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# Study of the Electroless Deposition of Pd on Cu-Modified Graphite Electrodes by Metal Exchange Reaction

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The electroless deposition of Pd on Cu-modified graphite electrodes using a metal exchange reaction was investigated. The modification procedure consisted in the electrodeposition of Cu on the graphite electrode, subsequently replaced by Pd at open circuit in a Pd-containing solution. The influence of experimental conditions on the exchange reaction rate, the chemical state and the distribution of Cu and Pd on the electrode surface are highlighted. The resulting deposits were studied using cyclic voltammetry, atomic absorption spectroscopy, scanning electron microscopy, energy-dispersive X-ray, and X-ray photoelectron spectroscopy. The last technique confirmed the spontaneous oxidation of Cu by the Pd complexes adsorbed on the electrode surface and also demonstrated that Pd/Cu atomic ratio increases by increasing the $PdCl_2$ concentration. An increase of the Pd electroactive surface area, estimated by cyclic voltammetry, was observed by increasing the initial Cu loading, the exchange reaction time or the $PdCl_2$ concentration. It was also demonstrated that the metal exchange reaction leads to the formation of a Cu core enveloped by a Pd shell for every $PdCl_2$ concentration investigated here. The corrosion rate for the corrosion of copper by a Pd complex was determined and compared with that of the corrosion of copper by oxygen. On the basis of our observations, a general model to describe the Cu−Pd exchange process and the resulting electrode surface composition was proposed.

## Introduction

Palladium-based catalysts play an important role in numerous industrial fields, including the catalytic hydrogenation,[1,2] the combustion of methane,[3,4] the oxidation and decomposition of ammonia,[5,6] and the removal of nitrate and nitrite from water.[7,8] However, the efficiency of these catalysts is strongly affected by the preparation technique. A wide variety of modification methods has been reported in the literature for the deposition of Pd on solid surfaces, such as ion exchange.[9] impregnation,[10,11] polyol process,[12] photocatalytic deposition,[13] and sol–gel method.[14,15] These techniques generally employ Pd with an active component precursor and are classified as nonselective depositions, because no interaction exists between Pd and the precursor. Their major disadvantage is the weak interaction between the two components.[16] Thus, selective depositions that should be more efficient to achieve a stronger interaction between both components were developed. One of the most appropriate techniques is the deposition of Pd via metal exchange reaction. In this case, the precursor is usually a non-noble metal M with standard electrochemical potential lower than the one of Pd. This technique involves, first, the deposition of a layer of M on the surface (M/surface). Second, this surface is immersed in a Pd-containing solution. The metal M is oxidized by Pd, which undergoes simultaneously a reduction and deposition on the surface (Pd/surface).[17] The irreversible replacement of M occurs spontaneously at open-circuit potential following this redox equation

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$$M^0\text{/surface}+(m/2)Pd^{2+} \rightarrow M^{m+}+(m/2)Pd^0\text{/surface} \quad (1)$$

The driving force for this exchange reaction is the positive difference between the equilibrium potential of Pd in contact with its complexes, $E(Pd^{2+}/Pd)$, and the equilibrium potential of the metal M present on the surface, $E(M^{m+}/M^0\text{/surface})$.[18] Through this mechanism, the amount of Pd could be determined theoretically by the stoichiometry of the redox reaction. Recently, a number of researchers have used successfully such exchange reaction for different applications. Kokkinidis et al. deposited Pt on Ti substrate at open-circuit potential for the catalysis of the hydrogen evolution reaction.[19] Adžić and co-workers have also succeeded in depositing spontaneously a Pt layer on Au(111) and Pd(111) substrates by the replacement of a upd Cu layer.[17,20] Such a technique was very attractive since the spontaneous deposition of Pt on noble metals is thermodynamically impossible. Afterward, Van Brussel et al. used the same technique to prepare gold-supported Pt electrocatalysts by replacing a upd Cu layer for the catalysis of the oxygen reduction reaction.[21] Very recently, gold nanocages were synthesized for biomedical applications and also Pt nanofilms were formed following a metal exchange mechanism.[22,23] Such a technique allows the deposition of various metallic films structure by controlling the electronic charges of both metals. When Pd and M present the same oxidation state ($m = 2$ in eq 1), one Pd atom replaces one M atom, i.e., the M monolayer is replaced by a Pd monolayer and the exchange reaction may be considered as a replacement reaction.[24] On the other hand, when the metal M supplies one electron per one Pd atom, the M monolayer is replaced by a half-of Pd monolayer and the exchange reaction become a replacement-displacement reaction.[21] Finally, the formation of Pd multilayer on a Cu-modified gold electrode was achieved by using repetitive upd/replacement cycle.[23,24] In this case, the relevant standard potentials (given versus Ag/AgCl) are as follows: $Pd^{2+}/Pd$, 0.72 V; $PdCl_4^{2-}/Pd$, 0.44 V.[25] These equilibrium potentials are much more positive than that for $Cu^{2+}/Cu$ couple, 0.15 V,[25] confirming therefore that eq 1 is thermodynamically favorable.

In this study, Pd is deposited onto a Cu-modified pyrolytic graphite electrode via an exchange reaction process. The pyrolytic graphite is one of most interesting substrates for further industrial application since it presents suitable electrical and mechanical properties, a high thermal stability and a low price. The bimetallic system generated in this way will be applied for the nitrate reduction reaction and investigated in a further publication.[26] As described elsewhere,[27,28] the Cu−Pd system has been successfully applied for the electrocatalysis of the nitrate reduction showing the highest activity and an appropriate selectivity among transition and coinage metals. Because of the roles of both Cu and Pd in the nitrate reduction mechanism, the experimental conditions for the replacement of Cu by Pd in this work should ensure the presence of both metallic sites on the surface. The system developed here offers the formation of a thin Pd film, which present a great advantage because the Pd price restrains its industrial application. Moreover, the exchange reaction is kinetically rapid and simple and leads to an excellent contact between both metals. A number of studies have focused on the replacement of a upd Cu layer, which generally leads to the formation of a uniform noble metal monolayer.[17,23] In the present work, the exchange reaction is performed on Cu particles deposited on a graphite substrate and, consequently, depending on the experimental conditions used the formation of Cu−Pd clusters and/or submonolayer Pd coverage could be achieved.

The aim of the present study is the simultaneous control of the composition and the morphology of the modified electrode surface. The physicochemical properties of the deposited catalyst are also investigated here. To the best of our knowledge, few articles have focused on the metal exchange mechanism.[23,24,29] This article presents a detailed study of the exchange reaction process of Cu metal islands deposited on the graphite electrode by Pd as a function of the deposited Cu mass, the $PdCl_2$ concentration in the solution and the exchange time. The exchange reaction was studied by following the open-circuit potential with time of Cu-modified graphite electrodes in contact with Pd complex solutions. The electrochemical characterization was based on cyclic voltammetry. The morphology and composition of the modified surfaces were determined by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS) techniques.

## Experimental Section

The typical geometrical surface areas of the graphite electrodes (Electrolytica SG-202) varied from 2.0 to 3.5 cm$^2$. The electrodes were treated before each use; by first washing with nanopure $H_2O$ (18 MΩ, obtained from a Sybron/ Barnstead Nanopure system) and polishing with alumina (Buhler) powder 0.05 $\mu$m. Then, the electrodes were repeatedly washed with ultrasound successively in nanopure $H_2O$, 1 M $HNO_3$ (ACS grade, EMD), and $CH_3OH$ (HPLC grade) for 30 min. Finally, the electrodes were dried in a vacuum at 100 °C for 6 h to remove solvents.

The electrochemical modification and characterization of the graphite surface were performed in a conventional three-electrode cell composed by a pyrolytic graphite working electrode, a Pt grid as a counter electrode, and Ag/AgCl (3 M KCl) as a reference electrode in the presence of acidic media, while Hg/HgO (1 M NaOH) was employed as a reference electrode in the presence of

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highly alkaline media. The electrochemical experiments were carried out with a potentiostat/galvanostat (Solartron SI-1287) interfaced with a PC and the electrochemical setups were controlled with CorrWare 2 and CorrView 2 software (Scribner Associates).

Before the electrochemical modification, graphite electrodes were electrochemically pretreated by cycling (3 times) between 0 and −0.5 V, at 10 mV $s^{-1}$, in 1.8 M $H_2SO_4$ aqueous solution (ACS grade, Fisher Scientific). The electrodeposition of Cu on the graphite electrode was performed from 0.1 M $Cu(NO_3)_2 \cdot 6H_2O$ (99.999%, Alfa Aesar) in a 1.8 M $H_2SO_4$ aqueous solution, as described elsewhere.[30] The Cu deposition was carried out potentiostatically over a wide potential range (from 20 to −500 mV), under quiescent conditions and the deposition time was fixed at 20 s. Typically, the volume of the electrolyte solution was about 20 mL. After each modification, the graphite electrode was thoroughly washed with nanopure $H_2O$. The amount of Cu deposited on the resulting modified electrode was estimated by stripping voltammetry performed in the modification medium between the open-circuit potential and 0.5 V, at 5 mV.$s^{-1}$. The electroless deposition of Pd was carried out from an aqueous solution containing $PdCl_2$ (99%, Aldrich) in 0.1 M $HClO_4$ (ACS grade, BDH). The $PdCl_2$ concentration was varied between 1 and 10 mM. The deposition times were 30 s or 3 min, and a typical electrolyte volume was about 5 mL. The electrolyte solutions were prepared using nanopure $H_2O$ and deaerated before measurements by bubbling of $N_2$ (99.998%, Praxair). Following the exchange reaction, the graphite electrode was rinsed in 1 M $HNO_3$ and nanopure $H_2O$ and the concentration of Cu present in the electrolyte solution was determined by atomic absorption spectroscopy (Varian SpectrAA 220FS) at 324.8 nm.

The morphology of Cu−Pd deposits was examined using a Hitachi S-4300 scanning electron microscope (SEM) equipped with an Energy Dispersive X-ray (EDX) detector. The data were taken at an incident electron beam energy of 20 kV. The probe depth/volume of EDX is about 1 $\mu$m/1 $\mu$m. The detection limit of EDX measurements with our equipment is 0.05% (500 ppm) for Cu and Pd and 1% for C and O and the experimental parameters were optimized to increase the S/N ratio. X-ray photoelectron spectra (XPS) were obtained for the modified graphite plates with an Axis Ultra spectrometer (Kratos Analytical) equipped with a hemispherical analyzer and an Al anode (monochromatic $K_\alpha$ X-rays at 1486.6 eV) used at 12–14 kV and 10–20 mA. The theoretical energy resolution of the XPS instrument is 0.58 eV for Ag $3d_{5/2}$ full peak width at half-maximum. The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below $1 \times 10^{-9}$ Torr. XPS survey and core level spectra were recorded for the modified electrodes. For the survey and the high-resolution spectra, the step was 330 and 120 meV and the analyzer pass energy was fixed at 160 and 20 eV in the CAE mode, respectively. The used calibration method was based on the C 1s peak of carbon at 284.5 eV. The core level spectra were peak-fitted using the CasaXPS software. The data were treated by a Shirley background type. The core level spectra were used to evaluate the atomic concentrations of the species present at the graphite plate. The atomic concentration (at %) of each element was determined from the relative peak area of the spectra ($A_i$) and the corresponding sensitivity factors ($s_i$) according to the following equation at % $= (A_i/s_i) / \Sigma(A_i/s_i)$

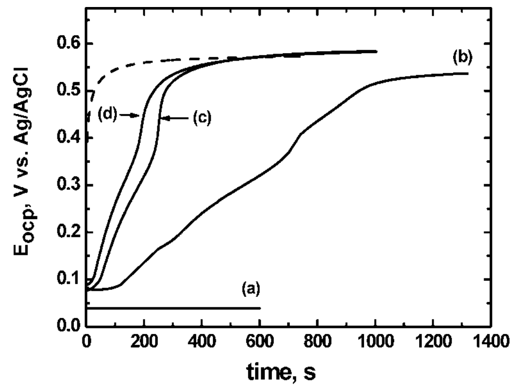

**Figure 1.** Variation of $E_{ocp}$ with time of Cu-modified graphite electrode immersed in a $PdCl_2$ + 0.1 M $HClO_4$ solution. The Cu loading is about 10 $\mu$g $cm^{-2}$ (dashed line) and 80 $\mu$g $cm^{-2}$ (solid lines). The $PdCl_2$ concentration is 0 (a), 3 (b), 7 (c), and 10 mM (d, dashed line).

The sensitivity factor used for C 1s, N 1s, O 1s, Pd 3d, and Cu $2p_{3/2}$ components were, respectively, equal to 1, 1.8, 2.93, 16, and 25.4 and obtained from CasaXPS, based on conventional Scofield values.[31]

## Results and Discussion

**Metal Exchange Reaction Followed by the Open-Circuit Potential.** The metal exchange reaction occurs by a spontaneous irreversible redox reaction in which one $Pd^{2+}$ ion from the solution oxidizes one Cu atom to generate $Cu^{2+}$. Simultaneously, $Pd^{2+}$ is reduced to $Pd^0$ and deposited on the electrode surface as described by the following equation

$$Cu^0/\text{graphite} + Pd^{2+} \rightarrow Pd^0/\text{graphite} + Cu^{2+} \qquad (2)$$

To characterize the Cu oxidation process during the exchange reaction, the change of the open-circuit potential ($E_{ocp}$) with time was determined for the Cu/graphite electrode in contact with Pd complexes (Figure 1). For a Cu loading of 80 $\mu$g.$cm^{-2}$, a positive variation of $E_{ocp}$ from 0.08 V to a steady-state value of 0.55 V is observed after 500 s of exchange time in the presence of 7 or 10 mM $PdCl_2$ (curves c and d in Figure 1, respectively). This time corresponds to the one required to complete the exchange reaction process. Previous studies have shown that the replacement of an upd Cu layer by Pd is complete after 180 s of exchange reaction time in a 10 mM Pd-containing solution.[17] On the other hand, the steady-state value of $E_{ocp}$ is reached after 1000 s when the $PdCl_2$ concentration is reduced to 3 mM (Figure 1, curve b).

Figure 1 also demonstrates that the change of $E_{ocp}$ with time depends on the Cu loading. In fact, for a smaller Cu mass (10 $\mu$g $cm^{-2}$, dashed line), the potential shifts to 0.55 V after only 50 s of exchange time, comparatively to 500 s for a larger deposited Cu mass (80 $\mu$g $cm^{-2}$, Figure 1, curve d). In that case, the variation of $E_{ocp}$ with time presents two steps that might correspond to different phenomena occurring during the replacement mechanism (vide infra). The rapid oxidation of Cu at the electrode surface reflects a fast

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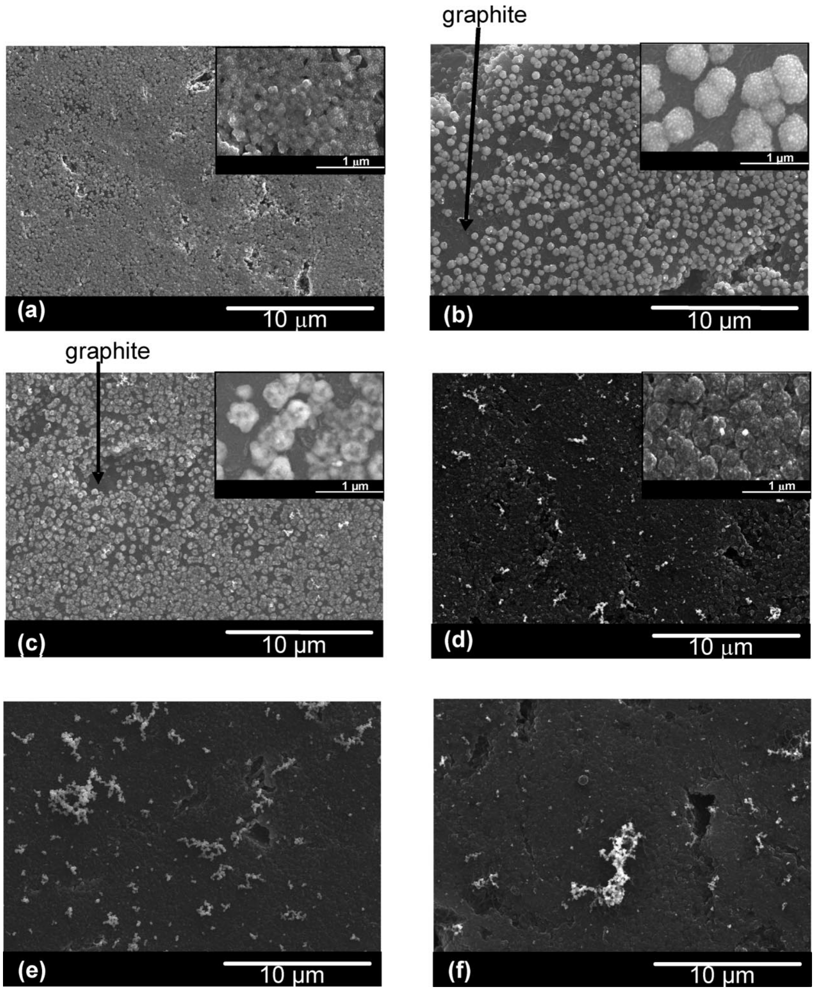

**Figure 2.** (a) SEM photomicrograph of a Cu/graphite electrode. Cu was deposited in a 0.1 M $Cu(NO_3)_2$ + 1.8 M $H_2SO_4$ solution at –0.2 V for 20 s; SEM photomicrographs of Cu−Pd/graphite electrodes, the exchange reaction was performed during 30 s in a $PdCl_2$ + 0.1 M $HClO_4$. The $PdCl_2$ concentration was (b) 1, (c) 3, (d) 5, (e) 7, and (f) 10 mM. In figures (b) and (c), an area of the underlying graphite substrate is indicated.

reduction of $Pd^{2+}$ and corresponds then to an instantaneous nucleation type.[32] In the absence of Pd complexes in the solution (Figure 1, curve a), the $E_{ocp}$ of Cu-modified graphite electrode is 0.04 V and remains unaffected.

**SEM Observations.** The SEM micrographs of Cu and Cu-Pd deposits obtained from different concentrations of $PdCl_2$ are presented in Figures 2a and 2b−f, respectively. Copper is deposited at a potential of −0.2 V during 20 s, which led to a Cu loading about 80 $\mu$g cm$^{-2}$ corresponding to a film thickness of 90 nm, according to Faraday law. Figure 2a shows that the graphite surface is completely covered by a homogeneous film of Cu and the mean diameter of Cu particles is about 200 nm. Figures 2b−f shows that the immersion of the Cu/graphite electrode for 30 s in a Pd-containing solution involves dramatic morphological and structural changes of the surface. For low $PdCl_2$ concentrations (1, 3, and 5 mM), the presence of voids is observed at the electrode surface. The darker areas of the micrographs correspond to the graphite substrate. The SEM micrographs also show that the mean particle size varies from 200 nm for the Cu/graphite electrode to 600 and 400 nm for the Pd-Cu/graphite prepared from 1 and 3 mM $PdCl_2$ solutions, respectively. Figure 2d−f shows that increasing the Pd concentration causes the formation of aggregates. The mean aggregate size increases with the Pd concentration and, at the same time, their number decreases. EDX analysis revealed that the darker surface observed in Figure 2d−f below the agglomerates corresponds to a Cu−Pd film. The same behavior was obtained, as a function of the $PdCl_2$ concentration, with a graphite electrode modified by a submonolayer of Cu (data not shown).

For low $PdCl_2$ concentrations, the presence of voids (uncovered surface) on specific sites of the graphite electrode surface indicates that the replacement reaction was initiated locally, at the most energetic sites.[29] rather than over the entire surface. Some of the copper atoms were oxidized and desorbed from areas of the surface where Pd was not deposited. The replacement of one Cu atom by one Pd atom should not leave void on the graphite surface since the atomic volume of Pd is higher than the Cu one (8.9 vs 7.1 cm$^3$ mol$^{-1}$). Prior to the replacement of Cu atoms, the Pd complexes should adsorb on the Cu/graphite surface and following electron transfer (eq 2) form a Pd adatom. When the $PdCl_2$ concentration is small, the Cu atoms present on the graphite surface are partially covered by Pd adatoms even for the experimental conditions investigated here, the amount

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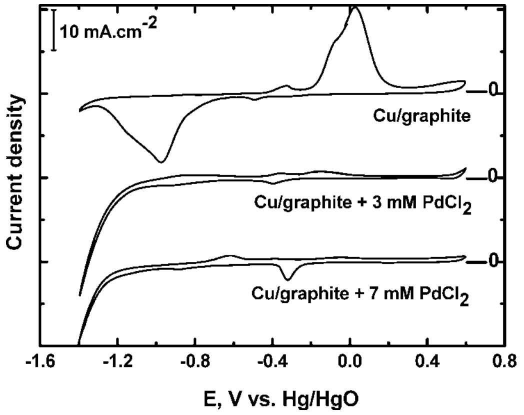

**Figure 3.** Cyclic voltamograms of Cu/graphite electrode and Pd−Cu/graphite electrodes recorded in 1 M NaOH at 50 mV/s. Cu was deposited on the graphite electrode from a 0.1 M Cu(NO$_3$)$_2$ + 1.8 M H$_2$SO$_4$ solution at –0.2 V for 20 s. Pd was deposited for 30 s in a 3 or 7 mM PdCl$_2$ + 0.1 M HClO$_4$ solution.

of Pd present in the electrolyte ($5 \times 10^{-6}$ mol for 1 mM PdCl$_2$) is slightly in excess comparatively to the deposited Cu amount ($4 \times 10^{-6}$ mol). In this case, the Cu atom covered by Pd adatom as well as their neighboring (and noncovered) Cu atoms can dissolve. The reaction is like a corrosion process, where Cu is being oxidized at the anodic site and the released electrons can reduce Pd(II) to Pd atoms at the cathodic site. A similar behavior was observed elsewhere for low concentrations of the noble metal.[24,29] According to Mrozek et al., the formation of a pinhole-free film was not evident even after multiple replacement cycles of upd Cu.[24] However, Sun and Xia demonstrated that when the noble metal concentration is high enough, the size of each hole on the surface would start to shrink due to a mass diffusion process, leading to the formation of a boxlike structure.[29] Thus, the Pd coating can become thicker as more as Pd atoms were generated by the exchange reaction. In the present case, the increase of the PdCl$_2$ concentration prevents the formation of voids on the electrode surface. The presence of aggregates at higher PdCl$_2$ concentrations follows a coalescence and agglomeration process created by a diffusion-coupling mechanism between neighboring particles.[17,19] Increasing the PdCl$_2$ concentration should lead to an increase in the amount of Pd adatoms and a decrease of the distance between neighboring Pd adatoms which facilitates their overlapping and agglomeration. The formation of such Pd aggregates can free some Cu surface atoms and then the metal exchange mechanism can carry on, which might explain the "multi-step" increase in the $E_{\text{ocp}}$ with time in case of a large Cu deposited mass (Figure 1). On the other hand, Van Brussel et al.[21] reported that once thin film of electrodeposited Cu is covered by a Pt layer the displacement rate drops to zero because the metal exchange mechanism occurs only when Cu is in direct contact with Pt complexes.[17,21]

**Quantification of the Exchange Reaction by Cyclic Voltammetry.** The exchange reaction of Cu with Pd was characterized by cyclic voltammetry. The presence of both Cu and Pd atoms on the modified electrodes is confirmed in Figure 3, which compares the cyclic voltammograms of Cu/graphite and Pd-Cu/graphite electrodes recorded in 1 M NaOH. The cyclic voltamogram of the Cu/graphite electrode is similar to that of a Cu electrode recorded in alkaline media.[33–36] The growth of an oxide film occurs on the electrode surface during the positive sweep of the potential. Initially, this process leads to the formation of Cu$_2$O at −0.33 V, then CuO and/or Cu(OH)$_2$ at 0 V, and finally Cu$_2$O$_3$ at 0.54 V. After switching the sweep direction, the reduction peaks of Cu oxides appear at −0.33, −0.50, and −0.98 V. The corresponding reactions are attributed to the formation of CuO, Cu$_2$O and Cu$^0$, respectively. A significant modification of the cyclic voltamogram is observed following the exchange reaction. In fact, the cyclic voltamogram of the Pd-Cu/graphite electrode generated by metal exchange with a 3 mM PdCl$_2$ solution shows an onset of the hydrogen evolution reaction (HER) at about −1.1 V followed by a continuous increase in the cathodic current. In addition, a decrease in the current density is observed for the main Cu oxidation and reduction peaks, while a cathodic wave appears at −0.38 V and corresponds to the reduction of the Pd oxide layer formed during the positive potential sweep.[37] On the other hand, the cyclic voltamogram of the Pd-Cu/graphite electrode performed from 7 mM PdCl$_2$ shows smaller Cu oxidation and reduction peaks. The cathodic peak observed at −0.9 V and the anodic peak at −0.6 V represent the hydrogen adsorption and desorption processes on Pd sites, respectively.[38,39] Also, an increase in the current density is observed for the Pd oxide wave situated at −0.32 V. These results suggest that, independently on the PdCl$_2$ concentration, Cu is not completely replaced by Pd since the Cu oxidation peak is still observed on the cyclic voltamograms of Pd−Cu/graphite electrodes. Nevertheless, a lower amount of Cu is still present on the electrode surface after an exchange reaction in the presence of 7 mM rather than 3 mM PdCl$_2$.

Figure 4 presents the cyclic voltamograms used to evaluate the reduction charge of the Pd surface oxides as a function of the switching potential which was varied from −0.1 to 0.7 V. The data show that the voltammetric charge increases and the peak potential become more negative as the positive limit of the sweep increases, as previously observed for the Pd-Sn system.[37] The electrochemical surface of Pd ($S_{\text{Pd}}$) was estimated from the charge involved during the reduction of one monolayer of oxide (405 $\mu$C.cm$^{-2}$), assuming that Pd oxides are PdO and Pd(OH)$_2$.[40,41] The inset of Figure 4 shows that $S_{\text{Pd}}$ increases linearly with the anodic limit until a potential where the slope changes. That point corresponds to the formation of a complete Pd oxide monolayer. At more positive potential, further oxidation occurs on the surface

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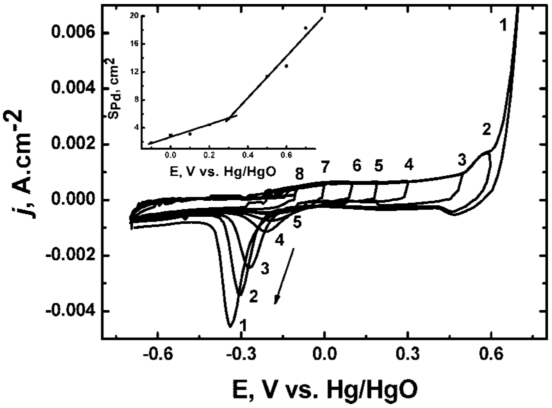

**Figure 4.** Cyclic voltamograms of Pd−Cu/graphite electrode recorded in 1 M NaOH at 50 mV/s. The positive potential limit was varied from –0.1 to 0.7 V. The window inset shows the variation of Pd electroactive surface area ($S_{Pd}$) versus the positive potential limit. Cu was deposited on the graphite electrode from a 0.1 M $Cu(NO_3)_2$ + 1.8 M $H_2SO_4$ solution at –0.5 V for 20 s. Pd was deposited for 3 min. in a 10 mM $PdCl_2$ + 0.1 M $HClO_4$ solution.

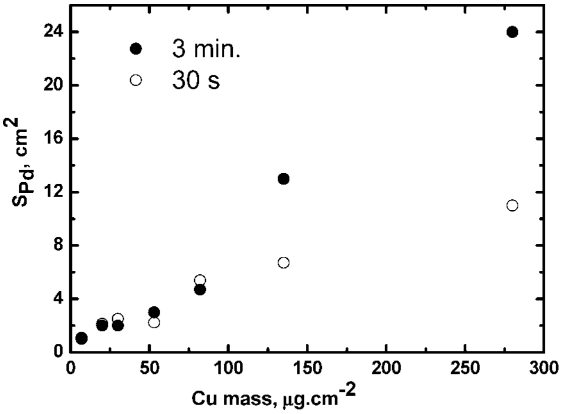

**Figure 5.** Variation of Pd electroactive surface area ($S_{Pd}$) versus Cu deposited mass. Cu was deposited at different potentials in 0.1 M $Cu(NO_3)_2$ + 1.8 M $H_2SO_4$ solution. Time deposition was 20 s. Pd was deposited in 10 mM $PdCl_2$ + 0.1 M $HClO_4$ solution during 30 s (○) and 3 min (•).

and leads to higher valence Pd oxides.[37] Similar experiments with electrodes having various Cu/Pd ratios revealed that the potential where the break in the straight lines is observed is equal to 0.3 V ± 5%. Even for high loaded Cu surfaces, the CuO reduction does not interfere with that of PdO. In addition, the potential and the intensity of the cathodic peak were not affected by saturating the electrolyte solution by either oxygen or nitrogen. This observation indicates that the $O_2$ reduction do not overlap with the PdO reduction. Henceforth, the $S_{Pd}$ values were evaluated systematically using 0.3 V as the anodic potential limit.

The $S_{Pd}$ values are calculated for Cu deposited masses between 0 and 300 $\mu$g cm$^{-2}$ for exchange times of 30 s or 3 min in presence of 10 mM $PdCl_2$. The different Cu masses are obtained by varying the deposition potential from 20 to −500 mV while keeping the deposition time constant. Figure 5 shows that the $S_{Pd}$ value increases with increasing the Cu deposited mass. However, the $S_{Pd}$ values do not appear to be affected by the exchange time when the deposited Cu mass is below to 80 $\mu$g cm$^{-2}$. Otherwise, the $S_{Pd}$ grows with increasing the reaction time. This behavior may be due to the longer exchange time required at higher Cu loading (Figure 1).

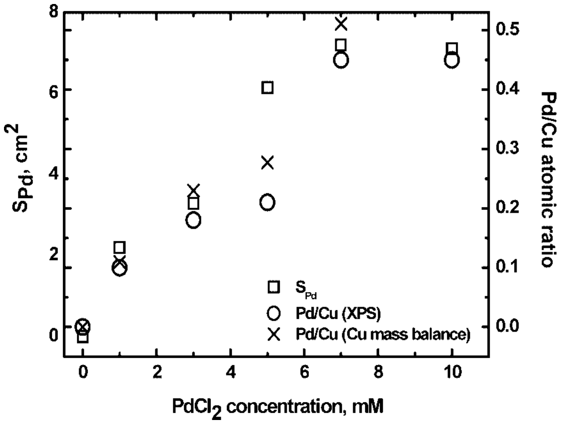

**Figure 6.** Variation of the electroactive Pd surface area ($S_{Pd}$) (□) and of the atomic ratio of Pd/Cu, estimated by XPS (○) and from the Cu mass balance (×), as a function of the $PdCl_2$ concentration. Cu was deposited at –0.2 V for 20 s. The exchange reaction time was 30 s.

The $S_{Pd}$ was also estimated for a bare graphite electrode that was polarized at −0.5 V in a 1.8 M $H_2SO_4$ solution for 20 s prior to being placed in the Pd-containing solution. In that case, palladium adsorbs spontaneously on the graphite surface and its electroactive surface area is about 2 cm$^2$. The electroless deposition of Pd on carbon electrode, without the presence of reducing agents, was investigated elsewhere and considered as the result of direct redox reactions between metallic ions and the carbon surface.[42]

The effect of the $PdCl_2$ concentration on $S_{Pd}$ was also investigated and displayed in Figure 6 (open squares) for an exchange reaction time of 30 s and a Cu loading of 80 $\mu$g cm$^{-2}$. As expected, the $S_{Pd}$ value increases by increasing the Pd concentration. This behavior is attributed to the growth of the agglomerates size induced by the increase of the Pd concentration (Figure 2). However, Figure 6 shows that the $S_{Pd}$ value saturates at a $PdCl_2$ concentration of about 7 mM and reaches a maximum of 7.1 cm$^2$. Such a rough structure is quite attractive for further catalytic applications. Note that higher $S_{Pd}$ can be obtained by increasing the exchange reaction time and the Cu deposited mass as seen in Figure 5.

**Quantification of the Exchange Reaction by EDX and XPS Measurements.** The EDX analysis of the modified electrodes revealed the presence of Cu and Pd on their surfaces. More specifically, a mean Cu/Pd atomic ratio about 3/1 is found for the aggregates (Figures 2d−f). This is consistent with a previous report indicating that a Cu core exists underneath the Pd overlayer.[43] On the other hand, the EDX analysis of the remainder of the surface gives a mean Cu/Pd atomic ratio about 7/1. The presence of residual Cu on the electrode surface after the replacement reaction was also observed elsewhere.[21] Table 1 presents the chemical composition, determined by EDX, for the Pd−Cu/graphite electrodes as a function of the Pd concentration in the metal exchange solution. These values are considered as semi-quantitative and the analyzed depth reaches 1 $\mu$m. For that

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**Table 1. EDX Analysis of the Cu−Pd/Graphite Electrodes Versus $PdCl_2$ Concentration for Different Surface Coverage by Cu**[a]

| $[PdCl_2]$ (mM) | % Cu | % Pd | % O |
|---|---|---|---|
| 0 | 100 | 0 | 0 |
| 1 | 100 | 0 | 0 |
| 3 | 100 | 0 | 0 |
| 5 | 66 | 7.0 | 27 |
| 7 | 45.5 | 4.5 | 50 |
| 10 | 40 | 10 | 50 |

[a] The Cu loading was 80 $\mu g\ cm^{-2}$. The exchange reaction time with $PdCl_2$ was 30 s. Carbon was not taken into account in the calculation.

reason, the amount of Pd is not detected for the small concentrations (1 and 3 mM) despite that cyclic voltammetry clearly demonstrated the presence of Pd at the electrode surface. This is due to the low amount of Pd at the surface and the relatively poor sensitivity of the EDX in our experimental conditions. Nevertheless, our results demonstrate that some Cu is still present on the electrode surface after the exchange reaction in our experimental conditions.

The Cu/graphite and Pd−Cu/graphite electrodes were further characterized by XPS. Figure 7 shows the high-resolution Cu $2p_{3/2}$, O 1s and Pd 3d core level spectra. For the Cu/graphite electrode, the Cu $2p_{3/2}$ core level spectrum shows a main peak envelope curve-fitted into two components centered at 932.4 and 934.5 eV, followed by a low intensity satellite peaks envelope consisting of a pair of peaks centered at 942.5 eV (Figure 7a). The peak at 932.4 eV could be attributed to either metallic copper or $Cu_2O$.[44] The component at 934.5 eV arises from the presence of $Cu(OH)_2$ at the electrode surface. In the case of Pd−Cu/graphite electrodes, the Cu $2p_{3/2}$ region shows three components at 932.1 ± 0.2, 933.7 ± 0.2, and 934.6 eV assigned to Cu/$Cu_2O$, CuO and $Cu(OH)_2$ respectively, in addition to the satellite peaks envelope centered at 942.5 eV.[45] The identification of the Cu components, especially the need for an additional peak for CuO, can be confirmed by the analysis of O 1s core level spectra presented in Figure 7b. The curve-fitting of O 1s spectrum of the Cu/graphite electrode yielded three main peaks at binding energies of 530.6, 531.6 and 532.6 eV, which can be assigned to $Cu_2O$, $Cu(OH)_2$, and CO/adsorbed $H_2O$, respectively.[46–48] However, four main peaks are observed on the Pd-Cu/graphite electrode at 529.3 eV (CuO), 530.6 ± 0.1 eV ($Cu_2O$), 531.7 eV ($Cu(OH)_2$), and 532.9 ± 0.1 eV. The peak fitting results are summarized in Table 2. It can be seen that an increase in the Pd concentration induces the appearance of the CuO component on the Cu−-Pd/graphite electrodes and also an increase in the satellite peaks. By determining the peak area for both O 1s and Cu $2p_{3/2}$ spectra, the relative abundance of Cu, $Cu_2O$, $Cu(OH)_2$, and CuO onto the different electrode surfaces was calculated and presented in Figure 7a. The Cu/graphite electrode surface contains the highest percentage of metallic copper, i.e., 59 at %, with 5 at % $Cu_2O$ and 36 at % $Cu(OH)_2$. Following the exchange reaction in a 3 mM $PdCl_2$ solution, a decrease in metallic copper at the surface is observed (42 at % $Cu^0$) with an increase of the total oxygen content with 8 at % $Cu_2O$, 3 at % CuO, and 47 at % $Cu(OH)_2$. When the exchange reaction is performed in a 7 mM $PdCl_2$ solution, only 27 at % metallic copper is present at the surface. Moreover, this surface presents the highest oxygen content with 12 at % $Cu_2O$, 2 at % CuO, and 58 at % $Cu(OH)_2$. These observations confirm that the exchange reaction and the deposition of Pd on the Cu/graphite surface are associated with the oxidation of Cu. On the other hand, the high-resolution Pd 3d spectra indicate the presence of a single component attributed to metallic Pd at 335.5 eV (Figure 7c). The peak intensity of Pd 3d increases with the concentration of $PdCl_2$, whereas the binding energy of the peak is not affected.

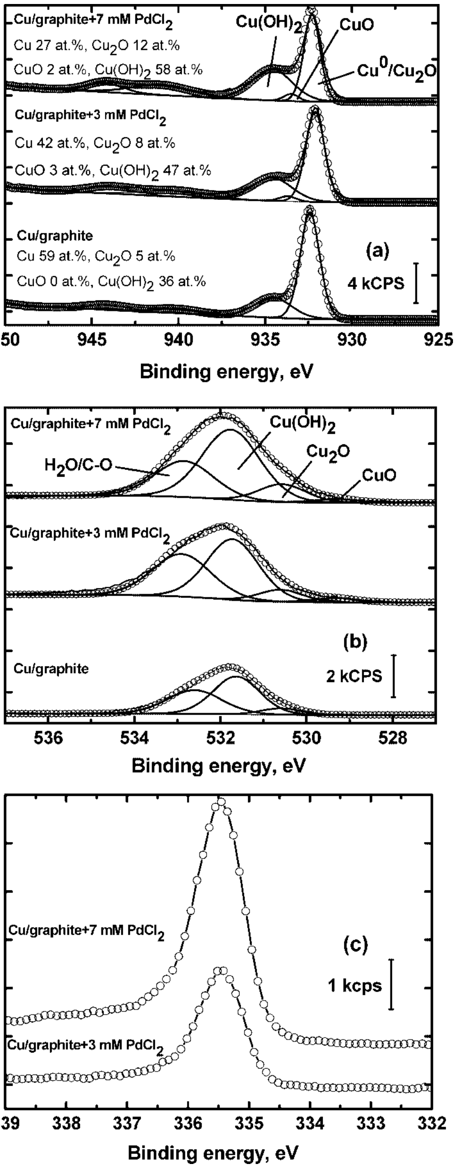

**Figure 7.** XPS high-resolution spectra of (a) Cu 2p3/2, (b) O 1s and (c) Pd 3d as a function of the $PdCl_2$ concentration. Cu was deposited at –0.2 V for 20 s in a 0.1 M $Cu(NO_3)_2$ + 1.8 M $H_2SO_4$ solution. Pd was deposited for 30 s in a $PdCl_2$ + 0.1 M $HClO_4$ solution.

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**Table 2. XPS Data for the Cu $2p_{3/2}$ and O 1s Core Level Spectra[a]**

| | | Cu/graphite | | | Cu/graphite + 3 mM $PdCl_2$ | | | Cu/graphite + 7 mM $PdCl_2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| species | | B.E.[b] (eV) | fwhm[c] (eV) | area (%) | B.E (eV) | fwhm (eV) | area (%) | B.E (eV) | fwhm (eV) | area (%) |
| $Cu2p_{3/2}$ | $Cu^0/Cu_2O$ | 932.4 | 1.3 | 63.9 | 932.1 | 1.2 | 50 | 932.3 | 1.1 | 38.4 |
| | CuO | | | | 933.7 | 1.1 | 2.5 | 933.5 | 1.0 | 2.8 |
| | $Cu(OH)_2$ | 934.5 | 2.5 | 23.2 | 934.6 | 2.7 | 26.8 | 934.6 | 2.7 | 33.8 |
| | $Sat_1$ | 940.1 | 3.0 | 6.0 | 940.1 | 4.5 | 11.6 | 941 | 4 | 16.1 |
| | $Sat_2$ | 944.1 | 3.0 | 6.9 | 944.0 | 3.2 | 9.1 | 944.2 | 2.5 | 8.8 |
| O1s | CuO | | | | 529.3 | 1.2 | 2.9 | 529.3 | 1.2 | 2.2 |
| | $Cu_2O$ | 530.6 | 1.1 | 7.9 | 530.6 | 1.2 | 8.3 | 530.5 | 1.3 | 11.8 |
| | $Cu(OH)_2$ | 531.6 | 1.3 | 53 | 531.7 | 1.4 | 49.7 | 531.7 | 1.5 | 56.6 |
| | $H_2O$ | 532.6 | 1.5 | 39 | 532.9 | 1.6 | 39.1 | 532.8 | 1.6 | 29.3 |

[a] The Cu loading was 80 μg $cm^{-2}$. The exchange reaction time with $PdCl_2$ was 30 s. [b] Binding energy. [c] Full width at half-maximum.

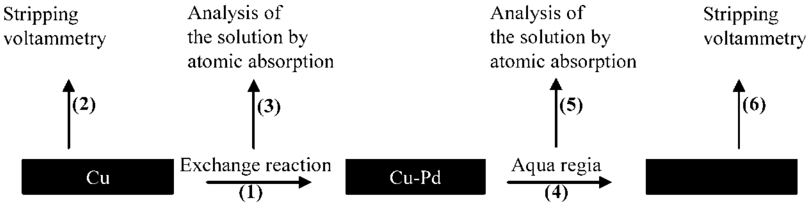

**Figure 8.** Diagram representing the different steps performed for the determination of the mass balance of the exchange reaction of Cu species. The graphite electrode is represented by the black rectangle.

According to Mårtensson et al., reducing the Pd concentration in the $Cu_xPd_{1-x}$ alloy from 100 to 30% induces a monotonous shift about 0.6 eV for the Pd 3d peak toward higher binding energies.[49] In the present study, the formation of a Cu−Pd alloy is not occurring because no shift in the Pd 3d peak position was observed when the Pd concentration changes. Because the interdiffusion rate between Cu and Pd is greatly reduced at room temperature, this might hinder the alloy formation. Note that the formation of a product with heterogeneous or "mosaic" structure rather than a homogeneous one is not excluded. In comparison, Sun and Xia succeeded in forming an alloy between Ag and Au by performing the exchange reaction at 100 °C with a vigorous magnetic stirring maintained during the entire process.[29] They mentioned that increasing the temperature tends to form a more stable alloy rather than heterogeneous pure metals. Also, the interdiffusion can be considerably increased by elevating the temperature or reducing the deposited layer thickness, which both facilitate the spontaneous alloying process.

Figure 6 also shows that the Pd/Cu atomic surface ratio (open circles), determined from the appropriate XPS data, increases when the $PdCl_2$ concentration increases as observed for $S_{Pd}$ determined electrochemically. It is found that following the exchange reaction, the surface concentration of Cu is still higher than the Pd one for every $PdCl_2$ concentration investigated here. In fact, the Pd atomic concentration represents from 10 to 30% of the surface layer probed by XPS. It should be noted that the reaction time employed here (30 s) is much lower than the one required to complete the exchange reaction process, i.e., 500 s (Figure 1).

**Mass Balance of the Exchange Process.** The metal exchange reaction was characterized further by establishing a complete mass balance of Cu species for Cu electrodes (deposited mass 80 μg $cm^{-2}$) following the exchange reaction with $PdCl_2$ solution of various concentrations from 1 to 10 mM. The total amount of Cu is quantified by combining various analytical methods as described in the flowchart shown in Figure 8. First, the nondisplaced Cu, i.e., Cu present on the electrode surface after the exchange reaction (step #1), is estimated by stripping voltammetry (step #2).[30] Second, the displaced Cu, i.e.. Cu present in the electrolyte solution, is analyzed by atomic absorption spectroscopy (step #3). Third, the Cu covered by a Pd layer that cannot be determined by stripping voltammetry of step #2 was analyzed by atomic absorption spectroscopy (step #5) after dissolving the residual metallic species present at the electrode surface in aqua regia (step #4). The total Cu mass is evaluated by the sum of all of the amounts described above added to the amount of Cu lost during the washing procedure of the Cu/graphite electrode.

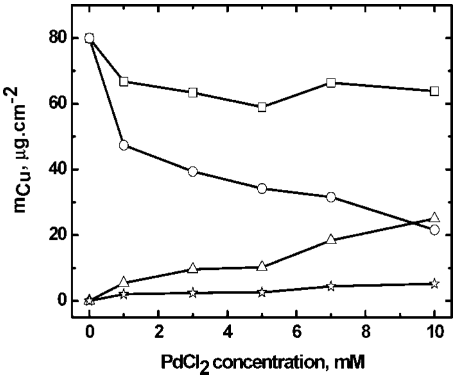

**Figure 9.** Variation of Cu mass ($m_{Cu}$) as a function of $PdCl_2$ concentration. Exchange reaction time is 30 s. Stars present the Cu enveloped by Pd. Triangles present the Cu displaced by Pd. Circles present nondisplaced Cu. Squares present the total quantified mass of Cu (including the mass of Cu lost during the washing procedure).

Figure 9 shows that the total Cu mass is about 66 μg.$cm^{-2}$ for every $PdCl_2$ concentration, which represents only 83% of the initial mass. This loss of Cu (17%) is intriguing. In order to verify the effectiveness of the aqua regia treatment of the electrode, the electrode was analyzed by stripping

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**Table 3. Amounts of Cu Displaced by Pd and Cu Corrosion Rates Obtained at Various $PdCl_2$ Concentration[a]**

| $[PdCl_2]$ (mM) | 1 | 3 | 5 | 7 | 10 |
|---|---|---|---|---|---|
| mass of Cu displaced by Pd ($\mu$g cm$^{-2}$) | 5.4 | 9.6 | 10.2 | 18.4 | 25 |
| Cu corrosion rate ($1 \times 10^{-9}$ mol cm$^{-2}$ s$^{-1}$) | 2.8 | 5.0 | 5.4 | 9.6 | 10.3 |

[a] The Cu loading was 80 $\mu$g cm$^{-2}$. The exchange reaction time with $PdCl_2$ was 30 s.

voltammetry (Figure 8, step #6). In all cases, no Cu was detected on the electrode surface. Thus, we believe that this apparent loss in Cu mass (17%) reflects the inaccuracy of all the analytical techniques used here. Nonetheless, the amount of replaced Cu increases and the one of nondisplaced Cu decreases considerably with an increase in the $PdCl_2$ concentration. These observations are consistent with the SEM, EDX, and XPS data. It is noteworthy that an amount of Cu that is presumably covered by a Pd layer is always detected. This fact demonstrates that, in our experimental conditions, Cu could never be completely replaced by Pd atoms (Figure 8, step #1) and that a Cu core exists independently of the $PdCl_2$ concentration used for the exchange reaction. The amount of Cu presents on the graphite surface after the exchange reaction, i.e., the sum of nonreplaced Cu and enveloped Cu, varies between 30 and 70% of the total deposited Cu mass. On the other hand, the amount of Pd deposited could be determined theoretically from the stoichiometry of the redox reaction (2). Thus, considering that one Pd atom replaces one Cu atom the maximum loading of Pd can be evaluated at about 90 $\mu$g cm$^{-2}$ assuming a maximum Cu replacement rate of 70% on the basis of Figure 9.

On the other hand, the mean Cu/Pd atomic ratio was also evaluated from the mass balance data and compared to that obtained by XPS measurements (Figure 6, curve ×). The atomic concentration of Cu was deduced from the total amount of Cu present on the electrode surface after the exchange reaction, i.e., the nondisplaced Cu and the Cu covered by a Pd layer. The atomic concentration of Pd was estimated from the amount of displaced Cu, assuming that one Pd atom replaces one Cu atom (eq 2). Figure 6 shows the relatively good agreement between the Cu/Pd atomic ratios estimated by both methods (XPS and mass balance), except for the highest Pd concentration (10 mM). This result confirms the reliability of the XPS technique even for the characterization of complex surface structures.

**Corrosion Kinetics.** Because the metal displacement reaction investigated here involved the dissolution of copper, the process was assimilated to the corrosion of copper and compared to the corrosion by oxygen. Thus, to further characterize the exchange reaction and the Cu corrosion kinetics, the Cu corrosion rate was determined for $PdCl_2$ concentration ranging from 1 to 10 mM. The corrosion rates (Table 3) are estimated from the amount of Cu displaced by Pd (Figure 9, triangles) during a reaction time of 30 s and as expected, it is found that the corrosion rate increases by increasing the $PdCl_2$ concentration. The corrosion rate values are similar to those obtained in the literature for the corrosion of Cu by oxygen.[50,51] In addition, the corrosion rates are also a function of the Pd salt concentration as was the case for the corrosion of Cu by oxygen.[51]

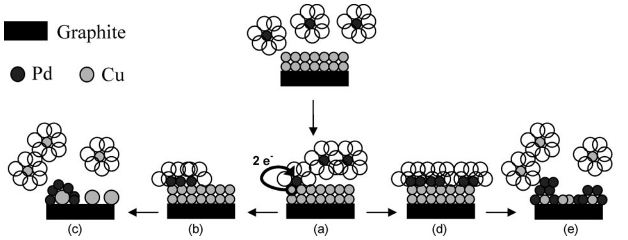

**Figure 10.** Schematic mechanism proposed for the exchange reaction between Cu deposited on a graphite electrode and Pd complexes present in the aqueous solution phase. (a) The first step is the adsorption of Pd at a specific site of the Cu surface. The second step depends on the $PdCl_2$ concentration; for is presented for the $PdCl_2$ concentrations lower than 5 mM (b, c) and higher than 5 mM (d, e).

**General Discussion.** Obviously, a combination of physical phenomena occurs on the electrode surface during the exchange process. Independently on the $PdCl_2$ concentration, the modified electrodes always contain Pd with a considerable amount of Cu. Also, the thickness of the Cu deposited film plays an important role in the duration of the exchange reaction. In fact, the presence of a multilayer Cu film allows a continual growth of the Pd deposits on the Cu-modified graphite surface, leading to Pd coatings thicker than those obtained in previous studies, where the exchange process was performed on an upd Cu deposited layer.[17,21]

However, the surface morphology is obviously affected by the $PdCl_2$ concentration. Based on the quantitative analysis of Cu and on the EDX, SEM and XPS measurements, a general model to describe the exchange process and the surface composition is presented (Figure 10). The first step of the exchange reaction involves the adsorption of the Pd complex at specific high surface energy sites of the Cu film, resulting in the formation of Pd adatoms (Figure 10a). The second step depends on the coverage of the Cu surface by Pd adatoms and consequently, two different pathways are proposed depending on the concentration of $PdCl_2$. For a concentration below 5 mM, the Cu film is partially covered by Pd adatoms (Figure 10b). In this case, the Cu atoms covered by Pd as well as bare Cu atoms are oxidized and dissolved from the surface. This phenomenon involves the formation of a Pd shell on a Cu core and leads, at the same time, to the appearance of voids on the graphite surface (Figure 10c). SEM micrographs revealed that the mean diameter of Cu particles increases after the exchange reaction (Figures 2b, c). On the other hand, for a $PdCl_2$ concentration higher than 5 mM, most of Cu atoms are covered by Pd adatoms (Figure 10d). Subsequently, Pd atoms may diffuse at the surface and overlap, to form agglomerates (Figure 10e). This will constitute the Pd shell enclosing a core of copper. The presence of voids is minimized when the $PdCl_2$ concentration increases. This could be attributed to a highest coverage of the Cu surface by the Pd adatoms.

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## Conclusions

Copper deposited on the pyrolytic graphite electrode was successfully replaced by Pd via a metal exchange reaction at open circuit. The Pd/Cu atomic surface ratio, evaluated by XPS, increased as the $PdCl_2$ concentration grows. The XPS data confirmed also the spontaneous oxidation of Cu and the simultaneous deposition of metallic Pd on the electrode surface. The replacement of Cu by Pd was more rapid when the amount of deposited Cu was lower and the $PdCl_2$ concentration was increased. A higher Pd electroactive surface was obtained by increasing the Cu mass, the exchange reaction time or the $PdCl_2$ concentration. The mass balance of Cu by stripping voltammetry and atomic absorption spectroscopy showed that the replacement of Cu by Pd is not complete after the exchange reaction. Regardless of the concentration of $PdCl_2$ in the electrolyte solution, an amount of Cu was present on the surface and the Pd shell covered always a Cu core. Such metallic surface structures should be very attractive for catalytic applications. The deposition of Pd on the Cu-modified graphite electrode was highly dependent on the Pd concentration. In the case of a $PdCl_2$ concentration below 5 mM, the SEM results have shown the presence of voids on the surface and an increase in the Cu particles diameter. When the $PdCl_2$ concentration was higher than 5 mM, the modified surfaces were completely covered and were characterized by the presence of Cu−Pd agglomerates, explained by the planar diffusion and the coalescence of Pd adatoms on the surface.

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