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Electrochemical production of perchlorates using conductive diamond electrolyses

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ABSTRACT

In this work, the electrochemical production of perchlorates with conductive-diamond electrodes is studied. The use of different chlorine raw materials, and the effect of several operation parameters (current density and pH) are studied in order to increase knowledge about production of chlorine oxoanions. Results show that the conductive-diamond electrolysis of different raw chlorine solutions leads to the production of a chlorine oxospecies mixture with significant concentrations of hypochlorite, chlorite, chlorate and also of perchlorate, and that complete conversion to perchlorate can be achieved if large current charges are passed through the cell. Alkaline pH and high current density seems to favor the production of perchlorate. The very significant increase in the perchlorate production with the current density may be related to the fact that in conductive-diamond electrolysis high current densities favor hydroxyl radicals formation. The counter ion of the chloride salts used as raw materials does not seem to influence the efficiency of the electrochemical process but on the stability of the perchlorate electrogenerated. On the contrary, the type of chlorine raw matter does not affect to the efficiency, but just on the stoichiometric current charge needed to complete the process.

1. Introduction

The electrolysis of chloride solutions with dimensionally stable anodes (DSA) is a process used presently to produce chlorine and hypochlorite. It is very simple and well-known, with fully developed technologies, and this allows its use even on in situ applications, such as the dosing of hypochlorites to swimming pools for disinfection purposes [1,2]. As well, DSA is also use to produce chlorates for a long time [3–5], being a very important industrial process, although chlorate synthesis has also been studied with hypochlorite as raw material [6].

With respect to perchlorate, the majority of the studies of perchlorate production use chlorate as raw material [7–9]. Nevertheless, some studies also use chloride as a raw material to produce perchlorates, even with graphite electrodes [10,11] and recently [12–15], the occurrence of perchlorates during electrolyses of chloride solutions with conductive diamond electrodes have been discussed in literature. In this context, better properties of conductive-diamond electrodes compared with other more conventional ones have attracted much attention in the recent years; these electrodes has shown a higher chemical and electrochemical stability, and a higher current efficiency in many oxidative processes. In addition, the high overpotential for water electrolysis is the more important property of conductive-diamond in the processing of aqueous solutions. These properties characteristic of conductive-diamond anodes are responsible of the turn of electrochemical oxidation into a very promising technology in the electrosynthesis of powerful oxidants [16–20].

Perchlorate ion is the least reactive oxidizer of the chlorine oxoanions. This is apparently inconsistent, since higher oxidation numbers are expected to be progressively stronger oxidizers, and less stable. Perchlorate has in fact the highest redox potential and is the least stable thermodynamically, but the central chlorine is a closed shell atom, and well protected by the four oxygens. Perchlorate salts are used in pyrotechnics, in manufacture of matches, munitions, and in the chemical analytical industry. Other perchlorate compound uses include additives in lubricating oils, tanning, fabric fixes, etc. Industrially, perchlorates are exclusively prepared by the electrochemical method [7–11]. In the past, thermal decomposition of chlorate has been used but since this process is very inefficient it has been abandoned long ago. Chemical oxidation of chlorates is currently not very economical either.

The main aim of this work is to study the electrochemical production of perchlorates with conductive diamond electrodes in double-compartment electrochemical flow cells from different chlorine raw materials. To develop a realistic process, and taking into account that high concentration of chlorine compounds may damage the diamond layer of the electrodes in industrial processes, diluted solutions of raw matter were used. For this reason, not

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brines but raw chlorine solutions, are used in the study. In addition, it is aimed to quantify the effect of several parameters, such as the current density or the pH, on these processes, in order to increase knowledge about production of chlorine oxoanions, with the future aim of improving its industrial production or hypochlorite disinfection.

2. Experimental

2.1. Analytical procedures

Chlorine species were determined by ion chromatography (column, Metrosep A Supp 4; mobile phase, 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$; flow rate, 1 ml min^{-1}). In the case of hypochlorite, the peak of chromatogram interferes with the chloride peak, therefore, the determination is realized by titration with As_2O_3 in NaOH 2 M.

2.2. Electrochemical cell

The electrosynthesis was carried out in a double-compartment electrochemical flow cell. A cationic exchange membrane (STEREOM L-105) was used to separate the compartments. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 each and an electrode gap of 15 mm. The anolyte and the catholyte were stored in dark glass tanks and circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point. The pH was monitored by means of the WTW-InoLab pH meter. The pH was kept constant at the desired set point (±0.1 units) by the continuous addition of sodium hydroxide.

2.3. Preparation of the diamond electrode (BDD electrode)

Boron-doped diamond (BDD) films were provided by CSEM (Switzerland) and synthesised by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si⟨1 0 0⟩ wafers (0.1 Ω cm, Siltronix). The temperature range of the filament was 2440–2560 °C and that of the substrate was 830 °C. The reactive gas was methane in excess dihydrogen (1% CH_4 in H_2). The dopant gas was trimethylboron with a concentration of 3 mg dm^{-3}. The gas mixture was supplied to the reaction chamber at a flow rate of 5 dm^3 min^{-1}, giving a growth rate of 0.24 $\mu m\, h^{-1}$ for the diamond layer. The resulting diamond film thickness was about 1 μm. This HF CVD process produces columnar, random texture and polycrystalline films with an average resistivity of 0.01 Ω cm.

2.4. Experimental procedures

Bench scale electrolyses under galvanostatic conditions were carried out to determine the influence of the main parameters in the process. The anolyte consisted of 0.1 M solutions of NaCl, LiCl and $NaClO_3$, and 0.05 M solutions of $BaCl_2$, $Ca(OCl)_2$. The catholyte consisted of water with NaOH solutions. The range of current densities employed was 150–1000 A m^{-2} in the synthesis of peroxosalts. The range of pH studied was 2–10.

3. Results and discussion

Fig. 1a shows the time-course of intermediates formed during the electrolysis of a solution containing 0.1 M NaCl in a double-compartment cell equipped with DSA electrodes. As it can be observed, the electrolysis of chloride in alkaline conditions leads to the production of a mixture of hypochlorite, chlorite and chlorates.

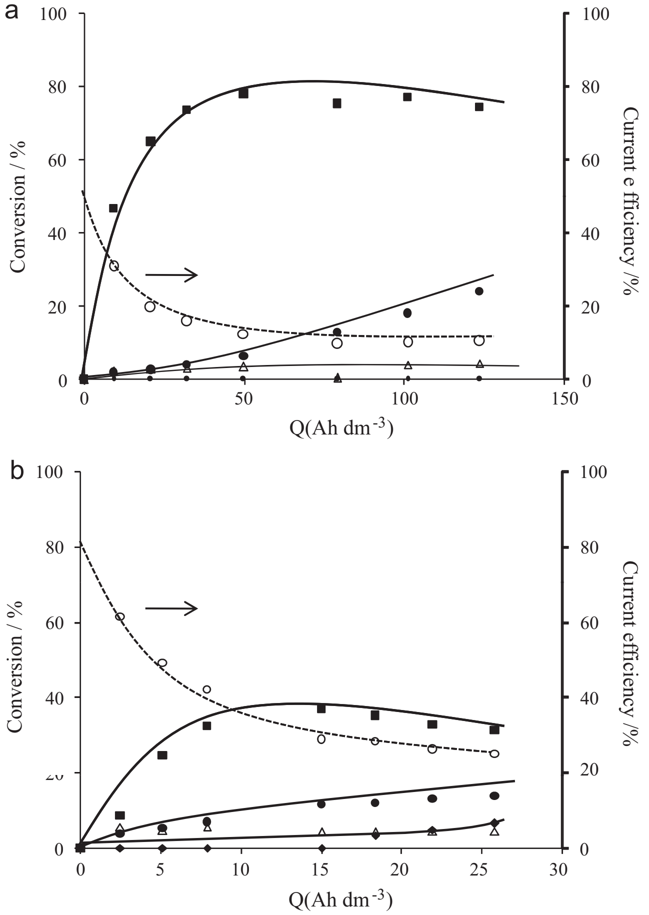

Fig. 1. Variation of the current efficiency (○) and of the conversion to chlorine species electrogenerated during (a) DSA and (b) BDD electrolysis of NaCl solutions (■) ClO^-, (△) ClO_2^-, (○) ClO_3^-, (●) ClO_4^- (0.1 M NaCl, *j* 300 Am^{-2}, *T* 35 °C, pH 10).

Conditions used are far from those typically used in the industrial production of hypochlorite and chlorates (room temperature and diluted raw material, not a brine) and the observed production of perchlorate is nil. Just on the contrary Fig. 1b shows the electrolysis of the same sodium chloride solution in double-compartment cells with conductive diamond electrodes. The use of these anodes also leads the production of a chlorine oxospecies mixture with significant concentrations of hypochlorite, chlorite, chlorate and, in this case, of perchlorate. As it can be observed, in both cases the current efficiency to global oxidants generation decreases during the experiment, being significantly greater for the electrolysis with the conductive-diamond electrode. The continuous decrease in the average current efficiency to global oxidants generation can be explained in terms of mass transfer limitations because in the batch system studied the concentration of reactant decreases continuously during operation of the process.

Likewise, the higher efficiencies obtained with BDD anodes may be related to the presence of hydroxyl radicals (Eq. (1)). It is reported [17,19,21] that large quantities of these radicals are formed during electrolyses of aqueous solutions. These radicals can oxidize other compounds in a region close to the anode surface (Eqs. (2) and (3)), or in the presence of chlorides, they can oxidize this raw material successively to different oxochlorinated compounds (Eqs. (3)–(7)). This may explain the higher current efficiencies obtained during the electrolyses, and also the occurrence of the perchlorates when using conductive-diamond as anode material [12], and not with DSA anodes, in which the occurrence of hydroxyl radicals during

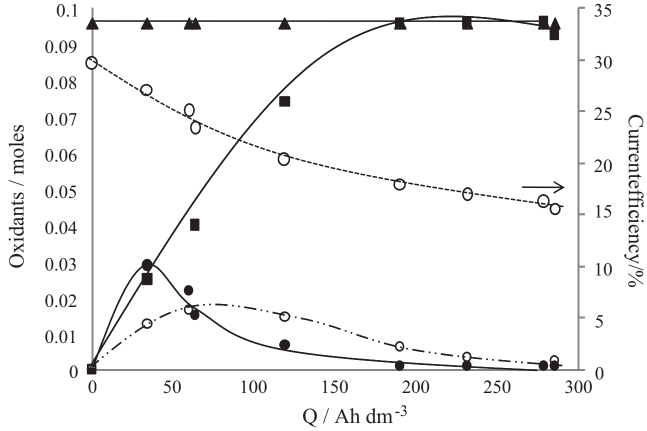

Fig. 2. Variation of chlorine oxospecies and current efficiency with electric charge in the electrolysis of NaCl solutions (●) ClO^-, (○) ClO_3^-, (■) ClO_4^-, and (▲) total chlorine (0.1 M NaCl, j 1000 Am^{-2}, T 35 °C, pH 10).

electrolyses of aqueous solutions is very questionable.

$$H_2O \rightarrow OH^{\bullet} + H^+ + e^- \quad (1)$$

$$2OH^{\bullet} \rightarrow H_2O_2 \quad (2)$$

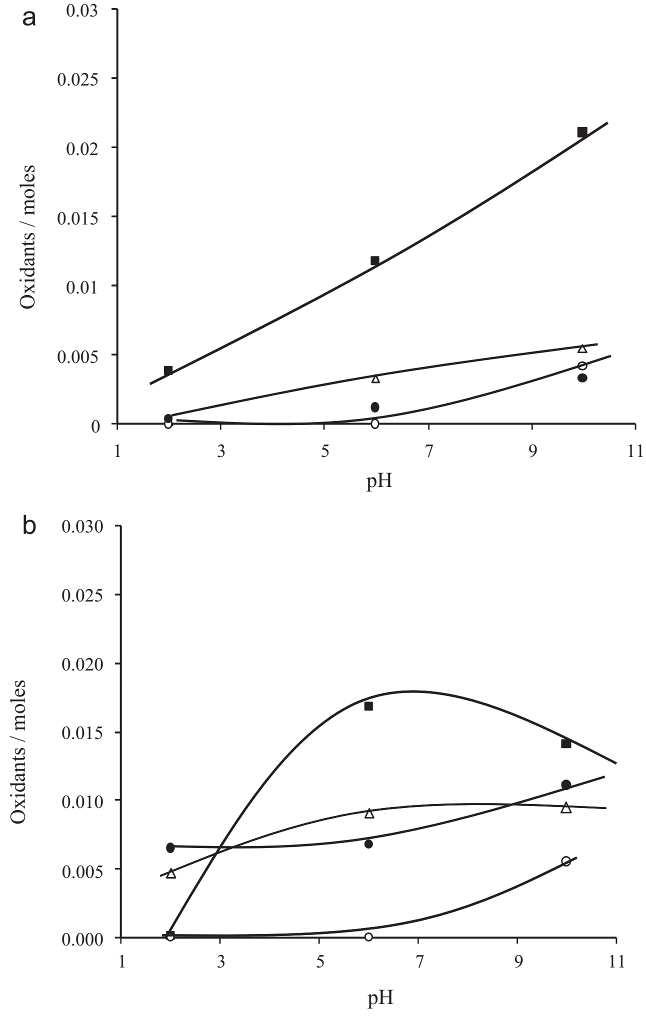

Fig. 3. Variation of chlorine oxospecies with pH during the electrolysis of NaCl solutions, (a) 10 Ah dm^{-3}, (b) 60 Ah dm^{-3}. (■) ClO^-, (△) ClO_2^-, (○) ClO_3^-, (●) ClO_4^- (0.1 M NaCl, T 35 °C).

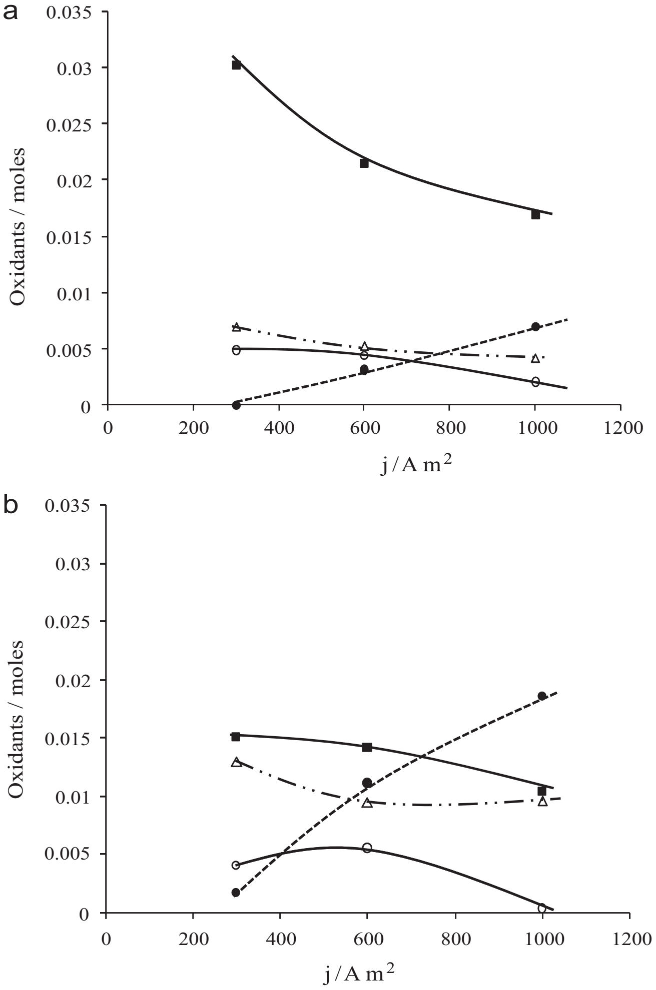

Fig. 4. Variation of chlorine oxospecies with current density during the electrolysis of NaCl solutions, (a) 10 Ah dm^{-3}, (b) 60 Ah dm^{-3}. (■) ClO^-, (△) ClO_2^-, (○) ClO_3^-, (●) ClO_4^- (0.1 M NaCl, T 35 °C, pH 10).

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$

$$Cl^- + OH^{\bullet} \rightarrow ClO^- + H^+ + e^- \quad (4)$$

$$ClO^- + OH^{\bullet} \rightarrow ClO_2^- + H^+ + e^- \quad (5)$$

$$ClO_2^- + OH^{\bullet} \rightarrow ClO_3^- + H^+ + e^- \quad (6)$$

$$ClO_3^- + OH^{\bullet} \rightarrow ClO_4^- + H^+ + e^- \quad (7)$$

The occurrence of perchlorates during the electrolyses of chlorine with diamond electrodes is of a great importance. It means that, initially, this type of electrodes should be avoided for direct disinfestations in supplying water, at least in conditions in which perchlorates can be formed, because perchlorates are associated to several serious health problems. However, it opens the possibility of using conductive-diamond electrolyses for the production of perchlorates, as this anion seems to be the final product of the oxidation of chlorine.

To check this possibility, an electrolysis at a higher current density and during a long time was carried out, using the double compartment cell equipped with diamond anodes and the same raw NaCl solution (Fig. 2). As it can be observed, at electric charges around 200 Ah dm^{-3}, oxidation to perchlorate is complete. Therefore, electrooxidation of NaCl with conduction diamond allows conversion of 100% to perchlorate. At initial stages, the hypochlorite formation is more favored than that of chlorate and perchlorate, but this compound is clearly an intermediate in the production of per-

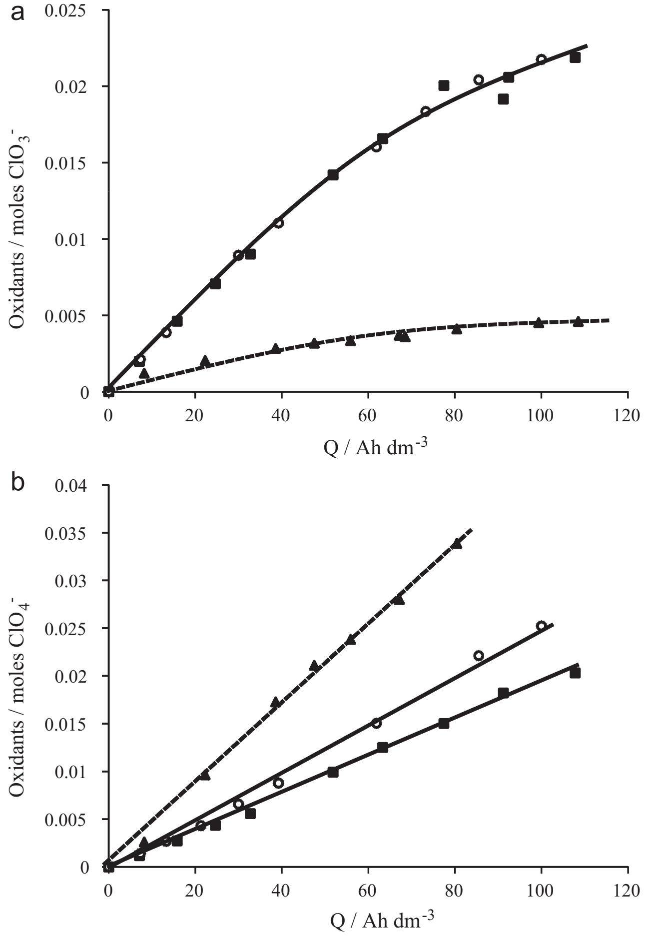

Fig. 5. Variation of (a) ClO_3^- and (b) ClO_4^- moles with electric charge during the electrolysis of (▲) $BaCl_2$, (○) NaCl, (■) LiCl. (j 1000 Am^{-2}, T 35 °C, pH 10).

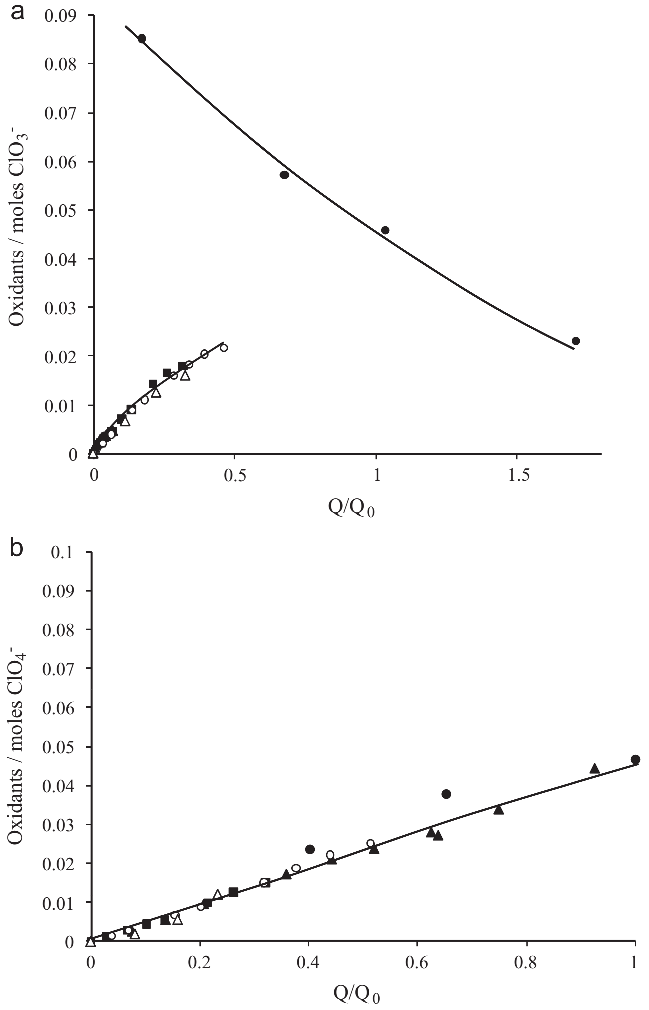

Fig. 6. Variation of (a) ClO_3^- and (b) ClO_4^- moles with Q/Q_0 during the electrolysis of (●) $NaClO_3$, (▲) $BaCl_2$, (○) NaCl, (△) $Ca(OCl)_2$. (j 1000 Am^{-2}, T 35 °C, pH 10).

chlorates. Average efficiency to global oxidants generation of the process is rather good, in spite of the small chloride concentration in the raw solution used in this study.

Fig. 3 shows the effect of the pH on the oxochlorinated anions distribution at two different specific electric current charges passed. As it can be observed, pH influences greatly in the process performance and only good yields are obtained in alkaline solutions. At acidic pH is favored the production of gaseous chlorine, and therefore there is less anionic oxochlorinated species available to be further oxidized. For these reason, all the later experiments shown in this work were carried out maintaining this parameter constant at pH 10.

Fig. 4 shows the effect of the current density on the oxichlorinated anion distribution, at the same specific current charge passed shown in Fig. 3. Perchlorate production is clearly favored operating at high current densities. In every case, hypochlorite is the more significant intermediate; however its concentration decreases when operation current density increases. The same behavior is observed in chlorate case, low current density favors chlorate production. Obviously, the hypochlorite and chlorate decreases match with perchlorate increment. One very important observation is that at low current densities (<300 Am^{-2}) and low electric charges passed, there is almost no perchlorate production. This opens the possibility of using conductive diamond in disinfection systems, only with very low current densities, because electrochemical disinfection processes need very low electric current charge passed [22], and in these conditions occurrence of perchlorates can be fully neglected. This observation can be enforced with the use of non-alkaline pHs, in which the formation of perchlorates is also non-promoted. On the other hand, the very significant increase in the perchlorate production with the current density may be related to the fact that high current densities favor hydroxyl radicals formation [17,19], and it indicates that these species could be involved in chloride oxidation to perchlorate, explaining the observed differences with respect to other electrodes and confirming the pathways proposed by Bergmann et al. [12,13].

The preparation of perchlorates by electrolysis of the corresponding chlorates has been studied in several works [7–9]. However, the electrolysis of chloride solutions to produce perchlorates is less studied and the effect of the counter ion on the electrolyses results could be of interest. In this context, Fig. 5 shows electrolysis of three different chloride salts (NaCl, LiCl and $BaCl_2$). As it can be observed, the perchlorate formation is favored when $BaCl_2$ is used as raw material, and accordingly the barium chlorate formation is less favored than lithium and sodium chlorates. This fact might be related to the stability of chlorate and perchlorate salts. The effect of the cation on the electrolysis is interesting indeed. The electrostatic stability work out the necessity of that positive charges and negative charges are neutralized in the structure [23]. A big anion is more stabilized with a big cation, so, $Ba(ClO_4)_2$ will be the compound more stable. This also explains the better performance of sodium versus lithium salts in the production of perchlorates.

The influence of the chlorine anion of the raw material on the electrolyses results is also of interest. Obviously, the further oxidized is the raw oxoanion, the smaller should be the current required to obtain conversion into perchlorates. For this reason, to compare the effect of the chlorine anion, Fig. 6 shows the production of chlorate (Fig. 6a) and perchlorate (Fig. 6b) in terms of the Q/Q_0 ratio, where Q_0 means the stoichiometric charge necessary to reach a 50% conversion to chlorate and perchlorate with a 100% efficiency, and it allows normalising process efficiency with respect to the type of chlorine anion.

As it can be observed, all experimental points lay over the same lines (for chlorate and perchlorate production). This indicates that in all cases the efficiency is the same and it does not depend on the type of chlorine raw matter, but just on the stoichiometric current charge needed.

4. Conclusions

From this work, the following conclusions can be drawn:

- The electrolysis of chloride solutions with both DSA and conductive-diamond electrodes leads to the production of a chlorine oxospecies mixture with significant concentrations of hypochlorite, chlorite and chlorate. Perchlorate occurrence is only observed with conductive-diamond and it behaves as the final product. Conversions of 100% to perchlorate can be achieved for larger current charge passed.
- The production of large quantities of hydroxyl radicals during BDD electrolysis may explain the higher current efficiencies and also the occurrence of the perchlorates when using conductive-diamond as anode material, and not with DSA anodes.
- Operation conditions and pH of the solutions influence greatly in the process performance. Perchlorate production is clearly favored operating at high current densities and at alkaline conditions.
- The efficiency of the perchlorate generation does not depend on the type of chlorine raw matter, but just on the stoichiometric current charge needed. However, the stability of chlorate and perchlorate electrogenerated seems to be related to the counter ion of the chloride salts used as raw material.

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