Electrochemical Production of Peroxocarbonate at Room Temperature Using Conductive Diamond Anodes

E. J. Ruiz-Ruiz[a], Y. Meas[b], R. Ortega-Borges[b], J. L. Jurado Baizabal[b]

[a]Universidad Autónoma de Nuevo León, UANL, Facultad de Ciencias Químicas,
Av. Universidad S/N, Ciudad Universitaria San Nicolás de los Garza, Nuevo León, México
[b] Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Departamento de Electroquímica Parque
Tecnológico Querétaro, Sanfandila, Pedro Escobedo, Querétaro C.P. 76703, México
e-mail: edgar.ruizr@uanl.mx

This work describes a method for synthesizing sodium peroxocarbonate by electoxidation of carbonate on conductive-diamond thin film electrodes in a sodium carbonate solution at room temperature. The effect of several parameters including: electrolyte concentration, current intensity, addition of Na_2SiO_3 as a stabilizing agent, and increments in temperature for sodium peroxocarbonate formation has been studied in an electrochemical *H* cell of two compartments separated by a cation-exchange membrane. The oxidant formation has been confirmed by cyclic voltammetry and *in situ* reduction during water electrolysis. The optimal experimental conditions are: the current density of 34.3 mA·cm^{-2}, an electrolyte concentration of 1M, and the addition of 4 g/L of sodium metasilicate in the two compartments of the electrochemical cell.

Keywords: peroxocarbonate, peroxosalts, diamond electrodes, electrosynthesis.

INTRODUCTION

Electro-synthetic processes for producing stable oxidant compounds of industrial or ecological interest, particularly anodic oxidation of inorganic ions on diverse electrode materials, have been intensively studied in recent years [1–3].

The electrochemical formation of those compounds is mainly carried out in strong acidic media with high oxygen overpotential in order to minimize the secondary reaction of oxygen evolution. Platinum (Pt) or metallic oxides, like PbO_2, are commonly used for the anode. Despite its lower overpotential platinum is usually the material of choice because PbO_2 anodes corrode slowly and release Pb-ions in solutions [4]. In this regard, over the last two decades many researchers have studied electrochemical oxidation as an alternative technology for the degradation of a wide variety of organic pollutants [4–6]. In addition, some studies have been focused on the use of diamond electrodes in the synthesis of oxidants that can be difficult to generate by more usual synthesis methods, most of them in acidic media [2, 7, 3, 8, 9]. Thanks to the high overpotential for water electrolysis and the large electrochemical window, enough to produce hydroxyl radicals (·OH) with high efficiency [4, 5, 10], boron-doped diamond (BDD) anodes have been shown to be suitable for electrosynthesis of powerful oxidants. These include: ferrates (FeO_4^{2-}) [6, 7, 11] peroxodiphosphate ($P_2O_8^{4-}$) [9], peroxyacetic acid (CH_3CO_3H) [12], peroxodisulfaphate ($S_2O_8^{2-}$) [3, 1, 8], perbromates (BrO_4^-) [13] or chlorine oxoanions [14], and even peroxocarbonate ($C_2O_6^{2-}$) in an alkaline medium [15, 16]. Synthesis of those compounds is very attractive, because they are strong oxidizing agents that can be used to degrade organic pollutants [17], and in other syntheses applications.

It has been reported [18] that there are two kinds of "percarbonates". One is chemical percarbonate ($Na_2CO_3 - 1.5H_2O_2$) and the other is electrolytic percarbonate. $Na_2CO_3 - 1.5H_2O_2$. The chemical percarbonate is usually obtained by simply mixing H_2O_2 and Na_2CO_3 in an alkaline solution. It is an effective oxygen-based bleaching agent used in textile, chemical, paper- and -wood industries as a source of active oxygen [19–21].

Among the oxidized forms of carbonate is $Na_2C_2O_6$, with a redox potential of 1.8 V (NHE) [22], which has a higher redox potential than perchlorate (1.201 V) or periodate (1.653 V). In this article the term SPOC will be used to refer to sodium peroxocarbonate ($Na_2C_2O_6$) in order to differentiate it from the sodium carbonate $Na_2CO_3 - 1.5H_2O_2$. The electrochemical production of SPOC has been investigated by direct oxidation of carbonate using Pt anodes [18, 23, 21] as well as BDD anodes [16, 15]. In the respective literature, the mechanism of their formation on BDD anodes implies the generation of free radicals (·OH):

$$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^-. \quad (1)$$
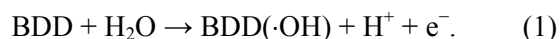
Free radicals (·OH) on the electrode surface react with bicarbonate or carbonate, oxidizing it into peroxocarbonate, according to reaction (2) [15, 22].

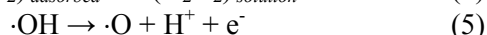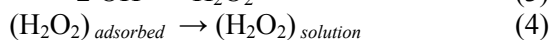$$2HCO_3^- + 2BDD(\cdot OH) \rightarrow C_2O_6^{2-} + 2H_2O. \quad (2)$$
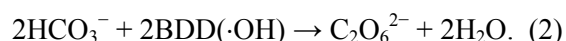
SPOC is obtained by electro-oxidation precipitates at 0–5°C, yielding a dry white powder with the

same XRD pattern as sodium percarbonate [15]. Unfortunately, peroxocarbonate in solution exhibits poor stability with a half-life estimated to be 1–2 min at 15ºC, pH 10, SPOC is hydrolyzed to peroxide [18]. In addition, heat or the presence of low levels of ions of heavy metals can accelerate its decomposition.

Certain inorganic salts, e.g. sodium metasilicate (Na_2SiO_3), have been used to stabilize sodium per-carbonate ($Na_2CO_3 - 1.5H_2O_2$) [24]. Some authors also have reported good results in stabilizing pero-xocarbonate $Na_2C_2O_6$ in solution [20, 16].

During electrosynthesis of peroxocarbonate on BDD anodes, some factors can cause the decomposition of this oxidant and decrease the generation efficiency. One of these factors is the increase of temperature due to high over voltages on the electrode surface and membrane resistance. In addition to ·OH production and formation of SPOC, several parallel parasite reactions can occur, like the generation of ozone O_3 and hydrogen peroxide.

$$2 \cdot OH \rightarrow H_2O_2 \qquad (3)$$
$$(H_2O_2)_{adsorbed} \rightarrow (H_2O_2)_{solution} \qquad (4)$$
$$\cdot OH \rightarrow \cdot O + H^+ + e^- \qquad (5)$$
$$\cdot O + O_2 \rightarrow O_3 . \qquad (6)$$

H_2O_2 generation is certainly not a parasite reaction, since it can be used to form sodium percarbonate as shown in the formula $Na_2CO_3 - 1.5H_2O_2$ by simple abduction of hydrogen peroxide to carbonate ions. The primary objective of this work is to study the effect of current density and electrolyte concentration on the electrochemical synthesis of peroxocarbonate or peroxodicarbonate at room temperature on a BDD anode.

EXPERIMENTAL

Materials and reagents

Analytical-grade Na_2CO_3 and Na_2SiO_3 were obtained from Aldrich and $KMnO_4$ from J.T. Baker and used as received. All electrolytic solutions were prepared with deionized water. BDD (from Fraunhofer IST) films were synthesized by the filament chemical vapor deposition technique on conducting p-Si substrates. The thickness of the diamond film was about 1 mm. The geometric area of the BDD anodes was 8 cm^2. Graphite was used as a cathode with a geometric area of 54 cm^2. All electrochemical experiments were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat connected to a PC for processing data.

Electro-synthesis of SPOC

Anodic oxidation of carbonate was carried out in a two-compartment H-type cell in order to insulate the anolyte and avoid SPOC reduction in cathode.

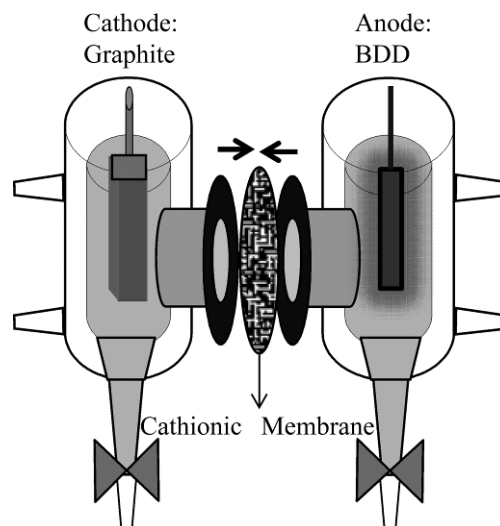Figure 1 shows a schematic representation of the experimental setup.

Fig. 1. Schematic representation of the *H* type electrochemical cell used to produce peroxocarbonate.

The anodic side of the cell contained 80 mL of carbonate solution Na_2CO_3 at different concentrations, and separated from the catholyte by a cation-exchange membrane (Asahi) with a cross-sectional area of 6.2 cm^2. No stirring was applied to the anolyte except prior to sampling. The distance from the membrane to the anode was 5 cm and it was 7 cm to the cathode. Constant-current electrolyses were conducted over a period for 3 h at current density levels from 31.2 mA·cm^{-2} to 37.5 mA·cm^{-2}. The temperature was initially 25±2°C and it was recorded during the electrolysis experiments. Every 30 min, a 5 mL sample was taken from each compartment and replaced by an equal volume of a fresh solution. Total peroxocarbonate concentration in the solution was measured using a titration by the standard $KMnO_4$ method [25].

Cyclic Voltammetry

Cyclic Voltammetry was carried out in a solution immediately after the anodic synthesis of SPOC in a conventional three-electrode electrochemical cell. In this cell, a BDD was used as the working electrode, a graphite bar as the auxiliary or counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The sweep rate was 10 mV/s^{-1} in the reduction sense.

In situ detection of SPOC was done using an H-type cell with 4 electrodes using and a potentiostat in the bi-potentiostat mode. In the cathodic compartment a graphite bar is used as the counter electrode. On the anodic side there was the reference electrode (SCE) and two work electrodes: BDD (8 cm^2) designated as the working electrode one (WE1) and another BDD (2 cm^2) designated as the working electrode two (WE2). The electrochemical

generation was done in WE1 for a sweep potential from 0 to 3.8 V (SCE) at 2.5 mV s^{-1}. The WE2 was maintained at − 1.45 V (SCE). The distance between the WE1 and WE2 was 1 cm.

Current efficiency was calculated using equation (7). Where n is the number of electrons consumed to generate one molecule of SPOC according to the mechanism in EQ ($n = 2$), F is the Faraday constant (96,487 Cmol^{-1}), C is the concentration of SPOC (mol L^{-1}), V_s is the solution volume (L), and I represents the applied current (A) at sampling time t (s).

$$\eta(\%) = \frac{nFCV_s}{\int_0^t idt} \times 100. \qquad (7)$$

RESULTS

Effect of the presence of stabilizer

Under open circuit conditions, no oxidant products were detected in any cell arrangement. The effect of the presence of sodium metasilicate Na$_2$SiO$_3$ (SMSC) as a stabilizer of peroxocarbonate was evaluated by adding 4 gL^{-1} of stabilizer. Figure 2 shows the concentrations of SPOC obtained applying a current density of 31.2 mA·cm^{-2} under different electrolysis conditions in Na$_2$CO$_3$ 1M at pH 10.8: i) without stabilizer; ii) with 4g L^{-1} of stabilizer. A BDD was used as the working electrode, a graphite bar as the auxiliary or counter electrode, and SCE as the reference electrode. The sweep rate was 10 mV s^{-1} in reduction sense.

Figure 2b shows that the presence of SMSC enhanced the production of SPOC, reaching about 25 mM after 3 hour of electrolysis. This is 10 mM more than is produced in the absence of a stabilizing agent.

During the first 1.5 hours of the synthesis, in both experiments, there was a linear increase in the concentration of SPOC. After that time, changes in concentrations were minimal. This can be attributed to chemical decomposition and to the effect of temperature [18], because the increment is about 6°C at the end of each experiment. The membrane also acted as a resistive element in the electrochemical cell. This was confirmed by an increase in the temperature of the solution mainly on the anodic side. It is worth mentioning that Na$_2$SiO$_4$ did not protect the SPOC molecules from destruction by temperature.

This behavior is also reflected in the current efficiency for SPOC production. In all cases the highest efficiencies for both electrodes were obtained in the first few minutes of polarization, with the current efficiency of 25% in the presence of a stabilizer and of 22% without SMSC. After that, the efficiency decreased over time as the rate of SPOC accumulation decreased until it reached the values of 15% and

9%, respectively. This result indicates that addition of sodium metasilicate increases the stability of SPOC and consequently the total current efficiency. However, efficiency also is affected by the decomposition of free radicals according to reactions (3)–(6) and by the oxygen evolution directly on the anode (reaction 8) [18]:
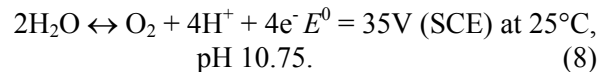
$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \; E^0 = 35V \text{ (SCE) at } 25°C,$$
$$\text{pH } 10.75. \qquad (8)$$

Figure 3 shows the influence of the concentration of Na$_2$CO$_3$ solution on the electrogeneration of SPOC. Experiments were carried out in 0.5, 1, and 2M of Na$_2$CO$_3$ solutions, applying 31.2 mA·cm^{-2} in a divided cell, with the addition of 4g L^{-1} of sodium metasilicate. In all cases, SPOC concentration increased rapidly for the first hour of electrolysis. However, after that, the velocity of accumulation decreased. The concentration as function of time became almost asymptotic in the 0.5M solution. In this case, the concentration of SPOC after one hour was 9.1 mM, which was more than 70% of the total oxidant that was synthesized within 3 hours (11.25 mM).

Changes in slopes using 1 and 2M solutions of Na$_2$CO$_3$ are similar but not as pronounced as in the 0.5M solution. The accumulated concentration of SPOC in 1M solution reached 26.5 mM. This was more than the double quantity obtained in the 0.5M solution of carbonate. However, when the concentration of electrolyte was doubled again, to the concentration of 2M, the SPOC produced was 30 mM at the end of electrolysis. Differences in SPOC concentrations obtained can be attributed primarily to the effect of temperature during electrolysis, because of the poor stability of SPOC. The final ΔT with respect to the initial room temperature were: 5.8°C for the 2M carbonate solution, 6.1°C for the 1M, and 7°C for the 0.5M concentration. This is attributed to the electrical resistance of the solution and membrane and corresponds to the high cell voltage shown in the Table for each current. Heating on the surface and around the anode may have caused accelerated decomposition of the product.

Evidently, since current efficiency is a function of the concentration of, it shows a similar behavior. Figure 3b presents the current efficiency for SPOC generation. The maximum efficiencies were 18.9, 25.7, and 29.1%, respectively, for each solution in the early phase of the experiment. Later, the efficiency decreased dramatically, to the final values of 6%, 15% and 17%, because of the difficulty of accumulation SPOC in a solution.

These results indicate that, although it is more efficient to use a 2M solution, this does not improve the carbonate/oxidant relationship. In order to determine the relationship of the oxidant to carbonate, the content of the active oxygen was calculated by
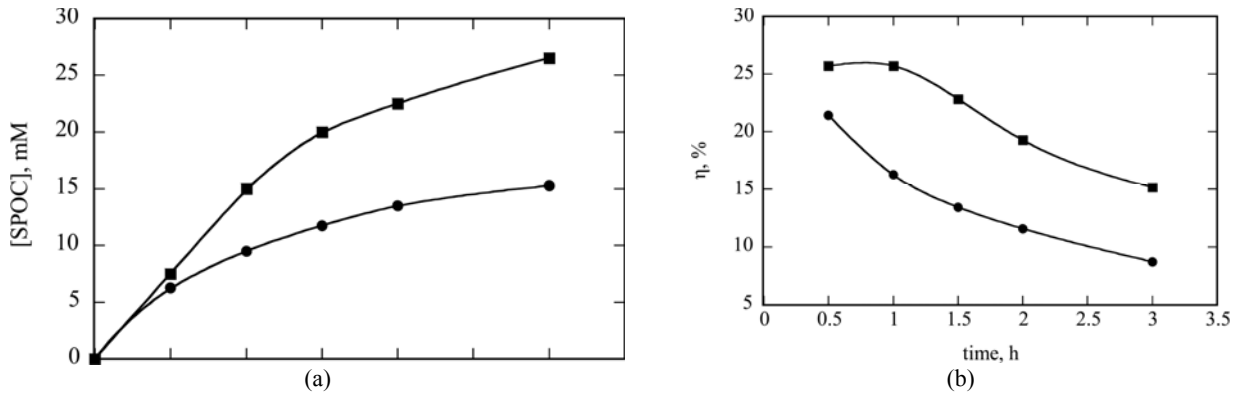
Fig. 2. Effect of addition of sodium metasilicate as stabilizer in a 1M Na₂CO₃ solution. (a) on SPOC concentration and (b) current efficiency at 31.2 mA·cm⁻². • in absence; ■ with addition of 4 mgL⁻¹ of sodium metasilicate.
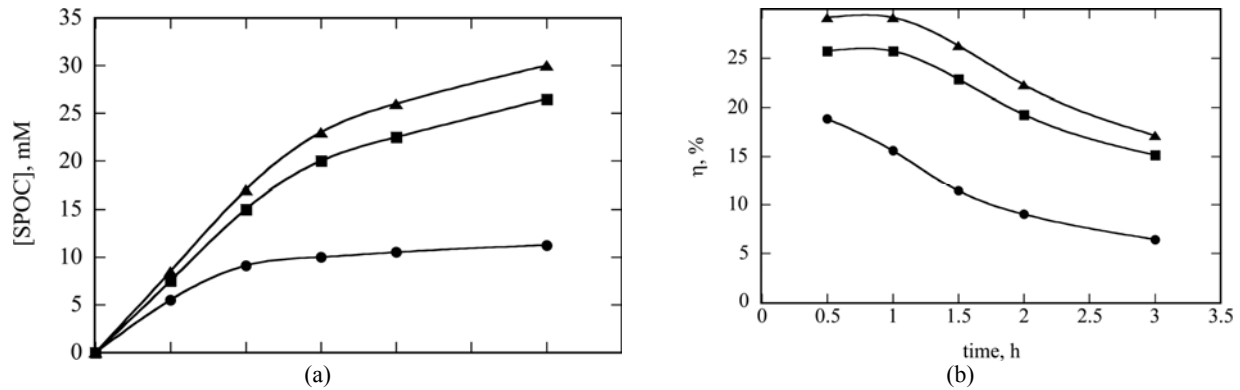

Fig. 3. Influence of concentration of Na₂CO₃ solution as supporting electrolyte and precursor of SPOC on (a) concentration and (b) current efficiency. ● 0.5M solution; ■ 1M solution; ▲ 2M solution current density applied 31.2 mA·cm⁻².

titration with the permanganate method, using the equation:

$$O\% = \left[(V - B) NA \times \frac{0.008}{W} \right] \times 100. \qquad (9)$$

Where O% represents the weight percentage of the active oxygen, V is the required volume of titrant, B is the required volume of titrant needed for the blank, N is the normality of titrant, A is the aliquot factor, and w corresponds to the grams of sample used (in solution).

The Table summarizes the effect of electrolyte concentration on the active oxygen content (O%), average current efficiency (η), cell potential (E), and final increase in temperature (ΔT) for producing SPOC on the BDD anode at 31.2 mA cm⁻². As shown in the Table, the highest SPOC content (30 mM) and average current efficiency (12%) were obtained in a carbonate 2M solution. However, the oxidant content (0%) was greater using only 1M with a value 0.404% obtained with an average efficiency of 22%. In a less concentrated carbonate solution, the oxidant power was weaker and efficiency lower. It can be accounted for in the following way: after reaching a certain concentration of SPOC, the charge transportation is limited to the charge transference on the electrode surface, but not to the diffusion on the electrolyte, as evidenced by high voltage

levels reached during electrolysis; the raise of temperature was registered in all experiments.

Table. Influence of electrolyte concentration on the SPOC production in function of Na₂CO₃ concentration at BDD anodes in a divided electrochemical cell applying 31.2 mA·cm⁻².

Na₂CO₃	[Na₂C₂O₆] mM	% O	average η/%	E/V	ΔT/°C
0.5M	11.25	0.171	12	9.8	7
1M	26.5	0.404	22	8.5	6.1
2M	30	0.243	25	7.8	5.8

SPOC reduction

Evidently, SPOC concentration depends on the duration of electrolysis, and different quantities of oxidant can be obtained by changing this duration. In order to confirm the formation and electrochemical reduction of SPOC, cyclic voltammograms were obtained after the electrolysis. The cyclic voltammograms in Fig. 4 show the cathodic part after electrolysis applying 37.5 mA·cm⁻². A for different times (0, 30, 120, and 180 min) in a 1M Na₂CO₃ solution in the presence of sodium metasilicate. A 5 mL sample was taken from the anodic compartment and SPOC was quantified by titration with thiosulphate. The concentrations obtained were 8, 22, and 26 mM. A cyclic voltammetry was made immediately in the reduction sense using the BDD as the work electrode
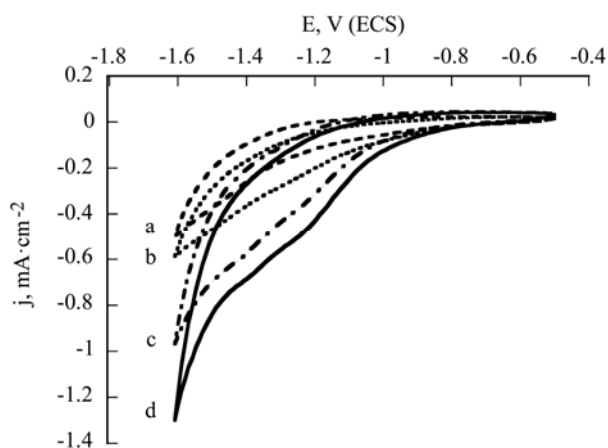
Fig. 4. Cyclic voltammograms of boron diad doped electrode after polarization of electrode in a 1M Na_2CO_3 solution. Sodium peroxocarbonate concentrations quantified: (a) 0; (b) 8; (c) 22; (d) 26 mM. Sweep rate 10 mV s^{-1}.
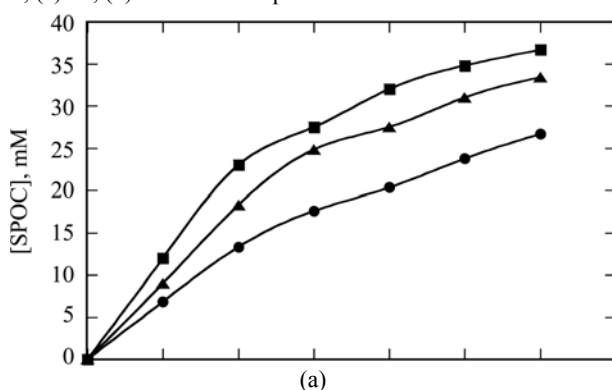

Fig. 5. *In situ* generation and detection of SPOC on BDD electrodes in 1M Na_2CO_3 solution. Lower line: polarization curve at sweep rate 2.5 mVs^{-1} in anodic sense (W1). Upper line: simultaneous response on BDD at -1.45 V vs ECS for SPOC reduction.

Fig. 6. Influence of current density on the anodic synthesis of SPOC in 1M Na_2CO_3 solution. (a) concentration and (b) current efficiency. ● 31.2 mA·cm^{-2}; ■ 34.3 mA·cm^{-2}; ▲ 37.5 mA·cm^{-2}.

in a typical three electrode electrochemical cell. A graphite bar was used as the counter electrode and SCE as the reference. The cyclic voltammograms in Fig. 4 show the cathodic part of the scans. Increases in current can be observed in potentials between 1 and 1.5 V vs. SCE with respect to non-electrolyzed solution. The peak current increases with SPOC concentration quantified. This behavior has been observed during synthesis of other peroxocompounds obtained under similar conditions. These peaks are attributed to the reduction of the electrogenerated $K_2S_2O_8$ [3].

An experiment was carried out in a four-electrode electrochemical cell, using a 1 cm^2 BDD as a working electrode 1 (W1) and a 5 cm^2 BDD as W2. In W1, a linear sweep at 2 mV s^{-1} in the oxidation direction was carried out, while in electrode W2 the potential was set at -1.45 V (SCE), enough to reduce the SPOC formed during polarization on W1 electrode.

The lower graph shows the polarization curves in the oxidation direction at 10 mV s^{-1} over DDB (W1). The upper graph shows the reduction current response at the W2 electrode. It was observed that there was not a substantial response in W2 after the electrolysis of water in W1. Upon initiation of water oxidation (> 2 V) in the diamond electrode W1,
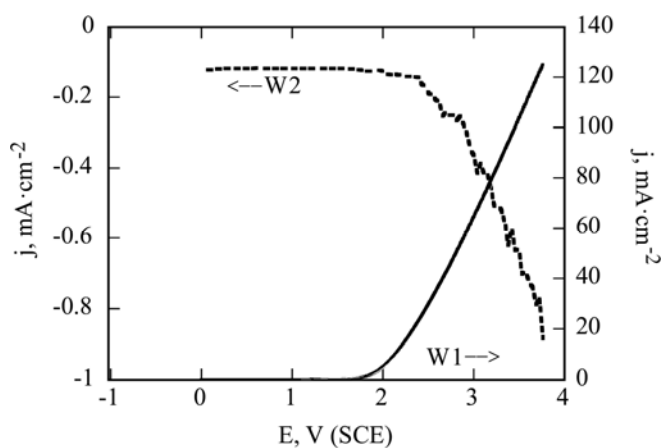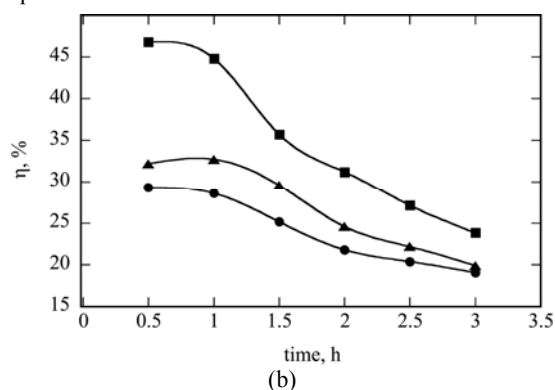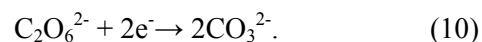
sodium percarbonate is formed. Then it is carried by diffusion to the second electrode where SPOC is reduced, with a consequent increase in the reduction current in the electrode. SPOC reduction can be represented by equation (10). However, Osetrova and co-workers [21] have suggested that several organic compounds, such as methane, ethylene and formaldehyde, are also formed in a complex reduction mechanism.

$$C_2O_6^{2-} + 2e^- \rightarrow 2CO_3^{2-}. \qquad (10)$$

When the anodic process is insulated by using a cationic membrane, the SPOC that is generated cannot pass to the cathodic compartment, which avoids its destruction by electro reduction in the cathode.

These results confirm that SPOC is formed as the result of CO_3^{2-} oxidation by free radicals during water discharge according to equation 2. Then SPOC is carried by diffusion to the second electrode, where SPOC is reduced, with a resultant increase in the reduction current in the electrode.

Effect of current on sodium peroxocarbonate generation

Figure 6 shows the effect of current density in the range 31.2–37.5 mA·cm^{-2} on anodic production of SPOC in a 1M Na_2CO_3 solution in a two compart-

ment electrochemical cell. It can be observed that peroxocarbonate generation is strongly dependent on current density. The highest SPOC concentration reached was 37 mM. This was obtained after 3 hours of polarization applying 34.3 mA·cm^{-2}. Applying higher current density (37.5 mA·cm^{-2}) decreased the final accumulation of SPOC considerably to 33 mM.

This behavior is reflected in the current efficiency (Fig. 6b), where the best values were obtained during the early stages of polarization. The graphic shows a big difference in the values obtained when applying currents densities of 31.2, 34.3 and 37.5 mA·cm^{-2}. SPOC is produced with efficiencies up to 45% by applying a current density of 34.3 mA·cm^{-2}. Clearly, the decrease in current efficiency is due to a diminution of the generation rate. Some authors explain this in terms of mass transfer limitations or by some sort electrochemical or chemical destruction of the oxidants that were formed [26]. However, there is another important factor that could cause the chemical degradation of SPOC.

This other factor which could affect the efficiency is temperature. The temperature increase after 3 hours was 12°C for 37.5 mA·cm^{-2}, 10°C for 34.3 mA·cm^{-2}, and 6°C for 31.2 mA·cm^{-2}. This is attributed to the electrical resistance of the solution and membrane and corresponds to the high cell voltage. The heating on the surface and around the electrode may cause accelerated decomposition of the product (4) despite the presence of stabilizier.

CONCLUSIONS

Sodium peroxocarbonates ($Na_2C_2O_6 + Na_2CO_4$) in solution are formed by oxidation of Na_2CO_3 in a process that implies there are free radicals on the BDD anode. The effects of these parameters including: electrolyte concentration, current, addition of stabilizer agent composition, and temperature on the formation of sodium peroxocarbonate have been studied. SPOC can be electro reduced at the cathode, and for that reason, the use of a membrane is recommended. Active oxygen content is better when SPOC is synthesized in a 1M solution than it is in either a 2M or 0.5M solution under these experimental conditions. The best current efficiency was obtained by applying 34.3 mA·cm^{-2} in a Na_2CO_3 solution in the presence of 4 g L^{-1} of Na_2SiO_3 as a stabilizer. Temperature is an important factor in the decomposition of SPOC.

ACKNOWLEDGMENTS

REFERENCES

1. Michaud P.A., Mahé E., Haenni W., Perret A., Comninellis C. Preparation of Peroxodisulfuric Acid using Boron- Doped Diamond thin Film Electrodes. *Electrochem Solid State.* 2000, **3**(2), 77–79.

2. Cañizares P., Sáez C., Sánchez-Carretero A., Rodrigo M.A. Synthesis of Novel Oxidants by Electrochemical Technology. *J Appl Electrochem.* 2009, **39**(11), 2143–2149.

3. Serrano K., Michaud P.A., Comninellis C., Savall A. Electrochemical Preparation of Peroxodisulfuric Acid using Boron-Doped Diamond thin Film Electrodes. *Electrochimica Acta.* 2002, **48**(4), 431–436.

4. Michaud P.A., Panizza M., Ouattara L., Diaco T., Foti G., Comninellis C. Electrochemical Oxidation of Water on Synthetic Boron-Doped Diamond thin Film Anodes. *J Appl Electrochem.* 2003, **33**(2),151–154.

5. Marselli B., Garcia-Gomez J., Michaud P.A., Rodrigo M.A., Comninellis C. Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes. *J Electrochem Soc.* 2003, **150**(3), D79–D83.

6. Sáez C., Rodrigo M.A., Cañizares P. Electrosynthesis of Ferrates with Diamond Anodes. *American Institute of Chemical Engineers J.* 2008 **54**(6), 1600–1607.

7. Villanueva-Rodríguez M., Sánchez-Sánchez C.M., Montiel V., Brillas E., Peralta-Hernández J.M., Hernández-Ramírez A. Characterization of Ferrate Ion Electrogeneration in Acidic Media by Voltammetry and Scanning Electrochemical Microscopy. Assessment of its Reactivity on 2,4-dichlorophenoxyacetic Acid Degradation. *Electrochimica Acta.* 2012, **64**, 196–204.

8. Khamis D., Mahé E., Dardoize F., Devilliers D. Peroxodisulfate Generation on Boron-Doped Diamond Microelectrodes Array and Detection by Scanning Electrochemical Microscopy. *J Appl Electrochem.* 2010, **40**(10), 1829–1838.

9. Weiss E., Sáez C., Groenen-Serrano K., Cañizares P., Savall A., Rodrigo M.A. Electrochemical Synthesis of Peroxomonophosphate using Boron-Doped Diamond Anodes. *J Appl Electrochem.* 2008, **38**(1), 93–100.

10. Chaplin B.P., Hubler D.K., Farrell J. Understanding Anodic Wear at Boron Doped Diamond Film Electrodes. *Electrochimica Acta.* 2013, **89**, 122–131.

11. Sánchez-Carretero A., Rodrigo M.A., Cañizares P., Sáez C. Electrochemical Synthesis of Ferrate in Presence of Ultrasound using Boron-Doped Diamond Anodes. *Electrochem Commun.* 2010, **12**(5), 644–646.

12. Cotillas S., Sánchez-Carretero A., Cañizares P., Sáez C., Rodrigo M.A. Electrochemical Synthesis of Peroxyacetic Acid using Conductive Diamond Electrodes. *Ind Eng Chem Res.* 2011, **50**(18), 10889–10893.

13. Sáez C., Cañizares P., Sánchez-Carretero A., Rodrigo M.A. Electrochemical Synthesis of Perbromate using Conductive-diamond Anodes. *J Appl Electrochem.* 2010, **40**(10), 1715–1719.

14. Sánchez-Carretero A., Sáez C., Cañizares P., Rodrigo M.A. Electrochemical Production of Perchlorates using Conductive Diamond Electrolyses. *Chem Eng J*. 2011, **166**(2), 710–714.

15. Saha M.S., Furuta T., Nishiki Y. Electrochemical Synthesis of Sodium Peroxycarbonate at Boron-Doped Diamond Electrodes. *Electrochem Solid St*. 2003, **6**(7), D5–D7.

16. Ruiz E.J., Ortega-Borges R., Jurado J.L., Chapman T.W., Meas Y. Simultaneous Anodic and Cathodic Production of Sodium Percarbonate in Aqueous Solution. *Electrochem Solid St*. 2009, **12**(1), E1–E4.

17. Costa C.R., Montilla F., Morallón E., Olivi P. Electrochemical Oxidation of Acid Black 210 Dye on the Boron-Doped Diamond Electrode in the Presence of Phosphate Ions: Effect of Current Density, pH, and Chloride Ions. *Electrochimica Acta*. 2009, **54**(27), 7048–7055.

18. Zhang J., Oloman C. Electro-Oxidation of Carbonate in Aqueous Solution on a Platinum Rotating Ring Disk Electrode. *J Appl Electrochem*. 2005, **35**(10), 945–953.

19. Koukabi N. Sodium Percarbonate: A Versatile Oxidizing Reagent. *Synlett*. 2010 (EFirst), 2969–2970.

20. Manoharan G.M., Raghavendran N.S., Narasimham K.C. Electrolytic Preparation of sodium and Potassium Percarbonate. *Transactions of the SAEST*. 2000, **35**(2), 69–72.

21. Osetrova N.V., Bagotzky V.S., Guizhevsky S.F., Serov Y.M. Electrochemical Reduction of Carbonate Solutions at Low Temperatures. *J Electroanal Chem*. 1998, **453**(1–2), 239–241.

22. Saha M.S., Furuta T., Nishiki Y. Conversion of Carbon Dioxide to Peroxycarbonate at Boron-doped Diamond Electrode. *Electrochem Commun*. 2004, **6**(2), 201–204.

23. Petrucci E., Montanaro D. Anodic Oxidation of a Simulated Effluent Containing Reactive Blue 19 on a Boron-Doped Diamond Electrode. *Chem Eng J*. 2011, **174**(2–3), 612–618.

24. Zhubrikov A.V., Legurova E.A., Gutkin V., Uvarov V., Khitrov N.V., Lev O., Tripol'skaya T.A., Prikhodchenko P.V. XPS Characterization of Sodium Percarbonate Granulated with Sodium Silicate. *Rus J Inorganic Chemistry*. 2009, **54**(9), 1455–1458.

25. ASTM International WC, PA, 2003, ASTM D2180-89 (2008). *Standard Test Method for Active Oxygen in Bleaching Compounds*. ASTM. 2008.

26. Martínez-Huitle C.A., Brillas E. Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods: A General Review. *Appl Catal B-Environ*. 2009, **87**(3–4), 105–145.

Реферат

В работе описан метод синтеза пероксокарбоната натрия при комнатной температуре путем электроосаждения карбоната на проводящие алмазные тонкопленочные электроды. Целью было изучение роли таких параметров, как концентрация электролита, интенсивность тока, добавление Na_2SiO_3 в качестве стабилизирующего компонента, а также повышение температуры при образовании пероксокарбоната натрия в электрохимической ячейке водорода, состоящей из двух отделений, разделяемых катионобменной мембраной. Образование окислителя подтверждено циклической вольтамперометрией и восстановлением *in situ* при электролизе водного раствора. Оптимальные условия эксперимента: плотность тока 34,3 мА·см$^{-2}$, концентрация электролита 1М, при добавлении 4 g/L метасиликата натрия в оба отделения электрохимической ячейки.

Ключевые слова: пероксокарбонат, пероксосоль, алмазные электроды, электросинтез.