

## Al<sub>2</sub>O<sub>3</sub> Coated with 3-*n*-Propyl-1-azonia-4-azabicyclo[2.2.2]octane Silsesquioxane Chloride and its use for Immobilization of Cobalt(II) Tetrasulfonated Phthalocyanine in Oxalic Acid Electrooxidation

André R. Ramos, Jacqueline Arguello, Hérica A. Magosso and Yoshitaka Gushikem\*

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13084-862 Campinas-SP, Brazil

Um polímero solúvel em água, preparado pelo método sol-gel e designado cloreto de 3-*n*-propil-1-azonia-4-azabicyclo[2.2.2]octano silsesquioxano, foi adsorvido sobre a superfície da alumina. Essa alumina recoberta com o polímero foi capaz de imobilizar efetivamente complexos de ftalocianina tetrassulfonada metalada com Co(II) como contra-íons. A ftalocianina de cobalto imobilizada dessa forma fica fortemente aderida sobre a superfície do cloreto de Al<sub>2</sub>O<sub>3</sub>/3-*n*-propil-1-azonia-4-azabicyclo[2.2.2]octano silsesquioxano. Além disso, quando incorporada a um eletrodo de pasta de carbono mostra uma boa resposta eletrocatalítica para a oxidação de ácido oxálico. Foi obtida uma relação linear ( $r = 0,998$ ) para o gráfico de correntes de resposta obtidas por cronoamperometria e a concentração de ácido oxálico na faixa de  $7.4 \times 10^{-5}$  a  $9.1 \times 10^{-4}$  mol L<sup>-1</sup>. O limite de detecção determinado foi igual a 18 μmol L<sup>-1</sup>.

A water-soluble polymer prepared by sol-gel process, 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride, was adsorbed on alumina surface. This polymer-coated alumina was able to effectively immobilize cobalt(II) tetrasulfonated phthalocyanine complexes as counter ions. Cobalt phthalocyanine immobilized in this way is well and tightly adsorbed on Al<sub>2</sub>O<sub>3</sub>/3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride surface. Furthermore, when incorporated to a carbon paste electrode showed a good electrocatalytic response toward the acid oxalic oxidation, making it a suitable electrode material. A linear relationship ( $r = 0.998$ ) between the current responses obtained by chronoamperometric measurements and the oxalic acid concentration in the range of  $7.4 \times 10^{-5} - 9.1 \times 10^{-4}$  mol L<sup>-1</sup> was observed. A detection limit of 18 μmol L<sup>-1</sup> was also determined.

**Keywords:** 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octanesilsesquioxane chloride, cobalt(II) tetrasulfonated phthalocyanine, oxalic acid electrocatalytic oxidation

### Introduction

Organic functionalization of mesoporous silica is an attractive research area in constant growth due to its many and varied technological applications in catalysis, ion exchange, optical and electronic devices field.<sup>1-6</sup> The preparation of hybrid materials with functionalized internal surface by a sol-gel processing technique can be easily achieved by cohydrolysis and polycondensation of tetraethylorthosilicate and an organotrialkoxysilane RSi(OR')<sub>3</sub>. Thus, 3-chloropropyltrimethoxysilane as the organosilane precursor has been already used in the preparation of 3-chloropropylsilsesquioxane, in which the chloropropyl group reacts with pyridine, leading to the

formation of 3-*n*-propylpyridiniumsilsesquioxane chloride polymer.<sup>7</sup> In the same way 1,4-diazabicyclo[2.2.2]octane has been employed in the synthesis of 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride.<sup>8</sup>

The interest on this kind of quaternary ammonium salts, as well as, other resemblances is mainly associated to their application as ionophores in polymeric membrane ion-selective electrode.<sup>9,10</sup> For example, 1,4-diazabicyclo[2.2.2]octane has been successfully employed in the preparation of anion-exchange membranes for removing of Cr(VI) and Cd(II) from aqueous medium.<sup>11,12</sup>

Besides, polycations prepared by attaching quaternized pyridine groups to a polysiloxane chain have proven to be reliable supporting material for immobilization of negatively charged electro active species.<sup>13,14</sup> Since this approach has provided effective

\*e-mail: gushikem@iqm.unicamp.br

attachments for electro active molecules the scope of this paper is to describe the immobilization of cobalt(II) tetrasulfonated phthalocyanine on alumina coated with 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane polymer and its electrochemical behavior as modifier for a carbon paste electrode in electrocatalytic application.

The coating of 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride on alumina surface can be easily accomplished by mixing alumina particles with the polymer aqueous solution for a period of time, followed by solvent evaporation. A good adhesion is expected since the free aluminol group, Al-OH, on the alumina surface has a high affinity by the terminal silanol group, Si-OH, of the polymer.<sup>15</sup>

The ability of the alumina-coated 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride polymer to immobilize electroactive species will be tested by adsorbing cobalt(II) tetrasulfonated phthalocyanine and its electrochemical behavior as a carbon paste electrode modifier will be evaluated as well. Moreover, in this study the electrocatalytic activity of adsorbed cobalt phthalocyanine for the oxalic acid oxidation will be investigated.

## Experimental

### Materials and methods

All chemicals were analytical grade and used as received. Solutions were prepared with doubly distilled water.

### Synthesis and characterization of 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride

3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride was prepared following a procedure described elsewhere,<sup>16</sup> but with some modifications. 89 mL of tetraethylorthosilicate (TEOS, Aldrich) were first prehydrolyzed with 35 mL of 1 mol L<sup>-1</sup> HCl and 150 mL of ethanol. The solution was stirred at room temperature for 2.5 h. 106 mL of 3-chloropropyltrimethoxysilane (Aldrich) were added, and stirred for another 2 h at room temperature. Then, the temperature was raised to 328 K and the system was allowed to stand at this temperature for 60 h to promote the condensation process. The solvent was slowly evaporated to dryness at 383 K. The solid obtained was powdered and exhaustively washed with ethanol. The remaining solvent was removed under vacuum at 340 K. About 30 g of this solid were immersed in 160 mL

of toluene, and 20 g of 1,4-diazabicyclo [2.2.2.]octane (DABCO) were added to the mixture and stirred under reflux temperature for 2 h. The solid obtained finally was filtered, washed with ethanol and dried at 333 K under vacuum. 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride will be abbreviated as SiDbCl. SiDbCl structure was confirmed by IR and <sup>13</sup>C NMR spectroscopy.

### Alumina coating with SiDbCl

For alumina coating with SiDbCl, about 40 g of Al<sub>2</sub>O<sub>3</sub> (S<sub>BET</sub> = 107 m<sup>2</sup> g<sup>-1</sup>) were immersed in 300 mL of 1.2 % SiDbCl aqueous solutions, and the reaction was promoted by heating the mixture at 348 K for 48 h. The solvent was allowed to evaporate until dryness at 373 K, and the solid product obtained was exhaustively washed with water to remove unreacted SiDbCl. The material obtained will hereafter be designated as Al<sub>2</sub>O<sub>3</sub>/SiDbCl.

### Immobilization of CoTsPc on Al<sub>2</sub>O<sub>3</sub>/SiDbCl

Cobalt(II) tetrasulfonated phthalocyanine tetrasodium salt was prepared as described elsewhere.<sup>17</sup> About 2 g of Al<sub>2</sub>O<sub>3</sub>/SiDbCl were immersed in 25 mL of 0.1 mmol L<sup>-1</sup> CoTsPc aqueous solution, and stirred for 30 min to promote the adsorption process mainly occurring by electrostatic interaction. The resultant blue solid was separated by filtration and washed with deionized water until a colorless supernatant was observed, and finally dried under vacuum.

CoTsPc adsorption on Al<sub>2</sub>O<sub>3</sub>/SiDbCl was confirmed by the characteristic bands associated with phthalocyanine complex in the UV-Vis region and the anodic peak corresponding to the oxidation of Co(II) to Co(III).

### Equipments

IR spectra in 4000-400 cm<sup>-1</sup> range were obtained on a BOMEM FTIR MB-Series infrared spectrophotometer with the sample investigated as KBr disc (1 wt.%). A solid-state <sup>13</sup>C NMR spectrum was obtained on a Bruker AC 300/P spectrometer at 75.4 MHz in the CP-MAS mode. Elemental analysis was also performed with a Perkin-Elmer 2400 series II elemental analyzer. Specific surface area was obtained on a Flow Sorb II 2300 apparatus (Micrometrics). Diffuse reflectance measurement between 200 and 800 nm was performed on a CARY 5G UV/Vis spectrophotometer. Barium sulfate was used as a reference white.

### Electrochemical study

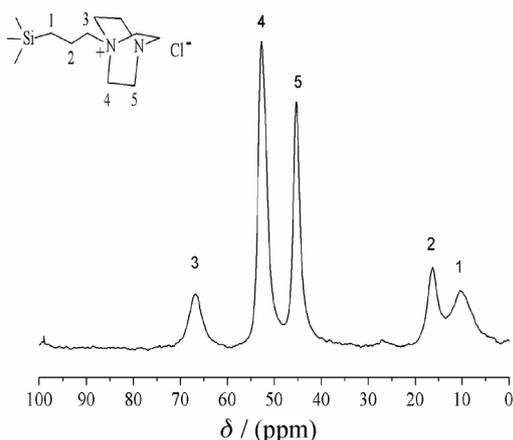
Characterization of  $\text{Al}_2\text{O}_3/\text{SiDbCl}/\text{CoTsPc}$  as electrode material was carried out using a three-electrode system, with a carbon paste electrode containing the material as working electrode, a saturated calomel electrode (SCE) as reference and platinum wire as counter electrode. The carbon paste electrode, with a geometric area of  $0.2 \text{ cm}^2$ , was prepared by mixing 50% of  $\text{Al}_2\text{O}_3/\text{SiDb}/\text{CoTsPc}$  with graphite (Fluka) and a drop of mineral oil (Nujol). The experiments were performed on an Autolab PGSTAT 20 potentiostat-galvanostat apparatus in a  $1.0 \text{ mol L}^{-1}$  KCl deaerated solution. A scan rate of  $5 \text{ mV s}^{-1}$  was used for DPV with pulse amplitude of  $10 \text{ mV}$  and  $20 \text{ ms}$  pulse width.

## Results and Discussion

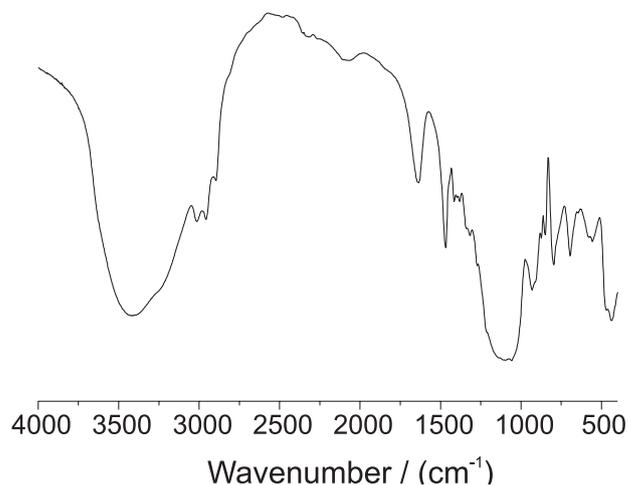
### Synthesis and characterization of $\text{Al}_2\text{O}_3/\text{SiDbCl}$

The covalent attachment of 1,4-diazabicyclo [2.2.2.] octane to propylsilsequioxane framework was confirmed by  $^{13}\text{C}$  NMR and IR spectroscopy. The solid-state  $^{13}\text{C}$  NMR spectrum and the respective assignments are shown in Figure 1, in which the peaks observed at 10, 16 and 68 ppm were attributed to  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$  carbon atoms of the *n*-propyl group. However, the peaks at 53 and 45 ppm were assigned to the  $\text{C}_4$  and  $\text{C}_5$  DABCO atoms, respectively.<sup>18</sup>

Figure 2 shows the FTIR spectra of SiDbCl. The characteristic vibrational mode band observed at  $1464 \text{ cm}^{-1}$  is assigned to the  $\delta \text{CH}_2$  of DABCO molecule attached to the



**Figure 1.** Solid state  $^{13}\text{C}$  NMR spectrum of SiDbCl. Marked peaks corresponds to the C atoms assignments shown in the inset structure.



**Figure 2.** Infrared spectra of the SiDbCl.

*n*-propyl group.<sup>16</sup> The peaks observed at  $2,962\text{--}2,840 \text{ cm}^{-1}$  are assigned to the CH stretching modes.<sup>19,20</sup> The peaks assigned to the silica network are observed at  $1,000\text{--}1,200 \text{ cm}^{-1}$  ( $\nu \text{ Si-O-Si}$ ) and  $936 \text{ cm}^{-1}$  ( $\nu \text{ Si-OH}$ ).<sup>21</sup>

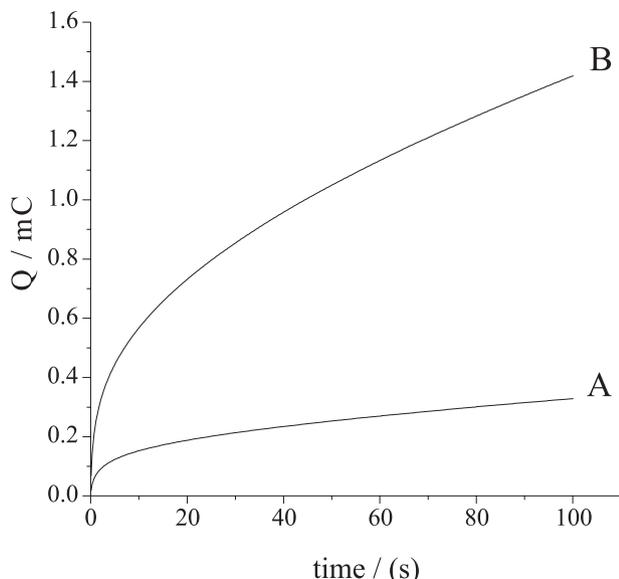
The ion exchange capacity (IEC) of SiDbCl was determined by analyzing the ionized chloride by potentiometric titration using a standard  $\text{AgNO}_3$  solution. The quantity of released chloride ions found (mol *per* gram of material) was  $2 \text{ mmol g}^{-1}$ . This value is very close to that obtained by elemental analyses ( $\text{C} = 21.1 \text{ wt.}\%$  ( $17.6 \text{ mmol g}^{-1}$ ),  $\text{H} = 4.64 \text{ wt.}\%$  ( $46 \text{ mmol g}^{-1}$ ),  $\text{N} = 4.90 \text{ wt.}\%$  ( $3.5 \text{ mmol g}^{-1}$ ), since a mole ratio  $\text{N}/\text{Cl}^- = 2$  is expected, so the total organic content of 30.6% in SiDbCl was found. When  $\text{Al}_2\text{O}_3$  was coated with 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride the IEC value of the new material,  $\text{Al}_2\text{O}_3/\text{SiDbCl}$ , decreased four times ( $0.5 \text{ mmol g}^{-1}$ ) as a result of the coating process.

The surface area of alumina after the polymer coating formation was analyzed. A specific surface area  $S_{\text{BET}} = 113 \text{ m}^2 \text{ g}^{-1}$  was found. Considering this value, it is noticeable that the surface area of porous aluminum oxide ( $S_{\text{BET}} = 107 \text{ m}^2 \text{ g}^{-1}$ ) was almost not affected by the coating process.

### Immobilization of CoTsPc on $\text{Al}_2\text{O}_3/\text{SiDbCl}$

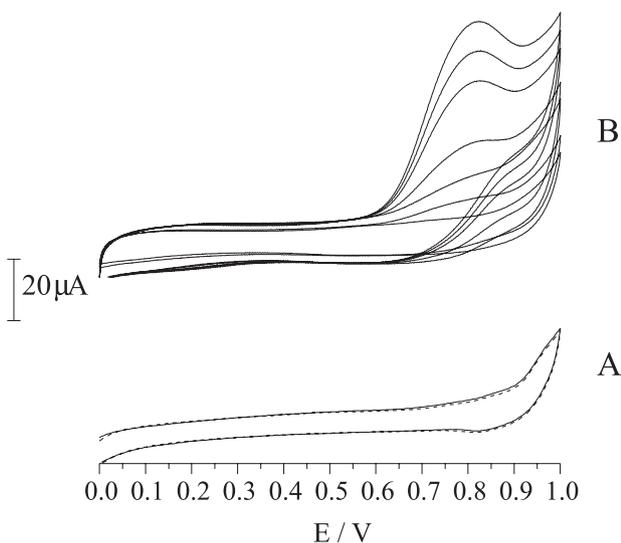
Quaternary nitrogen with the positive charge in the 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane framework gives the  $\text{Al}_2\text{O}_3/\text{SiDbCl}$  surface the ability to immobilize negatively charged redox species like cobalt(II) tetrasulfonated phthalocyanine, where the attachment preferably occurs by electrostatic interactions, as schematically represented in Figure 3. It seems that CoTsPc is strongly adsorbed on the  $\text{Al}_2\text{O}_3/\text{SiDbCl}$





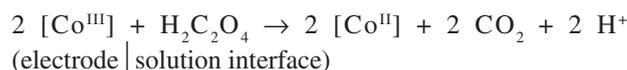
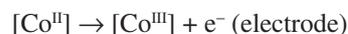
**Figure 6.** Charge-time curves of  $\text{Al}_2\text{O}_3/\text{SiDb}$  carbon paste electrode (A) and  $\text{Al}_2\text{O}_3/\text{SiDb}/\text{CoTsPc}$  carbon paste electrode (B) for potential step from 0 to 0.9 V in 1.0 mol  $\text{L}^{-1}$  KCl.

modified carbon paste electrode toward the oxidation of oxalic acid. Upon the addition of 0.1 to 1.1 mmol  $\text{L}^{-1}$  of oxalic acid in the electrolytic solution (1.0 mol  $\text{L}^{-1}$  KCl) an enhancement in the anodic current was clearly observed (Figure 7), indicating that an electrocatalytic process is occurring at the electrode surface. This statement is based on the fact that oxalic acid did not oxidize at a carbon paste electrode containing only  $\text{Al}_2\text{O}_3/\text{SiDb}$ , *i.e.* in absence of CoTsPc (not shown). Thus, oxalic acid oxidation on

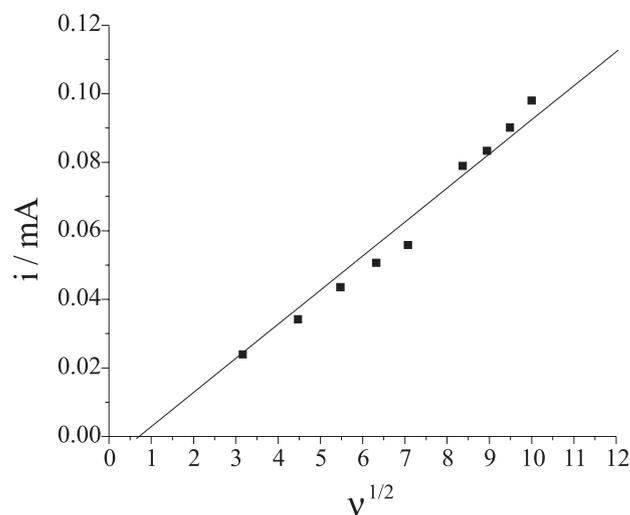


**Figure 7.** A) Cyclic voltammograms of  $\text{Al}_2\text{O}_3/\text{SiDb}$  carbon paste electrode in absence (dashed line) and presence of 1 mmol  $\text{L}^{-1}$  of oxalic acid (solid line); B) Cyclic voltammograms of  $\text{Al}_2\text{O}_3/\text{SiDb}/\text{CoTsPc}$  carbon paste electrode in presence of different concentrations of oxalic acid (0.0, 0.1, 0.2, 0.4, 0.7, 0.8 and 1.0 mmol  $\text{L}^{-1}$ ). Scan rate of 10  $\text{mV s}^{-1}$ , in 1 mol  $\text{L}^{-1}$  KCl.

$\text{Al}_2\text{O}_3/\text{SiDb}/\text{CoTsPc}$  modified carbon paste electrode is an EC process, which can be described by the following reaction steps:<sup>26</sup>



The behavior of the electrocatalytic anodic current as a function of the scan rate (*i* versus  $v^{1/2}$ ) resulted in a linear relationship in the range of 10–100  $\text{mV s}^{-1}$  (Figure 8) suggesting that the current is controlled by a semi-infinite linear diffusion.



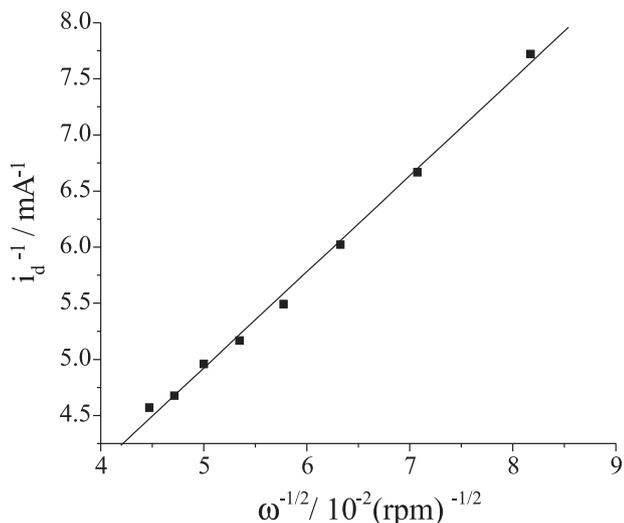
**Figure 8.** Plot of the electrocatalytic anodic current peak versus  $v^{1/2}$ .

Looking for more detailed information about the oxalic acid oxidation process, hydrodynamic voltammetry experiments were performed at an  $\text{Al}_2\text{O}_3/\text{SiDb}/\text{CoTsPc}$  modified carbon paste rotating electrode ( $A = 0.29 \text{ cm}^2$ ). The scan rate was 10  $\text{mV s}^{-1}$ , while the rotation rate was varied between 150 and 500 rpm. The Koutecky-Levich equation was used to determine the diffusion coefficient of oxalic acid.<sup>27</sup> This equation is valid for a first-order process with respect to the diffusion species, according to:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62nFAD_0^{2/3}\omega^{1/2}v^{-1/6}C_0}$$

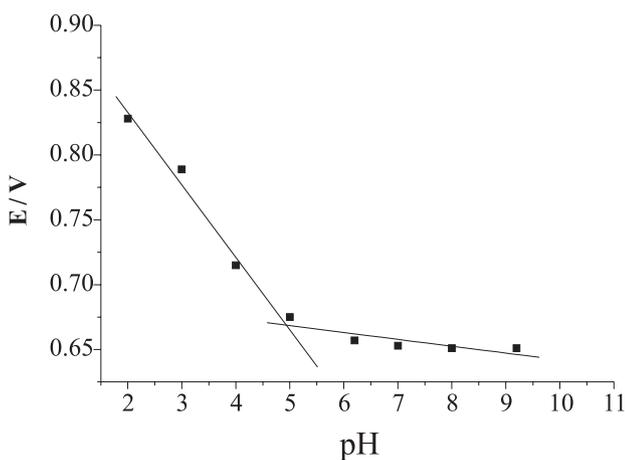
The first expression of this equation ( $1/i_k$ ) is related to the current under kinetic control while the second one is associated to the current under a diffusion-controlled regime. The symbols  $v$  and  $\omega$  represent the kinematic viscosity and the angular speed of the rotating electrode, respectively. Other parameters have their conventional meanings. Assuming values of  $v \approx 0.01 \text{ cm}^2 \text{ s}^{-1}$  and  $n = 2$ ,

the diffusion coefficient (*D*) of 1 mmol L<sup>-1</sup> of oxalic acid was evaluated from the slope of the linear graph in Figure 9 (*i*<sup>-1</sup> versus  $\omega^{-1/2}$ ).<sup>28</sup> The found value (*D* = 2.6 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) is similar to that previously reported.<sup>29</sup>



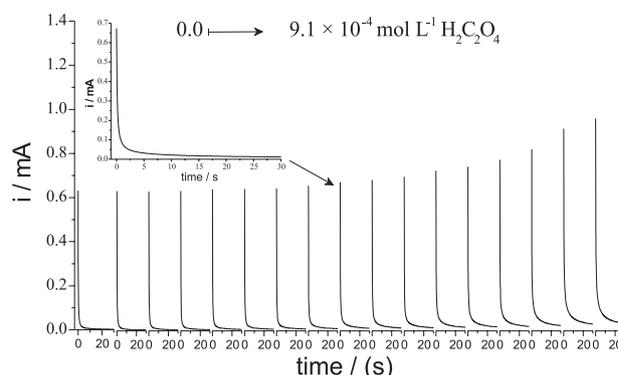
**Figure 9.** Plot of  $i_d^{-1}$  versus  $\omega^{-1/2}$  using an Al<sub>2</sub>O<sub>3</sub>/SiDb/CoTsPc modified carbon paste rotating electrode, in 1 mol L<sup>-1</sup> KCl and 1 mmol L<sup>-1</sup> oxalic acid.

pH effect on the electrooxidation potential of oxalic acid was also investigated in pH 2-9 range. *E* = *f* (pH) plot for 10 mmol L<sup>-1</sup> of oxalic acid solution as shown in Figure 10 depicts two regions with an intersection point very close to p*K*<sub>a2</sub> = 4.17 of oxalic acid,<sup>30</sup> corresponding to the dissociation of HC<sub>2</sub>O<sub>4</sub><sup>-</sup> species (HC<sub>2</sub>O<sub>4</sub><sup>-</sup> ⇌ C<sub>2</sub>O<sub>4</sub><sup>2-</sup> + H<sup>+</sup>). The potential peak remains pH-independent at pH higher than 5 because at pH > p*K*<sub>a2</sub> C<sub>2</sub>O<sub>4</sub><sup>2-</sup> are the dominant species, and since no-dissociation occurs before the electron transfer rate-determining step, the oxidation potential remains pH-independent.

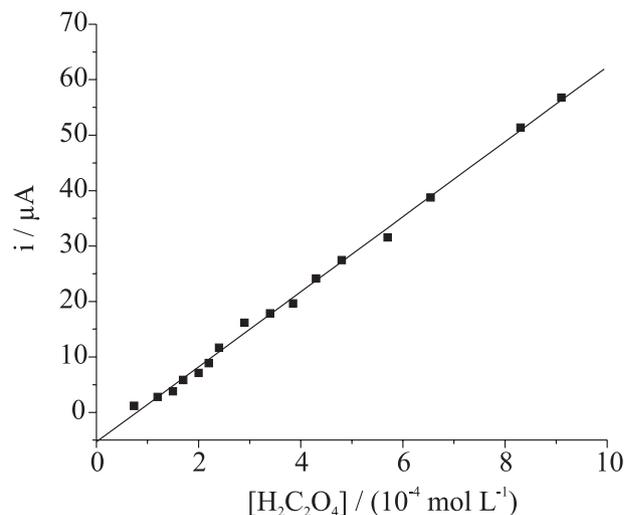


**Figure 10.** Dependence of peak potentials on the pH, for the oxidation of 10 mmol L<sup>-1</sup> oxalic acid in a solution of constant ionic strength (1 mol L<sup>-1</sup> KCl).

Finally, the current-concentration profile was plotted using the data from chronoamperometric curves. Figure 11 depicts the chronoamperograms after successive additions of aliquots of oxalic acid solution in a fixed applied potential of 0.8 V for 30 s. A very fast electrode response time was observed after addition of each aliquot of oxalic acid, about 1 s. In Figure 12, the electrocatalytic current increases linearly with the amount of oxalic acid added (*r* = 0.998), in the concentration range of 7.4 × 10<sup>-5</sup> - 9.1 × 10<sup>-4</sup> mol L<sup>-1</sup>. The detection limit, calculated as three times the standard deviation of measured blanks, is 18 μmol L<sup>-1</sup>. This value is better, comparing with that reported in previous study,<sup>15</sup> carried out on CoTsPc adsorbed on Al<sub>2</sub>O<sub>3</sub>-coated 3-*n*-propylpyridinium chloride silsesquioxane (0.5 mmol L<sup>-1</sup>) and is comparable to another carbon paste electrode modifier such as palladium nanoparticles (20 μmol L<sup>-1</sup>).<sup>31</sup> This result point out to a promising future application of Al<sub>2</sub>O<sub>3</sub>/SiDb as substrate to attach negatively charged electroactive species, building modified electrodes for electrocatalytic purposes.



**Figure 11.** Chronoamperometric curves for different oxalic acid concentrations, in 1 mol L<sup>-1</sup> KCl. Potential applied = 0.8 V for 30 s.



**Figure 12.** Plot of anodic current (*i*) versus oxalic acid concentration [H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>].

## Conclusions

The water-soluble polymer 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane silsesquioxane chloride was effectively adsorbed onto alumina surface making it a reliable material to immobilized negatively charged electroactive species. Electrostatic interaction between cobalt(II) tetrasulfonated phthalocyanine and Al<sub>2</sub>O<sub>3</sub>/SiDb was sufficiently strong since the electroactive species were not released to the solution phase during the electrochemical experiments. The Al<sub>2</sub>O<sub>3</sub>/SiDb/CoTsPc modified carbon paste electrode showed a good electrocatalytic response toward the oxalic acid oxidation. This result is quite promising if it is compared with the coating polymer previously mentioned (3-*n*-propylpyridinium silsesquioxane chloride), and some other useful application should be expected.

## Acknowledgments

This work has received financial support from FAPESP: research grant 00/11103-5, doctoral (H.A.M., 04/00920-3), and postdoctoral (J.A., 06/50563-8) fellowships. A.R.R. is in indebted to CNPq for a doctoral scholarship. The authors thank Prof. Carol H. Collins for her kindly suggestions to the manuscript.

## References

- Templin, M.; Franck, A.; Du Chesne, A.; Leist, H.; Zhang, Y.; Ulrich, R.; Schädler, V.; Wiesner, U.; *Science* **1997**, *278*, 1795.
- Lee, K.; Itharaju, R. R.; Puleo, D. A.; *Acta Biomaterialia* **2007**, *3*, 515.
- Yuan, J.; Zhou, S.; You, B.; Wu, L.; *Chem. Mater.* **2005**, *17*, 3587.
- Fujiwara, M.; Nishiyama, M.; Yamamura, I.; Ohtsuki, S.; Nomura, R.; *Anal. Chem.* **2004**, *76*, 2374.
- Sayari, A.; Hamoudi, S.; *Chem. Mater.* **2001**, *13*, 3151.
- Tien, P.; Chau, L. K.; Shieh, Y. Y.; Lin, W. C.; Wei, G. T.; *Chem. Mater.* **2001**, *13*, 1124.
- Gushikem, Y.; Alfaya, R. V. S.; Alfaya, A. A. S.; *Br PI* 9.803.053-A, **1998**.
- Arenas, L. T.; Langaro, A.; Gushikem, Y.; *J. Sol-Gel Sc. Tech.* **2003**, *28*, 51.
- Tundo, P.; Venturello, P.; Angeletti, E.; *J. Am. Chem. Soc.* **1982**, *104*, 6547.
- Wotring, V. J.; Johnson, D. M.; Bachas, L. G.; *Anal. Chem.* **1990**, *62*, 1506.
- Scindia, Y. M.; Pandey, A. K.; Reddy, A. V. R.; *J. Membr. Sci.* **2005**, *249*, 143.
- Arenas, L. T.; Vaghetti, J. C. P.; Moro, C. C.; Lima, E. C.; Benvenuti, E. V.; Costa, T. M. H.; *Mater. Lett.* **2004**, *58*, 895.
- Kobayasbit, J.; Anson, F. C.; *J. Phys. Chem.* **1991**, *95*, 2595.
- Ribeiro, E. S.; Gushikem, Y.; *Electroanalysis* **1999**, *11*, 1280.
- Lucho, A. M. S.; Pissetti, F. L.; Gushikem, Y.; *J. Sol-Gel Sc. Tech.* **2004**, *275*, 251.
- Arenas, L. T.; Aguirre, T. A. S.; Langaro, A.; Gushikem, Y.; Benvenuti, E. V.; Costa, T. M. H.; *Polymer* **2003**, *44*, 5521.
- Castellani, A. M.; Gonçalves, J. E.; Gushikem, Y.; *J. New Mat. Electrochem. Syst.* **2002**, *5*, 169.
- Arenas, L. T.; Dias, S. L. P.; Moro, C. C.; Costa, T. M. H.; Benvenuti, E. V.; Lucho, A. M. S.; Gushikem, Y.; *J. Colloid Interface Sci.* **2006**, *297*, 244.
- Min Jin, Z.; Jiang Pan, Y.; Feng Li, X.; Lin Hu, M.; Shen, L.; *J. Mol. Struct.* **2003**, *660*, 67.
- Marzocchi, M. P.; Sbrana, G.; Zerbi, G.; *J. Am. Chem. Soc.* **1965**, *87*, 1429.
- Fidalgo, A.; Ilharco, L. M.; *Chem. Eur. J.* **2004**, *10*, 392.
- Ray, S.; Vasudevan, S.; *Inorg. Chem.* **2003**, *42*, 1711.
- Tackley, D. R.; Dent, G.; Smith, W. E.; *Phys. Chem. Chem. Phys.* **2001**, *3*, 1419.
- Anson, F. C.; *Anal. Chem.* **1966**, *38*, 54.
- Xuan, G. S.; Jang, S.; Kwag, G.; Kim, S.; *Bull. Korean Chem. Soc.* **2005**, *26*, 671.
- Lucho, A. M. S.; Oliveira, E. C.; Pastore, H. O.; Gushikem, Y.; *J. Electroanal. Chem.* **2004**, *73*, 55.
- Bard, A. J.; Faulkner, L. R.; *Electrochemical Methods. Fundamentals and Applications*, 2<sup>nd</sup> ed., Wiley: New York, 2001, ch. 9.
- Yamazaki, S.; Yamada, Y.; Fujiwara, N.; Ioroi, T.; Siroma, Z.; Senoh, H.; Yasuda, K.; *J. Electroanal. Chem.* **2007**, *602*, 96.
- Casella, I. G.; *Electrochim. Acta* **1999**, *44*, 3353.
- Mandanias, M. M.; Shaffer, W.; Adair, J. H.; *J. Am. Ceram. Soc.* **2002**, *85*, 2156.
- Shaidarova, L. G.; Chelnokova, I. A.; Gedmina, A. V.; Budnikov, G. K.; Ziganshina, S. A.; Mozhanova, A. A.; Bukharaev, A. A.; *J. Anal. Chem.* **2006**, *61*, 375.

Received: September 29, 2007

Web Release Date: April 30, 2008

FAPESP helped in meeting the publication costs of this article.