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Comparative Study of Different Methods for the Preparation of Co_xO_y/C for the Electrosynthesis of Hydrogen Peroxide

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A comparative study of the sol-gel method (SGM) and polymeric precursor method (PPM) for the synthesis of Co_xO_y/C electrocatalysts has been performed. Co_xO_y/C electrocatalysts can electrogenerate hydrogen peroxide (H_2O_2), which is desirable for the electrochemical treatment of effluent containing organic pollutants in aqueous or non-aqueous medium. The results showed that SGM was superior for the synthesis of Co_xO_y/C catalysts for H_2O_2 electrogeneration. Analysis of X-ray diffraction for Co_xO_y/C prepared by PPM identified only one phase comprising Co_3O_4. Besides for Co_xO_y/C prepared by SGM a mixture of oxides was observed: CoO and Co_2O_4. The average size of crystallites in this material was 5 nm. A rotating ring-disc electrode was used for electrochemical analysis of the oxygen reduction reaction (ORR). The results showed that the SGM was better than PPM for H_2O_2 electrogeneration since it showed the highest ring-currents. Results also indicate that the number of electrons transferred in the ORR for SGM and PPM were 2.4 and 3.5, while the percentage of H_2O_2 formed was 78 % and 23 %, respectively. The results were obtained in a 1 M NaOH and 1 M H_2SO_4 electrolytes. Co_xO_y/C synthesized with SGM is a promising material for the production of H_2O_2.

Keywords: Oxygen reduction reaction, electrogeneration of hydrogen peroxide, cobalt oxides, electrochemical treatment.

1. INTRODUCTION

The significance of pollutants is related to the quantity emitted into the environment and many technologies have been developed to remove pollutants in large concentrations from urban wastewaters [1]. However, most organic compounds are resistant to conventional chemical and biological treatments and these substances accumulate in the environment after discharge [2].

For this reason, alternative methods, such as adsorption and stripping, are being studied as a substitute for biological and classical physico-chemical processes [3]. Of these, advanced oxidation processes (AOPs) are the best option because only chemical and advanced oxidation technologies have the ability to mineralize organic pollutants. Furthermore, these methods are the only processes able to achieve satisfactory results [3-6].

Different routes for the production of hydroxyl radicals ($^{\bullet}OH$), such as Fenton and Fenton-like reactions, are used in AOPs and cover a wide range of treatment processes under specific conditions [6,7]. Among then, the Fenton reaction is one of the cleanest and most efficient processes for the elimination of toxic compounds from wastewaters and soil [6].

Fenton’s reagent generates $^{\bullet}OH$ by reacting H_2O_2 and iron (II) salts [9-11]. The global reaction for the production of $^{\bullet}OH$ in acidic medium is:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$

The mechanism of the ferric ion catalyzed decomposition of H_2O_2 in acidic solution has been widely described by Walling and Goosen [12].

Use of Fenton’s reagent as an oxidant is attractive because iron is a highly abundant and non-toxic element, and H_2O_2 breaks down to environmentally benign products [13].

In the last decade, there has been great interest in producing H_2O_2 *in situ* to increase the efficiency of the subsequent oxidation reaction and lower the costs associated with transportation as well. H_2O_2 generated *in situ* is consumed prior to decomposition to H_2O and O_2 and leads to higher yields and selectivity for the favored reaction [3].

H_2O_2 can be generated by the two-electron reduction of oxygen at an appropriate cathodic potential. Electrogenerated H_2O_2 by the cathodic reduction of oxygen on an electrode occurs via the following equations [14-16]:

$$\text{In acid aqueous solutions: } O_2 + 2H^+ + 2\,e^- \rightarrow H_2O_2 \qquad (2)$$

$$\text{In alkaline aqueous solutions: } O_2 + 2H_2O + 2\,e^- \rightarrow H_2O_2 + 2OH^- \qquad (3)$$

Therefore, there is a continuous search for an improved electrochemical synthesis of H_2O_2 from oxygen in aqueous media [17]. However, production of H_2O_2 via electroreduction of oxygen has two main drawbacks. The low solubility of oxygen in water, sluggish kinetics [18] and low current efficiencies limit the use of the electroreduction of oxygen.

Carbon is a well known cathode for the two electron reduction of oxygen to H_2O_2 in alkaline solution [19, 20]. Graphite has been widely used in the reaction, but a gas diffusion electrode (GDE) is more common and is used to overcome the low solubility of oxygen, which causes mass transfer limitations at the cathode surface.

To enhance oxygen electroreduction to H_2O_2 at low pH (less than a pH of 12), previous research has focused on electrode materials [21–23], the influence of the pH [24], and the use of surfactants [25]. Additionally, electroreduction mediated by 2-ethyl 9,10-anthraquinone [26, 27] and the use of electrodes modified with electrocatalytic materials [28–33] has been researched. Non-noble catalysts often catalyze a two-electron process of O_2 reduction to produce H_2O_2 [34].

Considering the high activity of cobalt compounds for the production of H_2O_2 [35], the aim of this work was to compare two methods for the preparation of an electrocatalyst material (Co_xO_y/C) for H_2O_2 electrogeneration. The methods investigated include the PPM [36, 37] and the SGM [38, 39]. The performance of Co_xO_y/C materials for the reduction of oxygen to H_2O_2 in 1 M NaOH and 1 M H_2SO_4 was evaluated.

2. EXPERIMENTAL

2.1. Co_xO_y/C *materials*

Co_xO_y/C 20% (w/w) on black carbon was prepared using PPM as described by De Souza *et al.* [36, 37]. The precursor solution was prepared by dissolving citric acid - CA (Sigma-Aldrich) into ethylene glycol - EG (Synth) in 50:400 ratio at 60^oC. $CoN_2O_6.6H_2O$ (Sigma-Aldrich) was added to this solution, maintaining a ratio of 1:50:400 (metal: CA: EG). The catalysts were prepared by placing a pre-determined volume of the resin in an appropriate amount of Vulcan XC-72R carbon (Cabot Corporation), followed by the addition of EG to cover the carbon powder. These mixtures were homogenized in an ultrasonic bath for 60 min and thermally treated at 400 ºC for 2 hours under N_2 atmosphere.

In the SGM [38,39], the cobalt solution was prepared by adding the salt to 25 mL of a solution containing isopropyl alcohol (Synth) and acetic acid (Synth) 3:2 (v/v). The resultant sol–gel solutions were subjected to ultrasonic treatment (Sanders SW2000FI) for 20 min. After the homogenization step, carbon powder was impregnated with the organometallic compound and thermally treated at 400 ºC for 1 h. The final product was a CoO_X/C composite powder.

2.2. Co_xO_y/C *materials characterization*

2.2.1. Electrochemical characterization

Electrochemical measurements were conducted with a potentiostat / galvanostat Autolab PGSTAT 302 N, with a rotating disc electrode system. A platinum wire, two reference electrodes, Hg/HgO and Ag /AgCl / KCl (sat.) and a rotating ring-disk electrode (RRDE) were used as counter electrode, reference electrodes and work electrode, respectively. 1 M NaOH and 1 M H_2SO_4 were prepared from supra-pure grade reagents purchased from Merck and used as electrolytes.

The working electrodes were constructed as proposed by Paulus *et al.* [40] by dispersing 5 mg of the powder in 5 mL of water and mixing for 60 min in an ultrasonic bath. After that, 20 µL aliquots of the dispersion were pipetted onto the glassy carbon substrate of the disc. After the evaporation of the water in a nitrogen stream, 20 µL of a diluted Nafion® solution (5 wt%, Fluka) were pipetted onto the electrode surface to attach the catalyst particles onto the glassy carbon. The ratio of H_2O/ Nafion® in the solution was ca. 100/1.

For RRDE experiments an Au–Glassy carbon electrode from Pine Instruments was used as working electrode. This electrode consists of a central glassy carbon disk (area = 0.2475 cm^2) and an Au ring (area = 0.1866 cm^2). The collection efficiency of the RRDE was N = 0.37. This value was constant for all measurements.

An EDI101 rotator and CTV101 speed control unit were also used. The electrode rotation rate was varied from 100-3600 rpm and the experiments were controlled with General Purpose Electrochemical System (GPES) software.

The oxygen reduction reaction was studied in the two electrolytes. The electrolytes were saturated with oxygen for approximately 40 minutes, and the oxygen flow was maintained over the electrolyte during the entire analysis of the ORR. The measurements were obtained at a scan rate of 5 mV s^{-1}. All measurements were carried out at room temperature.

An AAnalyst 200 flame atomic absorption spectrometer (PerkinElmer, Massachusetts, USA), equipped with deuterium background correction and cobalt hollow-cathode lamps as radiation sources, was used for cobalt determination in electrolyte solutions after 20% Co_xO_y/C catalysts were prepared by PPM and SGM. The instrumental parameters were adjusted according to the manufacturer's recommendations.

3. RESULTS AND DISCUSSION

3.1. X-Ray diffraction analysis of the Co_xO_y/C

The materials were physically characterized using X-Ray Diffraction (XRD). Figure 1 shows the XRD patterns of the catalysts produced by PPM and SGM.

In the XRD patterns of the catalyst prepared by PPM, characteristic diffraction peaks were observed and attributed to Co_3O_4, according to JCPDS PDF # 76-1802. In the pattern derived from the catalyst prepared by SGM, a mixture of oxides was observed. These oxides were determined to be CoO and Co_2O_4, according to JCPDS PDF # 72-1474 and JCPDS PDF # 80-1534, respectively.

The average size of the crystallites of cobalt oxide particles were estimated using the Debye-Scherrer equation [41] at crystalline planes ((311): $2\theta = 36.8\ ^o$) for material prepared by PPM and ((111): $2\theta = 61.7\ ^o$) SGM. The values obtained were 4 and 5 nm, respectively.

Cobalt containing materials for the reduction of oxygen are generally PtCo/C or materials based on Pt [42 - 45]. These materials are frequently composed of PtCo alloys. Phase such as Co_2O_4

have not yet been observed. Even when using Co with triethylenetetramine chelate, the predominant phase is Co [46]. However, Douin *et al.* [47] study cobalt phases including Co^{4+} and using XANES, Lima and Ticianelli [48] concluded that a large fraction of Co atoms in PtCo/C electrocatalysts under alkaline conditions were present as Co_3O_4. In this study, it is important to point out that Co_3O_4 predominates in the phase and exists almost exclusively when prepared by PPM while the CoO and Co_2O_4 is present in SGM.

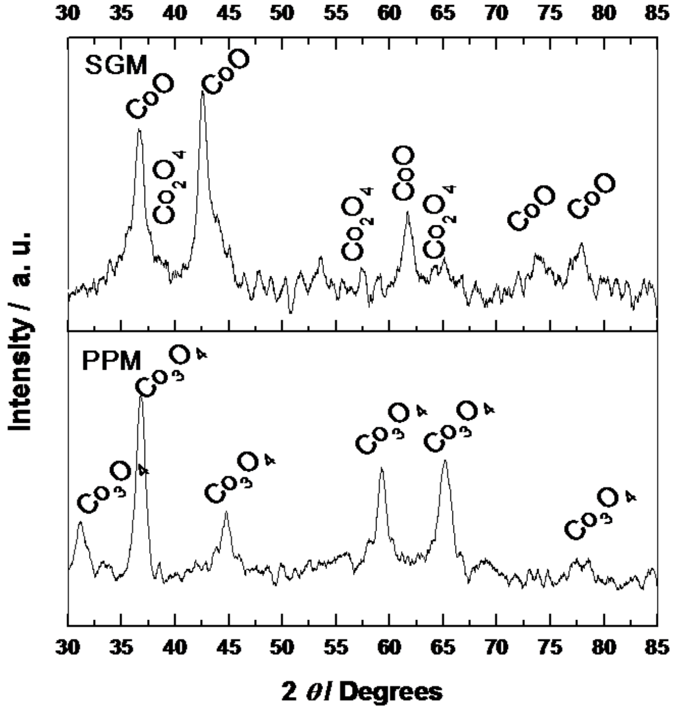

Figure 1. XRD patterns of Co_xO_y prepared by the PPM and SGM.

Wu *et al.* [49] identified that compared to commercially provided CoO, which presents submicron sizes, nanoscale CoO is more potential as conductive agent considering the dispersancy in among the active material and that nanoscale CoO particles have previously been synthesized via a sol–gel process, what is in agreement with the results obtained in Figure 1. After that, Douin *et al.* [46] affirmed that the presence of tetravalent cobalt allows reaching a good conductivity. Considering that in SGM two phases were observed including Co_2O_4 and CoO, it could give more conductivity, consequently leading to a higher activity in the ORR for H_2O_2 production.

3.2. ORR on Co_xO_y/C

The electrocatalytic activity of electrocatalysts toward the reduction of oxygen was evaluated using the ring-disk electrode method. Figure 2 compares the oxygen reduction current-potential polarization curves for SGM, PPM, Vulcan XC 72R, and Pt/C E-TEK for a rotating Au-ring/Carbon-disc electrode with 0.2475 cm^2. In this figure, the current-potential curves for the disc show the same general shape for all materials investigated. The well defined limiting current plateau indicates that ORR is controlled by diffusion in this region [44]. The carbon's disc current is two times lower than the Pt/C, as expected, since carbon features a 2-electron pathway in the ORR being the reference material for H_2O_2 production [24] while Pt/C is the reference material for the 4-electron pathway or water production. Results showed that SGM disc current was much similar to carbon, indicating a 2-eletron transferred for the H_2O_2 production. In contrast the PPM showed a disc current much similar to Pt/C featuring a 4-electron transferred or the H_2O production. Ring currents are in agreement with disc currents since the SGM showed the highest ring-current corresponding to the higher amount of H_2O_2 production.

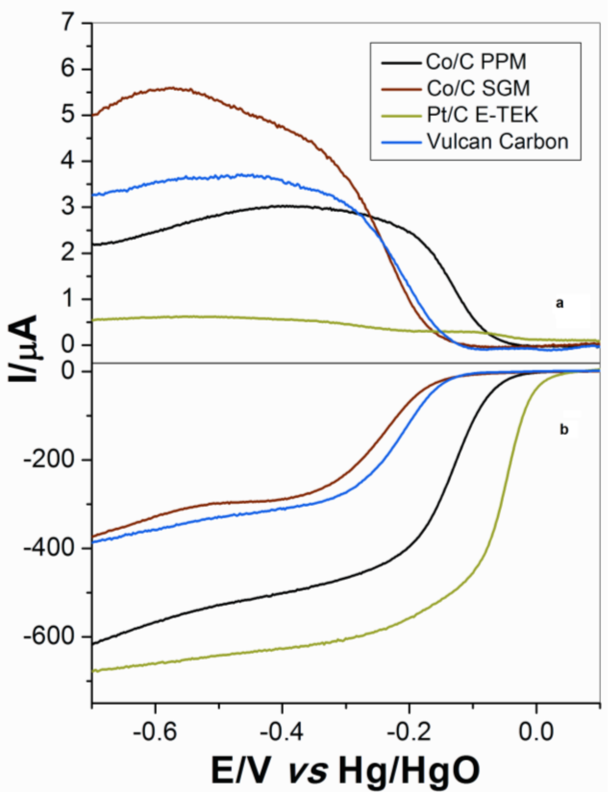

Figure 2. Current-potential polarization curves in a stationary state for ORR with different Co_xO_y/C electrocatalysts in oxygen-saturated 1 M NaOH: (a) ring current and (b) disc current. ϖ = 1600 rpm. Ring potential = 0.2 V.

To our knowledge, there are no literature references for Co/C prepared by PPM and SGM in alkaline medium or data associated with ORR polarization curves for Co/C. However, Lima *et al.* [48] showed that lower amounts of peroxide ions were formed for higher Pt/C ratios, which is in agreement with the results obtained from this study. Marcotte *et al.* [35] showed that CoAc on different carbon supports produces catalysts that are more active than the carbon supports alone for the production of H_2O_2. P. Hernández-Fernández *et al.* [44] showed that the onset potential of ORR and the performance of PtCo/C-875 throughout the polarization range were superior to other catalysts studied, such as Pt/C and Pt/C-875.

Because the ring current is proportional to the amount of H_2O_2 produced at the disc [35], the results in the literature [35, 44, 48] are in agreement with the results obtained here, where Pt/C showed the lowest ring current and the highest disc current and Co/C prepared by SGM showed the lowest disc current and the highest ring current.

The data regarding oxygen reduction for all materials studied were analyzed using the Koutechy-Levich (K-L) equation (Equation 4) and the results are displayed in the Koutechy-Levich (K-L) plot shown in Figure 3.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{-1}{nFAKC^0} - \frac{1}{\{0.62nFAD_{O2}^{2/3}\,\nu^{-1/6}C^0\omega^{1/2}\}} \qquad (4)$$

where i is the measured current, i_k and i_d are the kinetic and diffusion limited currents, respectively, k is the rate constant for the ORR, F is Faraday's constant (96484 C mol^{-1}), A is the effective projected area covered with catalyst, ω is the rotation rate, C^o is the saturated concentration of oxygen in the bulk solution, Do_2 is the diffusion coefficient of oxygen and υ is the kinematic viscosity of the solution.

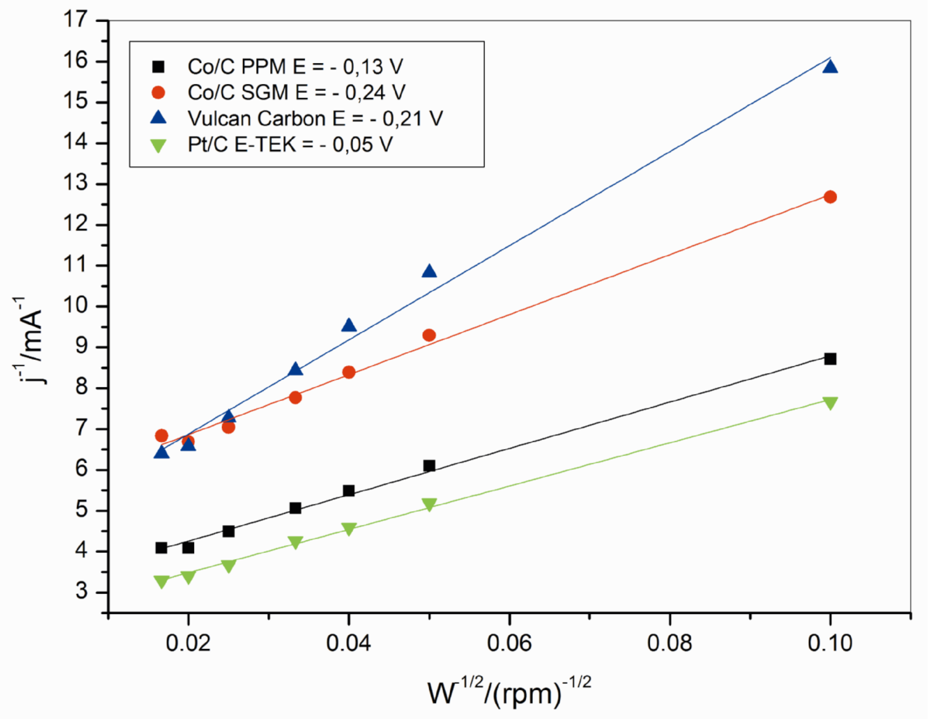

Figure 3. The Koutechy-Levich plot for 1 M NaOH. Pt/C and Vulcan carbon plots were inserted for comparison.

Figure 3 shows the Koutechy-Levich (K-L) plots for ORR with electrocatalysts prepared by PPM and SGM. Pt/C and Vulcan carbon were inserted for comparison. Carbon is the reference material for the 2-electron reduction of oxygen to H_2O_2 and Pt/C is the reference material for the 4-

electron reduction of oxygen to water. These plots are straight lines with distinct slopes and a nonzero y-intercept.

Oxygen can be directly reduced to water with the concomitant consumption of four electrons per O_2 molecule. Alternatively, oxygen can be reduced indirectly, forming H_2O_2 as an intermediate and only two electrons per O_2 molecule are consumed [43]:

$$O_2 + 3H_2O + 4e^- \rightarrow H_2O + 4OH^- \quad (5)$$

$$O_2 + 2H_2O + 2\,e^- \rightarrow H_2O_2 + 2OH^- \quad (6)$$

From the analysis of the Koutecky-Levich diagram, ORR with the material prepared by SGM followed the 2-electron transfer pathway and showed a similar slope to Vulcan carbon. In fact, materials prepared by SGM showed superior results compared to black carbon, which is the reference material for a mechanism involving 2 electrons and the formation of H_2O_2 [24].

3.2.1 Number of electrons transferred and percentage of H_2O_2.

The reaction pathway of the ORR, i.e., the relative formation rates of H_2O and H_2O_2, can be determined quantitatively with a RRDE. Feng *et al.* [50] calculated the H_2O_2% by the following equation:

$$H_2O_2\% = \frac{200 \text{ x } Ir / N}{Id + Ir / N} \quad (7)$$

where I_r is the ring current, I_d is the disk current, and N is the collection efficiency, equal to 0.37 for the present case. The procedure here used to calculate the number of electrons transferred during the ORR was the same adopted by Feng *et al.* [50].

Table 1. Values of H_2O_2 percentage and number of electrons transferred.

Electrocatalyst	n^o. electrons	% H_2O_2
Pt/C	3.9	4
vulcan carbon	2.9	51
Co/C PPM	3.5	23
Co/C SGM	2.4	74

Table 1 shows the calculated percentage of H_2O_2 produced using each material. The results were in agreement with the ring currents in Figure 3 because it is possible to confirm that SGM, which had the highest ring current, also had the highest percentage of H_2O_2 produced and Pt/C which had the lowest ring current had the lowest H_2O_2 percentage.

From the results in Table 1, Co_xO_y/C prepared using SGM transferred 2.4 and it is able to generate considerable amounts of H_2O_2 in the bulk solution, more than the Vulcan carbon, while Co_xO_y/C prepared using PPM transferred 3.5 electrons during ORR and it can be used as electrocalyst for fuel cells.

The activity tests of the electrocatalysts were also performed in acidic medium (1 M H_2SO_4) because the electrocatalysts could participate in the Fenton reaction, which is the reaction in Equation 1. However, after the utilization of 20% w/w Co_xO_y/C prepared by PPM and SGM in oxygen reduction under acidic conditions, cobalt concentrations of 1.13 $\pm$ 0.10 mg L^{-1} and 0.750 $\pm$ 0.015 mg L^{-1} were observed in the electrolyte solutions. Thus, the Co_xO_y/C prepared by both methods was soluble in acidic media.

4. CONCLUSIONS

All methods were effective for obtaining cobalt oxides supported on carbon. The Co_xO_y/C material prepared by SGM is a promising material for the H_2O_2 electrogeneration. This material forms a mixture of oxides, CoO and Co_2O_4, which conferee more conductivity and more activity toward 2-electrons transferred in ORR in 1 M NaOH. The results indicate that SGM is a superior method to PPM for producing Co_xO_y/C with the ability to generate H_2O_2. However, the PPM Co_xO_y/C PPM material can be tested as an electrocatalyst in fuel cells since it transferred 3.5 electrons for ORR without presence of Pt.

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