Unusual behaviour of perfluorinated cobalt phthalocyanine compared to unsubstituted cobalt phthalocyanine for the electrocatalytic oxidation of hydrazine. Effect of the surface concentration of the catalyst on a graphite surface

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Abstract: It was found that CoPc and 16(F)CoPc when adsorbed on a graphite electrode exhibited voltammograms in alkaline solution (0.2 M NaOH) that show the typical redox peaks attributable to the reversible Co(II)/(I) redox process. The peak potential for CoPc was independent of the surface concentration of the catalyst. In contrast, for 16(F)CoPc, the Co(II)/(I) redox process shifted to more negative potentials with increasing surface concentration of the catalyst. In a volcano correlation of log $(i/\Gamma)_E$ (activity per active site) *versus* the Co(II)/(I) formal potential of the catalyst (using several CoN4 chelates), CoPc appeared in the ascending portion (the activity increased with the Co (II)/(I) redox potential), whereas 16(F)CoPc appeared in the region where the activity decreases with the redox potential. In a plot of log $(i/\Gamma)_E$ *versus* the Co(II)/(I) formal potential of 16(F)CoPc, the declining portion of the volcano was reproduced for one single complex. Thus, 16(F)CoPc at different surface concentrations behaved as Co complexes, having different redox potential in the declining portion of the volcano plot, when the activity is normalized to the surface concentration. This was not observed for CoPc.

Keywords: cobalt phthalocyanine; cobalt-hexadecafluoro-phthalocyanine; surface concentration-dependent redox potential; hydrazine oxidation; electrocatalysis.

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INTRODUCTION

Hydrazine (N_2H_4) is a powerful reducing agent, which can be employed in the anode in fuel cells.[1–5] Hydrazine and its derivatives are frequently found in the environment and are used as essential raw materials and/or intermediates in some industrial preparations, such as in the production of pesticides, but they are also suspected of being carcinogenic and mutagenic.[6] However, in spite of its high reactivity, hydrazine presents a rather large oxidization overpotential on most electrode materials.[7] One approach for minimizing the overpotential of the reaction is the use of chemically modified electrodes (CMEs), which contain specifically selected redox mediators immobilized on conventional materials, such as glassy carbon and graphite. Metallophthalocyanine-modified electrodes have been extensively studied due to their electrocatalytic activity for numerous reactions.[8–20] In the past years, various chemically modified electrodes have been prepared and employed in the determination of hydrazine, including cobalt phthalocyanine-modified carbon paste electrodes, ruthenium cyanide film-coated electrodes, cobalt tetraphenylporphyrin-modified electrodes, an inorganic mixed-valent Prussian Blue film-coated electrode, an oxymanganese film-modified electrode and an adsorbed vitamin B_{12} electrode.[21–38] However, in spite of the great variety of modified electrode systems studied for the oxidation of hydrazine, there are only a few systematic studies on the parameters that control the activity of these electrodes,[29–32,38,39] including theoretical calculations.[40–43] In particular, one reactivity parameter that has been studied in some detail is the effect of M(II)/(I) or M(III)/(II) formal potential of MN4 catalysts on their electrocatalytic activity, with the employed formal potential depending on the reaction.[22–24,29–32,38,39] For example, when comparing catalytic activities as currents at a constant potential, normalized to the surface concentration of the catalyst, Γ (mol cm^{-2}), nonlinear correlations of log $(i/\Gamma)_E$ *vs*. $E^{\circ\prime}$ (the formal potential of the M(II)/(I) catalyst) were obtained,[29–32,38,39] and this was not only true for hydrazine oxidation, but for other reactions as well.[11,16,17,18,32] The correlations have the shape of a volcano, indicating that the formal potential of the catalysts need to be "tuned" to a given value for the highest catalytic activity to be obtained. For hydrazine oxidation, this was corroborated for Fe and Co MN4 macrocyclic complexes.[29–32,38,39] For typical volcano correlations, the activity is plotted *versus* a parameter that accounts for the degree of interaction of the reacting molecule with the active site. Thus, the "ascending" portion of the volcano corresponds to catalysts where the binding energy of the reacting molecule is weak but increases gradually until the optimal condition (not too weak, not too strong according to the Sabatier principle) is achieved. For gradually stronger binding energies, the catalytic activity decreases since the active sites become gradually blocked by adsorbed intermediates. Hence, it is of interest to compare catalysts that are in different branches of the volcano correlation. As shown in previous studies for

the oxidation of hydrazine, Co phthalocyanine (CoPc) is located on the ascending portion of the volcano correlation (see Fig. 1), whereas perfluorinated Co phthalocyanine 16(F)CoPc, which exhibits the most positive Co(II)/(I) formal potential of the studied phthalocyanines, appears on the extreme side of the "falling region" of the volcano correlation.[29,32,39] In this work, it was found that the redox properties of 16(F)CoPc were dependent on the surface concentration of the catalysts and this affects the intrinsic activity of this complex. For this reason, there are two data points for 16(F)CoPc in Fig. 1 and reported in different publications.[29,32]
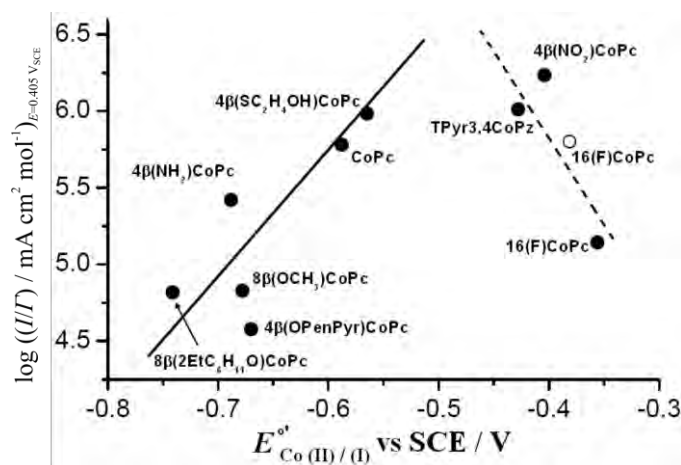

Fig. 1. Volcano correlation for the oxidation of hydrazine in 0.05 M $[N_2H_4]$ N_2 saturated 0.1 M NaOH solutions (data $\bullet$[32] and data $\circ$[29]). Reproduced by permission of the Electrochemical Society.

EXPERIMENTAL

Cobalt phthalocyanine (CoPc) and cobalt-hexadecafluoro-phthalocyanine (16(F)CoPc) were obtained from Aldrich and used as provided. All other products were of analytical reagent grade and used as received. The working electrode was an ordinary pyrolytic graphite (OPG) disk electrode from Pine Instruments (USA) with a geometrical area of 0.44 cm^2. The electrodes were polished before each experiment with 800 and 2400 grit emery paper followed by an extensive ultrasonic rinsing with ultra-pure Milli-Q water to remove solid particles. The electrochemical experiments were performed with a conventional three-electrode cell and a BAS-100 potentiostat (USA) or Autolab PGST30 potentiostat/galvanostat (The Netherlands). A spiral platinum wire of 2 cm^2 geometric area was used as the counter electrode and a saturated calomel electrode, SCE, as the reference electrode. Electrolytic solutions were routinely deoxygenated with pure nitrogen. All the potential values are given *versus* the saturated calomel electrode SCE. The electrolyte was aqueous 0.2 M NaOH, solution prepared in double-distilled water and deaerated with ultra pure N_2. CoPc and 16(F) $CoF_{16}Pc$ were adsorbed onto the OPG electrode by, respectively, placing a drop of 0.1 mM solution of the CoPc and 16(F)CoPc complexes in dimethylformamide (DMF) for various time intervals,

ranging from 10 to 1200 s on the graphite surface. After this procedure, the electrodes were rinsed with DMF, ethanol and double-distilled water, in order to remove any excess of the metal complexes. This procedure avoids the presence of microcrystals on the graphite surface, so the electrochemical response of the electrode can be attributed solely to molecules that are adsorbed on the electrode. Adsorption of all complexes was verified by the appearance of typical current peaks in the cyclic voltammograms of the modified electrodes.[21-25,29,31,32,38,39] Hydrazine was obtained from Riedel-de Haën and used as provided. NaOH was A.R. grade from Merck.

RESULTS AND DISCUSSION

The structure of Co phthalocyanine and perfluorinated Co phthalocyanine and also the Fukui profiles, obtained from theoretical calculations[44] to graphically illustrate the effect of electron-withdrawing groups located on the ligand on the charge distribution on the Co central metal, are illustrated in Fig. 2. The blue colour indicates high electron density and the red colour indicates low electron density on the Co centre. As a result of substitution of H atoms by F in the Co phthalocyanine ligand, the electron-withdrawing substituents cause a large increase in the ionization potential (IP) of 16(F)CoPc and a lowering of the energy of the frontier orbitals,[40,45] compared to CoPc, which could be written as 16(H)PcCo, to indicate that the –H groups have been replaced by –F groups on the phthalocyanine ligand. This effect causes the Co(II)/(I) formal potential to shift to more positive values, as it becomes more difficult to oxidize the Co(II) centre in 16(F)CoPc compared to CoPc. This is clearly illustrated in Fig. 3, which shows the cyclic voltammograms obtained with an OPG electrode modified with adsorbed
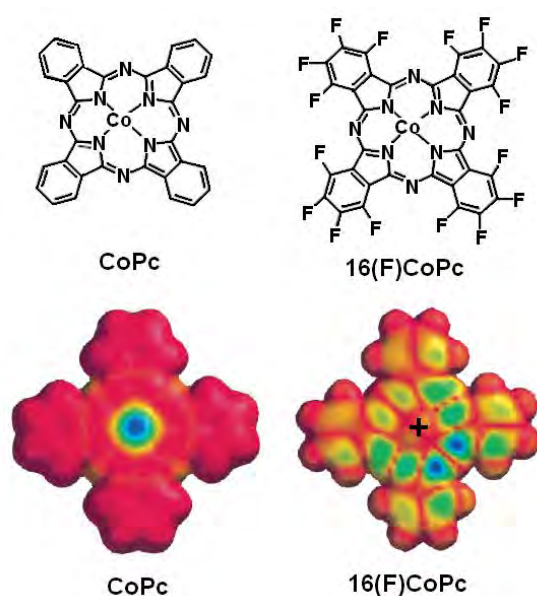

Fig. 2. Structures of CoPc (that can be written as 16(H)CoPc) and 16(F)CoPc) and the calculated Fukui profiles that illustrate the electron donating effect of the fluoro groups located on the ligand that shift electron density from the Co centre to the macrocycle ligand.[44] Reproduced by permission of the American Chemical Society.

layers of the examined cobalt phthalocyanines in a 0.2 M NaOH oxygen-free solution. CoPc exhibited a reversible peak at –0.59 V assigned to the reversible Co(II)/Co(I) couple.[9,21–24,29,39] For 16(F)CoPc, this process is shifted to more positive potentials (–0.33 V) by the effect of the electron-withdrawing groups, as discussed above. Indeed, it was shown in previous studies[9,11,17,18,21–24] that it is possible to "tune" the Co(II)/(I) formal potential of the catalyst by preparing CoPc phthalocyanines with groups on the ligand with different electron-withdrawing properties. Furthermore, a plot of Co(II)/(I) formal potential *versus* the sum of the Hammett parameters of the groups located on the ligand gave a linear correlation; hence, the redox properties of these complexes can be "tailored" to desired values, as discussed by Lever,[9] depending of the reaction and this is clearly demonstrated in the volcano correlation of Fig. 1.
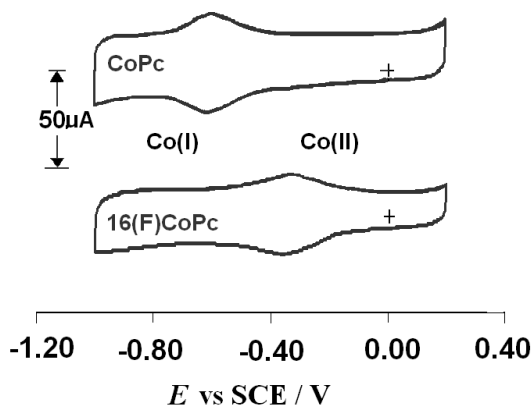

Fig. 3. Cyclic voltammograms of CoPc and 16(F)CoPc pre-adsorbed on an ordinary pyrolytic graphite electrode. Scan rate 0.1 V s^{-1}, N_2 saturated 0.2 M NaOH solution.

The surface concentration of the catalysts in Fig. 3 corresponded to the conditions where the OPG surface was saturated with phthalocyanine molecules, and this could be controlled by using different contact times between the solution of the complexes and the graphite surface during the modification procedure. For example, from the charge under the peaks in Fig. 3, it can be calculated that CoPc saturation was achieved at a surface concentration of 10×10^{-10} mol cm^{-2}, whereas for CoPc, surface saturation corresponded to a surface concentration of 6.8×10^{-10} mol cm^{-2}. This is not surprising since the size of the 16(F)CoPc molecule is larger than that of CoPc; hence, a lower surface concentration is expected for this particular complex, as 16(F)CoPc takes more room on the graphite than CoPc, assuming that they adsorb flat on the electrode surface.[46] The gradual increase in the surface concentration with modification time is illustrated in Fig. 4. For both complexes, the surface concentration exhibits an asymptotic behaviour with modification time, illustrating that the surface becomes saturated with the complexes after 800 s.
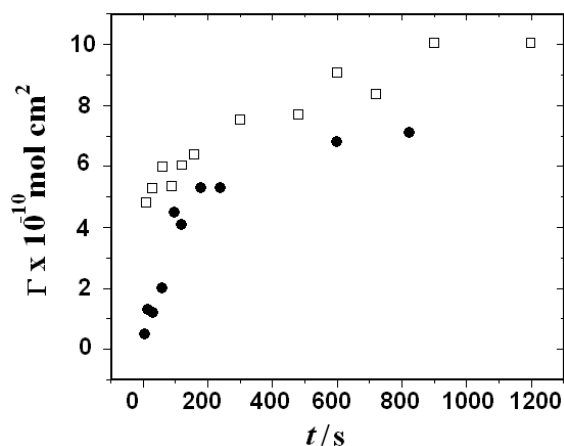
Fig. 4. Variation of the surface concentration for (□) CoPc and (●) 16(F)CoPc as a function of immersion time in 10^{-4} M solutions of the complexes at 20 °C, in the presence of air.

The cyclic voltammograms of the OPG electrode coated with different surface concentrations of 16(F)CoPc are shown in Fig. 5. The surface concentrations were estimated from the different electrical charges under the current peak, subtracting the capacitive currents. One interesting feature about the data in Fig. 5 is that, in contrast to that observed with CoPc, the peak potential shifts to more negative values with increasing concentration of the perfluorinated phthalocya-
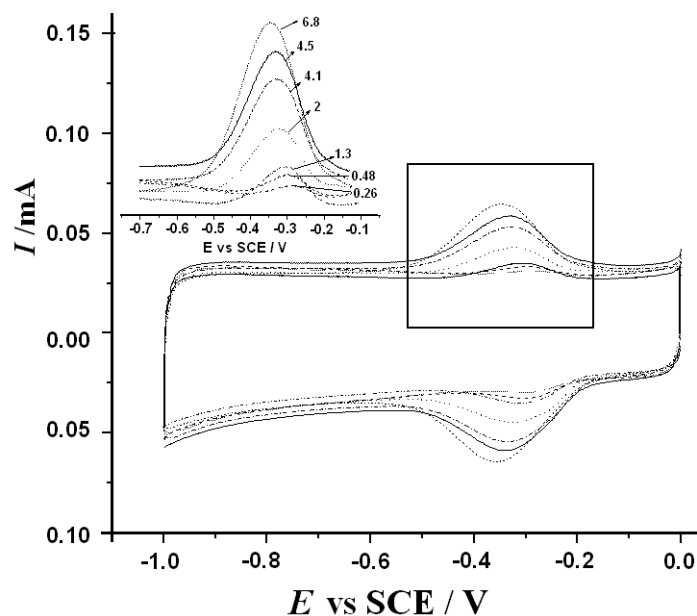

Fig. 5. Cyclic voltammograms of an OPG electrode modified with different surface concentrations of 16(F)CoPc. Potential scan rate: 0.2 V s^{-1}, electrolyte: 0.2 M NaOH, N$_2$ saturated.

nine. This effect is better illustrated in Fig. 6, in which the logarithm of surface molar concentration, Γ, is plotted *versus* the Co(II)/(I) formal potential found for the different concentrations.
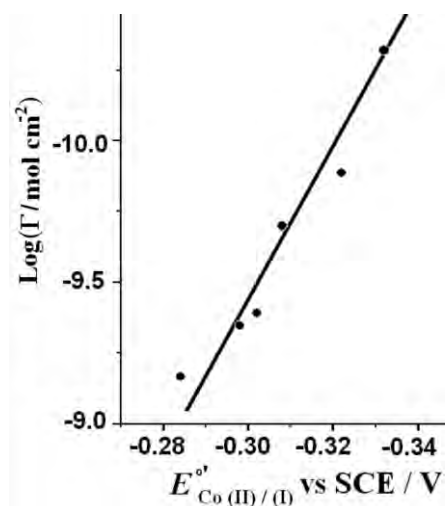

Fig. 6. Effect of the surface concentration of 16(F)CoPc on the Co(II)/(I) formal potential.

The slope of the linear correlation in Fig. 6 is –0.036 V per decade of log Γ. If there were no interactions between the l6(F)CoPc molecules, there would be no shift in the $E^{\circ\prime}$ Co(II)/(I) formal potential with variation of complex surface concentration, as was observed with CoPc.[29] The negative slope indicates that when Γ decreases, it is harder to oxidize the Co centre, *i.e.*, higher concentrations of l6(F)CoPc facilitate the reduction of Co(II); thus neighbouring molecules act as electron-withdrawing agents on the Co centre in one single molecule. The manner in which l6(F)CoPc is adsorbed on the graphite is unknown, but if they were to form stacks,[47] then only the molecules at the outermost should be active for a catalytic reaction, such as hydrazine oxidation. The catalytic activity of l6(F)CoPc should be independent of the surface coverage, at least in certain region of surface concentrations but, as it will be shown further on, this was not the case. From previous studies,[29,32,38] as illustrated in Fig. 1 (data taken from the literature,[30,32] shifting the formal potential to more negative values increases the catalytic activity of CoN4 macrocyclics when comparing to different complexes in one region of the volcano correlation. Thus, the activity per l6(F)CoPc molecule should decrease with dilution of the catalysts on the surface. To check this, the activity of OPG electrodes coated with different surface concentrations of 16(F)CoPc was examined and the same was realized with CoPc for comparison. This is illustrated in the polarization curves in Fig. 7. This data was further analysed in the Tafel correlations of Fig. 8. Correlations between $(\log i)_E$, current

densities at a constant potential taken from Fig. 8, and the logarithm of the surface concentration of the catalyst Γ are presented in Fig. 9.
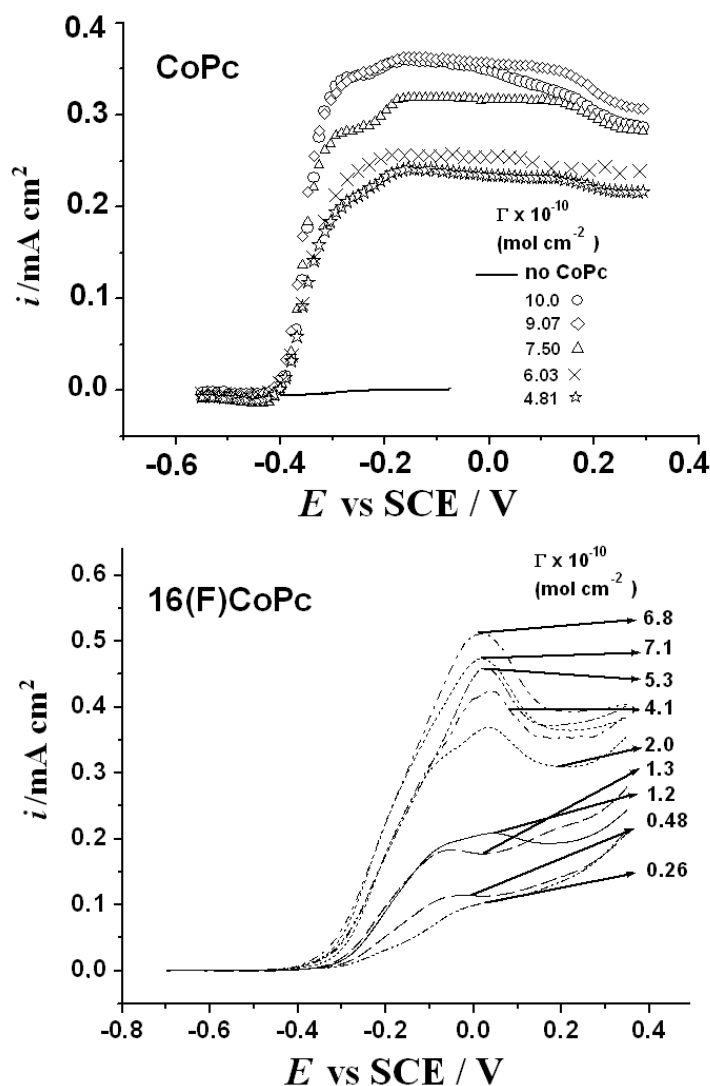

Fig. 7. Polarization curves of the chemically modified OPG electrode with different surface concentration of CoPc and 16(F)CoPc, in the presence of 5×10^{-4} M of hydrazine in 0.2 M NaOH solution saturated with N_2. Scan rate: 0.005 V s⁻¹.

Further analysis of the electrocatalytic process to assess the reaction order in surface concentration of the catalysts CoPc and 16(F)CoPc was performed by plotting log i at constant potential ($E = -0.35$ V) *versus* log Γ (shown in Fig. 9).
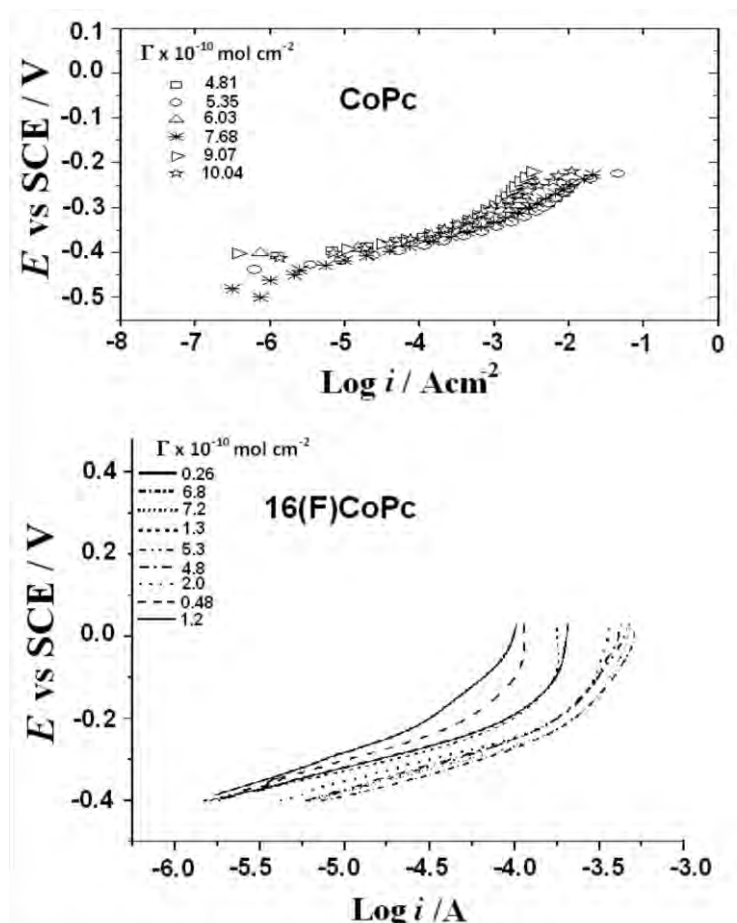
Fig. 8. Tafel plots for the oxidation of hydrazine on OPG modified with CoPc and 16(F)CoPc. Effect of surface concentration of the catalyst on the oxidation currents. Data obtained from Fig. 7.

In both cases, a linear correlation was observed, indicating that the catalytic currents increase linearly with the surface concentration of the catalyst. The order of the reaction in catalyst surface concentrations is $(d(\log I)/d\Gamma)_E$ and can be obtained from the slopes of the linear correlations in Fig. 9. For CoPc the slope was 1.2, so the reaction order could be considered to be one. However, for 16(F)CoPc, a fractional order of 0.58 was obtained. It might be difficult to explain an order close to 1/2 for this particular catalyst. However, further information could be obtained from kinetic data for this particular catalyst by plotting log (i/Γ) at constant potential *versus* the Co(II)/(I) redox potential for each particular surface concentration Γ of 16(F)CoPc. An interesting result was obtained that is illustrated in Fig. 10A. The activity normalized per surface concentration of the
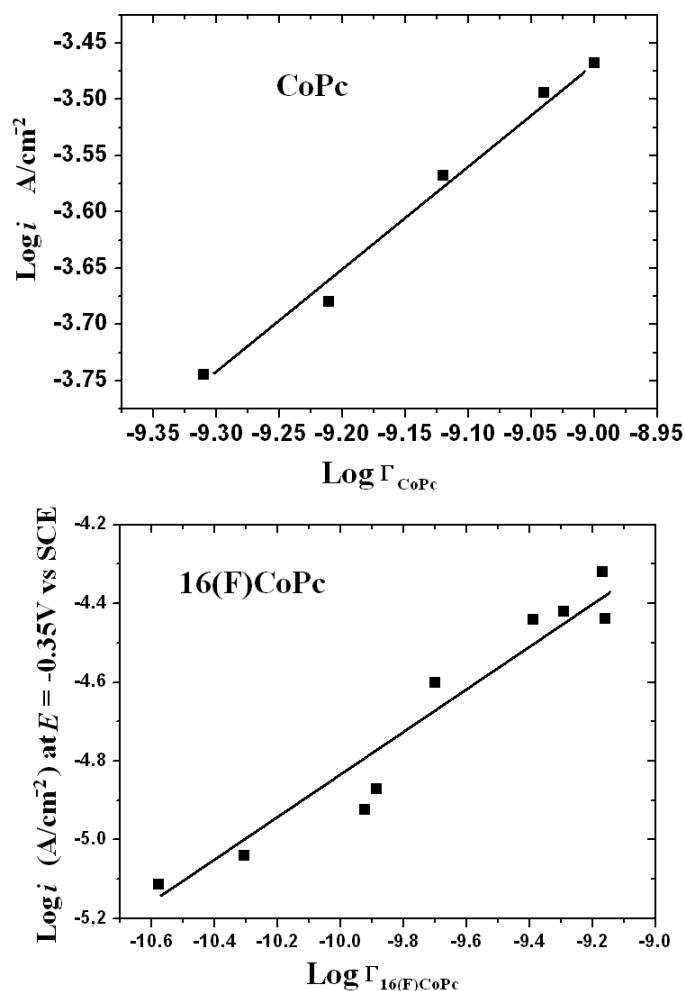
Fig. 9. Effect of catalyst surface concentration on the currents (as log *i* at constant potential) for the oxidation of hydrazine for CoPc and 16(F)CoPc. Data taken from Tafel plots in Fig. 8.

catalyst decreased with the formal potential, in a similar fashion to that observed in one of the branches of the volcano correlation of Fig. 1. Thus 16(F)CoPc at different surface concentrations behaves as if it were different Co complexes, so essentially it agrees with that observed in Fig. 1, *i.e.*, with one single complex, 16(F)CoPc, it is possible to reproduce the falling region of the volcano correlation. Since the activities were compared at –0.35 V, which is close to the Co(II)/(I) formal potentials observed for different surface concentration of 16(F)CoPc, it could be of interest to plot log $(i/\Gamma_{Co(II)})_E$, *i.e.*, current divided by the surface concentrations of Co(II) calculated form the Nernst equation, assum-
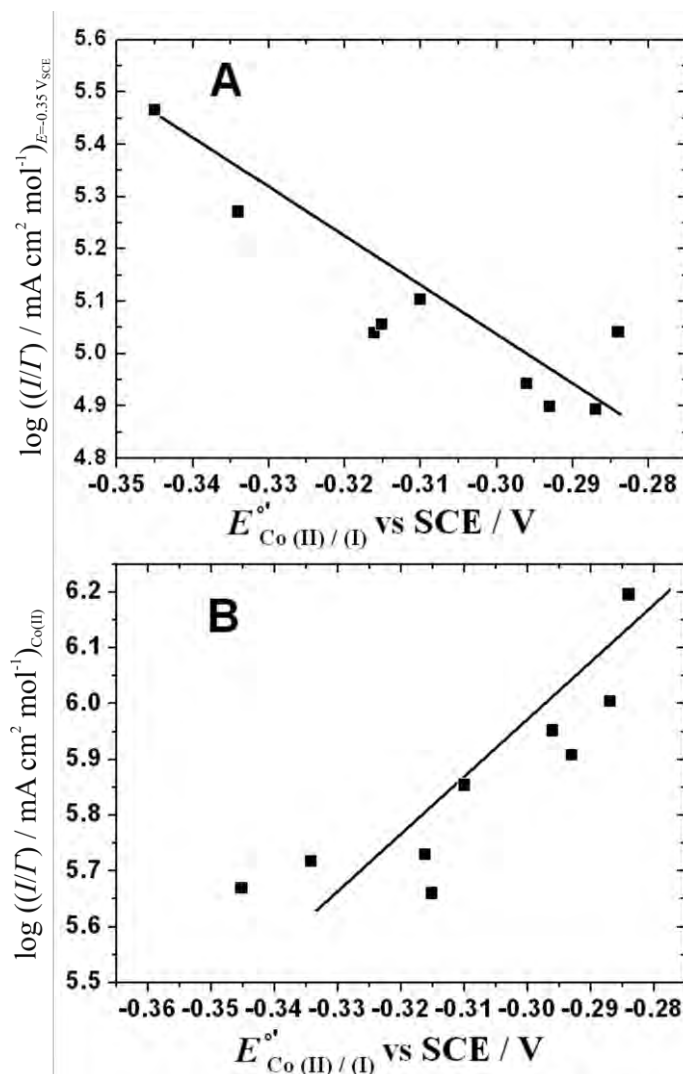
Fig. 10. A) Plot of log (i/Γ) at $E = -0.35$ V *vs.* the formal potential of the catalyst for a given Γ, the total surface concentration of 16(F)CoPc. Currents taken from the region of Tafel plots of Fig. 7 under kinetic control. B) The same as in (A) but currents are divided by the surface concentration of 16(F)Co(II)Pc, *i.e.*, the real surface molar concentrations of the Co(II) active sites.

ing that the active sites are Co(II). Such a plot is illustrated in Fig. 10B. A linear correlation was again obtained but with a positive slope, *i.e.*, the catalytic activity per Co(II) active site increased with increasing Co(II)/(I) redox potential of the catalyst. Fig. 10B is a free energy correlation since $i/\Gamma_{Co(II)}$ is proportional to the rate constant k at that electrode potential and the redox potential is proportional

to the driving force of the system. This type of behaviour was also observed for the catalytic oxidation of Fe phthalocyanines,[38] by comparing different Fe macrocyclics in a volcano correlation, when the currents in the falling regions were divided by the surface concentration of Fe(II) active sites, and the volcano becomes a linear correlation. The slope of the linear correlation in Fig. 10B is close to 0.120 V decade^{-1}, which is the same slope as that observed for the "linearized" volcano correlation for Fe complexes reported previously.[38] Furthermore, the linear correlation shown in Fig. 10B is similar to a linear Tafel correlation when the applied potential is the driving force of the reaction. In Fig. 10B, where the activities are compared at constant electrode potential, the "extra" driving force is provided by the M(II)/(I) redox potential of the catalyst.

CONCLUSIONS

It was found that the Co(II)/(I) formal potential of 16(F)CoPc adsorbed on graphite shifted to more negative values with increasing surface concentration of this catalyst. This was not observed for the unsubstituted CoPc. It is not clear why this phenomenon was observed for 16(F)CoPc since the exact orientation of these molecules on the graphite surface is unknown. If they formed stacks, instead of monolayers, it would be expect that only the molecules located at the outermost position in a stack would exhibit activity, since hydrazine molecules would not have access to 16(F)CoPc molecules located below. In this case, the correlations between $(\log i)_E$ might not be linear or should show linear behaviour only at low concentrations of 16(F)CoPc. This was not observed. However, some interaction between neighbouring 16(F)CoPc molecules could occur to affect the Co(II)/(I) formal potential, which does not occur with CoPc. When comparing the catalytic activities of electrodes coated with different surface concentrations of 16(F)CoPc, as $\log(i/\Gamma)$ (Γ is the total surface concentration of 16(F)CoPc) *versus* the Co(II)/(I) formal potential, it was possible to reproduce the falling region of a volcano correlation obtained by comparing the activity of several CoN4 macrocyclics and reported previously.[11,29,32,39] If the same plot is repeated using the surface concentration of Co(II) active sites at the potential used for the comparisons, *i.e.*, $\Gamma_{Co(II)}$, the activity per active site increases with the driving force of the catalyst, producing what could be considered a linear free energy correlation, with a slope close to 0.120 V decade^{-1}.

ИЗВОД

НЕУОБИЧАЈЕНО ПОНАШАЊЕ ПЕРФЛУОРОВАНОГ КОБАЛТ-ФТАЛОЦИЈАНИНА У ПОРЕЂЕЊУ СА НЕСУПСТИТУИСАНИМ КОБАЛТ-ФТАЛОЦИЈАНИНОМ У ЕЛЕКТРОКАТАЛИТИЧКОЈ ОКСИДАЦИЈИ ХИДРАЗИНА. ЕФЕКАТ ПОВРШИНСКЕ КОНЦЕНТРАЦИЈЕ КАТАЛИЗАТОРА НА ПОВРШИНИ ГРАФИТА

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Циклични волтамограми CoPc и 16(F)CoPc адсорбованих на графитној електроди у алкалној средини (0,2 M NaOH) показују типичне реверзибилне редокс пикове који потичу од Co(II)/(I) реакције. Потенцијал пика за CoPc не зависи од површинске концентрације катализатора, али се за 16(F)CoPc са повећањем површинске концентрације катализатора помера ка негативнијим вредностима. У делу „вулканске" корелације log (*i*/*Г*)$_E$ (активност по активном месту) према Co(II)/(I) формалном потенцијалу катализатора, понашање CoPc (у неколико CoN4 хелата) показује тенденцију раста (активност се повећава са Co(II)/(I) редокс потенцијалом), док се 16(F)CoPc појављује у области у којој активност опада са редокс потенцијалом. Област опадања активности 16(F)CoPc репродукована је само за један појединачни комплекс. Отуда се 16(F)CoPc различитих површинских концентрација понаша као Co комплекси који имају различите редокс потенцијале у опадајућој области „вулканске" криве, ако се активност нормализује по површинској концентрацији. Ово није опажено за CoPc.

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