Int. J. Electrochem. Sci., 7 **(2012)** 9738 - 9747

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Glassy Carbon Modified Electrode: Polymer and Supramolecular Assembly of Co(II)-[Tetra(O-Aminophenyl) Porphyrin] New Material for Electrocatalytic Assays

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Received: 20 July 2012 / *Accepted:* 6 September 2012 / *Published:* 1 October 2012

A glassy carbon electrode was electrochemically coated with a Co(II)[tetra(o-aminophenyl) porphyrin] (Co(II)TAPP) polymeric layer. The poly-Co(II)TAPP modified electrode presented Z 60.26 nm and RMS 4.73 nm values. In addition, a supramolecular assembly of Co(II)TAPP physisorbed on the polymeric film of the same porphyrin modified electrode was prepared (SMA-Co(II)TAPP/poly-Co(II)TAPP/GC). This supramolecular assembly presented Z 115.55 nm and RMS 37 nm values obtained by atomic force microscopy (AFM) surface characterization. The polymer film and the π-π staking supramolecular assemblies were characterized by atomic force microscopy, scanning electron microscopy (SEM) and cyclic voltammetry (CV). These modified electrodes were compared as electrocatalysts for oxygen reduction reaction at pH 6.8, phosphate buffer. Oxygen electrocatalytic reduction at the supramolecular modified electrode started at 0.20 V vs. Ag/AgCl, shifting the potential *ca*. 0.15 V with respect to the polymer modified electrode. On the other hand, under the same experimental conditions the catalytic current increased *ca*. 30 %. Carbon dioxide electrocatalytic reduction assays afforded similar results at both modified electrodes. Nevertheless, within the studied potential range for the reaction, hydrogen evolution takes place decreasing thus the carbon dioxide electrocatalytic reduction.

Keywords: Supramolecular; O2; Porphyrin; Cobalt; Modified Electrode

1. INTRODUCTION

There is an increasing need for simple, inexpensive, and rapid analytical procedures to measure the concentration of biological and environmental compounds. To this purpose electrochemical techniques have been widely studied and much interest has been focused on the use of carbon as cheap substrate. However, oxidation or reduction at carbon surface often proceed with very high activation overpotential, hence this substrate seldom lends itself to direct environmental analysis. In this regard, a field that opens up great possibilities is chemically modified electrodes (CMEs) [1-4]. These electrodes have been assembled by means of systematic surface modification with a variety of redox mediators. These compounds facilitate charge transfer between the electrode and electroactive species in solution at much lower potentials than would otherwise be possible. Occasionally the new monomeric and polymeric layer upon carbon electrodes are not morphologically characterized. Therefore the conclusions present some important omissions about surface features, *e.g.* are the monomeric or polymeric surface molecule films or particles? or are these surfaces mono- or multilayered coated? These questions are very important in order to explain the behaviour of these molecules as mediators in electrocatalytic processes [5].

Amidst the various mediators used as electrode modifier, porphyrin macrocycles have attracted considerable attention owing to their high stability and redox potential that can be modified by changing the metal coordinated to the macrocycle [6-14].

In the current work, a (Co(II)TAPP) polymeric layer coated glassy carbon electrode, obtained by oxidative electropolymerization, is reported. Upon this a polymer layer of supramolecular Co(II)TAPP (SMA-Co(II)TAPP) film formed by π-π interactions was obtained. Both electrodes were compared as electrocatalyst for oxygen reduction.

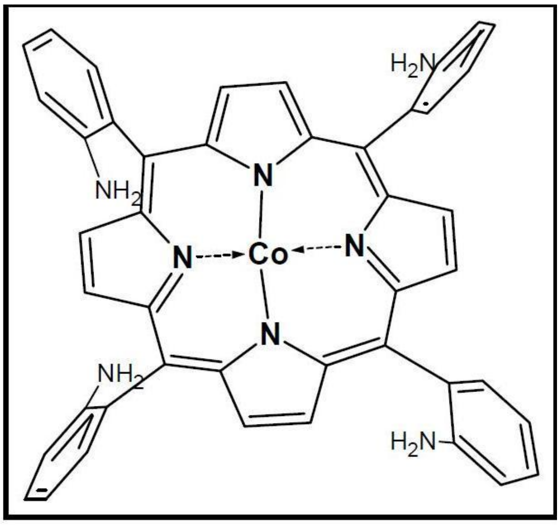

Figure 1. Co(II)-[tetra(2-aminophenyl)porphyrin] molecular structure

The supramolecular electrode proved to be a better catalyst than the polymeric one. On the other hand, a series of blank electrodes were compared, namely a monomeric modified electrode and composites of monomeric and polymeric electrodes, in order to corroborate the catalytic supramolecular nature of the SMA-Co(II)TAPP modified electrode.

Figure 1 depicts the molecular structure of Co(II)-[tetra(2-aminophenyl)porphyrin] molecule used in the present study. Blank and polymer modified electrodes as well as assembled supramolecular electrodes were characterized by SEM, AFM, and CV techniques. Finally, theses modified electrodes were attempted as electrocatalyst in oxygen reduction reaction (ORR) and carbon dioxide reduction and subsequently compared with bare glassy carbon.

2. EXPERIMENTAL

2.1. Characterization techniques

SEM measurements were performed on a JEOL JSM-6300 SCANNING ELECTRON MICROSCOPE.

AFM analysis was accomplished on a NANOSCOPE III A (Digital Instruments Inc. Santa Barbara CA). All images were collected in tapping mode to avoid film damage. All electrochemical measurements were carried out in a conventional three-compartment electrochemical cell. The glassy carbon modified electrode and a Pt foil were respectively the working and counter electrode. All quoted potentials are referred to a saturated Ag/AgCl,KCl,(sat'd) electrode. Voltammetric instrumentation was a Voltalab PGZ 100, Radiometer Potentiostat.

2.2. Modified electrodes preparation

1. Monomer modified electrode, (M) or Co(II)TAPP/GC, preparation. One drop of 1 mM porphyrin in DMF solution was deposited on the glassy carbon surface and then dried with air.
2. Polymer modified electrode, (P) or (poly-Co(II)TAPP/GC), preparation utilizing electropolymerization.

The oxidative electropolymerization of Co(II)TAPP was performed on the glassy carbon electrode by successive potential scans between − 0.9 and 1.20 V at 150 mVs^{-1} in a solution containing 1 mM of porphyrin in DMF and 0.1 M tetrabuthylamonioum perchlorate. At the positive limit, oxidation of the amino groups sets out and the film starts growing producing a current increase as the number of cycles increases (Fig. 2A). After 50 sweeps the electrode was removed from the electrochemical cell, washed with distilled water and dried. The modified electrode was characterized by cyclic voltammetry in a complex-free solution (Fig. 2B).

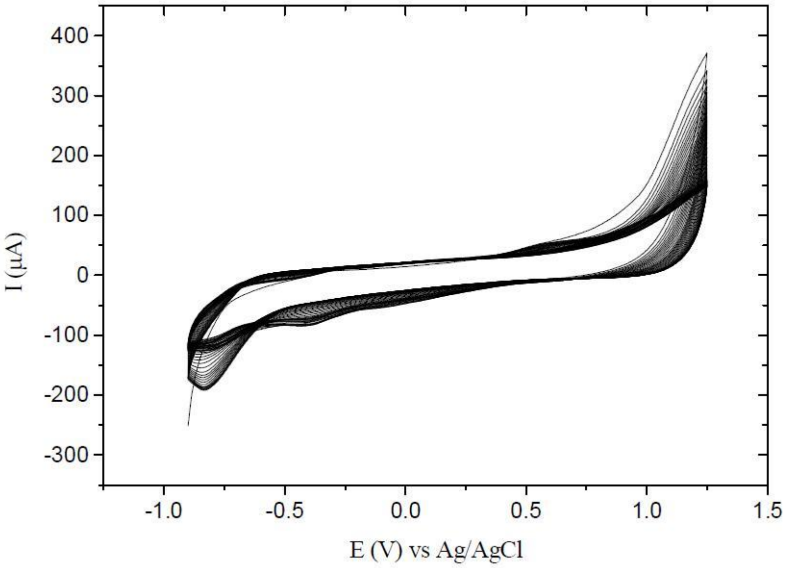

Figure 2A. Co(II)TAPP electropolymerization at glassy carbon. 50 cycles at 150 mV s^{-1}.

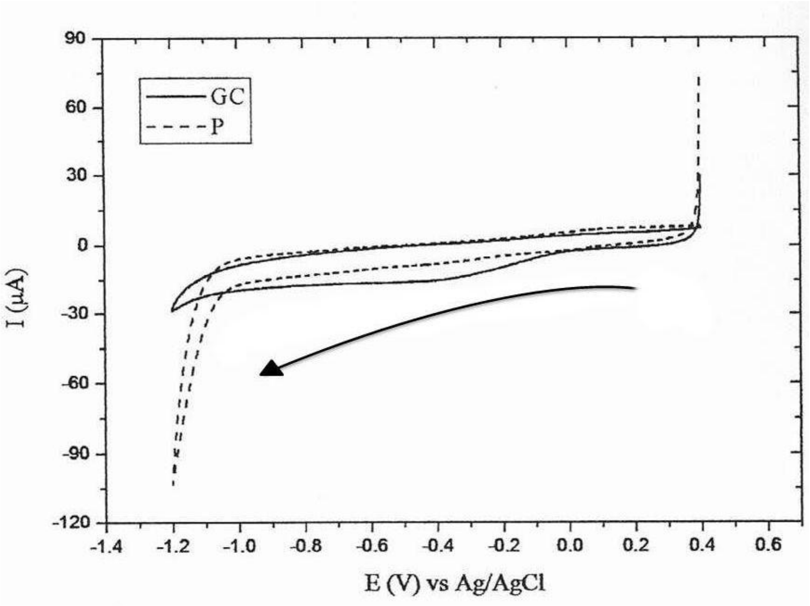

Figure 2B. Voltammetric response of a poly-Co(II)TAPP/GC modified electrode compared with a bare glassy carbon electrode at 10 mV s^{-1}. pH 6.8 (PBS).

2.3. Supramolecular electrode, (P+R) or (SMA-Co(II)TAPP/polyCo(II)TAPP/GC), preparation.

The poly-Co(II)TAPP/GC electrode was boiled in a 1 mM Co(II)TAPP/DMF solution for 90 minutes. The obtained supramolecular modified electrode was rinsed with distilled water and dried at room temperature. A scheme of the supramolecular electrode is shown in Fig 3A. The SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrode was characterized by cyclic voltammetry in a complex-free solution under nitrogen atmosphere (Fig. 3B). The modified electrode was stable at room temperature throughout the experiment.

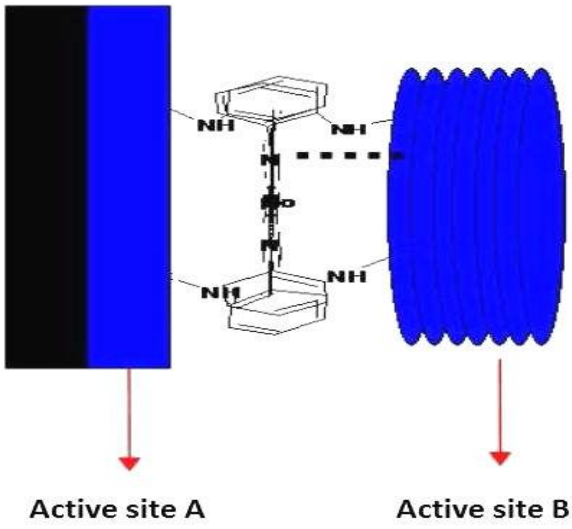

Figure 3A. Scheme of the supramolecular SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrode.

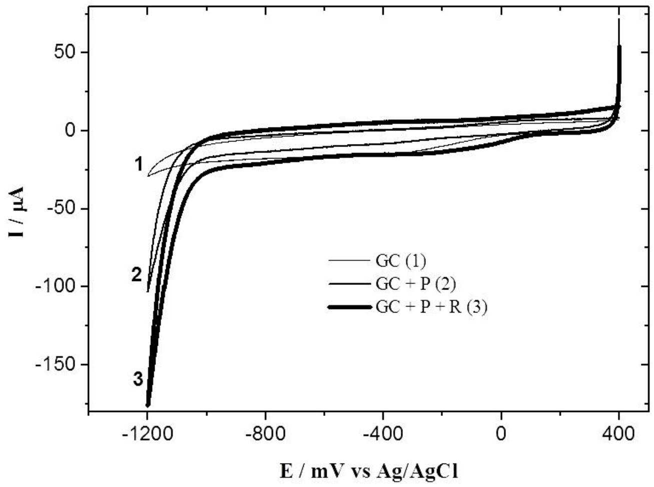

Figure 3B. Voltammetric response of 1) bare glassy carbon, 2) SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrode. pH 6.8 (PBS) and □□=10 mV s^{-1}

2.4. Refluxed porphyrin modified electrode (R) preparation

The GC electrode was boiled in a 1 mM Co(II)TAPP/DMF solution for 90 minutes. The obtained modified electrode was rinsed with distilled water and dried at room temperature.

2.5. Monomer + polymer modified electrode (M+P) preparation

One drop of 1 mM porphyrin in DMF solution was deposited on the (P) or (poly-Co(II)TAPP/GC) surface and then dried with air.

3. RESULTS AND DISCUSSION

3.1. Modified electrodes morphological characterization

3.1.1. SEM

Figure 4 shows the surface morphology of the various modified electrodes prepared in the current study. The SEM image of smooth and homogeneous surface corresponds to the unmodified glassy carbon electrode (GC in the figure). M micrograph corresponds to monomer species (physisorbed by the dry-drop method) on glassy carbon. The surface is rough with some particles of different forms and sizes, and is not fully covered. P image corresponds to the poly-(Co(II)TAPP/GC) electrode and exhibits a homogeneous and compact layer with small particles and full coverage. The P+M image corresponds to monomer species absorbed on the polymeric film. This surface is similar to M image but here the polymer base in not 100% coated. On the other hand, the P+R image of SMA-Co(II)TAPP/poly-(Co(II)TAPP/GC electrode exhibits a homogeneous and compact layer with small- and medium-size particles. This micrograph is different from the P+M image demonstrating that the deposit of porphyrin species during the preparation of the supramolecular assembly modifies the surface as compared with the simple modification due to a porphyrin-containing drop of solution on the previously prepared polymer (P+M modified electrode). Moreover, thin particles can be seen corresponding to DMF solvent used in the preparation of the SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrode showed in R image. Also, the R electrode does not coincide with the P+R electrode. This is the first evidence that the new material corresponds to the P+R electrode.

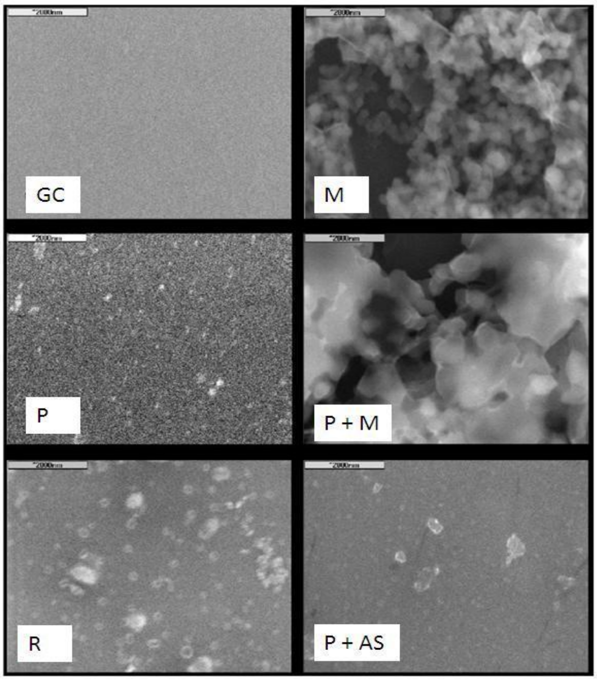

Figure 4. SEM micrographs of GC) glassy carbon, M) monomeric species of Co(II)TAPP absorbed on glassy carbon P) poly-Co(II)TAPP/GC, P+M) monomeric species of Co(II)TAPP absorbed on poly-Co(II)TAPP/GC, R) refluxed monomeric species of Co(II)TAPP adsorbed on glassy carbon and P+R) SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrodes.

3.1.2. AFM surface characterization

Bare glassy carbon showed a homogeneous surface with fine lines corresponding to mechanical alumina polishing (see Fig. 5, GC image). Besides, the poly-o-Co(II)TAPP/GC electrode exhibits a surface with small grains, but in some areas these grains are larger, in agreement with preferential electropolymerization, but the glassy carbon display total coverage (Fig. 5, P micrograph). The M and P+M images exhibit irregular coverage with channels and higher agglomeration on the surface. Therefore these procedures (deposition of monomer on different surfaces) make the electrode surface to become irregular and not fully coated. The R and P+R images of the SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrode showed different AFM images as compared to the poly-Co(II)TAPP/GC electrode. This revealed that Co(II)TAPP molecules deposited on a poly-Co(II)TAPP/GC electrode by π-π supramolecular interaction (P+R electrode) afford a compact and homogeneous surface.

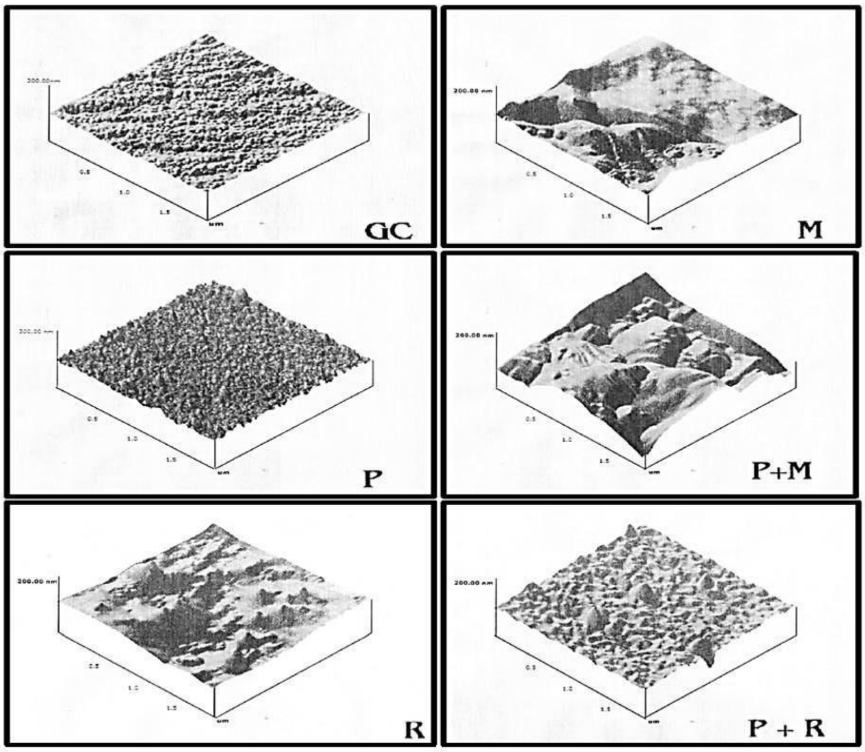

Figure 5. AFM images of GC) glassy carbon, M) monomeric species of Co(II)TAPP absorbed on glassy carbon P) poly-Co(II)TAPP/GC, P+M) monomeric species of Co(II)TAPP absorbed on poly-Co(II)TAPP/GC, R) refluxed monomeric species of Co(II)TAPP adsorbed on glassy carbon, and P+R) SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrodes.

SMR and Z parameters obtained from AFM images of bare glassy carbon (GC), poly-Co(II)TAPP/GC, and SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrodes are listed in Table 1.

Table 1. SMR and Z parameters of glassy carbon poly-Co(II)TAPP/GC and SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrodes. Data calculated from AFM experiments.

Electrode	Z range (nm)	SMR (nm)
Glassy Carbon	16.865	2.011
Poly-Co(II)TAPP/GC	60.258	4.725
SMA-Co(II)TAPP/poly-Co(II)TAPP/GC	115.55	6.374

The supramolecular electrode displayed the largest Z and SMR values, consistent with the formation of a new supramolecular assembly by π-π staking of Co(II)TAPP on poly-Co(II)TAPP/GC. Consequently, a good performance of this modified electrode as redox mediator in electrocatalytic processes is expected.

3.2. Electrocatalytic assays

Figure 6 shows polarization curves of oxygen reduction at the supramolecular electrode, poly-Co(II)TAPP modified electrode and bare glassy carbon. M-GC and P-M electrodes were unstable and no electrocatalytic tests were performed.

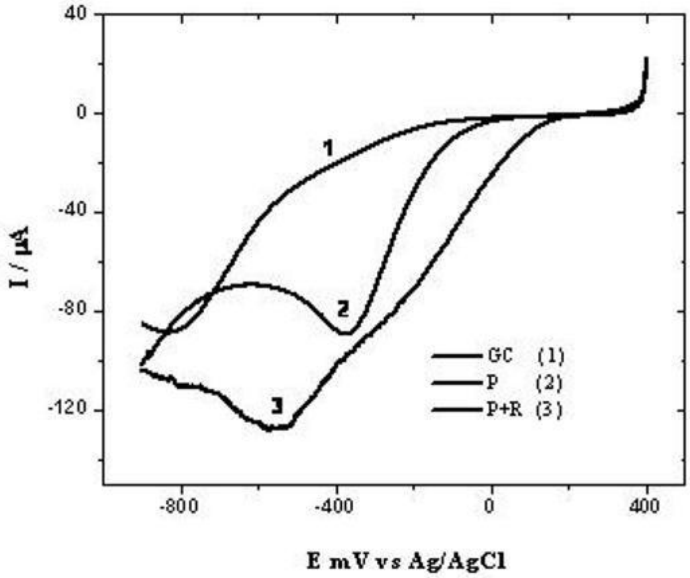

Figure 6. Cyclic voltammetry study of 1) glassy carbon 2) poly-Co(II)TAPP/GC and 3) SMA-Co(II)TAPP/poly-Co(II)TAPP/GC electrodes in oxygen saturated solution. pH 6.8 (PBS) and ν□=10 mV s^{-1}.

These results indicated that the supramolecular electrode presented the best performance as electrocatalyst shifting the oxygen reduction potential about 0.4 V with respect to bare glassy carbon and 0.15 V with respect to poly-Co(II)TAPP electrodes. At the poly-Co(II)TAPP electrode the ORR starts at +0.05 V with a current peak at – 0.40 V. The ORR at the supramolecular electrode SMA-Co(II)TAPP/poly-Co(II)TAPP/GC starts at 0.20V and presented two peaks at – 0.20V and – 0.55 V for the ORR electrocatalytic process. R. W. Murray et al. [8] observed a similar behaviour for poly Co(III) TAPPCl in 0.5 M H_2SO_4. However, in this work the supramolecular electrode showed this behaviour for ORR in PBS at pH 6.8. This fact is very important for practical applications as cathode in fuel cells configuration. The substantial enhancement of the voltammetric current is consistent with the greater number of active sites in the supramolecular electrode. The two catalytic waves observed for the supramolecular assembly were associated to oxygen reduction taking place at different sites of the supramolecular porous film.

Comparison of the polarization curves for carbon dioxide electrocatalytic reduction using glassy carbon, poly-Co(II)TAPP/GC, and supramolecular electrode (SMA-Co(II)TAPP(II)/poly-Co(II)TAPP/GC) (Figure 7) indicates that neither the supramolecular SMA-Co(II)TAPP/poly-Co(II)TAPP/GC nor poly-Co(II)TAPP electrodes can catalyses carbon dioxide electroreduction. The current discharge showed in Fig. 7 corresponds to the electroreduction of hydrogen.

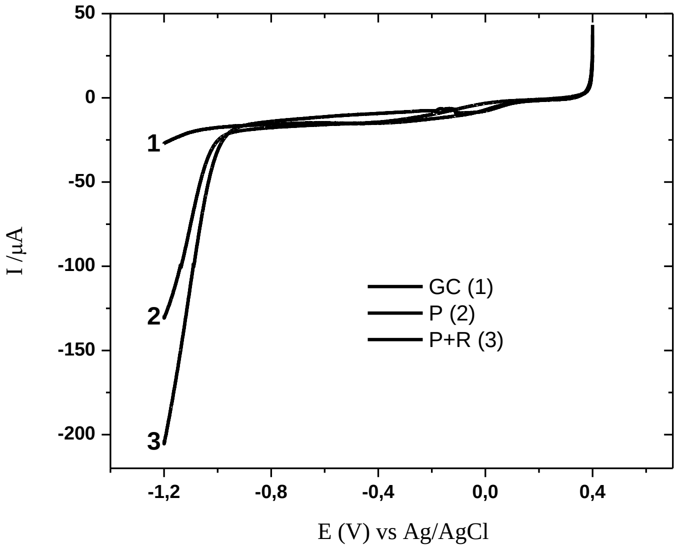

Figure 7. Voltammetric curves for carbon dioxide reduction using :1) Glassy carbon 2) poly-Co(II)TAPP/GC, and 3) SMA-Co(II)TAPP/poly-Co(II)TAPP/GC modified electrodes(PBS pH=6.8). From +0.4 to -1.2V vs Ag/AgCl, at 10 mV/s scan rate.

4. CONCLUSIONS

A novel and simple method for assembling a supramolecular device by π-π staking of Co(II)[tetra-(o-aminophenyl)porphyrin] on glassy carbon modified with a polymeric film of the same porphyrin was developed. SEM and AFM results corroborated that the electrochemically prepared poly-o-APPCo(II) was a stable multilayer polymeric film on glassy carbon as substrate. Besides, the supramolecular assembly formed by π-π staking of the same porphyrin on a polymeric modified electrode proved to be a stable porous film.

The electrode modified with SMA-Co(II)TAPP/ poly-Co(II)TAPP/CG was better suited as catalyst than poly-Co(II)TAPP/GC and bare glassy carbon for ORR processes in aqueous solution at pH 6.8 (PBS).

ACKNOWLEDGMENTS
Financial support from, Fondecyt projects 1120071 and 1120049, project AECI (PCI-A/025043/09 , PCI- A/030500/10) and Dicyt-USACH are gratefully acknowledged. J.V. thanks support through Fondecyt 3100066 project. A.H-C thanks support through CTQ2008-06017/BQU and ACIISI ID20100152 projects

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