Inorg. Chem. **2005**, *44*, 4366–4371

Inorganic Chemistry

Article

Stability of $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$-Modified Graphite Electrodes during Indirect Electrolyses

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Received December 16, 2004

The stability of a graphite felt electrode modified by covalent attachment of $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ is investigated during the indirect electrolyses of alcohols in a flow cell. The continuous increase of the local potential of the electrode during the electrolyses attests to its degradation. Cyclic voltammetry analyses of the modified electrode after electrolyses show a total decrease of 80–90% of the wave corresponding to the $Ru^{III/II}$ couple. The concentration of remaining alcohol measured at the outlet of the cell is almost constant during all the electrolyses but increase when the potential exceeds 0.95 V_{SCE}. At low potentials, the electrode can be regenerated by reaction with $Ru^{II}Cl_2(DMSO)(tpy)$ and then CF_3SO_3H, followed by hydrolysis, showing that the bipyridine ligand remains covalently attached to the electrode. At high potentials, the graphite is oxidized and the catalyst is partly lost in the reaction medium. XPS analyses of Ru core levels reveal that the ruthenium disappeared after electrolysis, showing that the degradation of the modified electrode is due to the demetalation of the oxidized complex.

Introduction

High oxidation state polypyridyl complexes of ruthenium have been largely used as oxidants in indirect electrolysis, owing to their remarkable reactivity and to the fact that they can be prepared by electrochemical oxidations of their corresponding aqua complexes.[1−7] Instead of being dissolved in the reaction medium, the catalysts are usually immobilized on electrodes for several reasons. First, the amount of required catalyst is lower for high concentrations at the electrode. Second, the catalyst is located at the interface where the reaction takes place. Third, the purification of the catalyst is easier and the modified electrode can be used several times.

A determining factor for the use of modified electrodes is their stability. The degradation of the electrode during the electrolyses can come from the loss of the catalyst in solution or from its deactivation. It has been shown that the catalyst immobilization usually improves its stability compared with the catalyst in solution. For example, Meyer et al.[8] observed that *cis*-$[Ru(bpy)_2(O)_2]^{2+}$ (bpy is 2,2′-bipyridine) is much more stable when it is covalently attached to a polymer film than in solution. The explanation given by the authors is the large amplitude displacement required to open a bipyridine ring, which is inhibited in rigid environments.

The method for immobilization has also an influence on the stability of the electrode. Polypyridyl complexes of ruthenium have been immobilized onto electrodes using a polymer coating. A first method consists of the encapsulation of the catalyst into cation-exchange membranes such as perfluorinated Nafion.[9−16] Anson et al.[10] have incorporated

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10.1021/ic048231k CCC: $30.25

$[Ru(tpy)(bpy)(OH_2)]^{2+}$ (tpy is 2,2′:6′,2″-terpyridine) at Nafion-coated electrodes. They observed that the catalyst was gradually converted into a catalytically inactive compound during the electrocatalysis of benzyl alcohol using the modified electrode. Meyer et al.[11,13] explained that this phenomenon could be due to the displacement of an aqua ligand by the sulfonate sites of the Nafion polymer. In the case of the catalytic oxidations of chloride anions to chlorine, the anation of the complex by Cl^- could also be responsible for the loss of its catalytic activity.[14]

In another approach, the catalyst has been attached to a polymer film, deposited on the electrode either by dipping the electrode in a solution of polymer and drying[9,17] or by electropolymerization of vinyl or pyrrole groups.[8,18−27] The degradation of the modified electrode during electrocatalyses has also been mentioned there. First, the polymer support can be reactive as it was observed for a poly(vinylpyridine) coating, where the polymer was oxidized during the electrolysis.[9,10] Second, the stability of the modified electrode depends on the method for preparation of the polymer film. For example, it has been noticed for polypyrrole that when the monomer contained several pyrrolic units, the electropolymerization led to a more stable film than when it contained only one pyrrolic unit.[22,24,27]

We have previously reported that $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ could be immobilized onto a graphite felt electrode by a covalent bond with the bipyridine ligand.[28] The modified electrode showed catalytic activity toward primary and secondary alcohols.[29] However, the volume concentrations of the immobilized catalyst, measured by cyclic voltammetry, substantially decreased during the electrolyses.

This work focuses on the stability of the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ modified graphite felt electrode during the electrocatalysis of alcohols. Cyclic voltammetry and XPS analyses will show that the major degradation of the electrode is not due to the break of the covalent bond between the bipyridine ligand and the carbon electrode but to the decomposition of the oxidized catalyst. Plane graphite electrodes were also used especially for XPS analysis, as surface sensitivity can be increased by measurements at the grazing incidence.

Experimental Section

Reagents and Materials. Graphite felt was obtained from Le Carbone Lorraine (RVG 4000). Its specific area measured by the BET method is 0.7 $m^2\ g^{-1}$, and its volume density is 0.088 g cm^{-3}. The plane graphite electrode was obtained from Le Carbone Lorraine (PAPYEX).

4-Nitrobenzyl alcohol, benzyl alcohol, and α-methylbenzyl alcohol were purchased from ACROS, and water was distilled using an autostill 4000X apparatus (Jencons). The felts were sonicated in water from Carlo Erba (Water Plus for HPLC) before XPS analyses.

Instrumentation. Cyclic voltammetry, controlled potential electrolyses, and constant current intensity electrolyses were performed in a divided flow cell, fitted with a graphite felt electrode (10 mm diameter, 10 mm thickness) located between two counter electrodes. Two cationic exchange membranes (Ionac 3470) were used for cell division. The reference electrode (saturated calomel electrode) was positioned at the surface of the felt, at an equal distance from the entry to the exit of the porous electrode.[30]

The controlled potential electrolyses using plane working electrodes (26 mm diameter) were performed in a homemade cell.[31]

XPS spectra were recorded using a VSW HA100 spectrometer with Al or Mg Kα excitation radiation at 1486.6 and 1283.6 eV, respectively, under a base pressure of 10^{-9} mbar.

HPLC experiments were performed on a Waters 600 instrument equipped with a Nova-Pak C_{18} column (3.9 × 150 mm). The mobile phase was methanol−water (50:50, v/v), and the flow rate was 1 $mL \cdot min^{-1}$ (UV−vis detector 254 nm).

Preparation of the $[Ru^{II}(tpy)(bpy)OH_2]^{2+}$-Modified Electrodes. $[Ru^{II}(tpy)(bpy)OH_2]^{2+}$ was immobilized onto the carbon felt according to a previously described procedure, which we recall here.[28] The bipyridine ligand was first attached to the electrode by anodic oxidation of the lithium salt of 4′-methyl-(2,2′-bipyridine)-4-acetic acid in a pH = 2.2 phosphate buffer solution. The electrode was sonicated in water (3 × 30 min). Reactions with $Ru^{II}Cl_2(DMSO)(tpy)$ and then CF_3SO_3H, followed by hydrolysis, afforded the $[Ru^{II}(tpy)(bpy)OH_2]^{2+}$- modified electrode.

The modified plane graphite electrode was prepared in the same way. However, the bipyridine immobilization was achieved by anodic oxidation at 1.6 V_{SCE} for 1 h of 10 mg (2.1×10^{-3} mol L^{-1}) of the lithium salt of 4′-methyl-(2,2′-bipyridine)-4-acetic acid, dissolved in 20 mL of a pH = 2.2 phosphate buffer solution (0.25 M NaH_2PO_4; 0.25 M H_3PO_4).

The modified electrodes were sonicated in water (3 × 30 min) before using.

General Procedure for the Electrocatalytic Oxidation of 4-Nitrobenzyl Alcohol Using the $[Ru^{II}(tpy)(bpy)OH_2]^{2+}$-Modified Electrodes. 4-Nitrobenzyl alcohol ($n_{alcohol} \simeq 500 n_{catalyst}$; $n_{catalyst}$ estimated by cyclic voltammetry) dissolved in 100 mL of a pH = 7.2 phosphate buffer solution (0.25 M NaH_2PO_4; 0.25 M Na_2HPO_4) was oxidized in the flow cell[30] under nitrogen, with a

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Table 1. Volume Concentrations of Grafted Catalysts on the Graphite Felt Electrodes Measured by Cyclic Voltammetry

flow rate (mL min^{-1})	vol concentration (10^{-8} mol cm^{-3}) before electrolysis	vol concentration (10^{-8} mol cm^{-3}) after electrolysis^{a,b}
0.74	4.2	0.6^{c} (14)
3.6	4.4	0.6 (14)
5.3	3.5	0.5 (14)
6	4.2	0.7 (16)
7.5	2.9	0.4 (14)

[a] Electrolysis of 100 mL of 4-nitrobenzyl alcohol ($n_{\mathrm{alcohol}} \simeq 500n_{\mathrm{catalyst}}$). [b] The ratio of remaining catalyst (%) is given in parentheses. [c] The volume concentration could not be calculated after the second and the third electrolyses.

constant current intensity distributed as 2/3 for the upstream electrical circuit and 1/3 for the downstream one. The electrolyte flowed through the porous electrode without recycling. For each experiment performed at a given flow rate r (see Table 1), the current intensity is calculated as follows:

$$I = \frac{4Frn_{\mathrm{alcohol}}}{60V}$$

n_{alcohol} is the number of moles of 4-nitrobenzyl alcohol, F is the Faraday constant, r is the flow rate (mL min^{-1}), and V is the volume of the reaction medium (mL).

For the electrolyses performed at a flow rate of 0.74 mL min^{-1}, the working electrode was used three times in succession to oxidize 4-nitrobenzyl alcohol, under the same experimental conditions. Particularly, the initial concentration of 4-nitrobenzyl alcohol is the same at the beginning of each electrolysis: $n_{\mathrm{alcohol}} \simeq 500n_{\mathrm{catalyst\ initial}}$ in 100 mL of a pH = 7.2 phosphate buffer solution.

Sample Preparation for XPS Analyses. The [Ru$^{\mathrm{II}}$(tpy)(bpy)-OH$_2$]$^{2+}$-modified electrodes were prepared as described above. The graphite felts were cut before XPS analyses to analyze the inner part of the felt.

A modified graphite felt electrode ($n_{\mathrm{catalyst}} = 1.6 \times 10^{-8}$ mol) was used to oxidize α-methylbenzyl alcohol (1.7×10^{-6} mol) in 100 mL of a pH = 7.2 phosphate (0.5 M) buffer solution. The electrolysis was carried out in the flow cell at 0.7 V$_{\mathrm{SCE}}$ for 7 h under nitrogen. The electrolyte solution flowed through the electrode with recycling at a flow rate of 8 mL min^{-1}. The electrode was sonicated 3 × 30 min before being analyzed.

The modified plane graphite electrode was used to oxidize benzyl alcohol (1.5×10^{-2} mol L^{-1}) in 13 mL of a pH = 7.2 phosphate (0.5 M) buffer solution at 0.7 V$_{\mathrm{SCE}}$ for 15 h under nitrogen. The surface concentration of grafted catalyst on the plane graphite electrode could not be measured by cyclic voltammetry analyses.

The modified electrodes were sonicated, under argon, in water (3 × 30 min) before XPS analyses.

Results

The electrocatalytic oxidation of 4-nitrobenzyl alcohol using the [Ru$^{\mathrm{II}}$(tpy)(bpy)(OH$_2$)]$^{2+}$-modified electrode **1** (Scheme 1) was performed in a flow cell[32] at constant current intensity and constant flow rate without recycling.

Figure 1a shows for different flow rates the remaining alcohol concentration measured by HPLC on the samples taken at the outlet of the flow cell during the electrolyses.

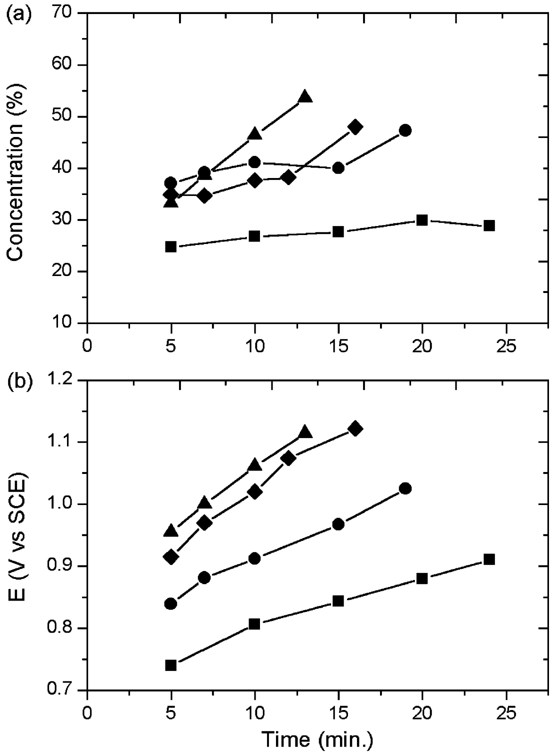
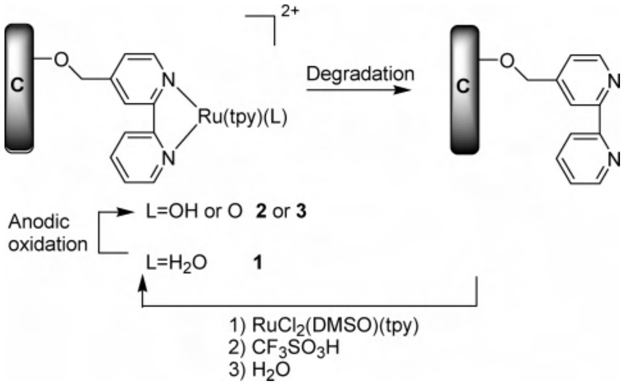


Figure 1. (a) Percentage of remaining 4-nitrobenzyl alcohol measured at the outlet of the flow cell and (b) potential of the modified electrode during the electrolysis performed at 7.5 (▲), 6 (◆), 5.3 (●), and 3.6 (■) mL min^{-1}.

Scheme 1



The corresponding local potential of the electrode is shown in Figure 1b. For each experiment, the potential increased during the electrolysis. We noticed that when the potential reached 0.95−1.05 V$_{\mathrm{SCE}}$, the concentration of remaining 4-nitrobenzyl alcohol suddenly increased.

Similarly, three successive anodic oxidations of 4-nitrobenzyl alcohol using the same grafted felt were performed at a low flow rate (0.74 mL min^{-1}). The potential of the working electrode continuously increased during the three experiments (Figure 2).

The stability of the modified electrodes was checked by cyclic voltammetry analyses of the grafted felts, as depicted in Figure 3[33] for the electrolyses performed at 0.74 and 5.3 mL min^{-1}.

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(33) The most visible region corresponding to the cathodic reduction of Ru$^{\mathrm{III}}$ is shown here as a proof of the presence of [Ru$^{\mathrm{II}}$(tpy)(bpy)-(OH$_2$)]$^{2+}$ on the electrode.

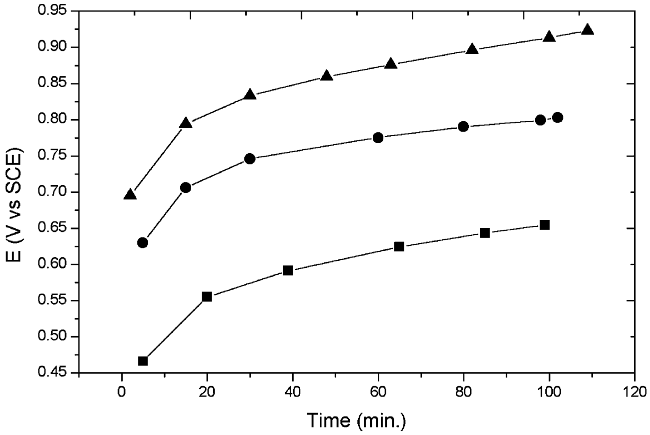

Figure 2. Potential of the working electrode during the first (■), the second (●), and the third (▲) electrolysis performed at 0.74 mL min^{-1}.

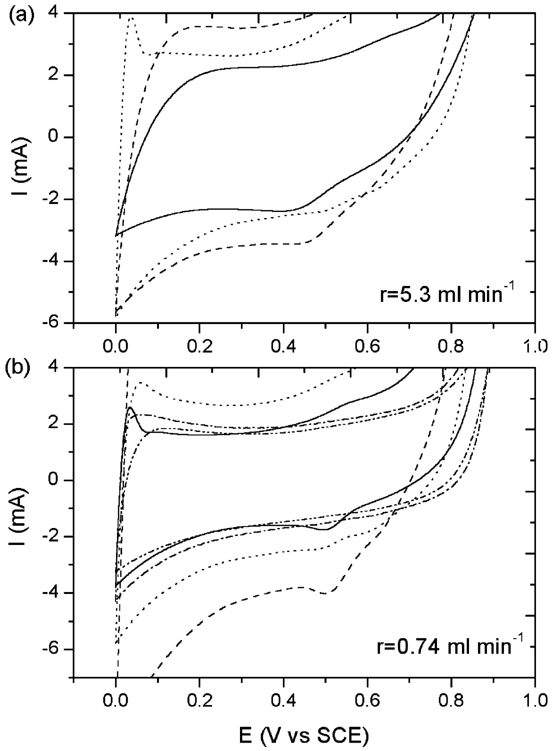

Figure 3. Cyclic voltammograms of the [Ru^{II}(tpy)(bpy)(OH_2)]$^{2+}$-modified electrode in a pH = 7.2 phosphate (0.5 M) buffer for electrolyses performed at (a) 5.3 and (b) 0.74 mL min^{-1}. Voltammograms are shown for grafted felts before electrolysis (---), after the first (•••), the second (- • -), and the third (- •• -) electrolyses, and after regeneration (—). Scan rate: 20 mV s^{-1}.

The volume concentrations of grafted catalyst were evaluated before and after electrolysis, by integration of the peak, corresponding to the $Ru^{III/II}$ couple,[28,29] using the Faraday law (Table 1).

The remaining catalyst concentration is as low as 10–20%, as it was previously observed with electrochemical oxidations performed at controlled potential.[29] The variation of the flow rate did not seem to influence the decrease in volume concentrations. Moreover, the reversible wave corresponding to the $Ru^{III/II}$ couple rapidly decreased when the potential was repeatedly cycled between 0 and 0.8 V_{SCE} (Figure 4) and reached about 20% of its initial value after 50 scans.

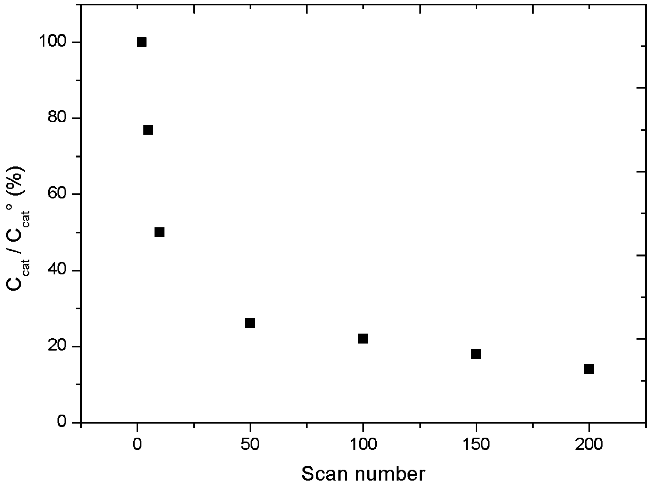

Figure 4. Ratio of catalyst remaining on the felt after repetitive cycling between 0 and 0.8 V_{SCE}.

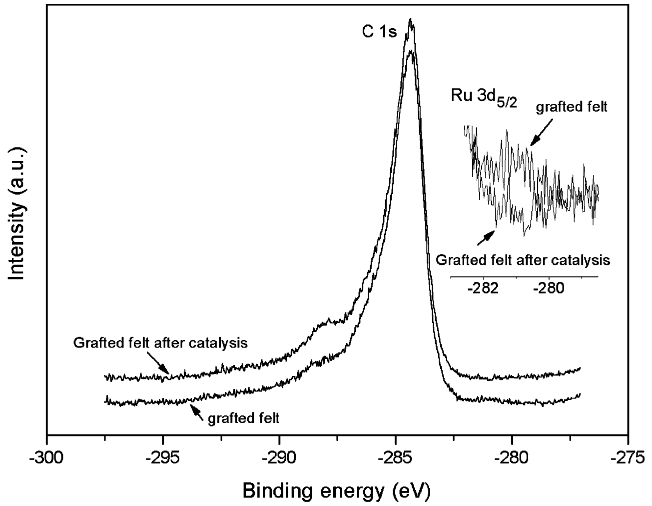

Figure 5. C 1s and Ru 3$d_{5/2}$ spectra of the grafted felt before and after electrocatalysis and zoom of the Ru 3$d_{5/2}$ region. The curves have been background subtracted and normalized to a constant intensity. Spectra were shifted vertically for clarity.

Cyclic voltammetry analyses showed that the grafted catalyst could be regenerated by treatments with $Ru^{II}Cl_2$(DMSO)(tpy) and then CF_3SO_3H, followed by hydrolysis (Figure 3). Initial volume concentrations of grafted catalyst could be recovered even if the modified electrode was used in three successive electrolyses. Curiously, the wave shape of the voltammograms (Figure 3) was modified after electrolysis: the capacitive current decreased and the water oxidation potential was higher. Thus, the $Ru^{III/II}$ reversible system could be more easily observed. However, if the modified electrode was used in the electrocatalysis of 4-nitrobenzyl alcohol at 1.1 V_{SCE} for 2 h, only 50% of the grafted catalyst could be regenerated.

The [Ru^{II}(tpy)(bpy)(OH_2)]$^{2+}$-modified electrode was also analyzed by XPS. Figure 5 shows the C 1s and Ru 3$d_{5/2}$ spectra of a grafted felt. The presence of oxides on the surface of the grafted felts, resulting from the grafting process,[28,34] was ascertained by the shoulder at 298 eV on the high-energy side of the C 1s peak. A small peak at 281 eV, corresponding to Ru 3$d_{5/2}$, could be observed. The

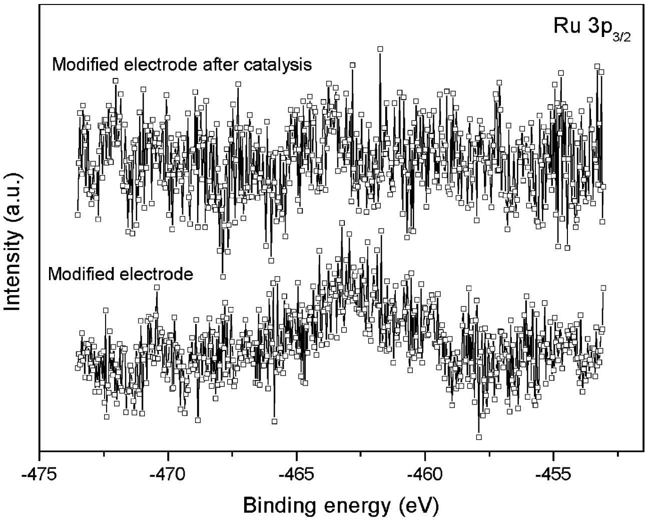

Figure 6. Ru $3p_{3/2}$ spectra of a modified carbon electrode before and after electrocatalysis. The curves have been background subtracted and normalized to a constant intensity.

electrocatalysis using this modified electrode was not performed at controlled intensity to avoid potential variation and possible destruction of the electrode. The electrolysis was carried out in a pH = 7.2 phosphate buffer solution at 0.7 V_{SCE}, using 1 mol % of catalyst. After 7 h of electrolysis, the electrode was analyzed by cyclic voltammetry. The $Ru^{III/II}$ wave was very small, and the volume concentration was estimated to be around 5×10^{-10} mol·cm^{-3}. XPS analysis on this electrode shows that the C 1s peak shape did not change after the electrolysis, so no more oxides were formed at the electrode during the electrocatalysis at 0.7 V_{SCE} (Figure 5).

The Ru $3d_{5/2}$ peak, previously observed, disappeared after the electrolysis (see zoom in Figure 5). To confirm this result, $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ was immobilized onto a plane graphite electrode according to the procedure described before (see Experimental Section). The photoelectrons emitted were collected at an electron takeoff angle of 30° from the plane of the surface to minimize the bulk signal and maximize the signal of the topmost layer corresponding to the grafted species. The modified electrode was analyzed before and after electrocatalysis in a pH = 7.2 phosphate buffer solution at 0.7 V_{SCE} for 15 h (Figure 6).

The peak corresponding to Ru $3p_{3/2}$ was clearly observed at 462.8 eV with the fresh modified carbon electrode and disappeared after the electrolysis. The N 1s peak region was also investigated. We noticed that, for both porous and plane electrodes, the initial N 1s concentration (around 3%) slightly increased after electrolysis.

Discussion

The use of different flow rates (r) for the oxidations of 4-nitrobenzyl alcohol with the $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$-modified electrode allows the current intensity (I) to vary, while keeping the total charge (Q) used in the reaction constant ($Q = I(V/r)$; V is the volume of the reaction medium). As the substrate concentration, the flow rate, and the current intensity do not vary during the electrolyses, the potential of the working electrode should remain constant. However, the measured potential of the working electrode increases during the electrolyses (Figures 1 and 2). For the experiments performed at a flow rate of 0.74 mL min^{-1}, the initial potential increases from the first to the third electrolysis (Figure 2). This unexpected increase of potential during the electrolyses is indicative of a decrease of the current intensity corresponding to the Ru^{II} oxidation and so of a degradation of the modified electrode. Indeed, a growing part of the current is used for the oxidation of water at more anodic potential, because the oxidation of the catalyst requires less and less current.

The concentration of the remaining alcohol[35] measured at the outlet of the flow cell increases very slowly during the electrolysis until the potential reaches 0.95−1.05 V_{SCE} (Figure 1). This result shows that the activity of the grafted catalyst involved in the oxidation of 4-nitrobenzyl alcohol slowly decreases in this range of potential. However, when the potential is higher, the concentration of remaining alcohol suddenly increases, showing a faster degradation of the modified electrode. Moreover, when the electrolysis is done at 1.1 V_{SCE} for 2 h, only 50% of the catalyst can be regenerated. In this range of potentials (0.95−1.1 V_{SCE}), three electrochemical processes occur: catalyst oxidation; water oxidation; graphite oxidation. When the graphite is oxidized, it undergoes a nucleophilic attack of water leading to damage to the graphite lattice.[36,37] In this case, the loss of catalyst in solution owing to graphite oxidation is probably responsible of the acceleration of the degradation of the modified electrode.

If the potential of the working electrode does not reach this limit, a single mechanism of degradation of the modified electrode occurs. Indeed, the electrode can be regenerated by reactions with $Ru^{II}Cl_2(DMSO)(tpy)$ and then CF_3SO_3H, followed by hydrolysis (Scheme 1). This result is important because it shows that the bipyridine ligand remains covalently attached to the modified electrode and that, in this case, the degradation is due to the deactivation of the catalyst during the electrolysis.

We previously observed that the deactivation of the catalyst occurs even if the substrate is not added in the reaction medium.[29] Moreover, the modified electrode exhibits poor stability by continuous cycling of potential (Figure 4), whereas it can be stored at room temperature several months without any degradation. Thus, the deactivation of the catalyst occurs when it is oxidized in $[Ru^{III}(tpy)(bpy^*)(OH)]^{2+}$ (**2**) or $[Ru^{IV}(tpy)(bpy^*)(O)]^{2+}$ (**3**) (bpy* is the grafted 2,2′-bipyridine; Scheme 1). Indeed, even if only one wave corresponding to the $Ru^{III/II}$ system can be observed in cyclic voltammetry, we have previously shown by differential pulse

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(34) During the grafting process, the graphite electrode is anodically oxidized and undergoes nucleophilic attack of water, leading to the formation of oxides onto the electrode.

(35) As the oxidation of 4-nitrobenzyl alcohol is not complete, the oxidation of water probably simultaneously occurred.

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voltammetry that the catalyst is oxidized in Ru^{IV} at about 0.6 V$_{SCE}$.[29] We also noticed that, during the electrolyses, the higher is the current intensity, the faster is the increase of the potential (Figures 1 and 2) and so the degradation of the electrode. This result seems also to support a mechanism of degradation connected with a deactivation of the catalyst, when it is in an oxidized form.

The rapid decrease of the wave corresponding to the Ru$^{III/II}$ couple by repeated cyclic voltammetry scanning (Figure 3) or by electrolysis[29] is not in accordance with the stability of the concentration of the remaining alcohol measured at the outlet of the flow cell (Figure 1). This phenomenon is not well understood yet, but it suggests that only 20% of the grafted catalyst is involved in the electrocatalysis of the alcohol.

To understand the mechanism responsible of the deactivation of the catalyst, the grafted electrodes were analyzed by XPS before and after electrocatalyses performed at 0.7 V$_{SCE}$. Information about the deactivation of the catalyst could not be obtained from the N 1s analyses, because the N 1s concentration increased after electrolyses for both porous and plane electrodes. The nitrogen pollution probably comes from the phosphate buffer solution used as reaction medium, which contains traces of nitrogen-containing compounds.[38]

Interestingly, C1s analysis (Figure 5) does not reveal a real enhancement of the oxides on the surface of the graphite felt after electrocatalysis, confirming that the graphite is not more oxidized at this potential. However, the wave shape of the cyclic voltammograms changes after electrolysis (Figure 3). As this phenomenon persists after regeneration of the modified electrode, partial oxidation of the oxides of the electrode[34] could occur during the electrolyses, leading to a surface modification of the graphite felt.

We then focused our attention on the Ru atom. The XPS analyses highlight the decrease of the ruthenium after electrocatalysis. As cyclic voltammetry experiments show that the bipyridine ligand remains covalently grafted on the graphite felt (see above), a demetalation of the complex is responsible of the deactivation of the catalyst (Scheme 1). The mechanism of deactivation of the grafted catalyst is different from those reported for [Ru^{IV}(tpy)(bpy)(O)]$^{2+}$ in homogeneous catalysis. Indeed, Meyer et al.[3] observed that the oxo complex decomposes into an oxo-bridged dimer during electrolysis. This discrepancy is not surprising as the oxo-bridged formation is unlikely with the immobilized catalyst.

Conclusion

In conclusion, the stability of the [Ru^{II}(tpy)(bpy)(OH$_2$)]$^{2+}$-modified electrode depends on the potential. For potentials above 0.95−1.05 V$_{SCE}$, the oxidation of graphite leads to damage on the fibers surface and to the loss of the catalyst in solution. For lower potentials, only the demetalation of the oxidized catalyst occurs. Thus, for low potentials, the degradation of the modified electrode is due to the deactivation of the catalyst and not to the break of the covalent bond between the bipyridine ligand and the graphite. The stability of the link between the catalyst and the electrode and the simplicity of the grafting process emphasize the interest in the method to modify electrodes. A second outcome of the current work is the evidence of a mechanism of degradation of the oxidized polypyridyl complex involving a demetalation process, whereas a dimerization has been observed in homogeneous catalysis. To improve the stability of the modified electrode, it would be interesting in future work to investigate the immobilization of catalysts with more stable metal−ligand bonds and containing only one polydentate ligand covalently bonded on the electrode.

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(38) For introduction of nitrogen onto carbon surface by nitrogen-containing compounds, see for example: Jansen, R. J. J.; Van Bekkum H. *Carbon* **1995**, *33*, 1021−1027. Alexander, M. R.; Jones F. R. *Carbon* **1996**, *34*, 1093−1102.