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

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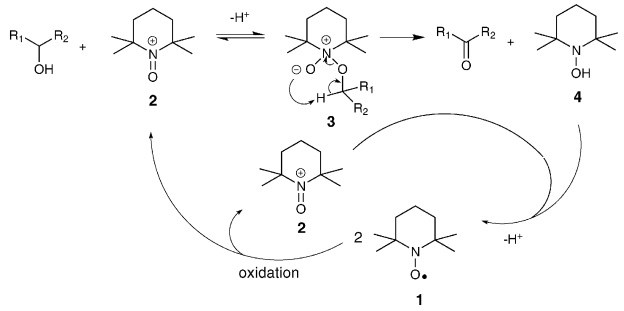
This work describes a simple method to attach TEMPO by an amide link to a graphite felt electrode. The derivatization of the electrode is highlighted by cyclic voltammetry and XPS analyses. Cyclic voltammetry analyses showed the catalytic activity of the grafted TEMPO in both organic and aqueous media. The electrolyses revealed improved stability of the grafted catalyst in aqueous medium compared to 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 not due to a break of the amide link between the graphite felt and TEMPO.

Introduction

Oxidation of alcohols to aldehydes, ketones or carboxylic acids is a fundamental reaction in organic synthesis. In the search for an environmentally friendly and economical method, stable organic nitroxyl radicals such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) **1** have been widely studied as catalysts for alcohol oxidation.[1,2] Actually, the oxidation reagent is the oxoammonium salt **2**, usually prepared *in situ* by chemical or electrochemical oxidation of **1** (Scheme 1).[1–5]

In alkaline medium a mechanism involving a cyclic transition state **3** has been proposed.[1] The intermediate **3** undergoes a cyclic elimination to give the hydroxylamine **4**. Above pH 3, a rapid symproportionation (comproportionation) 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 such as polymers,[6,7] silica[8,9] and MCM-41.[10,11] 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 using polymer coatings. Thus, TEMPO has been encapsulated into Nafion, a perfluorinated anionic polyelectrolyte which exhibits permselectivity towards cations such as oxoammonium salts.[12,13] Nafion polymers were of particular interest in this study as 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.



Scheme 1 Mechanism of alcohol oxidation by TEMPO in alkaline medium.

Other methods deal with the covalent attachment of nitroxyl radicals onto a polymer film. Thus, the electropolymerization of TEMPO-substituted pyrrole or thiophene has been performed on platinum or carbon electrodes.[14,15] The oxidation of benzyl alcohols to their corresponding carbonyl compounds has been achieved in acetonitrile, in the presence of sodium carbonate, using a modified carbon electrode. However, the authors have reported 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 of the attachment of 4-amino-TEMPO derivatives by an amide bond on polyacrylic acid, previously coated on a graphite felt electrode.[16,17] These modified electrodes have been used to oxidize alcohols in acetonitrile, in the presence of a base.[16–21] 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.[17]

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 of 4-amino-TEMPO at low potential.[22]

The approach taken in this work involves the chemical reaction between COOH groups present on the surface of the electrode and NH_2-containing compounds, with the formation

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of an amido linkage.[23–25] The anodic oxidation of graphite electrodes in aqueous acidic medium leads to the formation of surface COOH and OH groups. The 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 (eqn (1) and (2)).[26–29]

$$[C_x] + y(HSO_4^-, solv) \rightleftharpoons [C_x^{y+}, y(HSO_4^-, solv)] + ye^- \quad (1)$$

$$[C_x^{y+}, y(HSO_4^-, solv)] + yH_2O \rightleftharpoons [C_x(OH)_y] + yH_2SO_4 + ysolv] \quad (2)$$

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

We report here that the covalent attachment of TEMPO with a volume concentration of around 10^{-7} mol cm^{-3} can be achieved using this method. An analytical study of the electrocatalytic activity of the grafted TEMPO shows that the modified electrode is active towards the oxidation of 4-nitrobenzyl alcohol in aqueous and acetonitrile solutions. The deactivation of the modified electrode observed during the grafting process is investigated by photoelectron spectroscopy, showing that the degradation is not due to the loss of the catalyst into the solution.

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^2 g^{-1} and its density is 0.088 g cm^{-3}. 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% 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,[30] 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-electrode 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 served as the reference electrode.

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. The X-ray source used either Al or Mg Kα 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. The C1s level (284.4 eV) on clean felt served as a reference for all spectra. Simulation of the experimental peaks was carried out using a Gaussian–Lorenzian mixed function after background subtraction.

HPLC experiments were performed on a Waters 486 chromatograph equipped with a 3.9 × 150 mm Nova-Pak C18 column. The mobile phase was methanol–water (50 : 50, v/v) and the flow rate was 0.5 mL min^{-1}. The identification of the products and 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 outgassing at 250 °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,[31] either in a pH = 2.2 phosphate buffer solution (NaH_2PO_4 0.25 M; H_3PO_4 0.25 M) or in a pH = 9.2 borate buffer solution (H_3BO_3 0.25 M; H_2BO_3Na 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[31]) (the measured potential was around 1.5 V_{SCE}).

OH test: the felt was heated at 40 °C for 3 h with 4-nitrobenzoyl chloride (100 mg) in toluene.

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

Immobilization of TEMPO: the oxidized 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 10 days.

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

Samples of 10 mm diameter and 10 mm thickness were taken from the modified electrodes to carry out the analyses and the indirect electrolyses.

Indirect anodic oxidation of 4-nitrobenzyl alcohol at pH 10.3

The anodic oxidation of 4-nitrobenzyl alcohol (9.8×10^{-6} mol, $n_{alcohol} \approx 100 \times n_{catalyst}$ with $n_{catalyst}$ measured by cyclic voltammetry of the TEMPO modified electrode used for the electrolysis) in a pH 10.3 carbonate buffer solution (100 ml) (Na_2CO_3 0.25 M; $NaHCO_3$ 0.25 M) was carried out in a divided flow cell at 0.7 V_{SCE} (saturated calomel electrode). The electrolyte flowed through the porous electrode with recycling (7 mL min^{-1}). The reaction was stopped when the current fell to 40–45 μA (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 × 30 min) in water from Carlo Erba (Water Plus for HPLC) before XPS analyses. Due to differences in volume concentrations observed between samples, the same sample (and the same surface of this sample) was analysed after each electrochemical step.

Indirect anodic oxidation of 4-nitrobenzyl alcohol in acetonitrile

A solution of 4-nitrobenzyl alcohol (1.6×10^{-5} mol, $n_{alcohol} \approx 100 \times n_{catalyst}$ with $n_{catalyst}$ measured by cyclic voltammetry of the TEMPO modified electrode used for the electrolysis), using anhydrous acetonitrile (100 ml) and 2,6-lutidine (10 μl) and in lithium perchlorate (0.2 M) was electrochemically oxidized at 0.9 V_{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 the reaction medium dry. The electrolyte flowed through the porous electrode with recycling (7 mL min^{-1}). The reaction was stopped when the current fell to 1–5 μA (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 using a flow cell[31] in phosphate buffer (pH = 2.2) with an applied current of 150 mA for 1 h. First, the oxidized felt was analysed by XPS. The C1s spectrum showed two well-resolved peaks (Fig. 1 and 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 may 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 the C–O peak is at 285.9 eV, the C═O peak at 287.4 eV and the COO peak at 288.9 eV.[32,33] 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.[32,34,35] The oxidized felt also contained nitrogen with a peak at 400.5 eV, as shown by the N1s analysis (Table 1). The comparison with fresh felt showed that the presence of nitrogen (0.7%) on this sample was due to the electrochemical treatment of the graphite electrode. The pollution by nitrogen probably comes from the phosphate buffer solution used as reaction medium, which contains traces of nitrogen-containing compounds.[36] To improve the N1s analysis, an electrochemical oxidation of the graphite felt was performed 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. This position consists mainly of 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 oxidized 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 reaction with NO_2-containing species (Scheme 2).

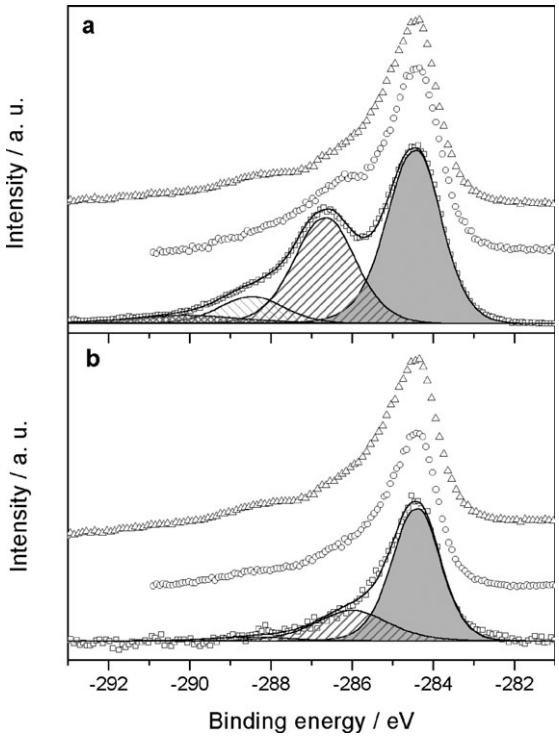


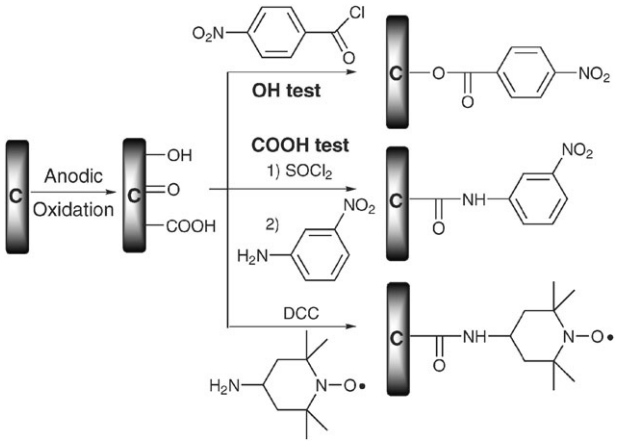
Fig. 1 XPS spectra of the C1s region of the graphite felt oxidized in pH = 2.2 phosphate buffer (0.5 M) (a, □) or in pH = 9.2 borate buffer (0.5 M) (b, □) with the corresponding deconvolution for which parameters are given in Table 1. The C1s spectra of the grafted felts before (○) and after (△) electrocatalysis are also given in both cases. The peaks have been background subtracted.

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

Nature of the felt		Binding energy/eV[a]	FWHM/eV[a,b]	% Peak area ratio[a,c]
Oxidized 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
	N1s	400.5 (–)	3.3 (–)	0.7 (0)
Grafted felt	C1s	284.4 (284.4)	1.4 (1.0)	63.4 (67.8)
		286.3 (285.9)	1.9 (2.2)	30.5 (24.1)
		288.1 (288.5)	1.7 (2.3)	6.1 (8.1)
	N1s	400.0 (400.2)	2.2 (2.2)	3.6 (3.0)
		402.1	2.0	0.4
Grafted felt after electrocatalysis	C1s	284.4 (284.4)	1.5 (1.0)	62.4 (62.7)
		286.1 (285.7)	1.9 (2.3)	22.5 (26.3)
		288.1 (288.3)	1.8 (1.6)	10.0 (5.6)
		289.3	3.5	5.1
	N1s	400.4 (400.2)	2.3 (2.3)	3.5 (3.7)

[a] The results of the sample used as an XPS reference (anodic oxidation in a pH = 9.2 borate buffer solution) are given in brackets. [b] Full-Width Half-Maximum of peaks. [c] 100*(C1s or N1s)/C1s total with the intensity of the N1s peaks corrected for the ionization cross-section (1.77 relative to the C1s cross-section).

Cyclic voltammetry analyses of the grafted felts were performed in sulfuric acid (0.5 M) and the NHOH/NO reversible system was observed with a peak separation of 80–100 m V_{SCE} at 0.3 V_{SCE}[37] after reduction of the NO_2 group into NHOH group at −0.5 V_{SCE} (Fig. 2).[38] Two scans between 0 V_{SCE} and −0.5 V_{SCE} were sufficient to reduce all the grafted NO_2 compounds into hydroxylamines. The integration of the cyclic voltammograms (see Fig. 2) using the Faraday law gave volume concentrations of 1–3 × 10^{-7} mol cm^{-3} for the OH groups and 0.9–3 × 10^{-7} mol cm^{-3} for the COOH groups. The range of values is given on the basis of three different oxidized felts. The derivatization reactions were carried out on two samples taken from each oxidized felt to measure the OH and COOH volume concentrations. It is worth noting that the value obtained for the volume concentration also depended on the analysed sample (10 mm diameter, 10 mm thickness) taken from the modified electrode (48 mm diameter, 10 mm thickness). Thus, the difference in volume concentration of several samples taken on a same modified felt was ±1 × 10^{-7} mol cm^3. The specific area of the oxidized felt measured by the BET method (2.0 m^2 g^{-1}) 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



Scheme 2 Preparation of the modified graphite felt electrodes.

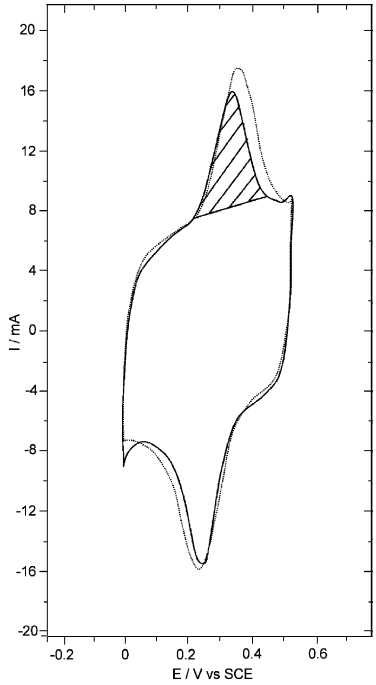


Fig. 2 Typical voltammograms of NHOH/NO system obtained in 0.5 M H_2SO_4 for nitro species attached onto the felt by an amide group (—) or by an ester group (···). Scan rate: 0.1 V s^{-1}. Only the bottom of the wave (*e.g.* hatched area) was considered for calculation of the volume concentration.

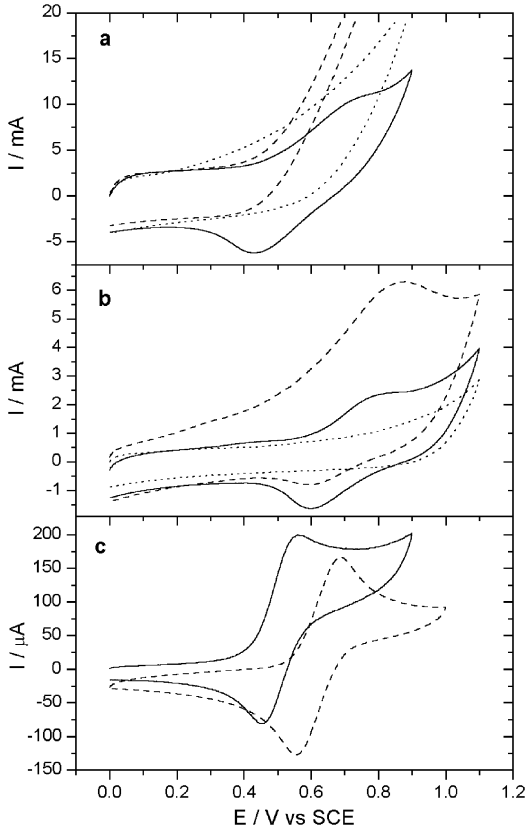


Fig. 3 (a) Cyclic voltammetry in pH 10.3 sodium carbonate buffer (0.5 M) of a TEMPO grafted felt (—), and of an oxidized felt (···) and a TEMPO grafted felt (--) in the presence of 4-nitrobenzyl alcohol (6.5×10^{-3} mol l^{-1}). Scan rate: 0.1 V s^{-1}. (b) Cyclic voltammetry in acetonitrile + 0.2 M $LiClO_4$ of a TEMPO grafted felt (—), and of an oxidized felt (···) and a TEMPO grafted felt (--) in the presence of 4-nitrobenzyl alcohol (6.5×10^{-3} mol l^{-1}) and 2,6-lutidine (4.3×10^{-3} mol l^{-1}). Scan rate: 0.01 V s^{-1} (c) Cyclic voltammetry of TEMPO (4.9×10^{-3} mol l^{-1}) at a glassy carbon electrode in pH 10.3 sodium carbonate buffer (0.5 M)–acetonitrile (8 : 2) at 0.1 V s^{-1} (--) and acetonitrile + 0.2 M Bu_4NClO_4 at 0.01 V s^{-1} (—).

estimated to be $0.6–1.7 \times 10^{-10}$ mol cm^{-2} for the OH groups and $0.5–1.7 \times 10^{-10}$ mol cm^{-2} for the COOH groups.

The reaction between amino-TEMPO and carboxylic acids present on the surface of the oxidized felt, in the presence of 1,3-dicyclohexylcarbodiimide (DCC), led to the covalent attachment of TEMPO onto the electrode (Scheme 2). Compared with the oxidized felt, the XPS analysis of the modified electrode (Table 1 and Fig. 1) showed a slight decrease of the peaks at 286.3 and 288.1 eV, and an increase of the peak at 284.4 eV corresponding to the graphitic carbons. The comparison of N1s photoelectron lines of the oxidized 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[39] and the NO[40] groups. The deconvolution also gave another small peak at 402.1 eV, which could be assigned to other nitrogen-containing functionalities present on the oxidized felt. For the electrode oxidized in a pH = 9.2 borate buffer solution, a similar behaviour was observed: a peak at 400.2 eV (CONH, $NO^{\bullet}$) 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 (Fig. 3a and b).

The $NO^{\bullet}/N{=}O^{+}$ reversible system was observed at 0.59 V_{SCE} and 0.73 V_{SCE} with a peak separation of 290 and 250 m V_{SCE} in a carbonate buffer solution and acetonitrile, respectively. The potentials were anodically shifted by 80 to 100 mV compared to TEMPO in homogeneous solution (Fig. 3c).

The volume concentration of grafted TEMPO, estimated by integration of the cyclic voltammograms (see Fig. 2), was 0.9–3×10^{-7} mol cm^{-3} in acetonitrile and in a carbonate buffer solution. As for the OH and COOH tests, the range of values is given on the basis of three different modified felts and the difference in volume concentrations of several samples taken on a same modified felt was $\pm 1 \times 10^{-7}$ mol cm^{-3}. A surface concentration of $0.5–1.7 \times 10^{-10}$ mol cm^{-2} was 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 ($NO^{\bullet}$ to NO^{+}) in a carbonate buffer solution, while its reverse cathodic peak was totally suppressed (Fig. 3a). In acetonitrile, the addition of 2,6-lutidine and 4-nitrobenzyl alcohol led to a less meaningful modification of the wave shape of the cyclic voltammogram (Fig. 3b).

The electrolysis 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_{SCE} and 0.9 V_{SCE}, 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 of 290. Using oxidized felt as the working electrode, 4-nitrobenzaldehyde was not oxidized after 1 h of electrolysis in acetonitrile and a conversion yield of only 39% (39% of aldehyde and 4% of acid) was observed after 4.5 h of electrolysis in a carbonate buffer solution (Table 2). At the end of the electrolyses, the grafted felts were analysed by cyclic voltammetry. The $NO^{\bullet}/N{=}O^{+}$ reversible system was not observed in both cases.

The stability of the TEMPO modified electrode was also tested by cyclic voltammetry. The current–voltage response

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

Electrolysis medium	Time/h	Conversion yield[a] (%)	Yield[a] (%)		Charge passed/C	Current efficiency[b] (%)	TON[c]
			Aldehyde	Acid			
Acetonitrile	1	8	10	0	0.32	99	20
Carbonate buffer	4.5	91 (39)	39 (39)	54 (4)	4.01 (4.03)	70 (22)	290

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

gradually decreased on repeated scans in acetonitrile and water with a loss of 50% after 50 scans (Fig. 4).

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 (Fig. 5) and the amount of nitrogen remained constant.

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

Discussion

It has been reported that anodic oxidation of HOPG, at potentials as high as 1.95 V_{SCE}, in aqueous solutions containing phosphate did not lead to intercalation or lattice damage of the electrode.[27,28] In contrast, the anodic oxidation of 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.[41] As previously observed,[30] the formation of shallow blisters on the surface of the fibres occurs simultaneously leading to an increase of the surface area of the graphite felt. This method of oxidation allows the functionalization 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 oxidized 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 oxidized in a borate buffer solution is used in this work as a reference for XPS measurements.

The covalent immobilization of OH or NH_2-containing molecules onto the electrode can be easily achieved by chemical reaction, with 0.6–1.7 × 10^{-10} mol cm^{-2} of grafted molecules on the surface of the electrode. This value is fairly high for a sub-monolayer covalent grafting process. Indeed, surface concentrations of 6–28 × 10^{-10} mol cm^{-2} on HOPG[42–44] and 0.7–1.7 × 10^{-10} mol cm^{-2} on graphite felt[45] have been reported for the multilayer[46] grafting process involving the reduction of diazonium salts. Other methods such as the oxidation of amines[47,48] and carboxylates[49] lead to monolayer coverage with surface concentrations of 3.2–7.3 × 10^{-10} mol cm^{-2} and 1.4–2.5 × 10^{-10} mol cm^{-2}, respectively.

Thus TEMPO modified electrodes can be prepared by reaction between 4-amino-TEMPO and the COOH groups formed on the oxidized felt. The immobilization of TEMPO onto the graphite felt was shown by the N1s analysis, showing the increase of the peak at 400.0 eV corresponding to the CONH and NO• groups (see Table 1: from 0.7 to 3.6%). This result was confirmed with the felt oxidized in a borate buffer solution by the appearance of a similar peak at 400.2 eV after immobilization 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[39]) cannot lead to substantial modification of the C1s photoemission spectrum. Thus, the C1s spectrum is the same before and after immobilization of TEMPO for felt previously oxidized in borate buffer. However, the felt oxidized in phosphate buffer exhibited 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 attenu-

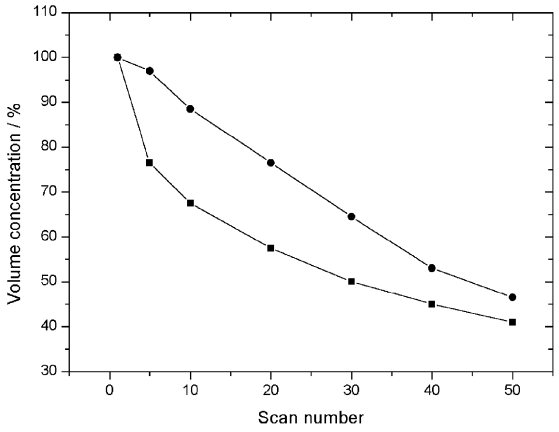


Fig. 4 Variation of the volume concentrations of immobilized TEMPO, estimated by cyclic voltammetry in acetonitrile + 0.2 M Bu_4NClO_4 at 0.01 V s^{-1} (●) and in pH 10.3 sodium carbonate buffer (0.5 M) at 0.1 V s^{-1} (■), as a function of scan number. The initial values of the volume concentrations were set to 100%.

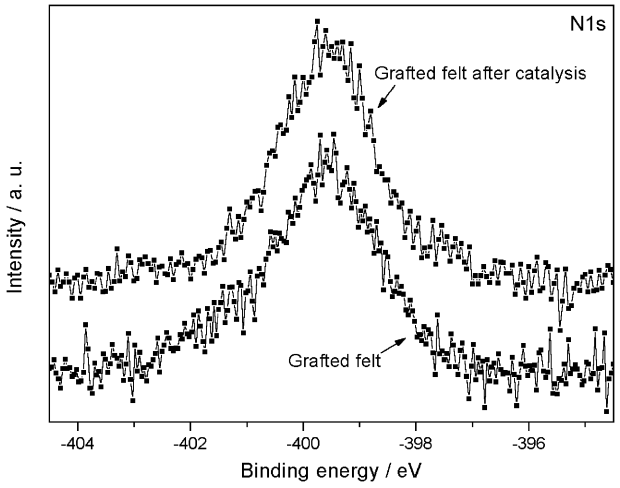


Fig. 5 XPS spectrum of the N1s region of the grafted felt before and after electrocatalysis. The curves have been background subtracted and normalized to a constant intensity.

ated by the presence of oxides on the electrode surface. The decrease of C=O on the grafted felt is not, as yet, well understood.

The presence of TEMPO on the surface of the electrode was also shown by cyclic voltammetry. Surface-confined, diffusionless species generally lead to a symmetric wave without any peak separation between the anodic and cathodic peak positions. The large peak separation observed for TEMPO-modified surfaces can be explained by the potential gradient inside the volumic electrode. The fact that a lower peak separation was observed for nitrobenzyl-modified surfaces indicated that charge-transfer kinetics and/or ohmic drop also interfere. The $NO^{\bullet}/N{=}O^{+}$ reversible system can be observed in both aqueous and nonaqueous solutions. This result highlights the possibility of using the modified electrode in any reaction medium. This is the great advantage of the direct covalent attachment of molecules onto a 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.[50] The volume concentration is fairly high for a covalent grafting process, compared with polymer coating (4–8 $\times$ 10^{-6} mol cm^{-3}),[12,20,21] where the catalyst is in all the thickness of the film. This can be explained by the increase of the graphite surface during the anodic oxidation of the felt. Indeed, we previously observed that the oxidation of amines led to higher volume concentrations (2.4 $\times$ 10^{-7} mol cm^{-3} against 1.2 $\times$ 10^{-8} mol cm^{-3}) when the felt was oxidized during the grafted process.[22] The surface concentration is roughly estimated to be 0.5–1.7 $\times$ 10^{-10} mol cm^{-2}. This value is of the same order of magnitude to the value (around 10^{-10} mol cm^{-2}) expected for monolayer coverage.[51] 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 oxidized in the corresponding aldehyde and carboxylic acid derivatives in a carbonate buffer solution. The loss 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.[1] Even if the reaction is not complete, the turnover number (290) is high compared to homogeneous catalysis. Indeed, the turnover number was around 5–40 in acetonitrile,[3] and in water, the ratio of substrate to catalyst used for the oxidation of carbohydrates was around 5.[4] It seems that the immobilization of the catalyst improves its stability, as it has been previously noticed for electrodes modified by electropolymerization.[14] Moreover, the authors reported that whereas 4-methoxybenzyl alcohol could be oxidized into the corresponding aldehyde with a yield of 87%, after 4 h of electrolysis in acetonitrile, the oxidation of other aromatic alcohols led to lower yields (23% for benzyl alcohol). This result seems to be consistent with the low yield (10%) obtained for the oxidation of 4-nitrobenzyl alcohol in acetonitrile with the TEMPO grafted felt.

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 the observation of a possible increase in 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 oxidized in a phosphate buffer solution, nor with the reference felt previously oxidized in a borate buffer solution, it shows that the graphite felt is not oxidized at the potential of the electrocatalysis. It is worth noting that the anodic oxidation of the felt, followed by the nucleophilic attack of water (eqn (1) and (2)) could have caused damage on the surface of the electrode. Thus, another phenomenon is responsible for the electrode degradation. 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 species 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 (Fig. 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 volume concentrations around 10^{-7} mol cm^{-3}. 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. The electrolyses led to the formation of the expected products with a turnover of up to 290. XPS analysis of the grafted felt before and after electrolysis shows that the degradation of the modified electrode during the electrolysis is not due to the breaking of the amide link between TEMPO and the graphite felt. These results are encouraging and the aim of our further investigations will be to increase the amount and the stability of grafted TEMPO to achieve large scale electrolyses.

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

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

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

When the nitro group is partially reduced into arylhydroxylamine (Ar-NHOH), the interconversion between Ar-NHOH and Ar-NO can occur

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