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ORIGINAL PAPER

Electrochemical synthesis of perbromate using conductive-diamond anodes

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Abstract In this work, a new method for the synthesis of perbromate, based on the use of conductive-diamond electrodes is described. The procedure developed is able to produce significant amounts of perbromates by electrolyses of bromate solutions. Hydroxyl radicals seem to play a very important role in the process. For this reason, high current densities (that promotes its occurrence) and raw material concentrations around 0.1 M of bromates are required to obtain an efficient process. Temperature in the range 20–30 °C seems to be recommended to obtain good efficiencies of the electrosynthetic process although the explanation of this observation is still unclear.

Keywords Electrosynthesis · Perbromate · Conductive-diamond

1 Introduction

Perbromates are not found in nature, and many attempts to produce perbromates in the laboratory were unsuccessful [1–3] mainly due to kinetic reasons, rather than thermodynamic ones. The radiochemical synthesis of BrO_4^- in 1968 using the β-decay of radioactive ^{83}Se, whilst not providing a viable route to macroscopic quantities of perbromate, proved that this mysterious species could exist. This stimulated the search for a chemical synthesis. Electrolytic oxidation of aqueous $LiBrO_3$ produced a 1% yield of perbromate, but the first isolation of a solid perbromate salt ($RbBrO_4$) was achieved by oxidation of BrO_3^- with aqueous XeF_2 [4, 5] according to the scheme shown in Eq. 1.

$$BrO_3{}^- + XeF_2 + H_2O \rightarrow BrO_4^- + Xe + 2HF \qquad (1)$$

A more practical synthesis of perbromate is obtained with the use of fluorine directly as the oxidizing agent [6] (Eq. 2).

$$NaBrO_3 + F_2 + 2NaOH \rightarrow NaBrO_4 + 2NaF + H_2O \qquad (2)$$

Perbromates are quite stable at room temperature in crystal form or in aqueous solutions. The general inertness of BrO_4^- at room temperature stands in sharp contrast to its high thermodynamic oxidizing power, which is greater than that of any other oxohalogen ion that persists in aqueous solutions. Thus, its reduction potential (E^0: 1.853 V) is higher than those of perchlorate (E^0: 1.201 V) and periodate (E^0: 1.653 V).

Thermochemical measurements [7] further show that $KBrO_4$ is thermodynamically stable with respect to its elements, but less so that the corresponding $KClO_4$ and KIO_4. There is not a satisfactory explanation of these facts, though they are paralleled by the similar reluctance of other elements following the completion of the 3d subshell to achieve their higher oxidation states.

Since the successful preparation of perbromates, only a limited amount of work on perbromate chemistry has been published due to the non commercial availability and the very expensive and complicated experimental production. In this context, during the recent years, the appearance of diamond thin-film electrodes has allowed the development of highly efficient electrochemical processes in the production of oxidants. In addition to the excellent chemical and electrochemical properties [8, 9], its main remarkable

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characteristic is its high overpotential for water electrolysis [10] (large enough to allow the generation of large amounts of hydroxyl radicals). This radical is a very powerful oxidant (E^0: 2.80 V vs. SHE) and it seems to be directly involved in the oxidation mechanisms that occur on diamond surfaces. In this way and once established the availability of the generation of inorganic oxidants from the oxidation of supporting electrolyte during conductive diamond electrolysis, some works [11] have also been focused on the electrochemical synthesis with diamond anodes of powerful oxidants such as persulphates [12], perphosphates [13], percarbonates [14] and ferrates [15–17]. The results obtained showed that the use of conductive diamond anode allows achieving great process efficiencies in comparison to more known synthesis methods.

With this background, the aim of this work is to study the electrosynthesis of perbromates with conductive diamond electrode and to clarify the effect of the most relevant parameter on the efficiency of the process.

2 Experimental

2.1 Analytical procedures

Bromate and bromide standard solutions (10–500 ppm) were prepared by dissolving the appropriate amount of $KBrO_3$ or KBr in water. Despite the not commercial availability of BrO_4^-, is not possible to carry out a calibration with standard solutions.

The oxidants produced were identified and quantified by ion chromatography. The column is a Metrosep A Supp (4 mm × 250 mm) (macroporous particles with 9 μm diameter, total capacity of 71 μmol of Cl^-). The detector is a conductimetric detector. The selected mobile phase was sodium phenate 20 mM of pH 11, prepared dissolving phenol in equimolar solution of NaOH. This phase presented high resolution between adjacent peaks, high sensitivity, high detectability and high precision.

Electrochemical measurements were made using a conventional three-electrode cell in conjunction with a computer-controlled potensiostat/galvanostat (Autolab model PGSTAT 30, Ecochemie B.V., Utrecht, The Netherlands). Diamond was used as the working electrode, Ag/AgCl as a reference electrode and stainless steel (AISI304) as a counter electrode. Voltammetric experiments were performed in unstirred solutions (200 mL).

Thermogravimetric analyses were carried out in a thermobalance SDT 600 (TA Instruments). The experimental conditions used were: nitrogen flow: 100 NmL/min, heating temperature range: 50–450 °C and heating rate: 10 °C/min.

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 pHmeter.

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 <100> 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 μm 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 and the catholyte consisted of solutions of $NaBrO_3$ (0.05–0.2 M). The range of current densities employed was 240–1000 A m^{-2} in the synthesis and the operation temperatures from 10 to 60 °C.

3 Results and discussion

Figure 1 shows the changes in the amount of bromate in the anodic chamber of a double compartment electrochemical cell, during the electrolysis with a conductive-diamond anode of an alkaline aqueous solution of sodium bromate (0.05 M $NaBrO_3$, pH 10) at a current density of 660 A m^{-2}, regulating the temperature at 17 °C during the process.

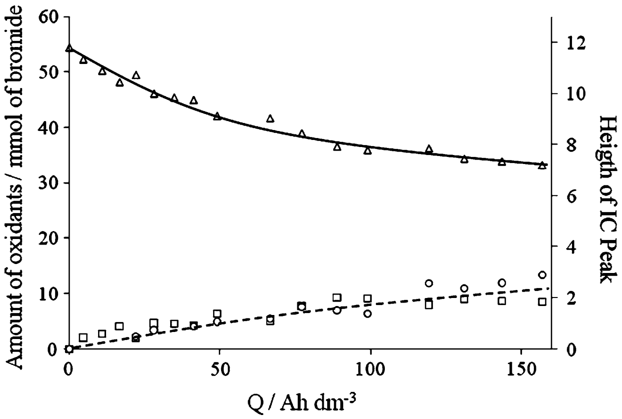

Fig. 1 Variation of the moles of bromate (*open triangle*), moles of perbromate (*open square*) and height of the new peak in the ionic chromatograph (*open circle*), in the anodic compartment for several oxospecies during the electrolysis of 0.05 M $NaBrO_3$ (pH 10, T 17 °C; j 660 Am^{-2})

It can be observed that the amount of bromate decreases significantly during the electrolysis. This figure also shows the height of a new peak that appears in the IC chromatograms during the electrolysis. This peak increases with the decrease of the bromate concentration and, as it can be observed in the figure, it matches the mass balance of bromine species in the cell. Permeability of bromine species through the membrane was checked and it was confirmed to be nil. Thus, the amount of bromine in the cathodic chamber remains constant and just the reduction of bromate to bromide is observed (Fig. 2).

Initially, these observations can be explained with the formation of perbromate in the electrolyzed solution. However, there are no commercial perbromate standards available to check the retention time of perbromate with the IC method used, and there is just one reference [18] that states that the peak obtained at the same retention time (and with the same chromatographic method) corresponds to perbromates. Anyway, to confirm the presence of perbromates, it was decided to look for other indirect methods.

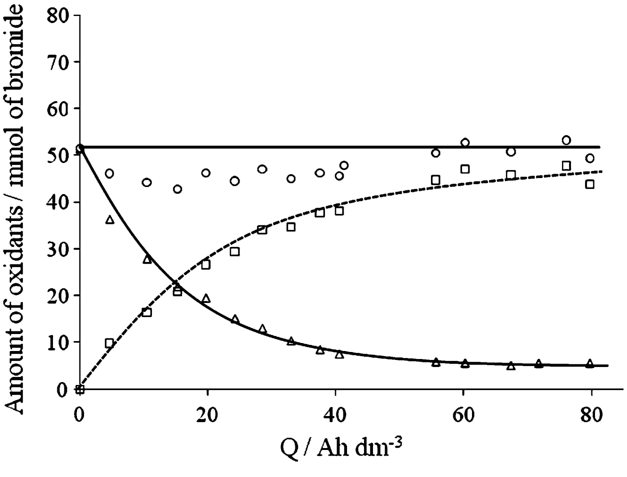

Fig. 2 Variation of the moles of oxospecies of bromine in the cathodic compartment during the electrolysis of 0.05 M $NaBrO_3$ (pH 10, T 17 °C; j 660 Am^{-2}); (*open circle*) total moles of bromine, (*open triangle*) moles of bromate, (*open square*) moles of bromide

Unfortunately, the chemistry of bromates is not well-described in the present moment and, in literature, it was just found a valuable study about the thermal stability of perbromates [4]: thermogravimetric measurements of perbromates seemed to show an exothermic decomposition at 275–280 °C to potassium bromate, which did not decompose to KBr until around 390–395 °C. The sharpness of the decomposition to bromate seemed to be strongly dependent on the purity of the perbromate. As it can be observed in Fig. 3, this behavior is just the obtained when it was carried out a thermogravimetric analysis of a pure $KBrO_3$ solution (raw material of the electrolysis) and of the solution after electrolysis. The decomposition peak of $KBrO_3$ to KBr appears in both cases; however, in the solution obtained after $KBrO_3$ electrolysis, it was also observed what it seemed to be the peak corresponding to perbromate decomposition. This confirms the formation of this species during the electrolysis with conductive-diamond anodes. Another evidence of the formation of perbromates is obtained by comparing the voltammetric behaviour of the raw bromate solution and that of the solution obtained in the anodic chamber after the electrolysis of this raw solution. Both voltammograms are shown in Fig. 4 and, as it can be observed, in both cases the behavior is completely different, being the electrolyzed solution more electrochemically active towards reduction. This is consistent with the presence of perbromates in this solution.

Figure 5 shows the influence of the current density in the production of perbromate for a given specific current charge passed (150 Ah dm^{-3}). To calculate the amount of

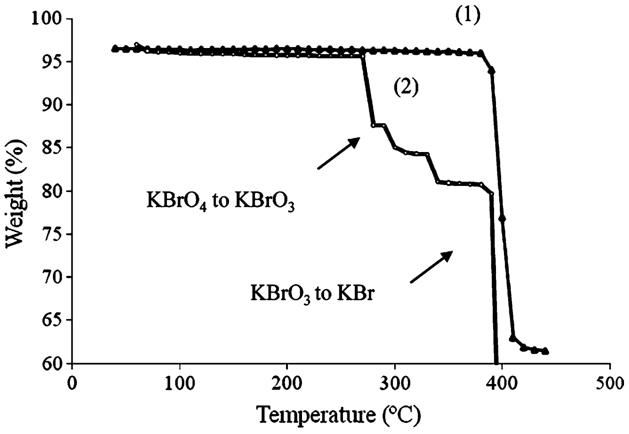

Fig. 3 Analysis thermogravimetric of: (1) initial bromate solution, (2) final solution of bromate electrolysis

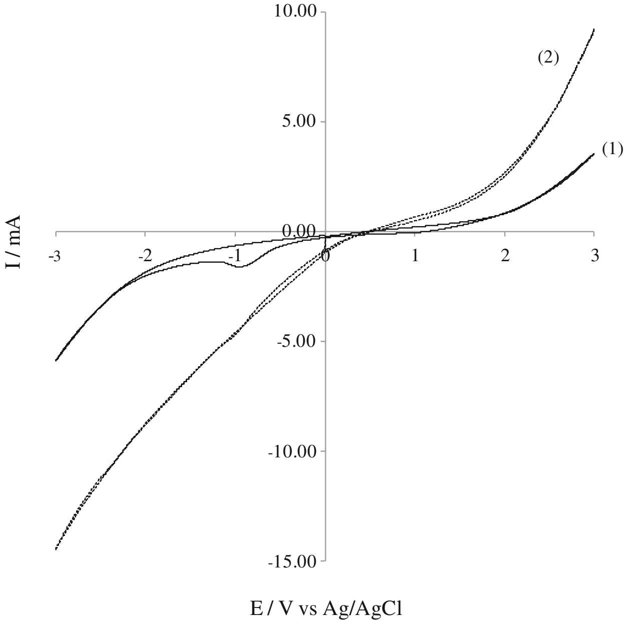

Fig. 4 Cyclic voltammograms on BDD anodes. Auxiliary electrode: Stainless steel AISI 304. Reference electrode: Ag/AgCl. Scan rate: 100 mV s^{-1}. (*1*) Bromate solution, (*2*) final solution of bromate electrolysis

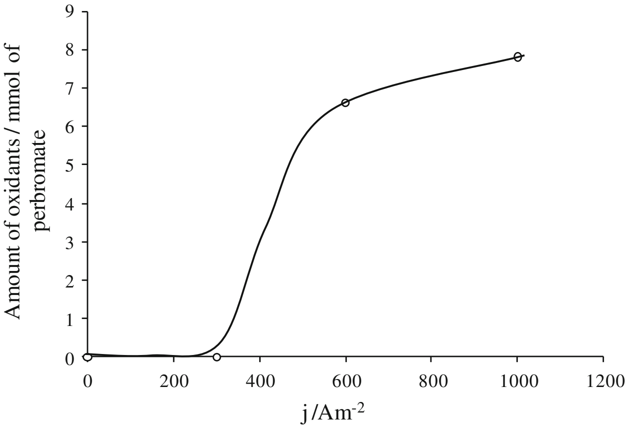

Fig. 5 Variation of millimoles of perbromate with the current density at an electrical charge passed of 150 Ah dm^{-3} in the electrolysis of 0.05 M $NaBrO_3$ solutions with boron doped diamond electrodes (pH 10, 17 °C)

perbromates (mmol) data from bromine mass balance and IC measurement were correlated.

As it can be observed, the perbromate generation strongly depends on the current density. Densities higher than 300 A m^{-2} were necessary to get any conversion. This fact is difficult to explain by means of bromate chemistry, but it can be related to the mechanisms of oxidant formation in the surface of conductive-diamond anodes, and it has been reported previously for other oxidants produced by anodic oxidation with conductive-diamond anodes, such as peroxophosphates [13] and ferrates [17].

The bromate oxidation towards perbromate was only achieved chemically with fluorine (2.87 V), and it has not been possible with other powerful oxidants, such as ozone (2.07 V) or $S_2O_8^{2-}$ (2.01 V) [19]. The oxidation potential of fluorine can only be compared to that of hydroxyl radicals (2.80 V), species which are known to be produced [20] during the electrochemical oxidation of water solutions with conductive-diamond electrodes (Eq. 3)

$$H_2O \rightarrow (OH)^{\bullet} + H^+ + e^- \quad (3)$$

The nil production of perbromates at low current densities suggests that this product can not be produced by direct electrolysis of bromate solutions but only by hydroxyl-radical mediated oxidation according to Eq. 4.

$$BrO_3{}^- + OH^{\bullet} \rightarrow BrO_4^- + H^+ + e^- \quad (4)$$

This fact can explain the production of this product in electrolyses with conductive-diamond anodes and not with other anodic materials, as diamond is the lone anodic material that has demonstrated the occurrence of significant amounts of hydroxyl radicals during the electrolysis of water.

Figure 6 shows the changes in the production of perbromates with the operation temperature (monitored at the anolyte reservoir). The production of perbromates obtained is clearly dependent on the temperature of the electrosynthesis, and the generation process seems to be favoured at temperatures around 20–30 °C. In fact, a very important change is observed for temperatures around 20 °C with a significant increase in the production. At the light of the present knowledge of the chemistry of perbromates is difficult to explain such observations, although they should be related to the reactivity of hydroxyl radicals with

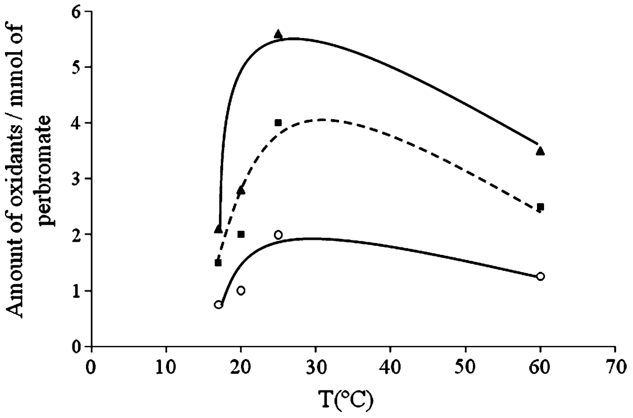

Fig. 6 Variation of mmoles of perbromate with temperature in the electrolysis of 0.05 M $NaBrO_3$ solutions with boron doped diamond electrodes (pH 10, 1000 Am^{-2}); (*open circle*) 25 Ah dm^{-3}, (*filled square*) 50 Ah dm^{-3}, (*filled triangle*) 70 Ah dm^{-3}

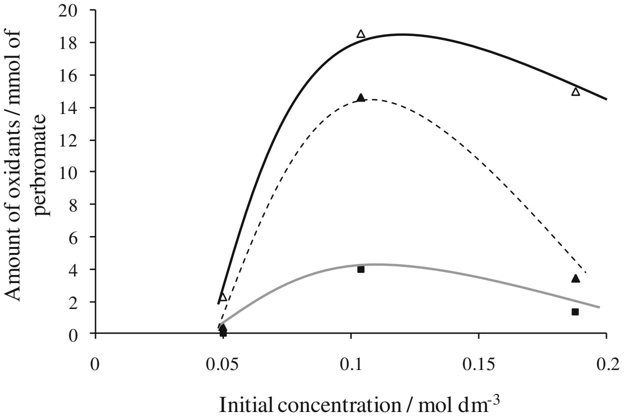

Fig. 7 Variation of mmoles of perbromate generated in the electrosynthesis of bromate as a function of the initial concentration of $NaBrO_3$ (pH 10, 1000 Am^{-2}); (*filled square*) 15 Ah dm^{-3}, (*filled triangle*) 40 Ah dm^{-3}, (*open triangle*) 70 Ah dm^{-3}

bromate which could be strongly dependent on the temperature. Solubility of perbromate and improvement in mass transfer coefficients can also help to explain this behaviour. The small decrease in the efficiency for very high temperatures could be interpreted as some sort of decomposition of perbromate.

Figure 7 shows the changes in the amount of perbromate electrogenerated during the electrolysis of different solutions of bromate (initial concentrations ranging from 0.05 to 0.20 mol dm^{-3}). The pH, current density and temperature were maintained during these electrolyses essays in values close to pH 10, 20 °C and 1000 A m^{-2}, respectively. As it can be observed, the concentration of oxidant obtained is significantly influenced by the concentration of the bromate. The amount of perbromate increases significantly with the amount of BrO_3^- ions available to be oxidized until achieving a maximum value (around 0.1 M $NaBrO_3$) and then, a decrease in the amount perbromate generated is observed. As a result, it can be suggested that 0.1 M $NaBrO_3$ is the optimum concentration for the perbromate synthesis with conductive-diamond anodes in the operating conditions used in this work. This fact could be related to the complex interaction between hydroxyl radicals and bromate ions which can lead, in case of non optimum ratios, to the decomposition of hydroxyl radicals towards oxygen and to the loss of efficiency of the process. In this point, it is important to state that a similar trend was observed in the formation of monoperoxophosphoric acid using the same technology [21]. This electrosynthesis process was explained by a similar mechanism of that of perbromate, with an important role of the hydroxyl radicals formed in the surface of the conductive-diamond, and it suggests that the important influence of the concentration of raw material can be a characteristic of this technology.

4 Conclusions

From this work it can be drawn that conductive-diamond electrolysis can be successfully used to synthesize perbromate from bromates solutions. Hydroxyl radicals seem to play a very important role in the process and explain the influence of current density and concentration of raw material in the efficiency of the process.

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