Carbon fibre based conductive ion exchangers as support for metal and ligand charged metalloporphyrin electrocatalysts

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

Institute of Physical Chemistry, Aristotelian University, Thessaloniki, Greece

J. O. BESENHARD

Institute of Inorganic Chemistry, Westfällische Wilhelms University, Münster, Germany

The behaviour of a new kind of metalloporphyrin catalyst electrode for reduction of oxygen, characterized by a metal and ligand charged (MLC) water soluble metalloporphyrin system and a surface oxidized carbon fibre substrate exhibiting cation exchanger properties, is investigated by cyclic voltammetry and by impedance spectroscopy. Results with Fe- and Co-MLC-metalloporphyrins clearly indicate that they are electrocatalytically active so long as the transition metals exist in their + 3 oxidation state. Compared to conventional metalloporphyrin electrodes, which are obtained after adsorption procedures, this new kind of electrode has several advantages, i.e. it bears larger quantity of catalytically active monomeric metalloporphyrin molecules, it is more resistant to rinsing and can be reactivated by addition of the metalloporphyrin to the aqueous electrolyte solution. These advantages allow the application of this electrode in fuel cells.

1. Introduction

The behaviour of water insoluble metalloporphyrins with non-ionic ligand systems has been investigated in previous studies [1–3]. It was found that the adsorption of these compounds can be carried out from methanolic solutions on surface oxidized, as well as on non-oxidized, carbon fibres. The electrochemical behaviour of the attached metalloporphyrins and their catalytic activity in oxygen-electroreduction and H_2NNH_2-electrooxidation was studied.

The present study extended to water soluble metalloporphyrins with a cationic ligand system, in order to examine the adsorption behaviour of these metal and ligand charged (MLC) metalloporphyrins on surface oxidized carbons. Due to their hydrophylic character, MLC-metalloporphyrins are not adsorbed on uncharged surfaces, such as non-oxidized carbons [4].

However, the presence of cation exchanging groups on pulse oxidized carbon fibres [5, 6] favours the attachment of cationic porphyrin species. Moreover, by addition of such water soluble MLC-metalloporphyrins to the electrolyte solution, 'worn out' catalyst electrodes may be reactivated. As the most appropriate metalloporphyrin salt for this purpose, the meso-tetra (4-N-methylpyridyl) porphyrin tetraiodide

was selected:
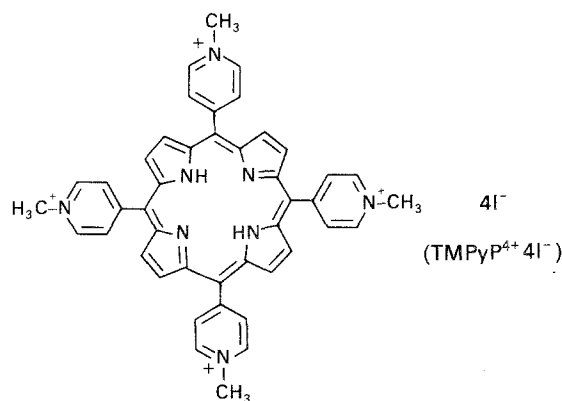
(TMPyP^{4+}4I$^-$)

2. Experimental details

The insertion of Fe^{3+} and Co^{3+} in the porphyrin ligand was carried out by us and was based on methods described in the literature [7, 8].

15 μmol TMPyP^{4+}4I$^-$ (Ventron) were dissolved in 100 ml H_2O and a 20-fold quantity of $FeSO_4 \cdot 7H_2O$ (Merck) or $Co(NO_3)_2 \cdot 6H_2O$ (Carlo Erba) with a few NaCl crystals were added. The solution was heated at ca. 90° C for an average period of 30 min and was allowed to stand in air for about 10 min, so that auto-oxidation to the trivalent metal complex could take

place [8]. The excess of metal ions was removed from the solution in the form of the corresponding hydroxide as follows: in the hot freshly prepared solution of metalloporphyrin, 50 ml NaOH 0.1 M were added and the mixture was left to cool. The metal hydroxide was separated from the metalloporphyrin solution by successive filtrations.

The attachment procedure of the metalloporphyrin was accomplished by dipping the fibres in a 10^{-4} M solution at 20° C for sufficient time so that equilibrium could be established. The fibres were then rinsed with water and used for the electrochemical measurements.

The carbon fibres used in this study were from BASF–Celanese Corp. U.S.A. (type Celion GY 70). These polyacrylonitrile-based fibres are characterized by high orientation along the fibre axis, stiffness (Young modulus 5.15×10^{11} N m^2) and considerable electrical conductivity (specific resistance 7×10^{-4} Ω cm) [9, 10].

The electrochemical oxidation of the carbon fibres was achieved by application of alternative oxidative and reductive potentiostatic square wave pulses in aqueous solutions of Na$_2$SO$_4$ 0.5 M, for time periods varying from 0 up to 6 min. The applied potential range extended from $+2.3$ V to -0.3 V/SCE and the duration of the oxidative pulse was six times longer than that of the reductive pulse. These conditions were experimentally found to be the most appropriate for the formation of intercalation compound of type C_n^+ HSO$_4^-$ and subsequent hydrolysis to a thick layer of surface oxides consisting mainly of –COOH and –OH groups [5, 6]. The procedure is favoured by the acidic environment due to the electrolysis of water [5, 11].

Impedance measurements in the controlled potential mode were performed with a system consisting of a potentiostat (Jaissle IMP 88 -10 ± 10 V, 0.5 A) and a Lock-In Amplifier (EG&G PARC Model 5210), connected to a computer (AT Acer 910).

Frequency sweeps extended from 10^5 Hz to 0.5 Hz using a sinusoidal perturbance signal of 5 mV peak to peak. High frequency measurements were obtained using a resistor (of known value) placed in series with a counter electrode. Frequencies lower than 0.5 Hz could not be obtained.

Aqueous buffer solutions of pH = 9 were prepared from H$_3$BO$_3$ and NaOH.

All measurements were carried out at 25° C.

3. Results and discussion

3.1. Modification of carbon fibres by MLC-metalloporphyrins

The adsorption of TMPyP^{4+} 4I$^-$, as well as of the corresponding metalloporphyrins, on pristine carbon fibres is negligible as proved by the absence of characteristic peaks in the corresponding cyclic voltammograms. From Fig. 1 it is obvious that the carbon fibres can be used as electrodes over a wide potential range (from $+1$ up to -1.5 V/SCE, for the pH 9 solution).
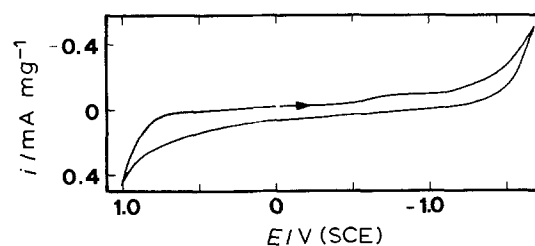

Fig. 1. Cyclic voltammogram (v = 100 mV s^{-1}, pH 9) of non-oxidized carbon fibres after their immersion in solutions of TMPyP^{4+} 4I$^-$ and of the corresponding metalloporphyrins.

On pulse oxidized carbon fibres the porphyrin ligand, as well as the Fe(III)- and Co(III)-metalloporphyrins, are strongly attached via an ion exchange process. This is verified by the appearance of characteristic redox peaks in the corresponding cyclic voltammograms (Fig. 2).

The pairs of peaks a, a′ and b, b′ are attributed to the reduction and oxidation of the double bonds C=N of the porphyrin ring.

Earlier studies on the electrochemical behaviour of TMPyP^{4+} 4I$^-$ on mercury and gold electrodes in acidic aqueous solutions showed that the primary step of the overall mechanism involves the reduction of the porphyrin ring C=N bonds [12].

Peaks c, c′ and d, d′ are attributed to the reversible redox reaction of the central metal ion, i.e. Fe(III) + $e^- \rightleftharpoons$ Fe(II) and Co(III) + $e^- \rightleftharpoons$ Co(II).

In previous studies it was found that the adsorbed metalloporphyrin exists in two forms, monomeric and dimeric, which exhibit two reversible pairs of peaks, respectively [1, 2]. The monomeric form proved to be catalytically active since it has the ability to produce an intermediate adduct with the molecule of the species that undergoes electrocatalytic reduction or oxidation [13–15].
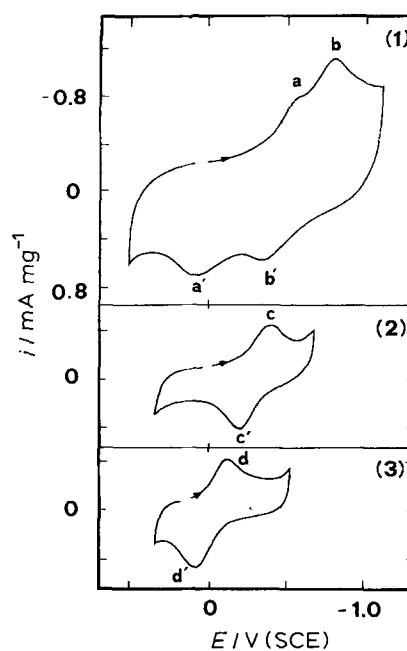

Fig. 2. Cyclic voltammograms (v = 100 mV s^{-1}, pH 9) of oxidized carbon fibres (m = 1 mg, t = 1 min) after attachment through cation exchange of TMPyP^{4+} (1), Fe(III)TMPyP^{5+} (2) and Co(III)TMPyP^{5+} (3).

It is known from the literature that numerous porphyrins and metalloporphyrins exist in solution in several forms, i.e. as monomers, dimers and even higher aggregates [16].

In the case of $TMPyP^{4+}4I^-$ and its metal complexes it has been established that they exist as monomers, except the iron porphyrin which has been found to aggregate [16–18].

Nevertheless, the appearance of a single pair of redox peaks of the central metal ion in the corresponding cyclic voltammograms (curves 2 and 3 in Fig. 2) indicates the attachment of the monomeric form of $Fe(III)TMPyP^{5+}$ and $Co(III)TMPyP^{5+}$ exclusively, through cation exchange. Further evidence of the ion-exchanging character of the attachment process is provided by the fact that the cationic porphyrin components are totally removed by concentrated solutions of $Ca(NO_3)_2$ (e.g. 0.5 M).

From the area under peaks c and d in the cyclic voltammograms of Fig. 2 it is estimated that the attached quantity of metalloporphyrin is 7×10^{-3} mmol per g of carbon fibre (1 g of 1 min oxidized carbon fibres corresponds to $0.25\,m^2$ of electrochemically active electrode area). This value is almost 20 times lower compared to the quantity of Ag^+ cation-exchanged on 1 min electro-oxidized carbon fibres. This difference is attributed to the fact that the metalloporphyrin cation is much larger; it covers simultaneously many active sites and cannot penetrate the micropores of the oxidized carbon substrate. Nevertheless, this quantity is significantly greater compared to metalloporphyrins not carrying charges on their ligand systems. For example, the amount of the monomeric $Co(III)TMPyP^{5+}$ was found to be 10-fold compared to the monomeric form of the non-ionic $Co(II)$-protoporphyrin kept on the oxidized carbon fibre surface by adsorption interactions.

The arrangement of the metalloporphyrin components is expected to be perpendicular to the electrode surface since the methylpyridyl rings are out of the porphyrin plane and the positive charges delocalize the π electron density across the surface of the molecule and thus inhibit π–π interactions between the porphyrin ring and the carbon substrate [17]. These arguments imply that the ion exchange is performed via the peripheral charged groups.

The investigated charged metalloporphyrins show much less tendency to be removed from the electrode, by long storage in water or in aqueous electrolyte solutions, than ordinary uncharged metalloporphyrins. Moreover, the removed small quantity of the ion-exchanged metalloporphyrin system can be easily replaced by addition of MLC-metalloporphyrins to the aqueous electrolyte solution, whereas this is not possible in the case of water insoluble metalloporphyrins.

3.2. Catalysis of O_2-electroreduction

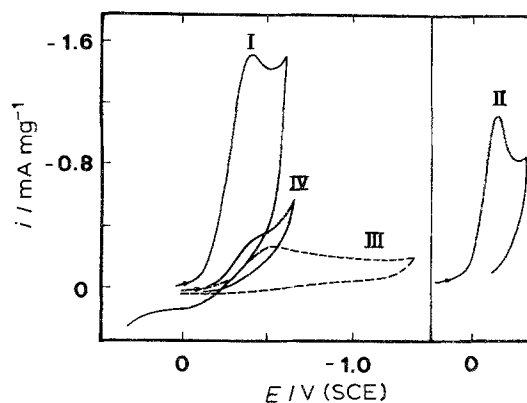The electroreduction of oxygen is catalysed on the metalloporphyrin modified carbon fibre electrodes.

Fig. 3. Cyclic voltammograms ($v = 100\,mV\,s^{-1}$, pH 9) of oxygen-reduction (saturated solution) on oxidized carbon fibres $m = 1\,mg$, $t = 1\,min$) after cation exchange with $Fe(III)TMPyP^{5+}$ (I) and $Co(III)TMPyP^{5+}$ (II). Cyclic voltammograms III and IV correspond to the oxygen electroreduction on non-oxidized and oxidized fibres respectively (on curve IV the beginning of the reduction of the surface oxide layer is discerned).

The reduction peak appears at the potential region of the peak pair of the central metal ion (Fig. 3).

The peak current i_p for the oxygen reduction is proportional to the square root of the scan rate, varying from 0.02 to $0.4\,V\,s^{-1}$. The slopes of the plots of i_p against $v^{1/2}$ for Fe-porphyrin and Co-porphyrin modified carbon fibres were found 4.93×10^{-3} and $2.65 \times 10^{-3}\,A\,V^{-1/2}\,s^{1/2}$, respectively.

According to the equation of irreversible electrode processes $i_p = 3.01 \times 10^5 n(\alpha n_\alpha)^{1/2}ACD^{1/2}v^{1/2}$ [19], considering $\alpha n_\alpha = 0.5$, $A = 1\,cm^2$, $C = 1.23 \times 10^{-3}\,M$ (for saturated solution) and $D = 2.32 \times 10^{-5}\,cm^2\,s^{-1}$ [1], it was estimated that the number of electrons involved in the oxygen reduction is 4 in the case of Fe-porphyrin and 2 in the case of the Co-porphyrin modified electrodes. These results prove that O_2 is reduced to H_2O in the presence of Fe-porphyrin and to H_2O_2 in the presence of Co-porphyrin. The same results are obtained after comparison of the charges under the corresponding reductive peaks (curves I and II in Fig. 3). Further confirmation is provided by the fact that electrochemical reduction of H_2O_2 to H_2O occurs only in the presence of $Fe(III)TMPyP^{5+}$.

The five coordinate $Fe(III)TMPyP^{5+}$ and $Co(III)$-$TMPyP^{5+}$ exhibit a square pyramidal configuration having the metal ion at the top [20]. The axial position of the trivalent central metal ion is occupied by oxygen under formation of an intermediate adduct [13], which is crucial for the electrocatalytic reduction.

The initial step of this electrocatalytic process involves the reduction of M(III) to M(II):

$$P\text{–}M(III)\cdot O_2 + e^- \longrightarrow P\text{–}M(II)\cdot O_2$$
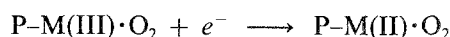
In the latter species a resonance between $M(II)\cdot O_2$ and $M(III)\cdot O_2^-$ states exists as has already been proved for other metalloporphyrin complexes [14, 15]. The next steps of the electrocatalytic reduction of oxygen on the modified electrodes have already been described in a previous study [1].

The catalytic activity of the oxidized carbon fibres modified with MLC-metalloporphyrins increases for
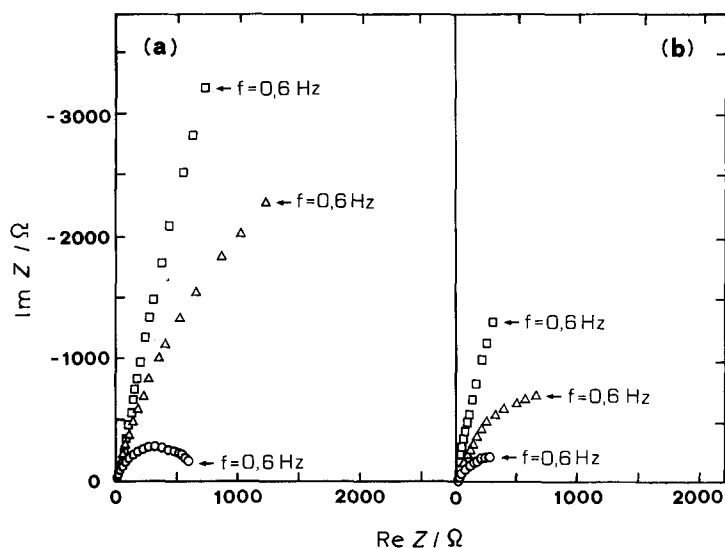
Fig. 4. Impedance spectra of oxygen-reduction on carbon fibres (1 mg) in buffer-solution (pH 9) saturated with oxygen, at (O) − 500, (△) − 300 and (□) − 150 mV/SCE. (a) As received fibres, and (b) preoxidized fibres (1 min pulse oxidation). (Frequency at the beginning of all the curves: 10^5 Hz).

periods of oxidation varying from 0 to 1 min, whereas it remains practically the same for periods of oxidation extending from 1 up to 6 min. Prolonged oxidation seriously decreases the conductivity and the mechanical stability of the carbon fibres.

3.3. Impedance spectroscopy

The electrocatalytic process in the case of oxygen reduction on the carbon fibre modified by MLC-metalloporphyrins electrodes was also followed by potential controlled impedance spectroscopy. The results verify that the MLC-metalloporphyrin systems of Fe and Co catalyse the electroreduction of oxygen if the transition metals are in the + 3 oxidation state.

The electrocatalytic activity of as received and surface oxidized carbon fibres is very poor and can be neglected compared to the activity of the attached metalloporphyrins.

The behaviour of as received and surface oxidized carbon fibres is demonstrated by Fig. 4, showing impedance spectra of O_2-reduction at − 500 mV and − 300 mV/SCE. At more positive potentials (e.g. − 150 mV) these fibres are practically inactive for oxygen-reduction, in accordance with the cyclic voltammetric study.

Figure 4 shows that at − 150 mV the faradaic current is negligible, whereas at − 300 mV and − 500 mV it is more pronounced. The corresponding curves tend to a semicircle and this trend is more apparent on the electrooxidized fibres compared to the pristine fibres.

According to the non linear least square method, it was estimated that the charge transfer resistance (R_{ct}) is 750 Ω per mg of pristine fibres and 550 Ω per mg of 1 min electrooxidized fibres, at − 500 mV/SCE.

It is evident that the double pulse oxidation does not significantly affect the charge transfer resistance of the electrode for the oxygen-reduction, despite the fact that it is related to a considerable increase of the carbon fibre surface [21]. By contrast, the double layer capacity is drastically increased after the double pulse oxidation procedure. The values obtained were 30 μF per mg of pristine carbon fibres and 500 μF per mg of 1 min oxidized carbon fibres. This considerable

increase reflects not only the increase in real surface area, but also the much higher double layer capacities of edge, i.e. functionalized, carbon sites compared to basal plane sites [5, 22].

Figure 5 shows impedance spectra of oxygen-reduction on Fe- and Co-metalloporphyrin modified carbon fibre electrodes at different potentials. The potential of − 500 mV/SCE was chosen to ensure that the transition metals were present mainly in their + 2 oxidation state. At this potential the electrodes behave almost as pure capacitors, i.e. the faradaic current is negligible. The more positive potentials were set at levels where at least large fractions of the transition metals were present in the + 3 state. These potentials, i.e. − 300 mV for Fe and − 150 mV/SCE for Co, were determined from the cyclic voltammetric study, since they lie in the region of the peak pair of the corresponding central metal ion.
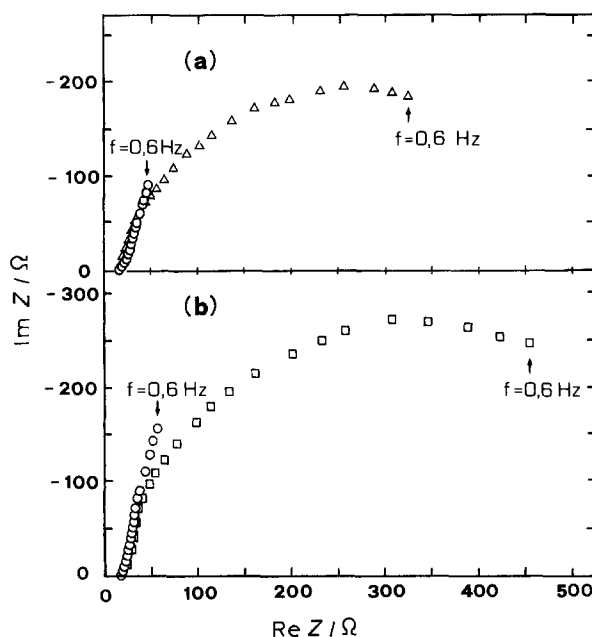

Fig. 5. Impedance spectra of oxygen-reduction on carbon fibres (1 mg) in buffer-solution (pH 9) saturated with oxygen at potentials: (□) − 150; (△) − 300 and (O) − 500 mV/SCE. (a) Fe-porphyrin modified fibres, and (b) Co-porphyrin modified fibres. (Frequency at the beginning of all the curves: 10^5 Hz).

On oxidized non-modified fibres at $-300\,\text{mV}$ the charge transfer resistance is $1600\,\Omega$ per mg (Fig. 4b), whereas on oxidized and modified by Fe(III)porphyrin fibres the corresponding value is $400\,\Omega$ per mg (Fig. 5a). Analogous calculations at $-150\,\text{mV}$ gave values of R_{ct} greater than $10^4\,\Omega$ per mg oxidized non-modified fibres (Fig. 4b) and $600\,\Omega$ per mg of oxidized and modified by Co(III)porphyrin fibres (Fig. 5b).

The small values of the charge transfer resistance for oxygen-electroreduction on carbon fibre electrodes modified by metalloporphyrins verify that the electro-catalytic activity of these electrodes is apparent at the potential region of the redox couple of the central metal ion.

4. Conclusions

The combination of cation-exchanging carbon-based supporting materials with metal and ligand charged metalloporphyrins is a new way of making catalytically active electrodes. This new kind of electrode has several fundamental advantages over conventional metalloporphyrin electrodes. These are:

(i) The strong interactions between the negative charges on surface oxidized carbons and the positive charges (up to 5) on MLC-metalloporphyrins make possible higher surface concentrations of metalloporphyrins than conventional impregnation of carbons with ordinary metalloporphyrins not carrying charges on their ligand system.

(ii) MLC-metalloporphyrins attached to the carbon surface by strong electrostatic interactions are more resistant against 'washing out' processes than ordinary metalloporphyrins, which are kept on the carbon surface mainly by much weaker adsorption interactions.

(iii) MLC-metalloporphyrins show much less tendency to be transformed into catalytically inactive dimers or oligomers than ordinary metalloporphyrins.

(iv) As MLC-metalloporphyrins are soluble in water, 'worn out' catalyst electrodes can be reactivated by addition of MLC-metalloporphyrins to the electrolyte solution.

These advantages might be further developed and exploited for practical applications, for example in fuel cells.

References

[1] S. Antoniadou, A. D. Jannakoudakis and E. Theodoridou, *Synth. Met.* **30** (1989) 283.
[2] *Idem, ibid.* **30** (1989) 295.
[3] S. Antoniadou, A. D. Jannakoudakis, P. D. Jannakoudakis and E. Theodoridou, *ibid.* **32** (1989) 309.
[4] T. Kuwana, M. Fujihira, K. Sukanawa and T. Osa, *J. Electroanal. Chem.* **88** (1978) 299.
[5] E. Theodoridou, A. D. Jannakoudakis, J. O. Besenhard and R. F. Sauter, *Synth. Met.* **14** (1986) 125.
[6] A. D. Jannakoudakis, P. D. Jannakoudakis, E. Theodoridou and J. O. Besenhard, *J. Appl. Electrochem.* **20** (1990) 619.
[7] D. B. Marell, J. Barrett and P. S. Clezy, *Biochem. J.* **78** (1961) 793.
[8] J. H. Fuhrhop and K. Smith, in 'Porphyrins and Metalloporphyrins' (edited by K. Smith), Elsevier Scientific (1975) p.803.
[9] J. B. Donnet and P. Ehrburger, *Carbon* **15** (1977) 143.
[10] D. J. Johnson, in 'Chemistry and Physics of Carbon' (edited by P. A. Thrower) Vol. 20, Marcel Dekker, New York (1987) p.1.
[11] S. Antoniadou, A. D. Jannakoudakis, P. D. Jannakoudakis and E. Theodoridou, *Chim. Chron. N.S.* **18** (1989) 141.
[12] B. P. Neri and G. S. Nilson, *Anal. Chem.* **44** (1972) 2257.
[13] A. Bettelheim and T. Kuwana, *ibid.* **51** (1979) 1002.
[14] A. J. Appleby, M. Savy and P. Caro, *J. Electroanal. Chem.* **111** (1980) 91.
[15] K. Shigehara and F. C. Anson, *J. Phys. Chem.* **86** (1982) 2776.
[16] W. I. White, in 'The Porphyrins' (edited by D. Dolphin) Vol. 5, Academic Press, New York (1978) p.303.
[17] P. Hambright, in 'Porphyrins and Metalloporphyrins', *op. cit.* [8], p.266.
[18] D. G. Davis, in 'The Porphyrins' (edited by D. Dolphin) Vol. 5, Academic Press, New York (1978) p.140.
[19] A. J. Bard and L. R. Faukner, 'Electrochemical Methods', J. Wiley & Sons, New York (1980) p.220.
[20] J. L. Hoard, in 'Porphyrins and Metalloporphyrins', *op. cit.* [8], p.317.
[21] J. O. Besenhard, J. Jakob, P. Möller, M. Wicher, A. D. Jannakoudakis and E. Theodoridou, 'Werkstoffe in der Elektrochemie', Dechema Monographien, Vol. 121 (1989) p.355.
[22] A. J. Bard, 'Encyclopedia of Electrochemistry of the Elements', Vol. VII, Marcel Dekker, New York (1976) p.38.