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Effects of carbonate on the electrolytic removal of ammonia and urea from urine with thermally prepared IrO₂ electrodes

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Abstract Recent studies have shown that electrolysis can be an efficient process for nitrogen removal from urine. These studies have been conducted with urea solutions or fresh urine, but urine collected in NoMix toilets and urinals has a substantially different composition, because bacteria hydrolyse urea quickly to ammonia and carbonate. In this study, we compared electrochemical removal of nitrogen from synthetic solutions of fresh and stored urine using IrO₂ anodes. We could show that in fresh urine both ammonia and urea are efficiently eliminated, mainly through chlorine-mediated oxidation. However, in stored urine the presence of carbonate, arising from urea hydrolysis, leads to an inhibition of ammonia oxidation. We suggest two parallel mechanisms to explain this effect: the competition between chloride and carbonate oxidation at the anode and the competition between chlorate formation, enhanced by the buffering effect of carbonate, and ammonia oxidation for the consumption of active chlorine in the bulk. However, further experiments are needed to support the latter

mechanism. In conclusion, this study highlights the negative consequences of the presence of carbonate in urine solutions, but also in other wastewaters, when subjected to an electrolytic treatment on IrO₂ in alkaline media.

Keywords Ammonia electrooxidation · Urea electrooxidation · Inhibition by carbonate · Carbonate electrooxidation · Urine treatment

1 Introduction

Ammonia removal is a main objective of municipal wastewater treatment, since free ammonia is a fish toxic and high ammonia loads can cause eutrophication especially in coastal waters [1]. About 80 % of the nitrogen in municipal wastewater originates from urine and recent research has shown that separate treatment of urine is a sensible approach to improve nutrient removal from wastewater [2].

A wide range of processes has been proposed for nitrogen treatment in urine [3]. Some aim to remove nitrogen as gaseous N₂, others to recover nitrogen as a fertilizer. Nitrification [4], nitritation/anammox [5] and ammonia stripping [6] are the most extensively tested technologies. Electrolysis is another interesting technology for nitrogen removal from urine. This process could be particularly suitable for small decentralised reactors due to simple process control, high resilience to inflow variations, simple reactor setup and low demand for chemicals [7].

Electrochemical oxidation of ammonia and urea has received considerable attention in the last years, since novel, efficient, and stable electrodes have been developed [8]. Besides ammonia removal from wastewater, electrolysis has also been tested for ammonia sensors [9] and for hydrogen recovery from ammonia and urea [10, 11].

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In wastewater treatment the most common mechanism for electrochemical ammonia oxidation is indirect oxidation with chlorine [12]: electrochemically generated hypochlorous acid reacts with ammonia in a mechanism known as breakpoint chlorination [13]. Direct electrochemical oxidation of ammonia has been investigated intensively on platinum, but also on other noble metals and their alloys [14]: at low overpotential, nearly all ammonia is oxidised to N_2 following a mechanism that involves the adsorption and dehydrogenation of ammonia (NH_3) molecules [15]. At higher potentials, electrodes are deactivated by adsorbed nitrogen (N_{ads}), but if the potential is increased above a certain threshold, Pt is oxidised to PtO_x and nitrogen oxides such as nitrite and nitrate are formed [14].

Recently, several research groups have presented novel electrodes for direct ammonia oxidation, for example boron-doped diamond electrodes (BDD) [16], Ni/Ni(OH)₂ [17] and dimensionally stable anodes (DSA) such as Ti-IrO₂ [18, 19]. Despite preliminary studies on the mechanism of ammonia oxidation on these electrodes [20, 21], the mechanisms are not completely understood. Bunce and Bejan [14] suggested that the mechanism could be considered to be analogous to a metallic Pt or Ir anode that has become covered by an oxide surface. This theory implies that nitrogen oxides can be produced at higher potentials. Kapalka et al. [21] reported another similarity with noble metals electrodes: intermediates of ammonia oxidation are the likely reason for Ti-IrO₂ electrode deactivation at high potentials.

Electrochemical urea degradation has been studied to a much lower extent than ammonia degradation. Simka and Piotrowski [22] tested several DSA electrodes and could show that N_2 and CO_2 were the main products. In their experiments, urea degradation was mediated by electrochemically formed chlorine. Direct urea degradation was described by Boggs et al. [11] on several noble metals and their alloys. The highest activity, however, exhibited nickel. The low stability of nickel could be improved by electrodepositing rhodium [23].

Few studies have been reported on electrochemical nitrogen removal from urine. Recently, Boggs et al. [11] proposed to use urine as a source of hydrogen, by electrolysis of urea with nickel electrodes. They applied the process on a solution containing 1 mol L⁻¹ KOH and human urine. By adding the KOH solution, a high pH value was ensured, which is beneficial for the direct oxidation of urea. Whether the system would also work with unchanged human urine, was not tested. Ikematsu et al. [24] tested an electrochemical reactor consisting of an iron electrode positioned between two PtIr electrodes. By changing the direction of the current they could switch between total nitrogen removal and iron dissolution for phosphate precipitation. Most of the experiments were conducted with diluted urine solutions.

To our knowledge, no study on urine electrolysis has considered that the composition of source-separated urine changes considerably in the toilets, pipes and storage tanks. Ubiquitous ureolysing bacteria degrade urea [25]. According to medical literature, fresh urine has an average pH value of 6.2, low total ammonia (480 mgN L⁻¹) and 90 % of the nitrogen is bound as urea. After urea hydrolysis, the same urine has an average pH value of 9.1, more than 90 % of the nitrogen exists as total ammonia (NH_3 and NH_4^+) and the total carbonate concentration increased from nearly zero to 3,200 mgC L⁻¹. Concomitantly, the alkalinity of the solution increases as well [26]. All these changes can have a considerable effect on the electrochemical removal of nitrogen, as we will show in this study.

2 Materials and methods

Two synthetic solutions featuring human urine immediately after excretion (“fresh urine”) and after storage in a urine collection-system (“stored urine”) were used. Both solutions were prepared based on the composition given by Udert et al. [26] (details on Table 1 and in supplementary information).

Table 1 shows that the fresh urine solution contained mainly urea as nitrogen species, whereas in the stored urine solution, urea is replaced by ammonia and carbonate. This modification represents the fact that urea is hydrolysed by the enzyme urease produced by microorganisms [25]. As the only organic compound with chemical oxygen demand (COD) (urea does not have a COD), acetate was added to

Table 1 Concentrations of the species initially present in synthetic solutions of fresh and stored urine. The recipes for the solutions are given in Tables 1 and 2 of the supplementary information

	Fresh urine (mol L ⁻¹)	Stored urine (mol L ⁻¹)
Urea	0.266	–
Ammonia/ammonium	0.0337	0.568
Chloride	0.107	0.118
Bicarbonate/carbonate	–	0.271
Acetate	0.125	0.125
Sodium	0.184	0.111
Potassium	0.0563	0.0563
Magnesium	0.00389	–
Calcium	0.0046	–
Sulfate	0.0162	0.0162
Phosphate	0.0242	0.0175
Initial pH	6.1	8.8

stored urine. This compound was chosen as representative for the COD compounds, since it makes up about 50 % of the COD in stored urine (own measurements, data not shown). Acetate is formed by fermentation during storage. For the sake of simplicity, we also added acetate as COD source to fresh urine. However, COD was not measured in this experiment since our own experiments showed that it was not degraded at the electrode used (unpublished results).

Ti/IrO₂ (loading: 1 mg IrO₂ cm⁻²) electrodes were prepared by a thermal decomposition method. More details have been given elsewhere [27].

Electrolysis experiments were carried out at constant temperature ($T = 25 \pm 1$ °C, Polystat cc2, Huber, Germany), under galvanostatic conditions (15 ± 0.3 mA cm⁻², EA-PS 3065-03B, Conrad, Germany), in a 120 mL one-compartment cell with two zirconium cathodes and one Ti/IrO₂ anode (geometric surface area: 13.5 cm²) in between. Stirring was provided by a magnetic bar and a magnetic stirrer (ARE Heating Magnetic Stirrer, VELP Scientifica, Italy).

1 mL aliquots were taken at various time intervals. The solution pH was measured at every sampling (pH 213 Microprocessor pH-meter, Hanna Instruments, France), and, when necessary, it was adjusted with solutions of NaOH (Fluka Chemicals, Switzerland) or HClO₄ (60 %, ACS, Alfa Aesar, USA). The concentration of both solutions varied between 0.01 mmol L⁻¹ and 1 mol L⁻¹ depending on the experiment and the pH change. The pH was not adjusted between two consecutive samplings. The cell voltage was recorded at every sampling.

During electrolysis, the active chlorine concentration (sum of Cl₂, HOCl, NaOCl, and chloramines) was measured by iodometric titration [28], while the total nitrogen (sum of dissolved nitrogen species), total ammonia (sum of free ammonia and ammonium), nitrate and nitrite concentrations were measured photometrically with cuvette tests (Hach Lange GmbH, Germany).

The polarization curves were obtained in a 50 mL one-compartment cell with three electrodes: the working electrode was a Ti/IrO₂ electrode (geometric surface area: 0.785 cm²), the reference electrode was a mercurous sulfate electrode MSE (REF 621, Radiometer Analytical, France) with a potential of +0.64 V versus standard hydrogen electrode, and the counter electrode was a platinum wire. These electrodes were connected to the galvanostat-potentiostat (μ Autolab Type III, Eco Chemie BV, The Netherlands) and the data were recorded and analysed with the software GPES (Version 4.9.009).

The speciation of carbonate species was calculated with the computer program PHREEQC according to [17]. In the simulations, we used the Pitzer approach to calculate the ion activities.

3 Results

3.1 Electrolysis of synthetic urine solutions

Figure 1 shows the results of galvanostatic electrolysis (15 mA cm⁻²) of fresh urine (initial pH 6) and stored urine (initial pH 9) on IrO₂ anode, carried out at 25 °C. The electrical charge passed Q [Ah L⁻¹] was calculated as indicated in the supplementary information section.

During fresh urine electrolysis the pH value first increased. After passing $Q = 45$ Ah L⁻¹ it reached a maximum of 7, and then fell to a value of 5 towards the end of the electrolysis (charge passed 86 Ah L⁻¹). During electrolysis of stored urine the pH remained constant at a value close to 9.

Figure 1A and C show the measured concentrations of ammonia, nitrate, and total nitrogen species as a function of Q for both fresh urine and stored urine. In the former case, the total nitrogen concentration decreased clearly with time, total ammonia concentration remained low and dropped under the detection limit (2 mgN L⁻¹), and the concentration of nitrate increased, reaching a maximum of 1670 mgN L⁻¹ at the end of the experiment. In the case of stored urine, the concentration of total nitrogen, mainly consisting of ammonia, hardly changed. The total ammonia concentration dropped only slightly during the experiment, partially compensated by the increase of the nitrate concentration. Nitrite concentrations (not shown) remained low: they reached a maximum of 1.6 mgN L⁻¹ for fresh urine, and were below the detection limit (0.6 mgN L⁻¹) for stored urine. Figure 1B and D display the concentration of active chlorine as a function of Q in both solutions. A sharp increase is observed towards the end of the experiment for fresh urine, whereas the level of active chlorine remained very low and quite constant during the entire experiment for stored urine.

3.2 Effect of carbonate and high pH value on the electrolysis of fresh urine

In order to investigate the effects of carbonate on the electrochemical treatment of fresh urine, a first experiment was carried out in presence of 3.24 gC L⁻¹ of carbonate (or 28.6 gNa₂CO₃ L⁻¹). The resulting pH value was 10.2. To separate the effects of carbonate and high pH, a second electrolysis experiment was conducted by adjusting the pH value to 10.2 by adding NaOH. Figure 2 shows the nitrogen concentrations and the concentration of active chlorine for both experiments. In the experiment with carbonate, the pH value remained constant without addition of base, while in the experiment without carbonate, the pH had to be adjusted by adding NaOH to keep it at a value of 10.2. Figure 2A shows that urea oxidation was inhibited in the

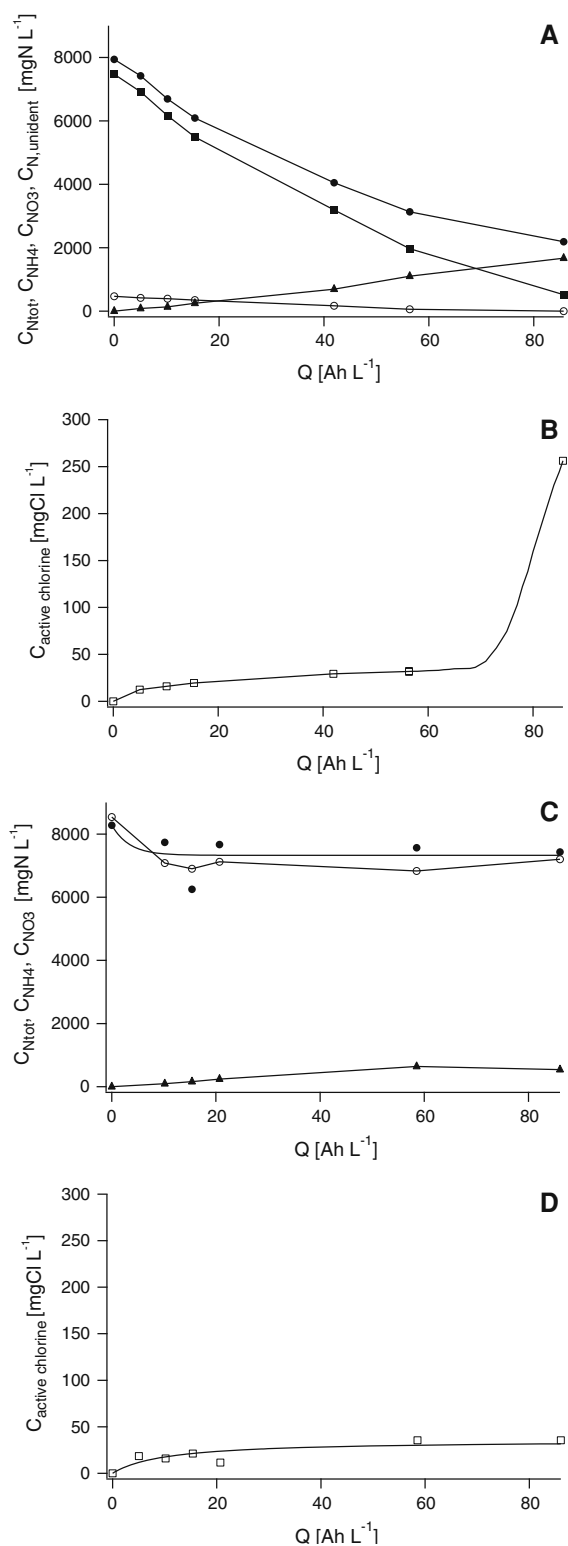


Fig. 1 Galvanostatic electrolysis of synthetic fresh urine, at pH 6 ± 1 (A, B) and synthetic hydrolysed urine at pH 9 (C, D). $j = 15 \text{ mA cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$. Filled circle total nitrogen (C_{Ntot}), open circle ammonium ($C_{\text{NH}_4^+}$), filled triangle nitrate ($C_{\text{NO}_3^-}$), filled square non-identified nitrogen-species ($C_{\text{N,unident}}$; at the beginning of the experiment, this must have been urea, but it was not identified by measurements during the experiment), open square active chlorine ($C_{\text{active chlorine}}$). The formulas for the fitted curves are given in the supplementary information

The initial current efficiency of urea oxidation was high (86 %). Nitrate was formed during the first part of the experiment. The level of active chlorine was similar in both experiments (Fig. 2B, D).

3.3 Carbonate study

In order to understand the effect of high carbonate concentrations on urea and ammonia oxidation, we measured polarization curves in solutions containing Na_2CO_3 (various concentrations) and NaClO_4 (1 mol L^{-1}), firstly as a function of pH (Fig. 3), and secondly as a function of carbonate concentration (Fig. 4). The curves show that carbonate was oxidised on IrO_2 anode at a pH higher than 9, with an onset potential of 0.35 V versus MSE. In both experiments, the height of the current density peak correlated with the concentration of carbonate (CO_3^{2-}) (inset of Fig. 3 and inset of Fig. 4). The speciation of carbonate was calculated using Pitzer parameters for the carbonate species, that allow incorporating the high ionic strength of the solution into the calculations.

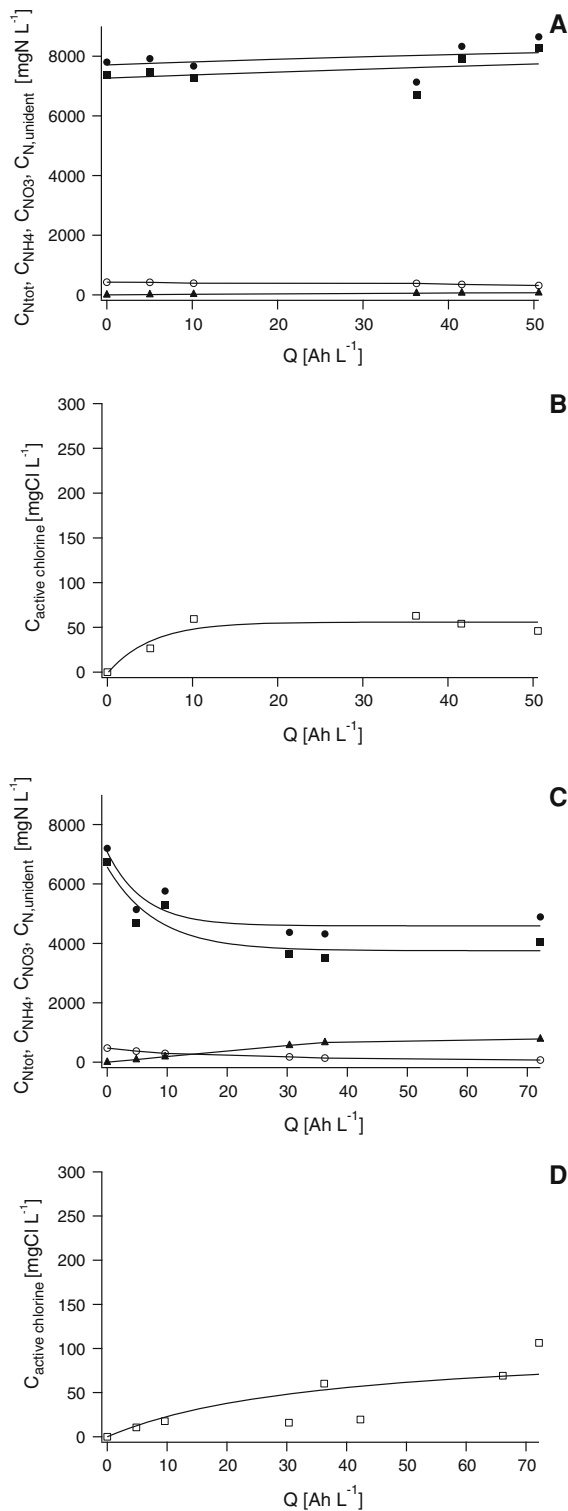
Galvanostatic electrolysis of 0.12 mol L^{-1} NaCl solutions was carried out in presence and in absence of carbonate (0, 1.68, 3.24 gC L^{-1}), for pH values varying between 6 and 10. The results revealed that carbonate strongly inhibited the formation of active chlorine in the bulk of alkaline solution, but more weakly in neutral and acidic solutions (Fig. 5). Without carbonate, the pH value had only a small effect on the production of active chlorine.

4 Discussion

4.1 Active chlorine formation

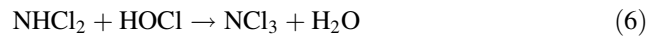
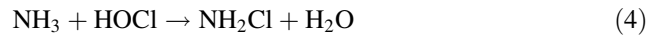
In all experiments, active chlorine was found in considerably high amounts. Equations 1–3 can describe the formation of active chlorine compounds: chloride was oxidised to chlorine at the IrO_2 anode (Eq. 1), and further on chlorine was hydrolysed in the bulk of the solution to form hypochlorous acid and hypochlorite ion (Eqs. 2, 3). These reactions were already observed on IrO_2 electrodes [29].

presence of carbonate. The solution without carbonate exhibited a different electrolysis behaviour: the nitrogen measurements depicted in Fig. 2C show that urea degradation was fast in the beginning of the experiment but essentially stopped when Q passed a value of 10 Ah L^{-1} .



◀ **Fig. 2** Galvanostatic electrolysis of synthetic fresh urine in presence of $3.24 \text{ gC L}^{-1} \text{ Na}_2\text{CO}_3$ (**A, B**) and in absence of carbonate (**C, D**). Conditions: pH 10.2, $j = 15 \text{ mA cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$. *Filled circle* total nitrogen ($C_{\text{N,tot}}$), *open circle* ammonium (C_{NH_4}), *filled triangle* nitrate (C_{NO_3}), *filled square* non-identified nitrogen ($C_{\text{N,unident}}$: at the beginning of the experiment, this must have been urea, but it was not identified by measurements during the experiment), *open square* active chlorine ($C_{\text{active chlorine}}$). The formulas for the fitted curves are given in the supplementary information

urea [30, 31]. In the reaction with ammonia, chloramines may be formed according to Eqs. 4–6 [13, 30].

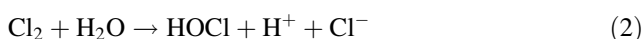
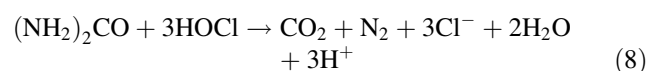
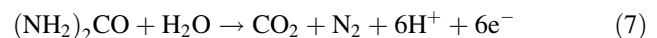


4.2 Urea degradation in fresh urine

Urea oxidation to nitrogen may occur either through direct oxidation, according to Eq. 7, or indirect oxidation, via electro-generated active chlorine, as indicated by Eq. 8 [32, 33]. Simka and Piotrowski [22] further differentiate indirect urea electrolysis through chlorine adsorbed at the anodic surface and through active chlorine present in the bulk of the solution. In the first case, the chloride concentration is almost constant along the experiment and no active chlorine is formed in the bulk, whereas in the latter case, active chlorine is clearly formed and participates in the oxidation of urea in the bulk of the solution.

The mechanism of urea oxidation and its products depend strongly on the process parameters, and especially on the initial concentration of chloride, the pH value of the solution, the applied current density, and the applied anodic potential [31, 33]. For instance, on RuO_2 anodes, a more efficient indirect oxidation was observed at higher pH values and high NaCl concentrations [33].

The main products of direct urea electrooxidation depend on the pH: for instance, in neutral conditions, CO_2 and N_2 are formed, but by-products such as nitrogen dioxide (NO_2), nitrous oxide (N_2O), and NO_3^- were also observed [34]. Concerning indirect urea electrolysis, it is known that ammonia and nitrate are the main products, and that ammonia can be further oxidised to N_2 and NO_3^- by active chlorine [35]. Possible reaction mechanisms for nitrate production from urea in absence and in presence of active chlorine are given in Eqs. 9 and 10. These two equations are solely based on stoichiometry, since the mechanism of the indirect electrochemical oxidation of urea to nitrate has not been clarified yet.



Hypochlorous acid is known to be a more potent oxidant than hypochlorite [30] and is able to oxidise ammonia and

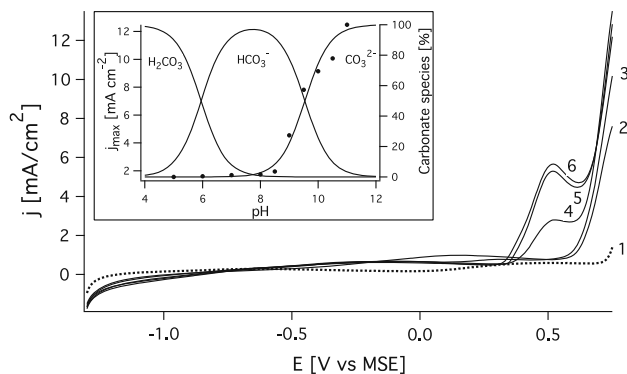


Fig. 3 Polarization curves for $1.20 \text{ gC}\cdot\text{L}^{-1}$ of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3^-$ in $1 \text{ mol}\cdot\text{L}^{-1}$ NaClO_4 . Scan rate = 50 mV s^{-1} , $T = 25^\circ\text{C}$, on IrO_2 anode. Curve 1: supporting electrolyte (blank) at pH 9, curves 2–6: pH 6, 8, 9, 10 and 11. In the inset the peak current density (dots), and the calculated carbonate species concentrations (lines) are shown as function of the pH value

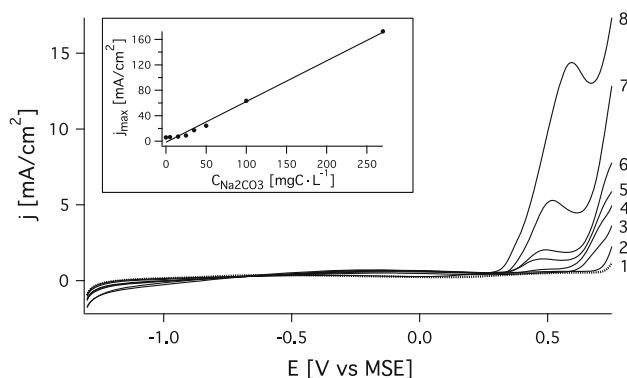
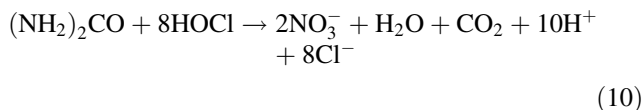
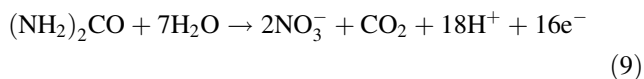


Fig. 4 Polarization curves for various concentrations of Na_2CO_3 in 1 mol L^{-1} NaClO_4 , at pH 10, scan rate = 50 mV s^{-1} , $T = 25^\circ\text{C}$, on IrO_2 anode. Curve 1: supporting electrolyte (blank), curves 2–8: $0.06, 0.18, 0.30, 0.42, 0.60, 1.20$ and $3.24 \text{ gC}\cdot\text{L}^{-1}$ Na_2CO_3 . The inset shows the peak current density as a function of the total carbonate concentration



The nearly parallel decrease of total nitrogen and urea in Fig. 1A shows that urea was mainly oxidised to gaseous compounds such as molecular nitrogen N_2 and possibly to N_2O , NO_2 , and nitric oxide (NO), while only a small fraction was oxidised to aqueous species, especially nitrate. The mechanism of urea oxidation may involve ammonia as intermediate, but in this case the reaction of ammonia with active chlorine was fast, as we did not observe any increase in ammonia concentration in the solution. In the present experiment, indirect oxidation by bulk active chlorine is probably the main pathway, since the concentration of

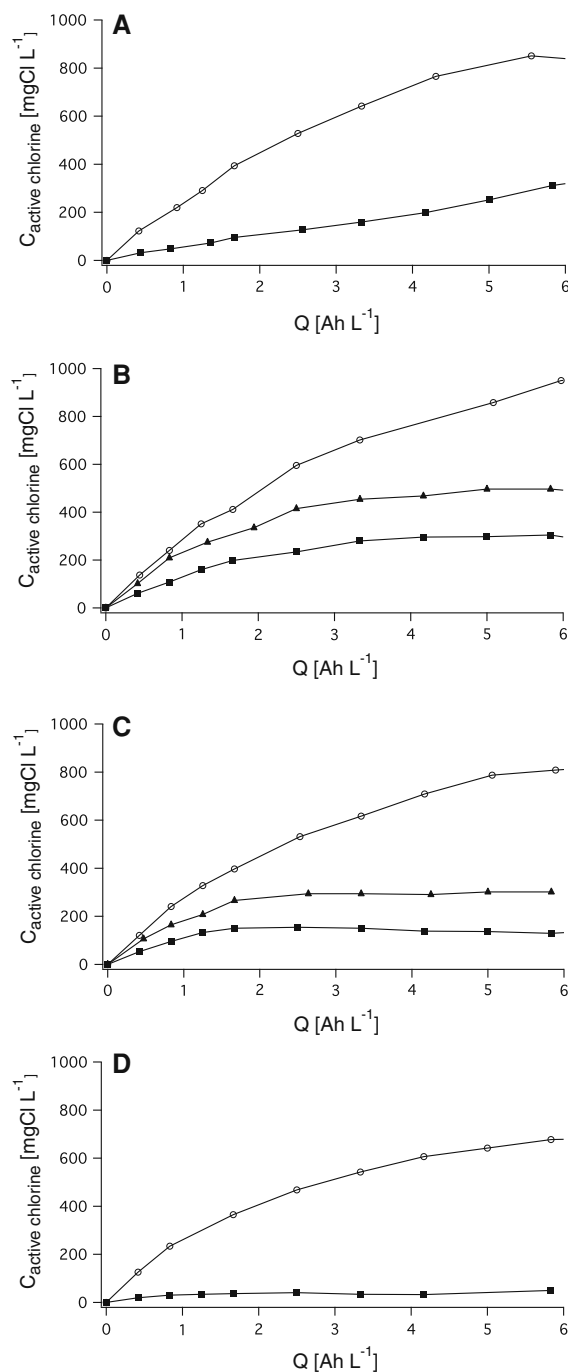


Fig. 5 Effect of carbonate on the rate of active chlorine formation during galvanostatic electrolysis in a 0.12 mol L^{-1} NaCl solution, at pH 6 (A), 8 (B), 9 (C) and 10 (D), on IrO_2 anode, at 15 mA cm^{-2} , $T = 25^\circ\text{C}$. Open circle $0 \text{ gC}\cdot\text{L}^{-1}$ Na_2CO_3 , filled triangle $1.68 \text{ gC}\cdot\text{L}^{-1}$ Na_2CO_3 , filled square $3.24 \text{ gC}\cdot\text{L}^{-1}$ Na_2CO_3

active chlorine remained very low during the whole process, and rose when the urea concentration became low, as shown by Fig. 1B. However, we cannot exclude some direct urea oxidation, since we have not measured the anodic potential during the present experiment, and since the low level of active chlorine may also be the result of the

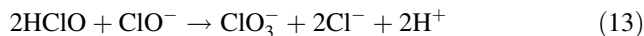
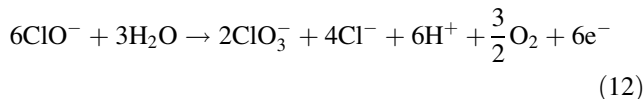
Table 2 Initial (η^{initial}) and overall (η^{overall}) current efficiencies for NO_3^- , N_2 and Cl_2 production and selectivity towards nitrate ($K_{\text{NO}_3}^{\text{R}}$) during electrolysis of synthetic fresh urine and synthetic stored urine. R denotes the sum of ammonia, ammonium and urea

	Fresh urine, pH 6	Stored urine, pH 9
Charge passed	86 Ah L ⁻¹	86 Ah L ⁻¹
(% of theoretical amount for complete elimination of urea or ammonia)	(190 %)	(250 %)
$\eta_{\text{Urea} \rightarrow \text{NO}_3^-}^{\text{initial}}$	23.7 %	–
$\eta_{\text{Urea} \rightarrow \text{N}_2}^{\text{initial}}$	70.3 %	–
$\eta_{\text{NH}_3 \rightarrow \text{NO}_3^-}^{\text{initial}}$	–	25.2 %
$\eta_{\text{NH}_3 \rightarrow \text{N}_2}^{\text{initial}}$	–	47.6 %
$\eta_{\text{Cl}^- \rightarrow \text{Cl}_2}^{\text{initial}}$	0.4 %	0.2 %
$\eta_{\text{R, total}}^{\text{initial}} = \eta_{\text{R} \rightarrow \text{NO}_3^-}^{\text{initial}} + \eta_{\text{R} \rightarrow \text{N}_2}^{\text{initial}} + \eta_{\text{Cl}^- \rightarrow \text{Cl}_2}^{\text{initial}}$	94.4 %	73.0 %
$\eta_{\text{Urea} \rightarrow \text{NO}_3^-}^{\text{overall}}$	31.9 %	–
$\eta_{\text{Urea} \rightarrow \text{N}_2}^{\text{overall}}$	37.9 %	–
$\eta_{\text{NH}_3 \rightarrow \text{NO}_3^-}^{\text{overall}}$	–	8.6 %
$\eta_{\text{NH}_3 \rightarrow \text{N}_2}^{\text{overall}}$	–	3.1 %
$\eta_{\text{Cl}^- \rightarrow \text{Cl}_2}^{\text{overall}}$	4.4 %	1.6 %
$\eta_{\text{R, total}}^{\text{overall}} = \eta_{\text{R} \rightarrow \text{NO}_3^-}^{\text{overall}} + \eta_{\text{R} \rightarrow \text{N}_2}^{\text{overall}} + \eta_{\text{Cl}^- \rightarrow \text{Cl}_2}^{\text{overall}}$	74.2 %	13.3 %
$K_{\text{NO}_3}^{\text{R}} = \frac{\eta_{\text{R} \rightarrow \text{NO}_3^-}^{\text{overall}}}{\eta_{\text{R, total}}^{\text{overall}}}$	24 %	31.8 %
Urea conversion ratio	93 %	–
Ammonia conversion ratio	100 %	16.9 %
Total nitrogen removal	72.4 %	10.3 %

inhibition or the consumption of active chlorine by other side processes. The oxidation of urea mediated by adsorbed chlorine, as defined by Simka and Piotrowski [22], did probably not occur since we clearly observed the formation of active chlorine in the bulk.

Current efficiencies for urea oxidation to molecular nitrogen and nitrate, and chlorine evolution were calculated based on the data of Fig. 1 (more details on the calculation are given in the supplementary information). Both the initial current efficiencies (initial slope of the concentration curve vs Q , when $Q \rightarrow 0$, see supplementary information for calculation) and the overall current efficiencies are given in Table 2; in the same table, the selectivity towards nitrate formation is also presented. For fresh urine electrolysis, the total current efficiency (sum of the identified main reactions) decreased with time, which means that some unknown side reactions became important or some losses occurred. A possible loss is the volatilization of gaseous chlorine. Furthermore, thermally prepared IrO_2 electrodes are known to show an electrocatalytic activity for oxygen evolution [36], and, as the cell potential slightly increased during the electrolysis, oxygen evolution (Eq. 11) may have

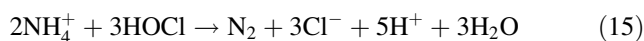
occurred. Then, some chloramines were probably formed according to Eqs. 4–6 [30]. Finally, both the chemical and electrochemical formation of chlorate (Eqs. 12, 13) have been reported in similar conditions [31].



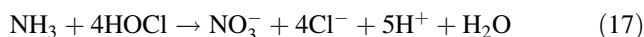
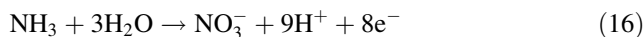
According to our data, most of the urea and ammonia were removed from fresh urine during the 48 h electrolysis experiment. Only 27.6 % of the nitrogen remained in the solution, from which 24 % in the form of nitrate. The overall current efficiency of the process was 74.2 %, which is a considerably good value.

4.3 Ammonia degradation in stored urine

Ammonia can be efficiently degraded by direct oxidation on IrO_2 electrode in alkaline pH solutions, but not in neutral and acidic conditions. Indeed, only the species NH_3 is oxidised, whereas ammonium (NH_4^+) remains electrochemically inert (Eq. 14) [18, 21]. Under non-alkaline conditions, ammonium can be oxidised indirectly by electro-generated active chlorine [18]. This process is supported by the speciation of active chlorine: at a pH value below 7.5, the major species is hypochlorous acid, which is a more potent oxidant than hypochlorite (Eq. 15) [30]. Indirect oxidation by active chlorine has also been proposed as major ammonia degradation mechanism for BDD and other DSA electrodes (see e.g. [13, 16, 37]).



During electrolysis of stored urine, total nitrogen and ammonia concentrations decreased only slightly at the beginning of the experiment and then remained constant within experimental errors (Fig. 1C). Apparently, ammonia was neither oxidised directly nor by electro-generated active chlorine. Hardly any nitrogen left the solution, suggesting that no volatile nitrogen compounds were produced. Only nitrate was formed in appreciable amounts, probably following Eqs. 16 [37] or 17. Equation 17 is based on stoichiometry, since the mechanism of nitrate formation from ammonia through active chlorine has not been completely clarified yet.



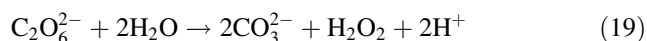
Initial and overall current efficiencies, for ammonia oxidation to molecular nitrogen and nitrate and for chlorine

formation are given in Table 2. The initial current efficiencies were high, but they strongly decreased until the end of the treatment. Overall, only 10.3 % of ammonia was removed, and 31.8 % of the removed ammonia was oxidised to nitrate. Figure 1D shows that the amount of active chlorine in the bulk of the solution remained very constant and low throughout the experiment. This suggests either an inhibition of active chlorine formation or the consumption of active chlorine by another competing reaction. Chemical and electrochemical formation of chlorate (Eqs. 9, 10) have been reported to occur in dilute active chlorine solutions and might have consumed active chlorine [31, 38].

The overall total current efficiency in the experiment with stored urine was only 13.3 %. This value is much lower than in the experiment on urea electrolysis. Side reactions at the surface of the electrode such as the oxidation of water (Eq. 11), the electrochemical formation of chlorate (Eq. 12) and the oxidation of carbonate (Eq. 18) may explain this difference.

4.4 Carbonate oxidation

During cyclic voltammetry of carbonate solutions at different pH values the peak maximum current density correlated well with the CO_3^{2-} species concentration (inset of Fig. 3). Zhang and Oloman, and Van der Wiel and Janssen [39, 40] suggested a mechanism for carbonate oxidation on platinum electrodes: carbonate is oxidised to percarbonate (Eq. 18), which is further hydrolysed to bicarbonate and hydrogen peroxide (Eq. 19). Hydrogen peroxide may finally be oxidised at the surface of the anode to oxygen (Eq. 20). During the overall reaction 2 mol of protons are released per mole of carbonate oxidised. This should lead to a pH decrease, if the solutions were not as strongly buffered as in our experiments. The half time of percarbonate was reported to be 1–2 min at pH 10 and 15 °C [40]. The oxidation of carbonate to percarbonate was also reported on BDD electrodes at alkaline conditions [41].



The electrochemical oxidation of carbonate not only lowered the current efficiency for ammonia oxidation, it is also the likely reason for the inhibition of ammonia and chlorine oxidation. This can be shown by comparing oxidation potentials: the observed oxidation potential of 3.24 gC L⁻¹ carbonate at pH 10 on our IrO₂ anode (onset potential = 0.35 V vs MSE, Figs. 3, 4) is lower than the potential for chloride oxidation (onset potential = 0.7 V vs MSE for 1 mol L⁻¹), and similar to the one of ammonia

oxidation (onset potential = 0.45 V vs MSE, for 0.1 mol L⁻¹) on IrO₂ electrodes [42]. Due to its lower oxidation potential, carbonate oxidation (Eq. 18) at the surface of the electrode competes and may overcome the reaction of chlorine evolution (Eq. 1), as well as the reaction of direct ammonia oxidation (Eqs. 14, 16).

4.5 Hypochlorite consumption

CO_3^{2-} oxidation alone cannot explain the low active chlorine production at lower pH values (Fig. 5A, B). In neutral and slightly acidic conditions, carbonate is predominantly present in the form of bicarbonate HCO_3^- and carbonic acid H_2CO_3 , which are not oxidised at the same low potentials as CO_3^{2-} (Fig. 3). One process that reduces the availability of active chlorine may be the formation of chlorate. Jung et al. [43] suggest that active chlorine electrochemical oxidation to chlorate is more efficient at pH values above 7.2. Based on their observations, they proposed that hypochlorite ion is the active chlorine species that is converted electrochemically to chlorate, whereas hypochlorous acid would rather be converted chemically to chlorate, but in a less efficient reaction. The electrochemical conversion of active chlorine to chlorate under alkaline and neutral conditions has also been proposed by several studies [38, 44]. In our experiments, the strong buffering effect of carbonate could have enhanced the electrochemical (in alkaline solutions) and chemical (in slightly acidic solutions) conversion of active chlorine to chlorate (Eqs. 12, 13) in the diffusion layer close to the electrode. However, a final conclusion is not possible, because we did not measure the chlorate concentrations.

4.6 Effect of carbonate on nitrogen removal

Based on these considerations, we propose that the inefficient ammonia and urea degradation at high carbonate (CO_3^{2-}) concentrations is mainly a consequence of the anodic oxidation of carbonate into percarbonate. An additional process that reduces the efficiency of ammonia and urea oxidation could be the removal of active chlorine through chlorate formation in the diffusion layer, enhanced by the buffering effect of carbonate. However, further experiments are needed to prove this hypothesis.

The results of Fig. 2C may be explained as follows: at the beginning of the electrolysis, no carbonate is present, and urea is degraded. However, urea degradation leads to the formation of CO_2 (Eqs. 7–10), which exists mainly as CO_3^{2-} under alkaline conditions, and thus inhibits further urea oxidation. This is an auto-inhibition mechanism of urea oxidation in alkaline conditions on IrO₂ electrode. However, under slightly acidic conditions (Figs. 1A, 5A), carbonate inhibits the formation of active chlorine only

slightly, which may affect the efficiency of indirect urea oxidation, but not direct urea oxidation.

5 Conclusions

- In fresh urine, urea and ammonia can be efficiently oxidised on IrO₂ electrodes, but in stored urine ammonia cannot be oxidised with the same electrode. If electrolysis is used for nitrogen removal from urine, the reactor should be located very close to the toilet in order to collect the urine, before urea has been hydrolysed in the pipes.
- High carbonate (CO₃²⁻) concentrations are responsible for the insufficient ammonia electrolysis in stored urine. Carbonate is oxidised at a relatively low potential (about 0.35 V vs MSE on IrO₂) and thereby outcompetes direct ammonia oxidation and formation of active chlorine. A second influence on the current efficiency could be the enhanced conversion of active chlorine to chlorate due to the high pH values in the carbonate buffer.
- The presence of carbonate might not only be a problem for the electrolytic removal of ammonia and urea from urine on IrO₂ anode but also for other solutions and processes that involve chlorine mediated oxidation at elevated pH values.
- Further research on ammonia removal from stored urine should focus on finding electrodes that have higher oxidation potentials for carbonate than for chloride and ammonia.

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