

ELECTROPOLYMERIZATION OF PYRROLE SUBSTITUTED METALLOPORPHYRINS – SYNTHESIS AND CHARACTERIZATION

L. M. Abrantes^{1*}, C. M. Cordas¹, J. P. Correia², F-P. Montforts³ and M. Wedel³

1- *CECUL, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1700 Lisboa, PORTUGAL.*

2- *Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1700 Lisboa, PORTUGAL.*

3- *Institut für Organische Chemie, Universität Bremen, Bibliothekstrasse, 28358 Bremen, DEUTSCHLAND.*

Abstract

The electropolymerization of substituted manganese and iron metalloporphyrins with two pyrrole groups bonded in lateral chains is investigated. It is shown that under potentiodynamic conditions the film formation can be successfully achieved. A methodology for the polymerization of the iron containing monomer on microelectrodes is also presented.

The behaviour of the polymer modified electrodes is studied for the O₂ reduction, as well as for the oxygen and hydrogen evolution reactions, revealing good electrocatalytic activity.

Keywords: Conducting polymers, Electropolymerization, Metalloporphyrins, Electrocatalysis

Introduction

In the last years the research concerning surface modified electrodes, namely incorporating transition-metal complexes, has been widely developed [1]. Among the possible immobilisation techniques, one can find direct adsorption, inert matrix incorporation and deposition by polymerization, including electropolymerization [2]. This last presents multiple advantages, namely, good reproducibility, simplicity and easy experimental control of the film thickness [3]. The grafting of transition-metal complexes to electrodes can be efficiently achieved through electropolymerization of an appropriate monomer, as pyrrole substituted metalloporphyrins [4-6]. The so-obtained modified electrodes have great interest due to their electrocatalytic properties, namely in O₂ reduction [6-8], hydrogenation processes [5] and electrocarboxylation of alkyl halides [9]. Recently it has also been described the possibility of their use in electrochemical detection of neurotransmitters [10].

Polymeric films of pyrrole substituted metalloporphyrin complexes have been grown on different materials such as mercury, platinum, graphite and glassy carbon [10]. Metalloporphyrins containing a flexible link with the pyrrole group, in order to reduce steric hindrance and cross-linking effects in the resulting polymeric film, have also been reported [5].

In this paper the electropolymerization of metalloporphyrin monomers with two pyrrole groups presenting two flexible links – figure 1 – is studied. Beyond the possible advantages already mentioned, the electropolymerization can occur by any of the pyrrole groups, increasing the probability of polymer formation.

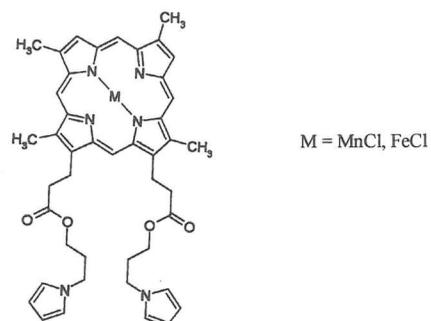


Fig.1 – Structure of two pyrrole groups substituted metalloporphyrin monomers used in the work.

The redox behaviour of the modified electrodes, in a monomer-free solution, was investigated, and the films electrocatalytic activity was tested for O₂ reduction as well as for oxygen and hydrogen evolution reactions.

Experimental

Electrochemical procedures

The electrochemical experiments were carried out in a conventional two compartments, three-electrode cell. The working electrodes were a Pt disk ($A=0.196\text{ cm}^2$) and a Pt microdisk ($A=7.85\times 10^{-7}\text{ cm}^2$); a Pt foil was used as counter electrode and the potentials are expressed against the saturated calomel electrode (SCE).

The electropolymerization on Pt disk was performed by continuous potential cycling at a sweep rate of 50 mV s^{-1} in solutions containing 0.5 mmol dm^{-3} of the monomer (manganese(III)-porphyrin pyrrol ester: Py-MnPor and iron(III)-porphyrin pyrrol ester: Py-FePor) and 0.1 mol dm^{-3} Bu₄NClO₄ in acetonitrile (Merck, uvasol spectroscopy grade), distilled under

argon atmosphere. The polymer synthesis (PPy-FePor) on the microelectrode was achieved potentiodynamically in a similar solution, at $v=500\text{ mV s}^{-1}$ with an anodic delay. Electrolyte solutions were routinely deoxygenated with argon (purity>99.9997%). Prior to the experiments, the working electrodes were mechanically polished with successively finer grades of alumina (down to $0.05\text{ }\mu\text{m}$), cleaned in an ultrasound bath, and rinsed with double distilled water and acetonitrile.

The films redox behaviour was studied by cyclic voltammetry in a monomer-free solution. The electrocatalytic ability of the modified electrodes was evaluated for the O₂ reduction by potential sweeping in an aqueous solution of 0.1 mol dm^{-3} NaCH₃COO, saturated with O₂. For the oxygen and hydrogen evolution reactions steady state polarisation curves in 0.1 mol dm^{-3} NaCH₃COO aqueous solutions were recorded.

Preparation of metalloporphyrin pyrrol esters

0.262 mmol of the metal(III)-methyl-ester [11] was dissolved in 15 cm^3 of THF. After addition of 15 cm^3 5M aqueous KOH, the reaction mixture was vigorously stirred under argon at 70°C for 22 hours. The colourless THF phase was rejected and 18 cm^3 5N HCl and 20 cm^3 *tert*-butylmethyl ether were carefully added to the aqueous phase. A precipitation resulted at the phase boundary. The aqueous phase was cooled to 0°C for one hour and filtered through a büchner funnel. Drying in high vacuum yielded the deuteroporphyrin dicarboxylic acid as a black solid, which was used in the next step without any further purification.

0.063 mmol metal (III) deuteroporphyrin dicarboxylic acid, 0.88 mmol 3-(1-pyrrolyl)-propane-1-ol and 0.176 mmol DMAP were dissolved in 20 cm^3 dry THF and stirred under argon at room temperature. After addition of 3 cm^3 triethylamine the mixture was cooled to 0°C , and 0.74 cm^3 of a 50% solution of *n*-propyl phosphonic acid anhydride in ethyl acetate was slowly added. The mixture was stirred for 30 min at 0°C then for 12 hours at room temperature. The mixture was taken up with 50 cm^3 of dichloromethane and extracted four times with 1N HCl and once with a solution of saturated sodium bicarbonate. The organic phase was filtered through cotton wool, evaporated and the residue chromatographed on aluminium oxide with dichloromethane/metanol (15+1). Crystallisation from chloroform/xylene results in pyrrol esters as metallic glittering dark solids with typical yields of 58%.

Results and discussion

The cyclic voltammograms in figure 2 present the electrochemical characterization and the electropolymerization of Py-MnPor at a Pt disk electrode. In the redox behaviour of Py-MnPor (figure 2A) the waves of the conversion processes of the couple Mn(III/II) approximately at -0.50

and -0.36 V (I_c and I_a) can be clearly seen. Besides the anodic peak at 1.0 V (III) followed by a current increase (IV) can be ascribed to the irreversible oxidation of pyrrole groups and the oxidation of porphyrin macrocycle, respectively. It must be noted that the electrochemical oxidation of the pyrrole groups occurs at potentials slightly inferior to those reported for other pyrrole-substituted metalloporphyrins [5, 12]. In the cathodic scanning a current increase develops at -1.2 V (II) corresponding to the macrocycle porphyrin ring reduction.

The electropolymerization was performed by continuous potential scanning over the range -1.6 to $+1.5$ V (figure 2B). The occurrence of two oxidation peaks at *ca.* 0.15 and 0.51 V increasing continuously in amplitude is indicative of the polymer phase growth. The anodic peak near 0.15 V shifts anodically as the film thickens, and it shall be assigned to the metal oxidation within the polymer matrix. The other anodic peak at about 0.51 V is probably due to the film oxidation. The current due to metal reduction shifts cathodically and merges in a cathodic process, which depicts the electroactivity of the polymer matrix.

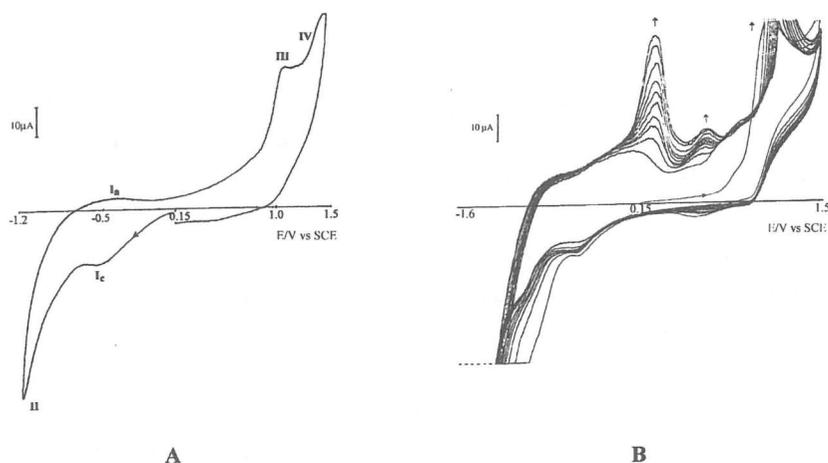


Fig. 2 - A - Cyclic voltammetry of Py-MnPor at Pt disk; $v=50$ mV s^{-1} ; $E_{in}=E_{oc}$.
B - Repeated potential scans of Py-MnPor at Pt disk; $v=50$ mV s^{-1} .

The redox behaviour and potentiodynamic polymerization of PPy-FePor at a Pt disk are displayed in figure 3. In the monomer electrochemical characterization (figure 3A), the peaks of Fe(III/II) redox couple appear reasonably defined, at about the potential values of -0.37 and -0.29 V (I_c and I_a), due to the cathodic and anodic processes, respectively. A cathodic process ascribed to the porphyrin macrocycle reduction takes place at -1.0 V (II). During the positive sweep two anodic peaks can be observed at 0.81 and 1.08 V (III and IV) that shall correspond to the

pyrrole groups and the porphyrin macrocycle oxidations, in this order. It should be noted the slightly lower potential value for pyrrole oxidation compared to the previous discussed monomer. In the reverse cathodic scan, it can be observed a wave at 0.5 V (V), likely due to the polymer reduction in some extent.

The electropolymerization has been performed by cyclic voltammetry over the potential window of -1.6 to $+1.5$ V (figure 3B) and presents the same main features as those discussed for the electrosynthesis of PPy-MnPor: two oxidation processes develop due to the polymer formation – a peak near 0.08 V and a band close to 0.94 V – both increasing their amplitudes as the film grows; the metal oxidation in the polymer matrix shifts anodically while the correspondent reduction process presents a cathodic shift.

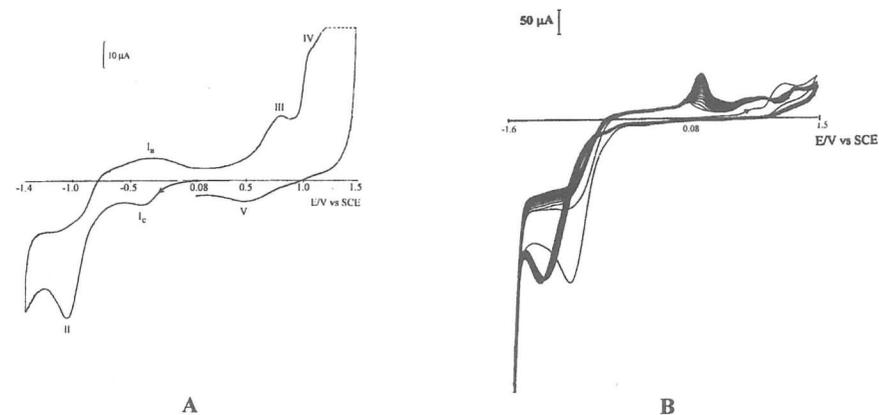


Fig. 3 - A - Cyclic voltammetry of Py-FePor at Pt disk; $v=50$ mV s^{-1} ; $E_{in}=E_{oc}$.
B - Continuous potential scanning of Py-FePor at Pt disk; $v=50$ mV s^{-1} .

The current intensities involved in the redox transformations of PPy-MnPor are lower than those observed for PPy-FePor, indicating a less electroactive conducting polymer when the Mn is the metal of the macrocycle. Both polymers, however, present low growth rates, which are an indication of their limited conductivities.

The redox behaviour of PPy-MnPor and PPy-FePor modified electrodes, in a monomer-free solution, is presented in figure 4.

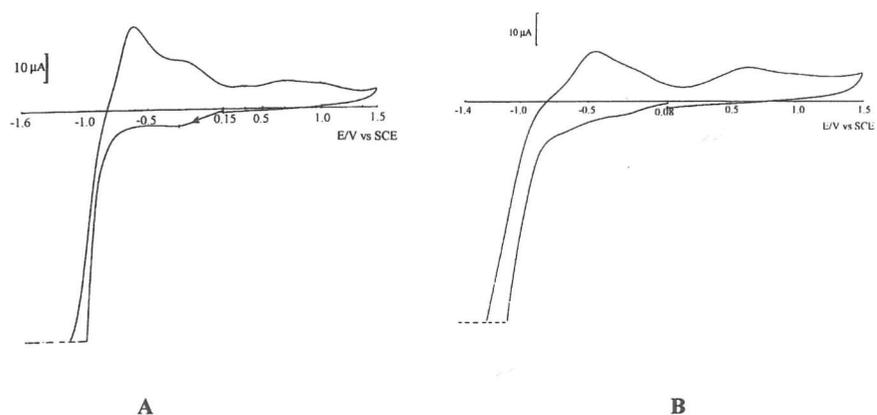


Fig. 4 – Cyclic voltammograms of (A) PPy-MnPor and (B) PPy-FePor modified electrodes, in a monomer free solution; 5 cycles of electropolymerization; $v=50 \text{ mV s}^{-1}$.

In the cyclic voltammogram of the PPy-MnPor film (5 cycles of growth) presented in figure 3A, the redox process of Mn(III/II) couple, at nearly the same potential values as for the monomer in solution, can be observed, which indicates that a polymer film was effectively formed on the electrode. However, a shoulder formation following the Mn oxidation peak can be seen. A large oxidation band is also noted where the polymer oxidation is likely to be merged. The PPy-FePor film (figure 3B) displays similar features: the metal redox processes recognised at the same potential range as for the Py-FePor, and a metal oxidation peak broadening. An anodic wave, presenting a peak at about 0.68 V, ascribed to the polymer oxidation, is also revealed.

Compared to the monomer redox behaviour, the metal anodic process widening, in both films, can be explained as a consequence of the oxidation that progressively comes to occur within the polymer matrix instead of over the platinum surface. Indeed, for a thicker polymer film (10 cycles of growth) – figure 5 – the metal anodic conversion shifts for more positive values, being the metal oxidation over the Pt electrode unnoticed. As the number of growth cycles increases, the porphyrin ring oxidation becomes clearly observed at $E = 1.2 \text{ V}$.

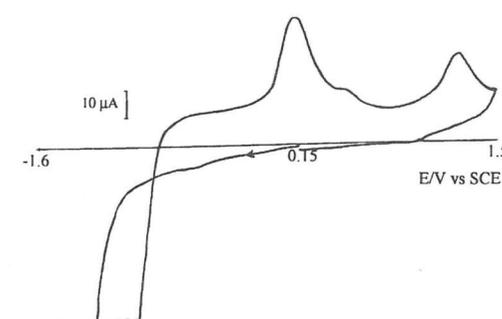


Fig. 5 – Cyclic voltammogram of PPy-MnPor modified electrode in a monomer free solution; 10 cycles of electropolymerization; $v=50 \text{ mV s}^{-1}$.

Once successfully achieved the polymer electrosynthesis on Pt disk, it was investigated the electropolymerization on microelectrodes. In figure 6 is presented the cyclic voltammograms of Py-FePor growth and its electrochemical characterization on a Pt microdisk. The film formation was performed potentiodynamically by a single cycle in the range -0.5 to +1.0 V, with a 40 s delay at the anodic limit.

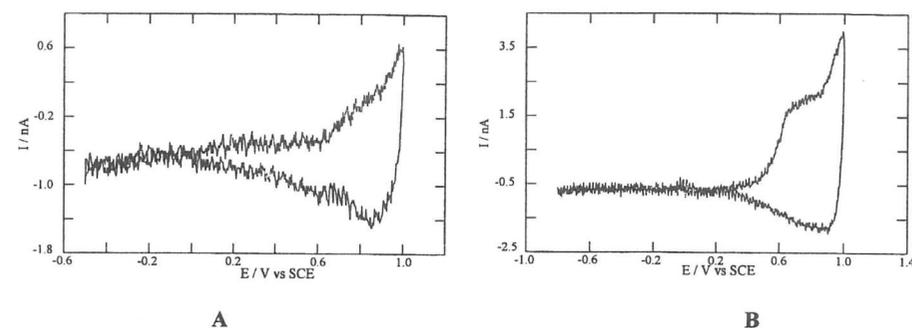


Fig. 6 – A – Electropolymerization of Py-FePor at Pt microdisk; 1 cycle; $v=500 \text{ mV s}^{-1}$; -0.5 V \leftrightarrow +1.0 V vs SCE; 40 s delay at the anodic limit.

B – Cyclic voltammogram of the modified microelectrode in a monomer free solution; $v=100 \text{ mV s}^{-1}$; -0.5 V \leftrightarrow +1.0 V vs SCE.

The pyrrole oxidation occurs *ca.* 0.8 V (figure 6A), which is in agreement with the values found for the Pt disk with the same monomer (figure 3A). The redox behaviour of the so-obtained modified microelectrode (figure 6B) displays a peak at $\approx 0.7 \text{ V}$ due to the polymer oxidation. In this

curve a cathodic broad wave, in which the polymer reduction is probably included, can be seen. An indication of the good electroactivity of the modified microelectrodes is given by the magnitude of the current intensities.

The electrocatalytic behaviour of the polymer modified Pt disk electrodes, with 50 cycles of electropolymerization, was tested for the oxygen and hydrogen evolution reactions (OER and HER, respectively) by means of steady state polarisation curves – figure 7. For comparison, the bare Pt behaviour under the same conditions is also shown. The best results for the OER were achieved for the Fe-containing polymer. The currents obtained for the PPy-MnPor, though smaller, are still superior to those of Pt (figure 7A). For the HER both modified electrodes have an inferior performance comparing to the Pt electrode, presenting the PPy-MnPor film, however, a response close to the achieved with the noble metal.

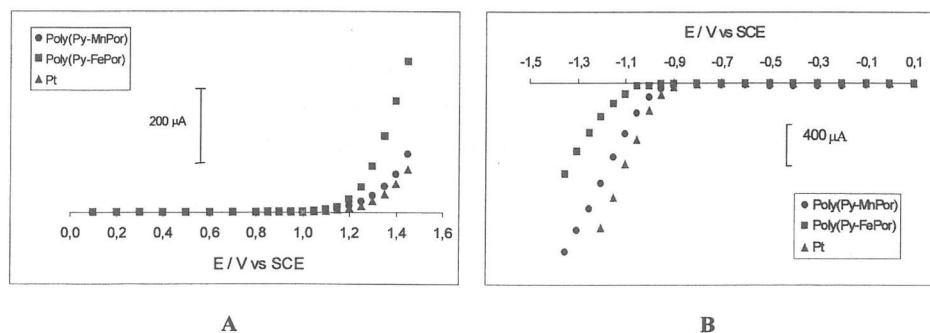


Fig. 7 – Steady state polarisation curves for bare Pt disk and modified electrodes in $0.1 \text{ mol dm}^{-3} \text{ NaCH}_3\text{COO}/\text{H}_2\text{O}$.
A – Oxygen evolution reaction, OER; B – Hydrogen evolution reaction, HER.

The films catalytic activity was evaluated for the O_2 reduction by cyclic voltammetry in the potential range +0.3 to -0.8 V – figure 8. Both polymer modified electrodes develop higher cathodic currents than Pt, giving the PPy-MnPor electrode the best results.

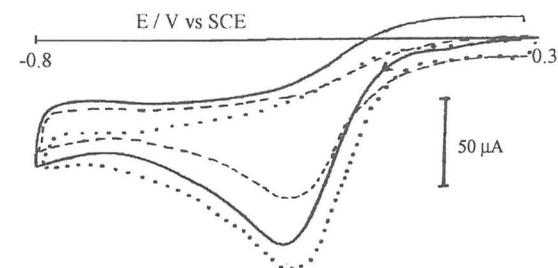


Fig. 8 – Cyclic voltammograms of polymer modified and bare Pt disk electrodes in $0.1 \text{ mol dm}^{-3} \text{ NaCH}_3\text{COO}/\text{H}_2\text{O}$ saturated with O_2 ; PPy-FePor: —; PPy-MnPor: •••••; bare Pt : - - - - - ; $\nu = 50 \text{ mV s}^{-1}$.

Conclusions

Under potentiodynamic control it is possible to obtain polymer modified electrodes by anodic oxidation of substituted metalloporphyrins with two pyrrole groups. It was observed in the Fe-containing metalloporphyrin monomer that the pyrrole oxidation takes place at lower potentials than in Py-MnPor, and the redox conversion of the porphyrin ring does not hinder the polymer growth on conventional size electrodes. The film growth rates are relatively low due to polymer poor conductivity. The electropolymerization of Py-FePor can also be achieved at Pt microelectrodes.

Polymer films electrosynthesized with 50 cycles at Pt disk electrodes reveal better catalytic activity for the O_2 reduction and the OER than bare Pt. For the HER the PPy-MnPor approaches the performance of the platinum, although inferior. Owing to their interesting electrocatalytic properties, studies of polymer films prepared from metalloporphyrins substituted with two pyrrole groups appear to be a promising field of research.

References

1. C. Armengaud, P. Moisy, F. Bedioui, J. Devynick and C. Bied-Charreton, *J. Electroanal. Chem.*, **277** (1990) 197.
2. B. Ballarin, S. Masiero, R. Seeber and D. Tonelli, *J. Electroanal. Chem.*, **449** (1998) 173.
3. J. Heinze, *Synthetic Metals*, **41-43** (1991) 2805.

4. T. Otten, T. Darbre, S. Cosnier, L. M. Abrantes, J. P. Correia and R. Keese, *Helvetica Chimica Acta*, **81** (1988) 1117.
5. F. Bédoui, M. Voisin, J. Devynck and C. Bied-Charreton, *J. Electroanal. Chem.*, **297** (1991) 257.
6. O. El Mouahid, C. Coutanceau, E. M. Belgsir, P. Crouigneau, J. M. Léger and C. Lamy, *J. Electroanal. Chem.*, **426** (1997) 117.
7. O. El Mouahid, A. Rakotondrainibe, P. Crouigneau, J. M. Léger, C. Lamy, *J. Electroanal. Chem.*, **455** (1998) 209.
8. S. Lj. Gojkovic, S. Gupta, R. F. Savinell, *J. Electroanal. Chem.*, **462** (1999) 63.
9. G. Zheng, M. Stradiotto, L. Li, *J. Electroanal. Chem.*, **453** (1998) 79.
10. B. Duong, R. Arechabaleta and N. J. Tao, *J. Electroanal. Chem.*, **447** (1998) 63.
11. S. Cosnier, A. Walter, F-P. Montforts, *J. Porphyrins Phtalocyanines*, **2** (1998) 39.
12. L. M. Abrantes, J. P. Correia, R. Fraga, T. Darbre, R. Keese, *Portugaliae Electrochim. Acta*, **16** (1998) 93.

Received, June 6, 1999
Revised, December 14, 1999

CONVERSION COATINGS FOR ALUMINIUM METAL MATRIX COMPOSITES

C.M. Rangel, T.I. Paiva

Instituto Nacional de Engenharia e Tecnologia Industrial
IMP/DM - Electroquímica de Materiais
Estrada do Paço do Lumiar, 22
1649 - 038 Lisboa, Portugal

Abstract

Al 6061 powder and F800 grade SiC particles (SiCp) were used as raw materials for the preparation of metal matrix composites (MMC), via a powder metallurgy route (PM), with 0% to 20 wt % of SiCp, the reinforcement material. Corrosion studies revealed a linear dependency of the pitting potential (E_p) with the logarithm of the concentration of NaCl with a slope of ~ -90 mV/decade, but there was no significant difference in the E_p values of the composite materials as a function of the concentration of reinforcement. Corrosion protection of PM Al SiC alloys was achieved by favouring the formation of a Ce/Mo-based conversion coating on the surface without the use of external polarisation. Pitting potentials were assessed in a 0.1 M NaCl solution after treatment. No increase in current density was evident for samples treated at pH 4.4 followed by post-treatment at 60°C for one hour, when polarised up to 0 mV (SCE). The role of Ce and Mo as inhibitors is analysed and discussed in terms of the protective character of the produced cerium-molybdenum conversion coatings.

Introduction

For aluminium metal matrix composites (MMC's), it is recognised that as a result of the incorporation of reinforcement, an increase in the corrosion of the matrix occurs with preferential attack at the reinforcement/ matrix interface. Pores, crevices, second phases and interfacial reaction products have a significant contribution to the corrosion susceptibility [1-15].

Since MMC's make attractive materials for a wide range of applications due to properties such as high strength and stiffness, lightness and low coefficient of thermal