JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 1060–1064

Anion exchange activity of electrochemically bonded ethylene diamine on carbon fibres

S. ANTONIADOU, A. D. JANNAKOUDAKIS, P. D. JANNAKOUDAKIS, E. THEODORIDOU

Institute of Physical Chemistry, Aristotelian University, Thessaloniki, Greece

Received 18 December 1991; revised 10 April 1992

Carbon fibre based anion exchangers were prepared through electrochemical oxidation and bonding of ethylene diamine on fibre electrodes in acetonitrile and subsequent formation of the chloride salts of the ammonium groups.

Catalytically active noble metals can be introduced into the carbon matrix after ion-exchange with complex salts, carrying the noble metal in their anionic component, and subsequent cathodic reduction of the noble metal ions to the metallic state, in aqueous solutions.

The free amino groups of the carbon fibres modified with oxidized ethylene diamine can be used for the preparation of chemically modified electrodes via an amidization reaction with acid chlorides.

The amount of the oxidized ethylene diamine attached to the carbon fibre surface exceeds a monolayer coverage, suggesting the formation of chain and bridge configurations on the carbon fibres. Investigation was performed by cyclic voltammetric, chrono-amperometric, potentiometric and impedance measurements. The order of magnitude of the anion-exchange capacity of the produced material for small anions was 1 meq per g carbon fibre.

1. Introduction

Previous studies carried out in the authors' laboratory involved the cation exchanging properties of electrochemically oxidized carbon fibres. The cation-exchanging groups (i.e. -COOH and -OH groups) of the fibres were used for the attachment of noble and heavy metal ions [1–4].

The cathodic reduction of the exchanged noble metal ions resulted in the creation of a material bearing highly dispersed metal atoms acting as electrochemical and/or chemical catalysts [1, 5–7]. Via the cation-exchanging groups of the carbon material, metal and ligand-charged catalytically active porphyrin components were also introduced into the graphitic substrate [8]. The electrochemically oxidized carbon fibres were further used for the preparation of chemically modified electrodes [9, 10].

The importance of the ion-exchanging properties of the carbon material, as well as the applications of the modified fibres as composites in plastics, used in the aerospace industry [11–13], introduced a need for the creation of an analogous material bearing anion-exchanging groups. The realization of this was achieved through electrochemical bonding of ethylene diamine on to the carbon fibre surface and subsequent formation of the respective chloride salts of the ammonium groups.

Electrochemical bonding of amines to carbon fibre surfaces toward improved carbon-epoxy composites has been recently reported in the literature [13]. Attachment of amines to pyrolytic graphite has also been achieved by exposing the graphite surfaces to gaseous amines following plasma etching in an argon atmosphere [14].

2. Experimental details

The carbon fibres used in the present study were from the BASF-Celanese Corporation, USA (type Celion GY70). These polyacrylonitrile-based fibres are characterized by high orientation along the fibre axis, stiffness and considerable electrical conductivity [8].

The electrochemical oxidation and bonding of ethylene diamine on the carbon fibres was carried out in acetonitrile and $(C_2H_5)_4NClO_4$ was used as the supporting electrolyte. The carbon fibres modified by oxidized ethylene diamine were immersed for 20 min in concentrated HCl, so that the corresponding chloride salts were formed. The anion exchange of the Cl^- ions with the anionic components of noble metal complex salts was carried out in aqueous solutions of $NH_4[Au(III)Cl_4] \cdot xH_2O$ (Aldrich Chemical Co.), of K_2PtCl_4 (BDH Laboratory Reagents) and of $(NH_4)_2PdCl_4$ (Aldrich Chemical Co.).

The amidization of the amino groups of the modified carbon fibres with 3,5-dinitrobenzoyl chloride was performed in a reflux set up at 65 °C in carbon tetrachloride solution for approximately 2 h. 3,5-dinitrobenzoyl chloride (Fluka, purum) was recrystallized from carbon tetrachloride solutions. The aqueous buffer solution of pH 4 was prepared from CH_3COOH and CH_3COONa.

Impedance measurements were carried out with a system consisting of a potentiostat and a 'lock-in' amplifier connected to a computer, as described in a

0021-891X

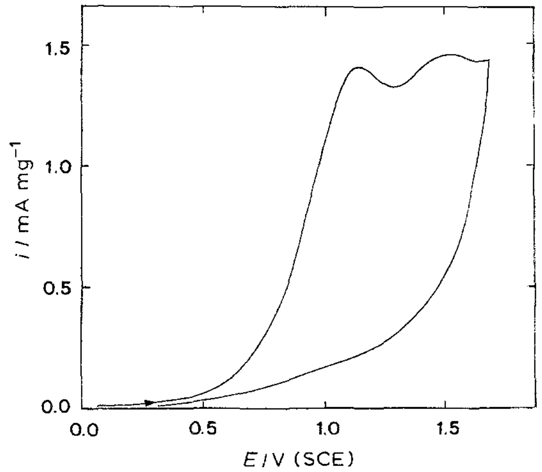


Fig. 1. Cyclic voltammogram ($\nu = 200 \mathrm{mV s^{-1}}$) of $H_2NCH_2CH_2NH_2$ ($c = 5 \times 10^{-3}$ M) on carbon fibre electrode in CH_3CN (Et_4NClO_4 0.1 M).

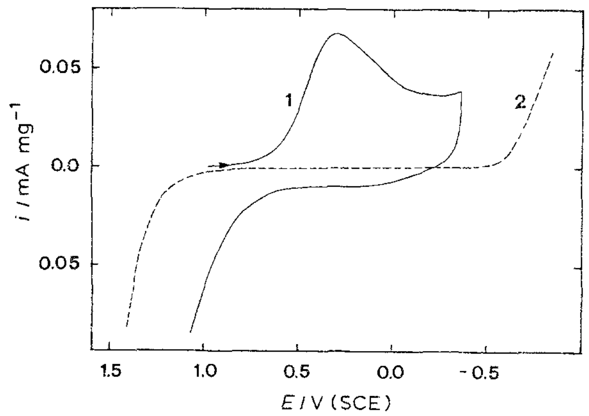


Fig. 2. Cyclic voltammogram ($\nu = 20 \mathrm{mV s^{-1}}$) of modified with oxidized $H_2NCH_2CH_2NH_2$ carbon fibres after the formation of the chloride salts of the ammonium groups and the subsequent anion-exchange with $[Au(III)Cl_4]^-$, in pH 4 buffer solution (curve 1). Curve 2 represents the cyclic voltammogram of the bare electrode in the same solution.

previous study [8]. All electrochemical measurements were carried out at 25 °C.

3. Results and discussion

The cyclic voltammetric study of ethylene diamine in acetonitrile solutions on a bundle of carbon fibres consisting of about 380 filaments, showed that two anodic irreversible waves appear with $E_{p1} = 1.15$ and $E_{p2} = 1.50$ V/SCE (Fig. 1). These peaks may be attributed to the oxidation of ethylene diamine to the corresponding mono and di-cation radicals respectively, which are bonded to the carbon fibres under H^+ subtraction.

During successive scans the heights of the oxidation peaks diminished gradually. After keeping the electrode at 1.6 V/SCE for 30 min and subsequent scanning, the oxidation peaks disappeared, implying passivation of the electrode due to the attachment of ethylene diamine oxidation product to the carbon fibre surface.

The modified electrodes were afterwards immersed in concentrated solution of HCl, so that the chloride salts of the ammonium groups were formed. Chloride anions of the latter material are expected to be replaced by anionic components of noble metal complex salts, such as $NH_4[Au(III)Cl_4]$, K_2PtCl_4 and $(NH_4)_2PdCl_4$. The anion-exchanging properties of the obtained material were verified through the characteristic electrochemical behaviour of the noble metals included in the anionic components.

Figure 2 shows the cyclic voltammogram of the material anion-exchanged with $[Au(III)Cl_4]^-$ and subsequently rinsed with water, in a pH 4 aqueous solution. During the cathodic scan, a well shaped wave due to the reduction of Au(III) to metallic Au appeared, while in the subsequent anodic scan gold oxides were formed [1]. The presence of these oxides resulted in the appearance of the anodic current at much less positive potential, compared to bare electrodes.

The electrodes bearing metallic Au, produced by cathodic reduction of Au(III), showed electrocatalytic activity in the reduction of aliphatic nitrocompounds [1] and in the oxidation of formic acid [15].

The electrodes with metallic platinum or palladium, obtained after reduction of the anion-exchanged $(PtCl_4)^{2-}$ or $(PdCl_4)^{2-}$ respectively, exhibited the characteristic hydrogen adsorption-desorption peaks in the corresponding cyclic voltammograms in 0.5 M H_2SO_4 solutions [5, 7]. The former electrodes proved to be suitable for the catalytic electrooxidation of methanol [5, 6], while the latter showed catalytic efficiency in the electroreduction of aromatic nitrocompounds and in the electrooxidation of formic acid [7]. The ion-exchange process was further confirmed by the fact that the anionic components of the complex metal salts were totally removed through 1 M NaOH solutions.

In order to examine whether the oxidized ethylene diamine attached to the carbon fibres has free amino-groups, we employed an amidization reaction which was carried out with an acid chloride. 3,5-dinitrobenzoyl chloride was chosen as the most suitable species for this reaction, since the nitro-groups can be easily identified electrochemically.

Figure 3 shows the cyclic voltammogram of the carbon fibres, bearing oxidized ethylene diamine, modified with the dinitrobenzene species, in a pH 4 aqueous solution. Peaks a and b in Fig. 3 correspond to the reduction of the two $-NO_2$ to $-NHOH$ groups, while the reversible peak pairs c, c′ and d, d′ are attributed to the reactions of $-NHOH$ to $-NO$ groups [9].

Quantitative results concerning the total amount of attached oxidized ethylene diamine, were obtained after chronoamperometric measurements conducted on large bundles of carbon fibres at 1.6 V/SCE, in acetonitrile. After a series of experiments it was estimated that 2.1 meq $H_2NCH_2CH_2NH_2$ are oxidized and bonded per g carbon fibres (1 g pristine carbon fibres corresponds to 0.17 m^2 of electrochemically active electrode area).

Evaluation of the total quantity of

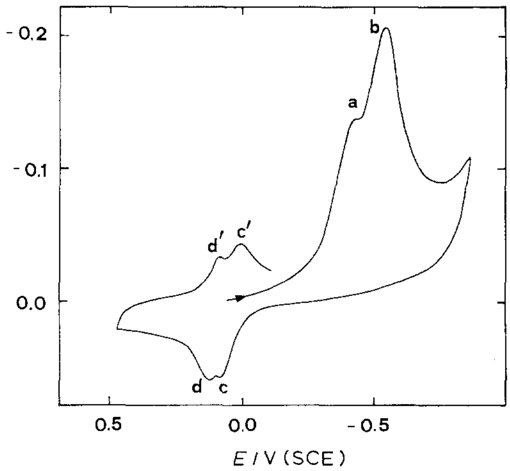


Fig. 3. Cyclic voltammogram ($\nu = 20\,\mathrm{mV\,s^{-1}}$) of modified with oxidized $H_2NCH_2CH_2NH_2$ carbon fibres after the amidization reaction with 3,5-dinitrobenzoyl chloride, in pH 4 buffer solution.

$H_2NCH_2CH_2NH_2$ molecules on the fibres was performed by potentiometric titration with HCl in aqueous solution at ground modified material. The result obtained was 2.2 meq $H_2NCH_2CH_2NH_2$ per g carbon fibres. Comparison of the above values implies that the majority of the $H_2NCH_2CH_2NH_2$ molecules undergo a two-electron oxidation, whereas just a small part of the molecules undergo a one-electron oxidation, suggesting the existence of non-oxidized amino groups.

The order of magnitude of the bonded amount of $H_2NCH_2CH_2NH_2$ exceeds a monolayer coverage, in contrast to the results of Barbier *et al.* [13], who refer to a monolayer coverage in the case of oxidation of *p*-nitrobenzylamine on carbon fibres.

The ethylene diamine molecules, which undergo a two-electron oxidation, may form mainly polymeric chains on the fibre surface. Formation of six-member rings with two more carbon atoms of the substrate (bridge configuration [13]) is also possible. The former feature explains the existence of terminating free amino groups. These two configurations may be schematically presented as shown in Fig. 4.

The formation of multiple polymer layers is expected to decrease the 'double layer' capacitance [16] and, consequently, to affect the impedance spectrum of the modified fibres. In Fig. 5, the impedance spectra of pristine carbon fibres and carbon fibres modified with oxidized ethylene diamine are shown at a potential (0.2 V/SCE), where no faradaic process occurs.

Figure 5 indicates that both electrodes exhibit a CPE-behaviour (constant phase element behaviour), which is attributed to the roughness of the electrode surface [16, 17]. It is obvious that the CPA angle φ (constant phase angle) is significantly greater in the case of the modified carbon fibres.

In order to obtain the double layer capacitance, C_0, for pristine and modified carbon fibre electrodes the method described by Sluyters *et al.* [16] was employed, which is applicable for rough electrodes at potentials where no faradaic process occurs (blocking electrodes).

For these calculations the relation

$$
\begin{aligned}
Z &= Z' - iZ'' \\
&= R_\Omega + \omega^{-(1-\alpha)} Q \left[\sin\left(\frac{\alpha\pi}{2}\right) - i\cos\left(\frac{\alpha\pi}{2}\right) \right] \qquad (1)
\end{aligned}
$$

was used, where R_Ω is the resistive limit of Z at $\omega \rightarrow \infty$, Q is a constant (with dimensions $\Omega\,\mathrm{cm^2\,s^{-(1-\alpha)}}$) representative of the CPE, and α is a dimensionless parameter which has a value between 0 and 1 and is related to the angle of rotation ($\varphi = \alpha\pi/2$). The values of R_Ω, Q and α were estimated by using complex non-linear least squares (CNLS) data fitting.

On the basis of the equations

$$Q^{-1} = C_0^{1-\alpha} R_\Omega^{-\alpha} \qquad (2)$$

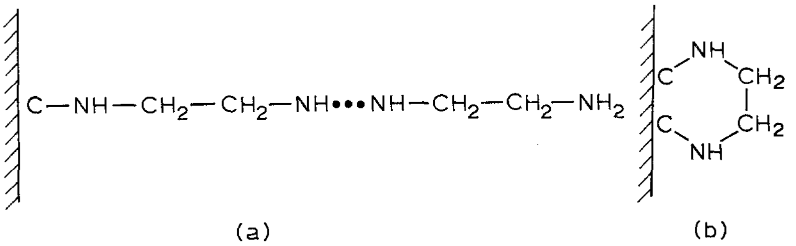
or

$$C_0 = (Q^{-1} R_\Omega^{\alpha})^{1/(1-\alpha)} \qquad (3)$$

the values of the double layer capacitance, C_0, for pristine and modified carbon fibre electrodes were found to be $15\,\mu\mathrm{F}$ and $7\,\mu\mathrm{F\,mg^{-1}}$ fibres or $9\,\mu\mathrm{F}$ and $4\,\mu\mathrm{F\,cm^{-2}}$, respectively.

The formation of multiple polymer layers of oxidized ethylene diamine on the carbon fibres caused inhibitory effects of electroreductions and/or electrooxidations of non-ionic depolarizers. For example, in the case of *p*-benzoquinone, which exhibited a normal redox behaviour on pristine fibres showing two pairs of reversible peaks (Fig. 7, curve 1) according to the reactions given in Fig. 6 it was found that on modified fibres the heights of the first reversible pair of peaks were diminished, whereas the second reversible pair of peaks disappeared, indicating complete inhibition of the dianionic radical formation (Fig. 7, curve 2). This behaviour was unaffected upon successive cycles.

Formation of multiple layers through electropolymerization on carbon fibres has also been observed in previous studies, in the case of naphthols and their



(a) (b)

Fig. 4. (a) Chain configuration; (b) bridge configuration.

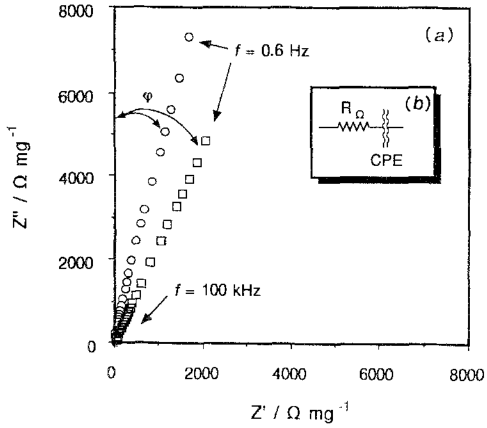


Fig. 5. (a) Impedance spectra of carbon fibres (1 mg) at 0.2 V/SCE, in CH$_3$CN (Et$_4$NClO$_4$ 0.1 M). (○) Pristine fibres ($\varphi = 0.15\pi/2$). Note: 1 mg corresponds to 1.7 cm^2; (□) modified by oxidized H$_2$NCH$_2$CH$_2$NH$_2$ fibres ($\varphi = 0.25\pi/2$). (b) Cell impedance analogue for an ideally polarized electrode. (Resistance in series with a CPE).

nitro and nitroso derivatives [18–20]. The presence of these layers on the electrode surface has been found to inhibit the performance of several electrochemical reactions [19, 20].

The primary amino groups of the bonded oxidized ethylene diamine are capable of reacting with dinitrobenzoyl chloride, whereas the secondary amino groups do not have this ability, due to steric hindrance effects. It is therefore predicted that the quantity of this species bonded to the modified material, corresponds only to a small number of the total amino-groups. Thus, chrono-amperometric measurements carried out on electrodes modified by the dinitrobenzene-group, at −0.65 V/SCE, in aqueous pH 4 solution, showed that about 1.8 × 10^{-2} meq of the dinitrobenzene species are attached per g carbon fibres.

Similar experiments performed on modified material by anion-exchanged [Au(III)Cl$_4$]$^-$ gave a value of 4 × 10^{-2} meq of Au per g carbon fibres. The increase in the deposited quantity in the latter case is attributed to less pronounced steric effects for [Au(III)Cl$_4$]$^-$ than for the -C$_6$H$_3$(NO$_2$)$_2$ group.

The ratio 4 : 1.8 also results from the correlation of the areas under the reduction peaks of Au^{3+} (to Au^0) and of the dinitrobenzene group in the corresponding cyclic voltammograms (Figs. 2 and 3), taking into account the 3 and 8-electron electrochemical reaction, respectively.

The results for the reaction of 3,5-dinitrobenzoyl chloride with primary amino groups are in agreement with literature data describing the behaviour of 4-fluoro-benzoyl chloride, which reacts only with the primary amino groups of derivatized carbon electrodes [13, 21].

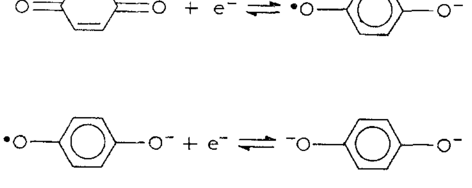


Fig. 6.

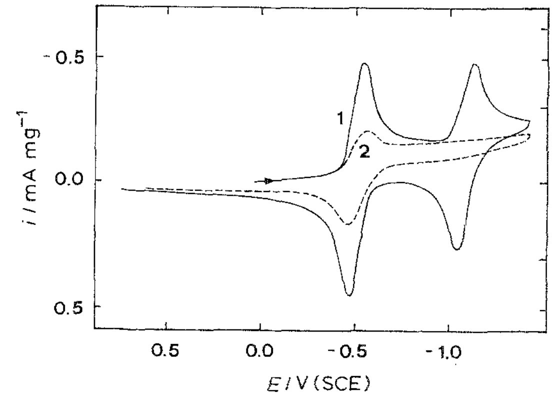


Fig. 7. Cyclic voltammogram (v = 100 mV s^{-1}) of p-benzoquinone (c = 10^{-3} M) in CH$_3$CN (Et$_4$NClO$_4$ 0.1 M) on pristine (1) and on modified carbon fibres (2).

The order of magnitude for the anion-exchange capacity of the produced material for small anions, such as F$^-$ and CN$^-$, was estimated to be about 1 meq per g carbon fibre.

4. Conclusions

Carbon fibres modified by electrochemical bonding of ethylene diamine can be used as precursors for the preparation of chemically modified electrodes via amidization of the free amino groups with acid chlorides.

Anion-exchangers produced by reaction of the modified fibres with HCl are suitable for the following applications:

(i) Carbon fibre based noble metal catalysts can be obtained through ion-exchange of the anionic components of complex metal salts, followed by electrochemical reduction to the metallic state.

(ii) Due to their relatively high anion-exchange capacity, these carbon fibres can be used for selective deionization and detoxication of waters from small anions.

References

[1] E. Theodoridou, A. D. Jannakoudakis and D. Jannakoudakis, *Synth. Met.* **9** (1984) 19.
[2] E. Theodoridou, A. D. Jannakoudakis, J. O. Besenhard and R. F. Sauter, *ibid.* **14** (1986) 125.
[3] E. Theodoridou, A. D. Jannakoudakis, P. D. Jannakoudakis, J. O. Besenhard and A. Kurtze, *in* 'Carbon '88' (edited by B. McEnaney and T. J. Mays), (1988) p. 537.
[4] E. Theodoridou, A. D. Jannakoudakis, P. D. Jannakoudakis and S. Antoniadou, *Can. J. Chem.* **69** (1991) 1881.
[5] A. D. Jannakoudakis, E. Theodoridou and D. Jannakoudakis, *Synth. Met.* **10** (1985) 131.
[6] E. Theodoridou, A. D. Jannakoudakis, J. O. Besenhard and R. F. Sauter, Proceedings of the 4th International Carbon Conference, Baden-Baden (1986) p. 623.
[7] A. D. Jannakoudakis, *Synth. Met.* **39** (1991) 303.
[8] E. Theodoridou, A. D. Jannakoudakis, P. D. Jannakoudakis, S. Antoniadou and J. O. Besenhard, *J. Appl. Electrochem.* **22** (1992) in press.
[9] P. D. Jannakoudakis, A. D. Jannakoudakis, E. Theodoridou and J. O. Besenhard, *ibid.* **19** (1989) 341.
[10] *Idem, ibid.* **20** (1990) 619.
[11] J. B. Donnet and P. Ehrburger, *Carbon* **15** (1977) 143.
[12] Y. S. Ko, G. P. Daumit and J. R. Crozier, Proceedings of the 4th International Carbon Conference, Baden-Baden (1986), p. 659.
[13] B. Barbier, J. Pinson, G. Desarmot and M. Sanchez, *J. Electrochem. Soc.* **137** (1990) 1757.

[14] N. Oyama, A. P. Brown and F. C. Anson, *J. Electroanal. Chem.* **87** (1978) 435.

[15] J. O. Besenhard, R. Parsons and R. M. Reeves, *ibid.* **96** (1979) 57.

[16] G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach and J. H. Sluyters, *ibid.* **176** (1984) 275.

[17] W. H. Mulder and J. H. Sluyters, *Electrochim. Acta* **33** (1988) 303.

[18] E. Theodoridou, P. Karabinas and D. Jannakoudakis, *Z. Naturforsch.* **37b** (1982) 112.

[19] S. Antoniadou, A. D. Jannakoudakis, P. Karabinas and E. Theodoridou, *J. Electroanal. Chem.* **207** (1986) 203.

[20] P. Karabinas, *Can. J. Chem.* **68** (1990) 275.

[21] R. W. Murray, *Electroanal. Chem.* **13** (1984) 270.