

Cyclic Voltammetric Studies of Heat Treated and Oxidized Carbon Fibres in Organic and Aqueous Solutions

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Summary. Cyclic voltammetry was used to compare the electrochemical behaviour of *PAN*-based carbon fibre electrodes in aqueous (different *pH*), acetonitrile and methanol solutions. The sets of fibres used were produced at three temperatures and were oxidized with conc. HNO_3 or left nonmodified. The electrode reaction mechanisms probably occurring on the carbon fibre surfaces were analyzed.

Keywords. Cyclic voltammetry; Carbon fibres; Surface functional groups.

Untersuchung thermisch behandelter und oxydierter Kohlefasern mittels zyklischer Voltammetrie in organischen und wässrigen Lösungen

Zusammenfassung. Es wurde das elektrochemische Verhalten von Kohlefaserelektroden in wässrigen (verschiedener *pH*-wert), acetonitrilischen und methanolischen Lösungen verglichen. Die Kohlefasern auf *PAN*(Polyacrylnitril)-Basis, die sich voneinander in der Temperatur der thermischen Behandlung unterscheiden und nicht oder mit konzentrierter Salpetersäure oxidiert wurden, wurden mittels zyklischer Voltammetrie untersucht. Der wahrscheinliche Verlauf der Elektrodeprozesse auf den Kohlefaseroberflächen wurde analysiert.

Introduction

The electrochemical properties of carbon fibres (*CFs*) depend on their thermal history and chemical pretreatment mode [1–5]. The heat treatment temperature of carbon fibres influences their microstructure, *e.g.* specific surface area, pore size distribution, and surface energy state. These factors influence the nature of the functional groups formed on the carbon surface during oxidative modification.

The course of electrode processes, such as oxygen electroreduction [6] or electroadsorption [7, 8], depends on the presence of a chemisorbed oxygen species on the *CF* surface.

In the studies of the electrochemical properties of *CFs*, these were used as working electrodes in various forms:

– single fibres (cylindrical) or their cross-sections [6, 9–10],

- single [2-3, 5, 9, 11] and faggots [12],
- cloths (felts) [1, 4, 7].

No comprehensive comparative studies on the electrochemical behaviour of *CF* electrodes with respect to the nature of the electrolyte solution, to the thermal history of the studied *CFs*, or their oxidation modification have been reported in the literature. These relationships are discussed in the present paper.

Results and Discussion

The cyclic voltammometric (CV) curves recorded for all carbon fibres investigated in aqueous solutions of neutral electrolyte (Na_2SO_4) are presented in Fig. 1. CV curves recorded in acetonitrile and methanol solutions are shown in Figs. 2 and 3, respectively.

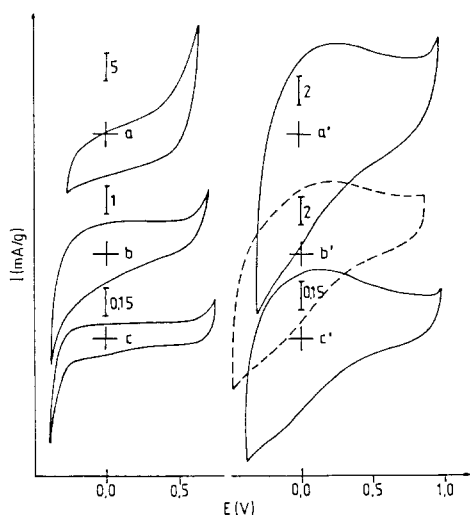


Fig. 1. Cyclic voltammograms of carbon fibres in $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ Na}_2\text{SO}_4$ aqueous solution; a, CF1100; a, CF1100ox; b, CF1400; b, CF1400ox; c, CF2400; c, CF2400ox

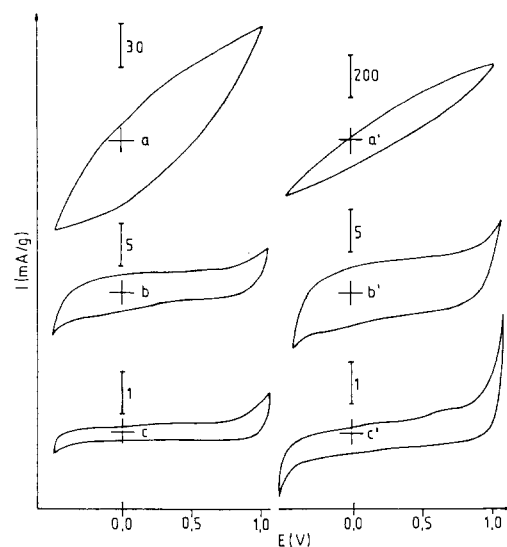


Fig. 2. Cyclic voltammograms of carbon fibres in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ LiClO}_4$ acetonitrile solution (a-c': see caption of Fig. 1)

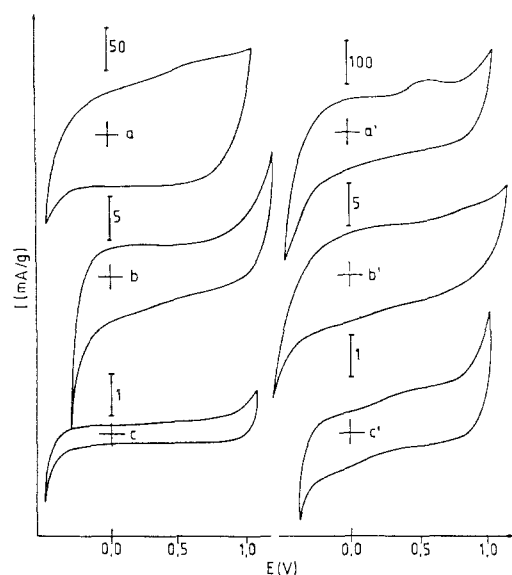


Fig. 3. Cyclic voltammograms of carbon fibres in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ LiClO}_4$ methanol solution (a–c': see caption of Fig. 1)

Comparison of the cyclovoltammetric curves recorded in both aqueous and non-aqueous solutions provided evidence of a considerable decrease in double electric layer capacity with increase in *CF* carbonization temperature (particularly between 1100 and 1400 °C). This observation applies to both unmodified and oxidized carbon fibres.

Oxidative modification leads to the appearance of a wide anodic peak with a potential between 0.1 and 0.3 V in neutral aqueous solutions (see Fig. 1). This peak is not observed in non-aqueous solutions. Presumably, in this potential range water molecules participate in the electrode process. At the same time, a slight cathodic peak ($E \approx 0.0 \text{ V}$) is observed more pronouncedly in solutions of higher *pH* for all fibres tested in aqueous solutions. The absence of any peak on CV curves recorded in acetonitrile solutions (Fig. 2) suggests that functional groups on the surface of the electrode material exhibit no electroactivity in non-protic systems.

On the CV curves recorded in methanol solutions (Fig. 3), marked anodic peaks ($E \approx 0.5 \text{ V}$) and poorly-shaped cathodic peaks ($E \approx 0.0 \text{ V}$) are observed for oxidized carbon fibres. In a low-protic environment, the oxidation of functional groups is believed to occur at a higher potential than in aqueous solutions. The lack of such a shift in cathodic peak potential can be explained by the electron transfer character of the process responsible for this peak. Therefore, the presence of protons in the electrolyte solution influences electrode processes in which chemisorbed oxygen species participate. To evaluate these influences, the CV curves for aqueous electrolyte solutions of different *pH* were recorded. The curves obtained for CF-2400ox is shown in Fig. 4. The shape of CV recorded for different *pH* values of electrolyte solutions indicates that reduction (partially reversible) occurs in acidic solutions (*pH* 1–4), and a distinct cathodic peak is observed. In neutral and basic solutions, however partially reversible or irreversible oxidation takes place.

Recently, the presence of similar peaks on CV curves recorded for glassy carbon electrodes (activated in air at 400–800 °C as well as oxidized by electrochemical pretreatment) was confirmed [14, 15]. The cyclic voltammograms recorded for

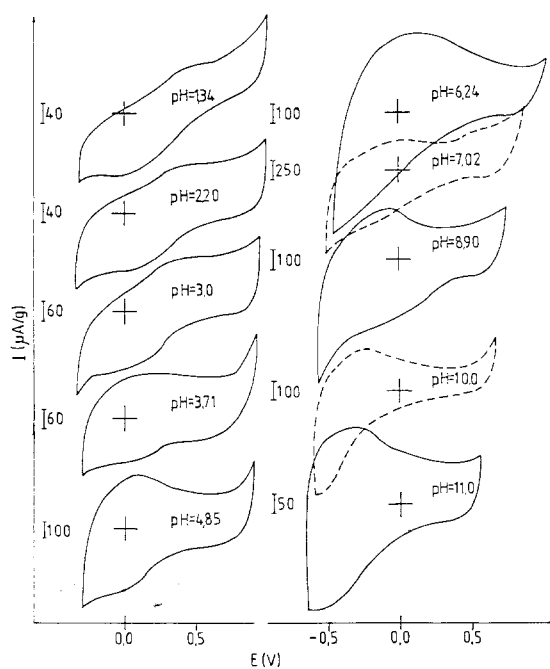


Fig. 4. Cyclic voltammograms of CF2400ox in aqueous solutions with different pH

activated carbons (modified carbon paste electrodes) did not reveal any specific redox peaks, but square wave voltammograms were characterized by some well-defined redox peaks [16]. The behaviour of all these peaks was consistent with that one expected for couples of the quinone/hydroquinone type [14–16].

The measured *Nernst* slopes were generally in the range of 0.30 to $-0.80 \text{ V}/pH$, most often near $-0.60 \text{ V}/pH$. This is close to the theoretical value of $-59 \text{ mV}/pH$ at 25°C for the $2e^-/2H^+$ redox couple.

A simple interpretation of the peaks observed on the recorded CV curves is not possible because of their large width. Species that do not have to diffuse to the electrode, such as adsorbates or groups chemically bound to the surface, tend to show sharp peaks [17].

The dependence of the estimated anodic peak potential on the pH of aqueous electrolytes for the selected fibre (CF 2400ox) is presented in Fig. 5. A fairly good straight line is obtained within the entire range of pH values with an average slope of $69.5 \text{ mV}/pH$. One contributing factor to the discrepancy in slopes (obtained and theoretical) could be the incomplete resolution of the overlapping peaks exhibiting differing electrochemical reversibilities. It would be expected to find hydroxylic groups (quasi-hydroquinones) in different local environments on the carbon surface. Carbon fibres are thought to possess localized graphitic planes, at the edge of which various electroactive functionalites could be expected to be formed during nitric acid oxidation [18].

A gradual hydrolysis of lactone-type surface groups (with increase of blanc electrolyte basicity) leads to an enhancement of the observed anodic peak (Fig. 4).

A distinct differentiation of the electrode process has been observed for the reduction of surface functional groups. In this case the estimated peak potentials are less dependent on pH .

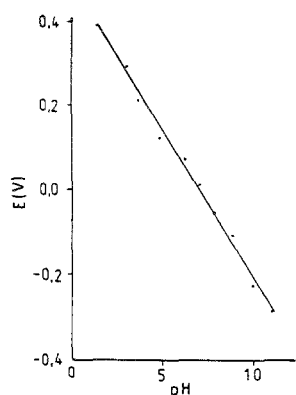


Fig. 5. Anodic peak potential of CF2400ox vs. *pH* of aqueous solutions

The observed similarity in the behaviour of the surface functional groups of oxidized carbon fibres and in that of the model system (some substituted organic quinones) [19, 20] does not exclude the presence of other functional groups on the carbon surface. This non-revealing of other functional groups may be due both to the lack of electrochemical activity and their relatively small quantities on the rough surface of the carbon fibres investigated.

The electrochemical reaction mechanisms occurring with the participation of active surface compounds in aqueous electrolytes can be studied by means of the method presented here. On the other hand, the lack of electrochemical activity of functional groups in aprotic media enable these systems to be applied in charge-transfer and electroadsorption.

Experimental

The investigated carbon fibre electrodes were produced from *PAN* (polyacrylonitrile) by carbonization at 1100, 1400, and 2400 °C [13]. Some electrodes were used in unmodified form (CF1100, CF1400, CF2400), while others were oxidized with conc. (65%) HNO_3 for 1 h at 80 °C (CF1100ox, CF1400ox, CF2400ox). Voltammetric experiments were carried out using a standard three-electrode glass cell and a typical setup. Cyclic Voltammograms were recorded in aqueous solutions ($0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaOH, $0.05 \text{ mol} \cdot \text{dm}^{-3}$ Na_2SO_4 , and $0.05 \text{ mol} \cdot \text{dm}^{-3}$ H_2SO_4 mixed in various proportions) over a wide range of *pH* (1–13) and in methanol and acetonitrile solutions of LiClO_4 ($0.1 \text{ mol} \cdot \text{dm}^{-3}$). The bundles of *CFs* acting as working electrodes weighed between 2 and 30 mg. A saturated calomel electrode was used as reference electrode (SCE) and a platinum wire as counter electrode. A salt bridge was used for the non-aqueous solutions. All measurements were carried out at room temperature in an oxygen-free atmosphere at a sweep rate of $33.3 \text{ mV} \cdot \text{s}^{-1}$. All reagents were of analytical grade and the aqueous solutions were prepared from double-distilled water. The non-aqueous solvents were additionally dried using methods described in the literature.

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References

- [1] Tanahashi I., Yoshida A., Nishino A. (1991) *J. Appl. Electrochem.* **21**: 28
- [2] Jannakoudakis A. D., Jannakoudakis P. B., Theodoridou E., Besenhard J. O. (1990) *J. Appl. Electrochem.* **20**: 619
- [3] Neffe S. (1987) *Carbon* **25**: 761
- [4] Yoshida A., Tanahashi I., Nishino A. (1990) *Carbon* **28**: 611
- [5] Kozłowski C., Sherwood P. M. A. (1984) *J. Chem. Soc., Faraday Trans.* **80**: 2099
- [6] Bednarkiewicz E., Kublik Z. (1990) 41st ISE Meeting, Extended Abstracts, Suppl. 4, Prague, Czechoslovakia
- [7] Woodard F. E., McMackins D. E., Jansson R. E. W. (1986) *J. Electroanal. Chem.* **214**: 303
- [8] Viedieniapin A. A. et al. (1991) *Elektrochimija* **27**: 842
- [9] Schulze G., Frenze W. (1984) *Anal. Chim. Acta* **159**: 95
- [10] Dayton M. A., et al. (1980) *Anal. Chem.* **52**: 946
- [11] Maeda Y., Harada S. (1989) *Synth. Met.* **31**: 389
- [12] Morita M., Nishimura N., Matsuda Y. (1993) *Electrochim. Acta* **38**: 1721
- [13] Błażewicz S. (1982) Polish Patent No 112, 180
- [14] Marsh J. H., Orchard S. W. (1992) *Carbon* **30**: 895
- [15] Young Y., Lin Z. G. (1994), *J. Electroanal. Chem.*, **364**: 23
- [16] Kaplan J. D., Marsh J. H., Orchard S. W. (1993) *Electroanalysis* **5**: 509
- [17] Wopschall R. H., Shain I. (1967) *Anal. Chem.* **39**: 1514
- [18] Donnet J. B., Bansal R. C. (1993) *Carbon fibre*. Marcel Dekker, New York, pp. 153–160
- [19] Bailey S. I., Ritchie I. M. (1985) *Electrochim. Acta.* **30**: 3
- [20] Tarasevich M. R., Bogdanovskaya V. A., Zagudaeva N. M. (1987) *J. Electroanal. Chem.* **223**: 161

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