, analyzing two areas on the sample and considering three measurements in each zone taken every 2 min for 10 min.

3. Results and discussion

3.1. CS-1018 electrode characterization

The SEM and AFM micrographs of the CS-1018 substrates are shown in **Figure 1**, where the lines attributed to the mechanical polishing are observed. The images show that the treated substrates, CS-1018 T, present a rougher surface due to chemical attack with HNO_3 . The observed roughness measurements were of $R_q = 0.0509 \text{ }\mu\text{m}$ and $R_q = 0.739 \text{ }\mu\text{m}$, for the untreated and treated surfaces, respectively. This difference in the roughness value will be important for the adhesion effect of the polymer material to be synthesized on it.

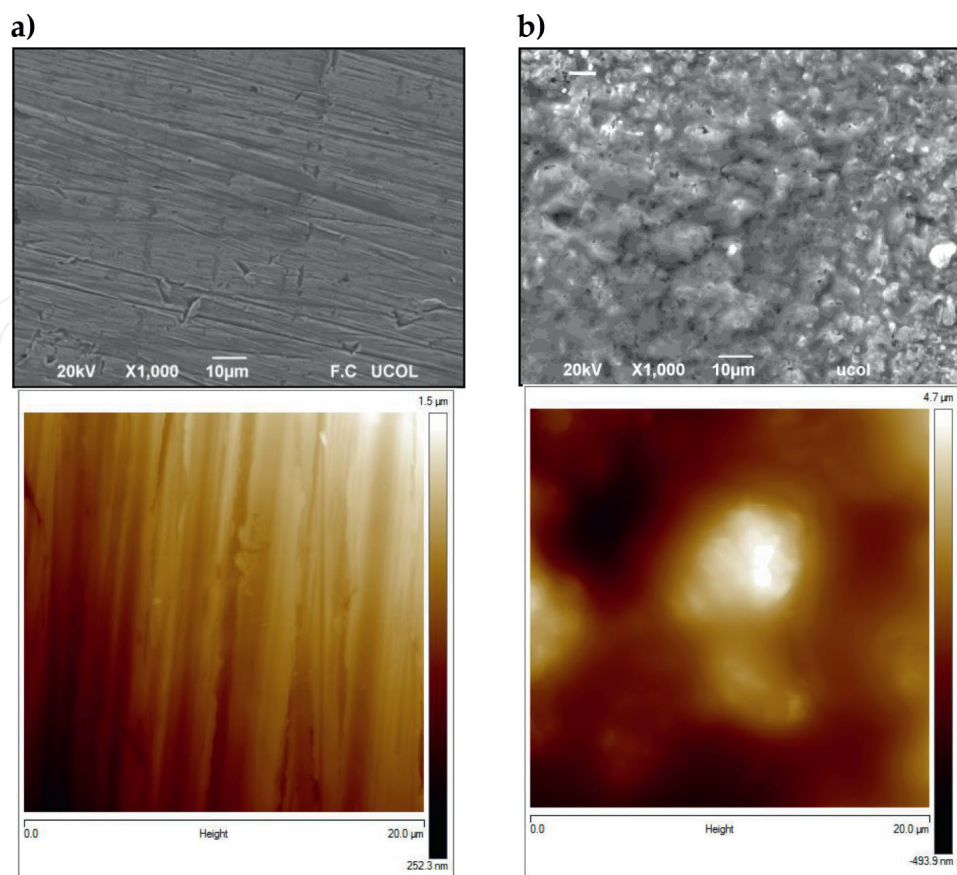


Figure 1. SEM and AFM micrographs of CS-1018: (a) untreated (NT) and (b) treated (T) in 10% HNO_3 .

3.2. PPy film electrodeposition

In this work, the results obtained by two electrochemical techniques are presented: CV and CA. The electrodeposits were made in four different electrolytes, in order to find the best characteristics of the film. **Figure 2a** shows an example with the cyclic voltammograms of the polymerization of polypyrrole in electrolyte of KNO_3 . The voltammograms show the characteristic signals [74–76]. **Figure 2b** shows the signal of PPy deposited with applied constant potential method [77].

3.3. PPy morphology on CS-1018

Figure 3 shows the deposited PPy films on the CS-1018 with and without treatment in the four different electrolytes, electrodeposited by CA technique. When KI and KF electrolytes were used, deposit films were not obtained, but when K_2SO_4 and KNO_3 were used as electrolytes, the formation of PPy films was obtained.

Figure 4a shows the SEM image of PPy deposited on CS-1018 NT, in which a homogeneous film is observed that completely covers the surface of the steel. However, it is possible to observe lines in said film due to the polishing process of the steel, indicating that the deposited film is thin. By contrast, in the PPy film deposited on AC-1018 T, non-uniform circular

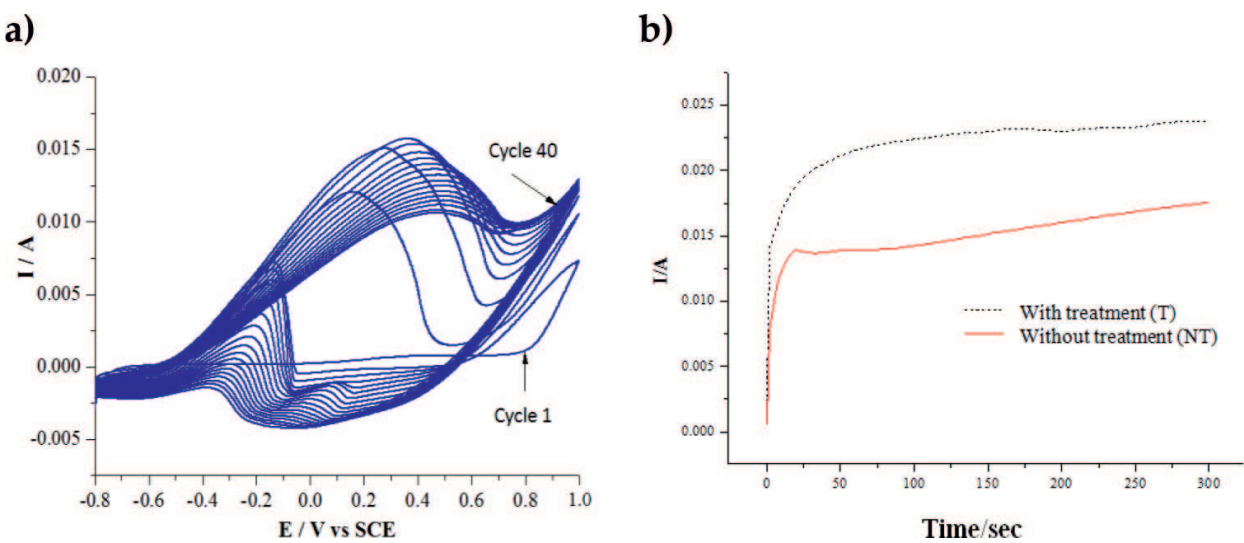


Figure 2. Electrochemical formation of PPy on CS-1018 with (a) CV and (b) CA.

agglomerates with needle-shaped scales are observed, as can be seen in **Figure 4b**. This suggests that acid treatment to the steel affected the morphology of the deposited polymer. This observed morphologies show a characteristic topography of conductive polymers [78].

3.4. Contact angle characterization of the PPy surface

In order to analyze the surface of deposited PPy films, contact angle measurements were performed with and without water and crude oil on selected samples, and steel substrates with and without acid treatment. The measurements were performed in two areas of the sample

Constant Potential (CP)				
	KI	KF	K ₂ SO ₄	KNO ₃
Without treatment (T)				
With treatment (NT)				

Figure 3. PPy films electrodeposited on CS-1018 substrates with and without treatment in four electrolyte media by CA technique.

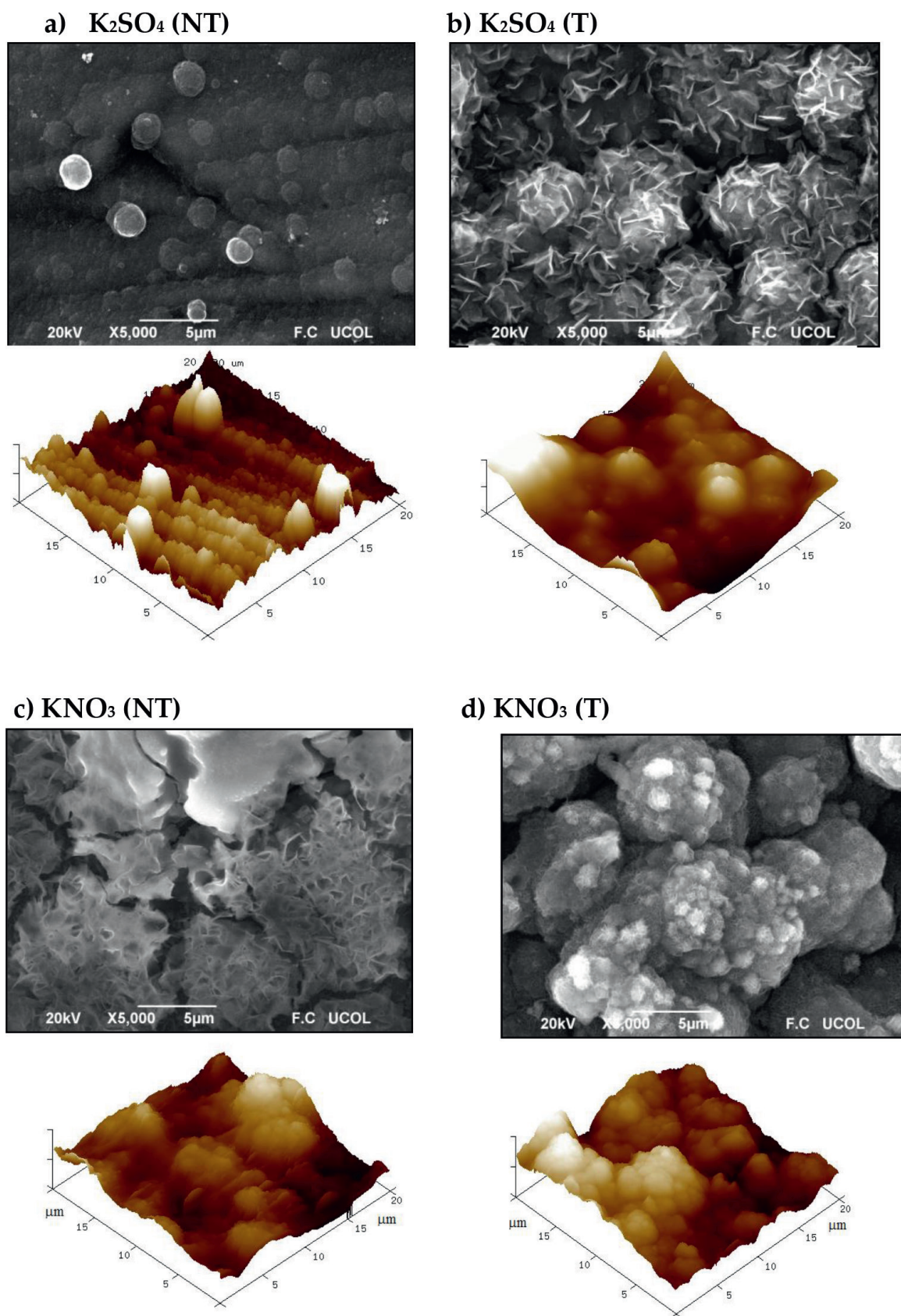


Figure 4. SEM and AFM micrographs of the PPy deposited by the chronoamperometry technique on untreated (NT) and treated (T) CS-1018 substrates: (a) in K_2SO_4 electrolyte untreated substrate, (b) K_2SO_4 electrolyte treated substrate, (c) KNO_3 at 0.1 mol L⁻¹ concentration on untreated and (d) treated substrates with 10% HNO_3 .

and in each zone, three measurements were taken every 2 min. The contact angle values were obtained from the averages of the measurements. **Figure 5** shows the experimental setup, wherein a drop of water makes contact with the substrate CS-1018 NT and how its image is projected to measure the contact angle.

Table 2 shows the values of the contact angle measurements with water and crude oil of the treated and untreated electrodes, and the respective formed polypyrrole films. It is noted that the contact angle of the CS-1018 NT surface is about 70° with water and crude oil. In other words, the untreated metal surface has the same affinity for both liquids. When the steel surface is subjected to acid treatment, CS-1018 T, the contact angle with water increases to 110° . This result indicates that nitric acid treatment induces a slightly hydrophobic behavior. On the other hand, the contact angle also increases slightly with crude oil and remains at a value close to 90° , that is, at the boundary between the oleophilic/oleophobic balances. Contact angle results show that the acid treatment to the metal surface provides hydrophobic properties to the surface; this measurement is in line with AFM results, showing greater surface roughness for electrodes exposed to acid medium. These results are consistent with those reported in the literature [52, 60, 74, 79].

According to this result, the polypyrrole films deposited on CS-1018 T presented rougher surfaces than those synthesized on CS-1018 NT. In both cases, after the synthesis and coating with PPy of the electrodes, the contact angle with water exhibited an increase as the surface roughness increases. PPy deposition on CS-1018 NT has a slightly hydrophilic behavior contrary to the case when the polymer is synthesized on a treated surface.

The contact angle values with crude follow the same trend as the water. This contact angle value is lower in the untreated surface, with apparently less roughness. However, these contact



Figure 5. Experimental setup for contact angle measurement.

Sample	Contact angle/(°)	
	Water	Oil
CS-1018 NT	70	70
CS-1018 T	110	85
PPy-KNO ₃ on CS-1018 NT by CV	80	83
PPy-KNO ₃ on CS-1018 T by CV	125	90
PPy-K ₂ SO ₄ on CS-1018 NT by CA	70	70
PPy-K ₂ SO ₄ on CS-1018 T by CA	90	80

Table 2. Contact angle values with water and oil of the electrodeposited polymers.

angle values in the presence of the polymer coating are close to 90°, the threshold value for determining the oleophilic nature of the electrode surface.

Contact angle measurements show that the surface CS-1018 T PPy-KNO₃ forms a contact angle greater than the surface of CS-1018 NT PPy-KNO₃. That is, that the greater the porosity of the metal surface, a higher roughness of the polymer deposited is obtained, and consequently the polypyrrole-oil interaction decreases.

The roughness plays an important role for the hydrophobicity of the polymer deposit. According to the literature [80], hydrophobicity increases as the roughness of the material grows. **Figure 6** shows the average values of contact angle with oil as a function of roughness of the deposited

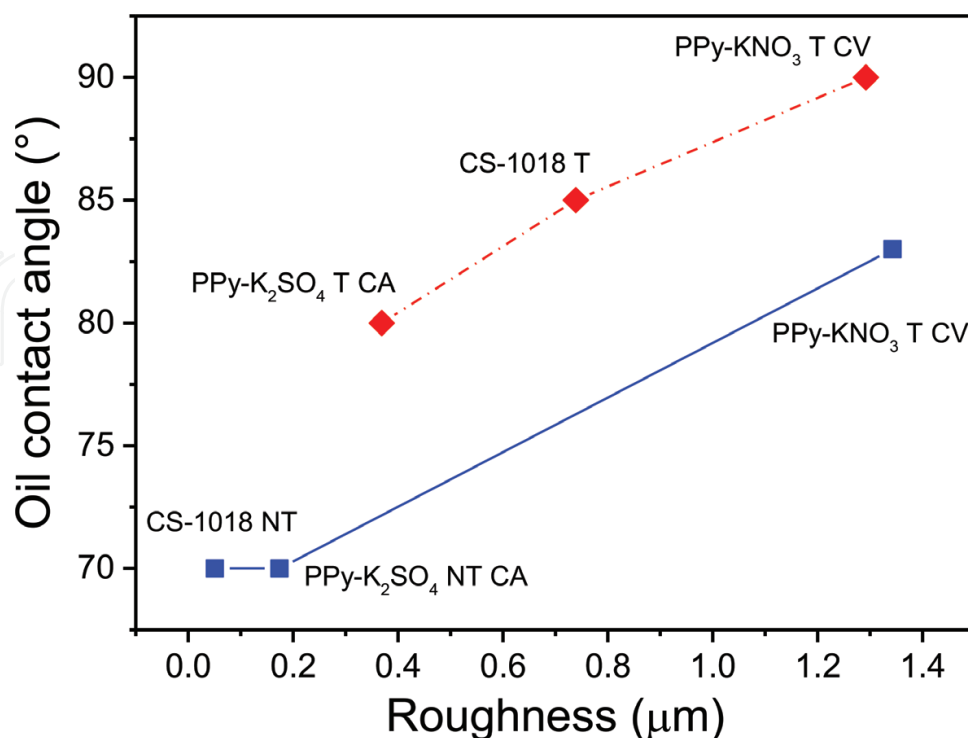


Figure 6. Relation between oil contact angle with the roughness of the polymer films.

polymer films. The materials with greater roughness presented greater contact angle than those with low roughness. It is observed that the contact angle of the PPy-KNO₃ with acid treatment by CV increased around 20° with respect to CS-1018 NT. Therefore, this result shows that such polymer under certain conditions is efficient to reduce contact of asphaltenes with CS-1018.

4. Conclusions

Acid pretreatment modifies the roughness of the CS-1018 substrate generating an oxide layer that influences both the morphology and the stability of electrodeposited PPy films, creating surfaces with different arrangements, which depends on the electropolymerization technique employed. The roughness difference is directly related to the stability of the polymer film formed and its surface properties (wettability). CV electrodeposition is the most appropriate method for this type of application. The PPy materials deposited with KNO₃ by CV, with and without treatment in an acid medium, presented a greater homogeneity and roughness. The roughness is directly proportional to the hydrophobicity of the PPy film, which was evidenced with an increase in contact angle values (lower affinity to crude oil). The inhibition of the asphaltene deposition is evidenced by obtaining contact angles of more than 90°. The results indicate that this methodology is cost-effective, versatile, and scalable for the synthesis of electrodes for applications to inhibit asphaltenes deposition.

Acknowledgements

O.E. Vázquez-Noriega acknowledges the scholarship granted by CONACYT-Mexico. We acknowledge the funding through CONACyT-Mexico projects No. 177480 and the Fis. D. Pozas of the University of Colima for the study of SEM-EDS microscopy. RD Martínez-Orozco appreciates the postdoctoral scholarship by Fondo Sectorial-CONACYT-SENER grant No. 2138.

Author details

Oscar E. Vázquez-Noriega¹, Javier Guzmán², Nohra V. Gallardo-Rivas¹, Reinaldo David Martínez Orozco¹, Ana M. Mendoza-Martínez¹, María Yolanda Chávez Cinco¹, Luciano Aguilera Vázquez¹ and Ulises Páramo-García^{1*}

*Address all correspondence to: uparamo@itcm.edu.mx

¹ Centro de Investigación en Petroquímica, División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Cd. Madero, Prol. Bahía de Aldhair y Av. De las Bahías, Parque de la Pequeña y Mediana Industria, Altamira, Tamaulipas, Mexico

² Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas, Col. San Bartolo Atepehuacán, Mexico D.F., Mexico

References

- [1] McSween HY, Richardson SM, Uhle ME. *Geochemistry: Pathways and Processes*, 2 ed., Columbia University Press, 2003. 432 p. ISBN: 9780231509039
- [2] Luo P, Wang X, Gu Y, Zhang H, Moghadam S. Asphaltene precipitation and its effects on the vapour extraction (VAPEX) heavy oil recovery process. In, *International Thermal Operations and Heavy Oil Symposium*, 20-23 October, Calgary, Alberta, Canada, SPE/PS/CHOA 117527, 2008. p. 1-9
- [3] Al-Sahhaf TA, Fahim MA, Elkilani AS. Retardation of asphaltene precipitation by addition of toluene, resins, deasphalted oil and surfactants. *Fluid Phase Equilibria*. 2002;**194-197**:1045-1057
- [4] Leontaritis KJ, Ali Mansoori G. Asphaltene deposition: A survey of field experiences and research approaches. *Journal of Petroleum Science and Engineering*. 1988;**1**:229-239
- [5] Rogel E, Miao T, Vien J, Roye M. Comparing asphaltenes: Deposit versus crude oil. *Fuel*. 2015;**147**:155-160
- [6] Panuganti SR, Vargas FM, Gonzalez DL, Kurup AS, Chapman WG. PC-SAFT characterization of crude oils and modeling of asphaltene phase behavior. *Fuel*. 2012;**93**:658-669
- [7] Maia Filho DC, Ramalho JBVS, Spinelli LS, Lucas EF. Aging of water-in-crude oil emulsions: Effect on water content, droplet size distribution, dynamic viscosity and stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2012;**396**:208-212
- [8] Speight JG. *The Chemistry and Technology of Petroleum*, 4th ed. CRC Press, 2006. 953 p. ISBN: 9781439873892
- [9] Hu G, Li J, Zeng G. Recent development in the treatment of oily sludge from petroleum industry: A review. *Journal of Hazardous Materials*. 2013;**261**:470-490
- [10] Afghoul AC, Amaravadi S, Boumali A, Calmeto JCN, Lima J, Lovell J, Tinkham S, Zemplak K, Staal T. Tubería flexible: La próxima generación. *Oilfield Review*. 2004;**16**:38-57
- [11] Santhana K, Van Gisbergen SJ, Harris J, Ferdiansyah E, Brady ME, Al-Harthy S, Pandey A. Eliminating multiple interventions using a single rig-up coiled-tubing solution. *SPE Production & Operations*. 2008;**23**(02):119-124
- [12] Frenier WN, Ziauddin M, Venkatesan R. *Organic deposits in oil and gas production*, Society of Petroleum Engineers, 2010. 362 p. ISBN: 978-1-55563-291-5
- [13] Park SJ, Ali Mansoori G. Aggregation and deposition of heavy organics in petroleum crudes. *Energy Sources*. 1988;**10**:109-125
- [14] Rocha Junior LC, Ferreira MS, da Silva Ramos AC. Inhibition of asphaltene precipitation in Brazilian crude oils using new oil soluble amphiphiles. *Journal of Petroleum Science and Engineering*. 2006;**51**:26-36

- [15] Castellano O, Gimón R, Soscun H. Theoretical study of the σ - π and π - π interactions in heteroaromatic monocyclic molecular complexes of benzene, pyridine, and thiophene dimers: Implications on the resin-asphaltene stability in crude oil. *Energy & Fuels*. 2011;**25**: 2526-2541
- [16] Warren LF, Anderson DP. Polypyrrole films from aqueous electrolytes. The effect of anions upon order. *Journal of the Electrochemical Society*. 1987;**134**:101-105
- [17] Su W, Iroh JO. Electrodeposition mechanism, adhesion and corrosion performance of polypyrrole and poly(N-methylpyrrole) coatings on steel substrates. *Synthetic Metals*. 2000;**114**:225-234
- [18] Patois T, Lakard B, Monney S, Roizard X, Fievet P. Characterization of the surface properties of polypyrrole films: Influence of electrodeposition parameters. *Synthetic Metals*. 2011;**161**:2498-2505
- [19] González MB, Saidman SB. Electrodeposition of bilayered polypyrrole on 316 L stainless steel for corrosion prevention. *Progress in Organic Coatings*. 2015;**78**:21-27
- [20] Su W, Iroh JO. Morphology and structure of the passive interphase formed during aqueous electrodeposition of polypyrrole coatings on steel. *Electrochimica Acta*. 1999;**44**: 4655-4665
- [21] Mollahosseini A, Noroozian E. Electrodeposition of a highly adherent and thermally stable polypyrrole coating on steel from aqueous polyphosphate solution. *Synthetic Metals*. 2009;**159**:1247-1254
- [22] Kowalski D, Ueda M, Ohtsuka T. The effect of counter anions on corrosion resistance of steel covered by bi-layered polypyrrole film. *Corrosion Science*. 2007;**49**:3442-3452
- [23] Tallman DE, Spinks G, Dominis A, Wallace GG. Electroactive conducting polymers for corrosion control. *Journal of Solid State Electrochemistry*. 2002;**6**:73-84
- [24] Spinks GM, Dominis AJ, Wallace GG, Tallman DE. Electroactive conducting polymers for corrosion control. *Journal of Solid State Electrochemistry*. 2002;**6**:85-100
- [25] Rajagopalan R, Iroh JO. Characterization of polyaniline-polypyrrole composite coatings on low carbon steel: A XPS and infrared spectroscopy study. *Applied Surface Science*. 2003;**218**:58-69
- [26] Tat'yana VV, Oleg NE. Polypyrrole: A conducting polymer; its synthesis, properties and applications. *Russian Chemical Reviews*. 1997;**66**:443
- [27] Otero TF. Polímeros conductores: Síntesis, propiedades y aplicaciones electroquímicas. *Revista Iberoamericana de Polímeros*. 2003;**4**:1-32
- [28] Arias J. Síntesis y caracterización de polímeros conductores basados en anilinas sustituidas y su aplicación en electrocatálisis [Thesis doctoral]. Universidad de Alicante, Spain; 2007
- [29] Deshpande PP, Jadhav NG, Gelling VJ, Sazou D. Conducting polymers for corrosion protection: A review. *Journal of Coatings Technology and Research*. 2014;**11**:473

- [30] Ohtsuka T. Corrosion protection of steels by conducting polymer coating. *International Journal of Corrosion*. 2012;**2012**:7, Article ID 915090
- [31] Tüken T, Yazıcı B, Erbil M. Polypyrrole/polythiophene coating for copper protection. *Progress in Organic Coatings*. 2005;**53**:38-45
- [32] Pekmez NÖ, Abacı E, Cinkılı K, Yağan A. Polybithiophene and its bilayers with polyaniline coatings on stainless steel by electropolymerization in aqueous medium. *Progress in Organic Coatings*. 2009;**65**:462-468
- [33] Basescu N, Liu Z-X, Moses D, Heeger AJ, Naarmann H, Theophilou N. High electrical conductivity in doped polyacetylene. *Nature*. 1987;**327**:403-405
- [34] Leising G, Tasch S, Brandstätter C, Graupner W, Hampel S, List EJW, Meghdadi F, Zenz C, Schlichting P, Rohr U, Geerts Y, Scherf U, Müllen K. Efficient full-colour electroluminescence and stimulated emission with polyphenylenes. *Synthetic Metals*. 1997;**91**:41-47
- [35] Gravert DJ, Janda KD. Organic synthesis on soluble polymer supports: Liquid-phase methodologies. *Chemical Reviews*. 1997;**97**:489-510
- [36] Li C, Bai H, Shi G. Conducting polymer nanomaterials: Electrosynthesis and applications. *Chemical Society Reviews*. 2009;**38**:2397-2409
- [37] Dai L, Soundarrajan P, Kim T. Sensors and sensor arrays based on conjugated polymers and carbon nanotubes. *Pure and Applied Chemistry*. 2002;**74**:1753-1772
- [38] Barlett PN, Cooper JM. A review of the immobilization of enzymes in electropolymerized films. *Journal of Electroanalytical Chemistry*. 1993;**362**:1-12
- [39] Peng H, Zhang L, Soeller C, Travas-Sejdic J. Conducting polymers for electrochemical DNA sensing. *Biomaterials*. 2009;**30**:2132-2148
- [40] Frackowiak E, Béguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*. 2001;**39**:937-950
- [41] Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP. A review of anode catalysis in the direct methanol fuel cell. *Journal of Power Sources*. 2006;**155**:95-110
- [42] Sivakkumar SR, Kim D-W. Polyaniline/carbon nanotube composite cathode for rechargeable lithium polymer batteries assembled with gel polymer electrolyte. *Journal of The Electrochemical Society*. 2007;**154**:A134-A139
- [43] Huang XH, Tu JP, Xia XH, Wang XL, Xiang JY. Nickel foam-supported porous NiO/polyaniline film as anode for lithium ion batteries, *Electrochemistry Communications*. 2008;**10**:1288-1290
- [44] Cho SI, Lee SB. Fast electrochemistry of conductive polymer nanotubes: Synthesis, mechanism, and application. *Accounts of Chemical Research*. 2008;**41**:699-707
- [45] Smela E. Conjugated polymer actuators for biomedical applications. *Advanced Materials*. 2003;**15**:481-494

- [46] Bar-Cohen Y. Artificial muscles based on electroactive polymers as an enabling tool in biomimetics. *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*. 2007;**221**:1149-1156
- [47] Otero TF. Soft, wet, and reactive polymers. Sensing artificial muscles and conformational energy. *Journal of Materials Chemistry*. 2009;**19**:681-689
- [48] Hu J, Zhu H, Ma Y, Yi T, Mao X, Lin A, Gan F. Corrosion protection of stainless steel by separate polypyrrole electrode in acid solutions. *Materials and Corrosion*. 2011;**62**:68-73
- [49] Kowalski D, Ueda M, Ohtsuka T. Corrosion protection of steel by bi-layered polypyrrole doped with molybdophosphate and naphthalenedisulfonate anions. *Corrosion Science*. 2007;**49**:1635-1644
- [50] Prissanaroon W, Brack N, Pigram PJ, Liesegang J. Co-doped polypyrrole coatings for stainless steel protection. *Surface Review and Letters*. 2006;**13**:319
- [51] Beck F, Michaelis R. Strongly adherent, smooth coatings of polypyrrole oxalate on iron. *The Journal of Coatings Technology*. 1992;**64**:59
- [52] Wencheng S, Iroh JO. Electrodeposition mechanism of polypyrrole coatings on steel substrates from aqueous oxalate solutions. *Electrochimica Acta*. 2000;**46**:1-8
- [53] Tüken T, Yazıcı B, Erbil M. A new multilayer coating for mild steel protection. *Progress in Organic Coatings*. 2004;**50**:115-122
- [54] Rohwerder M, Duc LM, Michalik A. In situ investigation of corrosion localised at the buried interface between metal and conducting polymer based composite coatings. *Electrochimica Acta*. 2009;**54**:6075-6081.
- [55] Chang JH, Hunter IW. Characterization and control of the wettability of conducting polymer thin films. *Materials Research Society*. 2010;**1228**:7-12
- [56] Mecerreyes D, Alvaro V, Cantero I, Bengoetxea M, Calvo PA, Grande H, Rodriguez J, Pomposo JA. Low surface energy conducting polypyrrole doped with a fluorinated counterion. *Advanced Materials*. 2002;**14**:1521-4095
- [57] Russell TP. Surface-responsive materials. *Science*. 2002;**297**:964-967
- [58] Langer R, Tirrell DA. Designing materials for biology and medicine. *Nature*. 2004;**428**:487-492
- [59] Luzinov I, Minko S, Tsukruk VV. Adaptive and responsive surfaces through controlled reorganization of interfacial polymer layers. *Progress in Polymer Science*. 2004;**29**:635-698
- [60] Lafuma A, Quere D. Superhydrophobic states. *Nature Materials*. 2003;**2**:457-460
- [61] Feng L, Li S, Li Y, Li H, Zhang L, Zhai J, Song Y, Liu B, Jiang L, Zhu D. Super-hydrophobic surfaces: From natural to artificial. *Advanced Materials*. 2002;**14**:1857-1860
- [62] Gao L, McCarthy TJ. The "lotus effect" explained: two reasons why two length scales of topography are important. *Langmuir*. 2006;**22**:2966-2967

- [63] Wang X, Berggren M, Inganäs O. Dynamic control of surface energy and topography of microstructured conducting polymer films. *Langmuir*. 2008;**24**:5942-5948
- [64] Xiangjun W, Kristofer T, Olle I. Single- and bilayer submicron arrays of fluorescent polymer on conducting polymer surface with surface energy controlled dewetting. *Nanotechnology*. 2005;**16**:437
- [65] Lee W, Jin M-K, Yoo W-C, Lee J-K. Nanostructuring of a polymeric substrate with well-defined nanometer-scale topography and tailored surface wettability. *Langmuir*. 2004;**20**:7665-7669
- [66] Xu L, Wang J, Song Y, Jiang L. Electrically tunable polypyrrole inverse opals with switchable stopband, conductivity, and wettability. *Chemistry of Materials*. 2008;**20**:3554-3556
- [67] Xu L, Chen W, Mulchandani A, Yan Y. Reversible conversion of conducting polymer films from superhydrophobic to superhydrophilic. *Angewandte Chemie International Edition*. 2005;**44**:6009-6012
- [68] Vargas G, Santillán J, Rincón R, Trejo A, Romero A. Determinación experimental del efecto de la temperatura sobre el ángulo de contacto de un crudo de 15° API sobre un núcleo de yacimiento, Memoria en extenso. In: XXVI Congreso Nacional de Termodinámica, 19-23 September 2011, México, D.F. pp. 751-759
- [69] Andersen SI, Christensen SD. The critical micelle concentration of asphaltenes as measured by calorimetry. *Energy & Fuels*. 2000;**14**:38-42
- [70] Liu L, Buckley JS. Alteration of wetting of mica surfaces. *Journal of Petroleum Science and Engineering*. 1999;**24**:75-83
- [71] Standal S, Haavik J, Blokhus AM, Skauge A. Effect of polar organic components on wettability as studied by adsorption and contact angles. *Journal of Petroleum Science and Engineering*. 1999;**24**:131-144
- [72] Kaminsky R, Radke CJ. Asphaltenes, water films, and wettability reversal. *Society of Petroleum Engineers Journal*. 1997;**2**:485-493
- [73] John R, Wallace GG. The use of microelectrodes to probe the electropolymerization mechanism of heterocyclic conducting polymers. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1991;**306**:157-167
- [74] Wang Y, Northwood DO. An investigation into the nucleation and growth of an electropolymerized polypyrrole coating on a 316L stainless steel surface. *Thin Solid Films*. 2008;**516**:7427-7432
- [75] Wang Y, Rajeshwar K. Electrocatalytic reduction of Cr(VI) by polypyrrole-modified glassy carbon electrodes. *Journal of Electroanalytical Chemistry*. 1997;**425**:183-189
- [76] Lehr IL, Saidman SB. Morphology and properties of polypyrrole electrosynthesized onto iron from a surfactant solution. *Synthetic Metals*. 2009;**159**:1522-1528
- [77] Vázquez-Noriega OE, Guzmán J, Gallardo-Rivas NV, Reyes-Gómez J, Mendoza-Martínez AM, Rivera-Armenta JL, Páramo-García U. Polypyrrole films deposited on

carbon-steel CS-1018 and its interaction with Mexican crude oil. *International Journal of Electrochemical Science*. 2015;**10**:6378-6391

- [78] Ansari Khalkhali R, Price WE, Wallace GG. Quartz crystal microbalance studies of the effect of solution temperature on the ion-exchange properties of polypyrrole conducting electroactive polymers. *Reactive and Functional Polymers*. 2003;**56**:141-146
- [79] dos Santos RG, Mohamed RS, Bannwart AC, Loh W. Contact angle measurements and wetting behavior of inner surfaces of pipelines exposed to heavy crude oil and water. *Journal of Petroleum Science and Engineering*. 2006;**51**:9-16
- [80] Gennes P-Gd, Brochard-Wyart FO, Quéré D. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*. New York, NY: Springer; 2004