Hypochlorite Oxidation on RuO₂-Based Electrodes: a Combined Electrochemical and In Situ Mass Spectroscopic Study

Kateřina Minhov Macounov¹ · Nina Simic² · Elisabet Ahlberg³ · Petr Krtil¹

Published online: 3 October 2018
© The Author(s) 2018

Abstract

The hypochlorite oxidation on RuO₂ doped with Co, Mg, Ni and Zn was studied by means of voltammetry combined with mass spectroscopy. The hypochlorite oxidation takes place in two distinct steps separated with at least 200 mV. While the first step can be assigned to the direct hypochlorite oxidation, the second one seems to be connected with the oxidation of strongly adsorbed in situ formed hypochlorite. In the oxidation process of hypochlorite, oxygen is the main product but also hydrogen peroxide can be detected. The number of electrons used to produce one molecule of oxygen (z) is less than expected from an electrochemical point of view. This fact, together with an accumulation of chloride ions in solution, indicates that the reaction mechanism of the hypochlorite oxidation involves the formation of radicals that can be regenerated by chemical redox reactions.

Keywords Hypochlorite oxidation · Chlorate process · Ruthenium dioxide · DEMS

Introduction

Chlorate production is one of the most important large-scale electrolytic technologies supporting environmentally friendly elemental chlorine free (ECF) bleaching of pulp. Chlorate is manufactured by electrolysis of sodium chloride in an undivided cell [1], where the electrochemically produced chlorine chemically disproportionates in alkaline media [2–4]. The desired electrode processes are rather straightforward and comprise the chlorine evolution at the anode (reaction (1)) and hydrogen evolution at the cathode (reaction (2)).

The scope of the processes involved in the chlorate production is, however, significantly wider, since the desired formation of chlorate from the electrochemically generated chlorine represents a complex reaction pathway starting with hydrolytical disproportionation of chlorine to hypochlorite and chloride according to reaction (3) [5]:

The hydrolytically formed hypochlorite may exist either in anionic form or as hypochlorous acid [6] and yields eventually chlorate according to reaction (4):

The efficiency of the whole processes is, however, adversely affected by several side reactions of chemical or of electrochemical nature [7, 8]. The oxidation or reduction of hypochlorite/ hypochlorous acid is considered to be the most serious parasitic reactions affecting the efficiency of the chlorate production at the anode [9, 10] as well as on the cathode [11, 12]. Particularly, the anode-related hypochlorite behaviour is of fundamental importance since it yields oxygen and represents, therefore, a significant safety risk [8, 13]. The hypochlorite to oxygen conversion is usually ascribed to the hypochlorite decomposition either by catalytic or electrochemical pathways. The corresponding processes for the catalytic decomposition may be formulated as follows [14, 15]:

✉ Elisabet Ahlberg
ela@chem.gu.se

✉ Petr Krtil
PetrKrtil@jh-inst.cas.cz

¹ J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague, Czech Republic

² AkzoNobel Pulp and Performance Chemicals, SE-445 80 Bohus, Sweden

³ Department of Chemistry and Molecular Biology, University of Gothenburg, SE-41296 Gothenburg, Sweden

An alternative mechanism reflecting possible electrochemical nature of the hypochlorite oxidation was formulated by Foerster [16] and by Kotowski [17], reactions (7) and (8), respectively:

The above outlined hypochlorite decomposition/oxidation-related oxygen production may indeed proceed in parallel with conventional electrocatalytic oxygen evolution by oxidation of water:

It ought to be noted that oxygen production unifies all above summarized anodic parasitic reactions. A suppression of the parasitic oxygen formation is therefore of paramount importance to improve efficiency and safety of the process [7, 13, 18]. The active strategies mitigating the parasitic oxygen production are, however, hindered by limited knowledge of the true mechanism of the anodic hypochlorite oxidation and of its sensitivity to selective control via electrode material selection/optimization.

The oxygen formation accompanying hypochlorite oxidation on polycrystalline Pt was reported recently [19]. A combination of linear sweep voltammetry with on-line mass spectroscopic detection of the produced oxygen revealed unusually high oxygen formation where the apparent number of electrons needed to produce an oxygen molecule dropped significantly below 4 encountered in conventional water oxidation. These results were interpreted in terms of a radical chain mechanism, where the initial hypochlorite oxidation yields the hypochlorite radical [19], which enters in radical-assisted water-splitting, yielding oxygen, hydrogen peroxide and protons [19]. The results obtained on Pt, despite their fundamental importance, are rather departed from the industrial conditions encountered in chlorate production which predominantly uses DSA-based anodes.

Keeping in mind that the industrial dimensionally stable anodes (DSA) are based on oxides of Ti and Ru, where Ru oxides are believed to be responsible for DSA's activity, one may obtain a better understanding of the hypochlorite oxidation behaviour under conditions relevant to the chlorate process by a systematic investigation of the hypochlorite oxidation on well-defined oxide electrodes based on Ru oxides and, therefore, related to DSA. The major advantage of such model

system lies in their well-defined nature [20, 21] as well as in the known selectivity towards chlorine and oxygen evolution reactions [22, 23]. This paper, thus, extends the previous mechanistic studies of hypochlorite oxidation on polycrystalline Pt, by employing electrode materials based on RuO₂ doped with different cations such as Ni, Co, Zn and Mg in a systematic study combining voltammetry with differential electrochemical mass spectroscopy (DEMS) detection of the reaction products.

Experimental

Ruthenium dioxide and Ru_{1-x}Me_xO₂ (Me = Co, Ni, Mg and Zn) were prepared by spray-freezing/freeze-drying approach as described in [21–24]. Aqueous solutions were prepared from ruthenium (III) nitrosyl nitrate (31.3% Ru, Alfa Aesar) and corresponding Ni, Co, nitrates (Aldrich, p.a.) and Mg and Zn acetate (Puratronic®, 99.997% metals basis, Alfa Aesar) in 100 mL of Millipore H₂O with a total concentration of metal cations of 8 mM. The solutions were then sprayed into liquid N₂ to create fine ice particles. The resulting ice slurries were transferred to an aluminum tray precooled with liquid N₂ and placed in the freeze dryer (FreeZone Triad Freeze Dry System 7400030, Labconco) precooled to –30 °C. The pressure was decreased to approximately 1.0 Pa, and the temperature was ramped according to the following programme: –30 °C (2 h), –25 °C (5 h), –20 °C (6 h), –15 °C (5 h), 30 °C (4 h). Afterwards, the resulting powder was annealed in the furnace at 400 °C for 1 hour. Crystallinity and phase purity of the prepared materials was checked using a Rigaku Miniflex 600 powder X-ray diffractometer with CuK_α radiation. The diffraction patterns of the resulting doped ruthenium dioxide samples conform to single-phase materials and are shown in Fig. 1.

The hypochlorite stock solution was prepared by letting chlorine gas into a 5 M NaOH (Scharlau, reagent grade, ACS ISO, Reag. Ph Eur). The hypochlorite concentration in the stock solution was 1.6 M, and the solution was cooled and stored cold in dark. Given the preparation technique, the hypochlorite stock solution contained an equimolar amount of NaCl. The oxidation of hypochlorite was studied in 0.1 M solution of NaClO₄ (Aldrich, p.a) containing variable amounts of hypochlorite. The pH of the hypochlorite solutions was adjusted to 9 by an addition of 1 M solution of NaOH (Aldrich, p.a.) in all experiments. The pH of the solution was checked using OK-104 conductometer (Radelkis, Hungary). The hypochlorite oxidation was studied by linear sweep voltammetry on RuO₂-based nanocrystalline electrodes. The linear sweep voltammetry experiments were carried out in a three-electrode arrangement in a home-made single compartment Kel-F cell with Pt and Ag/AgCl auxiliary and reference electrode, respectively. All experiments were carried out at polarization rate of 5 mV/s in the potential range between 0.3 and 1.3 V vs. Ag/AgCl. The

Fig. 1 XRD patterns of nanocrystalline RuO₂ and doped ruthenium dioxide conforming to average chemical composition Ru_{0.9}Me_{0.1}O₂ where Me stands for Ni, Co, Mg and Zn. The assignment of the curves is given in the figure legend

potential control was achieved using a PAR 263A potentiostat. The measured potentials were recalculated and are quoted in the reversible hydrogen electrode (RHE) scale to enable easy comparison of all samples.

The RuO₂-based catalysts were supported by a Ti mesh (GoodFellow, electrode area of 1 cm², open area 20%). The active catalysts were deposited on the Ti mesh by a procedure described in [20]. A water-based suspension of nanocrystalline RuO₂ catalyst (30 gL⁻¹) was deposited by adding 25 μ L aliquots to the Ti support and dried at 100 °C. The deposition procedure was repeated until the weight of the catalyst ranged between 1 and 2 mg. The total physical area of the catalyst corresponded to ca. 20 cm². All electrodes were calcined at 400 °C in air for mechanical stability before electrochemical experiments. The electrochemical characterization of the hypochlorite oxidation on RuO₂ catalysts was complemented by in situ spectroscopic detection of the volatile reaction products—namely of oxygen and chlorine. A differential electrochemical mass spectrometry (DEMS) apparatus consisting of a Prisma quadrupole mass spectrometer (QMS200, Balzers) connected with turbomolecular drag pump station (TSU071, Balzers) was used in these experiments.

The content of chlorides before and after electrochemical experiment was determined by argentometric titration with silver nitrate using potassium chromate as an indicator.

Results

The Role of the Electrode Material

A comparison of typical voltammograms of RuO₂-based electrodes in the hypochlorite containing systems are

shown in Figs. 2 and 3. As follows from comparison of the voltammograms taken for RuO₂ in presence and absence of hypochlorite (see Fig. 2), the hypochlorite oxidation shows a pronounced anodic peak appearing positive to 1.2 V (vs. RHE). The anodic process attributed to hypochlorite oxidation is accompanied by the formation of oxygen as reflected in the DEMS data (see Fig. 2b). It ought to be noted that while in the absence of hypochlorite, the signal of produced oxygen (the blue curve in the Fig. 2b) closely tracks the observed current. In the case of the hypochlorite oxidation, the onset of the oxygen production signal, however, lags behind the voltammogram reflecting the fact that the mass spectrometer is sensitive to the charge rather than to the current due to a limited transfer rate of the produced oxygen into the vacuum part of the DEMS apparatus.

Regardless of the catalyst composition, the oxidation of hypochlorite remains to be observed in the same potential interval 1.2–2.0 V (vs. RHE). This potential interval is restricted by the oxygen evolution at less positive potentials and chlorine evolution at the most positive potentials. The hypochlorite oxidation onset is the same for all studied RuO₂-based electrode materials. The course of the hypochlorite oxidation is characterized by two anodic peaks, the precise position of which depends on the type of the employed electrode material. The presence of the peaks in the voltammograms suggests that the anodic process is dominated by the oxidation of solution-based species rather than by conventional four-electron water oxidation at the electrode surface. In the case of Co-, Mg- and Zn-doped RuO₂, one finds the first anodic peak in the interval 1.5–1.6 V (vs. RHE). In the case of the non-doped RuO₂ and of the Ni-doped RuO₂, the position of the first anodic peak shifts towards more positive potentials. The first anodic peak

Fig. 2 A comparison of **a** voltammograms and **b** DEMS-based signals of oxygen production as a function of applied potential recorded on a nanocrystalline RuO₂ electrode-polarized in 20 mM NaCl in 0.1 M NaClO₄ solution (blue curve) and the same electrolyte solution complemented by 20 mM of NaClO (red curve). The applied polarization rate was 5 mV/s

is complemented by a second anodic maximum which appears at ca. 1.8 V (vs. RHE). In the case of non-doped and Ni-doped RuO₂, either a suppression of the second anodic peak or a shift towards significantly more positive potentials are observed, respectively. The activity of various RuO₂-based catalysts in

hypochlorite oxidation is comparable as shown in the similar peak currents obtained for different electrode materials. The above-described anodic behaviour—i.e. the presence of two resolved anodic peaks—is relatively weakly dependent on the initial hypochlorite concentration (see Fig. 4). The observed voltammograms remain qualitatively similar as long as the hypochlorite concentration remains below 0.05 M when the voltammograms gradually become dominated by a single wide peak without distinctive features. Note that the exact position of the resolved peak shifts with increasing hypochlorite concentration to more positive potentials reflecting the irreversible nature of the hypochlorite oxidation.

The presence of two anodic peaks reflects the complexity of the hypochlorite oxidation process. The identical value of the current onset for different electrode materials suggests that the initial hypochlorite oxidation is not catalytic in nature. While the first anodic peak may be attributed to the oxidation of the hypochlorite initially present in the system, the appearance of the second anodic peak may be assigned to an oxidation of surface-confined species as follows from pronounced electrode material-related change of the position as well as of the distinction of the second anodic peak. There are two possible mechanisms explaining the presence of the second voltammetric peak. The first one suggests a specific adsorption of the hypochlorite where the adsorption energy provides additional stabilization shifting the oxidation of the adsorbed hypochlorite to more positive potentials. This mechanism would assume that the current of adsorbed hypochlorite oxidation increases linearly with hypochlorite concentration until a complete coverage of the available surface sites is achieved. An alternative mechanism assumes the possibility of chloride adsorption on coordination-unsaturated oxygen atoms forming surface structures identical with adsorbed hypochlorite. Such a process is theoretically predicted at low pH by density functional theory (DFT) calculations [25]. Despite

Fig. 3 **a** Voltammograms and **b** DEMS-based signals of oxygen production as a function of applied potential recorded during the hypochlorite oxidation on various nanocrystalline RuO₂-based electrodes. The assignment of the individual curves to the electrode materials is given in the figure legend. Experimental conditions: 20 mM NaClO and 20 mM NaCl in 0.1 M NaClO₄, polarization rate 5 mV/s

Fig. 4 Voltammetric behaviour of hypochlorite oxidation at nanocrystalline RuO_2 -based electrodes with variable hypochlorite and chloride content. The assignment of the individual curves to the electrode materials is given in the figure legend. The applied polarization rate was 5 mV/s

the apparent disparity of the pH limiting the chloride adsorption (according to DFT) and of the actual pH at the beginning of the experiment, the chloride adsorption remains plausible due to a significant drop in the pH near the electrode surface due to oxidation of the solution-based hypochlorite. This mechanism should result in generally non-linear increase of the second voltammetric peak with increasing hypochlorite concentration. The effect of chloride on the overall anodic behaviour of RuO_2 -based electrodes can be tracked also in the change of the voltammogram shapes with increasing hypochlorite concentration (see Fig. 4). It needs to be noted that a linear increase of the observed current (in the hypochlorite oxidation region) is not observed in the entire hypochlorite concentration range $0.01 < c < 0.05$ M (see Fig. 5). This behaviour most likely reflects the pronounced chloride adsorption which affects the oxidation of hypochlorite. It has to be stressed that the hypochlorite concentration increase also leads to an increase in chloride content.

To obtain additional information regarding the mechanism of hypochlorite oxidation, the nature of possible reaction products needs to be assessed by an independent spectroscopic technique. Given the fact that the hypochlorite oxidation is known to produce large amounts of gaseous products, one may find the differential electrochemical mass spectroscopy

(DEMS) as the most convenient tool for the reaction product detection.

The primary detected reaction product is oxygen, the formation of which can be followed by mass spectroscopy as the fragment of $m/z = 32$ (see Figs. 2b and 3b). The onset of the oxygen production coincides with the onset of the anodic current. Closer investigation of the oxygen-related signal reveals that also oxygen is produced in two steps which can be aligned with the anodic peaks observed in the voltammograms. The oxygen production apparently culminates at the potential of the second anodic peak and decreases at the potentials above 2.0 V when the exponential current increase is observed. The peak-shaped character of the oxygen-related signal stresses the link between the oxygen formation and hypochlorite oxidation and rules out the conventional water electrolysis as a likely source of oxygen even at the most positive potentials. The oxygen production is accompanied with the production of hydrogen peroxide which can be followed by the mass fragment with $m/z = 34$ (see Fig. 6). Note that the detected hydrogen peroxide is solely produced at the or near the anode and is not attributable to any of the possible cathodic processes at the counter electrode. The relative amount of the detected hydrogen peroxide is affected by the electrode material—the formation of hydrogen peroxide

Fig. 5 Concentration dependence of the hypochlorite oxidation current in the second voltammetric peak on various nanocrystalline RuO₂-based electrodes. The experimental conditions were identical to those in

seems to be more facile on non-doped and Co- or Ni-doped RuO₂. The hydrogen peroxide formation on Mg- and Zn-doped RuO₂ seems to be suppressed. Regardless of the electrode material, the relative importance of the hydrogen peroxide formation expressed in terms of the hydrogen peroxide to oxygen ratio (see Fig. 6) is weakly potential dependent. However, the quantitative comparison of the data presented in Fig. 6 needs to be taken cautiously mainly due to a low selectivity of the DEMS towards hydrogen peroxide, which primarily decomposes to oxygen during fragmentation. This fact also prevents a direct comparison of the voltammetric charge with the DEMS-based signal of the produced oxygen. Even so, it needs to be stressed that although the hydrogen peroxide can be formed electrocatalytically [26], this reaction is thermodynamically disfavoured at the potentials employed in the reported experiments. The formation of highly oxidizing radicals is, therefore, a prerequisite for the hydrogen peroxide formation [19].

The chlorine production, which may be expected given the presence of chlorides, is confined to the highest electrode potentials above 1.8 V (see Fig. 7). The onset of the chlorine detection agrees well with the standard potential of the chlorine evolution reaction at the conditions of the experiment (please note that the standard potential of the chlorine

Fig. 4 The assignment of the individual curves to the electrode materials is given in the figure legend

evolution—a pH independent process—shifts in the reversible hydrogen scale by 59 mV per unit change of pH). This agreement also indicates that the local pH near the anode does not deviate significantly from the initial one on the time scale of the experiment. It has to be expected, though, that a prolonged oxidation eventually leads to an acidification of the electrolyte near the anode and consequently an enhancement of chlorine evolution. The course of the chlorine-related DEMS signals identifies the chlorine evolution as the processes restrict the accessible potential window in the hypochlorite oxidation experiments. Although the chlorine evolution most likely represents the potential window limiting process in the voltammograms, the corresponding DEMS-based chlorine-related signal is comparably low. This effect can be attributed to fast hydrolysis of the chlorine given the relatively high pH in the experiments [27].

Discussion

Quantification of the Oxygen Formation

Although the DEMS detects the oxygen ($m/z = 32$) as the primary reaction product of the studied anodic process, its

Fig. 6 DEMS-based signal of the hydrogen peroxide production (a) and in ratio with produced oxygen (b) as a function of applied potential during the hypochlorite oxidation on various nanocrystalline RuO_2 -based electrodes. Experimental conditions were the same as in Fig. 2. Presented DEMS data were smoothened using Savitzky-Golay filter to remove excessive noise. The assignment of the individual curves to the electrode materials is given in the figure legend

direct quantification—with respect to the passed current/charge—is complicated by simultaneous formation of hydrogen peroxide which aside of its molecular ion ($m/z = 34$)

Fig. 7 DEMS-based signal of the chlorine production during the hypochlorite oxidation on various nanocrystalline RuO_2 -based electrodes. Experimental conditions were the same as in Fig. 2. The assignment of the individual curves to the electrode materials is given in the figure legend

mainly produces oxygen upon ionization. The quantification of the oxygen formation efficiency is still possible provided that the formation of hydrogen peroxide (measurable from the course of the fragment with $m/z = 34$) is compensated for according to its fragmentation (obtained in calibration). In this manner, the measured signal with m/z of 32 can be separated into two contributions—a contribution from the hydrogen peroxide and a contribution from (electro)chemical processes proceeding in the hypochlorite oxidation. The efficiency of the latter one can be expressed in terms of an apparent average number of electrons needed to evolve one molecule of oxygen z [19]. This parameter is based on conversion of the recorded DEMS signal of oxygen to its theoretical charge equivalent. This charge equivalent is based on a calibration of the DEMS setup in conventional electrocatalytic oxygen evolution. The charge equivalent of the detected oxygen can be subsequently compared with the actual charge recorded by the potentiostat. The apparent number of electrons involved in the production of one oxygen molecule is calculated according to Eq. 10:

$$z = 4 \frac{Q_{EC}}{Q_{DEMS}} \quad (10)$$

where the Q_{DEMS} is the charge equivalent to the amount of oxygen detected spectroscopically, and Q_{EC} stands for the charge obtained by integration of the measured current. In the context of the electrolyte solution composition for hypochlorite oxidation, the value of z allows to distinguish between three qualitatively different cases. The z value higher than 4 indicates a situation when the overall electrode process encompassing the oxygen production integrates several parallel anodic reactions; sustaining z value equal to 4 is compatible with a situation that the detected oxygen is produced electrochemically either by water oxidation (Eq. 9) or in the Foerster reaction (Eq. 7); z value below 4 indicates that the detected oxygen is at least partially formed by a chemical process most likely involving radicals (see above), i.e. without charge transfer at the electrode–electrolyte interface.

The efficiency of the oxygen production in the hypochlorite oxidation process apparently depends on the electrode potential as it is outlined in Fig. 8. Based on the data presented in Fig. 8, it needs to be stressed that the efficiency of oxygen formation on all studied materials greatly exceeds that predicted by the Foerster's reaction stoichiometry. All tested electrode materials show z values in the range between 1.0 and 3.5 in the interval from 1.30 to 1.7 V (vs RHE). The z starts to increase at potential close and exceeding 1.7 V (vs. RHE) when the chlorine evolution-related processes start to play a significant role (see Fig. 8). The z vs. E curves also show two well-pronounced minima, the positions of which roughly coincide with the positions of the voltammetric peaks discussed in relation to Fig. 3a. The fact that the z value remains rather low in the potential range of both voltammetric peaks suggests

Fig. 8 Apparent average number of electrons involved in formation of one molecule oxygen, z , as a function of electrode potential during hypochlorite oxidation on various RuO_2 -based electrode materials. The presented values were extracted from the DEMS experiments at conditions identical to those in Fig. 2. The assignment of the experimental curves is given in the figure legend

that the anodic processes reflected in both voltammetric peaks are rather similar and both involve chemical formation of apparently over-stoichiometric oxygen. This behaviour is in agreement with the previously proposed radical-involving mechanism [19] of the hypochlorite oxidation. The gradual increase of the z at potentials positive to 1.7 V, i.e. in the potential range where also other oxidation processes can take place, is also in agreement with the assignment of the second (more positive) anodic peak to an oxidation of in situ surface confined hypochlorite-like species.

It needs to be noted that although the increase in the initial hypochlorite concentration affects significantly the observed voltammograms, the effect on the efficiency of the oxygen formation at potentials below 1.7 V where hypochlorite oxidation proceeds via radical mechanism is not dramatic. The efficiency of oxygen production shows, however, a complex dependence on the initial hypochlorite concentration (see Fig. 9) at potentials positive to 1.7 V (vs. RHE). The observed z data suggest a gradual suppression of the extent of the hypochlorite oxidation via radical mechanism in favour of electrocatalytic hypochlorite or conventional water oxidation. The electrocatalytic oxidation processes require sufficiently low surface pH, which, in turn, also enhances chloride adsorption. The concentration dependence in the z behaviour then reflects two contradicting trends. The extent of the radical-based hypochlorite oxidation naturally increases with increasing hypochlorite concentration. The radical-based hypochlorite oxidation, however, produces protons; hence, the increase in the hypochlorite oxidation extent also facilitates the acidification near the surface. Keeping in mind that an increase in hypochlorite concentration increases also the chloride content, one

Fig. 9 Apparent average number of electrons, z , involved in formation of one molecule of oxygen as a function of hypochlorite concentration on various RuO_2 -based catalysts. The presented values were extracted from the DEMS experiments at conditions identical to those in the Fig. 7. The assignment of the experimental curves is given in the figure legends

has also to expect that the hypochlorite and chloride adsorption are facilitated. The resulting z therefore reflects the balance between both types of hypochlorite oxidation and seems to be affected by the nature of the electrode material. The explored electrode materials can be divided into two groups, according to the observed z behaviour. The first one is composed by electrode materials known to have relatively low-to-moderate selectivity for chlorine formation [21, 22]—Zn- and Mg-doped RuO_2 —which are known to be primarily selective for oxygen evolution process [21–23], along with non-doped ruthenium dioxide. The second group is composed of Ni- and Co-doped RuO_2 where one observes the strongest chlorine evolution [20, 28] (see Fig. 6).

As shown in Fig. 9, gradual increase of z to values higher than 4 is obtained for materials showing high selectivity towards chlorine evolution (Ni- and Co-doped RuO_2), which is consistent with blocking of the electrocatalytic hypochlorite oxidation or water oxidation due to a preference for chloride oxidation/adsorption. For the materials with known preference for oxygen evolution, the increase in initial hypochlorite concentration leads to formation of a plateau with z of ca. 4 in the potential interval 1.7–2.0 V (vs. RHE). In the case of the

non-doped RuO₂, the observed values of z remain significantly lower than 4 in the potential interval 1.7–2.0 V (vs. RHE), regardless of the initial hypochlorite concentration. The observed experimental trends confirm the surface sensitivity of the hypochlorite oxidation process at potentials positive to 1.7 V (vs. RHE). It needs to be stressed, however, that the observed behaviour results from complex interplay between the OER, hypochlorite oxidation and CER with apparent interdependence of hypochlorite and chloride adsorption/oxidation.

The Hypochlorite Oxidation Mechanism

The disagreement of the Foerster reaction stoichiometry with the quantitative measure of the oxygen production along with hydrogen peroxide production found for all RuO₂-based anode materials forces us to reformulate the mechanism of the hypochlorite oxidation. Low apparent number of electrons needed for production of one molecule of oxygen, which indicates a mechanism with significant involvement of radicals, needs to be reconciled with (at least partial) electrochemical nature of the overall hypochlorite oxidation process as well as with the fact that it proceeds in two distinctive steps.

The proposed reaction mechanism assumes that the hypochlorite oxidation is initiated by a hypochlorite radical formation.

The formed ClO radical reacts with water or hydroxide ions producing a superoxide radical anion.

This anion radical can be involved in several follow-up reactions yielding either oxygen and hydrogen peroxide, reaction (13), and/or hydroxyl radical and chloride ions, reaction (14).

The hydroxyl radical has high reactivity and given the electrolyte composition, one can assume that it immediately reacts with either hypochlorite, reaction (15), or with chloride ions, reaction (16).

In short, the hypochlorite oxidation may proceed either as a sequence A, which encompasses reactions (11) through (15), or as a sequence B encompassing reactions steps (11), (12), (13), (14) and (16). It needs to be stressed that reaction (15) reforms the hypochlorite radical which can re-enter into step

(12) as a reactant. The reaction sequence A then attains in part a radical chain nature which decreases the apparent number of electrons needed to evolve one molecule of oxygen significantly below 4 as observed in the experiments. The reaction sequence B changes the overall course of the process by regeneration of the hypochlorite anion instead of the hypochlorite radical (compare reactions (15) and (16)). These two processes may be distinguished by following the chloride concentration change during the hypochlorite oxidation process (see below).

The above-outlined mechanism can be applied to processes underlying both anodic peaks observed in voltammograms. Given that the hypochlorite oxidation-related peaks are separated with at least 200 mV, it is reasonable to assume that the initial radical formation proceeds in a different manner in each of them. While the onset of the first anodic peak is mainly surface-insensitive, i.e. the process is exclusively controlled by the electrode potential indicating an outer sphere nature of the electron transfer (the radical is formed from solution-based hypochlorite), the second process, however, is weakly dependent on the surface composition. It indicates that the hypochlorite anion is adsorbed on the surface to a certain extent, stabilising the anion and making it more difficult to oxidize compared with the hypochlorite anion in solution.

The extent of the hypochlorite oxidation according the reaction sequences A and B may be visualized by following the chloride concentration change during the hypochlorite oxidation process (provided that the electrode potential remains confined to the hypochlorite oxidation region). The chloride content change connected with the hypochlorite oxidation can be expressed in a form of a parameter η which is calculated as a ratio of the chloride concentration after and before the hypochlorite oxidation experiment, Eq. 17.

$$\eta = \frac{c_{\text{Cl}}^{\text{after}}}{c_{\text{Cl}}^{\text{before}}} \quad (17)$$

The ratio η as a function of hypochlorite concentration is shown in Fig. 10. In the case of RuO₂-based catalysts, the η ranges between 1.2 and 1.7, which clearly indicate the prevalence of process (15) over process (16) in the entire concentration region. The variability of η with hypochlorite concentration indicates a change in the relative contributions of the processes (15) and (16) to the overall hypochlorite oxidation mechanism. The trends observed are similar to the once obtained on polycrystalline Pt electrodes [19]. However, the significantly lower values of η observed for Pt outline a specific role of the electrode material in the hypochlorite oxidation. There is no specific trend depending on the transition metal included in the RuO₂ structure and the average number of η is 1.4 ± 0.1 . The largest value of η is obtained for Ni-doped RuO₂, which is known to be particularly active for both oxygen and chlorine evolution [28, 29], respectively. One might

Fig. 10 Chloride accumulation η in the system connected with hypochlorite oxidation as a function of the initial hypochlorite concentration

attribute this effect to a specific interaction of the surface with either hypochlorite or chloride anions which is expected to be different between the metals and oxides as well as within the oxides alone.

The role of chloride seems to be reflected also in the concentration dependence of z depicted in Fig. 9. The data presented in Fig. 9 show opposite trends attributable to hypochlorite and chloride present in the system. The increase of hypochlorite concentration ought to, as a rule, decrease the z due to the promotion of the radical chain reaction pathway and due to the buffering effect of the hypochlorite which keeps the pH more alkaline and consequently pushes the bulk chlorine evolution to higher potentials (vs. RHE). Such a behaviour is generally observable in the z vs. E curves in the potential interval 1.5–1.8 V (vs. RHE).¹ The hypochlorite concentration increase, on the other hand, raises also the chloride concentration which increases the extent of the chlorine evolution leading in turn to an increase of the z . The increase of z is more pronounced for Ni- and Zn-doped RuO_2 electrodes while in the case of the non-doped or Mg-doped electrode materials, the concentration dependence of z remains rather weak.

The surface sensitivity of the observed behaviour, therefore, suggests active role of the surface chemistry and consequently the role of the adsorption phenomena on the electrode's activity in hypochlorite oxidation. It needs to be noted that this surface selectivity can be of a paramount importance in the actual chlorate electrolysis. The elucidation of the actual role of chlorides and hypochlorite anions in the anodic process related to the hypochlorite oxidation would, however, require

more systematic approach with respect to the electrolyte composition.

Conclusions

Hypochlorite oxidation on RuO_2 -based electrodes occurs in two steps in the potential window above 1.2 V (vs. RHE). The initial hypochlorite oxidation seems to be independent of the employed electrode material, while the second oxidation process appearing at higher potentials is affected by the nature of the electrode. The latter process is attributed to an oxidation of surface-confined hypochlorite-like species. Regardless of the electrode material, the dominating product of the hypochlorite oxidation is oxygen. The oxygen production shows a maximum at potentials corresponding to the peak position of the second anodic process. In addition, the hypochlorite oxidation leads to the formation of hydrogen peroxide and eventually of chloride ions. The efficiency of the oxygen production in the electrochemical hypochlorite oxidation is high as shown by the apparent number of electrons needed to evolve one molecule of oxygen z . The low z values suggest a radical-based mechanism of the hypochlorite oxidation process. The radical nature of the hypochlorite oxidation is further confirmed by an accumulation of chlorides in the system observed during the hypochlorite oxidation.

Funding Financial support from Akzo Nobel Pulp and Performance Chemicals AB is gratefully acknowledged.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. N. Ibl, H. Voght in *Comprehensive Treatise of Electrochemistry, Electrochemical Processes*, ed. By J. O. Bockris (Plenum Press, 1981), p. 167
2. K. Viswanathan, B.V. Tilak, *Chemical. J. Electrochem. Soc.* **131**(7), 1551 (1984)
3. J.E. Colman, *AIChE Symp. Ser.* **77**, 244 (1981)
4. V. De Valera, On the theory of electrochemical chlorate formation. *Trans. Faraday Soc.* **49**, 1338 (1953)
5. M. Spasojevic, N. Krstajic, P. Spasojevic, L. Ribic-Zelenovic, Modelling current efficiency in an electrochemical hypochlorite reactor. *Chem. Eng. Res. Des.* **93**, 591–601 (2015)
6. C.Y. Cheng, G.H. Kelsall, Models of hypochlorite production in electrochemical reactors with plate and porous anodes. *J. Appl. Electrochem.* **37**(11), 1203–1217 (2007)
7. A. Cornell, in *Encyclopedia of applied electrochemistry*, ed. by G. Kreysa, K.-I. Ota, R. F. Savinell. Chlorate Cathodes and Electrode Design (Springer, New York, 2014), p. 175

¹ The trends in the z values observed at potentials between 1.4 and 1.5 V (vs. RHE) should be taken with care since they are based on evaluation reading comparable with the resolution of the DEMS technique.

8. B. Endrődi, N. Simic, M. Wildlock, A. Cornell, A review of chromium(VI) use in chlorate electrolysis: functions, challenges and suggested alternatives. *Electrochim. Acta* **234**, 108–122 (2017)
9. K.L. Hardee, K.L. Mitchell, The influence of electrolyte parameters on the percent oxygen evolved from a chlorate cell. *J. Electrochem. Soc.* **136**(11), 3314 (1989)
10. J. Wanngård, The catalyzing effect of chromate in the chlorate formation reaction. *Chem. Eng. Res. Des.* **121**, 438–447 (2017)
11. G. Linbergh, D. Simonsson, The effect of chromate addition on cathodic reduction of hypochlorite in hydroxide and chlorate solutions. *J. Electrochem. Soc.* **137**(10), 3094 (1990)
12. M.-L. Tremblay, C. Chabanier, D. Guay, *J. Electrochem. Soc.* **137**, 3094 (1990)
13. J.E. Colman, B.V. Tilak, *Encyclopedia of chemical processing and design* (M. Dekker, New York, 1995), p. 126
14. M.W. Lister, Decomposition of sodium hypochlorite: the catalyzed reaction. *Can. J. Chem.* **34**(4), 479–488 (1956)
15. S. Sandin, R.K.B. Karlsson, A. Cornell, Catalyzed and uncatalyzed decomposition of hypochlorite in dilute solutions. *Ind. Eng. Chem. Res.* **54**(15), 3767–3774 (2015)
16. F. Foerster, *Trans. Amer. Electrochem. Soc.* **46**, 23 (1924)
17. S. Kotowski, B. Busse, in *Modern chlor-alkali technology*, ed. By K. Wall (Ellis Horwood Ltd, Chichester, 1986), p. 310
18. R.K.B. Karlsson, A. Cornell, Selectivity between oxygen and chlorine evolution in the chlor-alkali and chlorate processes. *Chem. Rev.* **116**(5), 2982–3028 (2016)
19. K.M. Macounová, N. Simic, E. Ahlberg, P. Krtíl, *J. Am. Chem. Soc.* **137**, 7262 (2015)
20. J. Jirkovský, M. Makarova, P. Krtíl, Particle size dependence of oxygen evolution reaction on nanocrystalline RuO₂ and Ru_{0.8}Co_{0.2}O_{2-x}. *Electrochem. Commun.* **8**(9), 1417–1422 (2006)
21. V. Petrykin, K. Macounová, M. Okube, S. Mukerjee, P. Krtíl, Local structure of Co doped RuO₂ nanocrystalline electrocatalytic materials for chlorine and oxygen evolution. *Catal. Today* **202**, 63–69 (2013)
22. V. Petrykin, K. Macounová, J. Franc, O. Shchlyakhtin, M. Klementová, S. Mukerjee, P. Krtíl, Zn-Doped RuO₂ electrocatalysts for selective oxygen evolution: relationship between local structure and electrocatalytic behavior in chloride containing media. *Chem. Mater.* **23**(2), 200–207 (2011)
23. V. Petrykin, K. Macounová, O.A. Shlyakhtin, P. Krtíl, Tailoring the selectivity for electrocatalytic oxygen evolution on ruthenium oxides by zinc substitution. *Angew. Chem. Int. Ed.* **49**(28), 4813–4815 (2010)
24. D.F. Abbott, V. Petrykin, M. Okube, Z. Bastl, S. Mukerjee, P. Krtíl, *J. Electrochem. Soc.* **162**, H23 (2015)
25. H.A. Hansen, I.C. Man, F. Studt, F. Abild-Pedersen, T. Bligaard, J. Rossmeisl, *Phys. Chem. Chem. Phys.* **12**, 283 (2010)
26. X. Shi, S. Siahrostami, G.L. Li, Y. Zhang, P. Chakthranont, F. Studt, T.F. Jaramillo, X. Zheng, J.K. Nørskov, Understanding activity trends in electrochemical water oxidation to form hydrogen peroxide. *Nat. Commun.* **8**(1), 701 (2017)
27. M. Gershenzon, P. Davidovits, J.T. Jayne, C.E. Kolb, D.R. Worsnop, *J. Phys. Chem. A* **106**, 7748 (2002)
28. K. Macounová, M. Makarova, J. Jirkovský, J. Franc, P. Krtíl, Parallel oxygen and chlorine evolution on Ru_{1-x}Ni_xO_{2-y} nanostructured electrodes. *Electrochim. Acta* **53**(21), 6126–6134 (2008)
29. N. Bendtsen, V. Petrykin, P. Krtíl, J. Rossmeisl, *Phys. Chem. Chem. Phys.* **16**, 13682 (2014)