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Formation of a Bifunctional Redox System Using Electrochemical Reduction of Platinum in Ferrocene Based Ionic Liquid and Its Reactivity with Aryldiazonium

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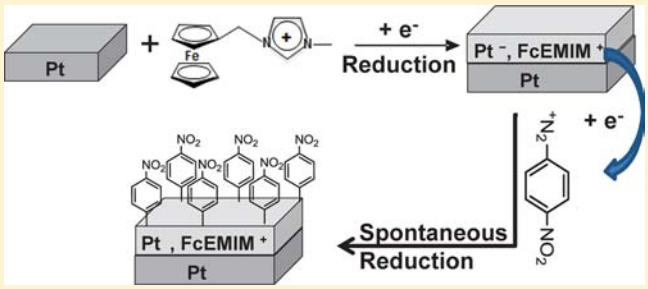
ABSTRACT: The electrochemical reduction of platinum in ferrocene based ionic liquid, 1-ferrocenylethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([FcEMIM][TFSI]), has been investigated on both macro and micro platinum electrodes. The electrochemical and X-ray photoelectron spectroscopy (XPS) analyses of the reduced platinum evidence the presence and the intercalation of the ferrocene imidazolium into the platinum surface. The resulting metal−organic phase was anticipated to be of the general formula [$Pt_n^{\delta-}$, $FcEMIM^{\delta+}$]. Next, the spontaneous reaction of the electrogenerated Pt phases as reducing agent with phenyl diazonium salts was performed. The "reduced platinum phase" reacts with nitrophenyl diazonium salts, without applying any external potential, and conduces to the attachment of nitrophenyl groups onto the surface. Detailed experiments based on cyclic voltammetry and XPS were carried out to follow the occurrence of the grafting. Indeed, both experiments evidence the presence of ferrocene and nitrophenyl groups on the Pt surface. As a result, a bifunctional active surface containing two redox systems has been obtained.



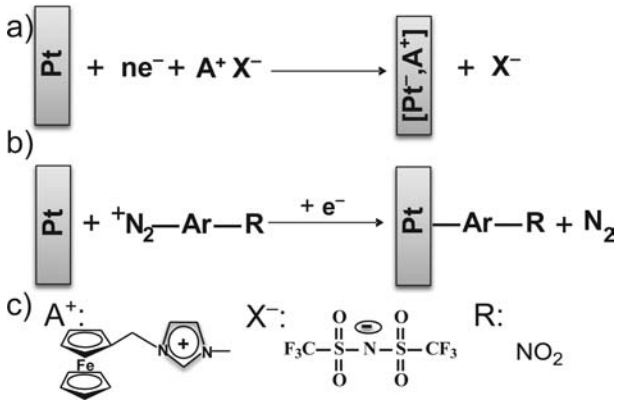
INTRODUCTION

Specific properties of materials are determined in part by the surface composition, and in this field modified electrodes represent a pertinent illustration of this phenomenon.[1] Surface modification of conducting or semiconducting substrates has been employed for the production of new superior products in terms of increased corrosion resistance, improvement of optical and electrical/electronic properties, electrocatalysis, sensing, and molecular electronics.[2,3] Various strategies have been proposed to form defectless mono- and multilayered structures leading to control of their physicochemical properties. Recently, interest has been devoted to the formation of molecular assemblies on surfaces that contain molecular components with a multitude of different functionalities.[4]

In this context, electrochemistry has been proposed as convenient method to produce modified and functionalized surfaces. Mainly two electrochemical processes have been reported in the literature leading to either the inclusion "solid phase" or the attachment of organic molecules to the electrode materials providing new and special properties to the interfaces.

The formation of so-called "solid phase" is a quite general phenomenon, which is based on the inclusion of the molecules into the electrode material after cathodic treatment (Scheme 1a).[5−8] Solid substances are also produced upon reduction of metallic electrodes in nonaqueous solutions containing alkyl ammonium salts as background electrolytes.[9] Among the metals that can be reduced electrochemically are those belonging to the IV and V main group of elements, which are known to form polyatomic anionic species, called Zintl ions,[10] e.g., antimony,[11] bismuth,[11] tin,[12] or lead.[12] Moreover, recent work reports the formation of 'platinides' such as BaPt, Ba_3Pt_2, Ba_2Pt,[13] or the

Scheme 1. Schematic Illustrating the Electrochemical Modifications of Platinum[a]



[a](a) Cathodic polarization in organic electrolytic solution. (b) Electrochemical reduction of diazonium salts. (c) A^+ and X^- are the cation and the anion of the used ionic liquid, R is the terminated group of diazonium.

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more complex $Pt_2In_{14}Ga_3O_8F_{15}$.[14] Moreover, the cathodic corrosion of platinum has been proposed as a facile and effective method to prepare clean metal nanoparticles.[15] The reduced platinum phases could be generated after a cathodic polarization of platinum in dry aprotic solvent containing organic or inorganic slats.[16,17] These electrogenerated phases resembling the Zintl phases are produced from an elemental electrochemical process, which should formally correspond to the reduction of the platinum metal. The resulting metal−organic phase was anticipated to be of the general formula [$Pt_n^{\delta-}$, $A^{\delta+}$, AX], where A^+ is the cation and X^- is the anion electrolyte. This puzzling reaction has been investigated by different electrochemical methods, scanning electron microscopy (SEM), and in situ electrochemical atomic force microscopy (EC-AFM), evidencing impressive morphological changes of the metal surfaces.[16−19] X-ray photoelectron spectroscopy (XPS) analysis of reduced platinum brought a clear evidence for the formation of negatively charged platinum and supported the idea that the cation of the supporting electrolyte was incorporated into the metal lattice.[20] Recently, our group has investigated the electrochemical response of ferrocene based ionic liquid,[21] and the electrochemical reduction of platinum in this media.[22] The use of the intrinsically electroactive ILs leads to bring a formal electrochemical proof for the presence of the ionic liquid cation onto and/or into the electrode material.

Besides this puzzling reaction, the most studied functionalization route occurs through covalent coupling which ensures a stable and strong attachment of the desired molecules onto the surface. The fast and versatile electrochemical reduction of diazonium, explored by Pinson, has been extensively used to build modified surfaces.[23−25] Briefly, it has been established that following one electron reduction and a subsequent elimination of dinitrogen, aryl diazonium salts provide highly reactive radicals allowing the formation of covalent bonds with surfaces materials (Scheme 1b). This reaction has been investigated in different media[26,27] using various materials (such as metallic surfaces, carbon, and silicon)[28,29] and several diazonium derivatives.[25,30,31] The presence of organic layers attached onto the electrode surface was evidenced using several techniques.[25,32] Recently, the grafted layers have been used to attach more complex moieties or to build hierarchically ordered multilayered devices.[33−35]

In this work, we purpose to combine two electrochemical processes, presented in Scheme 1a,b, for preparing the multifunctional layer. Before that, we reexamined in more detail the electrochemical reduction of Pt in ferrocene based ionic liquid, since this process has been characterized only from cyclic voltammetry studies.[22] We performed a series of electrochemical characterization on both macro and micro electrodes. Next, the change in the chemical nature that accompanies the modifications of the platinum surfaces upon the cathodic activation was followed by X-ray photoelectron microscopy measurements. The so-generated phases were used to induce the reduction of the diazonium salt. The resulting surface was characterized by electrochemical and XPS measurements. Besides the interest in potential applications for the development of such interfaces, our goal was also to improve the basic knowledge about the reactivity of these unconventional "reduced" platinum phases and to build multifunctional redox active surfaces, containing two redox systems, which are of interest in molecular electronic devices.

■ EXPERIMENTAL SECTION

Chemicals. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) purchased from Aldrich (electrochemical analysis grade, ≥99%) was used as supporting electrolyte at a concentration 0.1 M. Dry acetonitrile (ACN) was purchased from Fulka and stored over molecular sieves. The diazonium salt used for this study was 4-nitrophenyldiazonium tetrafluoroborate purchased from Across and was used as received.

Ionic Liquid. The electroactive ionic liquid, 1-ferrocenylethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([FcEMIM]-[TFSI]), was prepared according to standard procedures.[36] Prior to each experiment, vacuum pumping carefully dried RTILs overnight and the amount of residual water was measured with Karl Fischer titration (Karl Fischer 652 Metrohm). The amount of water measured in our samples ranged from 100 to 200 ppm.[37]

Electrochemical Experiments. For the electrochemical experiments a conventional three-electrode cell was used. Platinum wire was used as auxiliary electrode. Saturated calomel electrode SCE was used as reference electrode for the electrochemical measurements in acetonitrile media, while, for the experiments performed in ionic liquid a Pt/PPy quasi-reference electrode was used.[38] To minimize the solution contamination, the SCE electrode was placed in an electrode bridge tube with a Vycor frit. The electrode bridge tube was filled with 0.1 M Bu_4NBF_4 in ACN. In order to take into account the liquid junction potential, the reference electrode was calibrated with the internal reference system (ferrocenium/ferrocene) Fc^+/Fc couple as recommended by IUPAC, and all potentials were scaled versus Fc^+/Fc. Platinum disk electrode (3 mm diameter) and Pt ultramicroelectrode (20 μm diameter) were used as working electrodes. Prior to use the working electrodes were polished using successively SiC-paper 5 μm (Struers) and DP-Nap paper 1 μm (Struers) with Al_2O_3 0.3 μm slurry (Stuers). After polishing the electrode was thoroughly rinsed with ultrapure water (18.2 MΩ cm). Before any electrochemical measurements the solutions were deoxygenated by bubbling argon gas for 30 min, during the experiment the electrochemical cell remain under argon. The potentiostat used in this study was CHI 660C (CH Instruments, TX). All the experiments are performed at 25 °C. For XPS analysis a platinum foil 0.1 mm thick (from Goodfellow) was used as working electrode.

X-ray Photoelectron Spectroscopy Analyses. XPS measurements were performed using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al Kα ($h\nu$ = 1486.6 eV) 200 W X-ray source. The X-ray spot size was 500 μm. The samples were stuck on sample holders using conductive double-sided adhesive tape and pumped overnight in the fast entry lock at ∼5 × 10^{-8} mbar prior to transfer to the analysis chamber. The pass energy was set at 100 and 40 eV for the survey and the narrow scans, respectively. Data acquisition and processing were achieved with the Avantage software, version 4.67. Spectral calibration was determined by setting the main C(1s) component at 285 eV. Atomic percentages have been determined using this software and taking into account photoemission cross sections, analyzer transmission, and variation of electron mean free paths with kinetic energy.

■ RESULTS AND DISCUSSION

Cathodic Polarization of Pt Electrode in Ferrocene Based Ionic Liquid and Its Electrochemical Characterization. As explained above the proposed procedure for making the multifunctional redox active system occurs in two steps. The first step is based on the cathodic modification of the platinum electrode in ferrocene based ionic liquid [FcEMIM, TFSI]. It was shown that the electrochemical reduction of platinum in this media occurs at −2.1 V.[22] In this work, the surface modification was performed by cathodic polarization at −2.2 V during 200 s. Following that, the electrode was rinsed thoroughly in acetonitrile and then characterized by electrochemistry. Such study become straightforward since the incorporated species is bearing ferrocene redox probe which

is easier to characterize by cyclic voltammetry. Figure 1 shows the electrochemical response of the reduced platinum electrode in acetonitrile electrolytic solution.

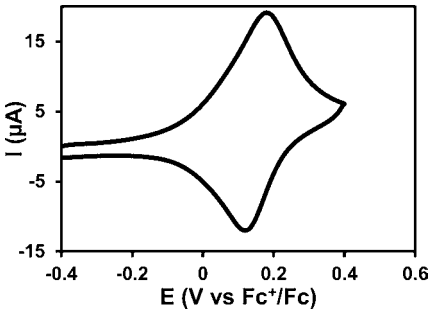


Figure 1. Electrochemical characterization of modified Pt electrode in solution containing 0.1 M of Bu4NBF4 in ACN. Scan rate was 0.1 V s^{-1}.

The recorded CV shows reversible redox system at 0.15 V which is assigned to the electrochemical response of the ferrocene/ferrocenium imidazolium redox couple. In addition, the peak-to-peak separation is around 20 mV indicating that the Fc moieties are immobilized onto and/or into the electrode surface. The presence of this signal confirms the existence of ferrocene groups onto or into the platinum electrode surface. One has to note that the characterization of Pt electrode after polarization, in ferrocene based ionic liquid, at a potential more positive than −1.4 V, did not show the presence of Fc signal. In our experimental condition, the only source of ferrocene species is the ionic liquid cation, thus the cathodic polarization at −2.2 V is the origin of the presence of Fc signal observed during the electrochemical characterization. By analogy with the previous works,[16−18,20,22] the cathodic polarization of Pt in ferrocene based ionic liquid conduces to the formation of solid phase where the ionic liquid cation (ferrocene imidazolium) is intercalated and/or attached onto the electrode material.

In order to check the stability of the reduced phase, the electrode was removed from the test solution and sonicated in ACN for 15 min. Following that, the electrode was characterized in electrolytic solution. Similar behavior as presented in Figure 1 is obtained with a negligible current variation, less than 5% after 50 cycles. This result suggests the high stability and the strong immobilization of Fc species and thus permits the investigation of the variation of both current and peak potential as a function of the scan rate. The obtained results are presented in Figure 2.

Figure 2A shows linear variation of the peak current versus the scan rate suggesting a nondiffusive redox process to and from the electrode surface and thus demonstrating that the Fc species, originating from the cathodic polarization in ferrocene based ionic liquid, are intercalated and/or attached onto the Pt electrode. Figure 2B exhibits the variation of the peak potential as a function of the scan rate. For a scan rate below 0.1 V s^{-1}, the peak potentials are not affected by the scan rate variation. Upon increasing the scan rate, the peak potentials shift in positive and negative direction relative to standard redox potential of Fc which reflects control of the voltammetry by the rate of electron transfer of the immobilized ferrocene moieties. Apparent rate constants for electron transfer, k_{app}, were calculated using Laviron's formalism[39] based on the classical Butler−Volmer theory.

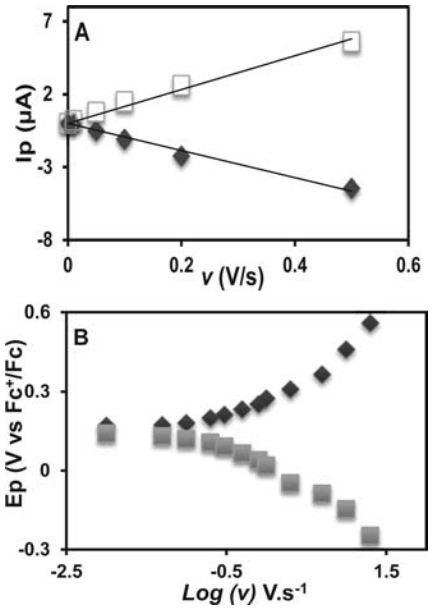


Figure 2. (A) Scan rate dependency of the anodic and cathodic peak current. (B) Variation of the anodic and cathodic peak potential as function of the log (v).

$$k_{app} = (1 - \alpha)nFv_a/RT$$

where α is the charge-transfer coefficient and v_a is the intersect of the two linear regions in the plot *Ep* vs log (v) obtained at low and high scan rates. The symmetry between the anodic and cathodic branches suggests that α is 0.5. From Figure 2B the calculated apparent rate constant is around 2 s^{-1}. This value has to be compared to the apparent rate constant measured when Fc units are covalently attached onto electrode material in self-assembled monolayer configuration.[40] Thus, the reported values in the literature range from 50 to 200 s^{-1}. This variation depends on the method used for the grafting and the surface density of Fc species. In our case, the apparent rate constant is at least 1 order of magnitude smaller; this difference could be ascribed to the organization of the Fc moieties in the platinum phase or onto the surface. Indeed, the modification process generates probably solid phase where the Fc species are intercalated in the Pt which, intuitively, will decrease the rate constant compared to Fc-SAM organization.

Cathodic Polarization of Pt Ultramicroelectrode in Ferrocene Based Ionic Liquid and Its Electrochemical Characterization. All the studies related to the generation of solid phases, by electrochemical reduction of metal electrodes, are performed using a millimeter size electrode. The use of ultramicroelectrodes, UME, allows high spatial and temporal resolution of the achieved measurements and offers direct distinguish between electrochemical process occurring in solution (steady state current) or at the electrode surface (peak current).[41] In this connection, the generation of reduced platinum phase was performed on a Pt ultramicroelectrode. The cathodic modification was performed in ferrocene based ionic liquid by applying −2.2 V during 200 s. Next, the UME was rinsed extensively in ACN and immersed in free electrolytic solution. Figure 3 shows the electrochemical response of the reduced Pt UME.

The electrochemical characterization exhibits a reversible redox system at potential around 0.15 V related to the ferrocene/ferrocenium imidazolium redox couple. Obtaining a

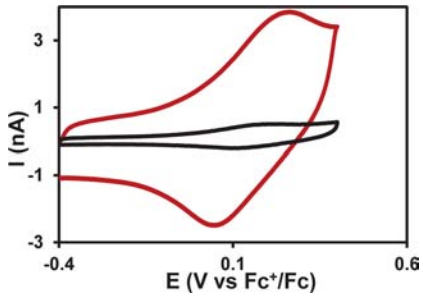


Figure 3. Cyclic voltammetry of the reduced platinum UME electrode (10 μm radius) in solution containing 0.1 M of Bu_4NBF_4 in ACN at 0.1 V s^{-1} (red line) and 0.01 V s^{-1} (black line).

peak shape rather than sigmoidal shape is characteristic of a process where the species involved do not diffuse to and from the microelectrode. In addition, lowering the scan rate to 0.01 V s^{-1} (black line) induces a decrease in the current intensity, linear variation with the scan rate, while maintaining the peak shape. Contrarily, for a redox species in solution the CV recorded at UME shows a sigmoidal shape, steady state current, which is independent of the scan rate variation (for a lower scan rate typically below 0.1 V s^{-1}). All these results indicate the possibility to generate reduced platinum phase, after cathodic polarization in ferrocene based ionic liquid, using microelectrode size, and confirm the immobilization of Fc onto and/or into the platinum. Moreover, the analysis of the electrochemical signal in Figures 1 and 3 could provide estimation of the amount of the Fc groups. The charge of the electroactive species could be measured, and the surface concentration is calculated using the formula $\Gamma = Q/nFS$. Where Q corresponds to the charge measured by integration of the anodic peak, n is the number of the electron, F is the faraday constant, and S is the area of the electrode. In the present case, the average surface concentration was found to be in the range of 10^{-8} mol cm^{-2}. This value is at least 1 order of magnitude higher compared to the theoretical maximum surface coverage for Fc alkanethiol monolayer which is 7.6×10^{-10} mol cm^{-2}.[42] Similar results were observed after the cathodic charge of glassy carbon in the presence of ω-iodoalkylferrocenes.[43] The high surface coverage combined with the low apparent rate constant supports again the idea of the occurrence of Fc imidazolium intercalation into the platinum surface, during the cathodic activation, rather than attachment onto the surface.

XPS Analyses of Reduced Pt Electrode. XPS is a versatile tool for accurately analyzing the surface chemical composition for a given material. Parts a and b of Figure 4 compare the XPS survey spectra and the high resolution spectra at the Pt(4f) core level, respectively, of the Pt substrate without any polarization (black line) and after cathodic polarization at −2.2 V during 200 s (red line). Figure 4c displays the high resolution spectra at the Fe(2p) core level of the reduced Pt.

The spectrum of the nonpolarized Pt substrate mainly displays the platinum signals, which originate from Pt(4f) core electrons. The Pt($4f_{7/2}$) and Pt($4f_{5/2}$) doublet is observed at 71.1 and 74.2 eV, respectively, in agreement with literature report.[20] Minor peaks are also identified such as C(1s) at 285 eV, oxygen O(1s) at 532.5 eV, and N(1s) at 400 eV, which are ascribed to classical surface contamination.

After the cathodic polarization in ferrocene based ionic liquid, the platinum signal is strongly attenuated (see Figure 4b) while the C(1s) relative intensity considerably increases

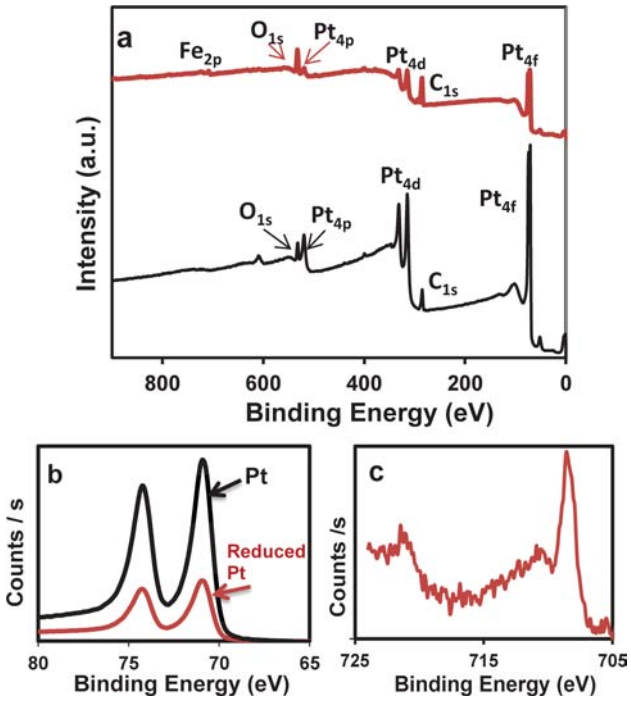


Figure 4. (a) XPS survey scans of platinum substrate (black line) without any polarization and (red line) after a 200 s cathodic polarization at −2.2 V in ferrocene based ionic liquid. High resolution XPS spectra for (b) Pt(4f) and (c) Fe(2p) core level.

(see Figure 4a). The increase of C(1s) at 285 eV corresponds to contributions from aromatic carbon. Moreover, a new peak corresponding to Fe(2p) core level became visible. The Fe(2p) spectrum (Figure 4c) is composed of two peaks at 708.6 and 721.1 eV corresponding to the Fe($2p_{3/2}$) and Fe($2p_{1/2}$) signals, these values being perfectly consistent with those previously published for ferrocene.[40] In addition, the N(1s) high resolution spectra show two contributions at 400 and 401.9 eV (data not shown). The peak at 400 eV can be attributed to some reduced nitrogen possibly from surface contamination of the Pt sample (this signal is visible on nonpolarized sample). According to the literature, the nitrogen component associated with the high binding energy 401.9 eV is due to imine group in the form of the imidazolic ring.[44] This analysis shows that the chemical composition of Pt surface is strongly modified upon the electrochemical activation. The IL cation has aromatic carbon originating from the imidazolium ring and Fe from the Fc attached to the imidazolium. The increase of C(1s) peak intensity at 285 eV, the attenuation of the Pt signal, and the appearance of the Fe(2p) signal and the N(1s) peak at 401.9 eV are indicative of the presence of ferrocene imidazolium species onto and/or into the Pt surface. A closer examination of the XPS spectra provides other information about the chemical nature of the reduced Pt phase. The background observed on nonmodified and modified Pt is completely different (Figure 4a). Indeed, background increase is observed for reduced platinum when increasing the binding energy. In addition, a background increase in the XPS spectra on the high binding energy side (lower kinetic energy side) of the C(1s) and Fe(2p) peaks is observed. Such a background shape means that a higher portion of C(1s) and Fe(2p) is located more deeply inside the substrate rather than attached or simply adsorbed onto the Pt substrate. Similar observations were reported on a series of solid state barium platinide compound.[45]

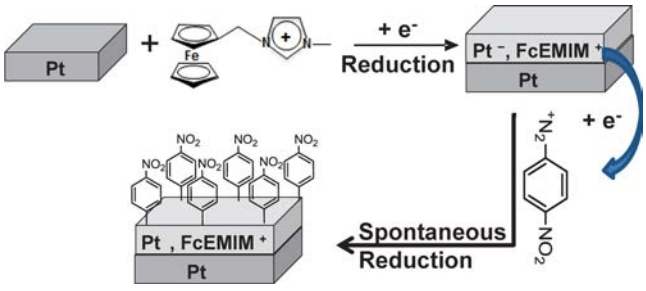
One has to note that the resulting modification, after the cathodic treatment of platinum, could not be explained by simple formation of chemically modified platinum, crystallization, or ionic liquid anion reduction. Indeed, the grafting of imidazolium based ionic liquid onto the electrode surface has been recently described, and this chemically modified electrode does not show any activation of the electrode material (spontaneous reactivity toward diazonium as described in the following paragraph).[46] The other explanation could be related to the reduction of the IL anion. Thus, the latter is susceptible to a series of electrochemically initiated breakdown reactions starting at a potential around −2.7 V, and the products of these eventually precipitate onto the electrode as film.[47] This possibility could be excluded since the applied potential (−2.2 V) is not negative enough to reduce the IL anion. In addition, the XPS data does not show the presence of peaks related to fluorine (F) or sulfur (S) suggesting the absence of ionic liquid anion (TFSI) onto the electrode surface. This observation suggests that the modification of Pt, after cathodic treatment in ferrocene based IL, could not be explained by electrocrystallization, chemical modification, and IL anion reduction process.

Collectively, electrochemistry at millimeter and micro size electrodes, XPS results, and literature results[7,11−14,16−18,20,22] indicate that the Fc imidazolium is intercalated in platinum surface after the cathodic activation. The reduced platinum corresponds to the interfacial formation of intermetallic phases with a general formula [$Pt_n^{\delta-}$, $FcEMIM^{\delta+}$]. In our previous work, we have shown that the formal oxidation degree of platinum varies from −0.9 to −1.6 depending on the injected charge during the electrochemical reduction process.[20] This behavior is analogous to a charging process. Compared to our previous results and taking into account the value of the injected charge (350 mC cm^{-2}), the formal oxidation state of platinum is around −1.5.

Reactivity of Cathodically Modified Pt with 4-Nitrophenyldiazonium. As explained previously, the reduced Pt can be used for triggering electron-transfer reactions. In that connection, we have previously reported on the activation of diazonium salts by the cathodically modified Pt in the absence of any externally applied potential.[48] This procedure allows the transformation of the reduced Pt to a functional organometallic interface. As a test system, we choose the 4-nitrophenyldiazonium salt. Scheme 2 summarizes the two-step procedure.

The experimental procedure involves the electrogeneration of the reduced platinum in ferrocene based ionic liquid as described in the previous part. Similar polarization conditions as described above were used (−2.2 V during 200 s), and then the sample was immediately transferred into a deoxygenated ACN solution containing 5 mM of 4-nitrophenyldiazonium tetrafluoroborate salt. The system was left to react for 15 min under argon to allow a sufficient time for the reaction to be completed without applying any external potential. One has to note that the open circuit potential of reduced platinum is around −1.8 V which is negative enough to reduce the diazonium. Next, the electrode was thoroughly rinsed several times with ACN and sonicated for 10 min to remove the organic material that is only weakly bound on the platinum surface. Finally, the electrode was transferred to a pure electrolyte solution and examined by cyclic voltammetry. Figure 5 shows the cyclic voltammetry of the step-wisely modified Pt substrate. The CV was performed by sweeping the potential from −0.4 to −1.9 V, during the backward scan the return potential was set at 0.4 V, and after three successive cycles the scan was stopped at −0.4 V.

Scheme 2. Schematic Illustrating the Spontaneous Grafting of Nitrophenyl Layer onto Activated Platinium



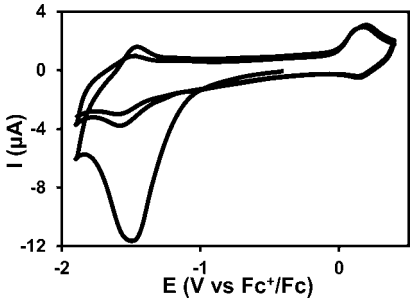


Figure 5. Cyclic voltammetry in a pure electrolyte solution (ACN + 0.1 M in NBu_4BF_4) of a Pt electrode after cathodic modification (in ferrocene based ionic liquid) followed by a 15 min immersion in ACN solution containing 4-nitrophenyldiazonium salts. Scan rate was 0.1 V s^{-1}.

During the first forward scan the CV shows a reduction peak at −1.5 V corresponding to the reduction of the attached nitrophenyl (NP) groups. The redox process is reversible as attested by the oxidation peak observed during the backward scan. Increasing the potential shows a reversible redox system at 0.15 V corresponding to the response of Fc^+/Fc imidazolium redox couple. For both redox processes, the peak-to-peak separation is close to 0 V indicating that the NP and Fc moieties are immobilized onto the Pt electrode. The electrochemical signal of Fc remains stable even after successive cycle (Figure 5) or after surface cleaning and sonication in ACN solution. The presence of the electrochemical signal of NP suggests the occurrence of self-grafting, without any external potential, onto reduced Pt surface. More interestingly, the Fc redox signal remains visible after the immobilization of NP layers which are known to act as an insulating layer. These results demonstrate the possibility of performing a multifunctional active system containing two different redox systems.

The electrochemical studies were complemented by a similar series of experiments using Pt foil as the working electrode followed by XPS analysis of the sample. Figure 6 shows the high resolution spectra at the N(1s) and Fe(2p) core level of the modified Pt substrate.

Compared to nonmodified Pt, the XPS spectra of the step-wisely modified platinum surface evidence several major features: (i) The platinum signal is strongly attenuated after the two modifications processes (cathodic polarization in ferrocene based IL followed by immersion in diazonium solution) from 31.6 at. % to 1.6 at. %, indicating the covering of

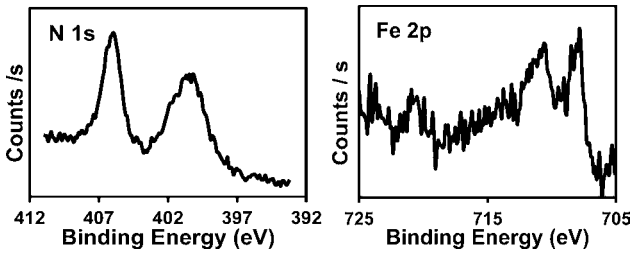


Figure 6. XPS high resolution spectra of N(1s) and Fe(2p) core level on platinum foil after cathodic polarization and reaction with 4-nitrophenyl diazonium.

the platinum surface by an organic layer. (ii) The C(1s) signal at 285 eV corresponding to aromatic carbon increases from 34.2 at. % to 71.7 at. %, indicating the presence of additional aromatic carbon onto the surface. (iii) As shown in Figure 6, a new peak appears at 406 eV, assigned to the N(1s) signal of the NO_2 groups. Another component of the N(1s) signal is also observed at 400 eV. This may be due both to some reduced nitrogen (possibly from the NO_2 group reduction under the X-beam, reduction by the reduced Pt phase) and to the surface contamination of the platinum sample (a similar signal is visible on the Pt sample before any treatment). (iv) The peak corresponding to the Fe(2p) core level is still visible as illustrated in Figure 6. The Fe(2p) doublet is ill defined compared to Figure 4C. This difference could be ascribed to the presence of the nitrophenyl added layer which attenuated the intensity of the peak. (v) All these results confirm the presence of the nitrophenyl layer and Fc groups onto the Pt surface, suggesting the formation of a redox multifunctional surface.

■ CONCLUSION

The cathodic polarization of a platinum electrode in ferrocène based ionic liquid, 1-ferrocenylethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide, deeply modifies the chemical nature of the starting material. With rather mild reactions conditions, ferrocène imidazolium platinide-like phases were produced. The electrochemical characterization of the reduced phase evidences the presence of the ferrocene signal and leads to the estimation of the apparent electron transfer rate which is found to 1 order of magnitude smaller than that reported when Fc units are covalently attached onto electrode material in a self-assembled monolayer configuration. The surface concentration of Fc moieties was found to be at least 1 order of magnitude higher than Fc-SAM. All these differences recommend the occurrence of Fc intercalation in platinum during the cathodic polarization. XPS investigations clearly show a significant change in the chemical nature of the Pt after treatment. Indeed, the strong attenuation of the Pt peak, the increase of the aromatic C(1s) signal, and the appearance of the Fe(2p) peak suggest strongly the presence of ferrocene imidazolium into or onto the platinum surface. Moreover, deep analyses of the XPS spectra confirm the intercalation of the ferrocenyl-imidazolium in platinum after the cathodic polarization.

The generated platinides phases display strong reductive properties that can be used to induce spontaneous grafting reactions such as the reduction of aryldiazonium salts. Cyclic voltammetry and X-ray photoelectron spectroscopy experiments show that the reaction results in the irreversible formation of strongly bound organic nitrophenyl layers. Interestingly, a bilayered active surface containing two redox systems (ferrocene and nitrophenyl) has been obtained. Consequently, it should be possible to extend the procedure presented here for the controlled preparation of several multifunctional metal−organic and structured interfaces.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bard, A. J.; Statmann, M.; Rubinstein, I.; Fujihira, M.; Rusling, J.-F. *Modified Electrodes Encyclopedia of Electrochemistry*; Wiley: New York, 2007; Vol. *10*.

(2) (a) Hermelin, E.; Petitjean, J.; Lacroix, J. C.; Chane-Ching, K. I.; Tanguy, J.; Lacaze, P. C. *Chem. Mater.* **2008**, *20*, 4447−4456. (b) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271−1308.

(3) (a) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437. (b) Hauquier, F.; Ghilane, J.; Fabre, B.; Hapiot, P. *J. Am. Chem. Soc.* **2008**, *130*, 2748−2749.

(4) Gooding, J. J.; Ciampi, S. *Chem. Soc. Rev.* **2011**, *40*, 2704−2718.

(5) Melendres, C. A. *J. Electrochem. Soc.* **1977**, *124*, 650.

(6) (a) Baranski, A. S.; Fawcett, W. R. *J. Electrochem. Soc.* **1982**, *129*, 901. (b) Kariv-Miller, E.; Nanjundiah, C.; Eaton, J.; Swenson, K. E. *J. Electroanal. Chem.* **1984**, *167*, 141.

(7) (a) Garcia, E.; Cowley, A. H.; Bard, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 6082. (b) Aberdam, D.; Salem, C.; Durand, R.; Faure, R. *J. Electroanal. Chem.* **1990**, *239*, 71. (c) Radovic, B. S.; Edwards, R. A. H.; Jovicevic, J. N. *J. Electroanal. Chem.* **1997**, *428*, 113.

(8) (a) Aberdam, D.; Salem, C.; Durand, R.; Faure, R. *J. Electroanal. Chem.* **1990**, *239*, 71. (b) Svetlicic, V.; Lawin, P. B.; Kariv-Miller, E. *J. Electroanal. Chem.* **1990**, *284*, 185.

(9) (a) Fidler, M. M.; Svetlicic, V.; Kariv-Miller, E. *J. Electroanal. Chem.* **1993**, *360*, 221. (b) Kariv-Miller, E.; Lehman, G. K.; Svetlicic, V. *J. Electroanal. Chem.* **1997**, *431*, 87.

(10) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

(11) Zintl, E.; Dullenkopf, W. *Z. Phys. Chem. B* **1932**, *16*, 183.

(12) Zintl, E.; Harder, A. *Z. Phys. Chem. A* **1931**, *154*, 47.

(13) Karpov, A.; Nuss, J.; Wedig, U.; Jansen, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4818.

(14) Köhler, J.; Chang, J.-H.; Whangbo, M.-H. *J. Am. Chem. Soc.* **2005**, *127*, 2277.

(15) (a) Rodriguez, P.; Tichelaar, F. D.; Koper, M. T. M.; Yanson, A. I. *J. Am. Chem. Soc.* **2011**, *133*, 17626−17629. (b) Yanson, A. I.; Rodriguez, P.; Garcia-Araez, N.; Mom, R. V.; Tichelaar, F. D.; Koper, M. T. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 6346−6350.

(16) (a) Cougnon, C.; Simonet, J. *Platinum Met. Rev.* **2002**, *46*, 94. (b) Cougnon, C.; Simonet, J. *Electrochem. Commun.* **2002**, *4*, 266. (c) Cougnon, C.; Simonet, J. *J. Electronal. Chem* **2002**, *531*, 179. (d) Simonet, J. *Electrochem. Commun.* **2003**, *5*, 439.

(17) (a) Ghilane, J.; Guilloux-Viry, M.; Lagrost, C.; Hapiot, P.; Simonet, J. *J. Phys. Chem. B* **2005**, *109*, 14925. (b) Bergamini, J.-F.; Ghilane, J.; Guilloux-Viry, M.; Hapiot, P. *Electrochem. Commun.* **2004**, *6*, 188.

(18) Bard, A. J.; Zoski, C. G. *Electroanalytical Chemistry, A Series of Advances*; Marcel Dekker: New York, 2010; Vol. *23*.

(19) Ghilane, J.; Guilloux-Viry, M.; Lagrost, C.; Simonet, J.; Hapiot, P. *J. Am. Chem. Soc.* **2007**, *129*, 6654−6661.

(20) Ghilane, J.; Lagrost, C.; Guilloux-Viry, M.; Simonet, J.; Delamar, M.; Mangeney, C.; Hapiot, P. *J. Phys. Chem. C.* **2007**, *111*, 5701−5707.

(21) Fontaine, O.; Lagrost, C.; Ghilane, J.; Martin, P.; Trippé, G.; Fave, C.; Lacroix, J.-C.; Hapiot, P.; Randriamahazaka, H. *J. Electroanal. Chem.* **2009**, *632*, 88−96.
(22) Ghilane, J.; Fontaine, O.; Martin, P.; Lacroix, J.-C.; Randriamahazaka, H. *Electrochem. Commun.* **2008**, *10*, 1205−1209.
(23) Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883.
(24) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429.
(25) Bélanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995.
(26) (a) Brooksby, P. A.; Downard, A. J. *Langmuir* **2004**, *20*, 5038−5045. (b) Delamar, M.; Desarmot, G.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *Carbon* **1997**, *35*, 801. (c) Santos, L.; Ghilane, J.; Martin, P.; Lacaze, P.-C.; Randriamahazaka, H.; Lacroix, J.-C. *J. Am. Chem. Soc.* **2010**, *132*, 1690.
(27) (a) Ghilane, J.; Martin, P.; Fontaine, O.; Lacroix, J.-C.; Randriamahazaka, H. *Electrochem. Commun.* **2008**, *10*, 1060−1063. (b) Fontaine, O.; Ghilane, J.; Martin, P.; Lacroix, J.-C.; Randriamahazaka, H. *Langmuir* **2010**, *26*, 18542−18549.
(28) (a) Bernard, M. C.; Chaussé, A.; Cabet-Deliry, E.; Chehimi, M. M.; Pinson, J.; Podvorica, F.; Vautrin-Ul, C. *Chem. Mater.* **2003**, *15*, 3450. (b) Chaussé, A.; Chehimi, M. M.; Karsi, N.; Pinson, J.; Podvorica, F.; Vautrin-Ul, C. *Chem. Mater.* **2002**, *14*, 392−400.
(29) (a) Henry de Villeneuve, C.; Pinson, J.; Bernard, M. C.; Allongue, P. *J. Phys. Chem. B.* **1997**, *101*, 2415. (b) Adenier, A.; Bernard, M. C.; Chehimi, M. M.; Cabet-Deliry, E.; Desbat, B.; Fagebaume, O.; Pinson, J.; Podvorica, F. *J. Am. Chem. Soc.* **2001**, *123*, 4541. (c) McCreery, R. L. *Chem. Mater.* **2004**, *16*, 4477−4496.
(30) (a) Fave, C.; Noel, V.; Ghilane, J.; Trippe-Allard, G.; Randriamahazaka, H.; Lacroix, J.-C. *J. Phys. Chem. C.* **2008**, *112*, 18638. (b) Ernst, S.; Aldous, L.; Compton, R. G. *Chem. Phys. Lett.* **2011**, *511*, 461−465. (c) Garrett, D. J.; Jenkins, P.; Polson, M. I. J.; Leech, D.; Baronian, K. H. R.; Downard, A. J. *Electrochim. Acta* **2011**, *56*, 2213−2220.
(31) (a) Tessier, L.; Deniau, G.; Charleux, B.; Palacin, S. *Chem. Mater.* **2009**, *21*, 4261−4274. (b) Deniau, G.; Azoulay, L.; Bougerolles, L.; Palacin, S. *Chem. Mater.* **2006**, *18*, 5421−5428. (c) Stockhausen, V.; Ghilane, J.; Martin, P.; Trippé-Allard, G.; Randriamahazaka, H.; Lacroix, J.-C. *J. Am. Chem. Soc.* **2009**, *131*, 14920−14927.
(32) (a) Chen, P.; McCreery, R. L. *Anal. Chem.* **1996**, *68*, 3958. (b) Paulik, M. G.; Brooksby, P. A.; Abell, A. D.; Downard, A. J. *J. Phys. Chem. C* **2007**, *111*, 7808−7815. (c) Brooksby, P. A.; Downard, A. J. *Langmuir* **2004**, *20*, 5038−5045. (d) Deniau, G.; Azoulay, L.; Bougerolles, L.; Palacin, S. *Chem. Mater.* **2006**, *18*, 5421−5428.
(33) (a) Santos, L.; Ghilane, J.; Lacroix, J.-C. *J. Am. Chem. Soc.* **2012**, *134*, 5476−5479. (b) Harper, J. C.; Polsky, R.; Wheeler, D. R.; Lopez, D. M.; Arango, D. C.; Brozik, S. M. *Langmuir* **2009**, *25*, 3282−3288. (c) Liu, G.; Liu, J.; Böcking, T.; Eggers, P. K.; Gooding, J. J. *Chem. Phys.* **2005**, *319*, 136−146. (d) Louault, C.; d'Amours, M.; Bélanger, D. *Chem. Phys. Chem.* **2008**, *9*, 1164−1170. (e) Liu, G.; Paddon-Row, M. N.; Gooding, J. J. *Electrochem. Commun.* **2007**, *9*, 2218−2223. (f) Brooksby, P. A.; Downard, A. J. *Langmuir* **2005**, *21*, 1672−1675.
(34) (a) Jin, Z.; McNicholas, T. P.; Shih, C.-J.; Wang, Q. H.; Paulus, G. L. C.; Hilmer, A. J.; Shimizu, S.; Strano, M. S. *Chem. Mater.* **2011**, *23*, 3362−3370. (b) Leroux, Y. R.; Hui, F.; Noël, J.-M.; Roux, C.; Downard, A. J.; Hapiot, P. *Langmuir* **2011**, *27*, 11222−11228. (c) Barras, A.; Szunerits, S.; Marcon, L.; Monfilliette-Dupont, N.; Boukherroub, R. *Langmuir* **2010**, *26*, 13168−13172. (d) Corgier, B. P.; Bélanger, D. *Langmuir* **2010**, *26*, 5991−5997.
(35) (a) Majumder, M.; Zhan, X.; Andrews, R.; Hinds, B. J. *Langmuir* **2007**, *23*, 8624−8631. (b) Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620−5686. (c) Vase, K. H.; Holm, A. H.; Norrman, K.; Pedersen, S. U.; Daasbjerg, K. *Langmuir* **2007**, *23*, 3786−3793.
(36) (a) Thomas, J.-L.; Howarth, J.; Hanlon, K.; McGuirk, D. *Tetrahedron Lett.* **2000**, *41*, 413. (b) Thomas, J.-L.; Howarth, J.; Kennedy, A. M. *Molecules* **2002**, *7*, 861. (c) Gao, Y.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 3406.
(37) Rogers, E. I.; Sljukic, B.; Hardacre, C.; Compton, R. G. *J. Chem. Eng. Data* **2009**, *54*, 2049−2053.
(38) Ghilane, J.; Hapiot, P.; Bard, A. J. *Anal. Chem.* **2006**, *78*, 6868−6872.
(39) Laviron, E. *J. Electroanal. Chem.* **1979**, *101*, 19−28.
(40) Fabre, B.; Hauquier, F. *J. Phys. Chem. B.* **2006**, *110*, 6848−6855.
(41) Janin, M.; Ghilane, J.; Randriamahazaka, H.; Lacroix, J. C. *Electrochem. Commun.* **2009**, *11*, 647−650.
(42) Walczak, M. M.; Popenoe, D. D.; Deinhammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687.
(43) Jouikov, V.; Simonet, J. *Langmuir* **2012**, *28*, 931−938.
(44) Chi, Y. S.; Hwang, S.; Lee, B. S.; Kwak, J.; Choi, I. S.; Lee, S. G. *Langmuir* **2005**, *21*, 4268.
(45) Karpov, A.; Konuma, M.; Jansen, M. *Chem. Commun.* **2006**, 838.
(46) Ghilane, J.; Trippe-Allard, G.; Lacroix, J. C. *Electrochem. Commun.* **2013**, *27*, 73−76.
(47) (a) MacFarlane, D. R.; Forsyth, M.; Howlett, P. C.; Pringle, J. M.; Sun, J.; Annat, G.; Neil, W.; Izgorodina, E. I. *Acc. Chem. Res.* **2007**, *40*, 1165−1173. (b) Howlett, P. C.; Izgorodina, E. I.; Forsyth, M.; MacFarlane, D. R. *Z. Phys. Chem.-Int. J. Res. Phys. Chem. Chem. Phys.* **2006**, *220*, 1483−1498.
(48) Ghilane, J.; Delamar, M.; Guilloux-Viry, M.; Lagrost, C.; Mangeney, C.; Hapiot, P. *Langmuir* **2005**, *21*, 6422−6429.