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# Covalent attachment of TEMPO onto a graphite felt electrode and application in electrocatalysis

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## Abstract

This work describes a simple method to attach TEMPO by an amide link to a graphite felt electrode. The derivatization of the electrode is highlighted by cyclic voltammetry and XPS analyses. The catalytic activity of the grafted TEMPO is observed by cyclic voltammetry in both organic and aqueous media. Macroscale electrolyses reveal a better stability of the grafted catalyst in aqueous medium than in acetonitrile. Furthermore, the catalyst is more stable when it is immobilized onto the electrode than when it is in homogeneous solution. The XPS analyses of the grafted felt after electrocatalysis in aqueous medium shows that the degradation of the modified electrode during the electrolysis is due to a chemical modification of the catalyst rather than to a break of the amide link between the graphite felt and TEMPO.

## Introduction

Oxidations of alcohols in aldehydes, ketones or carboxylic acids are fundamental reactions in organic synthesis. In the search for a green and economical method, stable organic nitroxyl radicals like 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) **1** have been widely studied as catalysts in the alcohol oxidation.<sup>1,2</sup> Actually, the oxidation reagent is the oxoammonium salt **2**, usually prepared in situ by chemical or electrochemical oxidation of **1** (Scheme 1).<sup>1-5</sup>

## Scheme 1

In alkaline medium a mechanism involving a cyclic transition state **3** has been proposed.<sup>1</sup> The intermediate **3** undergoes a cyclic elimination to give the hydroxylamine **4**. Above pH 3, a rapid symproportionation between the oxoammonium salt **2** and the hydroxylamine **4** occurs leading to TEMPO **1**.

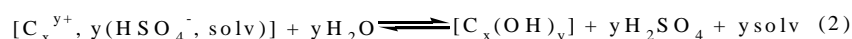
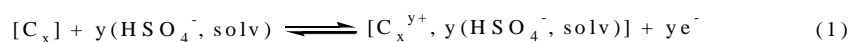
To facilitate separation and catalyst recycling, nitroxyl radicals have been immobilized onto solid supports like polymers<sup>6, 7</sup>, silica<sup>8, 9</sup> and MCM-41<sup>10, 11</sup>. Modified electrodes have also been widely studied because they have the great advantage of being active supports. The immobilization of nitroxyl radicals onto electrodes has been achieved by polymer coatings. Thus, TEMPO has been encapsulated into Nafion, a perfluorinated anionic polyelectrolyte which exhibits permselectivity towards cations such as oxoammonium salts.<sup>12, 13</sup> Nafion polymers were of particular interest in this study because they are stable in water. Thus, the oxidation of carbohydrates has been achieved in a carbonate buffer solution (pH=10). However, a gradual decrease in the initial TEMPO density has been observed, probably due to the extraction of the catalyst from the polymer layer during the reaction with the carbohydrate molecule.

Other methods deal with the covalent attachment of nitroxyl radicals onto a polymer film. Thus, the electropolymerisation of TEMPO-substituted pyrrole or thiophene has been performed on platinum or carbon electrodes.<sup>14, 15</sup> The oxidation of benzyl alcohols in their corresponding carbonyl compounds has been achieved in acetonitrile, in the presence of sodium carbonate, using the modified carbon electrode. However, the authors have observed that the addition of a base required for the regeneration of the active oxoammonium salt **2** from the hydroxylamine **4**, led to the degradation of the polymer film.

Another approach consists in the attachment of 4-amino-TEMPO derivatives by an amide bond on polyacrylic acid, previously coated on a graphite felt electrode.<sup>16, 17</sup> These modified electrodes have been used to achieve alcohol oxidations in acetonitrile, in the presence of a base.<sup>16-21</sup> The authors have observed a better stability of the immobilized catalyst than in homogeneous solutions and a good tolerance of the polymer film towards alkaline medium.<sup>17</sup>

The direct covalent bonding of molecules onto graphite electrodes has the advantage of providing modified electrodes with stable attachment of compounds onto their surface. Moreover, these modified electrodes are easy to use in both aqueous and nonaqueous solutions. We have previously achieved the covalent attachment of TEMPO onto a graphite electrode by addition of an aminyl radical electrogenerated by oxidation at a graphite felt anode of 4-amino-TEMPO at low potential.<sup>22</sup>

In this work, the approach involves chemical reactions between COOH groups present on the surface of the electrode and NH<sub>2</sub>-containing compounds with the formation of an amido linkage.<sup>23-25</sup> The anodic oxidation of graphite electrodes in aqueous acidic medium leads to the formation of surface COOH and OH groups. A mechanism proposed for the electrochemical oxidation of graphite in sulfuric acid involves a simultaneous intercalation of anions and solvent into the lattice followed by a nucleophilic attack of water (Eq. (1) and (2)).<sup>26-29</sup>



This reaction leads to the formation of C-O functionalities subsequently oxidised to C=O species such as carboxylic acids.

We report here that TEMPO can be covalently attached onto the carbon electrode by this method. The electrocatalytic activity of the grafted TEMPO towards alcohol oxidation is studied in both aqueous and nonaqueous solutions. The surface of the graphite electrode after electrochemical treatments is also investigated by photoelectron spectroscopy.

## Experimental

### Reagents and materials

The graphite felt was obtained from Le Carbone Lorraine (RVG 4000). Its specific area measured by the BET method is 0.7 m<sup>2</sup> g<sup>-1</sup> and its density is 0.088 g cm<sup>-3</sup>. 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl (4-amino-TEMPO), 1,3-dicyclohexylcarbodiimide (DCC), thionyl chloride, 4-nitrobenzyl alcohol, 4-bromobenzyl alcohol, 4-nitrobenzoyl chloride, 3-nitrobenzylamine, tetrabutylammonium perchlorate (contains maximum 10% of water) and lithium perchlorate were used as purchased (Acros) and water was distilled using an autostill 4000X apparatus (Jencons).

### Instrumentation

Cyclic voltammetry analyses and controlled potential electrolyses using the modified electrodes were performed in a divided flow cell<sup>30</sup>, fitted with the graphite felt samples (10 mm diameter, 10 mm thickness) located between two counter-electrodes. The anodic and cathodic compartments were separated by cationic exchange membranes (Ionac 3470). A

standard three-electrodes electrochemical cell (glassy carbon electrode as working electrode and Pt wire as counter-electrode) was used for cyclic voltammetry analyses of TEMPO in solution. In all cases, a saturated calomel electrode serves as a reference.

XPS analyses were performed under a base pressure of  $10^{-9}$  mbar using a VSW HA100 spectrometer. The analyser was operated with a constant pass energy of 22 eV. X-ray source used either Al or Mg  $K\alpha$  excitation radiation at 1486.6 eV and 1283.6 eV respectively. The spectrometer binding energy scale was initially calibrated against the Au 4f (84.0 eV) level. C1s level (284.4 eV) on as-received clean felt serves as a reference for all spectra. Simulation of the experimental peaks was carried out using a Gaussian-Lorentzian mixed function after background subtraction.

HPLC experiments were performed on a Waters 486 chromatograph equipped with a 3.9 x 150 mm Nova-Pak C18 column. The mobile phase was methanol-water (50:50, v/v) and the flow rate was  $0.5 \text{ mL}\cdot\text{min}^{-1}$ . The identification of the products and the calculation of their concentration were based on HPLC comparison with authentic samples (UV-Vis detector 254 nm).

BET measurements were performed on a Micromeritics FlowSorb II 2300 apparatus using a 30% mixture of nitrogen in helium flowing gas, after 30 min. outgasing at  $250^\circ\text{C}$ .

### **Preparation of modified graphite felt electrodes**

The anodic oxidation of the graphite felt (48 mm diameter, 10 mm thickness) was performed for 1 h in a divided flow cell<sup>31</sup>, either in a pH=2.2 phosphate buffer solution ( $\text{NaH}_2\text{PO}_4$  0.25 M;  $\text{H}_3\text{PO}_4$  0.25M) or in a pH=9.2 borate buffer solution ( $\text{H}_3\text{BO}_3$  0.25 M;  $\text{H}_2\text{BO}_3\text{Na}$  0.25 M), with current intensities of 150 mA or 300 mA, respectively (2/3 of the current between the cathode located at the electrolyte entry and 1/3 between the cathode located at the electrolyte outlet<sup>31</sup>) (the measured potential was around  $1.5 \text{ V}_{\text{SCE}}$ ).

OH test: the felt was heated at  $40^\circ\text{C}$  for 3h with 4-nitrobenzoyl chloride (100 mg) in toluene.

COOH test: acyl chlorides were prepared by heating for 3h the electrode at  $40^\circ\text{C}$  in toluene in the presence of thionyl chloride (1 ml). The felts were rinsed in toluene and subsequently heated for 3h at  $40^\circ\text{C}$  in toluene in the presence of 3-nitrobenzylamine (100 mg) and triethylamine (1 ml).

Immobilization of TEMPO: the oxidised electrodes were treated with 4-amino-TEMPO (15 mg, 0.096 mmol) and 1,3-dicyclohexylcarbodiimide (21 mg, 0.102 mmol) in *N,N*-dimethylformamide (DMF) at room temperature for 80 hours.

The modified graphite felts were sonicated in DMF and water (3 x 30 min) before being analysed.

### **Indirect anodic oxidation of 4-nitrobenzyl alcohol at pH 10.3**

The anodic oxidation at the TEMPO modified electrode, of 4-nitrobenzyl alcohol ( $9.8 \times 10^{-6}$  mol,  $n_{\text{alcohol}} \simeq 100 \times n_{\text{catalyst}}$  with  $n_{\text{catalyst}}$  measured by cyclic voltammetry) in a pH 10.3 carbonate buffer solution (100 ml) ( $\text{Na}_2\text{CO}_3$  0.25 M;  $\text{NaHCO}_3$  0.25 M) was carried out in a divided flow cell at 0.7  $V_{\text{SCE}}$  (saturated calomel electrode). The electrolyte flowed through the porous electrode with recycling ( $7 \text{ mL min}^{-1}$ ). The reaction was stopped when the current fell to 40-45  $\mu\text{A}$  (the initial current was around 2 mA).

The same experiment was carried out for samples used in XPS analyses, except that 4-bromobenzyl alcohol was used instead of 4-nitrobenzyl alcohol to avoid any nitrogen source which could contaminate the electrode surface. The felts were sonicated (3 x 30 min) in water from Carlo Erba (Water Plus for HPLC) before XPS analyses. The same surface of the felt was analysed before and after electrocatalysis.

### **Indirect anodic oxidation of 4-nitrobenzyl alcohol in acetonitrile**

A solution of 4-nitrobenzyl alcohol ( $1.6 \times 10^{-5}$  mol,  $n_{\text{alcohol}} \simeq 100 \times n_{\text{catalyst}}$  with  $n_{\text{catalyst}}$  measured by cyclic voltammetry), using anhydrous acetonitrile (100 ml) and 2,6-lutidine (10  $\mu\text{l}$ ) and in lithium perchlorate (0.2 M) was electrochemically oxidised at 0.9  $V_{\text{SCE}}$  in a divided flow cell fitted with the TEMPO modified electrode, under nitrogen. Potassium hydroxide pellets were added to the solutions of both anodic and cathodic compartments to keep dry the reaction medium. The electrolyte flowed through the porous electrode with recycling ( $7 \text{ mL min}^{-1}$ ). The reaction was stopped when the current fell to 1-5  $\mu\text{A}$  (the initial current was around 0.2 mA).

## **Results**

The first step of the grafting process is the electrochemical oxidation of the graphite felt. It was performed in a flow cell<sup>31</sup> in phosphate buffer (pH=2.2) with an applied current of 150 mA for 1h. First, the oxidized felt was analysed by XPS. The C 1s spectrum showed two well-resolved peaks (Figure 1 and Table 1).

### **Figure 1**

### **Table 1**

The spectrum could be deconvoluted into four components. The main component at 284.4 eV corresponded to C=C groups (graphitic). The 286.6 eV peak could include C-O (C-OH, C-O-C) and C=O (carbonyl, quinone) surface moieties, as oxygen induces shifts to higher binding energies by 1.5 eV per C-O bond. This means that C-O peak is at 285.9 eV, C=O peak at 287.4 eV and COO peak at 288.9 eV.<sup>32, 33</sup> Thus, the peak at 288.4 eV corresponded to COO (carboxylic acid, lactone). The peak at 290.1 eV was attributed to the shake-up satellite ( $\pi \rightarrow \pi^*$ ) of C1s.<sup>32, 34, 35</sup> The oxidised felt also contained nitrogen with a peak at 400.5 eV, as shown by the N 1s analysis (Table 1). The comparison with a fresh felt showed that the presence of nitrogen (0.7 %) on this sample was due to the electrochemical treatment of the graphite electrode. The nitrogen pollution probably comes from the phosphate buffer solution used as reaction medium, which contains traces of nitrogen-containing compounds.<sup>36</sup> For improvement of the N1s analysis, an electrochemical oxidation of the graphite felt was accomplished in a pH=9.2 borate buffer solution. The C1s peak deconvolution showed the presence of oxides on the felt, with a peak at 286.0 eV. At this position, we have mainly C-O and C-O-C groups. It is worth noting that the concentration of C=O groups on the surface of the felt was lower, compared to the felt oxidised in a pH=2.2 phosphate buffer solution (Table 1). As expected, the region of N1s analysis showed the absence of nitrogen on the felt. The presence of the OH and COOH groups on the surface of the electrode was also confirmed by chemical reactions with NO<sub>2</sub>-containing species (Scheme 2).

## Scheme 2

Cyclic voltammetry analyses of the grafted felts were performed in sulfuric acid (0.5 M) and the -NHOH/-NO reversible system could be observed at 0.3 V<sub>SCE</sub><sup>37</sup> after reduction of the NO<sub>2</sub> group into NHOH group at -0.5 V<sub>SCE</sub> (Figure 2).<sup>38</sup> The integration of the cyclic voltammograms (see Figure 2) using the Faraday law gave volume concentrations of 6x10<sup>-8</sup> mol cm<sup>-3</sup> for the reacting OH groups and 9x10<sup>-8</sup> mol cm<sup>-3</sup> for the reacting COOH groups. The specific area of the oxidized felt measured by the BET method (2.0 m<sup>2</sup> g<sup>-1</sup>) was 2.8 times higher than the specific area of the reference non oxidized felt. As the variation of the density was not significant, the surface concentrations were estimated to 3 x 10<sup>-11</sup> mol cm<sup>-2</sup> for the OH groups and 5 x 10<sup>-11</sup> mol cm<sup>-2</sup> for the COOH groups.

## Figure 2

The reaction between amino-TEMPO and carboxylic acids present on the surface of the oxidised felt, in the presence of 1,3-dicyclohexylcarbodiimide (DCC), led to the covalent attachment of TEMPO onto the electrode (Scheme 2). Compared with the oxidised felt, the XPS analysis of the modified electrode (Table 1 and Figure 1) showed a slight decrease of the peaks at 286.3 and 288.1 eV, with an increase of the peak at 284.4 eV corresponding to the graphitic carbons. The comparison of N 1s photoelectron lines of the oxidised electrode before and after grafting of TEMPO revealed the increase of the peak at 400.0 eV for the grafted felt, corresponding to the CONH<sup>39</sup> and the NO<sup>40</sup> groups. The deconvolution also gave another small peak at 402.1 eV, which could be assigned to other nitrogen-containing functionalities present on the oxidised felt. For the electrode oxidised in a pH=9.2 borate buffer solution, a similar behaviour was observed: a peak at 400.2 eV (CONH, NO<sup>•</sup>) appeared (Table 1). However, the peak shape of the C1s spectrum did not change after grafting in this case.

The TEMPO modified electrode was also analysed by cyclic voltammetry in a pH=10.3 carbonate buffer solution and in acetonitrile (Figure 3 and 4).

### Figure 3 and 4

The NO<sup>•</sup>/N=O<sup>+</sup> reversible system was observed at 0.59 V<sub>SCE</sub> and 0.73 V<sub>SCE</sub> in a carbonate buffer solution and acetonitrile respectively. The potentials were anodically shifted by 80 to 100 mV compared to TEMPO in homogeneous solutions (Figure 5).

### Figure 5

It is worth noting that in both cases, the oxidation of the nitroxyl radical in the corresponding oxoammonium salt is easier in aqueous carbonate buffer than in acetonitrile.

The volume concentration of grafted TEMPO, estimated by integration of the cyclic voltammograms, was 3x10<sup>-7</sup> mol cm<sup>-3</sup> in acetonitrile and 9x10<sup>-8</sup> mol cm<sup>-3</sup> in a carbonate buffer solution. The difference between these two values is due to the error of measurement.

An average surface concentration of 10<sup>-10</sup> mol cm<sup>-2</sup> could be determined from the specific surface of the oxidized felt measured by the BET method (vide supra).

The catalytic activity of the immobilized TEMPO towards alcohol oxidation was first studied by cyclic voltammetry. The addition of 4-nitrobenzyl alcohol led to a dramatic enhancement of the oxidation peak (NO<sup>•</sup> to NO<sup>+</sup>) in a carbonate buffer solution, while its reverse cathodic

peak was totally suppressed (Figure 3). In acetonitrile, the addition of 2,6-lutidine and 4-nitrobenzyl alcohol led to a less significant modification of the waveshape of the cyclic voltammogram (Figure 4).

The preparative-scale oxidations of 4-nitrobenzyl alcohol using the TEMPO modified electrode was then attempted, in a flow cell, in an aqueous carbonate buffer solution and in acetonitrile in the presence of 2,6-lutidine, with 1 mol% of catalyst, at 0.7 V<sub>SCE</sub> and 0.9 V<sub>SCE</sub> respectively. The reactions were followed by HPLC. In acetonitrile, the reaction stopped after 1 h of electrolysis, leading selectively to the 4-nitrobenzaldehyde with an integral turnover number of 20 (Table 2). After 4.5 h of electrolysis in a carbonate buffer solution, a mixture of 4-nitrobenzoic acid and 4-nitrobenzaldehyde was obtained with a conversion yield of 91% and a turnover number around 290.

At the end of the electrolyses, the grafted felts were analysed by cyclic voltammetry. The NO<sup>•</sup>/N=O<sup>+</sup> reversible system could not be observed in both cases.

The stability of the TEMPO modified electrode was also tested by cyclic voltammetry. The current-voltage response gradually decreased on repeated scans in acetonitrile and water with a loss of 50% after 50 scans (Figure 6).

### Figure 6

The C1s analysis revealed some differences between the modified electrodes before and after electrocatalysis (Table 1). The peak at 286.1 eV (C-O), decreased in relative intensity after electrolysis, whereas the peak at 288.1 eV (COO) increased. It seems that the alcohols present on the carbon surface are oxidized into carboxylic acids during the electrolysis. However, no significant increase of the shoulder on the high binding energy side was observed. Moreover, the shape of the N1s peak of the grafted felt did not change after electrolysis (Figure 7) and the amount of nitrogen remained constant.

### Figure 7

Similar results were observed in the N1s region with the felt previously oxidised in a pH=9.2 borate buffer solution (Table 1). In this case, the C1s peaks before and after electrocatalysis were superimposable.

## Discussion

It has been reported that anodic oxidation of HOPG, at potentials as high as 1.95 V<sub>SCE</sub>, in aqueous solutions containing phosphate did not lead to intercalation or lattice damage of the electrode.<sup>27, 28</sup> In contrast, the anodic oxidation of the graphite felt, performed in a phosphate buffer solution, leads to the formation of oxides on the surface of the fibres as shown by XPS analysis.<sup>41</sup> As previously observed<sup>30</sup>, the formation of shallow blisters on the surface of the fibres occurs simultaneously leading to the increase of the surface area of the graphite felt. This method of oxidation allows the functionalisation of the felt without dramatic damage. The anodic oxidation of the graphite electrode can also occur in a borate buffer solution, although the applied current intensity has to be higher. Unlike the electrode oxidised in a phosphate buffer solution, the oxidation of the felt does not lead to the formation of nitrogen-containing functionalities on the surface of the fibres. As the N1s analysis is particularly important to attest the presence of TEMPO on the electrode, the felt oxidised in a borate buffer solution is used in this work as a reference for XPS measurements.

The covalent immobilization of OH or NH<sub>2</sub>-containing molecules onto the electrode can be easily achieved by chemical reactions, with a fairly high amount of grafted molecules on the surface of the electrode. Thus TEMPO modified electrodes can be prepared by reaction between 4-amino-TEMPO and the COOH groups formed on the oxidised felt. The immobilization of TEMPO onto the graphite felt is attested by the N1s analysis, showing the increase of the peak at 400.0 eV corresponding to the CONH and NO<sup>•</sup> groups (see Table 1: from 0.7 to 3.6%). This result is confirmed with the felt oxidised in a borate buffer solution by the appearance of a similar peak at 400.2 eV after immobilisation of TEMPO (see table 1: from 0 to 3%). As the peak at 288.1 eV, assigned to COO is large, the substitution of the COOH (288.9 eV) groups by CONH (0.9 eV lower than COOH groups<sup>39</sup>) cannot lead to substantial modifications of the C1s photoemission spectrum. Thus, the C1s spectrum is the same before and after immobilization of TEMPO for a felt previously oxidised in borate buffer. However, the felt oxidised in phosphate buffer exhibits a shift and a decrease of the second main component, which could indicate a decrease of the C=O groups. This decrease is compensated by the increase of the peak assigned to graphitic carbons, probably less attenuated by the presence of oxides on the electrode surface. The decrease of C=O on the grafted felt is not well understood yet.

The presence of TEMPO on the surface of the electrode is also attested by cyclic voltammetry. The NO<sup>•</sup>/N=O<sup>+</sup> reversible system can be observed in both aqueous and nonaqueous solutions. This result outlines the possibility of using the modified electrode in any reaction medium. This is a great advantage of the direct covalent attachment of molecules

onto graphite surface, compared with polymer coating. The anodic shift of the potential observed in acetonitrile and carbonate buffer compared with homogeneous solutions, can be explained by the presence of the amide substituent in the 4-position on the piperidine ring of the grafted TEMPO. Indeed, it has been reported that the difference between the half-wave potentials of 4-substituted-TEMPO and TEMPO could reach 130 mV, depending on the substituent.<sup>42</sup> The volume concentration is fairly high for a covalent grafting process, compared to polymer coating ( $4\text{-}8 \times 10^{-6} \text{ mol cm}^{-3}$  <sup>12, 20, 21</sup>), where the catalyst is in all the thickness of the film. The surface concentration is roughly estimated to be around  $10^{-10} \text{ mol cm}^{-2}$ , by cyclic voltammetry. This value is of the same order of magnitude to the value (around  $10^{-10} \text{ mol cm}^{-2}$ ) expected for monolayer coverage.<sup>43</sup> However, as several types of oxides are present on the graphite surface, only a sub-monolayer of TEMPO is probably present on the electrode.

The catalytic activity of the immobilized TEMPO towards 4-nitrobenzyl alcohol is clearly highlighted by cyclic voltammetry analyses in acetonitrile and carbonate buffer. In acetonitrile the reaction stops at the aldehyde stage with a turn-over of 20. In contrast, the alcohol can be oxidised in the corresponding aldehyde and carboxylic acid derivatives in a carbonate buffer solution. The less of selectivity in aqueous solution has already been observed in homogeneous catalysis and explained by the oxidation of the aldehyde in its hydrated form in the same way as the alcohol.<sup>1</sup> Even if the reaction is not complete, the turn over number (290) is high compared to homogeneous catalysis. Indeed, the turn over number was around 5-40 in acetonitrile <sup>3</sup>, and in water, the ratio of substrate over catalyst used for the oxidation of carbohydrates was around 5.<sup>4</sup> It seems that the immobilization of the catalyst improves its stability, as it has been previously noticed for electrodes modified by electropolymerisation.<sup>14</sup>

Cyclic voltammetry analyses of the felt before and after electrolysis in acetonitrile and water show a degradation of the modified electrode. To understand this phenomenon, the grafted felt was analysed by XPS, before and after the electrolysis in water. As a sub-monolayer of the redox active molecule is present on the surface of the carbon electrode, the carbon atoms of the graphite felt probably represent the largest contribution in the C1s analysis compared with the carbon atoms of TEMPO. Thus, the comparison of the C1s peaks before and after electrocatalysis allows us to observe a possible increase of the oxides on the surface of the electrode. As the shoulder on the high binding energy side observed on the C1s peak corresponding to C-O, C=O and COO increases after electrolysis neither with the felt previously oxidised in a phosphate buffer solution, nor with the reference felt previously

oxidised in a borate buffer solution, it shows that the graphite felt is not oxidised at the potential of the electrocatalysis. It is worth noting that the anodic oxidation of the felt, followed by the nucleophilic attack of water (Eq. 1 and 2) could have caused damage on the surface of the electrode. Thus, another phenomenon is responsible of the electrode degradation. An important information is also provided by the N1s analysis. The presence of nitrogen on the surface of the modified electrode is mainly due to the grafted TEMPO as shown by the increase of the N1s peaks after immobilization of TEMPO (vide supra). Interestingly, the N1s peaks remain constant after electrocatalysis for both felts (3.5% for the felt oxidized in a pH=2.2 phosphate buffer solution and 3.7% for the felt oxidized in a pH=9.2 borate buffer solution). As no source of nitrogen is present in the reaction medium during the electrocatalysis, this result shows that the grafted TEMPO, which is the only source of nitrogen, remains on the electrode surface after electrocatalysis. Consequently, the degradation of the modified electrode observed by cyclic voltammetry is not related to a break of the amide link between TEMPO and the graphite felt, which should lead to the loss of the catalyst in solution. The exact mechanism of degradation of grafted TEMPO is not known but it could be attributed to a problem of regeneration of the oxoammonium from the corresponding hydroxylamine or to a partial instability of the oxoammonium salt. This last point is confirmed by the cyclic voltammetry experiments since the volume concentration of a TEMPO-modified electrode decreases on repeated scans (Figure 5) in both aqueous and organic media.

## **Conclusions**

In conclusion, this work shows that TEMPO can be immobilized onto a graphite felt by direct covalent bonding, with good volume concentrations. One advantage of the modified electrode is that it can be used in both organic and aqueous media. Cyclic voltammetry analyses showed that the grafted TEMPO is active in catalysis in acetonitrile and water. Preparative scale electrolyses lead to the formation of the expected products with a turn over up to 290. This value, which is higher than the values reported for homogeneous catalysis, shows that the catalyst is more stable when it is immobilized onto the electrode than when it is in solution. XPS analysis of the grafted felt before and after electrolysis shows that a chemical modification of the catalyst is responsible of the degradation of the modified electrode during the electrolysis.

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 solution proceeds according to the following mechanism:

$$\text{Ar-NO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{Ar-NHOH} + \text{H}_2\text{O}$$

$$\text{Ar-NHOH} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{Ar-NH}_2 + \text{H}_2\text{O} \text{ at more cathodic potential}$$

$$\text{Ar-NHOH} \rightleftharpoons \text{Ar-NO} + 2\text{H}^+ + 2\text{e}^-$$

When the nitro group is partially reduced into arylhydroxylamine (Ar-NHOH), the  
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## Figure captions

**Figure 1** XPS spectra of the C 1s region of the graphite felt oxidised in pH=2.2 phosphate buffer (0.5 M) (**A**, -□-) or in pH=9.2 borate buffer (0.5 M) (**B**, -□-) with the corresponding deconvolution which parameters are given in Table 1. The C1s spectra of the grafted felts before (-○-) and after (-△-) electrocatalysis are also given in both cases. The peaks have been background subtracted.

**Figure 2** Cyclic voltammetry in 0.5M  $\text{H}_2\text{SO}_4$  of NHOH/NO system obtained from nitro species attached onto the felt by an amide group (—) or by an ester group (....). Scan rate: 0.1  $\text{V s}^{-1}$ . Only the bottom of the wave (e.g. hatched area) was considered to calculate the volume concentration.

**Figure 3** Cyclic voltammetry in pH 10.3 sodium carbonate buffer (0.5 M) of a fresh felt (...) and TEMPO grafted felts, in the presence (----) or not (—) of 4-nitrobenzyl alcohol ( $6.5 \times 10^{-3}$  mol l<sup>-1</sup>). Scan rate: 0.1 V s<sup>-1</sup>.

**Figure 4** Cyclic voltammetry in acetonitrile + 0.2M LiClO<sub>4</sub> of TEMPO grafted felts, in the presence (----) or not (—) of 4-nitrobenzyl alcohol ( $6.5 \times 10^{-3}$  mol l<sup>-1</sup>). Scan rate: 0.01 V s<sup>-1</sup>

**Figure 5** Cyclic voltammetry of TEMPO ( $4.9 \times 10^{-3}$  mol l<sup>-1</sup>) at a glassy carbon electrode in pH 10.3 sodium carbonate buffer (0.5 M) / acetonitrile (8 / 2) at 0.1 V s<sup>-1</sup> (----) and acetonitrile + 0.2M Bu<sub>4</sub>NClO<sub>4</sub> at 0.01 V s<sup>-1</sup> (—).

**Figure 6** Variation of the volume concentrations of immobilized TEMPO, estimated by cyclic voltammetry in acetonitrile + 0.2M Bu<sub>4</sub>NClO<sub>4</sub> at 0.01 V s<sup>-1</sup> (-●-) and in pH 10.3 sodium carbonate buffer (0.5 M) at 0.1 V s<sup>-1</sup> (-■-), as a function of scan number. The initial values of the volume concentrations were set to 100%.

**Figure 7** XPS spectrum of the N1s region of the grafted felt before and after electrocatalysis. The curves have been background subtracted and normalised to a constant intensity.

### Scheme captions

**Scheme 1** Alcohol oxidation by TEMPO in alkaline medium.

**Scheme 2** Preparation of the modified graphite felt electrodes.

**Table 1:** Parameters obtained from the XPS measurements of the oxidised felt and of the grafted felt with 4-amino-TEMPO before and after electrocatalysis.

Nature of the felt		Binding energy/eV <sup>a</sup>	FWHM/eV <sup>a, b</sup>	% Peak area ratio <sup>a, c</sup>
Oxidised felt	C1s	284.4 (284.4)	1.5 (1.3)	51.1 (71.8)
		286.6 (286.0)	1.7 (2.2)	34.5 (24.9)
		288.4 (288.5)	1.8 (2.2)	9.1 (3.3)
		290.1	3.5	5.2
Grafted felt	C1s	400.5 (-)	3.3 (-)	0.7 (0)
		284.4 (284.4)	1.4 (1.0)	63.4 (67.8)
		286.3 (285.9)	1.9 (2.2)	30.5 (24.1)
	N1s	288.1 (288.5)	1.7 (2.3)	6.1 (8.1)
400.0 (400.2)		2.2 (2.2)	3.6 (3.0)	
Grafted felt after electrocatalysis	C1s	402.1	2.0	0.4
		284.4 (284.4)	1.5 (1.0)	62.4 (62.7)
		286.1 (285.7)	1.9 (2.3)	22.5 (26.3)
	N1s	288.1 (288.3)	1.8 (1.6)	10.0 (5.6)
		289.3	3.5	5.1
		400.4 (400.2)	2.3 (2.3)	3.5 (3.7)

<sup>a</sup> The results of the sample used as an XPS reference (anodic oxidation in a pH=9.2 borate buffer solution) are given in brackets <sup>b</sup> Full-Width Half-Maximum of peaks <sup>c</sup> (C1s or N1s)/C1s total with the intensity of the N1s peaks corrected for the ionisation cross-section (1.77 relative to the C1s cross-section).

**Table 2:** Anodic oxidations of 4-nitrobenzyl alcohol using the TEMPO-modified electrode.

Electrolysis medium	Time/h	% Conversion yield <sup>a</sup>	% Yield <sup>a</sup>		Charge passed (C)	% Current efficiency <sup>b</sup>	TON <sup>c</sup>
			Aldehyde	Acid			
Acetonitrile	1	8	10	0	0.32	99	20
Carbonate buffer	4.5	91	54	39	4.01	71	290

<sup>a</sup> Approximate yields calculated using the concentrations determined by HPLC <sup>b</sup> Current efficiency=100xtheoretical charge/charge passed <sup>c</sup> Turnover number (TON) =  $(2n_{\text{aldehyde}}+4n_{\text{acid}})/n_{\text{catalyst}}$ , where  $n_{\text{aldehyde}}$ ,  $n_{\text{acid}}$  and  $n_{\text{catalyst}}$  are the number of moles of aldehyde, acid and catalyst respectively.

Figure 1

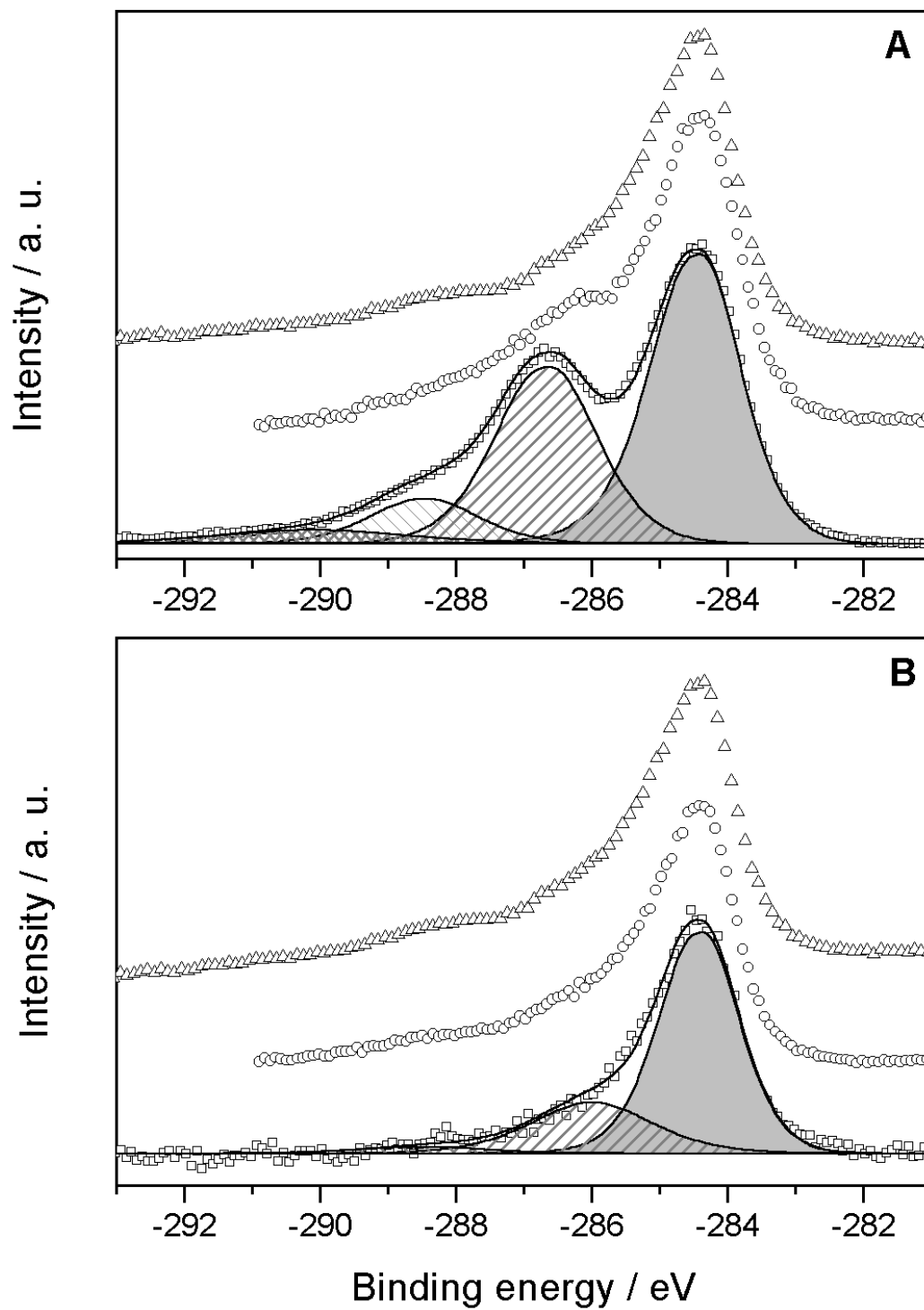


Figure 2

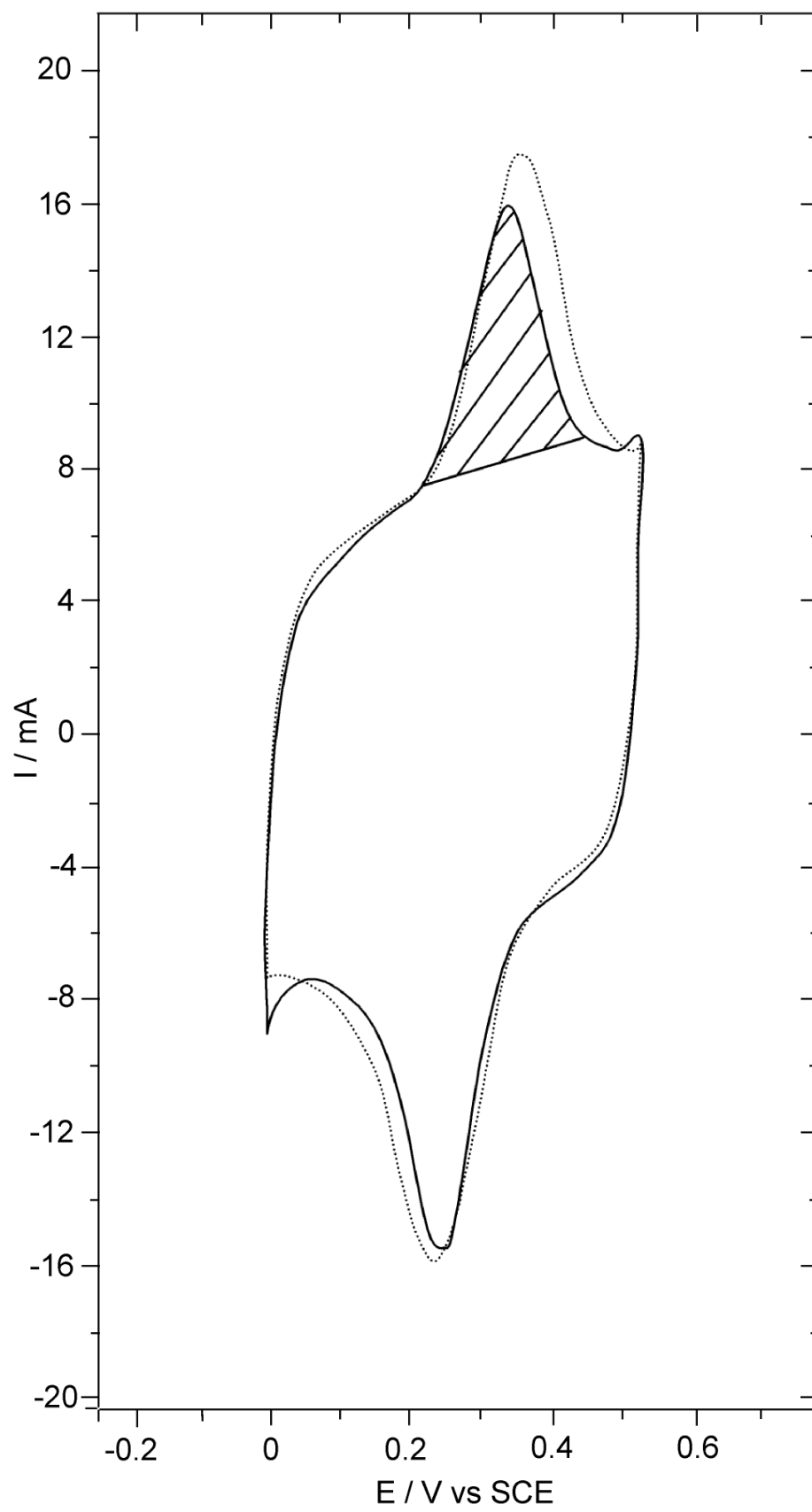


Figure 3

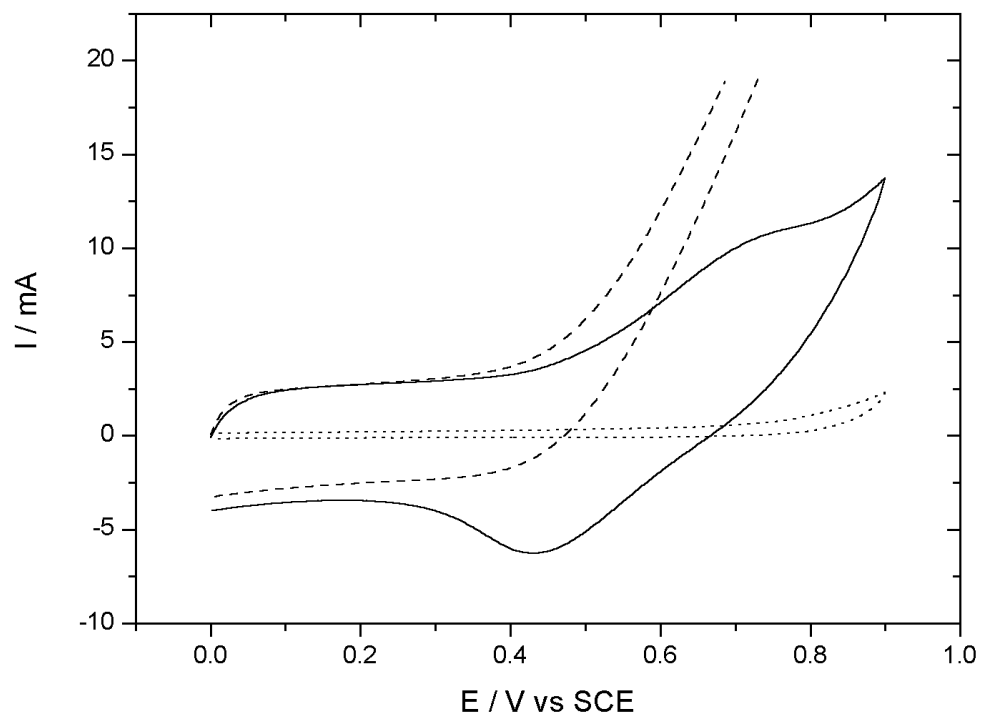


Figure 4

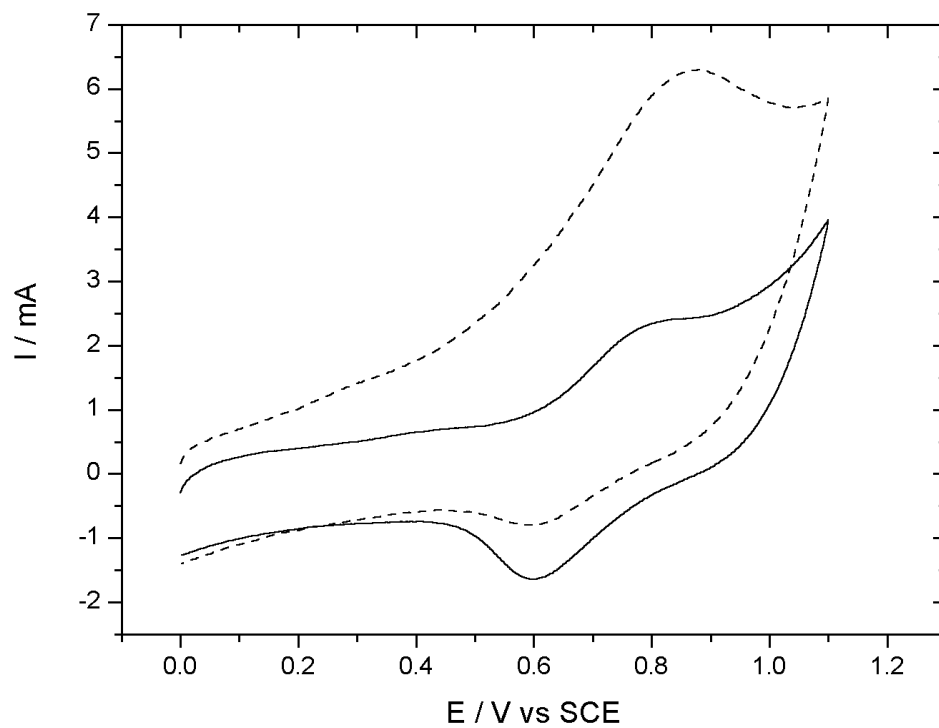
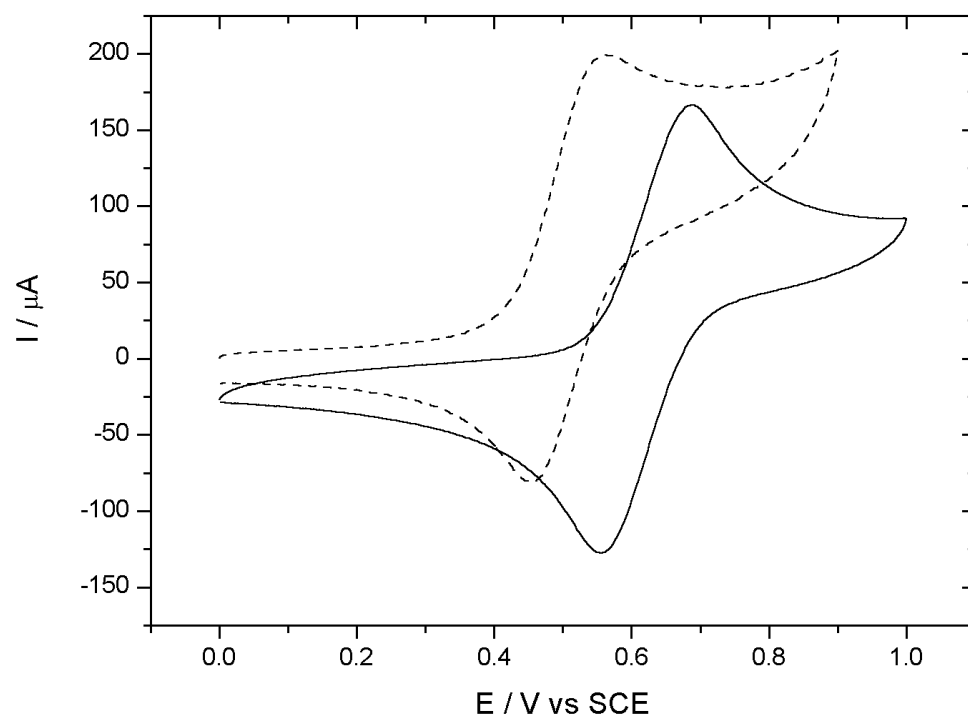


Figure 5



**Figure 6**

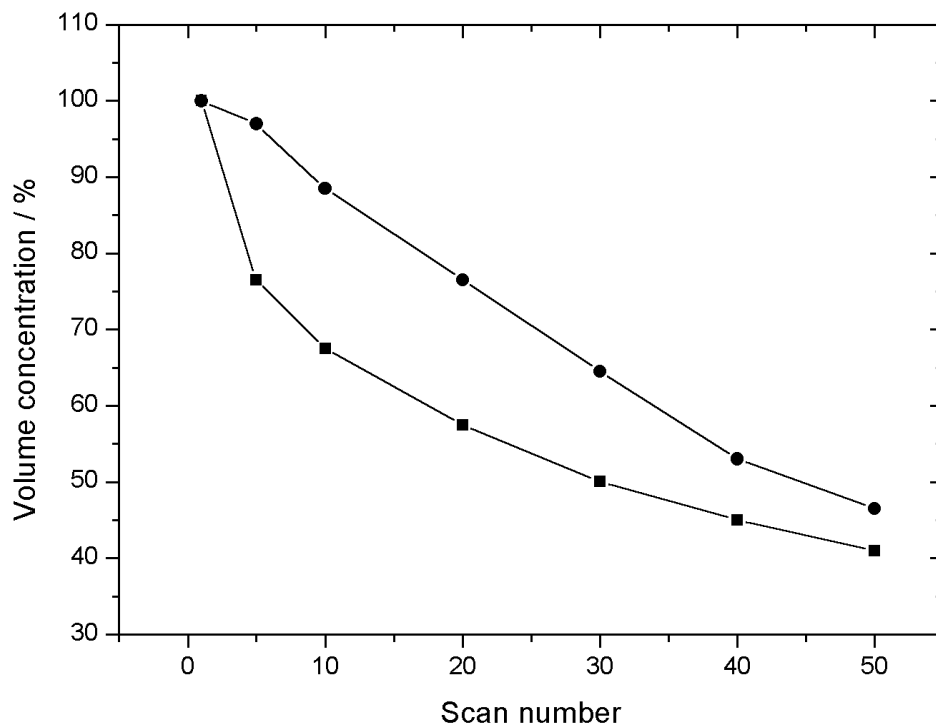
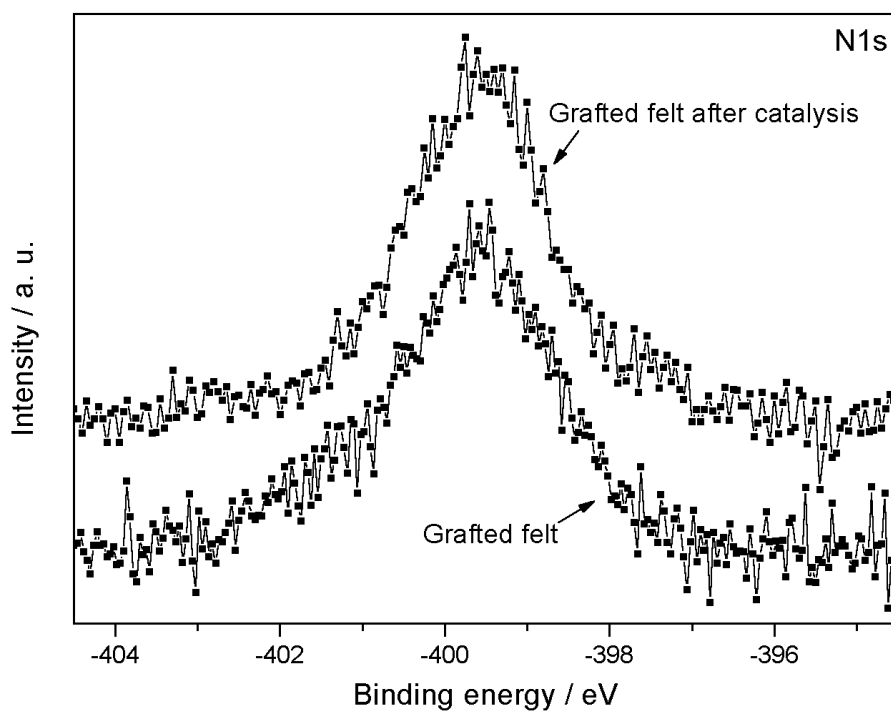
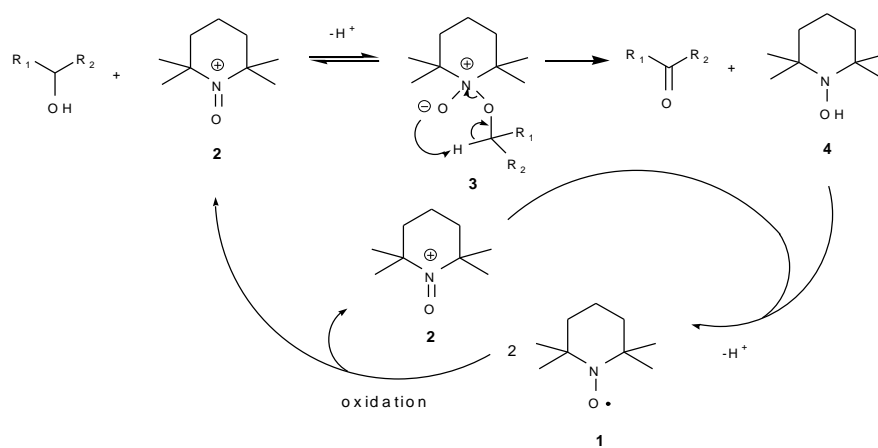


Figure 7



## Scheme 1



## Scheme 2

