LETTER

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Electrochemically linking TEMPO to carbon *via* amine bridges

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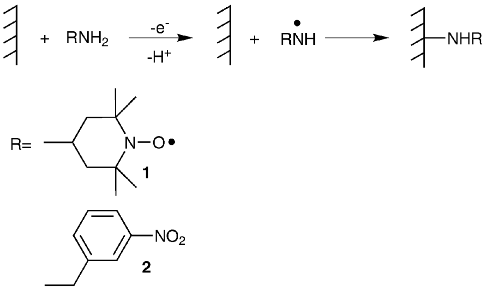
The immobilization of amino-containing compounds onto a graphite felt electrode is achieved by anodic oxidation in water. At high potentials, the specific surface of the felt increases during the grafting process, leading to high volume concentrations. The electrochemical reaction can also proceed at low potentials, giving rise to the successful covalent attachment of TEMPO onto the electrode.

Nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO; **1**), play an increasingly important role in organic synthesis, as catalysts for the oxidation of alcohols to aldehydes, ketones and carboxylic acids.[1–3] Although only small amounts of catalyst are usually used, it is desirable to develop a chemical process allowing simple product and catalyst purification, as well as catalyst recycling. In this aim, several methods for the immobilization of TEMPO have been developed.[4–13] However, to our knowledge, the solid covalent bonding of TEMPO onto the surface of electrodes has never been accomplished. In the search for methods to achieve covalent attachment of TEMPO onto graphite felt electrodes used as active supports, we were interested in a route involving a reaction between carbon surfaces and electrochemically generated radicals.[14] One modification method is based on the anodic oxidation of amine-containing compounds (Scheme 1).[15,16]

The mechanism proceeds *via* the one-electron oxidation of the amine group to the corresponding radical cation, which deprotonates to give a radical.[17] This radical reacts with the carbon surface, leading to covalent attachment of the compound *via* an amine linkage. Aliphatic and benzyl amines, as well as aminopyridine, could be immobilized by this method.[15,16,18–21] Although the procedure works well with primary amines, it only leads to low surface coverage with secondary amines and tertiary amines could not be immobilized. The amine anodic oxidation is usually carried out in anhydrous solvents. However, it has been noticed that aqueous solutions also support this process.[16]



Scheme 1 Mechanism of the derivatization of electrodes by oxidation of amines.

The use of an aqueous electrolytic medium for surface derivatization is advantageous, not only because it is a simple and green procedure, but also because it can lead to high amounts of grafted species at the electrode. Indeed, we outlined in a previous study that, when the derivatization of a graphite felt electrode by alcohols was performed in phosphate buffer solution, an increase of the surface area of the electrode occurred at the same time, leading to an increase of the volume concentration of the grafted catalyst.[22]

In this work, we report results on the immobilization of amines onto a graphite felt electrode by anodic oxidation in aqueous solutions. We will show that the covalent attachment of TEMPO by an amine link onto the porous electrode can be achieved by electrochemical oxidation reactions at low potentials.

The modification of a graphite felt electrode by anodic oxidation of amine-containing compounds in aqueous solutions was first investigated using 3-nitrobenzylamine **2**. The derivatization of the felt was performed in a flow cell by anodic oxidation of **2** in a pH = 2.2 phosphate buffer solution with an applied current of 1 A. The presence of immobilized nitro species on the electrode was ascertained by cyclic voltammetry, with the appearance of the NHOH/NO reversible system at 0.33 V_{SCE},[23] after electroreduction of the nitro group into hydroxylamine at −0.5 V_{SCE} (Fig. 1).[24]

The volume concentrations of the grafted felts were calculated from the Faraday law, by integration of the cyclic voltammograms (see Fig. 1) and are given in Table 1. The comparison of the double-layer capacity C_{dl} of the grafted felts with those of a fresh felt was used to estimate the increase of the surface area during the grafting process.[22] This information is necessary to calculate surface concentrations of grafted

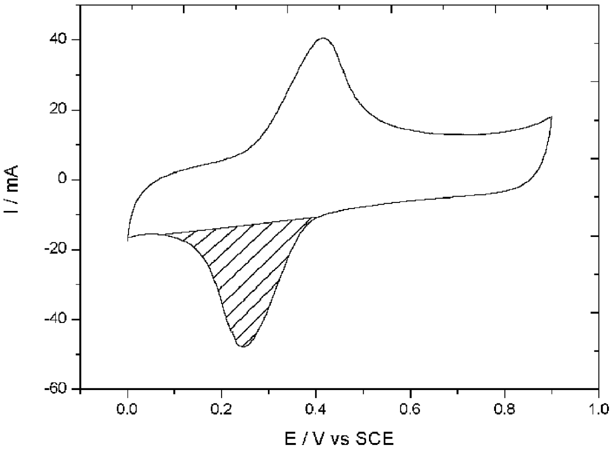


Fig. 1 Cyclic voltammetry in 0.5 M H_2SO_4 of the NHOH/NO system obtained from nitro species grafted onto the felt (10 min); scan rate = 0.1 V s^{-1}. Only the hatched area was considered to calculate volume concentrations.

Table 1 Characteristics of the modified felts upon varying grafting reaction conditions.

Substrate (concentration/10^{-3} mol l^{-1})	pH buffer[a]	Potential/ V_{SCE}	Electrolysis time/min	Q/C	Volume concentration/10^{-8} mol cm^{-3}	C_{dl}[bc] /μF cm^{-2}	Surface concentration /10^{-11} mol cm^{-2}
2 (3.5)	2.2	—[d]	2	120	3.4	36 (10)	2.5
	2.2	—[d]	5	300	5.9	72 (10)	2.2
	2.2	—[d]	10	600	24.4	186 (10)	3.5
	2.2	—[d]	18	1080	17.7	153 (10)	4.3
	2.2	—[d]	30	1800	3.9	139 (10)	0.7
3 (3.9)	7.2	0.45	4	4	0.8	4 (2)	0.6
	7.2	0.45	420	40	0.7	2 (2)	1.1
	9.2	0.35	12	4	1.2	3 (2)	1.3
	9.2	0.35	1440	101	0.2	2 (2)	0.3
	10.3	0.3	11	4	0.6	5 (2)	3.4
	10.3	0.3	1050	95	0.2	4 (2)	0.2

[a] pH = 2.2 and 7.2: phosphate buffer (0.5 M); pH = 10.3: carbonate buffer (0.5 M); pH = 9.2: borate buffer (0.5 M). [b] $C_{dl} = (I_a - I_c)/2Av$, where I_a and I_c are the anodic and cathodic currents taken at 0.7 V_{SCE} for cyclic voltammograms performed in 0.5 M H_2SO_4 and at 0.2 V_{SCE} for those performed at pH = 10.3, A is the initial electrode area and v is the scan rate. [c] The C_{dl} of a fresh felt is given in parentheses. [d] The oxidation was performed at constant current intensity (1 A).

species on the fibres of the felt (Table 1). The surface area of the graphite electrode fibres increased with the charge as it was varied during electrolysis from 120 to 600 C. This led to an increase of volume concentrations. However, if the charge was too high (1080 and 1800 C), the surface area decreased, leading to lower volume concentrations. Surface concentrations were almost the same in all experiments, except when the electrolysis was performed for 30 min. This phenomenon could be explained by the significant decrease of the concentration of **2** in the reaction medium.

Similarly, 4-amino-TEMPO (**3**) was immobilized onto the graphite felt by anodic oxidation in three different buffer solutions. Oxidation potentials were chosen to be just before the quasi-reversible waves observed by cyclic voltammetry for each buffer solution (Fig. 2). Cyclic voltammetry analyses of the grafted felts, performed in a pH = 10.3 carbonate (0.5 M) buffer solution , showed the presence of the $NO^{\bullet}/N{=}O^{+}$ reversible system at 0.63–0.64 V_{SCE} (Fig. 3).

It is interesting to note that the $NO^{\bullet}/N{=}O^{+}$ system was more reversible when **3** was immobilized on the electrode than when it was in solution. As amines can be oxidized by oxoammonium salts,[25] the low intensity of the cathodic wave in solution could be explained by the intermolecular reaction between the amino group of the compound and its corresponding oxoammonium salt. Such a reaction is not permitted when **3** is attached to the carbon surface.

The volume and surface concentrations obtained for each experiment are given in Table 1. In this case, the surface area did not increase, leading to volume concentrations lower than for **2** (the best results were 24.4 × 10^{-8} mol cm^{-3} for **2** compared to 1.2 × 10^{-8} mol cm^{-3} for **3**). Several attempts to immobilize **3** at higher potentials failed, probably due to a degradation of the oxoammonium salt during the grafting process. Unlike **2**, best results were obtained at low charges and the grafting process was finished in a few minutes. In the case of **2**, the surface area of the felt fibres increases during the grafting process. This phenomenon is directly linked to the electrochemical oxidation of graphite.[22] Taking into account these observations, the mechanism proposed in Scheme 2 could simultaneously occur with that of Scheme 1 during the grafting process.

Indeed, such a mechanism, involving the oxidation of graphite followed by a nucleophilic attack of the substrate, has already been proposed in the case of the derivatization of a graphite felt electrode by anodic oxidation of alcohols in water.[22] However, in the case of **3**, the surface area of the felt does not increase.[26] This result shows that the graphite is not oxidized during the derivatization and that the mechanism depicted in Scheme 2 cannot occur in this case. The pH of the reaction medium slightly influences the volume concentrations, even at pH = 7.2 (Table 1). As the pK_a of **3** is 8.97,[27] it seems that the grafting process can be achieved even with small amounts of unprotonated amine in the reaction medium. The anodic oxidation of the amine probably shifts the equilibrium of the protonation reaction in the direction of amine formation. These results seem to show that the amine form of **3** is

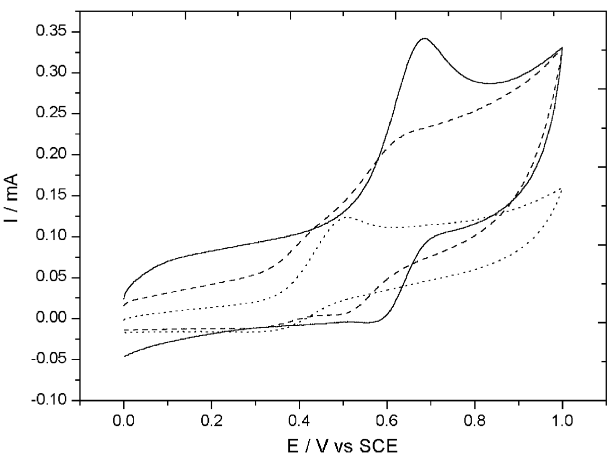


Fig. 2 Cyclic voltammograms of **3** (5.8 × 10^{-3} mol l^{-1}) at a glassy carbon electrode, at pH = 7.2 (—), pH = 10.3 (--) and pH = 9.2 (···); scan rate: 0.1 V s^{-1}.

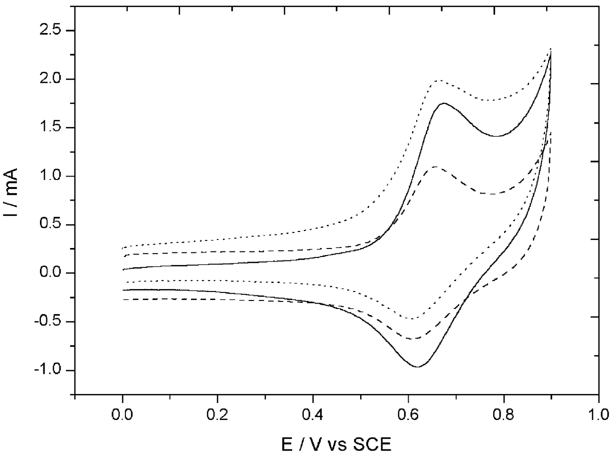
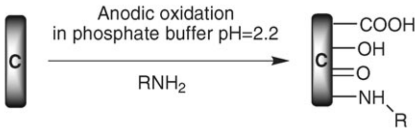


Fig. 3 Cyclic voltammograms of felts derivatized by anodic oxidation of **3** at pH = 9.2 (—), pH = 10.3 (--) and pH = 7.2 (···), measured in a pH = 10.3 carbonate (0.5 M) buffer solution; scan rate: 0.1 V s^{-1}.



Scheme 2 Mechanism involving a nucleophilic attack of NH_2-containing compounds onto the oxidized graphite felt.

oxidized at the potentials chosen to carry out the grafting process and that the general mechanism depicted in Scheme 1 occurs here.

In conclusion, TEMPO-modified graphite felt electrodes with volume concentrations around 10^{-8} mol cm^{-3} can be obtained by anodic oxidation of **3** in water at low potentials. This result is promising for the immobilization of a large range of substrates onto graphite electrodes. Moreover, when the derivatization can be performed in water at higher potentials, an increase of the specific area of the felt occurs at the same time, leading to higher volume concentrations.

Experimental

The graphite felt was obtained from Le Carbone Lorraine (RVG 4000, specific area 0.7 m^2 g^{-1}, volume density 0.088 g cm^{-3}). The average diameter of a fibre, estimated by scanning electron microscopy is 20 μm. Thus, the inside void volume of a felt can be estimated to be around two third of its external volume.

The derivatization of the felt was performed in a divided flow cell,[28] fitted with a graphite felt electrode (48 mm diameter, 10 mm thickness) located between two counter-electrodes. The flow cell was modified in order to introduce a reference electrode (saturated calomel electrode, SCE) located in the middle of the felt. Fifty milligrams of 3-nitrobenzylamine hydrochloride or **3** in 75 ml of phosphate buffer solution at pH = 2.2 (NaH_2PO_4 0.25 M; H_3PO_4 0.25 M) or pH = 7.2 (NaH_2PO_4 0.25 M; Na_2HPO_4 0.25 M), carbonate buffer solution at pH = 10.3 (Na_2CO_3 0.25 M; $NaHCO_3$ 0.25 M) or borate buffer solution at pH = 9.2 (H_3BO_3 0.25 M; H_2BO_3Na 0.25 M) were oxidized at controlled potentials or at 1 A, distributed as 0.67 A for the upstream and 0.33 A for the downstream electrical circuit (the measured potential was around 1.2–1.3 V_{SCE}, see Table 1). The electrolyte flowed through the porous electrode with recycling (4 ml min^{-1}). The modified graphite felts were sonicated in water (3 × 30 min) before being analyzed.

Cyclic voltammetry analysis of the grafted felts (10 mm diameter, 10 mm thickness) was performed in an analytical flow cell.[22] A standard three-electrode electrochemical cell (glassy carbon electrode as working electrode, Pt wire as counter-electrode) was used for the cyclic voltammetry analysis of the compounds in solution.

Acknowledgements

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$$\text{Ar-NO}_2 + 4H^+ + 4e^- \longrightarrow \text{Ar-NHOH} + H_2O$$

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

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