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Spontaneous Grafting of Iron Surfaces by Reduction of Aryldiazonium Salts in Acidic or Neutral Aqueous Solution. Application to the Protection of Iron against Corrosion

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The chemical grafting of iron surfaces at open-circuit potential by reduction of different aryldiazonium salts in aqueous acidic solution occurs spontaneously without the need of electrochemical assistance. X-ray photoelectron spectroscopy (XPS) and IR allowed to evidence the grafting of organic moieties without any adsorption of diazonium salts. The aryl groups are strongly bonded to the metal since they can withstand sonication in acetone. XPS measurements also show that spontaneous grafting in water is at least as efficient as electrochemical grafting and also indicate the presence of a multiphenyl layer coverage of the iron surface. The surface film of carboxyphenyl groups on iron was chemically derivatized further by octyltriethoxysilane. The anticorrosive effects of the different films were evaluated in 0.01 M H_2SO_4 aqueous solution, by polarization and impedance measurements. Grafting of the diazonium salt results in an inhibition efficiency up to 73%, which can be slightly increased up to 85% by derivatization of the film by octyltriethoxysilane. The inhibition efficiency can be significantly improved up to 97% when the grafted metal is left in the corrosion medium in the presence of the diazonium salt.

Introduction

Electrochemical reduction of aryldiazonium salts at various carbon electrodes in an organic medium leads to the covalent grafting of the organic groups to the electrode surface.[1−6] This has also been demonstrated at various other semiconductive or conductive surfaces, such as silicon,[7] iron and mild steel,[8] zinc, nickel, cobalt, copper, gold, platinum,[9] and so forth. The same electrografting reaction can be performed in acidic aqueous solution in the cases of carbon,[2] iron, and mild steel.[8] The grafting can also take place spontaneously without any electrochemical assistance in an aprotic medium onto carbon, copper, iron and zinc,[10,11] palladium, and semiconductors (Si and GaAs).[12] Moreover, McCreery and Hurley have described the spontaneous grafting of copper and aluminum alloys in acidic aqueous solution.[13]

The electrografted film protects the surface against corrosion in acidic media.[14] It acts as a corrosion inhibitor, whose efficiency can be compared to that of classical corrosion inhibitors described in the literature. Another advantage of covalently bonded organic films is that they can be further derivatized chemically or photochemically.[15]

Corrosion inhibitors can be divided in different categories depending on how they are obtained and how strong their bonding to the surface is.[16] Efficient iron protection methods against corrosion are used in the car industry. They involve several steps, including chromating and phosphating, that are harmful for the environment. Classical organic corrosion

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inhibitors for easily oxidizable metals are usually compounds containing a quaternary P atom,[17] derivatives of imidazole,[18] oxadiazole or thiadiazole,[19] acetylenic alcohols,[20] and so forth. They are adsorbed at the iron surface and must be used in the presence of the free compound in the solution. Another procedure described for engineering metals (Fe, mild steel, Cu) and gold consists of using organic molecules bonded onto a self-assembled monolayer or multilayers of alkyl-α,ω-bisphosphonic acid[21,22] or 16-hydroxyhexade-canoate ions in the case of passivated iron.[23] The latter method has also been used to immobilize biological molecules at the surface of Ti or by an organophosphoric acid at the surface of Si/SiO_2.[24,25] An electrochemical method in which organic layers of polypyrrole or polyaniline or a mixture of both are deposited by electro-oxidation at the surface of mild steel or zinc has also been reported.[26-28] The efficiency of all these methods against corrosion is limited by the poor bonding of the inhibitor onto the surface.

To circumvent this drawback, some protection methods have been proposed, which involve the covalent bonding of an organic layer to the substrate. For example, metallic surfaces of Fe, Ni, or Pt are covalently modified by electrochemical reduction of vinylic monomers such as acrylonitrile, methacrylonitrile, or butenenitrile.[29,30] Polymer films of about 10 nm thickness, which are prepared at highly negative potentials in an oxygen-free organic medium, are covalently bond to the metal. They have proven efficient for protection against corrosion.

In the present paper, we will show that it is possible to graft chemically aryl groups derived from diazonium salts onto iron surfaces in acidic aqueous or neutral water solution and that these groups protect iron against corrosion in a 0.01 M H_2SO_4 aqueous solution. For the sake of comparison, electrochemical grafting is also performed by biasing the iron sample several hundreds of millivolts more negative than the reduction peak potential of the diazonium salt.

The following diazonium salts have been used: $^+N_2ArBF_4^-$, with Ar = C_6H_5 (**1**); C_6H_4Br (**2**); $C_6H_4(CH_2)_{11}CH_3$ (**3**); and $C_6H_4CO_2H$ (**4**).

Experimental Section

Chemicals and Iron Samples. Chemical reagents were purchased from Aldrich (Saint-Quentin Fallavier, France) and used as received. Solvents were purchased from SDS (France).

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The synthesis of diazonium salts has been described in previous publications.[2,14] Salt **1** was used for infrared characterization, salt **2** for X-ray photoelectron spectroscopy (XPS) analysis, and salt **4** for further derivatization. Electrochemical measurements were performed on **1**−**4**.

Two types of iron samples were used: a disk microelectrode (diameter: 1 mm, Goodfellow, Great Britain, 99.99%) and plates ($1 \times 1 \times 0.1$ cm^3, Goodfellow, Great Britain, 99.99% for XPS or $4 \times 2 \times 0.15$ cm^3, Weber Métaux, France, 99% for spectral analysis). They were first polished on a polishing cloth (DP−Nap, Struers, Denmark) with 1 μm diamond paste and then with 0.02 μm alumina slurry (Presi, France) in nanopure water to avoid organic contaminants on the electrodes. They were finally rinsed in acetone.

Diazonium Salts Grafting onto Iron Samples. The iron samples were immersed into a 10 mM H_2SO_4 solution containing 10 mM of diazonium salt for 60 min. In the case of electrochemical grafting, the iron electrode was biased at −1.0 V/Ag−AgCl for 5 min. Following grafting, all samples were ultrasonicated in acetone for 10 min to remove any species adsorbed onto the surface.

Derivatization after Grafting. After chemical grafting by **4**, the iron electrode was immersed into a 50 mM acetone solution of octyltriethoxysilane [$C_8H_{17}Si(OC_2H_5)_3$, C_8TES] at 40 °C for 2 h under a dry atmosphere. Once rinsed with acetone, the electrode was treated in a 10 mM H_2O solution in acetone for 10 min at 40 °C and then rinsed in acetonitrile for a few minutes to form a polymer film. Finally the coated electrode was dried under a vacuum for 5 min.

Characterization. XPS spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al Kα X-ray source (1486.6 eV) and a magnetic lens that increases the electron acceptance angle and, hence, the sensitivity. An X-ray beam of 650 μm size was used at a power of 10 mA $\times$ 15 kV. The spectra were acquired in the constant analyzer energy mode, with a pass energy of 150 and 40 eV for, respectively, the survey and the narrow regions. The Avantage software, version 1.85, was used for digital acquisition and data processing. Spectral calibration was determined by setting the aliphatic C−C/C−H C1s peak at 285 eV.

Infrared analyses were carried out with a Magna-IR 860 IR-TF (Nicolet Instruments) equipped with a reflection accessory at 80° and a 13-mm-diameter mask.

Potentials were imposed and currents measured by a potentiostat/galvanostat (CH660A, CH Instruments, USA). The potentiodynamic polarization curves were carried out by applying a 1 mV/s scanning rate. Impedances were measured using the same equipment with a 5 mV amplitude at the open circuit potential, E_{op}, in the 10^4 to 10^{-2} Hz interval with six points per decade.

All measurements were performed at 20 °C in aerated solutions under unstirred conditions. Prior to any measurement, the electrodes were left for a few hours (1−3 h) in the measurement medium until the open potential, E_{op}, stabilized to a constant value.[31]

Results and Discussion

We have observed that aryldiazonium salts are spontaneously reduced by iron in acidic aqueous solution. This occurs because of the difference between the oxidation potential of iron ($E^\circ_{Fe^{2+}/Fe}$ = −0.68 V/SCE, SCE = saturated calomel electrode) and the reduction potential of aryldiazonium salts (peak potentials measured at a C or Fe electrode between −0.45 and 0.2 V/SCE in an aprotic medium).[2,14] The reduc-

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Scheme 1. Mechanism for the Aryl Groups Bonding onto Iron
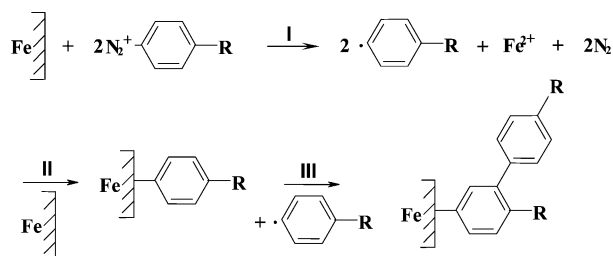
tion mechanism, which is depicted in Scheme 1, involves a first dissociative electron transfer that gives dinitrogen and aryl radicals (step I). The latter are linked to the iron surface (step II) to give organic mono- or multilayers (step III).

The grafting was observed by XPS and IR spectroscopies with iron plates as the substrates and its impact on the inhibition of iron corrosion by electrochemical measurements with iron electrodes.

XPS Analysis. The wide-scan XPS spectrum of an iron sample left 2 h in the air is represented in Figure 1a, and those of samples submitted to chemical and electrochemical grafting by **2** are respectively represented in Figure 1b and c. Grafting leads to (i) a dramatic increase of the C[1s] peak centered at 285 eV and (ii) the appearance of the characteristic peaks Br[3d], Br[$3p_{3/2}$–$3p_{1/2}$], and Br[3s] from bromine centered at $\sim$70, 184–191, and 258 eV, respectively.

It is noteworthy that the high-resolution Br[3d] spectra are both sharp and centered at 70.2 eV (see Figure 1b′ and c′ for either chemical or electrochemical grafting), a binding energy value that is consistent with bromine in C–Br covalent bonds. Indeed, the Br[3d] binding energy reported for poly(bromostyrene) is 70.5 eV[32] and is very comparable to the value reported in this work for a –C_6H_4– chemical environment. By comparison, Figure 1a′ shows no Br[3d] feature but only the spectral background from the uncoated iron plate.

The relative intensities of both C[1s] and Br[3d] peaks are lower for the electrochemical grafting. This can be explained, as we have already discussed, by the dependence of the electrochemical grafting of iron in dilute sulfuric acid on the electrode potential.[8] When the electrode potential becomes more negative than E_{corr}, the reduction of aryldiazonium ions competes with that of protons and, as a consequence, grafting becomes less efficient.

A smaller bromine to carbon ratio appears by XPS in the case of the electrochemical grafting of **2** onto iron relative to the spontaneous grafting. This cannot result from reduction since reduction of the C(aromatic)–Br bond during the experiment can occur neither spontaneously nor by electrochemistry at the potential used. However, reduction of the C–Br bond is possible under the XPS beam as already observed for nitro groups.[11,33,34] The difference may, therefore, result from different recording times of the XPS spectra.

The oxygen peak depends strongly on the nature of the iron surface. For the ungrafted sample, this peak, which is centered at 530.1 eV (see Figure 1a′′), corresponds to iron oxides and hydroxides (529.7–531.7 eV for FeOOH).[35] The oxygen peak of the chemically and electrochemically grafted samples is much smaller than that of bare iron and is centered at, respectively, 533.0 and 532.3 eV (see Figure 1b′′,c′′), which is in favor of Fe–O–C bonds as observed by XPS for copper (Cu–O–C)[13] or by time-of-flight–secondary-ion mass spectrometry for carbon (C–O–C).[36]

A small peak at 400.30 eV is present for nitrogen on all samples, and its surface is about 2 times higher for the grafted samples (see Figure 1b′′′ and c′′′) than for bare iron (see Figure 1a′′′). Its assignation is quite controversial. For the grafted samples, it could correspond, at least partly, to the formation of an azo bridge by reaction of the diazonium salt either (i) with an already grafted aryl group to give Fe–Ar–N=N–Ar or (ii) with the iron surface to give Fe–N=N–Ar. The formation of azo compounds during the spontaneous derivatization of copper has been thoroughly investigated by McCreery and Hurley,[13] who assigned the XPS peak at $\sim$400 eV to the formation of azo compounds corresponding to the reaction of diazonium cations on phenyl groups pertaining to the layer (i). We think this assumption is unlikely since diazonium salts react with phenol groups to give azo dyes[37,38] but are not known to react with unsubstituted aryl groups except in the presence of a reducing agent, but in this case, they give dimers along the Gomberg reaction.[39,40] In addition, we think that both i and ii would involve the reaction of a radical such as Ar–N=N$^\bullet$ onto the surface, which is unlikely since it has been shown that under the conditions used for electrografting reactions, the reaction does not go through this radical.[41] Azo bonds have also been advocated by Bélanger and co-workers to explain the presence of the $\sim$400 eV XPS peak during the electrografting of nitrobenzenediazonium on carbon.[4] We think that the reduction of the nitro group under the XPS beam is more likely, as mentioned above.[11,33,34] McCreery and Hurley also rejected the reaction of diazonium cations with surface oxide by observing a higher ratio of azo to phenyl groups on clean, bare Cu than on purposely oxidized copper.[13] He also argued that on a copper surface, the diazonium cation would immediately be reduced to the radical as in the Sandmeyer or Gattermann reactions. Since all these arguments are quite relevant, the origin of the $\sim$400 eV peak remains unclear, and fortuitous contamination cannot be excluded.

The characteristic peaks for diazonium at 403.8 and 405.1 (N[1s])[42] were not observed (see Figure 1a′′′,b′′′, and c′′′). This means that adsorption of the diazonium salt onto the iron

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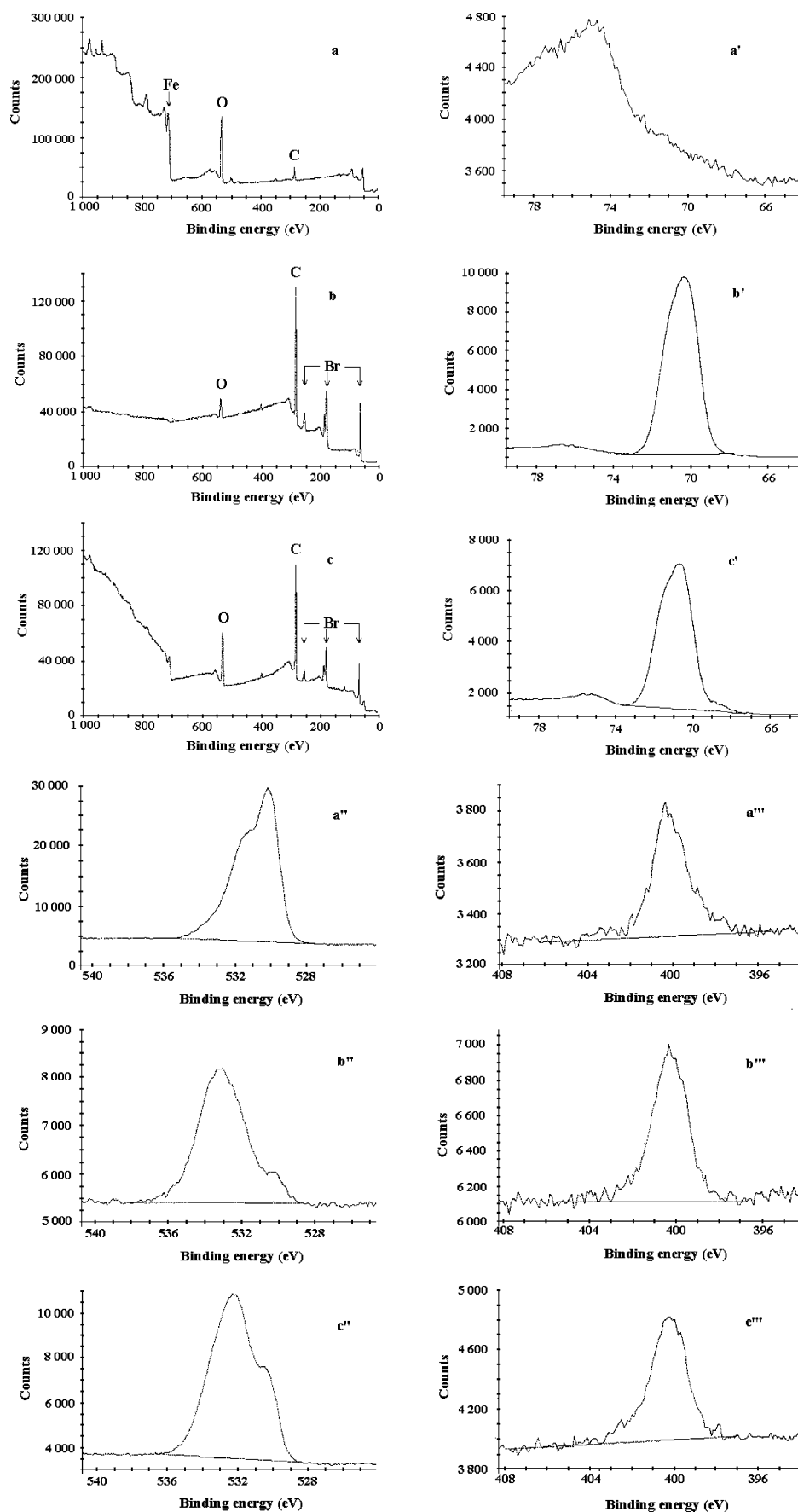(42) Finn, P.; Jolly, W. L. *Inorg. Chem.* **1972**, *11*, 1434.

Figure 1. X-ray photoelectron spectroscopy for iron plates. Wide scan (a, b, c). High-resolution scan in (a′, b′, c′) the Br region, (a″, b″, c″) the O region, and (a‴, b‴, c‴) the N region. (a, a′, a″, a‴) Left 2 h in air. (b, b′, b″, b‴) Chemically grafted by **2**. (c, c′, c″, c‴) Electrochemically grafted by **2**.

surface, if any, does not withstand the sustained ultrasonic rinsing of the iron samples in acetone prior to the measure-

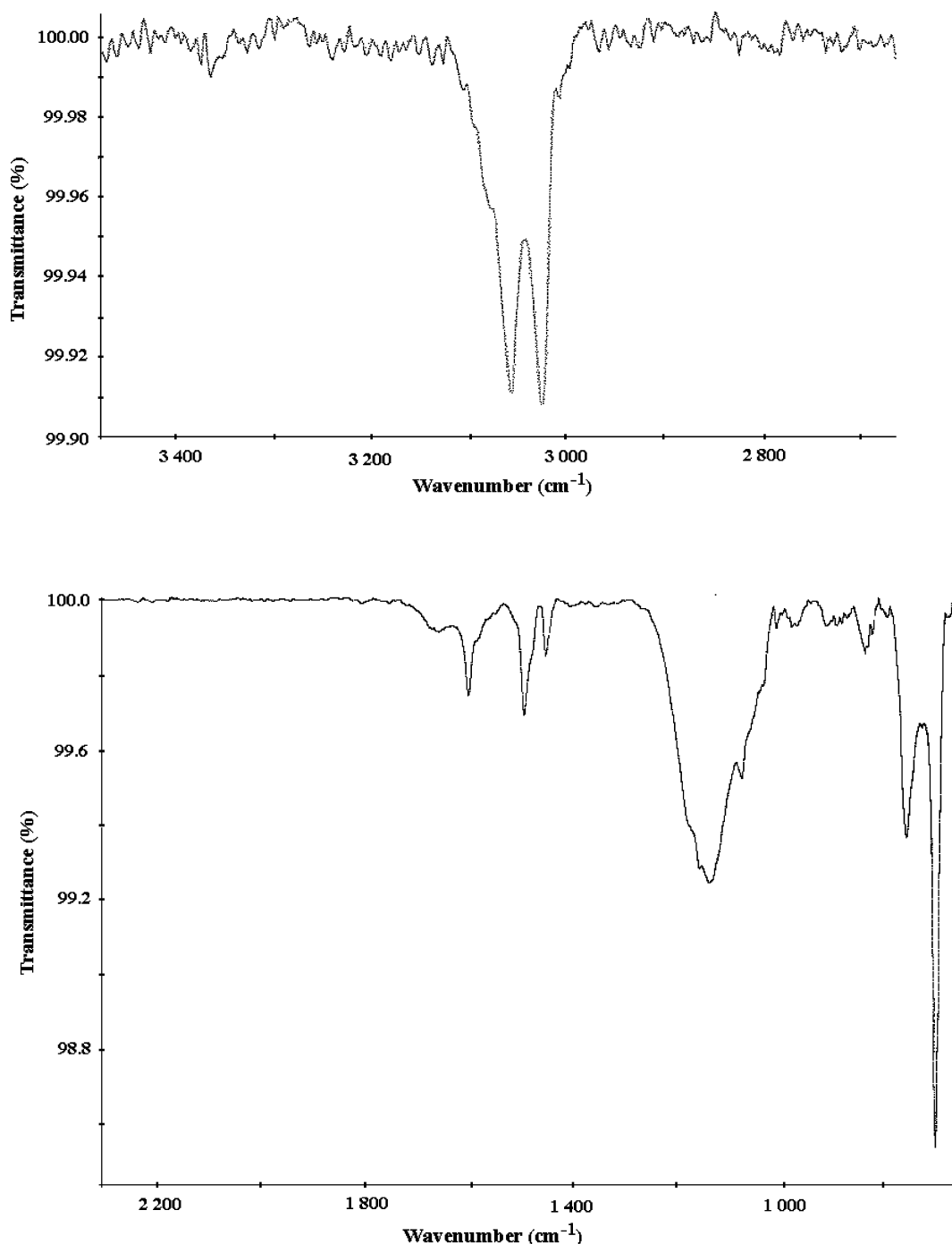ments. Similarly, no peak at 685 eV (F[1s]) for BF_4^- was observed.

Figure 2. Infrared spectrum for an iron plate chemically grafted by **1**.

For the electrochemically grafted films, one can observe an important increase of the background intensity for binding energies higher than the Fe[2p] peak, which is due to inelastically scattered Fe[2p] photoelectrons. In addition, the Fe[2p$_{3/2}$] peak centered at 706.7 eV (Figure 1c) is significantly attenuated by the grafted overlayer. For chemical grafting, the Fe[2p] doublet is very weak and the background at the higher binding energy side is almost flat (Figure 1b). This is a firm indication that the organic coating is continuous, dense, and thick enough to screen iron, which results in a dramatic change in the spectral background shape. However, the organic coating thickness is still comparable ($\sim$8$-$9 nm) to the sampling depth of Fe[2p] so that elastically and inelastically scattered Fe[2p] electrons can escape.

Similar observations concerning the thickness of organic layers have already been made where industrial and coinage metals were grafted electrochemically in organic solvents by aryl diazonium salts.[9] The formation of multilayer coatings by spontaneous grafting results from the S_H homolytic substitution mechanism of formation of such films.[36]

IR Spectroscopy. Chemical grafting by **1** was detected by IR spectroscopy (see Figure 2). No significant band can be observed in the 2300$-$2130 cm^{-1} region for the stretching of the N$\equiv$N bond in the diazonium salt.[43,44] This confirms

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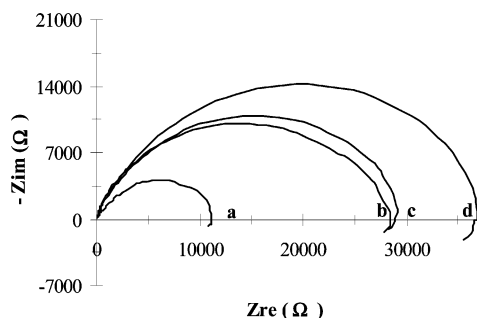
Figure 3. Impedance spectra of an iron electrode in a 0.01 M H$_2$SO$_4$ aqueous solution. (a) Bare, (b−d) modified chemically by, respectively, **1**−**3**. Electrode diameter = 1 mm.

Figure 4. Semilogarithmic polarization curves for iron in a 0.01 M H$_2$-SO$_4$ aqueous solution. Electrode: (a) bare; (b−d) chemically grafted by, respectively, **4**, **2**, and **3**; (e) left in a 10 mM solution of **2** after grafting. Electrode diameter = 1 mm. Scan rate = 1 mV/s.

the loss of dinitrogen during the grafting and is in agreement with the XPS measurements.

The spectrum exhibits two weak bands at 3060 and 3028 cm^{-1}, which correspond to the stretching of aromatic C−H bonds.[44] The medium-intensity bands at 1600 , 1493, and 1452 cm^{-1} correspond to the stretching of C=C bonds in aromatic rings. The band at 1600 cm^{-1} could also result from the presence of a phenyl multilayer film.[45,46] The formation of these multilayers has already been observed for the chemical grafting of aryl diazonium salts onto copper surfaces.[13] The broad and strong band at 1140 cm^{-1} can be attributed to iron oxides.[8] The strong bands (758 and 701 cm^{-1}) and the weak bands (839 and 662 cm^{-1}) correspond to out-of-the-plane vibrations of aromatic C−H. The presence of such bands can be assigned to monosubstituted and meta-disubstitued phenyl moieties. The IR spectra confirm, therefore, the presence of a polyphenylene film at the iron surface.

Electrochemical Measurements. The inhibition effect of the grafting has been assessed by determining the polarization resistance, R_p, by impedance measurements and the corrosion current, I_{corr}, by polarization curves on iron electrodes. R_p values were calculated from Nyquist impedance diagrams (see Figure 3). I_{corr} values were deduced from the semiloga-rithmic polarization curves by extrapolating the linear cathodic and anodic (its slope is fixed to a value of 58 mV per decade of current) branches at the corrosion potential[16] (see Figure 4). Polarization resistances for the bare iron electrode and the same electrode grafted by **1**−**3** are shown respectively in Figure 3a, b, c, and d, respectively. The polarization resistance value obtained with the three salts increases upon grafting, which indicates that the grafted film has inhibitor properties. The highest value is observed for the dodecylphenyl film **3**, for which the polarization resistance is about 1.5 times higher than for **1** and almost 4 times higher than for bare iron. The latter result strongly suggests that the hydrophobic alkyl chains are standing upright from the iron surface as we have already observed when iron was grafted electrochemically in an organic medium.[14]

In all cases, polarization curves exhibit a decrease of iron oxidation upon grafting (compare Figure 4, curves a−d),
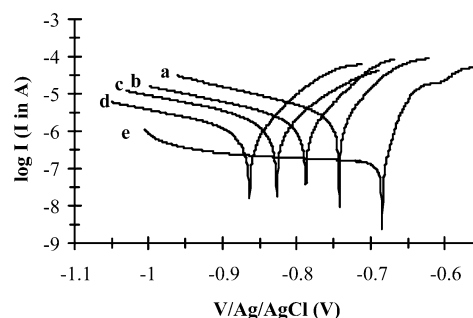
Table 1. Corrosion Currents and Inhibition Efficiencies of Bare and Modified Iron Electrodes by Chemical Grafting of Diazonium Salts[a]

diazonium salt, $^+$N$_2$ArBF$_4^-$	R_p kΩ	E_{corr} V/Ag−AgCl	I_{corr} 10^{-6} A	IE %
none	10.8	−0.742	3.20	
none[b]	16.0	−0.825	1.41	
C$_6$H$_5$[c] **1**	28.2	−0.830	1.05	68
C$_6$H$_5$[d] **1**	24.2	−0.841	0.71	50
C$_6$H$_4$Br **2**	28.7	−0.827	1.07	67
C$_6$H$_4$Br[c,e] **2**	54.2	−0.685	0.12	97
C$_6$H$_4$C$_{12}$H$_{25}$[c] **3**	36.6	−0.864	0.89	73
C$_6$H$_4$CO$_2$H[c] **4**	20.6	−0.787	1.60	50
C$_8$H$_{17}$Si(OC$_2$H$_5$)$_3$[f]	11.5	−0.778	2.44	25
C$_6$H$_4$CO$_2$H + C$_8$H$_{17}$Si(OC$_2$H$_5$)$_3$[c,g] **4**	41.3	−0.899	0.57	85

[a] Measurements in a 0.01 M H$_2$SO$_4$ aqueous solution. Electrode diameter = 1 mm. [b] Bare iron electrode maintained 1 h in a neutral aqueous solution. [c] Electrode grafted for 1 h by a 10 mM diazonium salt in 0.01 M H$_2$SO$_4$ aqueous solution. [d] Same as b in the presence of 10 mM diazonium salt. [e] Polarization measurements in the presence of 10 mM diazonium salt. [f] Iron electrode treated with octyltriethoxysilane but not by a diazonium salt. [g] Treatment by octyltriethoxysilane after grafting by **4**.

which means that the polyphenylene grafted organic film acts as a physical barrier between the metal and the aqueous medium. In all cases, we have also observed a negative shift of the open circuit potential when the modified electrode is immersed in a 0.01 M sulfuric acid solution. This shows that the grafted film plays the role of a cathodic inhibitor for iron. For the iron electrode chemically grafted by **4** (curve 4b), the impact of the grafted group (carboxyphenyl) is smaller than that of the other groups. This is likely due to the fact that carboxylic groups play the role of a relay for the transfer of charges toward the iron surface.

The inhibition efficiency, IE, was calculated from

$$\text{IE} = 100\left(1 - \frac{I_{corr}^{film}}{I_{corr}}\right)$$

where I_{corr}^{film} and I_{corr} represent the current intensities at, respectively, the coated and bare iron electrodes.

The results for the corrosion intensities and inhibition efficiencies are gathered in Table 1. The best results were obtained with salts **1**, **2**, and **3** after a 1-h grafting. We can observe a decrease of the corrosion current by ~70% upon grafting by **1**−**3**. This is in agreement with the above deter-mination of R_p by impedance measurements and also with previous results obtained upon electrochemical grafting.[14]

Figure 4 (curve e) shows that the corrosion current of an iron electrode decreases by 97% when, after grafting by **2**, the electrode has not been withdrawn from the diazonium

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Scheme 2. Mechanism for the Formation of a Polymer Film by Reaction of C$_8$TES with Iron Grafted Spontaneously by 4
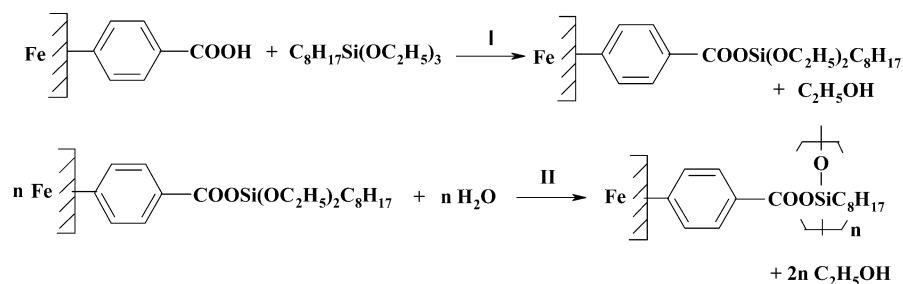
solution. The large decrease of the cathodic current confirms that the diazonium film acts as a cathodic inhibitor and that the inhibition of iron corrosion is under cathodic control. This effect is probably due to the stability of the grafted film, which can be repaired, if necessary, by the free diazonium salt molecules in the solution. At a potential of about -0.6 V/Ag−AgCl, one can observe that the rate of oxidation of iron is equal to that of a bare electrode because, following the oxidation of a certain amount of the metal, the organic film is cleaved from the surface.[14] One can compare this result with that of the literature using classical corrosion inhibitors in aqueous sulfuric acid solution: 2,5-bis(dimethylaminophenyl)-1,3,4-thiadiazole (IE = 95.2 for 10^{-5} M),[19] poly(4-vinylpyridine isopentyl bromide), and poly[4-vinylpyridine-poly(3-oxide-ethylene)tosyle] (IE up to 100 for an inhibitor concentration of 2.5×10^{-8} M).[47,48] Polypyrrole/polyphenol multilayer coatings can be compared to the present method since their inhibition efficiency is 98.3% in a 0.05 M sulfuric acid solution.[49]

We have observed by impedance and polarization measurements that the spontaneous grafting of diazonium salts also occurs in a neutral aqueous medium (pH = 6.8 at the beginning of the experiment). When the iron electrode has been immersed for 1 h in a 10 mM neutral solution of **2** (same treatment as in acidic aqueous solution), its R_p value increases and corrosion decreases, as can be seen in Figures S1 and S2 (Supporting Information). The effects are lower than those observed in an acidic medium, which could result from the lower stability of the diazonium salt in a neutral solution. Experiments performed at higher pH were not successful, certainly because of the poor stability of the diazonium salt at such high pH. To our knowledge, there is only one example in the literature of the grafting of a surface by diazonium salts at a basic pH; it involved carbon nanotubes that were grafted by **1** at pH = 10.[50]

As stated above, one advantage of the covalent grafting is the possibility to chemically derivatize the organic film with no risk of ungrafting the overlayer. Hence, following the chemical grafting of an iron electrode with diazonium salt **4**, the electrode was reacted with octyltriethoxysilane, C$_8$H$_{17}$Si(OC$_2$H$_5$)$_3$ (C$_8$TES), to overcoat the primary layer by a polymer film. We have used the procedure described by

Aramaki and Shimura,[23] who fabricated a one-dimensional polymer film on an iron electrode. First, they adsorbed 16-hydroxyhexadecanoate ion, HOC$_{16}$A$^-$, on a passivated iron electrode by immersion of the electrode into a NaHOC$_{16}$A methanol−water solution to obtain the self-assembled monolayer (SAM) of HOC$_{16}$A on iron. Then, they reacted this SAM with C$_8$TES or C$_{18}$TES for 2 h in acetone. In our case, the reaction, which was carried out in acetone at 40 °C for 2 h, consisted of two steps: the esterification of the acidic function of grafted iron by the silane (I, Scheme 2) and the polymerization of the silane into polysiloxane by reaction with water present in the medium and the elimination of ethanol (II).

To show the impact of the polymer film, the coated electrode was tested by linear voltammetry in a 0.01 M H$_2$SO$_4$ aqueous solution (see Figure 5). Polarization curves
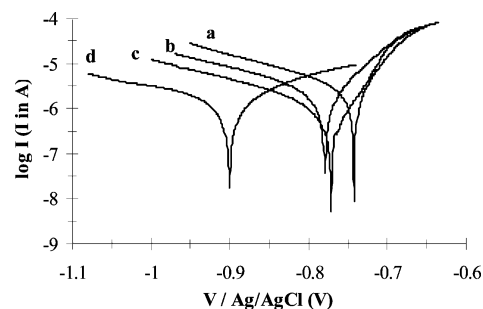

Figure 5. Semilogarithmic polarization curves in a 0.01 M H$_2$SO$_4$ aqueous solution for (a) bare iron electrode, (b) iron electrode simply immersed into a 0.01 M H$_2$SO$_4$ solution of water for 1 h and then treated with C$_8$-TES, (c) iron electrode chemically grafted by **4**, reacted with C$_8$TES, and left in a 0.01 M H$_2$SO$_4$ for 8 h, and (d) the same as c for 2 h in the corrosive medium instead of 8. Electrode diameter = 1 mm. Scan rate = 1 mV/s.

obtained with an iron electrode chemically grafted by **4**, reacted with C$_8$TES, and left in a 0.01 M H$_2$SO$_4$ solution for 2 h (see Figure 5, curve d) show that (i) the organic coating has a real impact on the decrease of the corrosion current, with an inhibition efficiency of 85%, and (ii) it acts as a mixed anodic and cathodic inhibitor. After 8 h of immersion in the corrosion medium, (i) the cathodic current increases and (ii) when the potential is displaced anodically, no more corrosion inhibition is observed since the organic film is cleaved from the surface of iron (see Figure 5, curve c). The electrochemical results could be reproduced after sonication.

In addition to the already-mentioned advantage of covalent grafting over adsorption, the present method shows several other advantages: (i) no passivation step is required and (ii) the modification of iron by grafting of the carboxyphenyl

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film takes less than 1 h. It has already been shown that when iron was immersed more than 1 h in the grafting solution in an organic medium, the inhibition efficiency did not vary considerably.[11]

Conclusion

Spontaneous grafting of iron in acidic aqueous solution has been reported, characterized by XPS and IR spectroscopies, and also detected electrochemically. The organic film is several layers thick and can be used either for direct protection of the metal against corrosion or for further derivatization. Grafting by the diazonium salt results in a maximum inhibition efficiency of 73%, which can be significantly increased to 97% when the grafted metal is left in the corrosion medium in the presence of the diazonium salt. These results compare well with those of the literature. We have also shown that spontaneous grafting is possible in neutral aqueous solution. The advantages of this method are that it operates under simple and environmentally friendly experimental conditions in water or *a fortiori* in any organic solvent and in the presence of air. Derivatization of grafted iron containing an acidic function by an alkoxysilane increases the inhibitor efficiency in acidic aqueous solution up to 85%.

Supporting Information Available: Impedance spectra and polarization curves of an iron electrode (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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