

ELECTROCATALYTIC ACTIVITY FOR O₂ REDUCTION OF UNSUBSTITUTED AND PERCHLORINATED IRON PHTHALOCYANINES ADSORBED ON AMINO-TERMINATED MULTIWALLED CARBON NANOTUBES DEPOSITED ON GLASSY CARBON ELECTRODES

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ABSTRACT

Amino-functionalized multiwalled carbon nanotubes (MWCNT-NH₂) were modified with Fe phthalocyanine (FePc) and perchlorinated Fe phthalocyanine (16(Cl)FePc) and deposited on glassy carbon electrodes (GCE). The electrocatalytic activity of these hybrid electrodes was examined for the reduction of molecular oxygen in alkaline media (0.2 M NaOH) using stationary and rotating disk electrodes. Electrodes containing 16(Cl)FePc are more active than those containing FePc. Electrodes containing CNTs are more active than electrodes without CNTs but the higher activity can be attributed to a greater real surface area, compared CGEs and not necessarily to a catalytic effect.

Keywords: Amino-terminated carbon nanotubes, Fe phthalocyanines, O₂ reduction, catalytic activity.

INTRODUCTION

MN₄ macrocyclic metal complexes are well known as catalyst for many electrochemical reactions, specially the reduction of O₂ and their activity is directly related to their redox properties^{6,7}. On the other hand, carbon nanotubes (CNTs) are interesting support materials for the modification of substrates⁸. CNTs increase the area of the electrodes and when this is combined with MN₄ macrocyclic complexes substantial improvements in the reactivity^{7,9-13} are observed. The specific chemistry of the surface of CNTs can be tailored by changing the nature of surface groups that can be created on their surface by appropriate chemical treatment, adapting them for a desired application⁸⁻¹³. A non-chemical way of modification of CNTs is by simple adsorption of macrocyclic complexes on the external walls of the CNTs where the molecules stick to them by π - π interactions. If carbon nanotubes are modified with amino groups -NH₂, they can coordinate to the axial position of the MN₄ complex¹³. The reduction of O₂ (ORR) is the most studied reaction using MN₄ complexes as catalysts, with the aim of replacing expensive Pt containing materials in the cathode of fuel cells¹⁴. In aqueous media ORR can proceed via two main pathways: via the transfer of 2-e⁻ to give peroxide and via 4 e⁻ to give water. The 4-e⁻ reduction of O₂ involves the breaking of the O-O bond and delivers more energy than the two-e⁻ reduction¹⁵. In alkaline media, Fe phthalocyanines promote the 4 e⁻ reduction of O₂ almost entirely to water¹¹. In this manuscript we have examined the ORR reaction in alkaline media (0.2M NaOH) using as catalysts Fe phthalocyanine (FePc) and perchlorinated Fe phthalocyanine (16(Cl)FePc) and incorporated on amino-terminated multiwalled carbon nanotubes.

EXPERIMENTAL

Iron phthalocyanine (FePc) and iron hexadecachlorophthalocyanine 16(Cl)FePc were obtained from Aldrich. Amino-functionalized multiwalled carbon nanotubes (amCNT) were purchased from DropSens. N,N-dimethyl formamide (DMF) was obtained from Merck. High purity N₂ and O₂ gases were obtained from Indura. All other reagents were of analytical grade and were used as received.

Prior to electrode modification different amCNT/FePcs dispersions were prepared. The amCNT was dispersed in 1 mgmL⁻¹ of the complex with the aid of ultrasonic stirring for 30 min. The dispersion was then left at room temperature for 24 h. The amCNT/FePcs dispersions were filtered and thoroughly washed with DMF and ethanol. The solid was dried at 40 °C for 24 h. The working electrode was a glassy carbon electrode disk (GCE, Pine instruments) of 0.196 cm². The GCE was polished with 2400 and 4000 grit emery paper followed by ultrasonic treatment in purified water for 1 min. In order to modify the GCE 1 mg of the dry amCNT/FePcs was dispersed in 1 mL DMF and sonicated for 15 min. 5 μ L of the amCNT/FePcs dispersion was cast on the GCE surface and allowed to dry at 60 °C for 15 min. Electrochemical measurements were conducted on an Epsilon Voltammetric Analyzer. An ASR Pine rotator unit

was used for the rotating disk electrode experiments., The counter electrode was a platinum spiral wire (99.99%, Aldrich), and a Ag/AgCl electrode saturated with KCl was the reference electrode. Measurements were conducted at 25 °C. wit 0.2 M NaOH was prepared using deionized, bidistilled water. CV curves were obtained in N₂ saturated solutions and polarization curves with O₂ saturated solutions.

RESULTS AND DISCUSSION

The structure of phthalocyanine (FePc) and hexadecachloro Fe phthalocyanine 16(Cl)FePc. Figure 2A compares two cyclic voltammograms obtained in 0.2 M NaOH, one, illustrating the response of the bare glassy carbon electrode and then, after the incorporation of the CNT nanotubes (GCE/amCNT). There are no faradaic currents in the potential region examined. The only effect of the addition of the carbon nanotubes is the increase in the capacitive currents by a factor or almost two, which reflects the increase in the real surface area of the electrode interface by the presence of the nanotubes. The dashed lines in Figure 2A illustrate the cyclic voltammograms obtained after modifying the amCNTs with FePc (GCE/amCNT/FePc). There is an increase in the capacitive currents by the presence of FePc and three redox peak appear -0.68 -0.49 and -0.22 V respectively. These peaks are more clearly visible in Figure AB that compares the square wave voltammograms of the same electrodes, i.e. the GCE/amCNT/FePc and GCE/amCNT. It is clear in Figure 3B that the electrode having unmodified carbon nanotubes does not show any faradaic currents in the potential region examined. The redox peaks at -0.49 V and -0.22 V have been assigned to the Fe(II)/(I) and Fe(III)/(II) reversible processes respectively. The electrical charge under each peak is ca. 5.8 x 10⁻⁶ C. One can estimate the amount of molecules by dividing the charge by the Faraday constant that is 96,485. C mol⁻¹ and this gives a value of 0.6 x 10⁻¹⁰ mol or 3.06 x 10⁻¹⁰ mol cm⁻² using the geometric area of the electrode. It is important to point out that the electrode is not smooth so this gives a rough idea of the amount of molecules present on the carbon nanotubes. However, Figure 2A shows that the capacitive currents under the presence of the carbon nanotubes increase by a factor of two so, the real surface area of the electrode is at least twice the geometric area of 0.196 cm².

Figure 3 shows similar results, but obtained with 16(Cl)FePc. The redox potentials for both Fe(II)/(I) and Fe(III)/(II) reversible processes are shifted to more positive potentials for 16(Cl)FePc compared to FePc. For example the Fe(II)/(I) moves 0.21 V in the positive direction by the effect of the -Cl groups whereas the Fe(III)/(II) redox pair moves 0.13 V, so the Fe(II)/(I) redox process is more sensitive to the effect of the -Cl groups than the Fe(III)/(II) redox process. The intensity of the peaks in Figure 3B attributed to the presence of 16(Cl)FePc are more intense compared to those observed with unsubstituted FePc. It is possible that the more electron deficient Fe center in 16(Cl)FePc coordinates better to the amino groups present on the CNTs than FePc, so this could explain the higher coverages observed with 16(Cl)FePc compared to FePc. The electrical charge under each peak is ca. 20.0 x 10⁻⁶ C and this gives

a value of 2.07×10^{-10} mol or 10.56×10^{-10} mol cm^{-2} , again using the geometric area of the electrode. Compared to FePc, the surface coverage of 16(Cl)FePc is about 3.44 times higher.

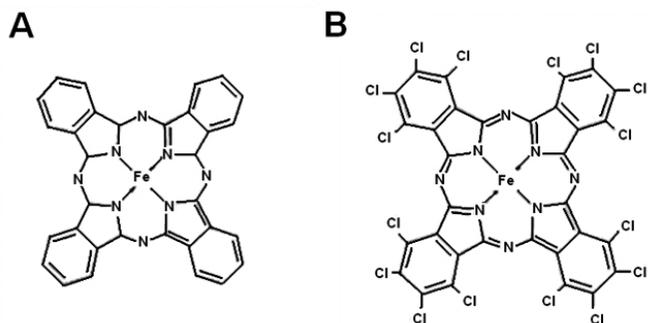


Figure 1. Structures of Fe phthalocyanines used in this study: (A) Unsubstituted Fe phthalocyanine (FePc) (B) Fe hexadecachloro phthalocyanine ($\text{FeCl}_{16}\text{Pc}$).

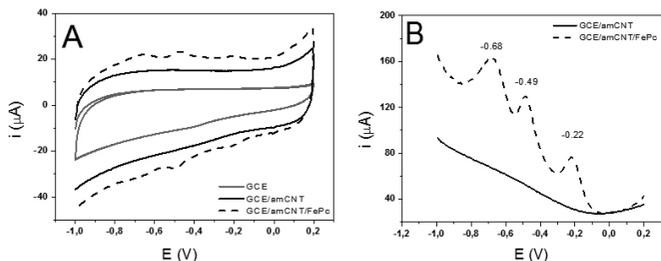


Figure 2. (A) Cyclic voltammograms of bare and modified GCE with amCNT and amCNT/FePc, in NaOH 0.2 M ($\nu = 100$ mV/s). (B) Square wave voltammetry of GCE/amCNT and GCE/amCNT/FePc. Parameters: amplitude 25 mV, frequency 15 Hz.

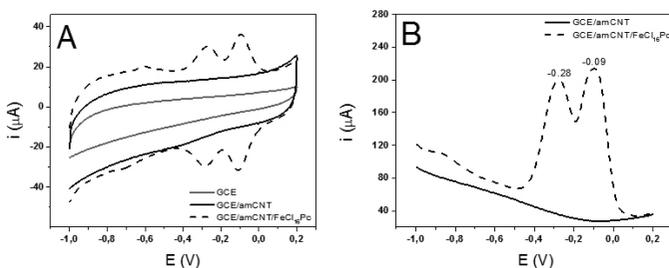


Figure 3. (A) Cyclic voltammograms of bare (grey) and modified GCE with amCNT and amCNT/ $\text{FeCl}_{16}\text{Pc}$, in NaOH 0.2 M ($\nu = 100$ mV/s). (B) Square wave voltammetry of GCE/amCNT and GCE/amCNT/ $\text{FeCl}_{16}\text{Pc}$. Parameters: amplitude 25 mV, frequency 15 Hz.

Figure 4 compares ORR rotating-disk polarization curves for 4 different types of electrodes namely: GCE, GCE/amCNT, GCE/amCNT/FePc and GCE/amCNT/16(Cl)FePc. The response of the bare GCE is known and essentially corresponds to the reduction of O_2 via $2e^-$ to give HO_2^- . The larger currents obtained with the GCE/amCNT electrode can be attributed almost entirely to an area effect, even though some catalytic effect of CNTs could be expected as the foot of the reduction wave is shifted by 0.1 V in the positive direction. After adding FePc to the CNTs the catalytic effect is evident since the currents increase by a factor of two or more and the foot of the wave is shifted in the positive direction by 0.3 V compared to bare GCE and by ca. 0.2 V compared to the GCE/amCNT electrode. The duplications of the diffusion limiting currents are attributed to a change in mechanism from a transfer of two electrons to a transfer of 4-electrons. It is known that FePc promotes the 4-electron reduction of O_2 in alkaline media¹. The presence of 16(Cl)FePc produces even larger currents and a shift in the foot of the wave in the positive direction. It is well established from previous work that electron-withdrawing substituents on the

phthalocyanine ligand favor the O_2 reduction process so this is not surprising. In fact the more positive the Fe(III)/(II) redox potential, the better for the catalytic activities of phthalocyanines¹⁷. The large currents of the GCE/amCNT/16(Cl)FePc electrode compared to GCE/amCNT/FePc can then be attributed to two factors namely, the more positive Fe(III)/(II) redox potential of 16(Cl)FePc compared to FePc and the higher surface coverage of 16(Cl)FePc on the CNTs compared to FePc. It is difficult to separate these two effects since it is possible that the 16(Cl)FePc molecules form multilayers on the CNTs and it is expected that only the outermost molecules will be accessible to O_2 . So the larger surface concentration of 16(Cl)FePc may not necessarily be reflected in a higher catalytic activity. We are currently investigating the possibility of preparing amCNTs with different surface concentrations of 16(Cl)FePc and see if this affects the catalytic currents for ORR.

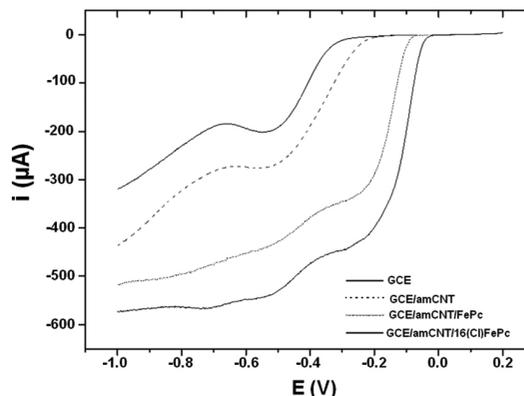


Figure 4. Polarization curves for ORR for a GCE (solid line) GCE/amCNT (dashed line), GCE/amCNT/FePc (dotted line) GCE/amCNT/16(Cl)FePc with a rotating disk electrode in NaOH 0.2 M O_2 saturated ($\nu = 5$ mVs⁻¹, $\omega = 1000$ rpm).

ACKNOWLEDGEMENTS

Work supported by Fondecyt Projects 1140199, Millennium Nucleus of Molecular Engineering for Catalysis and Biosensors RC120001 and Dicyt USACH P.C. thanks a postdoctoral position of the Millennium Nucleus.

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