

Cyclic voltammetry and XPS analyses of graphite felt derivatized by non-Kolbe reactions in aqueous media

Florence Geneste,^{*a} Maël Cadoret,^a Claude Moinet^a and Guy Jezequel^b

^a UMR 6509, Laboratoire d'Electrochimie et Organométalliques de l'Université de Rennes 1, Institut de Chimie de Rennes, Campus de Beaulieu, 35042, Rennes cedex, France

^b UMR 6627, Laboratoire de Physique des Atomes, Lasers, Molécules et Surfaces de l'Université de Rennes 1, Campus de Beaulieu, 35042, Rennes cedex, France

Received (in London, UK) 10th April 2002, Accepted 2nd July 2002

First published as an Advance Article on the web 19th July 2002

This present work describes a preliminary study of modification of graphite felt for future applications in indirect electrolysis. The anodic oxidation of electroactive carboxylate compounds was achieved in aqueous media. The derivatization of the electrode was highlighted by cyclic voltammetry and XPS analyses. Interestingly, the grafting process led to chemically stable covalent attachment of nitroaryl species on the graphite felt with simultaneous increase of its real surface area. The comparison with the process performed in acetonitrile underlines the role of graphite oxidation in the immobilization of the molecules on the felt.

Introduction

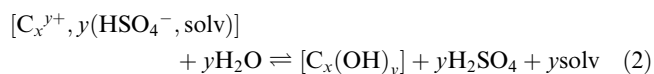
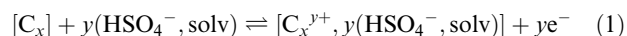
Indirect electrolysis¹ has attracted a lot of attention because it decreases the energy consumption and can offer higher selectivities than direct electrolysis. This process requires an electron carrier (the redox mediator) as illustrated in Scheme 1 with the example of an indirect electroreduction.

The mediator (Med_{red}) reacts with the substrate and is subsequently regenerated in its active form at the cathode. The immobilization of mediators on electrode surfaces makes the indirect electrolysis even more attractive. First, the electrolysis procedure is simplified: the problem of solubility of the redox catalyst in the reaction medium is avoided, and the purification process and the recovery of the mediator are easier. Second, small amounts of often expensive catalysts are necessary to obtain high concentrations at the electrode. Third, the immobilization process can result in the enhancement of the reactivity and the selectivity of the redox catalyst. Nevertheless, an important point to control is that the immobilization of the electroactive mediator does not inhibit its regeneration at the electrode. The stability and electrocatalytic activity of many compounds immobilized on planar electrodes has already been investigated.² However, a few results involving high surface felt electrodes were reported.

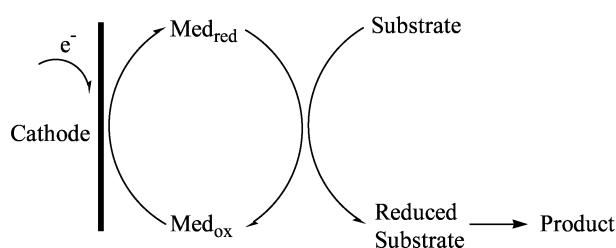
The immobilization of compounds on graphite felt has already been achieved using polymer coating.^{3,4} For example, the electrode was dipped in a solution of polyacrylic acid in methanol and dried, leading to a film of polymer on the

graphite felt.³ NH₂-containing compounds could then be attached to the coated electrode by reaction with the free carboxylic acid groups of the polymer film.

Covalent attachment of molecules directly to the graphite felt has also been accomplished.⁵ A graphite electrode can be electrochemically oxidized in acidic medium.⁶ A mechanism proposed for the anodic oxidation of graphite in sulfuric acid is given in eqns. 1 and 2:



The oxidation of graphite with a simultaneous intercalation of anions and solvent into the lattice is followed by a nucleophilic attack of water affording C–O functionalities at the graphite surface. Subsequent oxidation levels give C=O species such as ketones and carboxylic acids, so that covalent bonding can then be obtained at the graphite surface using standard chemical reactions. Thus, carboxylic acids formed at a planar carbon electrode were readily transformed into acyl chloride and subsequent reactions with NH₂-containing compounds led to the immobilization of amino species at the electrode.⁷ Graphite felt could be modified using the same procedure. For example, in our laboratory, Mn^{III}-5-(4-aminophenyl)-10,15,20-tris(phenyl)porphyrin acetate was successfully attached to the electrode by an amide bond.⁵ Another method involving a reaction between the surface of the graphite electrode and electrochemically generated species⁸ was recently employed by Pinson *et al.*⁹ to modify graphite felt. Thus, aryl radicals, generated by cathodic reduction of diazonium salts in acetonitrile, react with the graphite surface leading to carbon–carbon bonding. The authors noticed that approximately half of the grafting process occurred according to this mechanism whereas the other part was due to non-explained chemical reactions. The graphite felt was also successfully grafted by anodic oxidation of aryl acetate compounds in acetonitrile. A proposed mechanism¹⁰ involves an electrochemical oxidation of a salt of arylacetic acid leading after decarboxylation to an arylmethyl radical. At the potential of its formation, this radical can be immediately oxidized to the corresponding



Scheme 1 Principle of indirect electrolysis exemplified by a reduction.

carbocation according to a non-Kolbe reaction.¹¹ The resulting carbocation would react with one of the surface carbon atoms leading to carbon-carbon bond formation. For both methods involving diazonium salts or carboxylate compounds, the grafting process at the graphite felt was characterized by IR spectrometry, energy-dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS) and microanalysis. Surface concentrations around 10^{-10} mol cm⁻² were calculated from elemental analysis results. However, the facile characterisation by cyclic voltammetry of electroactive grafted molecules was not reported.

This work presents the first cyclic voltammetry analyses of electroactive molecules grafted at a graphite felt by anodic oxidation of carboxylate compounds or alcohol derivatives in aqueous media. A well-defined electrochemical response of grafted electroactive species constitutes a first step toward a possible application in electrocatalysis where the mediator has to be regenerated at the electrode. Two points are outlined in this study. Firstly, the nature of the graphite felt appears essential for cyclic voltammetry analysis. Secondly, the grafting process occurs when the anodic oxidation is performed in aqueous media, whereas a similar procedure fails in acetonitrile. Interestingly, the aqueous process allows not only the covalent bonding of molecules to the electrode but also results in the increase of its specific area, leading to an increase of the quantity of grafted species in the felt.

Experimental

Reagents and materials

Graphite felts were obtained from Le Carbone Lorraine (RVG 4000) and Actitex (ACTITEX-FC 1201). Their specific areas measured by the BET method are 0.7 m² g⁻¹ and 1200 m² g⁻¹ respectively. Carboxymethylferrocene was prepared as previously described.¹² 4-Nitrobenzeneacetic acid, 4-nitrobenzene methanol, tetrabutylammonium hydroxide (40 wt.% solution in water), tetrabutylammonium perchlorate were used as purchased (ACROS).

Instrumentation

Electrochemical treatments of the felt were performed at constant current intensity in a divided flow cell,¹³ fitted with a graphite felt electrode (52 mm diameter, 10 mm thickness) located between two counter-electrodes. Two cationic exchange membranes (Ionac 3470) were used for cell division.

XPS spectra were recorded using a VSW HA100 spectrometer with Al K α excitation radiation at 1486.6 eV. The sample was vacuum treated (10^{-8} mbar).

The SEM micrographs were obtained with a Jeol 6301F (9 kv) microscope.

HPLC analyses were carried out on a Waters 486 chromatograph equipped with a 3.9 \times 150 mm Nova-Pak C18 column and operated at a flow rate of 1 mL min⁻¹. The mobile phase was methanol-water (50:50, v/v). The identification of products was based on HPLC comparison with authentic samples (UV detector 240 nm).

Electrochemical analyses of the modified felts were performed in an analytical flow cell illustrated in Fig. 1.

The compartment containing the working electrode (graphite felt) was separated from the two interconnected stainless steel counter-electrode compartments by cationic exchange membranes (Ionac 3470). A good homogeneity of the potential distribution in the three dimensional working electrode was obtained when the felt was located between two counter-electrodes.¹⁴ The reference electrode (Saturated Calomel Electrode—SCE) was positioned in the middle of the felt. The potential control was performed using an EG&G Princeton Applied Research model 362 scanning potentiostat linked to

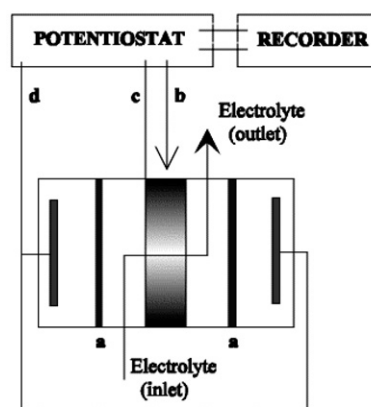


Fig. 1 Schematic diagram of the analytical flow cell: a, diaphragms (cationic membranes); b, saturated calomel electrode (SCE); c, working electrode (disc of graphite felt: 10 mm diameter, 10 mm thickness); d, auxiliary counter electrodes (stainless steel).

an XY recorder. The electrolyte solution (0.5 M H₂SO₄ for NO₂ moieties analysis) percolated the porous electrode with a constant flow rate monitored by a Gilson minipuls 2 peristaltic pump for aqueous solutions or Prominent gamma/4-I/W(RS) pump for acetonitrile.

Anodic oxidation of the sodium salt of 4-nitrobenzeneacetic acid in aqueous media

The derivatization of the felt was performed in a flow cell with 200 mg of 4-nitrobenzeneacetic acid, dissolved in 200 ml of phosphate buffer pH 7.2 (NaH₂PO₄ 0.25 M; Na₂HPO₄ 0.25 M) or pH 2.2 (NaH₂PO₄ 0.25 M; H₃PO₄ 0.25 M). The same buffer was used in cathodic and anodic compartments. The current intensity for the electrolysis was optimized to 300 mA calculated for 6 Faraday per mole of substrate (no passivation of the felt was observed but degradation of the felt occurred with higher current intensities) distributed in 200 mA for the upstream electrical circuit and 100 mA for the downstream one. The electrolyte flowed through the porous electrode without recycling (5.3 ml min⁻¹).

Anodic oxidation of 4-nitrobenzenemethanol in an aqueous medium

The anodic oxidation of 4-nitrobenzenemethanol (200 mg) in 200 ml of phosphate buffer pH 2.2 was performed according to similar experimental conditions used for 4-nitrobenzeneacetic acid.

Anodic oxidation of the tetrabutylammonium salt of 4-nitrobenzeneacetic acid in acetonitrile

The derivatization was realized in a flow reactor. 200 mg (1.1 mmol) of 4-nitrobenzeneacetic acid and 0.72 ml (1.1 mmol; 1 equiv.) of a solution of tetrabutylammonium hydroxide (40% in water) were added to 3.4 g (0.1 M) of tetrabutylammonium perchlorate dissolved in acetonitrile. The anodic oxidation was performed with an applied current of 300 mA (200 mA and 100 mA) corresponding to an excess of the current needed to transform all the substrate into 4-nitrobenzoic acid. The electrolyte solution flowed through the electrode without recycling (flow rate: 2 ml min⁻¹).

In a second experiment, the anodic oxidation of 4-nitrobenzeneacetic acid in acetonitrile was performed at controlled potential (1.2 V_{SCE}) using the analytical flow cell.

Samples for cyclic voltammetry and XPS analyses

In a typical procedure, a sample (10 mm diameter, 9 mm thickness) of derivatized felt was successively rinsed in water, acetone, soxhlet extracted in chloroform for 24 h before cyclic voltammetry and XPS analyses.

Results

Different kinds of carbon felts are commercially available. In order to choose an efficient material for electrochemical investigation, carboxymethylferrocene was analyzed by cyclic voltammetry using the ACTITEX-FC 1201 or CL RVG 4000 felt as working electrode. At a planar vitreous carbon electrode, the water soluble salt of carboxymethylferrocene gives rise to a ferrocene/ferrocenium ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$) reversible wave in aqueous electrolyte.¹⁵ Cyclic voltammograms, obtained at a graphite felt electrode used without percolation, are given in Fig. 2.

The ferrocene-ferrocenium reversible system was observed at a CL RVG 4000 felt used as working electrode whereas no response was obtained using the ACTITEX-FC 1201 one. Furthermore, in the same experiment the solution of carboxymethylferrocene flowed through the porous electrode maintained at 0.8 V_{SCE} . Interestingly, with the CL RVG 4000 electrode, a green solution was observed at the outlet of the flow cell, showing the presence of ferrocenium species in solution. The same experiment performed at a ACTITEX-FC felt anode did not show any change in the electrolyte color. The difference in the electrochemical response of the two felts in an aqueous medium could be due to their intrinsic morphology. This hypothesis was supported by the Scanning Electronic Microscopy results (Fig. 3). Contrary to the CL RVG 4000 fibers, the ACTITEX-FC fibers seem to be covered by a thick film as outlined in Fig. 3 (see the nodules in (b) and the excrescences in (c)).

These preliminary results lead us to consider the CL RVG 4000 felt as a suitable material for the present study. The direct oxidation of graphite electrodes in aqueous medium occurs at fairly mild potential¹⁶ and results in the increase of the real surface area of the electrode.¹⁷ Thus, in order to increase the surface area of the felt during the grafting process, we performed the anodic oxidation of substrates in aqueous media. The felt was derivatized in a flow cell¹³ by anodic oxidation of 4-nitrobenzeneacetic acid in phosphate buffers (pH = 7.2 and 2.2) with an applied current of 300 mA. HPLC analyses of the electrolyzed solution ascertained the presence of 4-nitrobenzeneacetic acid and 4-nitrobenzenemethanol. For comparison, the anodic oxidation of 4-nitrobenzenemethanol was performed

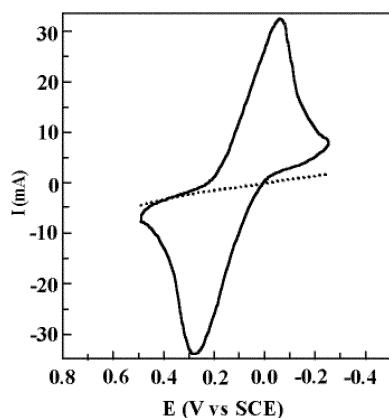


Fig. 2 Cyclic voltammetry of carboxymethylferrocene (20.5 mM) at a graphite felt electrode in carbonate buffer (NaHCO_3 0.25 M; Na_2CO_3 0.25 M) at 0.1 V s^{-1} ; solid lines are for the CL RVG 4000 felt and dotted lines are for the ACTITEX FC-1201 felt.

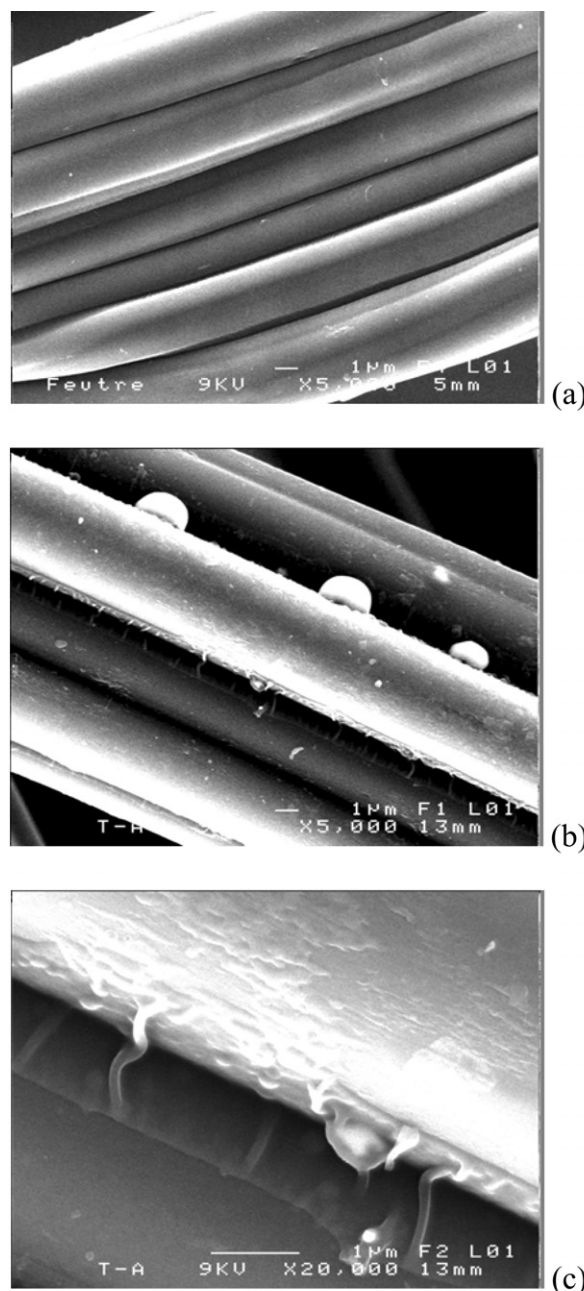


Fig. 3 SEM images of (a) the CL RVG 4000 felt ($\times 5000$), (b) the ACTITEX FC-1201 felt ($\times 5000$), (c) the ACTITEX FC-1201 felt ($\times 20000$).

in phosphate buffer pH 2.2 with an applied current of 300 mA. Moreover, the grafting process was also investigated in acetonitrile and the anodic oxidation of 4-nitrobenzeneacetic acid in acetonitrile (300 mA) was realized according to a similar procedure as the oxidation in water. The felts resulting from each experiment were rinsed (water, acetone) and soxhlet extracted in chloroform for 24 h in order to eliminate the substances adsorbed at the surface of fibers.⁹

Cyclic voltammograms of the grafted felts were realized in acidic electrolyte (0.5 M H_2SO_4) using the analytical flow cell described in the experimental section. The presence of homogeneously immobilized nitro species at the electrode was only characterized after oxidation of 4-nitrobenzeneacetic acid and 4-nitrobenzenemethanol in aqueous media (Fig. 4).

The presence of homogeneously immobilized nitro species was ascertained by the appearance of the nitroso-hydroxylamine reversible system¹⁸ formed after electroreduction of the nitro group at $-0.5 V_{\text{SCE}}$.

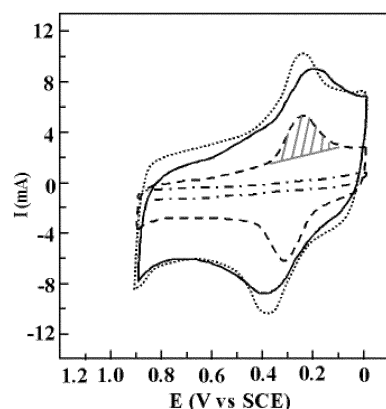


Fig. 4 Cyclic voltammetry in 0.5 M H₂SO₄ of a fresh felt (—), felts derivatized by anodic oxidation of 4-nitrobenzeneacetic acid in a phosphate buffer of pH 2.2 (—) and pH 7.2 (---) and by anodic oxidation of 4-nitrobenzenemethanol in a phosphate buffer pH 2.2 (···). Scan rate: 0.1 V s⁻¹. Only the top of the wave (e.g. hatched area) was considered to calculate the volume concentrations.

The volume concentrations¹⁹ of grafted molecules can be obtained by integration of the cyclic voltammograms (see Fig. 4) using the Faraday law and are given in Table 1. The volume concentrations of the OH groups present on the derivatized graphite surface were determined in the same way after reaction with 4-nitrobenzoyl chloride.²⁰

The increase of the capacitive envelope²¹ (Fig. 4) can be associated with the increase of the surface area of the felt during the electrochemical treatment.¹⁷ The comparison of the double-layer capacities C_{dl} (Table 1) with these of a fresh felt was used to estimate the increase of the surface area. The double-layer capacity was calculated from the cyclic voltammograms according to eqn. (3).

$$C_{dl} = (I_a - I_c)/2Av \quad (3)$$

I_a and I_c are the anodic and cathodic currents measured at 0.7 V_{SCE}, A is the initial electrode area and v is the scan rate. This expression previously used for planar carbon electrodes¹⁷ is in agreement with the model proposed by Conway *et al.*²² for porous materials such as graphite felt. The surface area of the grafted electrodes increased during the oxidation process, as outlined by the increase of the C_{dl} values of derivatized felts

Table 1 Chemical composition and double-layer capacities of fresh and grafted felts calculated from cyclic voltammograms

Felt treatment: electrolyte medium (applied current)	Nitro-containing molecules/ 10 ⁻⁸ mol cm ^{-3a}	Double-layer capacity C_{dl} / μF cm ^{-2b}	Free OH groups/ 10 ⁻⁸ mol cm ^{-3a}
Fresh felt	—	10	0.5
Phosphate buffer pH 7.2 (300 mA)	3.4 ^c	29 ^c	1.9
Phosphate buffer pH 2.2 (300 mA)	7.1 ^c	74 ^c	4.9
	8.7 ^d	87 ^d	
Acetonitrile (300 mA)	0.0 ^c	104 ^c	—

^a In order to eliminate the effect of the capacitive current, only the area of the top of each wave was considered and volume concentrations were calculated from the Faraday law ($Q = 2nF$, see Fig. 4).

^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}, A is the initial electrode area (480 cm² for a volume of 0.78 cm³ of analyzed felt), and v is the scan rate (100 mV s⁻¹). ^c Anodic oxidation performed with 4-nitrobenzeneacetic acid. ^d Anodic oxidation performed with 4-nitrobenzenemethanol.

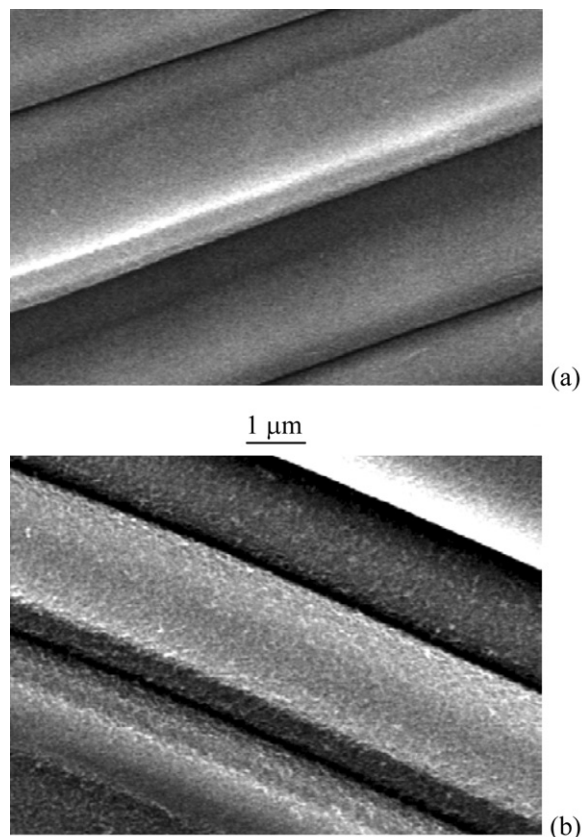


Fig. 5 SEM images of (a) fresh CL RVG 4000 felt and (b) oxidized CL RVG 4000 felt.

compared to a fresh felt. In order to check that the direct oxidation of the felt led to graphite lattice damage and was responsible for the modification of the surface area, a solution of phosphate buffer (pH = 7.2) was flowed through the felt with an applied current of 300 mA for 2 h. The rough appearance of the surface of fibers observed by Scanning Electronic Microscopy (Fig. 5) clearly confirmed that the increase of the surface area of the felt is due to the direct oxidation of graphite in water.

The cyclic voltammetry analyses were corroborated by XPS analyses. The presence of nitro groups at the graphite surface was confirmed by the peak at 406 eV after electrochemical oxidations accomplished in aqueous media (Table 2).

No peak corresponding to the NO₂ group was detected by XPS analysis for felts grafted at constant current intensity in acetonitrile. However, when the anodic oxidation of 4-nitrobenzeneacetic acid in acetonitrile was performed at controlled potential (1.2 V_{SCE}) in the analytical flow cell, the presence of NO₂ groups at the felt surface was observed by XPS. As reported with planar carbon electrodes,¹⁰ the XPS analyses of felts grafted with nitro species gave a signal between 399–401 eV, previously attributed to reduced forms of the nitro group. It is worth noting that this signal dramatically increased when the derivatization was realized in acetonitrile. Moreover,

Table 2 XPS analysis of graphite felts derivatized by anodic oxidation of 4-nitrobenzeneacetic acid

	Fresh felt	Phosphate buffer pH 2.2	Phosphate buffer pH 7.2	Acetonitrile (Bu ₄ NClO ₄)
% NO ₂ 406 eV ^a	0.0	2.0	1.7	0.0

^a NO₂/carbon ratio.

for all derivatized felts, the carbon signal could be decomposed in several peaks revealing the presence of different kinds of carbon at the electrode surface. Interestingly, for derivatization accomplished in acetonitrile, the surface area of the peak at 286.9 eV, most probably corresponding to a C=O group, was twice those obtained in aqueous electrolytes.

Discussion

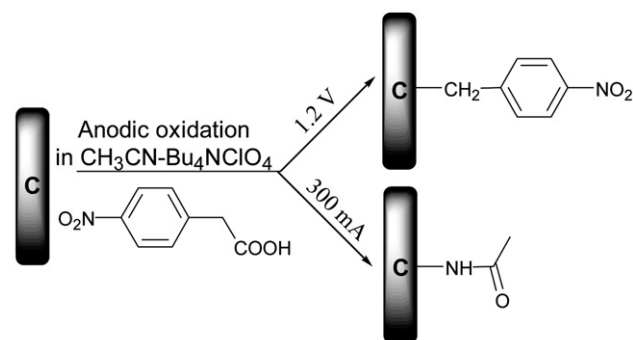
The choice of the graphite felt is of great importance for applications in indirect electrolysis. A larger quantity of mediators can be introduced on the felt if its specific area is larger, leading to a more efficient material. The ACTITEX felts are known for their high specific area ranging from $1000 \text{ m}^2 \text{ g}^{-1}$ to more than $1500 \text{ m}^2 \text{ g}^{-1}$. However, during the preliminary cyclic voltammetry experiments performed in aqueous medium with the ACTITEX-FC 1201 using a carboxymethylferrocene solution, the ferrocene/ferrocenium reversible wave was not observed (Fig. 2). This result was confirmed by the fact that the oxidation into ferrocenium species did not significantly occur even with an applied potential of $0.8 V_{\text{SCE}}$. The SEM images revealed the presence of a thick film on the surface of the fibers probably operating as an insulating sheath. In contrast, the very pure CL RVG 4000 felt containing 99.9% of carbon atoms showed a smooth bare surface. It led to a response comparable in potential to those of graphite planar electrodes and can be used in cyclic voltammetry studies.

The CL RVG 4000 felt has a lower specific area ($0.7 \text{ m}^2 \text{ g}^{-1}$) than the ACTITEX felts. However, the direct oxidation of the graphite lattice in aqueous electrolyte is known to increase the surface area of the electrode¹⁷ and we actually observed a direct oxidation of the felt at the potential of anodic oxidation of carboxylate compounds in aqueous media, as outlined by the increase of the apparent double-layer capacities C_{dl} of grafted felts compared to the fresh one (Table 1). The XPS analysis of the graphite surface confirmed the presence of NO_2 moieties on the felt with a $\text{NO}_2/\text{carbon}$ ratio of 1.7 to 2% (Table 2). This result can be compared to the XPS results previously reported for anodic oxidation of tetrabutylammonium salts of 4-nitrobenzeneacetic acid, in acetonitrile at planar carbon electrodes (1.7–2.9%).¹⁰

The grafted material obtained from a CL RVG 4000 felt afforded volume concentrations up to $7 \times 10^{-8} \text{ mol cm}^{-3}$, calculated from cyclic voltammograms. If we consider that 1 cm^3 of felt contains less than 1 cm^3 of solution, we can estimate that the concentration of catalyst was higher than $10^{-4} \text{ mol l}^{-1}$ in the felt. As a catalyst/substrate ratio usually is 1% to 10% in redox catalysis, the concentration of substrate in the electrolyte has to be around 10^{-2} to $10^{-3} \text{ mol l}^{-1}$. This rough estimation shows that the quantity of grafted compounds on the felt may be sufficient for future applications in indirect electrolysis.

The comparison of the volume concentrations obtained in the two different aqueous media (pH 2.2 and pH 7.2) revealed a higher quantity of grafted molecules in the acidic medium, although the electrochemical treatments were carried out in a similar way. As indicated above, XPS analysis showed that fairly similar concentrations of molecules on the felt surface were obtained for both phosphate buffers. The volume concentration at pH 2.2 was however significantly higher and increased with the surface area as outlined by the calculated C_{dl} (Table 1). Thus, it seems that the surface damage responsible for the increase of the surface area occurred preferentially in the acidic medium. It is worth noting that previous studies showed that the degradation process is not dependent on the pH but on the ability of electrolyte anions to intercalate the graphite lattice.^{17,23}

The mechanism leading to covalent grafting at a graphite surface is not yet well understood. It has been previously pro-



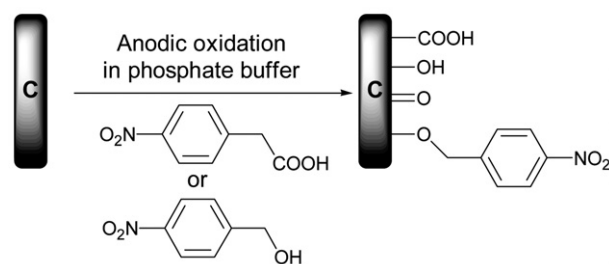
Scheme 2 Grafted species after acetonitrile treatment.

posed that a reaction between the carbocation resulting from the anodic oxidation of the salt of 4-nitrobenzeneacetic acid and a carbon atom of the graphite surface could be responsible for the grafting process performed in acetonitrile at the oxidation potential of the carboxylate.¹⁰ In our case, when the oxidation of 4-nitrobenzeneacetic acid in wet acetonitrile was realized at controlled potential ($1.2 V_{\text{SCE}}$), a similar derivatization takes place as confirmed by XPS analysis. But, when the experiment was accomplished at controlled current intensity corresponding probably to a more anodic potential, the direct oxidation of the graphite occurred and led to the increase of the surface area of the felt as outlined by the important variation of C_{dl} compared to a fresh felt (Table 1). The oxidized graphite felt should react predominantly with the most abundant nucleophile in the electrolyte, *i.e.* acetonitrile to give $-\text{N}=\text{C}^+-\text{CH}_3$ groups. Subsequent reaction of the iminium group with residual water should result in the formation of acetamides ($-\text{NHCOCH}_3$) at the graphite surface (Scheme 2) as outlined by the increase of the 399–401 eV (NH group) and 285.9 eV (C=O group) signals in XPS.

However, as no peak corresponding to the NO_2 group was detected by XPS analysis, it seems that the direct oxidation of the graphite felt in acetonitrile inhibited the grafting process.

In contrast, the covalent attachment at the felt of NO_2 -containing molecules resulting from the electrochemical treatment of 4-nitrobenzeneacetic acid or 4-nitrobenzenemethanol was observed simultaneously with the direct oxidation of the graphite electrode ascertained by the formation of OH groups (Scheme 3).

Taking into account the experimental results and the previously proposed mechanism for derivatization realized in alcohols,²⁴ the mechanism could involve an oxidation of graphite (eqn. 1) followed by a competitive nucleophilic attack of water leading to OH groups and 4-nitrobenzenemethanol used as starting compound or resulting from a non-Kolbe oxidation of 4-nitrobenzeneacetic acid. Subsequent oxidations of the OH groups also afford keto and carboxylic groups at the electrode.



Scheme 3 Grafted species after aqueous treatment.

Conclusion

This work shows the derivatization of graphite felts by anodic oxidation of acetic acids or alcohols in aqueous media leading to chemically stable bonding. It is worth noting that an increase of the specific area of the felt occurred at the same time. The volume concentrations obtained when the derivatization was performed in acidic medium are encouraging for future applications in indirect electrolysis. Moreover, a convenient cyclic voltammetry analysis of modified graphite felt is proposed. A good electrochemical response in cyclic voltammetry of species bonded to the felt is of great interest to control the rapid electrochemical regeneration of the active form of a grafted mediator and to check its stability. The application of this grafting process in the fabrication of modified electrodes for indirect electrolysis is in progress.

Acknowledgements

We are grateful to Mr S. Pronier for microphotographs and we thank Mr A. Quemerais for XPS analyses.

References

- (a) J. Simonet and G. Le Guillanton, *Bull. Soc. Chim. Fr.*, 1985, 180; (b) E. Steckhan, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 683; (c) S. Torii, *Synthesis*, 1986, 873.
- See for examples (a) W. Roman and E. Steckhan, *Electrochim. Acta*, 1997, **42**, 2027; (b) G. Cauquis, S. Cosnier, A. Deronzier, B. Galland, D. Limosin, J.-C. Moutet, J. Bizot, D. Deprez and J.-P. Pulicani, *J. Electroanal. Chem.*, 1993, **352**, 181; (c) E. Simon, E. Sablé, H. Handel and M. L'Her, *Electrochim. Acta*, 1999, **45**, 855; (d) A. Deronzier, D. Eloy, P. Jardon, A. Martre and J.-C. Moutet, *J. Electroanal. Chem.*, 1998, **453**, 179.
- (a) T. Osa, Y. Kashiwagi, K. Mukai, A. Oshawa and J. Bobbitt, *Chem. Lett.*, 1990, 75; (b) Y. Kashiwagi, A. Oshawa, T. Osa, Z. Ma and J. M. Bobbitt, *Chem. Lett.*, 1991, 581; Y. Kashiwagi, H. Ono and T. Osa, *Chem. Lett.*, 1993, 257; T. Osa, Y. Kashiwagi, Y. Yanagisawa and J. Bobbitt, *Chem. Commun.*, 1994, 2535; (c) Y. Yanagisawa, Y. Kashiwagi, F. Kurashima, J.-I. Anzai, T. Osa and J. Bobbitt, *Chem. Lett.*, 1996, 1043; (f) Y. Kashiwagi, Y. Yanagisawa, F. Kurashima, J.-I. Anzai, T. Osa and J. M. Bobbitt, *Chem. Commun.*, 1996, 2745; (g) E. M. Belgsir and H. Schäfer, *Electrochem. Commun.*, 2001, **3**, 32.
- (a) Y. Kashiwagi, Y. Yanagisawa, N. Shibayama, K. Nakahara, F. Kurashima, J. Anzai and T. Osa, *Electrochim. Acta*, 1997, **42**, 2267; (b) E. M. Belgsir and H. Schäfer, *Chem. Commun.*, 1999, 435.
- P. Jegou-Evanno, C. Moinet and G. Simonneaux, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2000, 711.
- (a) F. Beck, H. Junge and H. Krohn, *Electrochim. Acta*, 1981, **26**, 799; (b) D. C. Alsmeyer and R. L. McCreery, *Anal. Chem.*, 1992, **64**, 1528.
- (a) B. F. Watkins, J. R. Behling, E. Kariv and L. L. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 3549; (b) J. C. Lennox and R. W. Murray, *J. Electroanal. Chem.*, 1977, **78**, 395.
- A. J. Downard, *J. Electroanal.*, 2000, **12**, 1085.
- E. Coulon, J. Pinson, J.-D. Bourzat, A. Commerçon and J. P. Pulicani, *Langmuir*, 2001, **17**, 7102.
- C. P. Andrieux, F. Gonzalez and J.-M. Savéant, *J. Am. Chem. Soc.*, 1997, **119**, 4292.
- H. Hofer and M. Moest, *Ann. Chem. Pharm.*, 1902, **323**, 284.
- J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, 1958, **23**, 653.
- C. Moinet, *J. Phys. IV*, 1994, **4**, C1-175.
- C. Lamoureux, C. Moinet and A. Tallec, *Electrochim. Acta*, 1986, **31**, 1.
- P. Jegou-Evanno, J.-P. Hurvois and C. Moinet, *J. Electroanal. Chem.*, 2001, **507**, 270.
- P. Chen and R. L. McCreery, *Anal. Chem.*, 1996, **68**, 3958.
- F. Regisser, M.-A. Lavoie, G. Y. Champagne and D. Bélanger, *J. Electroanal. Chem.*, 1996, **415**, 47.
- M. Baizer and H. Lund, *Organic Electrochemistry*, Marcel Dekker, NY, 1991, p. 411. Oxidation/reduction reaction of the aryl nitro compounds in acidic solution proceeds according to the following mechanism:

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

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

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

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

- The volume concentrations are defined as the number of moles of electroactive grafted molecules per volume of felt. This term was preferred to the typically used surface concentration because it did not depend on the real surface area of the felt and directly accounted for the possibility of using the grafted three-dimensional electrode in indirect electrolysis.
- The introduction of an electroactive compound on the alcohol groups of the felt was realized by heating the felt at 40 °C during 3 hours with 4-nitrobenzoyl chloride and triethylamine in toluene. The felt was then successively rinsed with toluene, water, acetone and soxhlet extracted in chloroform for 24 h. The grafting process was achieved with benzenecarboxylic acid instead of 4-nitrobenzenecarboxylic acid to measure the volume concentrations with the best accuracy.
- For explanation of the double-layer theory, see for example: J. P. Diard, B. Le Gorrec, C. Montella, *Cinétique électrochimique*, Hermann, éditeurs des sciences et des arts, 1996, p. 40. When the surface of the electrode is charged, it generates a very strong electrical field that attracts opposite charged ions from the solution. It is admitted that the electrode/solution interphase behaves as a capacitor of capacity C_{dl} (double layer capacity). The resulting current is called capacitive current and is responsible for the capacitive envelope on cyclic voltammograms.
- W. G. Pell and B. E. Conway, *J. Electroanal. Chem.*, 2001, **500**, 121.
- K. W. Hathcock, J. C. Brumfield, C. A. Goss, E. A. Irene and R. W. Murray, *Anal. Chem.*, 1995, **67**, 2201.
- (a) H. Maeda, Y. Yamauchi, M. Hosoe, T.-X. Li, E. Yamaguchi, M. Kasamatsu and H. Ohmori, *Chem. Pharm. Bull.*, 1994, **42**, 1870; (b) H. Maeda, M. Hosoe, T.-X. Li, M. Itami, Y. Yamauchi and H. Ohmori, *Chem. Pharm. Bull.*, 1996, **44**, 559; (c) H. Maeda, T.-X. Li, M. Hosoe and M. Itami, *Anal. Sci.*, 1994, **10**, 963; (d) H. Maeda, M. Itami, Y. Yamauchi and H. Ohmori, *Chem. Pharm. Bull.*, 1996, **44**, 2294.