Electrolysis for the Treatment of Stored Source-Separated Urine

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DOCTOR OF SCIENCE of ETH ZURICH

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presented by

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Last but not least, I thank you, Barbara, for all you mean to me. You gave me decisive input for my work ;-) and supported me with so many things especially when I was having hard times. I love you.

Hanspeter, Mai 2015
Abstract

Electrolysis is a promising technology for the on-site treatment of source-separated urine. It is the many degrees of freedom (electrode material, electrode potential, current density, cell design), the electrical conductivity of urine and the high amenability to automation which make electrolysis attractive. It was the objective of this thesis to understand the electro-oxidation of organic substances and ammonia to apply electrolysis successfully for the removal of these compounds from stored source-separated urine. To achieve this goal, a variety of electrochemical experiments were conducted with anodes consisting of boron-doped diamond (BDD), thermally decomposed iridium oxide film (TDIROF) or graphite and a new experimental procedure was developed to assess the time dependent production of volatile organic chlorination by-products (OCBPs).

It was found that on BDD organic substances were preferentially oxidized via a fast reaction with hydroxyl radicals leading to very high removal rates ($r_{\text{COD}}$ above 420 gCOD·m$^{-2}$·d$^{-1}$, at 20 mA·cm$^{-2}$) compared to surface based biological systems (4 gBOD·m$^{-2}$·d$^{-1}$). On TDIROF, organics were mainly oxidized by chlorine mediated oxidation ($r_{\text{COD}} = 214 \pm 24$ gCOD·m$^{-2}$·d$^{-1}$, at 20 mA·cm$^{-2}$). However, chlorine evolution on BDD and TDIROF led to the formation of chlorination by-products (CBPs). Chlorate and perchlorate (at sufficiently high specific charge) were massively produced on both anodes (above 80% of initial chloride) but also the production of volatile OCBPs occurred (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloropropane, 1,2-dichloroethane, chlorobenzene) which were primarily emitted into the gas phase (40 – 100%). Ammonia was exclusively removed by chlorine mediated oxidation at elevated current densities ($r_{\text{NH}_4} = 43 \pm 20$ gN·m$^{-2}$·d$^{-1}$ on BDD, $r_{\text{NH}_4} = 227 \pm 16$ gN·m$^{-2}$·d$^{-1}$ on TDIROF at 20 mA·cm$^{-2}$). However, chlorine did not act as an ideal mediator but was removed in the form of CBPs resulting in residual ammonia in some cases.

The alternative direct oxidation of ammonia was shown to be feasible on graphite anodes preventing concomitant CBP formation and resulting in a lower specific energy demand ($E_{\text{sp,NH}_4} = 42$ Wh·gN$^{-1}$ at 12% ammonia removal) compared to chlorine mediated oxidation (BDD: 132 Wh·gN$^{-1}$ at 13% ammonia removal, TDIROF: 70 Wh·gN$^{-1}$ at 28% ammonia removal). However, even the lowest specific energy demand was an order of magnitude higher compared to biological nitrogen removal (4 Wh·gN$^{-1}$). The slow removal rates of direct electrochemical ammonia oxidation ($2.9 \pm 0.3$ gN·m$^{-2}$·d$^{-1}$) were likely the result of a pH drop in the anodic diffusion layer leading to the presence of non-reactive NH$_4^+$. Such a pH drop was demonstrated to be responsible for the fast inhibition of direct ammonia oxidation on TDIROF anodes. It was concluded that direct ammonia oxidation can be accelerated by reducing the thickness of the anodic diffusion layer through improved hydraulic conditions in the electrolysis cells.

In conclusion, this work confirmed the versatility of electrolysis as a treatment technology for source-separated urine. Moreover, it showed the complexity of the chemical and electrochemical processes during the electrolysis of a heterogeneous electrolyte such as urine. A more profound understanding of these processes is necessary to design efficient electrochemical systems. Additionally, electrode materials should be developed which are specific for the targeted reactions at low overpotentials.
Zusammenfassung

Die Elektrolyse ist eine vielversprechende Technologie für die Behandlung von Urin. Es sind die vielen Freiheitsgrade (Elektrodenmaterialien, Elektrodenpotential, Stromdichte, Zellendesign), die elektrische Leitfähigkeit des Urins sowie das hohe Automatisierungspotential, welche die Elektrolyse attraktiv machen. Es war das Ziel dieser Arbeit, die elektrochemische Oxidation von organischen Substanzen und Ammoniak zu verstehen, um diese für die dezentrale Behandlung von gelagertem Urin anzuwenden. Es wurden elektrochemische Experimente mit Bor-versetzten Diamant- (BDD), thermisch hergestellten Iridiumoxidfilm- (TDIROF) und Graphitanoden durchgeführt. Um dabei die Entstehung von leichtflüchtigen, chlorierten Nebenprodukten (CNPs) zu verfolgen, wurde eine neue experimentelle Methode entwickelt. Die Untersuchungen zeigten, dass an BDD organische Substanzen in einer Reaktion mit Hydroxylradikalen bevorzugt und mit hohen Raten \( r_{\text{CSB}} \) über 420 gCSB·m\(^{-2}\)·d\(^{-1}\), mit 20 mA·cm\(^{-2}\) oxidiert werden. An TDIROF waren mehrheitlich aktive Chlorspezies für die Oxidation organischer Stoffe verantwortlich (\( r_{\text{CSB}} = 214 \pm 24\) gCSB·m\(^{-2}\)·d\(^{-1}\), mit 20 mA·cm\(^{-2}\)). Allerdings führte die Entstehung von Chlor an beiden Elektroden zu CNPs. Große Mengen an Chlorat und Perchlorat (bei hoher spezifischer Ladung) wurden gebildet (über 80% von anfänglichem Chlorid) aber auch CNPs (Dichlormethan, Trichlormethan, Tetrachlormethan, 1,2-Dichlorpropaen, 1,2-Dichlorethan, Chlorbenzol), die in erster Linie in die Gasphase emittierten (40 – 100%), entstanden. Ammoniak wurde bei erhöhten Stromdichten ausschließlich von aktiven Chlorspezies oxidiert \( r_{\text{NH}} = 43 \pm 20 \) gN·m\(^{-2}\)·d\(^{-1}\) an BDD, \( r_{\text{NH}} = 227 \pm 16 \) gN·m\(^{-2}\)·d\(^{-1}\) an TDIROF mit 20 mA·cm\(^{-2}\)), was erheblichen Restammoniak zur Folge hatte, wenn die Bildung der CNPs zur totalen Erschöpfung des Chlorids führte. Es zeigte sich, dass Ammoniak alternative an Graphitelektroden mittels direktem Elektronentransfer oxidiert werden kann. Dies verhinderte die Entstehung von CNPs und führte zu geringerem spezifischem Energieverbrauch \( (E_{\text{sp,NH}} = 42 \) Wh·gN\(^{-1}\) nach 12% Ammoniakentfernung) im Vergleich zur Oxidation mit aktivem Chlor (BDD: 132 Wh·gN\(^{-1}\) nach 13% Ammoniakentfernung, TDIROF: 70 Wh·gN\(^{-1}\) nach 28% Ammoniakentfernung). Auch der tiefste Energieverbrauch war aber eine Größensordnung höher als in der biologischen Stickstoffentfernung (4 Wh·gN\(^{-1}\)). Die tiefen Raten der direkten elektrochemischen Ammoniakoxidation \( (2.9 \pm 0.3 \) gN·m\(^{-2}\)·d\(^{-1}\)) sind wahrscheinlich auf einen starken Abfall des pH-Wertes in der anodischen Diffusionsschicht zurückzuführen, welcher in nicht reaktivem NH\(_4\)\(^+\) an der Anode resultierte. Ein solcher pH-Abfall wurde als Ursache für die schnelle Hemmung der direkten Ammoniakoxidation an TDIROF Anoden eindeutig nachgewiesen. Eine Verkleinerung der Diffusionsschicht kann diesen Effekt minimieren, was durch verbesserte hydraulische Bedingungen in der Elektrolysezelle erreicht werden kann. Diese Arbeit bestätigte die Vielseitigkeit der Elektrolyse zur Behandlung von gelagertem Urin. Außerdem zeigte sie die Komplexität der chemischen und elektrochemischen Prozesse bei der Elektrolyse von Urin. Zur Effizienzsteigerung ist ein noch tieferes Verständnis dieser Prozesse notwendig. Zudem sollten Elektrodenmaterialien entwickelt werden, die spezifisch sind für die angestrebten Reaktionen und dabei geringe Überpotentiale aufweisen.
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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Active chlorine</td>
</tr>
<tr>
<td>AOB</td>
<td>Ammonia oxidizing bacteria</td>
</tr>
<tr>
<td>AOX</td>
<td>Adsorbable organic halogens (mgCl·L⁻¹)</td>
</tr>
<tr>
<td>BDD</td>
<td>Boron-doped diamond</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>CBP</td>
<td>Chlorination by-product</td>
</tr>
<tr>
<td>CE</td>
<td>Current efficiency (%), Current efficiency (%)</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>$c_{x,y}(t)$</td>
<td>Concentration of substance x at location y at time t.</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient (m²·s⁻¹)</td>
</tr>
<tr>
<td>DSA</td>
<td>Dimensionally stable anodes</td>
</tr>
<tr>
<td>E</td>
<td>Reduction potential of an electrode (V)</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard reduction potential (V)</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Equilibrium potential (V)</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Anode potential (V)</td>
</tr>
<tr>
<td>$E_{on-set}$</td>
<td>On-set potential (V)</td>
</tr>
<tr>
<td>$E_{sp,x}$</td>
<td>Specific energy demand (Wh·g⁻¹)</td>
</tr>
<tr>
<td>$E_{up}$</td>
<td>Upper return potential (V)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant (C·mol⁻¹)</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas chromatography / mass spectrometry</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>I</td>
<td>Current (A)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>$j$</td>
<td>(mA·cm$^{-2}$)</td>
</tr>
<tr>
<td>$j_{lim}$</td>
<td>(mA·cm$^{-2}$)</td>
</tr>
<tr>
<td>$k_m$</td>
<td>(m·s$^{-1}$)</td>
</tr>
<tr>
<td>LSV</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>(-)</td>
</tr>
<tr>
<td>NOB</td>
<td></td>
</tr>
<tr>
<td>OCBP</td>
<td></td>
</tr>
<tr>
<td>OER</td>
<td></td>
</tr>
<tr>
<td>RDE</td>
<td></td>
</tr>
<tr>
<td>$r_x$</td>
<td>(g·m$^{-2}$·d$^{-1}$)</td>
</tr>
<tr>
<td>SHE</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>(°C)</td>
</tr>
<tr>
<td>TDIROF</td>
<td></td>
</tr>
<tr>
<td>$U$</td>
<td>(V)</td>
</tr>
<tr>
<td>$\delta_N$</td>
<td>(m)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>(V)</td>
</tr>
</tbody>
</table>
### Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active chlorine</td>
<td>Denotes the chlorine species Cl(_2), HOCl, OCl(^-)</td>
</tr>
<tr>
<td>Active type anodes</td>
<td>Anodes that chemisorb activated oxygen, good electro-catalysts for oxygen evolution</td>
</tr>
<tr>
<td>Anode</td>
<td>Electrode at which substances from the electrolyte are oxidized</td>
</tr>
<tr>
<td>Cathode</td>
<td>Electrode at which substances from the electrolyte are reduced</td>
</tr>
<tr>
<td>Electro-coagulation</td>
<td>Coagulation of compounds by dissolving metal ions from an anode</td>
</tr>
<tr>
<td>Electro-flotation</td>
<td>Floating of compounds by tiny bubbles that are produced during electrolytic water splitting</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Ionic conductive phase between anode and cathode</td>
</tr>
<tr>
<td>Electron transfer control</td>
<td>Control of reaction kinetics by the transfer of electrons on the electrode (potential dependent)</td>
</tr>
<tr>
<td>Electro-oxidation</td>
<td>Oxidation of compounds by a direct or indirect electron transfer to an anode</td>
</tr>
<tr>
<td>Electro-reduction</td>
<td>Reduction of compounds by a direct or indirect electron transfer from a cathode</td>
</tr>
<tr>
<td>Fresh urine</td>
<td>Urine that contains nitrogen in the form of urea</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>The radical of the hydroxyl ion</td>
</tr>
<tr>
<td>Mass transfer control</td>
<td>Control of reaction kinetics by the mass transfer to the electrode</td>
</tr>
<tr>
<td>Non-active type anodes</td>
<td>Anodes that physisorb activated oxygen (hydroxyl radicals), bad electro-catalysts for oxygen evolution</td>
</tr>
<tr>
<td>On-set potential</td>
<td>Electrode potential at which an electrochemical reaction starts</td>
</tr>
<tr>
<td>Overpotential</td>
<td>Potential difference between the equilibrium potential and the on-set potential of an electrochemical reaction</td>
</tr>
<tr>
<td>Reference electrode</td>
<td>An electrode of known composition and potential which is used as a reference point against which other electrode potentials can be measured</td>
</tr>
<tr>
<td>Stored urine</td>
<td>Urine in which urea was hydrolyzed (ureolysis) to ammonia and carbonates</td>
</tr>
</tbody>
</table>
Chapter 1

General Introduction: Why Electrolysis for Urine Treatment?

Thesis chapter:
Zöllig, H., Morgenroth, E., Udert, K.M.
Background

This dissertation discusses electrolysis as an on-site treatment technology for stored source-separated urine. The thesis is focused on anodic oxidation processes of organic substances and ammonia. First, the role of different electrode types is discussed in chlorine mediated indirect electro-oxidation of organic substances and ammonia. During this process, harmful chlorination by-products (CBPs) can be produced. The formation of these CBPs and their emission pathways was studied in detail as a second part of this work. In a third and fourth part, direct oxidation of ammonia on the anode surface was investigated on two different electrode materials as an alternative process of electrolytic ammonia oxidation to prevent CBP formation.

In this introduction, the concept of source separation is briefly reviewed to understand the need for on-site urine treatment technologies. In the following, electrolysis is introduced and emphasis is put on its advantages to treat wastewater and urine on-site. The current knowledge about electrochemical technologies and especially about anodic oxidation processes is then reviewed to justify the objectives of this dissertation.

The present work was conducted within the technology part of the VUNA project (Etter et al., 2015, www.vuna.ch) which showed how sanitation and hygiene can be promoted by producing a fertilizer from source-separated urine. In this trans-disciplinary project a comprehensive set of studies was conducted covering all aspects (technological, organizational, economic, social and related to health) which are important for such a system.

The Need for On-site Urine Treatment Technologies

Sewer-based wastewater management has become a de-facto standard in industrialized countries. The basic approach is to flush all human excreta through a collection network to a centralized wastewater treatment plant where specific substances are eliminated (Gujer, 2002). This has led to a tremendous increase of public health (Hamlin and Sheard, 1998) and has reduced eutrophication of receiving water bodies to a large extent. Further advantages of this system are the high user comfort (“flush and forget”) and the robustness of the technology (Larsen and Gujer, 2013).

However, sewer-based wastewater management also has distinct disadvantages. It requires the supply of large amounts of water (180 L·p⁻¹·d⁻¹, Gujer, 2002) as the chosen means of transportation. In many cases, the flushing water is precious drinking water. After conveyance in the sewers, problematic substances are eliminated in the centralized wastewater treatment plants by investing a lot of energy mainly because the targeted substances were diluted in a big volume of water which needs to be aerated for sufficient oxygen supply to the biological treatment processes (Rittmann, 2013).

Furthermore, the sewers are a vast infrastructure that is expensive. In Switzerland, the total length of the public sewers alone is more than 47'000 km (Maurer and Herlyn, 2006). The replacement value of this infrastructure was estimated to be about 7'600 CHF per capita and the replacement value of the whole wastewater management system was calculated to be around 14’000 CHF per capita (Maurer and Herlyn, 2006). Thus, sewer-based wastewater management is costly mainly because it is a centralized system entailing an extensive built collection network.
In many parts of the world this centralized approach based on transport with fresh water in an expensive infrastructure is not a sustainable option. Often, fresh water is a too precious resource that cannot be used in huge amounts only to transport waste. Furthermore, the capital to build the sewerage is often missing (Evans, 2013). A solution to these problems might be decentralized, on-site wastewater management systems (Evans, 2013). As shown in Figure 1.1 on-site systems have the potential to be less expensive than sewerage systems especially with a low population density.

**Figure 1.1: Cost comparison of installing and operating conventional or simplified sewerage to onsite treatment systems in the city of Natal (Brazil). Sludge treatment costs are not included (from Evans, 2013, original source: Mara, 1996, copyright © 1996 by John Wiley & Sons, Inc).**

Urine source separation is a concept that goes hand in hand with decentralized wastewater management (Larsen and Gujer, 2013). Urine contains most of the nutrients (N (88%), K (74), P (61%)) that are excreted by humans in a concentrated form (Friedler et al., 2013). The separate collection of urine thus creates the opportunity to recycle nutrients or to eliminate them efficiently if recycling is not feasible. Currently, several technologies for the separate treatment of feces and urine are being developed (Larsen et al., 2013). Here, only the urine treatment technologies are briefly discussed because the scope of this dissertation is on-site urine treatment.

Urine treatment technologies may be divided into biological and physico-chemical processes (Larsen and Gujer, 2013) or into technologies that are more suited for nutrient recovery (nitrification/distillation (Udert and Wächter, 2012), precipitation (Grau et al., 2015; Etter et al., 2011), ammonia stripping/acid adsorption (Antonini et al., 2011), electrodialysis (Pröhn et al., 2007)) and others that primarily aim at pollutant removal such as nitritation/anammox (Udert and Jenni, 2013), membrane processes (Leslie and Bradford-Hartke, 2013), chemical oxidation (Von Gunten, 2013) or electrochemical processes (Udert et al., 2013)). Many of these processes have been tested at laboratory
scale (Maurer et al., 2006) and a good number was also applied at pilot scale (Udert et al., 2015).

Nevertheless, there is still a need for the development of urine treatment technologies especially for on-site implementation (Larsen and Gujer, 2013). Decentralized urine treatment will have an optimal performance only if technological solutions can be provided which are adaptable to specific circumstances. Thus, it is a big advantage to have several good technologies at hand. Second, it is not possible to simply downscale existing wastewater treatment technologies because decentralized systems have different properties than centralized systems (Table 1.1, Larsen and Gujer, 2013).

**Table 1.1: Comparison of characteristics of decentralized and centralized wastewater management systems (from Larsen and Gujer, 2013).**

<table>
<thead>
<tr>
<th>Topic</th>
<th>Properties of decentralized systems</th>
<th>Properties of centralized systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste flow and load</td>
<td>Highly variable, subject to individual events</td>
<td>Variable, but individual events not apparent</td>
</tr>
<tr>
<td>Rainwater</td>
<td>Hardly an effect</td>
<td>May define hydraulic design load</td>
</tr>
<tr>
<td>Waste composition</td>
<td>Rather homogeneous conditions between plants. Rather concentrated waste</td>
<td>Different for each plant, subject to individual industries. Rather dilute wastewater</td>
</tr>
<tr>
<td>Frequency of attendance</td>
<td>Irregular, long intervals</td>
<td>Daily to permanent</td>
</tr>
<tr>
<td>Cost of intervention</td>
<td>Large</td>
<td>Relatively low</td>
</tr>
<tr>
<td>Relative cost of sensors</td>
<td>High</td>
<td>Rather low</td>
</tr>
<tr>
<td>Calibration of sensors</td>
<td>Very low frequency and relatively very costly</td>
<td>Costly, but rather frequent</td>
</tr>
<tr>
<td>Sensor properties</td>
<td>Must be rugged and reliable, accuracy is of secondary importance, very infrequent maintenance</td>
<td>Must be sensitive, accurate and reliable but may require frequent maintenance</td>
</tr>
<tr>
<td>Data transmittance and control system</td>
<td>Due to on-going expansion of the number of systems, elements must be based on an adaptive grid</td>
<td>Typically fixed for one technological cycle</td>
</tr>
<tr>
<td>Control software</td>
<td>Highly standardized, but due to application in large numbers also highly optimized</td>
<td>May rely on modular design but adaptation to a specific plant typically required</td>
</tr>
<tr>
<td>Required process standardization</td>
<td>Very high, only standardized equipment can be produced in large numbers</td>
<td>Individual plants are typically designed as prototypes</td>
</tr>
<tr>
<td>Transport of pollutants and residues</td>
<td>Local extraction of concentrated residues and separate transport</td>
<td>Transported in sewers and extracted in the form of concentrated sludge</td>
</tr>
<tr>
<td>Handling of residues</td>
<td>May be centralized. An intermediate form may be transported to a central handling station</td>
<td>Typically occurs at the plant. Only small plants connect to larger ones</td>
</tr>
</tbody>
</table>

On-site urine treatment technologies need to be hygienically safe, energy efficient, versatile, robust, easy to automate and should require low maintenance (Larsen and Gujer, 2013). Many of the above mentioned technologies do have shortcomings with respect to these requirements. Biological processes can be affected severely by load variations (Larsen and Gujer, 2013), are sometimes difficult to control and require high maintenance. The physico-chemical processes often make use of the addition of chemicals which leads to maintenance and challenges with their automation (Grau et al., 2015). Electrolysis, on the other hand, is a promising technology for on-site urine
treatment especially because it is potentially robust, easy to automate and requiring low maintenance (Udert et al., 2013).

**Electrolysis: A Versatile and Robust Technology that is Easy to Automate**

In electrolysis, redox reactions are triggered on the surface of electrodes by applying an electric potential difference between two electrodes with an external power source (Figure 1.2). The anode (+) is by definition the electrode at which compounds from the electrolyte are oxidized. At the cathode (-), the electrons ($e^-$), that were released during anodic oxidation and transported via an external current, lead to the reduction of other compounds from the electrolyte. The induced charge difference within the electrolyte has to be equilibrated by an ionic current to guarantee electric neutrality. This is exemplified in the electrolysis cell in Figure 1.2 with the anodic evolution of oxygen and the cathodic evolution of hydrogen representing the well-known reactions involved in water splitting (Hamann and Vielstich, 2007).

![Figure 1.2: Basic scheme of an electrolysis cell. The positive electrode (+) is the anode and the negative electrode (-) the cathode. The anode is by definition the electrode where substances are oxidized. Electrons ($e^-$) are transported to the cathode where they reduce substances in the electrolyte.](image)

There are several factors that have an influence on the exact oxidation and reduction reactions going on at the anode and cathode, respectively (Panizza, 2010). A very important factor is the electrode potential ($E$ in [V]) usually given as a reduction potential. This potential can only be measured against a reference electrode, e.g. the standard hydrogen electrode (SHE), which is indicated with the unit (e.g. V vs. SHE). The electrode potential has to be large enough to overcome the activation energy of an electrochemical reaction so that it can proceed. The electrode potential at which a reaction starts is called the on-set potential ($E_{on-set}$ in [V]). If the electrode potential is further increased the reaction is accelerated because the overpotential ($\eta = E - E^0$, where $E^0$ is the equilibrium potential) becomes larger (Bard and Faulkner, 2001).
Another important factor is the electrode material which acts as an electro-catalyst. In other words, the activation energy (or the needed $\eta$) for an electrochemical reaction can be largely reduced by the electrode material. Therefore, the electrode material is decisive for the selection of reactions that will proceed on the electrode. Anode materials can be divided into two categories (Panizza, 2010; Rueffer et al., 2011): so called active type anodes (carbon, graphite or Pt, Ir and Ru based materials) which form higher surface oxides and thus chemisorbed active oxygen and non-active type anodes (boron-doped diamond (BDD) or Sn and Pb based materials) which form physisorbed active oxygen (hydroxyl radicals). Active type anodes typically show low overpotentials for the oxygen evolution reaction (OER) whereas non-active type anodes show high overpotentials for OER (Comninellis, 1994).

A third important factor is the electrolyte. The composition of the electrolyte at the electrode surface determines the availability of possible reactants. Thus, if substances from the bulk liquid should react on the electrode the mass transport of these substances to the electrode surface becomes important. Three transport processes are distinguished in an electrolysis cell: convection, migration and diffusion. The hydraulic conditions in a cell are therefore another important factor determining electrode reactions (Hamann and Vielstich, 2007).

The big advantages of electrolysis especially for the on-site treatment of urine lie in its mode of operation. Once the system is in place, energy is the only input required to drive the conversion processes. This energy is supplied by electricity which is easy to control. The induced external current flowing from anode to cathode further is directly related to the reaction rates at the anode and the cathode via Faraday’s law (Hamann and Vielstich, 2007). The reaction rate of a process is therefore easily accessible by measuring the current and the signals (current or voltage) can be used for process automation. Since electrolysis is a physico-chemical process it is ideally not susceptible to load variations in the influent and can be turned on and off as needed. Furthermore, no inhibition of the processes has to be expected as with biological systems in case undesired chemicals are dumped into the toilet. Another advantage of electrolysis is its versatility which results from the many degrees of freedom with this technology. These degrees of freedom mainly comprise the influencing factors (electrode material, electrode potential and hydraulic conditions) and the advantages described above.

**Potential Electrolytic Processes for the Treatment of Source-Separated Urine**

Electrolysis could be used in different ways for the treatment of urine similar to how the technology is used for wastewater treatment (Comninellis and Chen, 2010; Chen, 2004). One possibility is to oxidize or reduce compounds in urine at the anode or cathode, respectively. These two processes are known as electro-oxidation or electro-reduction. Electro-flotation and electro-coagulation are two technologies that combine electrolysis with another physico-chemical process for the removal of specific compounds from the electrolyte. Here, these electrolytic technologies are briefly reviewed. For a more detailed review on electrochemical and bioelectrochemical urine treatment processes see Udert et al. (2013). Before entering the topic of electrolytic treatment technologies the electrolyte shall be characterized.
Characteristics of Urine

The fresh urine excreted by humans (1,270 g·p⁻¹·d⁻¹) contains about 5% by weight of dissolved salts and the remaining 95% is water (all numbers in this subsection taken from Friedler et al., 2013). The relatively high content of dissolved salts leads to a high electrical conductivity of roughly 19 ± 2.4 mS·cm⁻¹. Additionally, fresh urine contains 90% of the nitrogen (11 ± 0.3 gN·p⁻¹·d⁻¹) in the form of urea and a high amount of organic substances (measured as chemical oxygen demand (COD), 13 ± 2.6 gCOD·p⁻¹·d⁻¹) containing the remaining 10% of the nitrogen.

However, the urea contained in fresh urine is quickly hydrolyzed (ureolysis) in urine collection systems and storage tanks due to an enzyme (urease) excreted by bacteria resulting in so called stored urine (Udert et al., 2003). Ureolysis releases all nitrogen contained in urea as ammonia (NH₄⁺ and NH₃) and the central C-atom in the form of carbonate (HCO₃⁻ and CO₃²⁻). This increases the pH value from 6.4 to a value of around 9.1 and adds a high alkalinity (carbonate) to stored urine (Udert et al., 2006). Consequences from these changes in the chemical composition are the precipitation of minerals (struvite, hydroxyapatite, calcite) and the volatilization of ammonia (Udert et al., 2006).

Electro-Oxidation

The goal of electro-oxidation in urine is to convert harmful into less harmful compounds by anodic oxidation. Two principle pathways exist for the course of such reactions (Panizza and Cerisola, 2009). In the first, the compounds are oxidized by a direct electron transfer on the anode surface in the so called direct oxidation. In the second pathway, a mediator substance (often active chlorine, Anglada et al., 2009) oxidizes the targeted compound in solution and gets regenerated again in a subsequent oxidation at the anode. This process is referred to as indirect oxidation. Both processes will be discussed in detail in the next section to identify the research gaps addressed in this dissertation.

Electro-Reduction

The counterpart of electro-oxidation is electro-reduction where specific compounds are reduced at the cathode. Similar to electro-oxidation also electro-reduction can proceed via two pathways (Rondinini and Vertova, 2010). Either the reduction proceeds by a direct electron transfer at the cathode surface or by a mediated reduction through a mediator species (e.g. Cp₂TiCl₅, Magdesieva et al., 2006) that is regenerated at the cathode. This process was mainly applied to remove halogen groups (F, Cl, Br and I) from organic halides such as chlorophenoxy herbicides, mono- and poly-halogenated phenols and other chlorinated aromatic substances (Rondinini and Vertova, 2010). Only recently, electro-reduction was used to remove halomethanes, haloacetonitriles, halopropanones, chloral hydrate and trichloronitromethane from water (Radjenovic et al., 2012).

Electro-Flotation

In electro-flotation, electrolysis produces fine bubbles of oxygen and hydrogen which attach to the compounds that are floated to the surface (Chen and Chen, 2010). This process was mainly used for the separation of oily substances or low-density suspended solids from municipal or industrial wastewater which is the reason why it is often
combined with electro-coagulation (Emamjomeh and Sivakumar, 2009). However, this process has not been used for urine yet although it might be applicable to remove small suspended particles from urine.

**Electro-Coagulation / Electro-Precipitation**

Electro-coagulation is a process in which coagulating agents are produced in-situ by the dissolution of metal ions (Liu et al., 2010). In most cases, Fe$^{3+}$ and Al$^{3+}$ ions are dissolved from sacrificial iron or aluminum anodes. Both ions quickly form hydroxides or polyhydroxides which act as the actual coagulating agents. Electro-coagulation was widely used for the treatment of wastewaters (Emamjomeh and Sivakumar, 2009) and was also applied for urine treatment to precipitate phosphorus (Udert et al., 2013). Phosphorus can be completely eliminated from urine with iron (Ikematsu et al., 2006; Zheng et al., 2009) and aluminum electrodes (Zheng et al., 2010b). Hug and Udert (2013) dissolved magnesium anodes and precipitated struvite achieving nearly complete recovery of phosphorus.

**Electro-Oxidation of Urine and other Wastewaters**

**Electro-Oxidation of Urine**

For real urine, electro-oxidation was only applied in a few studies to treat fresh urine. Ikematsu et al. (2006) used dimensionally stable anodes (DSA) composed of platinum (Pt) and iridium (Ir) and an iron (Fe) electrode for the subsequent removal of nitrogen / organic substances followed by phosphorus from fresh urine by first polarizing the DSAs as anodes followed by polarizing the Fe electrode as the anode. In these experiments, the urea and the organic substances were mainly removed by anodic oxidation on the DSA while phosphorus was removed by electro-coagulation when the cell polarization was reversed and the iron electrode acted as a sacrificial anode. Boggs et al. (2009) suggested the production of hydrogen at a platinum cathode while urea from urine was oxidized at a nickel hydroxide anode (Ni(OH)$_2$). Urea oxidation in fresh urine was studied by Kim et al. (2012). The authors used a bismuth oxide/titanium oxide anode (Bi$_x$-TiO$_2$) for the anodic urea oxidation while hydrogen was simultaneously produced at a stainless steel cathode. However, these studies contain little information about the use of electro-oxidation in stored urine.

In other studies, synthetic urine solutions have been used. A recent study compared the oxidation of organic substances and ammonia on non-active type boron-doped diamond (BDD) and active type iridium oxide (IrO$_2$) anodes (Li et al., 2015). The authors found that both processes depended on the type of anode that was used. Amstutz et al. (2012) compared the anodic oxidation of urea in synthetic fresh urine to the anodic oxidation of ammonia in synthetic stored urine. It was found that ammonia oxidation on an IrO$_2$ anode in stored urine was inhibited by the presence of carbonate. This was explained with two reactions competing with ammonia oxidation: the first being the direct oxidation of carbonate which outcompeted chloride oxidation and the second being chlorate formation from active chlorine which outcompeted ammonia oxidation by active chlorine. However, it was also reported in an earlier study that ammonia was oxidized in synthetic stored urine by anodic oxidation when a RuO$_2$-IrO$_2$-TiO$_2$/Ti anode was used (Zheng et al., 2010a). This might have been an effect of the different anode material that was used.
In any case, synthetic urine solutions can only roughly approximate the complexity of real urine especially regarding the organic substances.

**Electro-Oxidation of other Wastewaters**

Apparently, the experience with electro-oxidation for the treatment of stored urine is quite limited also with respect to the most promising processes of ammonia and organic substance oxidation. However, considerable knowledge about these processes is available from the treatment of other wastewaters (Anglada et al., 2009; Chen, 2004). The technology was mainly put forward for the treatment of wastewaters that cannot be treated with biological processes. Prominent examples are the treatment of landfill leachate (Perez et al., 2012), industrial wastewaters such as effluents from chemical (Rajkumar and Palanivelu, 2004), textile (Chatzisymeon et al., 2006), tannery (Szpyrkowicz et al., 2005; Panizza and Cerisola, 2004), food (Vijayaraghavan et al., 2006) or agro industry (Diaz and Botte, 2012) or recent applications to domestic wastewater (Cho et al., 2014b) and attempts to remove pharmaceutical residues (Sirés and Brillas, 2012; Radjenovic et al., 2011).

These studies reveal that also electro-oxidation of ammonia and organic substances can proceed via the two pathways of direct oxidation and indirect oxidation (Anglada et al., 2009, Panizza and Cerisola, 2009). This is shown schematically in Figure 1.3 for an arbitrary anode and described in the following two subsections.

![Figure 1.3: Scheme of the anodic oxidation processes of ammonia (NH₄⁺ / NH₃) and organic substances being the most relevant for the electro-oxidation of stored source-separated urine. Please note: direct oxidation is only represented for the case of ammonia oxidation but similar processes are possible with organic substances (Comminellis, 1994). Furthermore, it is indicated in which chapters of this thesis more relevant information can be found to these processes.](image-url)
Chapter 1

Ammonia Electro-Oxidation

The oxidation of ammonia was intensively investigated with respect to both pathways and on several anode materials (Bunce and Bejan, 2011; Muthuvel and Botte, 2009). Direct ammonia oxidation was thoroughly studied for the first time by Gerischer and Mauerer (1970) on platinum electrodes who also proposed a detailed mechanism for this route of ammonia oxidation. This mechanism was later generalized by de Vooys et al., 2001 for other transition and noble metal electrodes such as palladium, rhodium, ruthenium, iridium, copper, silver and gold.

Only recently, the activity for direct ammonia oxidation was also demonstrated for IrO$_2$ (Kapałka et al., 2011), BDD (Kapałka et al., 2010b) and Ni(OH)$_2$ (Kapałka et al., 2010a) electrodes. The dominant product of direct ammonia oxidation was generally found to be molecular nitrogen N$_2$ but also oxygenated gases such as NO, NO$_2$ and N$_2$O were found (Michels et al., 2010). Nevertheless, indirect ammonia oxidation was often reported to be the dominant pathway of ammonia oxidation in wastewater treatment since chloride is mostly present in wastewaters (Chen, 2004). Furthermore, the kinetics of indirect ammonia oxidation are usually faster than the kinetics of direct oxidation.

Electro-Oxidation of Organic Substances

Similar to the oxidation of ammonia also organic substances can be oxidized via both pathways (Panizza and Cerisola, 2009). Thereby, the mechanism of direct oxidation was found to depend strongly on the type of the anode material (Comninellis, 1994). The organic substances were found to be completely mineralized to CO$_2$ on non-active type anodes due to the oxidation with physisorbed hydroxyl radicals. On the other hand, the oxidation on active type anodes by chemisorbed oxygen rather resulted in partial oxidation of the organic substances. This was found to have a strong influence on the product distribution (Comninellis and Nerini, 1995) which potentially has important consequences if indirect oxidation proceeds in parallel.

In fact, organic substances can also be oxidized indirectly by active chlorine species. The product of indirect oxidation can be CO$_2$, which means that the organic substances are completely mineralized. However, if the oxidation is not complete organic chlorination by-products (OCBPs) can be formed (Anglada et al., 2011; Panizza and Cerisola, 2003; Comninellis and Nerini, 1995). Other by-products of indirect oxidation can be chlorate (ClO$_3^-$) and perchlorate (ClO$_4^-$). Chlorate and perchlorate formation from active chlorine were observed with active (Cho et al., 2014a; Jung et al., 2010; Bergmann et al., 2009) and non-active type anodes (Azizi et al., 2011) at elevated anode potentials.

The Objectives of this Thesis and Identified Research Gaps

The global objective of this dissertation was to evaluate electro-oxidation of ammonia and organic substances as an on-site urine treatment technology. This global objective was broken down into four, concrete goals. For each of these goals the research gaps were identified and research questions were formulated. The concrete goals, research gaps and questions leading to the chapters 2 to 5 are briefly presented in the next subsections.
Indirect Electro-Oxidation for Small Treatment Units (Chapter 2)

One goal for on-site urine treatment is the development of small treatment units. Especially indirect electro-oxidation was shown to remove organic substances and ammonia at very high specific removal rates leading to small reactors (Anglada et al., 2009, Kim et al., 2006). However, it is not known how indirect oxidation of organic substances and ammonia interact in real stored urine and it is not known whether active type or non-active type anodes are more suitable for these processes. The identified research questions are:

- How do the indirect oxidation of organic substances and ammonia interact in a complex matrix like urine?
- How fast are these processes and how energy efficient are they?
- What is the influence of the anode material?

Evaluating the Emissions of Chlorination By-products (Chapter 3)

The simultaneous presence of active chlorine and organic substances during indirect electro-oxidation of stored urine can lead to the formation of chlorination by-products (CBPs, Panizza and Cerisola, 2009) that are harmful to humans and the environment (Srinivasan and Sorial, 2009). It is the goal of this part of the thesis to quantify the CBPs during indirect electro-oxidation of stored urine and to assess the emissions into the gas phase and the treated urine. So far it remains unknown if, which and how many CBPs are formed during indirect electro-oxidation of stored urine and if this is depending on the type of anode used. Thus, the identified research questions are:

- Which are the dominant CBPs?
- Does the production of CBPs depend on the anode material?
- Which are the emission pathways of these CBPs?

Preventing CBP Formation by Using Direct Ammonia Oxidation (Chapter 4)

It was the goal of the next work package to evaluate direct oxidation of ammonia at the electrode surface as a less problematic alternative compared to indirect electro-oxidation given the risk of CBP formation. Direct ammonia oxidation was demonstrated for several anode materials but poisoning by N$_{ads}$ was often found to be a problem (de Voors et al., 2001). However, graphite, a versatile and cheap electrode material, was never evaluated for direct ammonia oxidation. The identified research questions are:

- Is graphite a catalytically active electrode material for direct ammonia oxidation?
- Which is the anodic potential window allowing ammonia to be oxidized without concomitant chlorine evolution?
- How efficient is direct ammonia oxidation for ammonia removal from urine?

The Reason for the Fast Inhibition of Direct Ammonia Oxidation (Chapter 5)

Direct oxidation of ammonia was demonstrated on thermally decomposed iridium oxide film (TDIROF) electrodes (Kapalka et al., 2011). This anode material would be
promising for urine treatment due to its longevity and because of the low overpotentials for direct ammonia oxidation. However, direct ammonia oxidation on this electrode was shown to be rapidly inhibited (Kapałka et al., 2011). It was the goal to identify the reason for this fast inhibition which so far has been attributed to the poisoning of the electrode surface by adsorbed elemental nitrogen (N_ads). However, the fast inhibition could also result from a strong pH drop in the vicinity of the electrode. The identified research questions are:

- What is the cause for the fast inhibition of direct ammonia oxidation on TDIROF anodes?
- Can the reason for this fast inhibition explain the slow ammonia removal kinetics found on the graphite anode?

**Outline of the Chapters**

The thesis is organized according to the relevant electro-oxidation processes presented in Figure 1.3. The first two chapters (chapters 2 and 3) are dealing with the indirect oxidation of ammonia and organic substances in stored urine. Chapters 4 and 5 subsequently discuss two specific aspects with respect to direct ammonia oxidation. Finally, chapters 7 and 8 give the general conclusions of the whole thesis and an outlook to potential future developments of electrolysis for the treatment of urine.

In chapter 2, the performance of chlorine mediated electro-oxidation is discussed for the removal of organic substances and ammonia from real stored urine. The presented data was collected in batch experiments in which high-concentration urine and low-concentration urine were treated at three different current densities (10, 15 and 20 mA·cm\(^{-2}\)) with BDD as a non-active type anode and TDIROF as an active type anode. The different mechanisms of organic substance oxidation and ammonia oxidation were discussed based on these data for the two types of electrodes. The removal rates, current efficiencies and the specific energy demand were calculated for each experiment and compared among each other. The use of two different types of real stored urine further allowed investigating the influence of the urine composition on the treatment performance of chlorine mediated electro-oxidation.

The investigation on the formation of CBPs during chlorine mediated electro-oxidation is presented in chapter 3. The CBPs were measured in selected batch experiments of the study introduced in chapter 2. For the measurement of the volatile OCBPs a new experimental set-up was developed consisting of two wash bottles filled with an organic solvent for the adsorption of the OCBPs. Together with the measurements of the OCBPs in the electrolyte, the total amounts of the OCBPs produced and their emission pathways could be elucidated. The relative importance of the different CBPs was discussed and the produced amounts were linked to the oxidation mechanisms at non-active BDD and active TDIROF anodes. Furthermore, the measurements of individual OCBPs in the urine were compared to a sum parameter of chlorinated substances (adsorbable organics halogen compounds, AOX) to assess the relative importance of the individually quantified OCBPs. In addition to the production of OCBPs, the formation of chlorate and perchlorate was also determined.
The results on the use of direct ammonia oxidation on graphite anodes for the by-product free removal of ammonia are shown in chapter 4. In this study, cyclic voltammetry (CV) experiments were performed in electrolytes that contained only ammonia, only chloride or ammonia and chloride as electro-active compounds. This allowed the identification of the potential range in which only the direct oxidation of ammonia without concomitant chloride oxidation had to be expected. With potentiostatic batch experiments in synthetic urine it was confirmed that in this potential range indeed only direct ammonia oxidation led to the removal of ammonia. In another batch experiment with real urine it was further confirmed that ammonia could be removed from real stored urine.

In chapter 5, the fast inhibition of direct ammonia oxidation on TDIROF anodes is discussed. CV experiments in ammonia containing electrolytes were used for these investigations. They were performed in stagnant electrolyte and on a rotating disc electrode (RDE) for an exact control of the Nernstian diffusion layer. First evidence for a pH induced inhibition was given by comparing the peak height of the ammonia oxidation in subsequent scans with changing lower return potentials. Similar experiments on an RDE later showed the importance of the Nernstian diffusion layer which increased the likelihood of a pH induced inhibition. Finally, the plausibility of the proposed pH induced inhibition mechanism was checked with a computer model simulating the diffusional behavior of all relevant species within the diffusion layer.

Finally, the chapters 6 and 7 present the conclusions over the whole dissertation project and an outlook with proposed research for more significant advances in this field.

References


Chapter 1


Chapter 2

Electrolytic Removal of Ammonia and Organic Substances from Real Stored Urine with Active and Non-Active Type Anodes

Thesis chapter:
Zöllig, H., Remmele, A., Morgenroth, E., Udert, K.M.
Graphical Abstract

Non-active Type Anode

Organic products

Active Type Anode

Intermediates

Organics / Intermediates

NH₄⁺

OH⁻

Cl⁻

H₂O

NO₃⁻

N₂

NH₄⁺

Organics

Cl⁻

BDD

TDIHF
Abstract

Electro-oxidation of organic substances and ammonia are promising processes for on-site treatment of source-separated urine. So far, mainly the electro-oxidation of fresh urine was investigated although it is known that urea hydrolyzes quickly in collection systems or storage tanks. Furthermore, in many studies synthetic urine instead of real urine was used. We investigated the direct and chlorine mediated indirect electro-oxidation of organic substances (measured as chemical oxygen demand (COD)) and ammonia in real high-concentration (4510 ± 290 mgCOD·L⁻¹, 2790 ± 170 mgN·L⁻¹) and low-concentration (1710 ± 50 mgCOD·L⁻¹, 1860 ± 40 mgN·L⁻¹) urine in which all urea was hydrolyzed. Non-active type boron-doped diamond (BDD) and active type thermally decomposed iridium oxide film (TDIROF) anodes were used for the experiments. We found that on BDD organic substances were removed with first order kinetics with respect to the COD concentration at very high rates (r₇COD above 420 gCOD·m⁻²·d⁻¹ at 20 mA·cm⁻² for COD concentrations above 1000 mgCOD·L⁻¹). This was because organics were preferentially removed over ammonia due to their high reactivity with hydroxyl radicals. On the TDIROF anode, COD was removed concomitantly with ammonia and mainly by indirect oxidation following zero order kinetics (r₇COD = 214 ± 24 gCOD·m⁻²·d⁻¹ at 20 mA·cm⁻²). It was further characteristic for both anodes that ammonia was exclusively removed by indirect oxidation. Thereby, the zero order kinetics in high-concentration urine were constant on TDIROF whereas two different regimes were observed on BDD due to the preferential removal of organics in a first phase followed by indirect ammonia oxidation without competing indirect oxidation of organic substances. The dependency of ammonia removal on active chlorine resulted in incomplete ammonia oxidation in low-concentration urine where chloride was exhausted too early. It can be concluded that non-active and active type anodes could be combined in series in order to achieve a fast, compact, complete and more energy efficient urine treatment with chlorine mediated indirect oxidation.

Keywords
Boron-doped diamond, BDD, iridium dioxide, IrO₂, complex wastewater, electrolysis

Introduction

Source separation and decentralization are novel sanitation concepts to deal with the challenges of urban water management (Larsen et al., 2013). The separate collection of urine allows nutrients to be eliminated efficiently on-site from a concentrated solution. Suitable on-site urine treatment technologies need to be stand alone, require low maintenance and provide a high user comfort. Electrolysis fulfills these requirements because it is operated by applying a constant voltage or constant current between two electrodes. This makes the technology easy to automate and the treatment progress can be monitored online (Anglada et al., 2009a). Low maintenance can be expected because the treatment processes are purely chemical and often the electrodes can be cleaned by reversing the electrode polarity for a short time (Le Vot et al., 2012). Nevertheless, there is still little knowledge about the interplay of the main chemical processes such as chlorine evolution, the oxidation of organic substances and ammonia oxidation in real stored urine.
In many cases electrochemical processes were investigated in synthetic urine solutions (Li et al., 2015; Amstutz et al., 2012; Zheng et al., 2010). However, synthetic solutions can only mimic the complexity of real urine. Especially the composition of the organic substances was often drastically simplified by substituting the total chemical oxygen demand (COD) with a combination of selected organic compounds. It remains unknown if the results for COD removal in such simplified synthetic urine can be transferred to the complex mixture of organic substances in real urine. If real urine was used, the studies were mainly about fresh urine (Ikematsu et al., 2006; Kim et al., 2013) although it is known that urea is hydrolyzed quickly (ureolysis) in urine collection systems and storage tanks (Udert et al., 2003). The consequences are an increased pH value around 9 and \( \text{NH}_4^+ \) and \( \text{NH}_3 \) being the main nitrogen compounds instead of urea. In practice, urine electrolysis systems will often have to treat ureolyzed urine because they are likely to be connected to a collection system or a storage tank.

The electrolytic oxidation of organic substances and ammonia has been demonstrated with various anode materials. They can be subdivided into two major categories: non-active type anodes and active type anodes (Panizza, 2010). Non-active type anodes are known to form physisorbed hydroxyl radicals (Fóti et al., 1999). The most popular material of this kind is boron-doped diamond (BDD) but also post-transition metals form oxides with such characteristics (SnO\(_2\) and PbO\(_2\)). On BDD, phenol was shown to be oxidized completely to CO\(_2\) under mass transfer control at elevated current density (\( j = 60 \text{ mA·cm}^{-2} \), Iniesta et al., 2001). Intermediate products were only formed when the oxidation was under electron transfer control (\( j = 5 \text{ mA·cm}^{-2} \)). This has been generalized to other organic compounds by Kapałka et al. (2008). Comninellis and Nerini (1995) showed that chloride did not increase the oxidation of phenol on a non-active type anode (SnO\(_2\)). Ammonia oxidation proceeded via a direct electron transfer on BDD at potentials between 1 and 2 V vs. an Hg/HgSO\(_4\)/K\(_2\)SO\(_4\) electrode (MSE, + 0.64 V vs. standard hydrogen electrode (SHE)) and elevated pH values (> 8, Kapałka et al., 2010a). In the presence of chloride, ammonia can also be oxidized by in-situ produced active chlorine (AC) at pH values below 8 (Kapałka et al., 2010a). These reaction mechanisms are distinctly different from the ones on active type anodes which could significantly impact the treatment of real urine.

The active type anodes form higher oxides at the surface making hydroxyl radicals unavailable for further reactions. Typical electrode materials of this kind are mixed metal oxides of transition metals such as IrO\(_2\) and RuO\(_2\) but also platinum-based electrodes and graphite (Panizza, 2010). On thermally decomposed iridium oxide films (TDIROF), phenol was degraded very inefficiently if no chloride was present (Comninellis and Nerini, 1995). It was argued that this was due to the selective but incomplete oxidation of phenol to other organic intermediates (hydroquinone, benzoquinone and catechol) on active sites of higher oxides similar to the oxidation of i-propanol to acetone (Fóti et al., 1999). When chloride was added, the AC that was formed in a parallel reaction further oxidized these intermediates which increased the current efficiency (Comninellis and Nerini, 1995). The TDIROF anode was also shown to be catalytically active for direct oxidation of NH\(_3\) in alkaline media at anode potentials between 0.25 and 0.75 V vs. MSE (pH > 9, Kapałka et al., 2011). In weakly buffered electrolytes this process was partially self-inhibited due to a strong pH drop in the anodic Nernstian diffusion layer (Zöllig et al., 2015a). In the presence of chloride, ammonia was oxidized at pH values around 6 by
AC species in a reaction zone close to the anode (Kapałka et al., 2010b). This indirect oxidation was shown to become more efficient with increasing chloride concentration (Liu et al., 2009). However, it remains elusive how all these processes interact in real stored urine.

In this study, we investigated if and how organic substances and ammonia are oxidized on non-active type BDD or active type TDIROF anodes in galvanostatic electrolysis of real stored urine. It was the goal to understand the interplay of chlorine mediated and direct oxidation of these substances on the two types of electrodes to achieve the most efficient treatment. To do so, we examined how the processes were affected by the variable composition of urine. Bulk electrolysis experiments were conducted in real, high-concentration urine and low-concentration urine. We further tested if there were major differences in the current efficiency or the specific energy demand depending on the current density.

**Materials and Methods**

**Urine Electrolysis**

The details to the setup of the electrochemical cell have been described in a previous publication (Zöllig et al., 2015b). The most important settings are given here for convenience.

An undivided glass cell (400 mL) was equipped with a BDD (Si/BDD, Adamant Technologies SA, La Chaux-de-Fonds, Switzerland) or a TDIROF (fabrication described elsewhere, Zöllig et al., 2015a) anode with 20 cm$^2$ of exposed surface area. The cathode with an equivalent surface area was made of steel (X5CrNi18-10, Hans Kohler AG, Zürich, Switzerland). The distance between the electrodes was between 9 and 10 mm. A mercury / mercurous sulfate (MSE) reference electrode was employed to measure the anode potential ($E_A$ in V) and was placed in a glass-blown Luggin capillary filled with saturated K$_2$SO$_4$. The cell was covered with a glass lid and sealed up gastight with Teflon tape. Temperature and pH were measured continuously (SenTix 41 connected to pH 196, WTW, Weilheim, Germany) and recorded with a data logger. Conductivity was measured with a handheld meter (TetraCon 325 connected to Cond 340i, WTW, Weilheim, Germany).

The electrolysis cell was filled with 350 mL of stored urine from the men’s or women’s urine storage tank at Eawag (Table 2.1). Electrolysis was performed with a potentiostat which registered $E_A$ (PGU 10V-1A-IMP-S, Ingenieurbüro Peter Schrems, Münster, Germany) under galvanostatic control at $j = 10, 15$ and $20$ mA·cm$^{-2}$. A magnetic stirrer was used to ensure turbulence and the temperature was controlled with a thermostat (K3 DS, Colora Messtechnik GmbH, Lorch, Germany) at a fixed temperature indicated for each experiment.
Table 2.1 - Composition of ureolyzed urine from the low-concentration women’s and high-concentration men’s storage tank at Eawag. The number of measurements was usually 6. (1) one measurement. (2) five measurements

<table>
<thead>
<tr>
<th></th>
<th>Low-concentration urine</th>
<th>High-concentration urine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>Total COD (mg·L⁻¹)</td>
<td>1710</td>
<td>50</td>
</tr>
<tr>
<td>Total Ammonia N (mg·L⁻¹)</td>
<td>1860</td>
<td>40</td>
</tr>
<tr>
<td>Nitrite N (mg·L⁻¹)</td>
<td>&lt;0.15</td>
<td>-</td>
</tr>
<tr>
<td>Nitrate N (mg·L⁻¹)</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>Chloride (mg·L⁻¹)</td>
<td>1250</td>
<td>130</td>
</tr>
<tr>
<td>Total Phosphate P (mg·L⁻¹)</td>
<td>88</td>
<td>9</td>
</tr>
<tr>
<td>Sulfate (mg·L⁻¹)</td>
<td>234</td>
<td>25</td>
</tr>
<tr>
<td>Conductivity (mS·cm⁻¹)</td>
<td>15.1</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>(-)</td>
<td>9.1</td>
</tr>
<tr>
<td>COD/Ammonia-N (mg·mg⁻¹)</td>
<td>0.92</td>
<td>0.04</td>
</tr>
<tr>
<td>COD/Cl⁻ (mg·mg⁻¹)</td>
<td>1.38</td>
<td>0.13</td>
</tr>
<tr>
<td>Ammonia-N/Cl⁻ (mg·mg⁻¹)</td>
<td>1.50</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Chemical Analysis

Aliquots (~13 mL) were taken with a syringe through a needle permanently installed in the glass lid for the wet chemical analysis. After the total COD was analyzed the samples were filtered with glass-fiber filters (0.45 μm, Chromafil GF/PET, Macherey-Nagel, Düren, Germany). Chloride, phosphate, sulfate, nitrite and nitrate were analyzed by ion chromatography (881 compact IC pro, Metrohm, Herisau, Switzerland). Ammonia and total COD were measured photometrically with cuvette tests (LCK 303 and LCK 314/614, Hach Lange, Berlin, Germany). The standard deviations of the wet chemical analyses were less than 5%.

Calculations

Under mass transfer controlled conditions the volumetric removal rate $r_x$ (g·m⁻³·d⁻¹) of a substance $x$ can be expressed as (Bard and Faulkner, 2001):

$$r_x = \frac{dc_{x,\infty}(t)}{dt} = -\frac{A}{V} \cdot k_m \cdot c_{x,\infty}(t) = -p \cdot c_{x,\infty}(t) \quad (2.1)$$

Where $c_{x,\infty}$ (mg·L⁻¹) is the bulk concentration of substance $x$, $A$ (m²) is the electrode surface area, $V$ (m³) is the volume of the electrolyte, $t$ is the time and $k_m$ (m·s⁻¹) is the apparent mass transfer coefficient. By integrating and rearranging equation (2.1) becomes:

$$ln \left( c_{x,\infty}(t) \right) = -p \cdot t + ln \left( c_{x,\infty}(0) \right) \quad (2.2)$$
The $k_m$ can then be calculated according to equation (2.3). In this calculation the initial electrolyte volume $V_{\text{init}}$ was used and the slope $p$ was calculated for the linear range in the logarithmic plot of the concentration against $t$:

$$k_m = \frac{p \cdot V_{\text{init}}}{A} \quad (2.3)$$

The area specific removal or production rate $r_{x,A}$ ($\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) of a substance $x$ that was removed under electron transfer control was calculated from the slope $a_x$ ($\text{g} \cdot \text{d}^{-1}$) of the linear regression of the remaining mass of substance $x$ (including mass in removed samples) vs. time as:

$$r_{x,A} = a_x \cdot \frac{1}{A} \quad (2.4)$$

Under the assumption that all ammonia not converted to nitrate or nitrite was oxidized to $\text{N}_2$, the total current efficiency for ammonia oxidation ($CE_{NH}$, in %) was estimated as:

$$CE_{NH}(t) = CE_{NO_3^-}(t) + CE_{NO_2^-}(t) + CE_{N_2}(t) \quad (2.5)$$

where

$$CE_x(t) = \frac{\Delta m_x(t) \cdot v_{e-x}^{-1} \cdot F}{M_N \cdot Q(t)} \quad (2.6)$$

and

$$CE_{N_2}(t) = \frac{(\Delta m_{\text{NH tot}}(t) - \Delta m_{NO_3^-}(t) - \Delta m_{NO_2^-}(t)) \cdot v_{e-N_2}^{-1} \cdot F}{M_N \cdot Q(t)} \quad (2.7)$$

Here $\Delta m_x(t)$ (gN) is the mass of substance $x$ produced in the cell until a time $t$, and $v_{e-x}^{-1}$ (mole$^{-1}$·molN$^{-1}$) is the number of electrons used per mole of ammonia oxidized to nitrate, nitrite or molecular nitrogen, respectively. $F$ is the Faraday constant (96,485 C·mole$^{-1}$), $M_N$ the molecular weight of nitrogen (14 gN·molN$^{-1}$) and $Q(t)$ (C) the transported charge, calculated from the current $I$ (A) as:

$$Q(t) = \int_0^t I(t) \cdot dt \quad (2.8)$$

The current efficiency for organic substance removal ($CE_{COD}$) was estimated on the basis of COD measurements:

$$CE_{COD}(t) = \frac{\Delta m_{\text{COD}}(t) \cdot F}{\text{TOD}_{e-} \cdot Q(t)} \quad (2.9)$$

As with the nitrogen species, $\Delta m_{\text{COD}}(t)$ (gO$_2$) is the mass of COD removed until a time $t$. TOD$_e$ is the theoretical oxygen demand of one mole of electrons (8 gO$_2$·mol$^{-1}$).

The specific energy demand for the removal of total ammonia ($x = \text{NH}$) or COD ($x = \text{COD}$) $E_{sp,x}$ (Wh·g$^{-1}$) was calculated from the average electrical power $\overline{U} \cdot \overline{I}$, which was calculated as the average of the product of the cell voltage $U$ (V) times $I$ (A) up to a time $t$ as:

$$E_{sp,x} = \frac{\overline{U} \cdot \overline{I} \cdot t}{\Delta m_x \cdot 3600 \cdot \overline{A}} \quad (2.10)$$
Results

Electrolysis of High-Concentration Urine

Oxidation on BDD

The removal of organic substances decreased with transferred charge which resulted in a linear trend of the COD concentration on a logarithmic scale (Figure 2.1). This can be explained with a first order-reaction with respect to COD indicating mass transfer control of the oxidation process. The apparent mass transfer coefficients $k_m$ calculated for the three applied current densities of 10, 15 and 20 mA·cm$^{-2}$ (Table 2.2) were in the same order of magnitude but showed a trend towards higher values with increasing current density indicating that the process was also electron transfer controlled.

Ammonia was eliminated at a rate of only 43 ± 20 gN·m$^{-2}$·d$^{-1}$ at 20 mA·cm$^{-2}$ in a first phase of the experiment up to a transferred charge of 6 Ah (Table 2.2, Figure 2.1). As with the other current densities, this resulted from low $CE_{NH}$ compared to $CE_{COD}$ in this initial phase showing the preferential oxidation of COD on BDD (Supplementary Information (SI), Figure A.2.1). In a second phase from 6 Ah to 14 Ah at 20 mA·cm$^{-2}$, ammonia was removed at a much higher rate (419 ± 17 gN·m$^{-2}$·d$^{-1}$) indicating that in this later reaction phase the indirect oxidation of organic substances and ammonia were competing reactions on BDD.

Table 2.2: Removal rates of COD, chloride and ammonia and the production rate of nitrate in the ranges that were linear with transferred charge (from 0 Ah to value indicated in subscript notation for each rate in Ah). In case of the BDD anode, the COD removal rate is given at 1000 mgCOD·L$^{-1}$ based on the calculated apparent mass transfer coefficients $k_m$.

<table>
<thead>
<tr>
<th>Urine type</th>
<th>Electrode</th>
<th>j (mA·cm$^{-2}$)</th>
<th>Removal of organic substances</th>
<th>Chloride removal</th>
<th>Ammonia removal</th>
<th>Nitrate production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r_{COD}$ (gCOD·m$^{-2}$·d$^{-1}$)</td>
<td>$k_m$ (m·s$^{-1}$)</td>
<td>$r_{Cl^-}$ (gCl$^-$·m$^{-2}$·d$^{-1}$)</td>
<td>$r_{NH}$ (gN·m$^{-2}$·d$^{-1}$)</td>
</tr>
<tr>
<td>High-concentration urine</td>
<td>BDD</td>
<td>20</td>
<td>421</td>
<td>38</td>
<td>4.9·10$^{-6}$</td>
<td>4.4·10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>334</td>
<td>26</td>
<td>3.9·10$^{-6}$</td>
<td>3.0·10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>190</td>
<td>4</td>
<td>2.2·10$^{-6}$</td>
<td>4.9·10$^{-8}$</td>
</tr>
<tr>
<td>Low-concentration urine</td>
<td>TDIROF</td>
<td>20</td>
<td>214</td>
<td>24</td>
<td>174.1</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>180</td>
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<td>20.6</td>
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<tr>
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<td>4.4·10$^{-7}$</td>
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<td></td>
<td></td>
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<td>549</td>
<td>28</td>
<td>6.4·10$^{-6}$</td>
<td>3.2·10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>467</td>
<td>26</td>
<td>5.4·10$^{-6}$</td>
<td>3.0·10$^{-7}$</td>
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<tr>
<td></td>
<td>TDIROF</td>
<td>20</td>
<td>163</td>
<td>13</td>
<td>164.1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>133</td>
<td>2</td>
<td>185.8</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>91.5</td>
<td>6</td>
<td>89.0</td>
<td>5</td>
</tr>
</tbody>
</table>
Removal of Ammonia and Organic Substances

Figure 2.1: Galvanostatic electrolysis of high-concentration urine on BDD. Full symbols: 20 mA·cm² (25.2 °C), grey symbols: 15 mA·cm² (25.1 °C) and empty symbols 10 mA·cm² (25.0 °C). Electrode gap: 9 mm.

The nitrate formation rate was 51 ± 9 gN·m⁻²·d⁻¹ and higher than the ammonia removal rate in the first phase up to 6 Ah at 20 mA·cm⁻² which indicates that nitrate was formed from other nitrogen sources than ammonia (e.g. organics). In the second phase of the experiment at 20 mA·cm⁻² the nitrate formation increased to 105 ± 2 gN·m⁻²·d⁻¹ which is only about a fourth of the ammonia removal rate. At the end of the experiments, the nitrate yields were 35%, 28% and 38% at 20, 15 and 10 mA·cm⁻², respectively. Nitrite
accumulated slowly at 10 and 15 mA·cm$^{-2}$ (Figure 2.1). At 20 mA·cm$^{-2}$, the samples were diluted too strongly such that nitrite could only be quantified above concentrations of 10 mgN·L$^{-1}$ in two samples. The nitrite concentrations in the other samples at 20 mA·cm$^{-2}$ were below 10 mgN·L$^{-1}$.

The chloride removal rate did not change significantly during the experiment when concentrations were getting lower (Figure 2.1). The increased ammonia oxidation at 20 mA·cm$^{-2}$ between 6 and 14 Ah thus cannot be explained with increased AC formation from more efficient chloride oxidation.

The pH value strongly decreased in the beginning of the experiments until a charge of about 4 Ah had been transferred (Figure 2.1). During the rest of the experiment, the pH value remained at a level of 7.5 except in the experiment with 20 mA·cm$^{-2}$ where the pH value dropped below levels of 2 when high amounts of charge had been transferred. This shows an imbalance of anodically produced and cathodically consumed protons.

**Oxidation on TDIROF**

On TDIROF in high-concentration urine, COD was constantly removed with transferred charge and did not depend on the bulk COD concentration indicating electron transfer control (Figure 2.2). In Table 2.2 it is shown that the COD removal rates increased with current density because the $CE_{COD}$ was almost not depending on the current density (SI, Figure A.2.1). A maximum COD removal rate of $214 \pm 24$ gCOD·m$^{-2}$·d$^{-1}$ was reached at a current density of 20 mA·cm$^{-2}$. This is low compared to the removal rate achieved on BDD at a much lower COD concentration of 1000 mgCOD·L$^{-1}$ and 20 mA·cm$^{-2}$ (Table 2.2).

Also ammonia was constantly removed ($r_{NH} = 227 \pm 16$ gN·m$^{-2}$·d$^{-1}$ at 20 mA·cm$^{-2}$) in parallel to the organic substances (Figure 2.2). The ammonia removal rates increased with the current density (Table 2.2) and were at least a factor two higher than on the BDD anode if the COD concentration was above 2000 mgCOD·L$^{-1}$. The highest nitrate production rate of $28 \pm 2$ gN·m$^{-2}$·d$^{-1}$ was observed at 10 mA·cm$^{-2}$ (Table 2.2) as a result of a high nitrate yield of 19% compared to the experiments at 15 and 20 mA·cm$^{-2}$. At these two current densities, the nitrate yield was significantly lower with only 7% in both experiments (Figure 2.2). The higher nitrate yield at 10 mA·cm$^{-2}$ resulted in a slightly higher $CE_{NH}$ compared to the experiments at 15 and 20 mA·cm$^{-2}$ (SI, Figure A.2.1). Nitrite was continuously formed resulting in slowly increasing concentrations.

Chloride was removed at a constant rate with comparable current efficiencies at all current densities (Figure 2.2). Accordingly, the removal rates rose with increasing current density (Table 2.2). The fastest chloride removal was observed at 20 mA·cm$^{-2}$ ($174 \pm 13$ g·m$^{-2}$·d$^{-1}$) which is almost double the chloride removal rate measured on BDD in high-concentration urine.

Similar to the BDD anode, the pH value dropped in the beginning of the experiments to reach a plateau at pH = 7.5 (Figure 2.2). About the same charge of 6 Ah was transferred to reach this level with current densities of 15 and 20 mA·cm$^{-2}$ whereas at 10 mA·cm$^{-2}$ only about 4 Ah were needed. The sudden pH drop with 20 mA·cm$^{-2}$ was caused by the detachment of the silicon sealing from the cathode which resulted in a strongly increasing cell voltage disturbing the pH measurement (SI, Figure A.2.1).
Figure 2.2: Galvanostatic electrolysis of high-concentration urine on TDIROF. Full symbols: 20 mA·cm\(^{-2}\) (25.1 °C), grey symbols: 15 mA·cm\(^{-2}\) (25.0 °C) and empty symbols 10 mA·cm\(^{-2}\) (25.0 °C). Electrode gap: 10 mm.
Electrolysis of Low-Concentration Urine

Oxidation on BDD

In low-concentration urine, the COD removal was also exponential as a function of the transferred charge but slowed down below concentrations of 100 mgCOD·L⁻¹ even though at 10 mA·cm⁻² there was still chloride left, so that indirect COD oxidation should have been possible (Figure 2.3). This indicates that some recalcitrant substances remained. In analogy to high-concentration urine, the $k_m$ values were increasing with current density and were generally at a higher level than what was observed in high-concentration urine (Table 2.2).

Initial ammonia removal can be noticed for the 15 and 20 mA·cm⁻² experiments but at 10 mA·cm⁻² the ammonia concentration remained constant until 2.5 Ah and started to decline thereafter until 7 Ah (Figure 2.3). Due to these unclear patterns, no ammonia removal rates were calculated for these experiments. It can be seen clearly from the experiments at 15 and 20 mA·cm⁻² that ammonia was not removed when no chloride was present.

Nitrate was formed constantly with transferred charge up to 5 Ah at all three current densities (Figure 2.3). Thereby, the formation rate increased with the current density up to $95 \pm 2$ gN·m⁻²·d⁻¹ at 20 mA·cm⁻² (Table 2.2). When more than 5 Ah were transferred, the nitrate concentration fell to values of about 50 mgN·L⁻¹ where it remained. At 20 mA·cm⁻², the rate of nitrate removal was $130 \pm 2$ gN·m⁻²·d⁻¹ calculated for the period between 5 and 9Ah. In that period, the concentration of ammonia slightly increased from 1480 to 1560 mgN·L⁻¹ indicating reduction of nitrate to ammonia at the cathode although this increase is within the measurement uncertainty. The concentrations of nitrite were very low until 2.5 Ah were transferred at all current densities. From then on, they increased sharply and reached values similar to those in high-concentration urine at about 7 Ah. During the remaining experiment, the nitrite concentrations started to gently decrease.

The chloride removal rate increased strongly from $65 \pm 5$ g·m⁻²·d⁻¹ at 10 mA·cm⁻² to $268 \pm 9$ g·m⁻²·d⁻¹ at 20 mA·cm⁻² (Table 2.2). This is more than a four-fold increase of the removal rate while the current density was only doubled and resulted from higher current efficiencies for chloride removal (Figure 2.3). The increasing current efficiencies, in turn, resulted from higher anode potentials at higher current densities (Zöllig et al., 2015b) which is consistent with the results obtained in high-concentration urine where lower anode potentials (SI, Figure A.2.1) resulted in slower chloride removal rates (Table 2.2).

The pH value declined from 9 to 7.5 within the first 2.5 Ah of transferred charge which was faster than in high-concentration urine. In contrast to those experiments, the pH value increased strongly between 5 and 7.5 Ah at current densities of 15 and 20 mA·cm⁻² whereas at 10 mA·cm⁻² the pH value increased more slowly. In the last phases, between 9 and 18 Ah at 15 and 20 mA·cm⁻², the pH increased slowly with transferred charge.
Figure 2.3: Galvanostatic electrolysis of low-concentration urine on BDD. Full symbols: 20 mA·cm\(^{-2}\) (16.5 °C), grey symbols: 15 mA·cm\(^{-2}\) (16.6 °C) and empty symbols 10 mA·cm\(^{-2}\) (16.2 °C). Electrode gap: 9 mm.

**Oxidation on TDIROF**

The removal of COD in low-concentration urine was constant as long as the COD concentration was higher than 800 mgCOD·L\(^{-1}\) (Figure 2.4). At lower COD concentrations, the COD removal followed first order kinetics. The transition in the kinetic regime coincided with the chloride being exhausted. This indicates that at high
concentrations COD was oxidized indirectly with chlorine and chlorine production was electron transfer limited. Direct oxidation may have become important when chloride was removed. Those kinetics can be explained by mass transfer limitation but we did not calculate $k_m$ because only few measurements were available in these periods.

Ammonia was removed steadily at comparable rates as in high-concentration urine as long as chloride concentrations were higher than approximately 500 mg·L$^{-1}$ (Table 2.2, Figure 2.4). The ammonia removal rates were increasing with current density since $CE_{NH}$ only initially depended on the current density (Figure 2.5). Ammonia removal slowed down when chloride concentrations dropped below approximately 500 mg·L$^{-1}$ at about 5 Ah. After a transition phase up to 7.5 Ah, ammonia was not removed any longer showing the indispensability of chloride for ammonia oxidation.

Nitrate was formed as long as ammonia was removed. The nitrate production rates were clearly higher than in high-concentration urine (Table 2.2), increased with current density and led to nitrate yields of 28%, 35% and 26% at 20, 15 and 10 mA·cm$^{-2}$, respectively. Thereafter, a slight nitrate removal appeared at 20 mA·cm$^{-2}$ between 8 and 12 Ah. While 40 mgN·L$^{-1}$ of nitrate were removed about 170 mgN·L$^{-1}$ of ammonia were produced indicating that nitrogen from other sources than nitrate was transformed to ammonia (e.g. from organics). Nitrite concentrations started to increase when chloride concentrations dropped below 500 mg·L$^{-1}$ but did not exceed 8 mgN·L$^{-1}$.

The behavior of the pH value was similar to what was observed with the BDD anode. At first, a strong pH drop was observed. The same minimum of 7.5 was reached but later than with the BDD anode. The pH value then started to increase gradually. This increase was slightly stronger the lower the current density was but much slower than in case of the BDD anode.
Removal of Ammonia and Organic Substances

Figure 2.4: Galvanostatic electrolysis of low-concentration urine on TDIROF. Full symbols: 20 mA·cm⁻² (16.4 °C), grey symbols: 15 mA·cm⁻² (16.4 °C) and empty symbols 10 mA·cm⁻² (16.6 °C). Electrode gap: 10 mm.

Current Efficiencies and Specific Energy Consumption

The specific energy consumptions of COD oxidation, \( E_{sp,COD} \), and ammonia oxidation, \( E_{sp,NH} \), depended on the \( CE_s \) of the respective processes and on the cell voltages which were both a function of the electrode material. Generally, we found that the \( E_{sp} \) were influenced more strongly by the \( CE_s \) than by the cell voltage which resulted from the
strong changes of the CEswith the concentration changes of the reactants during treatment progress. In the following this will be illustrated with the experiments in low-concentration urine. The results in high-concentration urine can be found in the SI section A.

**The case of BDD**

The resulting $E_{sp}$ and CEs of the experiments in low-concentration urine are presented in Figure 2.5. In case of the BDD anode, $E_{sp,COD}$ was steadily increasing. This increase in $E_{sp,COD}$ was mainly a result of the decreasing $CE_{COD}$. At 20 mA·cm$^{-2}$, the initial $E_{sp,COD}$ was 50 Wh·gCOD$^{-1}$ which increased to 104 Wh·gCOD$^{-1}$ to reach a concentration below 140 mg·L$^{-1}$ (94% COD elimination) after a transferred charge of 6.8 Ah. Within the same experimental period, the initial $CE_{COD}$ dropped from 42% to 23%. Thus, the two fold increase of $E_{sp,COD}$ mainly resulted from the reduction of $CE_{COD}$ by a factor of 2. Similarly, $E_{sp,NH}$ was mainly depending on $CE_{NH}$.

When comparing $CE_{COD}$ and $CE_{NH}$ it becomes apparent that in the beginning of the experiments the sum of $CE_{COD}$ and $CE_{NH}$ was close and sometimes even above 100%. Initially, at current densities of 15 and 20 mA·cm$^{-2}$, $CE_{COD}$ and $CE_{NH}$ were about 50% each. However, at a current density of 10 mA·cm$^{-2}$ $CE_{COD}$ was much larger than $CE_{NH}$. Much higher $CE_{COD}$ compared to $CE_{NH}$ were also observed in high-concentration urine (SI, Figure A.2.1) which clearly indicated the preferential oxidation of COD on BDD.

It can further be seen from Figure 2.5 that the cell voltage did not change strongly during a single experiment which led to a low influence of this parameter on $E_{sp,COD}$ and $E_{sp,NH}$ compared to the CEs. On the other hand, the higher cell voltages at higher current densities resulted in slightly higher $E_{sp,COD}$ or $E_{sp,NH}$, respectively, even if $CE_{COD}$ or $CE_{NH}$ were equal. This can be nicely seen in Figure 2.5 at a transferred charge of about 9 Ah with the BDD anode when comparing $E_{sp,COD}$ and $CE_{COD}$.

**The case of TDIROF**

On TDIROF, the $E_{sp,COD}$ was more or less stable during the phase of constant COD removal in each experiment. This was a consequence of the non-variable $CE_{COD}$ and the small changes of the cell voltage (Figure 2.5). At 20 mA·cm$^{-2}$, the initial $E_{sp,COD}$ was 170 Wh·gCOD$^{-1}$. The same value was reached after a transferred charge of 12 Ah when the COD concentration was 346 mg·L$^{-1}$ (80% COD elimination). Thus, COD removal on TDIROF required between 3 and 1.7 times more energy than COD removal on BDD even though the cell voltages were lower. This can be attributed to the low $CE_{COD}$ which decreased form 20% to 12% up to a transferred charge of 12 Ah.

The $E_{sp,NH}$, on the other hand, was smaller on TDIROF than on BDD (Figure 2.5). At a current density of 20 mA·cm$^{-2}$ the $E_{sp,NH}$ was 90 Wh·gN$^{-1}$ when the linear removal came to an end (5 Ah). On the BDD anode, $E_{sp,NH}$ was 270 Wh·gN$^{-1}$ after the same transferred charge. The better $E_{sp,NH}$ on TDIROF resulted from a slightly higher $CE_{NH}$ due to the longer presence of chloride and the lower cell voltages. However, despite the higher $CE_{NH}$ the sum of $CE_{COD}$ and $CE_{NH}$ did not reach 100%. Similar results were obtained in high-concentration urine (SI, Figure A.2.1).
Removal of Ammonia and Organic Substances

Discussion

The Oxidation of Organic Substances

On the BDD anode, the removal of COD and thus the oxidation of organic substances was electron and mass transfer controlled. The electron transfer control can be deduced from the increasing removal rates with increasing current densities (Table 2.2) and the mass transfer control from the apparent first order kinetics which was also observed in synthetic urine with BDD anodes (Li et al., 2015; Dbira et al., 2015). We postulate that the route of COD oxidation was twofold: oxidation by hydroxyl radicals and through indirect oxidation by AC. The reaction kinetics of COD oxidation by physisorbed hydroxyl radicals $c_{OH,rz}$ (mg·L$^{-1}$) in the reaction zone ($rz$) close to the anode may be expressed as:

$$\text{Discussion}$$

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\[ r_{\text{COD},rz} = \frac{dc_{\text{COD},rz}}{dt} = -k_{\text{OH,COD}} \cdot c_{\text{OH,rz}} \cdot c_{\text{COD,rz}} \]  

(2.11)

Where \( k_{\text{OH,COD}} \) (L·mgOH\(^{-1}\)·h\(^{-1}\)) is a second order rate constant as are the rate constants in the following equations (2.12) – (2.14). This process is fast which explains the electron transfer control by a limited availability of hydroxyl radicals. The mass transfer control resulted from the dependence of \( c_{\text{COD,rz}} \) on the bulk COD concentration \( c_{\text{COD,\infty}} \). The \( c_{\text{COD,rz}} \) decreased and led to a lower rate according to equation (2.11) when the diffusive mass flux of COD decreased as a result of a smaller gradient due to a smaller difference of \( c_{\text{COD,\infty}} \) and \( c_{\text{COD,rz}} \).

Nevertheless, some COD was also oxidized through indirect oxidation which is evident from the formation of organic chlorination by-products in the same experiments (Zöllig et al., 2015b). At an arbitrary location \( y \) in the Nernstian diffusion layer or the bulk liquid these process kinetics can be expressed as (Anglada et al., 2009b):

\[ r_{\text{COD,y}} = \frac{dc_{\text{COD,y}}}{dt} = -k_{\text{AC,COD}} \cdot c_{\text{AC,y}} \cdot c_{\text{COD,y}} \]  

(2.12)

The exact contribution of this process remains unclear. However, it was electron transfer controlled because of the electron transfer limited chloride oxidation.

The increasing \( k_m \) with increasing current density partially resulted from the electron transfer control of COD oxidation. Additionally, the thickness of the Nernstian diffusion layer may have been reduced due to a stronger formation of gas bubbles at higher current densities which was observed visually (SI, Figure B.2.1). Ibl et al. (1971) showed that evolving gases at an anode promote turbulence very efficiently by a hydrodynamic effect (gas bubbles rise close to the electrode and drag water with them) and by the penetration of the Nernstian diffusion layer by the detaching gas bubbles.

The comparatively low \( E_{\text{sp,COD}} \) in the beginning of the experiments on BDD in low- and high-concentration urine (SI, Figure A.2.1) underlines the preferential COD oxidation on BDD anodes by hydroxyl radicals. This preferential oxidation is also responsible for the higher \( CE_{\text{COD}} \) on BDD compared to TDIROF. The \( E_{\text{sp,COD}} \) value we found in low-concentration urine for a COD elimination of 94% (104 Wh·gCOD\(^{-1}\)) was close to the one recently found in synthetic urine (121 Wh·gCOD\(^{-1}\), Dbira et al., 2015). In high-concentration urine, however, a higher elimination (97%) was achieved with only half the specific energy demand (55 Wh·gCOD\(^{-1}\)). Thus, \( E_{\text{sp,COD}} \) strongly depended on \( CE_{\text{COD}} \) which in turn depended on the COD concentration whereas the applied current density and resulting cell voltage had a minor influence.

With the TDIROF anode, the COD removal was electron transfer controlled in all experiments at higher COD concentrations (800 – 4500 mgCOD·L\(^{-1}\)) but below 800 mgCOD·L\(^{-1}\), it became mass transfer limited. This was also observed in synthetic urine (Dbira et al., 2015) and in synthetic septic tank effluent with another active type anode (Cho et al., 2014). From our data it is not possible to judge if the removal of organic substances resulted from direct oxidation at the electrode surface or from chlorine mediated indirect oxidation. However, the presence of chloride was often found to have a strong impact on COD removal (Bagastyo et al., 2013; Panizza and Cerisola, 2009). It is therefore reasonable to assume that COD was mainly removed by indirect oxidation with AC.
The reaction kinetics of indirect COD oxidation can be expressed as in equation (12) similar to what was proposed by Cho et al. (2014). The apparent COD removal rate $r_{COD}$ then is the average of all $r_{COD,y}$. Apparently, the $r_{COD}$ was constant at high concentrations. Therefore, the average spatial product $c_{AC,y} \cdot c_{COD,y}$ must have been constant too. Since $c_{COD,y}$ was decreasing with time this implies that on average $c_{AC,y}$ increased with time. Very likely, the increase of $c_{AC,y}$ was stronger in the Nernstian diffusion layer towards the electrode surface since that is where AC is formed. Thus, it can be concluded that COD removal was limited by the production of AC.

The formation of AC resulted from the oxidation of chloride which showed similar CEs at all current densities. Therefore, the removal rate of chloride increased with increasing current density which resulted in accelerated AC supply and increasing COD removal rates. The elevated COD removal rates in high-concentration urine can at least partially be explained with less competing ammonia oxidation via AC which will be discussed in the next subchapter. Furthermore, all CEs were higher in high-concentration urine due to the better AC utilization by COD and ammonia oxidation at elevated concentrations. Consequently, also $E_{sp,cod}$ was lower in high-concentration urine (SI, Figure A.2.1).

**The Crucial Role of Chloride for Ammonia Removal**

On BDD, the formation of nitrate clearly indicated the oxidation of ammonia in all experiments (Figure 2.3, Figure 2.3). However, nitrate formation stopped when chloride was completely removed although the ammonia concentrations were still high. From this it can be concluded that ammonia was only removed by indirect oxidation via AC and in analogy to equation (2.12) it can be written:

$$r_{NH,y} = \frac{dc_{NH,y}}{dt} = -k_{AC,NH} \cdot c_{AC,y} \cdot c_{NH,y} \quad (2.13)$$

The apparent ammonia removal rate $r_{NH}$ is then again the average of all $r_{NH,y}$. The inhibition of direct oxidation might be explained with a pH drop in the Nernstian diffusion layer as was found for the TDIROF anode (Zöllig et al., 2015a). This mechanism can also be assumed for BDD, as Kapalka et al., (2010a) reported a high pH sensitivity for direct ammonia oxidation on BDD as well.

On BDD, chloride can be oxidized directly at the electrode surface or via hydroxyl radicals (Polcaro et al., 2009; Bergmann, 2010). The kinetics of the latter process in the reaction zone may be expressed as:

$$r_{Cl^{-},rz} = \frac{dc_{Cl^{-},rz}}{dt} = -k_{OH^{\cdot},Cl^{-}} \cdot c_{OH^{\cdot},rz} \cdot c_{Cl^{-},rz} \quad (2.14)$$

The strongly increasing chloride removal rate in low-concentration urine can be explained with preferentially accelerated kinetics of direct chloride oxidation due to increasing anode potentials (Zöllig et al., 2015b, Figure 2.5) and by less competition of equation (2.11) with equation (2.14).

These two mechanisms can also explain the low chloride removal rates in high-concentration urine. The slower direct chloride oxidation resulted from lower anode potentials than in low-concentration urine (SI, Figure A.2.1) and chloride oxidation by hydroxyl radicals was outcompeted by the fast reaction of organic substances with hydroxyl radicals which acted similar to radical scavengers (Donaghue and Chaplin,
2013). Consequently, indirect ammonia removal was slow in the beginning of the experiments with high-concentration urine (Figure 2.1). However, the benefit of the slow direct chloride oxidation was that chloride was still available later for the oxidation of ammonia when the COD was already removed mainly via hydroxyl radicals which resulted in complete ammonia removal at high rates.

On TDIROF, ammonia was also removed exclusively through indirect oxidation by AC and was not hindered by the oxidation of carbonate (CO$_3^{2-}$) as previously reported with synthetic stored urine (Amstutz et al., 2012). In analogy to the BDD case, it can be assumed that the ammonia removal rate anywhere in the electrolyte can be expressed with equation (2.13) resulting in a competition of indirect ammonia oxidation and indirect COD oxidation. Therefore, a higher COD to ammonia-N ratio should result in a higher ratio of $r_{\text{COD}}$ to $r_{\text{NH}}$. In high-concentration urine, we calculated $r_{\text{COD}}$ to $r_{\text{NH}}$ ratios of 1.02, 0.98 and 0.94 gCOD·gN$^{-1}$ for 10, 15 and 20 mA·cm$^{-2}$ whereas in low-concentration urine the ratios were 0.83, 0.73 and 0.63 gCOD·gN$^{-1}$, respectively (based on Table 2.2). This corresponds with the higher initial COD to ammonia-N ratio in high-concentration compared to low-concentration urine (Table 2.1).

The relative abundance of organic species and ammonia compared to chloride determines if COD and ammonia can be completely removed from urine at high rates with TDIROF. Complete removal should be feasible in high-concentration urine. In fact, chloride would be the last substance being used up based on an extrapolation of the removal rates for COD, ammonia and chloride. However, complete ammonia removal was not achieved in low-concentration urine because the initial COD/Cl$^{-}$ and ammonia-N/Cl$^{-}$ ratios were higher than in high-concentration urine (Table 2.1).

**The Products of Ammonia Oxidation**

In recent studies (Kapalka et al., 2010b, Kapalka et al., 2010a), evidence was reported that the main products of electrochemical, indirect ammonia oxidation are N$_2$ and nitrate as in conventional breakpoint chlorination (Pressley et al., 1972). The occurrence of N$_2$O, NO and NO$_2$ during electrolytic urine treatment seems unlikely. However, this point could be clarified with gas phase measurements.

The chronological distribution of the nitrogen species in all experiments may be explained with the reaction system (2.15) – (2.20) according to Perez et al. (2012).

\[
\begin{align*}
2NH_4^+ + 3ClO^- & \rightarrow N_2 + 3H_2O + 3Cl^- + 2H^+ \quad (2.15) \\
NH_4^+ + 3ClO^- & \rightarrow NO_2^- + 3Cl^- + 2H^+ + H_2O \quad (2.16) \\
NO_2^- + ClO^- & \rightarrow NO_3^- + Cl^- \quad (2.17) \\
NO_3^- + H_2O + 2e^- & \leftrightarrow NO_2^- + 2OH^- \quad E^0 = 0.017 \, V \quad (2.18) \\
NO_2^- + 5H_2O + 6e^- & \rightarrow NH_3(aq) + 7OH^- \quad E^0 = -0.165 \, V \quad (2.19) \\
2NO_2^- + 4H_2O + 6e^- & \rightarrow N_2(g) + 8OH^- \quad E^0 = 0.406 \, V \quad (2.20)
\end{align*}
\]

In high-concentration urine, the AC concentrations must have been low because anodically produced AC immediately reacted with organic substances or nitrogen species in the anodic diffusion layer (Kapalka et al., 2010b, Pressley et al., 1972). This resulted in some nitrite being able to escape from the anodic diffusion layer into the bulk solution.
where no AC was present. Additionally, some nitrite was presumably formed at the cathode by nitrate reduction (equation 2.18) since the cathode potential was clearly below -0.5 V vs. SHE in all our experiments (data not shown). As a result, nitrite concentrations increased in the bulk (Figure 2.1 and Figure 2.2). However, the dominant reactions in the anodic diffusion layer very likely were the oxidation of ammonia to N$_2$ (equation 2.15) and to nitrate (equations 2.16 and 2.17). The reasons for the higher nitrate yields with BDD and the very low nitrate yields with TDIROF at higher current densities (15 and 20 mA·cm$^{-2}$, Figure 2.2) remain elusive.

In low-concentration urine, the chloride removal rates and thus AC production rates were generally higher than in high-concentration urine (Table 2.2) which must have led to higher AC concentrations in these experiments presumably also in the bulk solution. Under these conditions, nitrite, being formed anodically or cathodically, was completely oxidized to nitrate resulting in low nitrite concentrations and nitrate accumulation as long as chloride was oxidized to AC. However, when the AC concentrations got lower because the chloride oxidation ceased, nitrite appeared in the bulk solution due to the still ongoing nitrate reduction at the cathode. The latter process led to decreasing nitrate concentrations since no nitrate was produced from ammonia anymore (Figure 2.3 and Figure 2.4). In this phase of the experiments, an equilibrium was established between direct nitrite oxidation at the anode to nitrate (backward reaction of equation 2.18) and nitrate reduction at the cathode to nitrite (forward reaction of equation 2.18) leading to a quasi-steady state. However, some nitrite was still reduced according to equation 2.19 and very little according to equation 2.20. Consequently, no net nitrogen removal could be observed.

In accordance with the chronological sequence of the above mentioned processes, the pH value dropped when ammonia oxidation to N$_2$ and nitrate (equations 2.15 and 2.16) were the dominant processes and increased when only nitrite was reduced to ammonia or N$_2$ (equations 2.19 and 2.20).

**Consequences for Improved Urine Treatment**

The initial composition of real stored urine had a strong influence on the electrolytic oxidation of organic substances and ammonia. Our experiments showed that in some cases the complete removal of ammonia is not feasible without adding chloride. The engineering of a treatment process needs to take this into account. Before designing the treatment process, the composition of the raw stored urine and its variability over time need to be assessed. Especially the ratios of COD/Cl$^-$ and ammonia-N/Cl$^-$ need to be known.

It was confirmed that organic substances were preferentially removed on BDD anodes even in the complex matrix of real stored urine due to their high reactivity with hydroxyl radicals (Dbira et al., 2015). Since this process was mass transfer limited even at very high COD concentrations it is possible to improve its selectivity by reducing the thickness of the Nernstian diffusion layer. This can be done by increasing the flow velocity between the electrodes or by working at higher current densities which induces higher turbulence via the evolving gases. If ammonia needs to be removed in the presence of organic substances, TDIROF anodes appear to be more suitable because
TDIROF led to higher $CE_{NH}$ values and required lower cell voltages resulting in lower $E_{sp,NH}$.

Low $E_{sp}$ mainly resulted from high $CE$ in function of high reactant concentrations and to a lower extent from the lower cell voltages due to the better conductivity of high-concentration urine. However, the lower conductivity in low-concentration urine did yield higher $E_{sp}$ at higher current densities. In order to minimize energy consumption and to maximize the removal rates the current density should be continuously adapted to the concentrations of COD and ammonia (Dbira et al., 2015). This could be realized in a cascade of electrolysis cells.

A cascade of non-active and active type anodes could be used to optimize the removal of COD and ammonia. In a first set of cells, BDD anodes would preferentially remove COD by oxidation with hydroxyl radicals while little chloride and ammonia would be removed. In a subsequent set of cells, ammonia could be removed in indirect oxidation with AC because chloride should still be left. Eventually, this allows the elimination of ammonia from solutions that initially show unfavorably low COD/Cl$^-$ and ammonia-N/Cl$^-$ ratios.

Conclusions

The hydroxyl radicals created at the BDD surface reacted very efficiently with the complex mixture of organic substances. In fact, at high concentrations the organic substances acted like hydroxyl radical scavengers which partly hindered the indirect oxidation of ammonia. The consequences were fast and preferential COD oxidation making BDD a good choice for the electrolytic removal of organic substances from urine.

On BDD and TDIROF, ammonia was only removed with chlorine mediated oxidation. Thereby, TDIROF showed better current efficiencies and a lower specific energy demands than BDD. However, chlorine did not act as an ideal mediator but was removed from urine. Thus, the ratios of chloride to COD and chloride to ammonia need to be high to achieve complete COD and ammonia removal.

The specific energy consumptions of organic substance and ammonia oxidation on BDD and TDIROF depended on the cell voltage and the current efficiencies. The current efficiencies were high at high reactant concentrations and did not depend heavily on the current density (in a range of 10 to 20 mA·cm$^{-2}$). However, at low reactant concentrations the current efficiencies were higher at low current densities. Accordingly, the current density needs to be adapted continuously to the reactant concentrations to achieve compact reactors with low specific energy demand.

The differences between non-active type (BDD) and active type (TDIROF) anodes for the electro-oxidation of organic substances and ammonia can be used beneficially for the treatment of urine. In a cascade of cells equipped with BDD and subsequently TDIROF anodes COD can be selectively removed on BDD which improves the later chlorine mediated removal of ammonia on TDIROF. Simultaneously, the current density can be set individually for each cell according to the COD and ammonia concentrations which improves the energy efficiencies and the cell size. In this way, electro-oxidation facilitating chlorine mediated oxidation can completely remove ammonia and organic substances from real stored urine. However, great care has to be taken due to the formation of chlorination by-products.
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References


Supplementary Information
A. Current Efficiencies and Energy Demand in High-Concentration Urine

A.1. The Case of BDD

The $E_{sp}$ and $CE$s of the experiments in high-concentration urine are shown in Figure A.2.1. As in low-concentration urine $E_{sp,COD}$ increased with transferred charge mainly due to a decrease in $CE_{COD}$. However, in high-concentration urine $CE_{COD}$ was much higher than in low-concentration urine and dropped from 90% to 61% from the beginning up to a transferred charge of 7.9 Ah at a current density of 20 mA·cm$^{-2}$. These higher $CE_{COD}$ resulted in values for $E_{sp,COD}$ of only 23 to 33 Wh·gCOD$^{-1}$. Thus, the increase of $E_{sp,COD}$ of one third was again resulting from a one third decrease of $CE_{COD}$. These results underline the preferential COD removal on BDD anodes.

In accordance with the high $CE_{COD}$, the $CE_{NH}$ was small especially in the beginning of the experiments. In agreement with $CE_{COD}$, the largest $CE_{NH}$ was achieved at the smallest current density of 10 mA·cm$^{-2}$. In the beginning, the sum of $CE_{COD}$ and $CE_{NH}$ were sometimes larger than 100% which of course is not possible. This must be attributed to measurement uncertainties mainly in the COD and total ammonia measurements. The low $CE_{NH}$ resulted in very high $E_{sp,NH}$ which culminated in a value of 766 Wh·gN$^{-1}$ at a current density of 20 mA·cm$^{-2}$ after a transferred charge of 6.25 Ah. However, when the stronger ammonia removal set in, $CE_{NH}$ increased to 45% yielding an $E_{sp,NH}$ of 127 Wh·gN$^{-1}$ after 14 Ah when ammonia was completely removed (see Figure 1 in the manuscript).

A.2. The Case of TDIROF

The $E_{sp,COD}$ on TDIROF increased much faster than in low-concentration urine and also faster than on the BDD anode. At 20 mA·cm$^{-2}$, the $E_{sp,COD}$ values increased from 28 to 67 Wh·gCOD$^{-1}$ until a transferred charge of 8 Ah was reached. Similar to the BDD case, this can be attributed to a fast decrease in $CE_{COD}$ from 59% to 34% since the cell voltage was not changing significantly with transferred charge. With that, the $CE_{COD}$ was higher than in low-concentration urine but still comparatively low with respect to the BDD anode.

$CE_{NH}$ was larger than on the BDD anode as already observed in low-concentration urine. However, especially in the beginning these values were shaky but always above 30%. Together with the lower cell voltages that were needed with TDIROF anodes, clearly lower $E_{sp,NH}$ values could be reached. In the same experimental period as discussed before for COD removal (0 to 8 Ah), $E_{sp,NH}$ increased from 42 to 77 Wh·gN$^{-1}$ at a current density of 20 mA·cm$^{-2}$ which is considerably less than what we observed on the BDD anode. As already mentioned in the manuscript, the strong increase of the cell voltage and the anode potential was observed due to an unintentional dismantling of the steel cathode.
Removal of Ammonia and Organic Substances

Figure A.2.1: Performance data from the experiments in high-concentration urine. Left: With the BDD anode. Right: With the TDIROF anode. Full symbols: 20 mA·cm$^{-2}$, grey symbols: 15 mA·cm$^{-2}$ and empty symbols 10 mA·cm$^{-2}$.

B. Gas Evolution at the BDD Anode

The formation of gas bubbles was observed visually. The picture in Figure B.2.1 shows the gas bubbles formed during the electrolysis of high-concentration urine. The bubbles that were formed at the electrode surface were very fine and can hardly be seen on the picture. After detachment, the bubbles moved upwards close to the electrode surface as described in Ibl et al. (1971) before they were dragged into the bulk liquid at a certain point by an eddy from the turbulence induced by magnetic stirring. These small gas bubbles in the bulk liquid are visible in the picture although very fuzzy because of their movement. Some of the small bubbles aggregated to bigger bubbles on the silicon sealing where they were immobilized. However, sooner or later also these bubbles were detached from the surface.
Figure B.2.1: Gas bubbles during the electrolysis of high-concentration urine. Small gas bubbles can be identified in the liquid which were in movement due to the turbulence induced by the magnetic stirrer. The larger bubbles were immobilized on the silicon sealing and formed as aggregates from the smaller bubbles.

References
Chapter 3

Formation of Chlorination By-Products and Their Emission Pathways in Chlorine Mediated Electro-Oxidation of Urine on Active and Non-Active Type Anodes

This chapter is based on the publication:
Chapter 3

Graphical Abstract

Electrolysis cell:

Wash bottles:

Air pump

Urine

ClO₃⁻, ClO₄⁻, CH₂Cl₂, CHCl₃, CCl₄
Abstract

Chlorination by-products (CBPs) are harmful to human health and the environment. Their formation in chlorine mediated electro-oxidation is a concern for electrochemical urine treatment. We investigated the formation of chlorate, perchlorate, and organic chlorination by-products (OCBPs) during galvanostatic (10, 15, 20 mA·cm⁻²) electro-oxidation of urine on boron-doped diamond (BDD) and thermally decomposed iridium oxide film (TDIROF) anodes. In the beginning of the batch experiments, the production of perchlorate was prevented by competing active chlorine and chlorate formation as well as by direct oxidation of organic substances. Perchlorate was only formed at higher specific charges (> 17 Ah·L⁻¹ on BDD and > 29 Ah·L⁻¹ on TDIROF) resulting in chlorate and perchlorate being the dominant CBPs (> 90% of initial chloride). BDD produced mainly short chained OCBPs (dichloromethane, trichloromethane, and tetrachloromethane), whereas longer chained OCBPs (1,2-dichloropropane and 1,2-dichloroethane) were more frequently found on TDIROF. The OCBPs were primarily eliminated by electrochemical stripping: On BDD, this pathway accounted for 40% (dichloromethane) to 100% (tetrachloromethane) and on TDIROF for 90% (1,2-dichloroethane) to 100% (trichloromethane) of what was produced. A post-treatment of the liquid as well as the gas phase should be foreseen if CBP formation cannot be prevented by eliminating chloride or organic substances in a pretreatment.

Introduction

Electrolysis is a versatile technology which is promising for on-site nutrient removal from urine because it allows for easy process control. The technology was applied for decentralized disinfection of drinking (Kerwick et al., 2005) and swimming pool water (Ghermaout and Ghermaout, 2010) and for on-site treatment of industrial wastewaters (Panizza and Cerisola, 2004; Szpyrkowicz and Radaelli, 2006) or land fill leachate (Anglada et al., 2009b). Electrolysis was also proposed to treat domestic wastewater on-site (Cho et al., 2014). Thereby, the final goal, being it the disinfection of water or the removal of chemical substances, was primarily achieved by oxidation with active chlorine (Cl₂, HOCl, and OCl⁻) which is produced in situ by the oxidation of chloride. This process is referred to as mediated or indirect electro-oxidation (Anglada et al., 2009a).

Urine contains high concentrations of chloride (Udert et al., 2006) potentially leading to strong active chlorine formation, high nutrient removal rates, and small reactors. It was shown that organic substances and ammonia can be readily removed with mediated electro-oxidation (Candido et al., 2013; Cho et al., 2014). However, the unspecific nature of indirect oxidation resulted in the formation of chlorination by-products (CBPs, Anglada et al., 2011; Bagastyo et al., 2013; Panizza and Cerisola, 2009) which could be a drawback of mediated electro-oxidation of urine.

Chlorate (ClO₃⁻) and perchlorate (ClO₄⁻) are important inorganic CBPs. They are the oxidation products of active chlorine species. Chlorate (Anglada et al., 2009b; Cho and Hoffmann, 2014; Cho et al., 2014; Lacasa et al., 2012) but also perchlorate (Li and Ni, 2012; Perez et al., 2012; Li et al., 2015) were reported as products of mediated electro-oxidation. It is not completely clear under which conditions chlorate or perchlorate is the main product. The electrode material is an important factor for the formation of
perchlorate. Perchlorate formation was reported to be a bigger problem with boron-doped diamond (BDD) anodes than with mixed oxide electrodes (Bergmann et al., 2009). Iridium oxide electrodes showed negligible perchlorate formation at low current densities. Furthermore, competing oxidation of chloride (Bergmann et al., 2009; Perez et al., 2012) or organic substances (Donaghue and Chaplin, 2013) was shown to reduce perchlorate formation. However, there is little knowledge about how these processes interact in a real, complex electrolyte such as urine and if competing reactions inhibit perchlorate formation. (Azizi et al., 2011)

A second group of CBPs are organic chlorination by-products (OCBPs). In batch electrolysis experiments, it was found that the concentration of OCBPs in the electrolyte increased initially, reached a maximum, and went back to zero (Panizza and Cerisola, 2003). This OCBP removal could result from the electrochemical degradation of OCBPs or from electrochemical stripping into the gas phase (Comninellis and Nerini, 1995). Most studies only analyzed the liquid phase while neglecting the gas phase as an emission pathway of OCBPs (Anglada et al., 2011; Bagastyo et al., 2013; Naumczyk et al., 1996; Panizza and Cerisola, 2003) or the complexity of real wastewaters was neglected by working with model substances if the gas phase was analyzed (Comninellis and Nerini, 1995; Johnson et al., 1999). It remains unknown if OCBPs are mainly removed by electrochemical stripping or by electrochemical degradation in complex wastewaters.

In this study, we report on the fate of chlorate, perchlorate, and OCBPs during chlorine mediated electro-oxidation of real stored urine with non-active type boron-doped diamond (BDD) and active type thermally decomposed iridium oxide film (TDIROF) anodes. We investigated if TDIROF leads to less perchlorate formation than BDD and if the high concentrations of chloride and organic substances prevent the formation of chlorate or perchlorate. We hypothesized that on TDIROF weaker chlorate and perchlorate formation would result in the formation of more OCBPs being eliminated primarily by electrochemical stripping into the gas phase.

**Experimental Section**

**Electrolysis Cell**

An undivided glass cell (400 mL) was equipped with a BDD (Si/BDD, BDD-film thickness: 3.0 μm, B-doping: 800 ppm, sp3/sp2 ratio: 250, Adamant Technologies SA, La Chaux-de-Fonds, Switzerland) or a TDIROF (fabrication described in Zöllig et al., 2015b) anode with 20 cm² of exposed surface area (A). The cathode was made of steel (X5CrNi18-10, Hans Kohler AG, Zürich, Switzerland) with equivalent surface area. The electrodes were not pretreated except for intense rinsing with nanopure water. The distance between the electrodes (d) was between 9 and 10 mm. A Hg/Hg₂SO₄/K₂SO₄ (MSE, 0.64 V vs standard hydrogen electrode (SHE), ref 601, Radiometer analytical, France) reference electrode was employed to measure the anode potential (Eₐ in V) and was placed in a glass-blown Luggin capillary filled with saturated K₂SO₄. A magnetic stirrer (IKAMAG RCT basic, IKA, Staufen, Germany) ensured turbulence at a rotational speed of 750 rpm in all experiments. The temperature in the reactor was controlled below ambient temperature as indicated for each experiment to prevent condensation of OCBPs during transfer into the wash bottles (Colora thermostat, Colora Messtechnik GmbH,
Lorch, Germany). The cell was covered with a glass lid and sealed up gastight with Teflon tape.

**Gas Wash**

The gas from the headspace was directed through Teflon tubes into two glass-blown wash bottles (WB, height: 40 cm, diameter: 2 cm, Glastechnik Rahm, Muttenz, Switzerland) filled with dodecane (≥ 99%, Merck, Darmstadt, Germany) to absorb volatilized OCBPs. The wash bottles were connected in series, and a constant air flow ($Q_g = 18.0 \pm 0.7 \text{ mL} \cdot \text{min}^{-1}$) was ensured in all experiments by sucking air through the system with a vacuum pump (N816.1.2KN.18, KNF Neuberger AG, Freiburg, Germany). The gas flow was measured at the inlet to the headspace of the electrolysis cell with a flow meter (F-111D-HB-22-P, Bronkhorst High Tech, AK Ruurlo, The Netherlands) and at the outlet of the vacuum pump with a gas meter (L1, Wohlgroth AG, Zürich, Switzerland) and a bubble meter (Optiflow 520, Humonics, Fairfield, USA). The total amounts of the OCBPs were calculated by summing up the measured and calculated amounts in the liquid and gaseous compartments of the system (Supplementary Information (SI), Figure A.3.1) and the mass removed in the aliquots. The amounts in the gaseous compartments were calculated by assuming equilibrium between the gas phase and the urine in the reactor or the gas phase and the dodecane in the wash bottles. Additionally, it was accounted for the mass lost out of wash bottle 2 ($m_{WB2,g}$). This mass was calculated according to equation 3.1. Thereby, the concentration in the off-gas was calculated by assuming equilibrium between the gas bubbles leaving WB2 and the dodecane phase. This was shown to be a reasonable assumption by modeling the OCBP concentrations in the rising gas bubble (SI, section B)

$$m_{WB2,g}(x) = \sum_{y=1}^{x} \left( \frac{1}{L_{16,OCBP}} \left( c_{\text{OCBP,WB2}(y-1)} + c_{\text{OCBP,WB2}(y)} \right) \cdot \int_{t_{y-1}}^{t_y} Q_g \cdot dt \right)$$

where $t_x$ (s) is the time when aliquot $x$ was taken, $L_{16,OCBP}$ (m$^3$ gas$\cdot$m$^{-3}$ hexadecane) is the partition coefficient of the particular OCBP between air and hexadecane (The partition coefficient for the air/dodecane system, which was not available, is very similar to the one of the air/hexadecane system (SI, section B)), and $c_{\text{OCBP,WB2}(y)}$ is the concentration of the OCBP in aliquot $y$.

**Recovery Experiment**

A recovery experiment was performed to show that OCBPs can be quantified with our experimental setup. Six OCBPs were quantified (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, chlorobenzene) because of their high abundance in two preliminary electrolysis experiments with stored urine on BDD and TDIROF anodes (results not shown). Additionally, chloromethane was detected in significant amounts in these experiments but could not be quantified later due to a very low $L_{16}$ value (SI, Table B.3.1). A spike solution (1 g·L$^{-1}$) of the targeted OCBPs was prepared in ethanol (Merck), and 1.1 mL of this solution was spiked to 350 mL of nanopure water at time zero. The total amounts of the OCBPs were calculated as mentioned above to close the mass balances at 9 points in time within 8 h of experiment duration. In this experiment, the temperature in the electrolysis cell was controlled at 19 °C.
Urine Electrolysis

The electrolysis cell was filled with 350 mL of stored urine from the women’s urine storage tank at Eawag (SI, Table C.3.1). Electrolysis was performed with a potentiostat which registered the current density $j$ and $E_A$ (PGU 10V-1A-IMP-S, Ingenieurbüro Peter Schrems, Münster, Germany) under galvanostatic control at three current densities: 10, 15 (the data of the experiments at these two current densities can be found in the SI, section J), and 20 mA·cm$^{-2}$. The temperature in the electrolysis cell was controlled at 16.5 °C.

Chemical Analysis

Aliquots (~13 mL) were taken with a syringe through a needle permanently installed in the glass lid for the wet chemical analysis. After the total COD analysis they were filtered with glass-fiber filters (0.45 μm, Chromafil GF/PET, Macherey-Nagel, Düren, Germany). After dilution, chloride, chlorate, perchlorate, phosphate, sulfate, and nitrate were analyzed by ion chromatography (881 compact IC pro, Metrohm, Herisau, Switzerland). Ammonia, nitrite, and total COD were measured photometrically with cuvette tests (LCK 303, LCK 341, and LCK 314/614, Hach Lange, Berlin, Germany). The standard deviations of the wet chemical analyses were less than 5%. OCBPs were extracted from urine by taking aliquots (~0.9 mL) with a gastight syringe. The unfiltered aliquots were added to 0.9 mL of dodecane in gas chromatography / mass spectrometry (GC/MS) glass screw-cap vials. The GC/MS vials were shaken for 10 s and the solvent was allowed to separate for 30 min. Thereafter, 0.8 mL of the segregated dodecane phase on top of the sample was pipetted into another GC/MS glass screw-cap vial (1.5 mL). The dodecane aliquots (~2 mL) from the wash bottles were taken through a valve located at the bottom and pipetted into a GC/MS glass screw-cap vial. The dodecane samples were then analyzed by GC/MS (Thermo Scientific DSQII single quadrupole GC/MS, Restek, Bellefonte, USA) as described elsewhere (Zöllig et al., 2015a). Adsorbable organic halogens (AOX) were analyzed in a certified laboratory according to DIN EN 1485 (DIN EN 1485:1996-11, 1996, Labor Veritas, Zürich, Switzerland).

Results

Recovery Experiment of OCBPs

The reliability of the new experimental setup for the measurement of OCBPs in the gas phase was tested with a recovery experiment prior to the actual experiments. The experiment showed that the experimental setup was suitable to quantify the targeted OCBPs during the electrolysis of urine. The average recovered masses over the 9 points in time were as follows: 95 ± 6% (dichloromethane), 99 ± 2% (trichloromethane), 97 ± 3% (tetrachloromethane), 98 ± 3% (1,2-dichloroethane), 100 ± 3% (1,2-dichloropropane), and 101 ± 3% (chlorobenzene). Detailed results are shown in section D of the SI.

Chloride Removal and the Formation of Chlorate and Perchlorate

At 20 mA·cm$^{-2}$, chloride was constantly removed from urine in the beginning of each experiment as shown in Figure 3.1 and Figure 3.2 for BDD and TDIROF, respectively. However, chloride oxidation was more efficient on BDD. The chloride removal rates in the linear regions were $8.3 \pm 0.3$ mol·m$^{-2}$·d$^{-1}$ on the BDD anode and $5.5 \pm 0.2$ mol·m$^{-2}$·d$^{-1}$.
on the TDIROF anode. This was surprising because in other studies TDIROF was shown to have a higher catalytic activity for chloride oxidation than BDD (Jeong et al., 2009; Kraft et al., 1999).

Figure 3.1: Concentrations in the cell and produced masses of OCBPs during the electrolysis of stored urine with a BDD anode at a current density of 20 mA·cm$^{-2}$. The solid lines denote the total mass of OCBPs produced. The data with full symbols were measured in urine. Temperature: 16.5 °C, electrode gap: 9 mm.

Figure 3.1: Concentrations in the cell and produced masses of OCBPs during the electrolysis of stored urine with a BDD anode at a current density of 20 mA·cm$^{-2}$. The solid lines denote the total mass of OCBPs produced. The data with full symbols were measured in urine. Temperature: 16.5 °C, electrode gap: 9 mm.
Figure 3.2: Concentrations in the cell and produced masses of OCBPs during the electrolysis of stored urine with a TDIROF anode at a current density of 20 mA·cm$^{-2}$. The solid lines denote the total mass of OCBPs produced. The data with full symbols were measured in urine. Temperature: 16.5 °C, electrode gap: 10 mm.

The constant chloride removal in the beginning of the experiments implies that chloride oxidation was under current limited control on BDD and on TDIROF because the rate did not depend on the bulk concentration. At low chloride concentrations, the removal of
Chlorine became mass transport limited which is apparent from the decreasing removal rate toward the complete removal of chloride (Kapałka et al., 2008a).

Chlorate was the dominant product of chloride oxidation on both electrodes (Figure 3.1 and Figure 3.2). On BDD, the chlorate production rate was $6.3 \pm 0.7 \text{ mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ until 5 Ah of transferred charge. On TDIROF, the production rate was $4.7 \pm 0.7 \text{ mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ up to 9 Ah corresponding to the slower oxidation of chloride on this anode. Neither the high concentration of chloride nor the one of organic substances prevented the formation of chlorate.

However, the presence of chloride or organic substances seemed to inhibit the formation of perchlorate in the beginning of the experiments (up to 3 Ah on BDD and up to 5 Ah on TDIROF), whereas impeding direct ammonia oxidation is unlikely due to low pH values close to the anode surface (Zöllig et al., 2015b). Strong perchlorate formation set in on both electrodes when the chloride concentration dropped below the chlorate concentration. At this point in time, the COD measurement was already comparatively low in the experiment with BDD (~400 mgCOD·L$^{-1}$), whereas with TDIROF it was still high (~1200 mgCOD·L$^{-1}$). This indicated that on BDD it might were the concentrations of chloride and organic substances that prevented perchlorate formation, whereas on TDIROF the presence of organics was less important. At the end of the experiments when all chloride was oxidized, the sum of chlorate and perchlorate accounted for 88% of the initial chloride concentration on BDD and for 96% on TDIROF, respectively.

**Formation of OCBPs on BDD and TDIROF**

Figure 3.1 shows that a strong net production of the targeted OCBPs took place in the beginning of the electrolysis on the BDD anode (up to 2.5 Ah). Tetrachloromethane was the only OCBP which was produced until 5 Ah were transferred. This is an indication that tetrachloromethane was built from dichloromethane or trichloromethane through successive chlorination. Chlorobenzene was only found in traces (< 3 µg) close to the quantification limit (0.03 mg·L$^{-1}$) in WB1. 1,2-Dichloropropane was detected (signal-to-noise ratio > 3) but could not be quantified.

After 2.5 Ah of transferred charge, the total amounts of the targeted OCBPs decreased dramatically except for tetrachloromethane. Since the OCBPs escaping in the off-gas of WB2 and the mass in the wash bottles were included in this calculation, the removal must have resulted from a process eliminating OCBPs in the system. More precisely, the elimination must have taken place in the electrolysis cell because the decrease in total mass came from a sharp drop in the mass measured in urine.

The formation of the targeted OCBPs on the TDIROF anode is shown in Figure 3.2. Dichloromethane and trichloromethane were the dominantly produced OCBPs. Tetrachloromethane was not found with this anode. Compared to the BDD anode, larger amounts of 1,2-dichloroethane, 1,2-dichloropropane, and chlorobenzene (close to 40 µg) were produced. The net formation of dichloromethane and trichloromethane was strongest before 2.5 Ah, whereas 1,2-dichloropropane and 1,2-dichloroethane were produced at a constant rate until all chloride was used up.
Adsorbable Organic Halogens (AOX)

Electrolysis with the TDIROF anode yielded higher AOX concentrations than electrolysis with the BDD anode in the beginning of the experiments (Figure 3.3). However, only with the BDD anode a large fraction of the AOX concentrations could be explained with the OCBPs measured in the liquid phase. A small part of the AOX measurements could also be attributed to the interference of chlorate and perchlorate (SI, section E). The unknown AOX fractions could be chloramines or longer chained OCBPs that could not be detected with our GC/MS method because their boiling point is higher than the one of dodecane. Another possibility are untargeted OCBPs. In the preliminary experiments we also found chloromethane, bromomethane, chloroethane, 1,1-dichloroethane, and 2-chloropropane with the BDD and chloromethane, cyanogen chloride, dichloroacetonitrile, and trichloronitromethane with the TDIROF anode.

Figure 3.3: AOX concentrations in urine and the explainable fractions (due to chlorate and perchlorate interference and the amount of OCBPs measured by GC/MS) during the electrolysis of stored urine at 20 mA·cm⁻². Temperature: 16.5 °C, electrode gap BDD: 9 mm, TDIROF: 10 mm.

Influence of the Current Density

Figure 3.4 shows that chloride was oxidized with increased current efficiency on BDD when the applied current density was increased. Therefore, also chlorate was produced more efficiently. This was not the case on the TDIROF anode. Chloride was removed equally efficient at all current densities and chlorate was formed accordingly.
Figure 3.4: Concentration profiles of chloride and chlorate in urine during the electrolysis on BDD and TDIROF at three different current densities (Symbols black: 20 mA·cm$^{-2}$, gray: 15 mA·cm$^{-2}$, white: 10 mA·cm$^{-2}$).

OCBPs were formed at all current densities with both anode materials. The sum of all the quantified OCBPs revealed that BDD produced more of the targeted OCBPs than TDIROF when high current densities were applied (Table 3.1). However, at the lowest current density of 10 mA·cm$^{-2}$ the TDIROF anode produced more of the targeted OCBPs. With both anodes, the sum of targeted OCBPs did not clearly depend on the current density. With BDD, the strongest formation was observed with a medium current density of 15 mA·cm$^{-2}$, whereas with TDIROF the production was similar at all three current densities.

Table 3.1: Totally produced OCBPs after the electrolysis of stored urine up to 9 Ah of transferred charge.

<table>
<thead>
<tr>
<th>Current density (mA·cm$^{-2}$)</th>
<th>BDD</th>
<th>TDIROF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Dichloromethane (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloromethane (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloropropane (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total OCBPs (mmolCl·L$^{-1}$)</td>
<td>0.15</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Chapter 3

Discussion

Experimental Setup for OCBP Measurement

In this paper, we present a novel method for the measurement of volatile OCBPs evolving from an electrolysis cell. The setup is simple and flexible and does not require sophisticated instrumentation. The cutoff in detectability of OCBPs, which is due to the boiling point of dodecane, can be circumvented by using other absorbents to extract OCBPs from urine and by combining different absorbents in the wash bottles connected in series or in parallel. Another advantage is that the dodecane samples can be stored easily and the analysis can be done with standard GC/MS equipment independently of the experiment itself.

The method allowed us to quantify OCBPs at a relatively high timely resolution compared to other methods. Johnson et al. (1999) used solid sorbent column traps which yielded a measurement point only after replacement every 8 h. Comninellis and Nerini (1995) probably analyzed directly the gas in the headspace of a recirculation vessel – but details for sampling and quantification remain unclear.

It is important to choose the right materials (i.e., glass, metal, or Teflon) for the tubing and the wash bottles to prevent OCBPs from adsorbing at the surfaces or diffusing through them. Furthermore, condensation of OCBPs at the walls of tubes and wash bottles has to be prevented by ensuring a lower temperature inside of the system compared to the ambient temperature. The wash bottles need to be tall, and the gas diffusors need to produce fine bubbles such that equilibrium between the gas phase and the absorbent phase is established. Representative samples are guaranteed due to the intense mixing of the absorbent by the rising gas bubbles.

Reaction Schemes on BDD and TDIROF

Before entering the discussion of our results we consider it useful to briefly review the current knowledge about the most relevant electrochemical oxidation processes on BDD and TDIROF. Chemical chlorate formation was briefly reviewed in section F of the SI, and schemes summarizing these processes are given in the SI, Figure F.3.1.

On TDIROF, there is a consensus that chloride is oxidized by a direct electron transfer yielding adsorbed chloride radicals. In a subsequent step, two of the latter recombine to form active chlorine in a heterogeneous reaction (Jeong et al., 2009; Trasatti, 1987) The products of chloride oxidation are assumed to be mainly active chlorine species (Jeong et al., 2009) although some studies also proposed direct oxidation of chloride to chlorate (Czarnetzki and Janssen, 1992; Jung et al., 2010). Organic substances can either be oxidized by a direct electron transfer at the electrode surface or by active chlorine species. The products can be smaller chained organic substances (intermediates), OCBPs, or CO₂. The latter one is an end-product, while the other substances can undergo further oxidation. Active chlorine species can be oxidized to chlorate by direct oxidation on the electrode surface via chlorite as a possible intermediate (Tasaka and Tojo, 1985).

The discussion on chlorine formation on BDD is controversial in the literature. Some studies proposed a similar direct oxidation mechanism as observed on active type electrodes resulting in chlorine evolution being a competitive reaction to hydroxyl radical
Chlorination By-products and Their Emission Pathways

formation (Bergmann et al., 2009; Polcaro et al., 2009). Other studies concluded that the oxidation by hydroxyl radicals led to the formation of active chlorine on BDD (Bergmann, 2010; Jeong et al., 2009). In the latter case, chloride is oxidized through indirect oxidation by hydroxyl radicals in a homogeneous reaction close to the anode (Bergmann, 2010). The products are again likely to be active chlorine species (Jeong et al., 2009). Organic substances were shown to be oxidized by hydroxyl radicals (Comninellis, 1994; Kapalka et al., 2008b) but they can also be oxidized by active chlorine species (Anglada et al., 2011). Similar to TDIROF, the products can be smaller chained organic substances (intermediates), OCBPs, or CO₂, and the first two might be further oxidized. Chlorate was reported to be formed by hydroxyl radical oxidation of active chlorine species (Bergmann, 2010). Perchlorate formation was argued to require a direct electron transfer followed by a homogeneous reaction with hydroxyl radicals (Azizi et al., 2011).

Efficiency of Chloride Oxidation

The higher current efficiency for chloride oxidation on BDD compared to TDIROF could result from the distinct oxidation mechanisms. On TDIROF, chloride oxidation was probably limited by the availability of active sites at high chloride concentrations. This would explain why the current efficiency for chloride oxidation is not depending on the bulk concentration of chloride and why chloride oxidation does not increase with current density. On the BDD anode, the chloride oxidation rates were also constant in each experiment. Either also because of limiting active sites (Bergmann et al., 2009) or because the probability of a chloride ion meeting a hydroxyl radical (Jeong et al., 2009) remained constant. This could be because the concentration of hydroxyl radicals in the reaction zone close to the anode increased with transferred charge, while the one of chloride and COD decreased. The higher concentration of hydroxyl radicals then also resulted in stronger oxidation of chlorate to perchlorate and stronger oxygen evolution.

The higher current efficiency of chloride oxidation on BDD with increasing current density likely resulted from more strongly accelerated kinetics of direct chloride oxidation (Bergmann et al., 2009; Polcaro et al., 2009) compared to the kinetics of other anodic processes. Jeong et al. (2009) reported a linear sweep voltammogram (LSV) on BDD which showed that the presence of chloride led to additional currents compared to a LSV in only supporting electrolyte indicating the faster acceleration of direct chloride oxidation with increasing anode potential. In our case, an increased current density led to an increased anode potential (SI, Figure G.3.1). If direct chloride oxidation on BDD happened at a lower on-set potential than other significant reactions, the increasing anode potential had a stronger effect on chloride oxidation due to the exponential character of the Butler-Volmer relationship (Bard and Faulkner, 2001). Nevertheless, also chloride oxidation by hydroxyl radicals might have proceeded simultaneously (Bergmann, 2010; Jeong et al., 2009).

Consequences for OCBP Formation

On BDD, the stronger breakdown of organic substances in the reaction with hydroxyl radicals (Comninellis and Nerini, 1995) led to more short chained intermediates which coexisted with higher concentrations of active chlorine. Consequently, more short
chained OCBPs were produced especially in the beginning when the reaction rates were high. The lower production of the targeted OCBPs at 20 mA·cm\(^{-2}\) (Table 3.1) may be explained with the more complete mineralization of organics to CO\(_2\) or by stronger formation and immediate stripping of chloromethane (not quantified) which could not be further chlorinated to dichloromethane or trichloromethane. With TDIROF on the other hand, the oxidative breakdown of organic molecules was less complete due to the weaker oxidizing environment (no hydroxyl radicals). The precursors for OCBP formation were therefore longer chained resulting in longer chained OCBPs.

The production of longer chained OCBPs also partially explains the higher amount of unknown AOX with the TDIROF anode. The GC/MS measurements showed that TDIROF was prone to form longer chained OCBPs. This indicated that on TDIROF OCBPs might have formed which were undetectable with our GC/MS method but which appear in the AOX measurements. Another explanation for unknown AOX are chloramines. On BDD, the stronger oxidation of chloride may have resulted in conditions also found in breakpoint chlorination (Kapałka et al., 2010). Consequently, ammonia would have been oxidized all the way to N\(_2\) leaving little chloramines in solution. It is less probable that such conditions were reached on TDIROF due to less chloride oxidation which may led to more chloramines showing up in the AOX measurements.

**Fate of OCBPs**

The fate of the measured OCBPs was considerably different on the two electrodes. On TDIROF, they were entirely removed from urine by electrochemical stripping. This is easily seen at the end of the experiment where OCBPs were transferred completely into the gas phase (Figure 3.2). In contrast to the BDD anode, there was no evidence for another process that would remove OCBPs. The fact that tetrachloromethane was not found on TDIROF indicates that it was not formed: if it had been formed, it would have been stripped into the wash bottles due to the low solubility in water and it would have been trapped in the wash bottles due to the high absorbability in dodecane (SI, Table B.3.1).

On BDD, the elimination of dichloromethane and trichloromethane may have resulted from further oxidation, to a small extent by chlorination to tetrachloromethane, or by complete mineralization (Randazzo et al., 2011) to CO\(_2\) which was indicated by the smaller production of OCBPs at 20 mA·cm\(^{-2}\) compared to 15 mA·cm\(^{-2}\) (Table 3.1). Another possibility is that they got reduced at the cathode (Rondinini and Vertova, 2010). However, we used a steel cathode for which, to our knowledge, electro-reductive properties of OCBPs have not been reported yet. Additional experiments are needed to clarify this aspect because reductive dehalogenation of trichloromethane was observed and found to be strongly dependent on the cathode material (Sonoyama et al., 1997; Sonoyama and Sakata, 1999).

**Relative Importance of CBPs**

Chlorate was formed much more strongly than OCBPs with both anodes. Since OCBPs and chlorate are supposed to be formed in reactions involving active chlorine, the two processes are in competition. The much weaker formation of OCBP could result from small amounts of organic precursors for OCBP formation or from slow reaction kinetics
of these reactions compared to chlorate formation. The strong chlorate formation likely resulted from simultaneous direct oxidation of chloride and active chlorine (TDIROF, Jung et al., 2010) or the oxidation of active chlorine via hydroxyl radicals (BDD, Bergmann, 2010) and chemical reactions of active chlorine species (Gordon and Tachiyashiki, 1991). Thereby, chemical chlorate formation could have been favored by an ideal pH range (between 6 and 9, Gordon and Tachiyashiki, 1991; Landolt and Ibl, 1970) due to the good buffer capacity of urine.

Perchlorate formation was low on both electrodes as long as chlorate was present at much lower concentrations than chloride and COD. This indicates that chloride, active chlorine, and COD were preferentially oxidized over chlorate. In contrast to earlier results (Li et al., 2015), strong production of perchlorate was observed on TDIROF toward the end of the experiments. This may be explained with chemical perchlorate formation due to ideal pH conditions in the diffusion layer (3.5 – 7.5; D’Ans and Freund, 1957; Landolt and Ibl, 1970) resulting from the moderate current densities applied and the good buffer capacity in real urine (detailed discussion in SI, section H). On the BDD anode, not only a competition of chloride and chlorate for active sites on the electrode was already suggested (Bergmann et al., 2009), but also a competition for hydroxyl radicals could be an explanation. Thus, high concentrations of chloride and COD could prevent perchlorate formation. However, if COD and chloride are completely eliminated after the same amount of transferred charge as in our experiments, there is a risk of strong perchlorate formation.

According to our results three risks exist with the chlorine mediated electro-oxidation of urine concerning CBPs: The first is the potentially massive formation of dissolved chlorate and especially perchlorate. These can be minimized by working at low current densities (BDD) and by respecting a maximum specific charge (residual chloride should be left). Second, targeted OCBPs and unidentified AOX can be left in solution at lower specific charges. Their toxicity remains unknown. However, in preliminary experiments (SI, section I) a nonspecific chlorophyll fluorescence test (Escher et al., 2005) indicated a positive effect of electrolysis (BDD, 10 mA·cm⁻²) on the baseline toxicity of urine, which means that the overall reduction of toxicity was higher than the increase by producing toxic OCBPs. Finally, we conclude that it is not sufficient to look at by-products in the liquid phase. The gas phase is equally important. In this work, the stripping of OCBPs into the gas phase accounted for 40% to 100% of the targeted OCBPs on BDD and for 95% to 100% on TDIROF. Accordingly, electrolysis units which produce OCBPs should be equipped with an off-gas treatment especially if they are placed in a closed room.

**Acknowledgments**

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References


Supplementary Information
A. Experimental Setup

The experimental setup for the measurement of organic chlorination by-products (OCPBs) is depicted in Figure A.3.1. The electrolysis cell and the wash bottles had a headspace above the liquid phase. The OCPBs in these headspaces were taken into account in the mass balances for the OCPBs in the recovery experiment as well as in the estimation of OCBP production.

Figure A.3.1: Experimental setup for the measurement of OCPBs in the liquid and the gas phase of an electrolysis cell. The electrolysis cell was filled with urine while the two wash bottles were filled with dodecane to absorb OCPBs from the off-gas. The air pump applied a low pressure in the headspace of wash bottle 2 leading to a constant air flow through the system.

B. Gas Exchange in the Wash Bottles

A numerical model was used to get a better understanding of the gas exchange in the wash bottles and to test if equilibrium can be assumed between the dodecane phase and the gas bubble leaving the wash bottle. For that purpose the rising gas bubble in the wash bottles was modeled mathematically. The mass transfer was modeled according to the two film theory (Tchobanoglous et al., 2003). We used the partition coefficients of the OCPBs in the hexadecane/air system because they can be shown to be very similar to the ones in the dodecane/air system (eq. S.3.1) which were not available. In fact, the partition coefficients in both alkane/air systems ($L = \frac{c_{\text{alkane}}}{c_{\text{air}}}$, $m_{\text{alkane}}^3 \cdot m_{\text{air}}^3$), $c_x$ being the concentration in solvent $x$) must be similar because it was shown that the partition coefficients in the dodecane/water system ($P = \frac{c_{\text{alkane}}}{c_{\text{water}}}$, $m_{\text{water}}^3 \cdot m_{\text{alkane}}^3$)) and the hexadecane/water system were very similar for a wide range of compounds (Seiler, 1974) and because the partition coefficients for the air/water system (Henry coefficients $H = \frac{c_{\text{water}}}{c_{\text{air}}}$, $m_{\text{water}}^3 \cdot m_{\text{air}}^3$) are constant (Table B.3.1).

\[ L = \frac{c_{\text{alkane}}}{c_{\text{air}}} = \frac{c_{\text{alkane}}}{c_{\text{water}}} \cdot \frac{c_{\text{water}}}{c_{\text{air}}} = P \cdot H \quad (S.3.1) \]

Since all OCPBs have a very large partition coefficient for hexadecane/air ($L_{16}$, Table B.3.1) the simplified mass flux equation for well soluble gases applied (Tchobanoglous et al., 2003). From this, the differential equation S.3.2 was found for the concentration of an OCBP in the rising gas bubble $C_{\text{OCBP},b}$:
Where $A_b$ (m$^2$) is the surface of the gas bubble as a perfect sphere calculated with a bubble diameter of 2.5 mm (estimated from a picture of rising gas bubbles in a wash bottle), $D_{OCBP}$ (cm·s$^{-1}$) is the diffusion coefficient in air (Table B.3.1), $c_{OCBP,b}$ (mg·L$^{-1}$) is the OCBP concentration in the gas bubble, $c_{OCBP, WB} = 0$ mg·L$^{-1}$ is the OCBP concentration in the dodecane of the wash bottle, $V_b$ (m$^3$) is the volume of the gas bubble and $d_b = 1.25$ mm is the diffusion layer thickness in the gas phase. This model was numerically implemented in Berkeley Madonna (Berkeley Madonna Inc., Berkeley, USA, Version 8.3.18) with an initial OCBP concentration in the bubble of $c_{OCBP,b,init} = 1$ mg·L$^{-1}$. The end time $t_{end}$ (s) of the gas exchange was calculated with the height of the wash bottle ($h_{WB} = 30$ cm) and a rising velocity of the gas bubble of $v_b = 0.3$ m·s$^{-1}$ as:

$$t_{end} = \frac{h_{WB}}{v_b} \quad \text{(S.3)}$$

The calculations presented in Figure B.3.1 show the OCBP concentrations in a gas bubble normalized with the initial concentrations ($c_{OCBP,init}$). The final concentrations in the gas bubble leaving the wash bottle were 0.7% (dichloromethane) to 2.9% (chlorobenzene), respectively. These amounts were in the range of the coefficient of variation of the GC/MS procedure (3.2% for dichloromethane and 2.8% for chlorobenzene). It was therefore reasonable to assume that the gas bubble was in equilibrium with the dodecane phase when the surface of the dodecane phase was reached.

**Table B.3.1: Physical properties of the OCBPs.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Henry coefficient$^1$</th>
<th>Partition coefficient hexadecane/air$^2$</th>
<th>Diffusion coefficient in air$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td>0.40$^4$</td>
<td>15</td>
<td>0.104</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>0.11</td>
<td>104</td>
<td>0.089</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>0.15</td>
<td>302</td>
<td>0.083</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>0.89</td>
<td>665</td>
<td>0.091</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.05</td>
<td>374</td>
<td>0.078$^4$</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>0.12$^2$</td>
<td>719</td>
<td>0.074</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.15</td>
<td>4560</td>
<td></td>
</tr>
</tbody>
</table>
Figure B.3.1: Fate of the OCBP concentration in a rising gas bubble in one of the wash bottles. Initial OCBP concentrations in the dodecane were zero. The rising velocity was assumed to be 0.3 m·s\(^{-1}\) and the bubble diameter 2.5 mm.

C. Characterization of the Urine

Hydrolyzed urine was taken from the women's urine storage tank in the main building at Eawag. The composition of the urine is given in Table C.3.1.

Table C.3.1: Composition of hydrolyzed urine from the women's storage tank at Eawag. The number of measurements was 6. (\(^1\)) only one measurement. (\(^2\)) 5 measurements

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total COD (mg·L(^{-1}))</td>
<td>1710</td>
<td>50</td>
</tr>
<tr>
<td>Total Ammonia N (mg·L(^{-1}))</td>
<td>1860</td>
<td>40</td>
</tr>
<tr>
<td>Nitrite N (mg·L(^{-1}))</td>
<td>&lt;0.15</td>
<td>-</td>
</tr>
<tr>
<td>Nitrate N (mg·L(^{-1}))</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>Chloride (mg·L(^{-1}))</td>
<td>1250</td>
<td>130</td>
</tr>
<tr>
<td>Total Phosphate P (mg·L(^{-1}))</td>
<td>88</td>
<td>9</td>
</tr>
<tr>
<td>Sulfate (mg·L(^{-1}))</td>
<td>234</td>
<td>25</td>
</tr>
<tr>
<td>Conductivity (mS·cm(^{-1}))</td>
<td>15.1(^1)</td>
<td>-</td>
</tr>
<tr>
<td>pH (-)</td>
<td>9.1(^2)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

D. Recovery Experiment to Assess the Experimental Setup for OCBP Measurements

The detailed results of the recovery experiment are presented in Figure D.3.1. The solid lines show that the mass of all OCBPs was conserved at all sampling points relative to the mass found in the beginning. Except dichloromethane, all OCBPs could be recovered by more than 90% for a period of nearly 8 hours. The stripping of the OCBPs from the water phase corresponded nicely to what would be expected according to the Henry coefficients (Table B.3.1). Tetrachloromethane, which has the highest Henry coefficient, was quickly removed, especially in the beginning, resulting in the lowest concentration in the electrolysis cell after 8 hours. The low concentration of tetrachloromethane in the first measurement was due to a high concentration of tetrachloromethane in the headspace of the electrolysis cell already at the very beginning. Dichloromethane, trichloromethane,
1,2-dichloropropane and chlorobenzene were removed from the nanopure water at very similar rates according to their comparable Henry coefficients. The substance with the lowest Henry coefficient, 1,2-dichloroethane, was removed more slowly. The observation that the stripping from the aqueous phase can be explained with the Henry coefficient indicated that the mass transport from water into air was not diffusion limited.

Similarly, the desorption of the OCBPs into the dodecane was not limited by mass transfer kinetics as shown in Figure B.3.1. Chlorobenzene, the compound with the highest \( L_{16} \) value, showed a strong increase in WB1 at the beginning and reflected very well the loss from the aqueous phase. Furthermore, almost no chlorobenzene was found in WB2 demonstrating that chlorobenzene was completely absorbed in WB1. Similar behavior was observed with tetrachloromethane and 1,2-dichloropropane. Likewise, these two compounds mirrored the removal from the aqueous phase in WB1 and showed little mass in WB2 corresponding to their high \( L_{16} \) values. The lower \( L_{16} \) values of trichloromethane and 1,2-dichloroethane resulted in an earlier transport into WB2. This was even more pronounced for dichloromethane with the lowest \( L_{16} \) value resulting in almost equal amounts in WB1 and WB2. The dodecane in WB1 was saturated early leading to an early transport into WB2.

Dichloromethane was only recovered by 85% during the first 8 hours of the experiment. This could result from a loss in the off-gas of WB2 that is higher than what we calculated. The calculation is based on the assumption that the gas leaving WB2 was in equilibrium with the dodecane phase. However, dichloromethane is the compound that has the lowest \( L_{16} \) value leading to faster saturation of the dodecane. This can be seen in the stagnating curve of the mass in WB1. Therefore, the assumption to have an equilibrium concentration in the off-gas of WB2 was probably not completely fulfilled towards the end of the experiment and the concentration in the gas phase might have been higher than what was calculated. Thus, the dichloromethane flux out of WB2 was slightly underestimated in our calculations.
Figure D.3.1: Recovery experiment for the selected OCBPs. The solid line denotes the total mass in all compartments and the dashed line the calculated mass lost in the off-gas of the second trap. The full symbols (●) denote measurements in nanopure water and the open symbols measurements in the wash bottles: WB1 (◊), WB2 (□). Temperature: 19.0 °C.

E. Interference of Chlorate and Perchlorate with the AOX Measurement

The interference of chlorate and perchlorate with the AOX measurements was calculated assuming linear correlations according to eq. S.3.4 and S.3.5.

\[
\begin{align*}
    c_{\text{AOX,ClO}_3^-} &= a_{\text{ClO}_3^-} \cdot c_{\text{ClO}_3^-} \\
    c_{\text{AOX,ClO}_4^-} &= a_{\text{ClO}_4^-} \cdot c_{\text{ClO}_4^-}
\end{align*}
\]  

Herein, \( c_{\text{AOX,x}} \) is the AOX concentration measured because of substance \( x \) and \( c_x \) is the concentration of substance \( x \). The correction coefficients \( a_{\text{ClO}_3^-} \) and \( a_{\text{ClO}_4^-} \) were estimated from two AOX measurements in nanopure water that was spiked with 500 mg·L\(^{-1}\) of chlorate \( (c_{\text{AOX,ClO}_3^-\text{,spike}} = 8.44 \mu g Cl \cdot L^{-1}) \) or perchlorate \( (c_{\text{AOX,ClO}_4^-\text{,spike}} = 25.68 \mu g Cl \cdot L^{-1}) \) and subtracting the blank value of nanopure water \( (c_{\text{AOX,blank}} = 1.96 \mu g Cl \cdot L^{-1}) \).

\[
    a_{\text{ClO}_3^-} = \frac{c_{\text{AOX,ClO}_3^-\text{,spike}} - c_{\text{AOX,blank}}}{c_{\text{ClO}_3^-}} = 1.08 \cdot 10^{-3} \text{ mgCl} \cdot \text{mmol}^{-1}
\]  

(S.3.6)
\[ a_{\text{ClO}_4^{-}} = \frac{c_{\text{AOX,ClO}_4^{-}_{\text{spike}}} - c_{\text{AOX,blank}}}{c_{\text{ClO}_4^{-}}} = 4.72 \cdot 10^{-3} \text{ mg Cl \cdot mmol}^{-1} \] (S.3.7)

**F. Schemes of Anodic Oxidation Processes on BDD and TDIROF**

The most relevant oxidation processes on BDD and TDIROF are represented schematically in Figure F.3.1 for a better understanding of the current knowledge about these processes. In addition to the electrochemical processes reviewed in the paper a brief review of chemical chlorate formation is given in the following.

It was shown that chemical chlorate formation from hypochlorous acid/hypochlorite and chlorous acid/chlorite can be important especially at medium pH values (6 to 9, (Gordon and Tachiyashiki, 1991) The involvement of that reaction was also discussed in a publication on electrochemical chlorate formation from NaCl on RuO$_2$-TiO$_2$/Ti (Czarnetzki and Janssen, 1992). The authors proposed that chlorate is formed in the acidic diffusion layer at the anode via a reaction of hypochlorous acid and chlorite. Such a reaction cannot be excluded in our experiments since a pH drop in the diffusion layer has to be expected. Although, urine is well buffered (Udert et al., 2003) which probably limited this pH drop.

The authors further came to the conclusion that significant direct oxidation of chloride to chlorate was mainly depending on a high ratio of the applied current density to the chloride concentration. They only found considerable direct chlorate formation at 2.76 kA\cdot m^{-2} if the chloride concentration was lower 300 mmol\cdot L^{-1}. This means that the ratio had to be above 0.92 mA\cdot L^{-1}\cdot cm^{-2}\cdot mmol^{-1} for substantial chlorate formation. In our experiments this ratio was 0.6 mA\cdot L^{-1}\cdot cm^{-2}\cdot mmol^{-1} in the beginning of the experiments at 20 mA\cdot cm^{-2}. It increased with the removal of chloride and reached much higher values than the critical value of 0.92 mA\cdot L^{-1}\cdot cm^{-2}\cdot mmol^{-1} due to the complete removal of chloride in some cases.

Another study on Pt/Ti found only low amounts of chlorate when the presence of active chlorine was suppressed but much higher amounts in presence of active chlorine (Jung et al., 2010). However, chemical and electrochemical chlorate formation from active chlorine was not distinguished. Nevertheless, also electrochemical oxidation of hypochlorite and chlorite to chlorate has been demonstrated on the Pt electrode (Tasaka and Tojo, 1985).
G. Anode Potential during Experiments with BDD

In Figure G.3.1 the time course of the anode potentials $E_A$ is shown for the three experiments with BDD anodes. Please note that the y-axis does not start at zero to make the differences clearer.

![Figure G.3.1: Anode potential ($E_A$) during the experiments with BDD as a function of transferred charge. MSE stands for “mercury / mercurous sulfate electrode” which was employed as a reference electrode.](image)

H. Possible Mechanism of Perchlorate Formation on TDIROF

So far, many results from other studies suggest that physisorbed hydroxyl radicals are required to form perchlorate (Azizi et al., 2011; Bergmann, 2010; Jung et al., 2010) However, many studies conclude that IrO$_2$ is an active type anode (Jeong et al., 2009; Panizza, 2010; Wu et al., 2014) and thus does not form such radicals. Another possibility would be direct oxidation of chlorate on the electrode with other reactive oxygen species however this would be in contradiction to many studies that did not find perchlorate with IrO$_2$ anodes (Bergmann et al., 2009; Lacasa et al., 2012). Nevertheless, perchlorate formation has been reported earlier on IrO$_2$ and other active type anodes as well (Bergmann, 2010; Bergmann et al., 2009).
Chlorination By-products and Their Emission Pathways

Perchlorate can be formed chemically in a reaction of hypochlorous acid/hypochlorite with chlorate (D'Ans and Freund, 1957). The kinetics of that reaction were found to be very slow, however, the authors did not take into account pH and hypochlorous acid/hypochlorite speciation which could be very important as the case of chemical chlorate formation shows (Czarnetzki and Janssen, 1992; Gordon and Tachiyashiki, 1991) Similar to the chemical formation of chlorate it is likely that chemical perchlorate formation is accelerated if hypochlorous acid instead of hypochlorite is present.

The most plausible mechanism for the strong perchlorate formation in our case, although quite speculative, therefore might be an electrochemically assisted chemical oxidation. D'Ans and Freund (1957) proposed the following mechanism for chemical perchlorate formation:

\[
\begin{align*}
\text{ClO}_3^- + \text{HClO} & \rightleftharpoons [\text{HCl}_2\text{O}_4]^-(\text{fast}) \quad (\text{S.3.8}) \\
[\text{HCl}_2\text{O}_4]^-(\text{slow}) & \rightarrow \text{ClO}_4^- + \text{Cl}^- + \text{H}^+ \quad (\text{S.3.9})
\end{align*}
\]

The buffering by phosphate (pK_{a2} = 7.2, Table C.3.1) and hypochlorous acid itself (pK_{a} = 7.5) probably resulted in an only moderate pH drop in the diffusion layer which facilitated the reaction S.3.8 in our system by making HClO available (Landolt and Ibl, 1970). The second step (eq. S.3.9) may have been accelerated at the anode by a destabilization of the chloronium perchlorate complex ([HCl_2O_4^-]) at the active sites once they were available. If it is assumed that chloride competed for the active sites and that the equilibrium of equation S.3.8 is strongly on the left hand side this could explain why perchlorate formation was retarded and why chlorate accumulated while chloride concentrations were high. However, once some active sites were free, reaction S.3.9 was accelerated which is in line with the observation that perchlorate formation was strongest at low chloride concentrations (Figure 3.2).

This may have not been observed before because either chloride was still left in solution or because more weakly buffered electrolytes have been used together with higher current densities (Lacasa et al., 2012; Li et al., 2015). This may resulted in a local pH drop which was too severe pushing the equilibrium of chlorine and hypochlorous acid towards chlorine. In such cases, the chloronium perchlorate complex may disappear which could strongly hinder perchlorate formation.

I. Preliminary Toxicity Tests

We assessed the toxicity of electrolytically treated urine in two preliminary experiments (on TDIROF at 5 mA·cm⁻² and on BDD at 10 mA·cm⁻² in high-load, stored urine (see Table I.3.1 for its composition)). After 32 hours of electrolysis, we did a chlorophyll fluorescence test recommended as a sum parameter for the toxicity of pharmaceuticals in urine (Escher et al., 2005). Since this method was optimized for universality rather than specificity it might work for the unidentified fraction of AOX as well.
Table I.3.1: Composition of high-load stored urine used in two preliminary experiments.

<table>
<thead>
<tr>
<th></th>
<th>High-load urine</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Std. Dev.</td>
<td></td>
</tr>
<tr>
<td>Total COD (mg L(^{-1}))</td>
<td>4510</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>Total Ammonia N (mg L(^{-1}))</td>
<td>2790</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>Nitrite N (mg L(^{-1}))</td>
<td>&lt; 10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nitrate N (mg L(^{-1}))</td>
<td>&lt; 10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Chloride (mg L(^{-1}))</td>
<td>3800</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Total Phosphate P (mg L(^{-1}))</td>
<td>242</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Sulfate (mg L(^{-1}))</td>
<td>822</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Conductivity (mS cm(^{-1}))</td>
<td>30.1</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>(-)</td>
<td>9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In Figure I.3.1 the inhibition of the bioluminescence is shown as a dose response curve for four different types of urine and the blank sample (nanopure water). The dose response curve for the untreated, stored urine showed a baseline toxicity resulting from ammonia, organic substances and xenobiotics such as pharmaceuticals as previously observed (Escher et al., 2005; Escher et al., 2006). The treatment of the urine with the TDIROF anode at 5 mA·cm\(^{-2}\) had little effect on the baseline toxicity. However, the treatment with BDD at 10 mA·cm\(^{-2}\) resulted in a shift of the dose response curve to the right which means a reduction of the non-specific toxicity. An even stronger toxicity reduction was observed in the treatment with a biological nitrification reactor (aerobic moving bed bio-reactor (MBBR)).

The reduction of the toxicity in the MBBR and the electrolysis with BDD very likely resulted from a reduction in the baseline toxicity due to the removal of ammonia, organic and xenobiotic substances. This can be concluded from the fact that in the MBBR about half of the ammonia is nitrified to nitrate and organic substances are almost completely removed with a removal efficiency of 90% (Udert and Wächter, 2012). On the BDD anode, the COD concentration decreased by 75% from 4.2 gCOD·L\(^{-1}\) to 1 gCOD·L\(^{-1}\) while ammonia was removed by 23% (Figure I.3.2). On the TDIROF anode, however, the COD concentration only decreased by 21% from 3.9 gCOD·L\(^{-1}\) to 3.1 gCOD·L\(^{-1}\) and ammonia by 20% (results not shown).
Figure I.3.1: Inhibition of the bioluminescence as a dose response curve of four types of urine and the blank sample (nanopure water): (■) untreated stored urine, (□) urine treated with TDIROF at 5 mA·cm\(^{-2}\), (˟) urine treated with BDD at 10 mA·cm\(^{-2}\), (▲) urine treated in a biological nitrification reactor (aerobic MBBR) and the blank (●). The relative enrichment factors (REF) refer to the original urine samples.

Figure I.3.2 presents the masses of the quantifiable OCBPs extracted from the urine during the experiment with BDD at 10 mA·cm\(^{-2}\) together with the concentrations of chloride, chlorate and COD. The OCBP masses were in a similar range as observed with the TDIROF anode at 20 mA·cm\(^{-2}\) and also present in significant amounts in the last sample which was analyzed with the bioluminescence test. On the other hand, only a low amount of chlorate was built probably because of the competing reactions resulting from the very high COD concentrations. Perchlorate was not measured but its formation was unlikely due to the high concentrations of chloride and the very low concentrations of chlorate (Bergmann et al., 2009).

From these preliminary tests we conclude that electrolysis has a beneficial effect on the non-specific toxicity of urine mainly due to the removal of the baseline toxicity caused by organic and xenobiotic substances. Moreover, the reduction of the baseline toxicity by electrolysis appears to be stronger than the potentially added toxicity of the OCBPs. The toxic effect of chlorate and perchlorate could not be assessed in these experiments. First of all, because little chlorate and probably no perchlorate were formed and second because the solid phase extraction (SPE) applied to remove some of the urine matrix effect would also have removed the effects of chlorate and perchlorate (Escher et al., 2005).

The effects of electrolysis on the toxicity of urine have to be investigated in more detail in future studies. The application of the chlorophyll fluorescence test appears to be a promising route of investigation to assess the non-specific toxicity. In combination with other pretreatment technologies than SPE it might also be used to investigate the added toxicity of chlorate and perchlorate.
Figure I.3.2: Masses of three OCBPs (dichloromethane, 1,2-dichloroethane, trichloromethane) measured by extraction from urine and concentrations of chloride and chlorate as well as COD during the electrolysis of high-load urine with a BDD anode at 10 mA·cm⁻².

References


http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf

Chapter 4

Direct Electrochemical Oxidation of Ammonia on Graphite as a Treatment Option for Stored Source-Separated Urine

This chapter is based on the publication:

Graphical Abstract

Anode Potential [V vs. SHE]
Exfoliation and by-product formation

Chlorine evolution and indirect oxidation

Direct oxidation and graphite mineralization

Cl₂
2 Cl⁻
1/3 N₂
2/3 NH₃

N-removal without harmful by-product formation and strong electrode corrosion

Organics
Chlorinated by-products

CO₂
0.5 N₂
NO₃⁻
2 NH₃
200 μm

Graphite Anode
Abstract

Electrolysis can be a viable technology for ammonia removal from source-separated urine. Compared to biological nitrogen removal, electrolysis is more robust and is highly amenable to automation, which makes it especially attractive for on-site reactors. In electrolytic wastewater treatment, ammonia is usually removed by indirect oxidation through active chlorine which is produced in-situ at elevated anode potentials. However, the evolution of chlorine can lead to the formation of chlorate, perchlorate, chlorinated organic by-products and chloramines that are toxic. This study focuses on using direct ammonia oxidation on graphite at low anode potentials in order to overcome the formation of toxic by-products. With the aid of cyclic voltammetry, we demonstrated that graphite is active for direct ammonia oxidation without concomitant chlorine formation if the anode potential is between 1.1 and 1.6 V vs. SHE (standard hydrogen electrode). A comparison of potentiostatic bulk electrolysis experiments in synthetic stored urine with and without chloride confirmed that ammonia was removed exclusively by continuous direct oxidation. Direct oxidation required high pH values (pH > 9) because free ammonia was the actual reactant. In real stored urine (pH = 9.0), an ammonia removal rate of 2.9 ± 0.3 gN·m^{-2}·d^{-1} was achieved and the specific energy demand was 42 Wh·gN^{-1} at an anode potential of 1.31 V vs. SHE. The measurements of chlorate and perchlorate as well as selected chlorinated organic by-products confirmed that no chlorinated by-products were formed in real urine. Electrode corrosion through graphite exfoliation was prevented and the surface was not poisoned by intermediate oxidation products. We conclude that direct ammonia oxidation on graphite electrodes is a treatment option for source-separated urine with three major advantages: The formation of chlorinated by-products is prevented, less energy is consumed than in indirect ammonia oxidation and readily available and cheap graphite can be used as the electrode material.

Keywords

NoMix technology, nitrogen removal, decentralized, on-site, potential controlled electrolysis, chlorinated by-products

Introduction

The separate collection and treatment of urine and feces (NoMix technology) has emerged as a new field in urban water management (Larsen et al., 2013). NoMix technology allows pollutants to be eliminated more efficiently (Pronk et al., 2007) or nutrients to be recovered from urine with processes such as struvite precipitation (Etter et al., 2011) and nitrification/distillation (Udert and Wächter, 2012). However, in some areas, especially in the cities of industrialized countries, nutrient removal rather than nutrient recovery might be a more economically viable solution. A promising technology for ammonia removal from urine is electrolysis (Udert et al., 2013) thanks to its high robustness, versatility and amenability to automation (Anglada et al., 2009).

During electrolysis, ammonia is removed by oxidation via two pathways: it is either oxidized indirectly through an oxidation mediator produced on the anode (e.g. active chlorine species: Cl₂, HOCI or OCI⁻) or through direct electron transfer on the anode surface (Anglada et al., 2009). Both processes can occur during electrolysis of stored urine, because chloride is present in high concentrations (up to 3.8 gCl·L^{-1}; Udert et al.,
Although indirect oxidation is the most common electrochemical process for ammonia removal in wastewaters (Chen, 2004), it has three major disadvantages: (1) toxic chlorinated by-products can be formed, (2) the specific energy demand for ammonia removal is high, and (3) active chlorine can increase electrode corrosion.

Stored urine contains high amounts of organic substances (the chemical oxygen demand (COD) can be as high as 10 g·L⁻¹, Udert et al., 2006). Thus, the risk of forming chlorinated organic by-products is high (Sirés and Brillas, 2012). Due to the high ammonia concentration, the formation of chloramines is also very likely. Chlorate and perchlorate are other inorganic chlorinated by-products that are formed chemically or electrochemically when chloride is oxidized at elevated anode potentials (Perez et al., 2012).

The specific energy demand is large due to the high cell voltages needed to reach the anode potentials at which active chlorine is formed. The side reactions occurring at elevated anode potentials (e.g. oxygen evolution, Kim et al., 2006) also contribute to the high specific energy demand. The negative effect that active chlorine can have on electrode stability is well known from the chlor-alkali industry (Hamann and Vielstich, 2007), especially in the case of graphite exfoliation (particle detachment caused by intercalated chloride).

In contrast to indirect oxidation, the use of direct oxidation should allow ammonia to be eliminated without producing chlorinated by-products. The specific energy demand can be expected to be lower and electrode corrosion should be reduced. The key to successful direct oxidation is to choose an electrode which is cheap and stable, and which is active and selective with respect to ammonia oxidation (Panizza, 2010). Despite its advantages, direct ammonia oxidation has not received much attention so far for the treatment of wastewaters or urine. One exception is the treatment of ammonia in highly alkaline media with Pt-Ir electrodes (Diaz and Botte, 2012; Boggs and Botte, 2010). The Pt-Ir electrode has the lowest overpotential for direct ammonia oxidation, resulting in high selectivity and a low energy demand. Other studies on direct ammonia oxidation mainly focused on the activity and mechanism of direct electron transfer with boron-doped diamond (BDD) or different types of dimensionally stable anodes (DSAs, Bunce and Bejan, 2011). However, one drawback of all these electrode materials is their high cost.

Another problem with direct ammonia oxidation can be the deactivation of the electrode. The thermally decomposed iridium oxide film (TDIROF, a DSA type electrode), was found to be deactivated, presumably due to surface poisoning by adsorbed nitrogen (Kapalka et al., 2011). The same deactivation mechanism had already been reported earlier for platinum and several transition metals (de Vooy et al., 2001). However, not all electrodes were poisoned. Continuously ongoing direct ammonia oxidation has been demonstrated by Bonnin et al. (2008) on Pt-Ir and by Kapalka et al. (2010a) on Ni/Ni(OH)₂ electrodes. Unfortunately, in the latter study it was pointed out that corrosion might be a critical problem with Ni/Ni(OH)₂ electrodes. Amstutz et al. (2012) further showed that ammonia oxidation on TDIROF at high pH values can be inhibited by competing oxidation of carbonate.

Compared to Pt-Ir, BDD or DSA, graphite could be an inexpensive alternative electrode material for direct ammonia oxidation. However, its activity, selectivity and stability for
Direct Ammonia Oxidation with Graphite Electrodes

direct ammonia oxidation have not yet been investigated in detail. Candido and Ponciano Gomes (2011) found indications of direct ammonia oxidation during an anodic polarization experiment, but were unable to confirm their findings in cyclic voltammetry (CV) experiments. Zheng et al. (2009) reported the use of graphite for ammonia removal from synthetic urine. However, indirect oxidation via active chlorine was likely to be the main mechanism for ammonia removal since chloride was present and high current densities were applied.

The aim of this study was to evaluate whether direct oxidation of ammonia on isostatically pressed fine-grain graphite is a technically feasible alternative to indirect electrolytic ammonia removal from source-separated urine. The use of direct ammonia oxidation should allow us to work at lower anode potentials, thereby preventing the formation of chlorinated by-products, avoiding graphite exfoliation induced by active chlorine and reducing specific energy demand. We studied the individual and combined reactions of ammonia oxidation and chlorine evolution in cyclic voltammetry experiments to find the anodic potential window for direct ammonia oxidation without concomitant chlorine evolution. In bulk electrolysis experiments, we subsequently evaluated the process stability, selectivity and efficiency of direct ammonia oxidation in synthetic and real stored urine.

Material and Methods

Cyclic Voltammetry (CV) Experiments

A one-compartment glass cell (50 mL, temperature controlled at 25 ± 0.1 °C with a Colora thermostat, Colora Messtechnik GmbH, Lorch, Germany) was used for CV. The electrolyte volume was 40 mL. The working electrode was a graphite rod (R 8650, SGL Carbon GmbH, Bonn, Germany). The cross-sectional area with a geometric surface of 0.385 cm$^2$ was exposed to the electrolyte. The reference electrode was an Ag/AgCl/KCl (Ag/AgCl, 0.21 V vs. SHE, InLab reference pro, Mettler Toledo, Greifensee, Switzerland) placed in a glass-blown Luggin capillary filled with 1 mol·L$^{-1}$ NaClO$_4$. The counter electrode was a graphite bar (Geometric surface area: 8 cm$^2$; R4340, SGL Carbon GmbH, Bonn, Germany). The cell was controlled with a potentiostat using EcmWin software (PGU 10V-1A-IMP-S, EcmWin V2.4, Ingenieurbüro Peter Schrems, Münster, Germany).

NaClO$_4$ (1 mol·L$^{-1}$) was used as the supporting electrolyte (Table 4.1: “support”). Two solutions were used to study individual reactions of ammonia and chloride: first, 1 mol·L$^{-1}$ NaClO$_4$ with 0.25 mol·L$^{-1}$ NH$_4$ClO$_4$ (“support + NH$_3$”) and, second, 1 mol·L$^{-1}$ NaClO$_4$ with 0.085 mol·L$^{-1}$ NaCl (“support + Cl”). The desired pH levels were adjusted with sodium hydroxide. The combined effect of ammonia and chloride was investigated in a solution with 1 mol·L$^{-1}$ NaClO$_4$, 0.25 mol·L$^{-1}$ NH$_4$ClO$_4$ and 0.085 mol·L$^{-1}$ NaCl (“support + NH$_3$ + Cl”). For all conditions, 5 scans were performed in a row at a scan rate of 200 mV·s$^{-1}$. Unless indicated otherwise, the lower return potential was -1.59 V and the upper return potential ($E_{up}$) was 2.01 V. The same working electrode was used for all experiments and was cleaned with 5 cycles (between: -1.59 to 2.01 V) in 1 mol·L$^{-1}$ NaClO$_4$ prior to new experiments.
Table 4.1: Composition of the electrolytes used for CV and solutions used in the bulk electrolysis experiments (calculated from amounts of substances added or measured values). The electric conductivity was temperature-compensated for 25 °C. Standard deviations due to measurement uncertainties were less than 5%. The pH values in synthetic urine are high because little acetate and ammonia was added. 1) Below detection limit; 2) NaOH for pH adjustment not considered.

<table>
<thead>
<tr>
<th>Electrolytes for cyclic voltammetry</th>
<th>Synthetic urine solutions Without chloride</th>
<th>With chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support</td>
<td>Support + NH₃</td>
<td>Support + Cl</td>
</tr>
<tr>
<td>Organics [mgCOD·L⁻¹]</td>
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<td>0</td>
</tr>
<tr>
<td>Total ammonia [mgN·L⁻¹]</td>
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</tr>
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<td>Sodium [mg·L⁻¹]</td>
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<td>23000</td>
</tr>
<tr>
<td>Potassium [mg·L⁻¹]</td>
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</tr>
<tr>
<td>Nitrate [mgN·L⁻¹]</td>
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<td>0</td>
</tr>
<tr>
<td>Nitrite [mgN·L⁻¹]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Chloride [mg·L⁻¹]</td>
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<td>0</td>
</tr>
<tr>
<td>Phosphate [mgP·L⁻¹]</td>
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<td>0</td>
</tr>
<tr>
<td>Carbonate [mg·L⁻¹]</td>
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</tr>
<tr>
<td>Sulfate [mg·L⁻¹]</td>
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<td>0</td>
</tr>
<tr>
<td>Perchlorate [mg·L⁻¹]</td>
<td>99500</td>
<td>124000</td>
</tr>
<tr>
<td>Conductivity [mS·cm⁻¹]</td>
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<td>37.0</td>
</tr>
<tr>
<td>Initial pH [-]</td>
<td>9.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

**Bulk Electrolysis Experiments**

In these experiments, a 400 mL glass cell was filled with 300 mL solution and covered with a Plexiglas lid to prevent ammonia volatilization. Two graphite plates (R 4340, SGL Carbon GmbH, Bonn, Germany) with an exposed surface of 20 cm² served as the anode and cathode, respectively. The graphite was connected to a copper wire with silver epoxy glue (EPO-TEK E4110, Epoxy Technology, Billerica, USA) and sealed onto PVC plates with silicon glue (CAF 1, Bluestar silicones, Saint-Fons cedex, France). The distance between the electrodes was 1 cm. The reference electrode was a Hg/Hg₂SO₄/K₂SO₄ (MSE, 0.64 V vs. standard hydrogen electrode (SHE), Ref 601, Radiometer analytical, France) placed in a glass-blown Luggin capillary filled with saturated K₂SO₄. All electrode potentials were recalculated to values against SHE. The solution was stirred with a magnetic stirrer and the temperature was controlled with a thermostat (25 ± 0.1 °C, Colora thermostat, Colora Messtechnik GmbH, Lorch, Germany). Aliquots of the solution (10 to 15 mL) were taken with a syringe through a needle permanently placed in the electrolysis cell. The samples were filtered (0.45 μm, Chromafil GF/PET, Macherey-Nagel, Düren, Germany) before chemical analysis (see below).

The anode potential (Eₐ) was controlled and measured continuously with a potentiostat (PGU 10V-1A-IMP-S, Ingenieurbüro Peter Schrems, Münster, Germany) and the current...
was recorded with the same device. The cell voltage was recorded with a data logger on a high impedance analogue input (Mikromec multisens, Technetics, Freiburg, Germany). The temperature and pH were measured continuously (SenTix 41 connected to pH 196, WTW, Weilheim, Germany) and recorded with the data logger. Conductivity was measured with a handheld meter (TetraCon 325 connected to Cond 340i, WTW, Weilheim, Germany).

Synthetic urine was prepared on the basis of the composition of stored urine given by Udert et al. (2006). Acetate was chosen as the only organic substance. Since low removal rates had to be expected, the ammonia and acetate concentrations were reduced to shorten the duration of the experiments. Chloride was completely eliminated from one solution to suppress indirect oxidation (Table 4.1). The recipes for the synthetic urine are given in the supplementary information (Table A.4.1).

Electrolysis of real urine was performed with urine from the women’s collection tank in the main building at Eawag (Table 4.1). In this experiment, the weight change of the anode and the cathode was monitored and six organic by-products (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, chlorobenzene) previously observed during electrolysis at elevated anode potentials were analyzed after extraction from the solution with dodecane (see below). The electrodes were weighed before and after electrolysis on a precision balance (Ag204 DeltaRange, Mettler-Toldeo GmbH, Greifensee, Switzerland). Before weighing, the electrodes were dried for 30 minutes at 105 °C.

**Chemical Analyses**

Chloride, phosphate, sulfate and nitrate were analyzed by ion chromatography (881 compact IC pro, Metrohm, Herisau, Switzerland) while ammonia and nitrite were analyzed photometrically with a flow injection analyzer (standard operating procedures: 45-1 and 45-3, FOSS, Hillerød, Denmark). Free and total chlorine, COD and nitrite at very low concentrations were measured with photometric cuvette tests (LCK 310, LCK 514 and LCK 341, Hach Lange, Berlin, Germany). Free and total chlorine as well as total COD were analyzed in unfiltered samples. The standard deviations of the chemical analyses were less than 5%.

Organic chlorinated by-products were extracted by adding 0.9 mL of the unfiltered sample to 0.9 mL dodecane in a gas chromatography / mass spectrometry (GC/MS) glass screw-cap vial. The sample was taken with a gastight glass syringe. The GC/MS vials were shaken for 10 seconds and the solvents were allowed to separate for 30 minutes. Thereafter, 0.8 mL of the segregated dodecane phases on top of the sample were pipetted into another GC/MS glass screw-cap vial (1.5 mL). The dodecane samples were stored in a freezer (-20 °C) until analysis with GC/MS. 1 µL of the dodecane sample was analyzed with a Thermo Scientific DSQII single quadrupole GC/MS (Restek, Bellefonte, USA). The samples were injected into the column with a CTC CombiPAL auto-sampler. The temperature increased from 40 °C (constant for 1 min) to 140 °C at 10 °C·min⁻¹ and from 140 °C to 200 °C (constant for 20 min) at 40 °C·min⁻¹. The column was a RTX-VMS, 60 m x 0.32 mm I.D. with 1.8 µm film thickness (Restek). Helium (100 kPa) was used as the carrier gas. The transfer line had a temperature of 220 °C and the MS source temperature
was set at 250 °C. The relative standard deviation of the GC/MS analysis was less than 3.6% for all compounds.

**Calculations**

**Cyclic Voltammetry**

The polarization of the graphite electrodes during cyclic voltammetry led to high background currents \( j_{\text{support}} \) \([\text{mA cm}^{-2}]\). To obtain the current caused by ammonia oxidation during the CV in ammonia-containing electrolyte, the current measured in the electrolytes without ammonia or chloride was subtracted from the original current \( j_{\text{support}+\text{NH}3} \) \([\text{mA cm}^{-2}]\). The peak current density of ammonia oxidation \( j_{\text{peak}} \) \([\text{mA cm}^{-2}]\), Figure 4.2) was then obtained by evaluating the maximum of the corrected current (Equation 4.1).

\[
 j_{\text{peak}} = \text{max}(j_{\text{support}+\text{NH}3} - j_{\text{support}}) \\
\text{(4.1)}
\]

The mole fraction of NH\(_3\), \( f_{\text{NH}3} \) [\%], was calculated as a function of the pH from the measured total ammonia concentrations \( c_{\text{NH tot}} \) with the chemical speciation software PHREEQC (Parkhurst and Appelo, 1999). Activity coefficients were calculated using the Pitzer approach with a database extended by Pitzer parameters for ammonium and perchlorate (Kapałka et al., 2010a).

**Bulk Electrolysis Experiments**

The removal or production rate of a substance \( x \) per electrode surface \( r_{A,x} \) \([\text{gN m}^{-2} \text{d}^{-1}]\) was calculated from the slope \( s_x \) \([\text{gN d}^{-1}]\) of the linear regression of the remaining mass of substance \( x \) (including mass in removed samples) vs. time as:

\[
 r_{A,x} = s_x \cdot \frac{1}{A} \\
\text{(4.2)}
\]

where \( A \) \([\text{m}^2]\) is the anode surface area.

The yields \( Y_x \) [%] of nitrite and nitrate were estimated from the concentration of substance \( x \), \( c_x \) \([\text{mgN L}^{-1}]\) in the cell at a time \( t \) \([\text{s}]\) and the total ammonia concentration \( c_{\text{NH tot}} \) \([\text{mgN L}^{-1}]\) in the cell by:

\[
 Y_x = \frac{c_x(t) - c_x(0)}{c_{\text{NH tot}}(0) - c_{\text{NH tot}}(t)} \\
\text{(4.3)}
\]

The yield of the gaseous nitrogen species \( Y_{N,\text{gas}} \) was estimated from the following mass balance:

\[
 Y_{N,\text{gas}} = 100 - Y_{\text{NO}_2} - Y_{\text{NO}_3} \\
\text{(4.4)}
\]

Under the assumption that all ammonia not converted to nitrate or nitrite was oxidized to \( N_2 \), the total current efficiency \( CE, \text{ in } \% \) was estimated as:

\[
 CE_{\text{tot}}(t) = CE_{\text{NO}_3}(t) + CE_{\text{NO}_2}(t) + CE_{N_2}(t) \\
\text{(4.5)}
\]

where
Direct Ammonia Oxidation with Graphite Electrodes

\[ CE_x(t) = \frac{\Delta m_x(t) \cdot \nu_{e^{-},x} \cdot F}{M_N \cdot Q(t)} \quad (4.6) \]

and

\[ CE_{N_2}(t) = \frac{\left( \Delta m_{N\text{Htot}}(t) - \Delta m_{NO_3^{-}}(t) - \Delta m_{NO_2^{-}}(t) \right) \cdot \nu_{e^{-},N_2} \cdot F}{M_N \cdot Q(t)} \quad (4.7) \]

Here \( \Delta m_x(t) \) [gN] is the mass of substance \( x \) produced in the cell until a time \( t \), and \( \nu_{e^{-},x} \) [mole·molN\(^{-1}\)] is the number of electrons used per mole of ammonia oxidized to nitrate, nitrite or molecular nitrogen, respectively. \( F \) is the Faraday constant (96,485 C·mole\(^{-1}\)), \( M_N \) the molecular weight of nitrogen (14 gN·molN\(^{-1}\)) and \( Q(t) \) the transported charge.

The current efficiency for organic substance removal was estimated on the basis of COD measurements:

\[ CE_{COD}(t) = \frac{\Delta m_{COD}(t) \cdot F}{TOD_e^{-} \cdot Q(t)} \quad (4.8) \]

As with the nitrogen species, \( \Delta m_{COD}(t) \) [gO\(_2\)] is the mass of COD removed until a time \( t \). \( TOD_e^{-} \) is the theoretical oxygen demand of one mole of electrons (8 gO\(_2\) mol\(^{-1}\)).

The transported charge \( Q \) [C] was calculated from the current \( I \) [A] as:

\[ Q(t) = \int_0^t I(t) dt \quad (4.9) \]

The specific energy demand for ammonia removal \( E_{sp} \) [Wh·gN\(^{-1}\)] was calculated from the average electrical power \( \bar{U} \cdot \bar{I} \), which was calculated as the average of the product of the cell voltage \( U \) [V] times the current \( I \) [A] up to a time \( t \) as:

\[ E_{sp} = \frac{\bar{U} \cdot \bar{I} \cdot t}{\Delta m_{N\text{Htot}} \cdot 3600 \cdot \pi} \quad (4.10) \]

Results

Direct Ammonia Oxidation on Graphite Anodes

The voltammogram in the presence of ammonia at pH 9 showed a clear anodic peak (a1), which was not observed in the supporting electrolyte without ammonia (Figure 4.1). This peak can be attributed to direct ammonia oxidation starting at an onset potential of 1 V. When a potential of 1.8 V was reached, the voltammograms with and without ammonia overlapped again, indicating the end of ammonia oxidation. The backward scans in the experiments with an upper return potential \( (E_{up}) \) of 2.01 V showed the same cathodic peak (c1) between 1.7 and 1.4 V with and without ammonia. However, when \( E_{up} \) was decreased to 1.81 V, no cathodic peak was visible in the backward scan, although the anodic ammonia oxidation peak was present in the forward scan. The cathodic peak c1 was most likely caused by surface functional groups on the graphite (hydroxyl, carbonyl and carboxyl groups), which are formed in the forward scan (Rueffer et al., 2011) above a potential of 1.8 V. Figure 4.2 shows the peak current density of ammonia oxidation as a function of the bulk pH value in nine CV scans: the peak currents follow the mole fraction of NH\(_3\), which indicates that NH\(_3\) was the reacting compound.
Figure 4.1: 5th scan of cyclic voltammograms in the supporting electrolyte (support, Table 4.1), and the supporting electrolyte with ammonia (support + NH$_3$, Table 4.1) recorded on graphite. Scan rate: 200 mV·s$^{-1}$; pH = 9; $T = 25$ °C.

Figure 4.2: Peak current density of ammonia oxidation on graphite ($\Delta$) and the mole fraction of ammonia (solid line) as a function of pH in supporting electrolyte with ammonia (support + NH$_3$, Table 4.1). Scan rate: 200 mV·s$^{-1}$; $T = 25$ °C.
Ammonia Oxidation on Graphite in the Presence of Chloride

The CV results with respect to chloride oxidation in the absence of ammonia are presented in Figure 4.3A. Figure 4.3B shows how chloride and ammonia oxidation interact if both substances are present. The presence of chloride alone resulted in a strong increase of anodic currents above an $E_a$ of 1.6 V in the forward scans, which indicates that chloride oxidation started at this potential. In the backward scans, the cathodic peak c1 vanished. Instead, a cathodic peak (c2) occurred between 1.2 and 0.75 V. The height of this peak depended on $E_{up}$ and disappeared when $E_{up}$ was smaller than 1.6 V. These observations indicate that the presence of chloride resulted in oxidation products (most likely $\text{Cl}_2$, $\text{HOCl}$ or $\text{OCl}^-$), which were reduced during the backward scan.

When ammonia and chloride were present, the anodic ammonia oxidation peak a1 appeared exactly as in the case when no chloride was present. Once the onset potential for chloride oxidation (1.6 V) was exceeded, higher anodic currents were measured than in electrolytes that contained no chloride. The identical occurrence of the peak a1 indicates that direct ammonia oxidation took place without any interfering oxidation of chloride between 1 V and 1.6 V. Chloride oxidation most likely started above 1.6 V, resulting in increased anodic currents. In the backward scan, both cathodic peaks c1 and c2 appeared if the upper return potential was 2.01 V. However, they were smaller than the peaks in the experiments, when only ammonia or chloride was present in the electrolytes. The peak c1 most likely resulted from the reduction of the same functional groups on graphite as hypothesized for Figure 4.1. The peak c2 likely originated from products of chloride oxidation, as shown in Figure 4.3A. In contrast to the case when only chloride was present, c2 disappeared completely with an upper potential limit of 1.81 V. This indicates that no chloride oxidation products (Cl$_2$, HOCl or OCl$^-$) were produced at anode potentials below 1.81 V if ammonia was present.

![Figure 4.3: 5th scan of cyclic voltammograms in the supporting electrolyte (support, Table 4.1), A: Chloride containing electrolyte (support + Cl, Table 4.1) and B: Chloride and ammonia containing electrolyte (support + Cl + NH$_3$, Table 4.1) recorded on graphite. Scan rate 200 mV·s$^{-1}$, pH = 9, T = 25 °C.](image-url)
Bulk Electrolysis of Synthetic Stored Urine

To determine the influence of chloride on ammonia removal at anode potentials below the chloride oxidation potential, bulk electrolysis experiments were conducted at $E_a = 1.31$ V in synthetic urine solutions with and without chloride. Figure 4.4 shows that ammonia was removed steadily in both experiments. At the end of the experiment, $38 \pm 2\%$ of the initial ammonia was removed, of which $77 \pm 4\%$ was oxidized to gaseous nitrogen species (not measured), $21 \pm 2\%$ to nitrate and $2 \pm 2\%$ to nitrite (not shown). In a control experiment without applied voltage, the ammonia concentration remained constant for 45 hours, indicating that ammonia loss by volatilization was negligible.

Ammonia removal proceeded at rates of $7.1 \pm 0.5 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (without chloride) and $6.2 \pm 0.4 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (with chloride). A student t-test revealed that these two rates are not significantly different ($\alpha = 0.05$). Nitrate production rates reached values of $1.1 \pm 0.05 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (without chloride) and $1.2 \pm 0.06 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (with chloride). Free chlorine did not exceed $0.2 \text{ mgCl}_2 \cdot \text{L}^{-1}$ and total chlorine was not higher than $0.4 \text{ mgCl}_2 \cdot \text{L}^{-1}$ in both experiments, while the chloride concentration was constant in the experiment with chloride ($3340 \pm 40 \text{ mgCl L}^{-1}$).

The specific energy demand for ammonia removal was $37 \text{ Wh} \cdot \text{gN}^{-1}$ without chloride while $35 \text{ Wh} \cdot \text{gN}^{-1}$ were needed with chloride. The current efficiencies for nitrate production were $21\%$ (without chloride) and $27\%$ (with chloride), and total current efficiencies for ammonia removal were $48\%$ (without chloride) and $56\%$ (with chloride).

No exfoliated graphite was observed in either experiment. Visual inspection of the solution revealed negligible turbidity and no graphite particles. In the experiment with chloride, where stronger graphite exfoliation would be expected, the COD values did not increase ($860 \pm 16 \text{ mgO}_2 \cdot \text{L}^{-1}$).
Direct Ammonia Oxidation with Graphite Electrodes

Figure 4.4: Concentration profiles during potentiostatic electrolysis of synthetic stored urine at $E_a = 1.31$ V with graphite anodes. Without chloride: (♦) ammonia and (▲) nitrate. With chloride: (◇) ammonia and (Δ) nitrate. $T = 25$ °C.

**Bulk Electrolysis of Real Stored Urine**

Real stored urine was treated at the same anode potential of $E_a = 1.31$ V to validate the results obtained with synthetic urine solutions. Indeed, the ammonia concentration profile in Figure 5 shows that ammonia was removed steadily from real urine. The removal rate was $2.9 \pm 0.3 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. The nitrate concentration was below the detection limit and the nitrite concentration did not exceed $0.3 \text{ mgN} \cdot \text{L}^{-1}$ in any sample. The products of ammonia oxidation in real urine must have been mainly gaseous nitrogen species (not measured). Organic substances (Figure 4.5) were removed at a rate of $20.6 \pm 3.5 \text{ gCOD m}^{-2} \cdot \text{d}^{-1}$ during the first four days of electrolysis. It was also during this period of time that the pH and the current density decreased, whereas both variables were constant after day four until the end of the experiment (Figure 4.5).
Figure 4.5: Potentiostatic electrolysis of real stored urine at $E_a = 1.31$ V. A: Concentration profiles of total ammonia nitrogen (♦), total COD (■) and dissolved COD (●); B: pH and C: Current density. $T = 25^\circ C$.

The chloride concentration increased from 1200 to 1880 mgCl·L$^{-1}$, probably due to electrolyte leakage from the pH probe. Free and total chlorine measurements could not be interpreted unambiguously due to a strong matrix effect in real urine. (Figure B.4.2, supplementary information). The selected chlorinated organic compounds (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, chlorobenzene) as well as chlorate and perchlorate were below the detection limits in all samples. This strongly suggests that neither active chlorine nor chlorinated by-products were formed.

The specific energy demand in real urine was higher than in synthetic urine solutions, with 42 Wh·gN$^{-1}$ needed to remove the first 12% of ammonia nitrogen. The higher
energy demand resulted from a lower total current efficiency of 33% and a higher cell voltage due to the lower conductivity of real urine. The gravimetric corrosion assessment showed a weight loss of the anode of 2.8 mg·g\(^{-1}\) and a weight gain of the cathode of 1.5 mg·g\(^{-1}\) (Figure 4.6). No graphite particles were noticed in the solution, which indicates that graphite exfoliation did not take place.

![Graph showing mass change of anode and cathode](image)

**Figure 4.6**: The mass of anode and cathode before (black) and after (grey) electrolysis of real stored urine at \(E_a = 1.31\) V. Error bars denote the standard deviation of three independent measurements.

**Discussion**

**Activity and Selectivity of Graphite for Direct Ammonia Oxidation in Stored Urine**

The activity of graphite for direct ammonia oxidation is clearly demonstrated by our CV results in Figure 4.1. The onset potential of 1 V is in good agreement with the onset potential found by Candido and Ponciano Gomes (2011) in a linear potential sweep experiment at pH 9.4. In contrast to our measurements, Candido and Ponciano Gomes (2011) did not observe clear ammonia peaks in their CV. We assume this is due to the use of a low upper return potential (only 1.34 V) in their experiment. The data presented in Figure 2 further shows that the reactive compound for direct ammonia oxidation is NH\(_3\), as has been demonstrated for other electrode materials such as TDIROF, Ni/Ni(OH)\(_2\) and BDD (Kapałka et al., 2011; Kapalka et al., 2010a; Kapalka et al., 2010b).

The results from the potentiostatic bulk electrolysis experiments in synthetic and real stored urine show that ammonia can be oxidized continuously on the graphite surface via the direct oxidation pathway. A considerable amount of ammonia was oxidized to nitrate in synthetic urine but not in real urine. Unfortunately, very little is known about nitrate
formation during direct oxidation of ammonia and our data as well do not allow an in-depth discussion of the formation of nitrate which would make any interpretation of the data speculative. This phenomenon could be subject of a follow-up study.

In contrast to other electrode materials, the graphite anodes were not poisoned nor did competing carbonate oxidation suppress ammonia oxidation completely as observed with TDIROF (Amstutz et al., 2012). Synthetic urine in particular contained large amounts of inorganic carbon and the initial pH was high. Thus, carbonate was present but its oxidation was too slow, if it occurred at all, to interfere with the direct ammonia oxidation. Poisoning was frequently observed with other electrode materials such as noble or transition metals (de Vooy et al., 2001). On these electrodes, strongly adsorbed elementary nitrogen blocked the active sites if ammonia was completely dehydrogenated during anodic oxidation. This kind of surface poisoning does not seem to occur with graphite. Otherwise, the ammonia removal rate and the nitrate production rate in the bulk electrolysis experiments would have changed with time. Our CVs in the presence and absence of ammonia (Figure 4.1) support this conclusion because the current densities were the same as soon as the ammonia oxidation peak was passed during the forward scan. If nitrogen were to poison the graphite surface, the oxidation of adsorbed nitrogen in the forward scan and the reduction of the oxidized nitrogen in the backward scan would produce a modified current profile as observed with platinum (de Vooy et al., 2001).

The graphite anodes were not very selective for ammonia oxidation: with synthetic urine, the current efficiencies did not exceed 56% and in the experiment with real stored urine the current efficiency was as low as 33%, indicating important side reactions. The most probable of these are the oxidation of organic substances, the oxidation of the graphite itself and the evolution of oxygen through water splitting. In the bulk electrolysis of real urine, the strong removal of organic substances during the first four hours would have required a current efficiency of 104% if anodic oxidation alone were responsible. Thus, organics were not removed by anodic oxidation alone in that period. COD may also have been removed cathodically by adsorption, which would explain the weight gain of the cathode. Another possible process is biological COD removal, but in that case we would not expect the process to stop after four days.

The current efficiency for ammonia oxidation was 32% in the period from day four to fourteen. Accordingly, the oxidation of organic substances cannot be the sole process responsible for the low current efficiency. According to Rueffer et al. (2011), the oxidation of graphite itself (mineralization to CO$_2$) occurs together with the evolution of oxygen from water splitting above potentials of 0.94 V. This anode potential is exceeded in our experiments. The weight loss of the anode measured in the experiment with real stored urine would require a charge of 0.5 Ah if the oxidation of graphite to CO$_2$ was the responsible process. Since the total charge was 1.65 Ah, the mineralization of graphite could account for about one third of the anodic current. The competition of direct ammonia oxidation, CO$_2$ formation and oxygen evolution on carbon fibers was pointed out by Webster et al. (2012). The low current efficiency for ammonia oxidation therefore most probably resulted from a combination of organics oxidation, graphite mineralization and oxygen evolution.
Influence of Chloride on Direct Ammonia Oxidation in Stored Urine

Janssen and Hoogland (1970) established the following mechanism for chlorine evolution:

\[ \text{Cl}^- \rightarrow \text{Cl}_{ad} + e^- \]  \hspace{1cm} (4.11)

\[ \text{Cl}_{ad} + \text{Cl}^- \rightarrow \text{Cl}_2 + e^- \]  \hspace{1cm} (4.12)

However, chloride ions are well known for their adsorption property in the inner Helmholtz plane by contact adsorption before faradaic currents occur (Bockris and Reddy, 1974). It has to be assumed that chloride ions are also present in direct contact with the graphite surface at potentials below 1.6 V. Therefore, the presence of chloride could have affected the direct ammonia oxidation in two ways: (1) it could have led to indirect oxidation increasing the ammonia removal and nitrate production with a risk of chlorinated by-product formation, or (2) the adsorption of chloride ions could have blocked active sites for direct ammonia oxidation, leading to decreased ammonia removal and nitrate production. Our results show that neither of these two scenarios was the case at anode potentials below 1.6 V. Three observations lead to this conclusion and are explained in the following subsection.

Influence of Chloride below 1.6 V

(i) The CV in Figure 4.3A does not show additional faradaic currents due to chlorine evolution in the forward scans compared to the CV in the supporting electrolyte up to potentials of 1.6 V. The reactions according to equations (4.11) and (4.12) thus did not take place until 1.6 V was reached. This conclusion is also supported by the fact that no reduction peak c2 appeared when the upper return potential was 1.6 V. In contrast, higher upper return potentials showed additional faradaic currents in the forward scans once 1.6 V was passed due to reactions (4.11) and (4.12). As a consequence, the reduction peak c2 was observed due to the reduction of Cl_{ad} and Cl_2 (or HOCl, OCl^-) in the backward scan.

(ii) The forward scans in the electrolyte that contained ammonia and chloride (Figure 4.3B) were identical to those in the electrolyte that contained only ammonia (Figure 4.1) up to a potential of 1.6 V. Thus, ammonia was either oxidized at different active sites than those adsorbing chloride or the oxidation happened at adsorbed chloride ions or both, resulting in the same ammonia oxidation currents as on the bare graphite surface.

(iii) In the potentiostatic bulk electrolysis experiments with synthetic urine presented in Figure 4.4, ammonia removal and nitrate production were not influenced significantly by the presence of chloride. The very low amounts of free and total chlorine found in these experiments support this interpretation.

Influence of Chloride above 1.6 V

Above 1.6 V, our CVs clearly show interactions of chlorine evolution and ammonia oxidation. The missing reduction peak c2 with \( E_{up} = 1.81 \) V in Figure 4.3B may have resulted from two possible processes. If ammonia was oxidized at adsorbed chloride, the presence of ammonia could prevent the oxidation of the chloride by replenishing the chloride electrons while being oxidized at the same time. Another possible process could...
be that chloride was oxidized in the reactions (4.11) and (4.12) to active chlorine, which immediately reacted with ammonia. Both processes can explain why no reduction peak c2 was observed, namely because no Cl$_{ad}$ and Cl$_2$ (or HOCl or OCl$^-$) were present during the backward scan.

The occurrence of the reduction peaks c1 and c2 in the backward scan of Figure 4.3B with $E_{up} = 2.01$ V most likely resulted from the fact that ammonia was completely used up at a certain point of the forward scan. This resulted in the formation of surface functional groups (hydroxyl, carbonyl and carboxyl groups) as in the supporting electrolyte, and of Cl$_{ad}$ and Cl$_2$ in the forward scans. These products were reduced in the corresponding reduction peaks c1 and c2 in the subsequent backward scan. The fact that c1 was observed in Figure 4.3B but not in Figure 4.3A shows that the formation of surface functional groups was prevented if only chloride was present but not when ammonia was also available. This could be an indication of competitive adsorption of chloride and ammonia leading to surface functional groups at active sites initially occupied by ammonia, whereas the surface is not functionalized at chlorine adsorption sites. Such a mechanism requires strong adsorption of NH$_3$, which was reported by Pittman Jr et al. (1999) at lateral planes of carbon fibers.

**Direct Ammonia Oxidation as a Treatment Process for Stored Urine**

The direct ammonia oxidation process on graphite has the advantage that no chlorinated by-products can be formed. The CV in chloride containing electrolyte showed that direct ammonia oxidation is feasible in the potential window from 1 to 1.6 V with no concomitant chlorine evolution. This was confirmed in the bulk electrolysis experiments with synthetic and real stored urine. As a consequence, no chlorinated organics were measured and chlorate and perchlorate were not produced either. The corrosion, and especially the exfoliation, of the graphite anode was significantly reduced because the anode potential was low and because the formation of active chlorine was hindered.

Other important aspects used to determine the applicability of direct ammonia oxidation are the products of the oxidized ammonia, the ammonia removal rate and the energy demand. Possible reactions involved in ammonia removal are:

$$2NH_3 \rightleftharpoons N_2(g) + 6e^- + 6H^+ \quad E^0 = 0.092 \ V \quad (4.13)$$
$$2NH_3 + H_2O \rightleftharpoons N_2O(g) + 8e^- + 8H^+ \quad E^0 = 0.511 \ V \quad (4.14)$$
$$NH_3 + H_2O \rightleftharpoons NO(g) + 5e^- + 5H^+ \quad E^0 = 0.726 \ V \quad (4.15)$$
$$NH_3 + 2H_2O \rightleftharpoons NO_2^- + 6e^- + 7H^+ \quad E^0 = 0.801 \ V \quad (4.16)$$
$$NH_3 + 2H_2O \rightleftharpoons NO_2(g) + 7e^- + 7H^+ \quad E^0 = 0.466 \ V \quad (4.17)$$
$$NH_3 + 3H_2O \rightleftharpoons NO_3^- + 8e^- + 9H^+ \quad E^0 = 0.812 \ V \quad (4.18)$$

We observed that a considerable amount of ammonia was oxidized to volatile nitrogen compounds. In other studies (Webster et al., 2012; Michels et al., 2010), it was demonstrated that the main gaseous nitrogen product from direct ammonia oxidation on carbon electrodes is molecular nitrogen which appears plausible also from a thermodynamic point of view since reaction 4.13 has the lowest standard reduction potential. Thus, it is very likely that N$_2$ was the main gaseous nitrogen compound in our
experiments. However, it cannot be excluded that some N₂O, NO or NO₂ was formed, as was found at BDD (Michels et al., 2010). This point could be clarified with GC or GC/MS measurements in the gas phase.

Direct ammonia oxidation was slow (2.9 ± 0.3 gN·m⁻²·d⁻¹, real stored urine) compared to indirect oxidation at an elevated anode potential (126 ± 6.7 gN·m⁻²·d⁻¹, supplementary information), but was still slightly faster than in conventional surface-based biological systems (2.5 gN·m⁻²·d⁻¹; Tchobanoglous et al., 2003). Assuming a urine volume of 1.5 L·p⁻¹·d⁻¹ with an ammonia concentration of 8.1 gN·L⁻¹ (Udert et al., 2006), the necessary graphite surface area is 4.2 m²·p⁻¹ for complete direct ammonia oxidation at the observed rate in real urine. In conventional bipolar cells, surface-to-volume ratios of 100 m²·m⁻³ can be achieved (Hamann and Vielstich, 2007), resulting in a liquid reactor volume of 42 L·p⁻¹. Space requirements for the actual treatment facility would be higher. This footprint can be reduced by increasing the ammonia removal rate. We currently prepare a manuscript (Zöllig et al., 2015) in which we discuss in detail whether this could be achieved by optimizing the hydraulic conditions in the electrolysis cell.

We estimated an electricity demand of 42 Wh·gN⁻¹ with direct ammonia oxidation, which is about eleven times more than in conventional nitrification/pre-denitrification of domestic wastewater (3.9 Wh·gN⁻¹; Maurer et al., 2003). This high energy demand was due to the anodic and cathodic overpotentials as well as the ohmic resistance in the solution. A considerable part of the energy losses had to be attributed to the low CE. As discussed in a section above, organic oxidation and graphite mineralization to CO₂ were probably the responsible side reactions. Energy requirements can be minimized if a cathode material is chosen with a lower overpotential for hydrogen formation (e.g. stainless steel). The ohmic resistance can be diminished with a smaller electrode gap in an improved cell design.

**Conclusions**

We investigated whether direct ammonia oxidation on graphite electrodes is a technically feasible alternative to indirect oxidation with active chlorine to remove ammonia from source-separated urine. We found that this process is promising for the following reasons:

Direct ammonia oxidation on graphite works at comparatively low anode potentials (1 – 1.6 V vs. SHE). No chlorine evolution occurs in this potential range. As a consequence, no chlorinated by-products are formed as is the case with indirect oxidation. Furthermore, the specific energy demand for ammonia removal is reduced compared to indirect oxidation because lower cell voltages are required.

The low potentials reduce graphite corrosion, since the exfoliation of graphite particles is prevented. This makes it possible to use readily available and cheap graphite as an electrode material for the process, although it has to be regarded as a consumable due to the mineralization to CO₂. The graphite electrode is not deactivated by nitrogen poisoning as frequently observed with other electrodes. Instead we found that the graphite electrode is continuously active for direct ammonia oxidation, leading to surface-specific removal rates that are slightly higher than in conventional biological surface-based nitrogen removal systems.
The challenge in applying direct ammonia oxidation efficiently for the treatment of stored urine lies in the low removal rates and the still high specific energy demand. Further research should focus on the causes of these low removal rates and on reducing the energy demand. This should include the question of whether direct ammonia oxidation is limited by electron transfer kinetics or by diffusion.

Acknowledgements

We thank Karin Rottermann and Claudia Bänninger-Werffeli for the chemical analysis. We acknowledge the help provided by Jakov Bolotin and Thomas Hofstetter and their very useful inputs with the GC/MS analysis. We thank Christos Comninellis at the Swiss Federal Institute of Technology in Lausanne (EPFL) for inspiring discussions. Furthermore, we thank the Bill and Melinda Gates Foundation for financing this study as part of the VUNA project (www.vuna.ch).

References


Supplementary Information


A. Bulk Electrolysis of Synthetic Stored Urine ($E_a = 1.31$ V)

The recipes for the synthetic urine are given in Table A.4.1. Chloride was removed completely from one solution. To keep similar ionic strength the NaCl in the solution without chloride was replaced by adding more NaHCO$_3$ and less KHCO$_3$ compared to the solution containing chloride.

Table A.4.1: Recipes for the synthetic urine solutions. All quantities are given in [g·L$^{-1}$]. All chemicals were anhydrous.

<table>
<thead>
<tr>
<th></th>
<th>no chloride</th>
<th>with chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>2.27</td>
<td>2.27</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>2.96</td>
<td>2.96</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>20.8</td>
<td>17.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>-</td>
<td>5.49</td>
</tr>
<tr>
<td>KHCO$_3$</td>
<td>2.20</td>
<td>6.15</td>
</tr>
<tr>
<td>NH$_4$CH$_3$COO</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>NH$_4$OH</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.02</td>
<td>2.99</td>
</tr>
</tbody>
</table>

B. Bulk Electrolysis of Real Stored Urine at High Anode Potential ($E_a = 1.94$ V)

Urine electrolysis at a high anode potential was performed in the same system as described in section 2.2 of the paper with urine from the men’s urine collection tank at the main building at Eawag (Table B.4.1).

Table B.4.1: Composition of the urine used for the bulk electrolysis experiment with real stored urine ($E_a = 1.94$ V). Electric conductivity was temperature compensated for 25 °C. Standard deviations were less than 5 %.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>[-]</td>
<td>9.0</td>
</tr>
<tr>
<td>El. conductivity</td>
<td>[mS·cm$^{-1}$]</td>
<td>27.2</td>
</tr>
<tr>
<td>Total Ammonia</td>
<td>[mgN·L$^{-1}$]</td>
<td>2870</td>
</tr>
<tr>
<td>Nitrate</td>
<td>[mgN·L$^{-1}$]</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Nitrite</td>
<td>[mgN·L$^{-1}$]</td>
<td>0.24</td>
</tr>
<tr>
<td>Phosphate</td>
<td>[mgP·L$^{-1}$]</td>
<td>221</td>
</tr>
<tr>
<td>Sulfate</td>
<td>[mg·L$^{-1}$]</td>
<td>705</td>
</tr>
<tr>
<td>Chloride</td>
<td>[mg·L$^{-1}$]</td>
<td>3500</td>
</tr>
</tbody>
</table>
Similar to our results (Figure B.4.1) Zheng et al. (2009) observed constant ammonia depletion although in synthetic urine. However, the removal rate calculated from their data at 10 mA·cm$^{-2}$ results in 238 gN·m$^{-2}$·d$^{-1}$ which is about two times higher than 126 ± 6.7 gN·m$^{-2}$·d$^{-1}$ in our case (~12 mA·cm$^{-2}$). The same factor 2 in the removal rate between synthetic and real urine was observed at lower potentials (see sections 3.3 and 3.4 of the paper) and is a consequence of the more complex composition of real urine.

The initial ammonia was removed by 34 % and the products were 57 % gaseous nitrogen species (not measured), 40 % nitrate and 3 % nitrite. Under the given assumptions the CE for ammonia removal was 32 % and the specific energy demand was 87 Wh·gN$^{-1}$ at the end of the experiment. The energy needs are in the range reported by other groups: Zheng et al. (2009) for instance found a value of 80.2 Wh·gN$^{-1}$ using graphite anodes (synthetic urine, initial ammonia: 6 gN·L$^{-1}$).

Visual inspection of the solution at the end of the experiment showed high turbidity and graphite flocks in the treated solution. Furthermore, corrosion was evident from a visual inspection of the anode surface. Rueffer et al. (2011) reported that a TOC increase in the solution due to graphite exfoliation starting at 1.3 V. This value is clearly lower than the potential applied in this experiment explaining our observation of strong electrode corrosion.

The high anode potential ($E_a$ = 1.94 V) was substantially higher than the onset potential for chloride oxidation (Figure 4.3), therefore chlorine formation was likely. One indication for chlorine formation is the drop of the chloride concentration from 3.5 g·L$^{-1}$ to 3.1 g·L$^{-1}$. Furthermore, the chlorination by-product chlorobenzene was only formed at high anode potentials (values up to 0.17 mg L$^{-1}$).
Unfortunately, direct chlorine measurements in real urine were not sufficiently reliable to compare chlorine formation at low ($E_a = 1.31 \text{ V}$) and high ($E_a = 1.94 \text{ V}$) anode potentials. Chlorine measurements in untreated urine resulted in substantial values, which must be due to interferences with the urine matrix (Figure B.4.2A). Attempts to eliminate the matrix effect were unsuccessful.

Figure B.4.2: A: The matrix effect of urine (women (triangles), men (circles), collected on 8.7.2014) onto the measurement of free (open symbols) and total chlorine (closed symbols). The chloride concentration is given as an indicator of the concentration of urine. B: Free (open) and total (closed) chlorine during electrolysis of women’s urine at $E_a = 1.31 \text{ V}$. C: Free (open) and total (closed) chlorine during electrolysis of men’s urine at $E_a = 1.94 \text{ V}$.

References


Inhibition of Direct Electrolytic Ammonia Oxidation Due to a Change in Local pH

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Graphical Abstract

Cyclic Voltammogram

1st scan: pH = 9.25
5th scan: pH = 9.09

Electrode potential / V (vs. MSE)

Current density / mA cm$^{-2}$

Anode

NH$_4^+$

NH$_3$ + H$^+$

0.5 N$_2$ + 3 H$^+$

NO$_3^-$ + 9 H$^+$

pH 9.25

Nernstian diffusion layer

9.09
Abstract
Electrochemical ammonia oxidation has gained a lot of attention recently as an efficient method for ammonia removal from wastewater, for the use in ammonia-based fuel cells and the production of high purity hydrogen. Thermally decomposed iridium oxide films (TDIROF) have been shown to be catalytically active for direct ammonia oxidation in aqueous solutions if NH$_3$ is present. However, the process was reported to be rapidly inhibited on TDIROF. Herein, we show that this fast inhibition of direct ammonia oxidation does not result from surface poisoning by adsorbed elemental nitrogen (N$_{ads}$). Instead, we propose that direct ammonia oxidation and oxygen evolution can lead to a drop of the local pH at the electrode resulting in a low availability of the actual reactant, NH$_3$. The hypothesis was tested with cyclic voltammetry (CV) experiments on stagnant and rotating disk electrodes (RDE). The CV experiments on the stagnant electrode revealed that the decrease of the ammonia oxidation peaks was considerably reduced by introducing an idle phase at open circuit potential between subsequent scans. Furthermore, the polarization of the TDIROF electrode into the hydrogen evolution region (HER) resulted in increased ammonia oxidation peaks in the following anodic scans which can be explained with an increased local pH after the consumption of protons in the HER. On the RDE, the ammonia oxidation peaks did not decrease in immediately consecutive scans. These findings would not be expected if surface poisoning was responsible for the fast inhibition but they are in good agreement with the proposed mechanism of pH induced limitation by the reactant, NH$_3$. The plausibility of the mechanism was also supported by our numerical simulations of the processes in the Nernstian diffusion layer. The knowledge about this inhibition mechanism of direct ammonia oxidation is especially important for the design of electrochemical cells for wastewater treatment. The mechanism is not only valid for TDIROF but also for other electrodes because it is independent of the electrode material.

Keywords
Iridium dioxide, low alkalinity, water treatment, Nernstian diffusion layer, acid-base equilibrium

Introduction
Direct ammonia oxidation at catalytically active surfaces can be used for the electrolytic removal of ammonia from wastewater (Bunce and Bejan, 2011; Muthuvel and Botte, 2009). Additionally, the process was suggested for the use in fuel cells where ammonia acts as a substitute for hydrogen (Lan and Tao, 2010) and for the production of high purity hydrogen in ammonia electrolyzers (Vitse et al., 2005). In contrast to indirect oxidation with active chlorine species, which is mostly employed for wastewater treatment, direct ammonia oxidation does not produce chlorinated by-products such as chlorate, perchlorate or organic chlorinated substances. Furthermore, direct oxidation usually proceeds at lower anode potentials than chlorine formation. Consequently, a high current efficiency and a lower specific energy demand can be achieved making direct ammonia oxidation attractive for wastewater treatment. Direct ammonia oxidation was shown to be technically feasible on isostatically pressed fine grain graphite without concomitant chlorine formation (Zöllig et al., 2015).
However, the ammonia removal rate was low in real stored urine (2.9 ± 0.3 gN·m⁻²·d⁻¹) and mineralization of the graphite electrode occurred as a side reaction. Although the mineralization was slow, the graphite electrode has to be considered a consumable. Corrosion problems were also reported with Ni/Ni(OH)₂ anodes (Kapałka et al., 2010a). In order to reduce maintenance and material consumption, it would be desirable to find more stable electrode materials that are suitable for direct ammonia oxidation.

The catalytic activity for direct ammonia oxidation was demonstrated for thermally decomposed iridium oxide films (TDIROF, Kapalka et al., 2011) or boron-doped diamond electrodes (BDD, Kapalka et al., 2010b). Both electrodes are stable when they are used as anodes. TDIROF electrodes further have the advantage that they are easy to fabricate and that they have a comparatively low overpotential for direct ammonia oxidation (Table 5.1). The low overpotential eventually leads to a high selectivity towards direct ammonia oxidation and to low specific energy requirements. However, the costs for the precious metal iridium are a drawback of this electrode.

Table 5.1: Comparison of onset potentials and peak potentials for direct ammonia oxidation on thermally decomposed iridium oxide films (TDIROF), isostatically pressed fine grain graphite and boron-doped diamond (BDD) at pH = 9.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>On-set potential [V vs. SHE]</th>
<th>Peak potential [V vs. SHE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDIROF (Kapałka et al., 2011)</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Graphite (Zöllig et al., 2015)</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Ni/Ni(OH)₂ (Kapałka et al., 2010a)</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>BDD (Kapałka et al., 2010b)</td>
<td>1.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Kapałka et al. (2011) found that ammonia oxidation peaks of consecutive cyclic voltammograms decreased dramatically on TDIROF if the lower return potential was above the hydrogen evolution region (HER). The authors interpreted these results as an electrode deactivation through surface poisoning by adsorbed intermediate nitrogen species (NH₃,ads, NH₂,ads, N₂,ads) formed during the direct ammonia oxidation process initially proposed by Gerischer and Mauerer (1970) for platinum (Pt, eqs. (5.1)-(5.5)).

\[
\begin{align*}
NH_3(aq) & \rightleftharpoons NH_3,ads \quad (5.1) \\
NH_3,ads & \rightleftharpoons NH_2,ads + H^+ + e^- \quad (5.2) \\
NH_2,ads & \rightleftharpoons NH_{ads} + H^+ + e^- \quad (5.3) \\
NH_{x,ads} + NH_{y,ads} & \rightleftharpoons N_2 + (x + y)H^+ + (x + y)e^- \quad (5.4) \\
NH_{ads} & \rightleftharpoons N_{ads} + H^+ + e^- \quad (5.5)
\end{align*}
\]

where x, y = 1 or 2.

This interpretation is often used to explain the decreasing activity of electrodes during direct ammonia oxidation in aqueous media (Zhong et al., 2013). It is mainly based on the findings of de Vooys et al. (2001) who identified N₂,ads as an electrode poison on
transition metal electrodes (such as Ru, Rh, Pd) and who generalized the mechanism of direct ammonia oxidation (Eqs. (5.1)-(5.5)) to transition metal electrodes.

However, deactivation of the electrode by surface poisoning might not be the only process leading to lower ammonia oxidation peaks in cyclic voltammetry (CV). In fact, it has been demonstrated for TDIROF (Kapalka et al., 2011) and other electrode materials (Kapalka et al., 2010a; Kapalka et al., 2010b; Zöllig et al., 2015) that direct ammonia oxidation is highly pH sensitive because the actual reactant is NH$_3$ while NH$_4^+$ cannot be oxidized directly. Apparently, direct ammonia oxidation itself (Eqs. (5.2)-(5.4)), but also many other anodic processes such as oxygen evolution (Eq. (5.6)), release a large number of protons.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{5.6}$$

This can lead to a strong pH drop in the Nernstian diffusion layer if the electrolyte is not buffered. The consequence is a shift in the local ammonia speciation according to the acid-base equilibrium, resulting in a low availability of reactive NH$_3$.

The hypothesis of this study is that decreasing ammonia oxidation peaks on TDIROF in subsequent scans could be due to a drop of the local pH in the Nernstian diffusion layer caused by acidic anodic reactions. To test this hypothesis, we evaluated the ammonia oxidation peaks of CV experiments with varying lower return potentials in stagnant electrolytes. Furthermore, we employed a rotating disc electrode (RDE) to control the thickness of the Nernstian diffusion layer under well-defined hydraulic conditions. These experiments were complemented with numerical simulations of the ammonia concentration profiles in the Nernstian diffusion layer to show that the proposed mechanism is plausible.

**Experimental**

The TDIROF electrodes were prepared by thermal decomposition of a precursor solution ($0.25$ mol·L$^{-1}$ H$_3$IrCl$_6$ (99.9%, ABCR GmbH & Co, Karlsruhe, Germany) in i-propanol (99.8%, Merck KGaA, Darmstadt, Germany)) on a titanium substrate (grade 2, BIBUS METALS AG, Fehraltorf, Switzerland) as previously reported (Kapalka et al., 2011). The titanium was sandblasted, treated in 1 mol·L$^{-1}$ oxalic acid (99.5%, Fluka Chemie GmbH, Buchs, Switzerland) at 95 °C for one hour, rinsed with nanopure water and dried in an oven at 105 °C for 5 minutes. Several layers were deposited to reach the final loading. Each IrO$_2$ layer was applied by pipetting the precursor solution onto one side of the substrate and distributing it evenly with a brush. The i-propanol was evaporated in an oven at 105 °C for 10 minutes followed by a tempering of the electrodes at 500 °C for 10 minutes. A pair of rectangular electrodes (5 cm · 4 cm) was loaded with $0.63 \pm 0.00$ mg·cm$^{-2}$ and three RDEs (diameter 15 mm) with $0.81 \pm 0.14$ mg·cm$^{-2}$. As a final step, the TDIROF was annealed at 500 °C for 1 hour. The electrodes were characterized using a scanning electron microscope (SEM, Nova NanoSEM 230, FEI, Hillsboro, USA). Elemental analysis was performed with an energy dispersive X-ray (EDX) system (INCA 4.15, X MAX 80, Oxford, UK) attached to the microscope. Results are provided in the supplementary information in section A.

The CV experiments in stagnant electrolyte were performed in a one-compartment cell (50 mL) with a three electrode setup. The rectangular TDIROF working electrode was
pressed against a hole in the bottom of the cell exposing a geometric surface area of 0.5 cm$^2$ to the electrolyte. The sealing between the electrode and the cell was made out of a silicon O-ring. The reference electrode (Hg/Hg$_2$SO$_4$/K$_2$SO$_4$ (MSE), Ref 601, Radiometer Analytical, Villeurbanne, France) was contained in a Luggin capillary filled with saturated K$_2$SO$_4$ (99%, Fluka). The tip of the Luggin capillary was placed 2 mm above the working electrode. A Pt-wire (geometric surface area: 1.26 cm$^2$) was used as the counter electrode. A potentiostat (PGU 10V-1A-IMP-S, Ingenieurbüro Peter Schrems, Münster, Germany) controlled the working electrode potential. The working electrode potential and the current density were recorded with the EcmWin software (EcmWin V2.4, Ingenieurbüro Peter Schrems). The temperature and pH were measured continuously (SenTix 41 connected to pH 196, WTW, Weilheim, Germany) but no temperature control was installed.

The same potentiostat and pH meter were used in the CV experiments on a RDE but another one-compartment cell (200 mL) with three electrodes was used. The TDIROF-RDE was sealed in a Teflon cylinder exposing a geometric surface area of 0.95 cm$^2$. The cylinder was plugged on the rotator (Jaissle Rotator, Jaissle Elektronik, Waiblingen, Germany) and inserted into the electrolyte from the top. The reference electrode (MSE, HgE 11, Sensortechnik Meinsberg, Waldheim, Germany) was contained in a Luggin capillary filled with saturated K$_2$SO$_4$ (99%, Fluka). The angled tip of the capillary was placed 3 mm from the RDE. A Pt-foil (geometric surface area: 10.62 cm$^2$) was utilized as the counter electrode. The electrolyte temperature was controlled at 25 ± 0.1 °C with a thermostat (Colora Messtechnik GmbH, Lorch, Germany). All experiments were performed in 0.5 mol·L$^{-1}$ Na$_2$SO$_4$ (99%, Merck) + 0.125 mol·L$^{-1}$ (NH$_4$)$_2$SO$_4$ (99.5%, Merck) dissolved in nanopure water. The pH value was adjusted by dosing NaOH (99%, Merck).

Calculations

We developed a dynamic numerical 1D-model to simulate pH, NH$_3$ and NH$_4^+$ concentrations in the Nernstian diffusion layer of the working electrode. The Nernstian diffusion layer was divided into segments of uniform thickness in which the concentrations were assumed to be homogeneous. The heterogeneous electrochemical reactions of direct ammonia oxidation and oxygen evolution were assumed to affect only the lowest of these segments which we will call the reaction zone. Oxygen evolution was taken into account according to Eq. (5.6) and direct ammonia oxidation was assumed to lead exclusively to molecular nitrogen for reasons of simplicity:

$$\text{NH}_3 \rightarrow 0.5\text{N}_2 + 3\text{H}^+ + 3e^-$$  \hspace{1cm} (5.7)

The surface specific reaction rate $r_x$ (mmol·cm$^{-2}$·s$^{-1}$) of the compound $x$ was estimated based on the measured current density $j$ (mA·cm$^{-2}$) according to Faraday’s law:

$$r_{NH_3} = \frac{-j_{NH_3}}{F \cdot n_{NH_3}}$$  \hspace{1cm} (5.8)

$$r_{O_2} = \frac{j_{O_2}}{F \cdot n_{O_2}}$$  \hspace{1cm} (5.9)

$$r_{H^+} = n_{O_2} \cdot r_{O_2} - n_{NH_3} \cdot r_{NH_3}$$  \hspace{1cm} (5.10)
where $F = 96485 \text{ C} \cdot \text{mol}^{-1}$ is the Faraday constant, $n_{O_2} = 4 (-)$ and $n_{NH_3} = 3 (-)$ are the number of electrons transferred according to Eq. (5.6) and (5.7).

The current density was allocated to the two electrochemical processes as follows:

$$j_{NH_3} = j_{NH} - j_b \text{ if: } 0.3 \text{ V} < E_w < 0.68 \text{ V and } j_{NH_3} > 0 \text{ mA} \cdot \text{cm}^{-2} \quad (5.11)$$

$$j_{O_2} = j_{NH} - j_b \text{ if: } 0.68 \text{ V} < E_w \text{ and } j_{O_2} > 0 \text{ mA} \cdot \text{cm}^{-2} \quad (5.12)$$

The subscript $NH$ denotes the current density measured during CV in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4 + 0.125 \text{ mol} \cdot \text{L}^{-1} (\text{NH}_4)\text{SO}_4 + \text{NaOH}$ and $b$ denotes the background current density measured in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4 + \text{NaOH}$. The $j_b$ was subtracted to account for non-faradaic currents. $E_w$ (V) is the potential of the working electrode.

The acid-base equilibrium of ammonia was modeled according to the mass action law in all segments individually and was assumed to be in equilibrium instantaneously. The conditional equilibrium constant ($K_c$) was calculated from $K = 10^{-pK_a}$ (pK$_a$ = 9.25 Haynes, 2012) with the activity coefficients of NH$_3$ ($\gamma_{NH_3} = 1$) and NH$_4^+$ ($\gamma_{NH_4} = 0.42$) accounting for the ionic strength $I_c = 1.88 \text{ mol} \cdot \text{L}^{-1}$ in the supporting electrolyte. The activity coefficients were estimated in the chemical speciation software PHREEQC (Parkhurst and Appelo, 1999) using the Pitzer approach with a database extended by Pitzer parameters for ammonium (Kapałka et al., 2010a). The pK$_c$-value was found to be 9.62. The concentration of $x$ was denoted with $c_x$ in mol·L$^{-1}$.

$$K_c = K \cdot \frac{\gamma_{NH_4}}{\gamma_{NH_3}} = \frac{c_{NH_3}c_{H^+}}{c_{NH_4^+}} \quad (5.13)$$

The mass flux $J_{x,i,i+1}$ (mmol·cm$^{-2}$·s$^{-1}$) of species $x$ from segment $i$ to segment $i+1$ was modeled with Fick’s first law of diffusion (Eq. (5.14)). The mass flux by migration was neglected because of the high conductivity of the used electrolytes (Hamann and Vielstich, 2007).

$$J_{x,i,i+1} = -D_x \frac{(c_x,i-c_x,i+1)}{\Delta y} \quad (5.14)$$

The values of the implemented diffusion coefficients were $D_{NH_3} = 1.5 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $D_{NH_4^+} = 1.957 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $D_{H^+} = 9.311 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (Haynes, 2012) and $\Delta y$ (cm) was the thickness of one segment in perpendicular direction to the electrode surface.

When an RDE was used, the thickness of the Nernstian diffusion layer $\delta_N$ (cm) was defined by the hydraulic conditions and could be calculated with Eq. (5.15) (Bard and Faulkner, 2001) depending on the angular velocity $\omega$ (s$^{-1}$), the kinematic viscosity of water $\nu = 8.93 \cdot 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$ and the diffusion coefficient of ammonia.

$$\delta_N = 1.6 \cdot \omega^{-1/2} \cdot \nu^{1/6} \cdot D_{NH_3}^{1/3} \quad (5.15)$$

This numerical model was implemented in Berkeley Madonna (Berkeley Madonna Inc., Berkeley, USA, Version 8.3.18).
Results

CV Experiments in Stagnant and Agitated Electrolytes

The cyclic voltammograms in Figure 5.1 show a strong inhibition of direct ammonia oxidation on our TDIROF electrodes in immediately consecutive scans confirming the findings of Kapałka et al. (2011). The ammonia oxidation peak in the forward scans (a1) as well as the ammonia oxidation peak in the backward scans (a2) decreased continuously from the first to the fifth scan. The peak a1 decreased in five scans by 32%. It is important to note that the scans were performed without interruption; the lag phase was 19 seconds between two consecutive ammonia oxidation peaks. Thus, the time for diffusion to equilibrate the reactant and pH gradients in the Nernstian diffusion layer was limited.

In compliance with the interpretation of Kapałka et al. (2011), the peak a2 appears because ammonia is not oxidized in the OER. It was hypothesized that NH$_3$ oxidation requires the redox couple IrO(OH)$_2$/IrO$_2$(OH) present at anode potentials of about 0.3 to 0.7 V vs. MSE. Above potentials of 0.7 V vs. MSE, the iridium is completely oxidized to IrO$_3$ which excludes the oxidation of ammonia in the OER. However, the oxidation to IrO$_3$ is reversible and therefore ammonia oxidation restarts in the backward scan.

The lower return potential was clearly above the HER in which protons would be consumed according to Eq. (5.16).

\[ 2H^+ + 2e^- \rightarrow H_2 \]  

(5.16)

As the HER was not reached, the protons released during the anodic reactions of ammonia oxidation (Eq. (5.2)–(5.4)) or oxygen evolution (Eq. (5.6)) were not consumed by hydrogen evolution during the cathodic polarization of the electrode. This means that the reduction of the peaks a1 and a2 could very well result from a reactant limitation due to a drop in local pH.
Inhibition of Direct Electrolytic Ammonia Oxidation

Figure 5.1: Five consecutive scans on a TDIROF electrode in 0.5 mol·L\(^{-1}\) Na\(_2\)SO\(_4\) + 0.125 mol·L\(^{-1}\) (NH\(_4\))\(_2\)SO\(_4\) + NaOH at pH = 9.25. Scan rate 200 mV·s\(^{-1}\), upper return potential: 0.8 V vs. MSE, lower return potential: -1.1 V vs. MSE, \(T = 25.2\, ^\circ\text{C}\), counter electrode: Pt-wire. The circles (○) at 0.3 and -0.5 V vs. MSE mark the points at which the concentration profiles in Figure 5.5 and Figure 5.7 were calculated.

Figure 5.2A shows five immediately consecutive CV scans in which the TDIROF electrode was polarized moderately into the HER (lower return potential -1.5 V vs. MSE). The ammonia oxidation peaks \(a_1\) and \(a_2\) were nearly identical, just the first scan showed slightly smaller peaks. An even more pronounced difference between the first and the consecutive scans can be seen in Figure 5.2B presenting the data of an experiment where the electrode was strongly polarized into the HER (lower return potential -1.7 V vs. MSE). In this case, the ammonia oxidation peaks of the scans two to five (again all nearly identical) were clearly higher than in the first scan.

In contrast to the experiment where the HER was not reached (Figure 5.1), the polarization of the working electrode into the HER resulted in the consumption of protons according to Eq. (5.16). The longer the electrode was polarized into the HER, the higher were the ammonia oxidation peaks \(a_1\) and \(a_2\) in the following anodic polarizations. This very likely resulted from a higher NH\(_3\) concentration in the reaction zone after strong hydrogen evolution.
Figure 5.2: A: Five consecutive scans on TDIROF in 0.5 mol·L⁻¹ Na₂SO₄ + 0.125 mol·L⁻¹ (NH₄)₂SO₄ + NaOH with a lower return potential of -1.5 V vs. MSE. B: The same as in A but with a lower return potential of -1.7 V vs. MSE. The red solid line marks the 5th scan. Scan rate 200 mV·s⁻¹, upper return potential: 0.8 V vs. MSE, pH = 9.25, T = 25.3 °C, counter electrode: Pt-wire.

Compared to the experiment with immediate consecutive scans (Figure 5.1), a considerably lower reduction of a1 and a2 was observed if an idle period of 4 minutes was inserted between individual scans, even if the lower return potential was kept above the HER (Figure 5.3). The peak a1 decreased by no more than 11% from the first to the ninth scan which is clearly less than with immediately consecutive scans. This finding corroborates our hypothesis of an effect in the diffusion layer. Due to the diffusion of protons, ammonia and ammonium, similar NH₃ concentrations must have been reached in the reaction zone prior to each anodic polarization which resulted in comparable ammonia oxidation peaks.

If the much lower decrease of a1 and a2 would have resulted from the reduction of poisonous N_ads, a reduction peak would have been expected in the backward scans. However, this was neither the case with or without idle periods between the scans (Figure 5.1 and Figure 5.3, respectively). Also the reduction of N_ads during the idle phase was very unlikely because the OCP was almost constant between the scans (mean OCP value of all idle periods -0.413 ± 0.003 V vs. MSE) and certainly did not reach values below the lower return potential (supplementary information B).
Figure 5.3: Three CV scans on TDIROF in 0.5 mol·L⁻¹ Na₂SO₄ + 0.125 mol·L⁻¹ (NH₄)₂SO₄ + NaOH at pH = 9.25. An idle period of 4 minutes was introduced between each scan during which the electrolyte was stirred. The points (4) at -0.4 V and (5) at 0.3 V vs. MSE at which the concentration profiles in Figure 5.5 were calculated are indicated with the circles (○). Scan rate 200 mV·s⁻¹, upper return potential: 0.8 V vs. MSE, lower return potential: -0.9 V vs. MSE, T = 23.4 °C, counter electrode: Pt-wire.

In Figure 5.4 we present five immediately consecutive cyclic voltammograms recorded on an RDE at an angular velocity of 91 rpm. In contrast to the scans in stagnant electrolyte without idle phase, the scans following the first scan on the RDE did not result in a strong decrease of the direct ammonia oxidation peaks a₁ or a₂. In fact, the peak a₁ only decreased by 5% from the first to the second scan. In the following scans, the decrease of peak a₁ was small (around 0.6% in each scan) resulting in a total peak decrease from the first to the fifth scan of 7%.

Also in this experiment, the lower return potential (-0.9 V vs. MSE) was chosen clearly above the HER and even 0.2 V higher than in the experiment in stagnant electrolyte (Figure 5.1). The time in which concentration gradients could even out was short (17 s) and the protons released during direct ammonia oxidation (Eq. (5.1)-(5.4)) and oxygen evolution (Eq. (5.6)) could not be consumed by hydrogen evolution. However, by making use of an RDE we were able to control the hydraulics at the working electrode and therewith to reduce δₙ. The consequences of this can be shown with our model calculations and are presented in the next section.
Figure 5.4: Five consecutive scans on a rotating TDIROF electrode in 0.5 mol·L\(^{-1}\) Na\(_2\)SO\(_4\) + 0.125 mol·L\(^{-1}\) (NH\(_4\))\(_2\)SO\(_4\) + NaOH at pH = 9.25. The circles (○) at 0.3 and -0.5 V vs. MSE mark the points at which the concentration profiles in Figure 5.7 were calculated. Scan rate 200 mV·s\(^{-1}\), upper return potential: 0.8 V vs. MSE, lower return potential: -0.9 V vs. MSE, \(T = 25.0\) °C, counter electrode: Pt-foil.

**Concentration Profiles in the Nernstian Diffusion Layer during CV**

The electrochemical measurements all supported our hypothesis but they did not show how the diffusion in the electrolyte proceeded and whether the proposed mechanism would be plausible on the observed special and temporal scale. To get more information about the concentration profiles in the diffusion layer we used the dynamic computer model. The initial conditions of the three state variables were chosen as \(c_{NH_3} = 0.07476\) and \(c_{NH_4^+} = 0.1752\) molN·L\(^{-1}\) and pH = 9.25 in all simulations.

In Figure 5.5, simulated concentration profiles are given for the characteristic points of the voltammogram in Figure 5.1. The concentration profiles show that the time between ammonia oxidation peaks in immediately subsequent scans was too short for the pH gradient to equalize (Figure 5.5A). Consequently, the regions in the vicinity of the electrode became more and more acidic with every scan. Due to the acid-base equilibrium, the change in pH resulted in a strong shift of ammonia speciation. Namely, the NH\(_3\) concentration dropped considerably (Figure 5.5B). Thus, the concentration of the reactant (NH\(_3\)) became lower during every anodic scan resulting in smaller direct ammonia oxidation peaks.
Inhibition of Direct Electrolytic Ammonia Oxidation

Figure 5.5: A: Calculated pH profiles in the vicinity of the electrode. B: NH$_3$ concentration profiles in the vicinity of the electrode. The profiles correspond to point (4) just before the ammonia oxidation peaks a1 appeared in the experiment presented in Figure 5.1 (immediately consecutive scans, bulk pH = 9.25).

Figure 5.6A and B display simulated concentration profiles at the points marked in Figure 5.3 during the experiment where an idle phase of 4 minutes was inserted between the scans. The profiles at the beginning of the first idle phase were calculated at the same point in time since the start of the experiment as the profiles calculated before the second scan in the experiment without an idle phase. These concentration profiles form Figure 5.5 and Figure 5.6 are directly comparable. The profiles in Figure 5.6A and B were less pronounced because the anodic currents in the foregoing scan were smaller. After the first idle phase, just before the second anodic polarization started (point (5) in Figure 5.3), there still was a small shift of ammonia speciation in the reaction zone (Figure 5.6B). This explains the small reduction of the ammonia oxidation peaks in the following scan and in all additional cycles until the ninth scan. The idle time between the scans allowed concentrations to equalize almost completely before a new anodic polarization so that comparable ammonia oxidation peaks were measured.
In stagnant electrolyte, the Nernstian diffusion layer has no limit and could theoretically expand deep into the bulk liquid. From the concentration profiles in Figure 5.5A it can be deduced that the maximal $\delta_N$ was close to 1.5 mm during the experiment presented in Figure 5.1. On the RDE, $\delta_N$ was hydraulically controlled and much thinner. With Eq. (5.15) it was calculated to be $\delta_N = 0.15$ mm for the applied rotational speed of 91 rpm. The consequences were the buildup of distinctly different concentration profiles of $\text{H}^+$, $\text{NH}_4^+$ and $\text{NH}_3$ compared to the stagnant electrolyte leading to a considerably different diffusion behavior.

A comparison of four concentration profiles between the first anodic polarization and the second anodic polarization in stagnant electrolyte (A, B, and C) and in agitated electrolyte (D, E, and F) is shown in Figure 5.7. In the stagnant electrolyte and on the RDE, a speciation shift due to a change in local pH appeared. However, when $\delta_N$ was hydraulically controlled on the RDE the concentration gradients evened out much faster. The reason for this was the more pronounced concentration gradients due to a thinner and limited Nernstian diffusion layer. The result was faster diffusion allowing concentrations to draw level quickly. Consequently, the concentration of $\text{NH}_3$ in the reaction zone at point 4 prior to the second anodic polarization was much closer to the one found prior to the first scan (compare the profiles 4 at distance 0 from the electrode in Figure 5.7B and E). This is remarkable and demonstrates the importance of $\delta_N$. It should be noted that the time until point 4 was reached in the CV on the RDE was shorter, because the lower return potential was higher than in the experiments with stagnant electrolyte (Figure 5.1).
Inhibition of Direct Electrolytic Ammonia Oxidation

Discussion

Mechanisms Inhibiting Direct Ammonia Oxidation

Gerischer and Mauerer (1970) distinguished between a fast and a slow passivation of direct ammonia oxidation on Pt. They found that the fast passivation was reversible by simply letting the working electrode rest at OCP. On the other hand, the slow passivation was found to be irreversible and was attributed to surface poisoning by N_{ads}. This also meant that the fast passivation could not result from surface poisoning by N_{ads} because the fast passivation was reversible.

Analogous to the platinum case, we argue that the fast inhibition of direct ammonia oxidation on TDIROF, as observed by Kapalka et al. (2011) and in our experiments (Figure 5.1), cannot result from surface poisoning by N_{ads}. The experiment presented in Figure 5.2 showed that it was enough to let the TDIROF electrode rest at OCP during an idle phase of 4 minutes to restore the catalytic activity of the electrode. Thus, the fast inhibition on TDIROF was reversible. Gerischer and Mauerer (1970) showed that N_{ads}...
can only be removed from Pt at high temperatures due to the high binding energy of $N_{ads}$. De Vooys et al. (2001) estimated the binding energy of $N_{ads}$ on Pt to be 394 kJ·mol$^{-1}$ and Wang et al. (2010) calculated a value of 373 kJ·mol$^{-1}$ on oxygen rich IrO$_2$. These binding energies are in the same order of magnitude. Therefore, the passivation of IrO$_2$ by $N_{ads}$ should be irreversible too but it was not. Furthermore, if surface poisoning by $N_{ads}$ would be the relevant mechanism, decreasing ammonia oxidation peaks would also be expected to appear on the RDE (Figure 5.4) but they did not. For these reasons, the fast inhibition of direct ammonia oxidation cannot result from surface poisoning by $N_{ads}$. However, our results do not reveal whether surface poisoning by $N_{ads}$ could appear during long term anodic polarization.

The formation of surface oxides can also be ruled out as the reason for the fast inhibition of direct ammonia oxidation in subsequent CV scans. In the study by Kapałka et al. (2011) it was argued that direct ammonia oxidation involves the surface redox couple IrO(OH)$_2$/IrO$_2$(OH). The complete oxidation of IrO$_2$(OH) to IrO$_3$ in the OER was therefore assumed to stop direct ammonia oxidation. However, the appearance of the peak a2, again resulting from ammonia oxidation on IrO(OH)$_2$/IrO$_2$(OH), indicated that IrO$_3$ was reduced at electrode potentials higher than 0.6 V vs. MSE. Thus, the passivation by IrO$_3$ was cleared away in the backward scans and the subsequent forward scan was not affected. Additionally, a passivation of the TDIROF surface by IrO$_3$ should have resulted in the same peak decrease in stagnant electrolyte (Figure 5.1) as on the RDE (Figure 5.4) but this was not the case.

Our experiments and the simulations of the processes in the Nernstian diffusion layer provided convincing evidence that direct ammonia oxidation can be strongly inhibited by a reactant limitation induced by a local pH drop in the vicinity of the electrode. This mechanism was already put forward by Kapałka et al. (2011) to explain their observation that deeper polarization of the electrode into the OER resulted in a reduced ammonia oxidation peak a2 due to the release of protons during oxygen evolution and it was mentioned in a recent work on ammonia oxidation kinetics (Diaz et al., 2013). The mechanism can also explain why the direct ammonia oxidation peaks increased when we strongly polarized the electrode into HER. The consumption of protons changed the local pH towards more positive values making more reactive NH$_3$ available in the subsequent forward scans. This resulted in higher peaks a1 and a2. Finally, our simulations showed that the proposed mechanism is reasonable on the observed spatial and temporal scale.

**Modeling the Nernstian Diffusion Layer**

The model shows the relative importance of the processes occurring in the reaction zone due to direct ammonia oxidation and oxygen evolution: the consequence of the NH$_3$ removal was that the total ammonia dropped close to the electrode (Figure 5.7C). However, the more important process leading to NH$_3$ limitation was the pH drop and the shift in ammonia speciation. A comparison of the profiles (1) in Figure 5.7B and C shows that the NH$_3$ concentration dropped by about 20 mmol·L$^{-1}$ while the concentration of total ammonia only declined by 5 mmol·L$^{-1}$. This led to concentration gradients of NH$_3$ but also of NH$_4^+$. It is interesting to note that the gradient of NH$_3$ was more pronounced than the one of NH$_4^+$ which resulted from the lower concentration of total ammonia towards the electrodes.
Figure 5.7C shows another interesting detail. The concentration of total ammonia went through a maximum higher than the value in the bulk liquid in all four profiles. This maximum moved towards the bulk electrolyte and formed a total ammonia wave propagating away from the electrode. The origin of this wave was the difference in the diffusion coefficients of NH$_3$ and NH$_4^+$. Even though the concentration gradient for NH$_3$ was more pronounced than the one of NH$_4^+$ the higher diffusion coefficient of NH$_4^+$ led to a stronger diffusion of that compound resulting in a higher ammonia mass flow away from the electrode in those regions that were not yet affected by ammonia depletion. Therefore, the shift in ammonia speciation not only resulted in a strong reactant limitation in the reaction zone but also in a transport of total ammonia away from the reaction zone.

**Overcoming the Inhibition Mechanism**

It should be feasible to use TDIROF for continuous ammonia oxidation in aqueous solutions, if the reactant limitation due to the proposed inhibition mechanism can be overcome. The reactant limitation may be resolved in three ways. The first possibility is to work at highly alkaline conditions although this bears the risk of ammonia volatilization and may require the dosage of a base. In these situations the excess of hydroxyl ions ensures sufficient alkalinity to prevent a pH drop. Such high pH conditions were applied in some laboratory studies showing continuous ammonia oxidation on other electrode materials. The group of Botte used Pt, Pt-Ir and Pt-Ir-Rh electro-catalysts (Boggs and Botte, 2009; Bonnin et al., 2008; Diaz et al., 2013) and made sure to have an excess of KOH present in the electrolyte. The same principle was applied in a study by Le Vot et al. (2012) using Pt in which a surplus of NaOH was ensured.

A drop in local pH can also be avoided by buffering the electrolyte. A naturally occurring buffer system in the suitable pH range is the carbonate/bicarbonate buffer system (pK$_a$ = 10.33, Haynes, 2012). However, it was shown that carbonate oxidation competes with direct ammonia oxidation on TDIROF which led to negligible ammonia oxidation at high pH values (Amstutz et al., 2012). On the other hand, very high carbonate to ammonia ratios did not influence direct ammonia oxidation on the graphite electrode (Zöllig et al., 2015). The small ammonia removal rates in that study probably resulted from low ammonia concentrations (< 400 mgN·L$^{-1}$) and pH values (< 9) in combination with non-optimized hydraulic conditions.

A third option was demonstrated with our RDE experiments and consists of reducing $\delta_N$ by controlling the hydraulic conditions at the electrode. The group of Eil-Hee Lee published several studies on the oxidation of ammonia in stacked electrolysis cells in which non-buffered electrolytes without chloride were recirculated (Kim et al., 2006a; Kim et al., 2005, 2006b). The induced convection at the electrodes probably reduced $\delta_N$ resulting in continuous direct ammonia oxidation. The very high removal rates (3000 gN·m$^{-2}$·d$^{-1}$, Kim et al., 2006b) may be explained with the high ammonia concentration (1 mol·L$^{-1}$) at elevated pH values (pH = 12) and the considerable current densities that were applied (80 mA·cm$^{-2}$). Process inhibition did not seem to be an issue. The ammonia oxidation rates were stable in an undivided cell during 1.5 hours of electrolysis.
Implications of the pH Effect for Electrolytic Processes

The proposed inhibition mechanism is primarily important for ammonia oxidation in weakly buffered and moderately alkaline aqueous solutions and therefore of outstanding importance for wastewater treatment. In such applications, it appears to be most promising to improve the hydraulic conditions in the electrolysis cells because neither working under highly alkaline conditions nor strong buffering of the wastewater are reasonable options because chemicals would need to be added.

For other important applications of direct ammonia oxidation such as the use in alkaline fuel cells or the production of high-purity hydrogen the pH effect can be avoided by working at strongly alkaline conditions or in non-aqueous media. It has been shown by Peng et al. (2011) that direct ammonia oxidation in saturated acetonitrile was not affected by any form of process inhibition on Pt and Pd electrodes. This indicates that in non-aqueous solutions a similar pH effect as in aqueous solutions must not necessarily exist.

However, similar pH effects as the one observed in the current study for direct ammonia oxidation might also play an important role for other electrochemical reactions that are sensitive to pH. For instance, an early study by Landolt and Ibl (1970) pointed out that the pH in the Nernstian diffusion layer influenced chlorate formation in concentrated NaCl solutions. Similar to the ammonia case, the protons released during hypochlorite oxidation itself (Eq. (5.17)) and oxygen evolution (Eq. (5.6)) were argued to result in lower amounts of the more reactive hypochlorite ion according to the acid-base equilibrium in eq. (5.18) leading to slower chlorate formation.

\[
\begin{align*}
6\text{OCl}^- + 3\text{H}_2\text{O} & \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 6\text{H}^+ + 1.5\text{O}_2 + 6\text{e}^- \quad (5.17) \\
\text{ClO}^- + \text{H}^+ & \rightleftharpoons \text{HClO} \quad (5.18)
\end{align*}
\]

Conclusions

Fast inhibition of direct ammonia oxidation on TDIROF electrodes is caused by a local pH drop in the Nernstian diffusion layer. The pH drop results from anodic processes such as oxygen evolution and direct ammonia oxidation itself. Thus, direct ammonia oxidation is partially self-inhibited. This pH effect can easily be mistaken for surface poisoning by \( \text{N}_{\text{ads}} \) because both effects are related to direct ammonia oxidation.

Since surface poisoning was found to play a minor role on short timescales, continuous ammonia removal by direct oxidation must be possible if optimal hydraulic conditions prevail in the electrolysis cell. Direct ammonia oxidation would be advantageous because lower anode potentials can be applied resulting in a higher current efficiency and a lower energy demand. Additionally, the formation of chlorinated by-products can be prevented. Nevertheless, surface poisoning may be an issue in long term operation of TDIROF anodes leading to slow process deactivation.

The inhibition mechanism we found is generally valid and not related to a specific type of electrode. Therefore, the challenge for successful application of direct ammonia oxidation for the treatment of wastewater is to overcome the local pH decrease. This could be achieved by reducing the Nernstian diffusion layer to a minimum.
Inhibition of Direct Electrolytic Ammonia Oxidation

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References


Supplementary Information
A. Characterization of TDIROF Electrodes

Scanning electron microscopy (SEM) images of a rectangular TDIROF electrode and a TDIROF-RDE are presented in Figure A.5.1A and B. Both images showed the typical, cracked dried-mud like structure also found in earlier studies (Hu et al., 2008). Energy-dispersive X-ray spectroscopy (EDX) analysis confirmed that the surface was covered with iridium dioxide. Figure A.5.1C shows the spectra of an TDIROF-RDE. The ratio of Ir to O was about 5.6 which is close to the expected ratio for IrO₂.

![Figure A.5.1: A: SEM image (backscattered electrons, BSE) of the rectangular TDIROF electrode used for CV in stagnant electrolyte. B: SEM image of TDIROF-RDE. C: EDX-spectrum of the TDIROF-RDE.](image)

B. OCP during Idle Period

The OCP was not continuously measured during the idle phase of the experiments presented in Figure 3 of the manuscript. However, we measured the OCP for 30 seconds prior to the scans. In this time, the OCP was slightly growing but almost constant (mean OCP value of all idle periods -0.413 ± 0.003 V vs. MSE). In another experiment under identical conditions where the OCP was measured for 30 seconds after 5 consecutive scans, the OCP dropped by 30 mV in the two seconds just after the end of the polarization and subsequently smoothly increased (Figure B.5.1). Therefore, it can be
assumed that the OCP between the scans did not vary much and certainly did not drop below the lower return potential.

![Graph showing OCP over time](image)

**Figure B.5.1:** Open circuit potential (OCP) of the TDIROF electrode at the beginning of an idle period.

**References**

Chapter 6

General Conclusions: The Use of Electrolysis for the Treatment of Stored Source-Separated Urine

Thesis chapter:
Zöllig, H., Morgenroth, E., Udert, K.M.
Implications for Decentralization and Source Separation

Decentralization and source separation requires many flexible technologies for the treatment of urine (Larsen and Gujer, 2013). This work confirmed that electro-oxidation can be one of them. Electro-oxidation meets the promise of being a technology that can provide very high reaction rates leading to small urine treatment units. Furthermore, the fact that electro-oxidation uses electricity as the only input makes the technology very attractive for on-site treatment and for complete automation. However, electro-oxidation is not yet a technology that can achieve every goal in urine treatment on its own and should be combined with other processes.

At the moment, electro-oxidation is a technology for the removal of organic substances and ammonia or urea from urine (Kim et al., 2013; Boggs et al., 2009). Therefore, electro-oxidation could be applied in places where the recovery of nutrients is not feasible for technical or economic reasons. Another application could be for the post-treatment of effluent waters from phosphorus recovering technologies such as the struvite precipitation process (Etter et al., 2011). Furthermore, it could be used for the disinfection of effluent waters by in-situ chlorine production. For the recovery of nutrients the electro-oxidative processes are not yet selective enough which results in too high nutrient losses. Electro-oxidation could be interesting for nutrient recovery, if ammonia were oxidized all the way to nitrate. The currently known processes, however, are not selective enough: most of the ammonia is oxidized to N₂ and the nitrogen is lost to the atmosphere.

Some important aspects need to be considered carefully if electrolysis is used for urine treatment. The formation of CBPs is a problem with chlorine mediated oxidation. CBP formation might be mitigated by appropriate pretreatments such as the selective removal of chloride or organic substances or by choosing operating conditions that prevent the formation of by-products. It was shown in this work that one possibility is to use direct oxidation of ammonia (chapter 4). However, to ensure practically useful ammonia oxidation rates, large electrode surfaces would be required. If it is not possible to prevent CBP formation, chlorate and perchlorate must be removed from the treated urine and OCBPs must be eliminated in the off-gas of the electrolysis cells. Another important aspect is the energy consumption of electrolysis. In this work, the energy demand of electrolytic nutrient removal was an order of magnitude higher than with biological processes. This can be improved with higher current efficiencies at lower overpotentials.

Mechanistic Insight into Electro-Oxidation of Stored Urine

The mechanisms involved in the electrolysis of urine are not straight forward due to the complex composition and the high but also highly variable concentrations in urine (chapter 1). This work revealed some mechanistic aspects which are caused by these particular characteristics of urine.

In chapter 2 it was shown that the chlorine mediated indirect oxidation of ammonia was retarded on the BDD anode in high-concentration urine. This could be attributed to a slower chloride oxidation in high-concentration but not in low-concentration urine. The reasons were lower anode potentials in high-concentration urine and a preferential oxidation of organic substances by hydroxyl radicals. Thereby, the strong oxidation of organic substances presumably led to high amounts of small chained intermediates.
reacting with AC which prevented indirect oxidation of ammonia. Under such conditions, the risk of forming OCBPs is high as was shown in chapter 3. The lower chloride removal in high-load urine further allowed ammonia to be removed completely at a later stage of the experiment because chloride was still present while COD was already drastically reduced resulting in fast indirect ammonia oxidation. Moreover, the experiments in low-load urine (chapter 2) showed that ammonia cannot be oxidized if all chloride is removed too early because direct oxidation of ammonia is not possible at elevated current densities neither on BDD nor on TDIROF due to a pH drop in the Nernst diffusion layer (chapter 5).

The pH drop in the Nernst diffusion layer (chapter 5) is also a good example for the importance of the chemical speciation, especially in the Nernst diffusion layer. The chemical speciation in this layer is decisive for the electrochemical reactions proceeding at the electrode and also influences the mass transfer of targeted compounds to the electrode. We found that the chemical speciation was mainly influenced by the chemical composition (buffer capacity) of the urine and the protons released during anodic reactions. Besides the influence on direct ammonia oxidation mentioned above (chapter 5) the chemical speciation in the diffusion layer was also likely to be responsible for the strong formation of chlorate and perchlorate (SI, chapter 3). In fact, the high buffer capacity of urine probably led to important chemical chlorate formation on BDD and on TDIROF by keeping the pH value in a range between 7.2 and 7.5 (phosphate and hypochlorite buffer system) making high concentrations of hypochlorous acid available. This might also have been the decisive factor for the formation of perchlorate on TDIROF.

**Performance of Electro-Oxidation for the Removal of Organic Substances and Ammonia**

The potentially high conversion rates are one of the main reasons why electro-oxidation is considered to be an attractive urine treatment technology. This eventually leads to small reactors that are of particular interest for on-site treatment. Indeed, the study presented in chapter 2 showed that extremely high specific removal rates of organic substances (measured as COD) and ammonia could be achieved: the maximum observed COD removal rate was $2110 \pm 190$ gCOD·m$^{-2}$·d$^{-1}$ and the maximum ammonia removal rate was $419 \pm 17$ gN·m$^{-2}$·d$^{-1}$ (with BDD at 20 mA·cm$^{-2}$). A comparison to surface-based biological systems shows the clear advantage of electro-oxidation in this respect (maximum BOD removal rate 4 gBOD·m$^{-2}$·d$^{-1}$ (Gujer, 2002); maximum ammonia removal rate 2.5 gN·m$^{-2}$·d$^{-1}$ (Tchobanoglous et al., 2003)).

If the constant ammonia removal rate on TDIROF at 20 mA·cm$^{-2}$ ($257 \pm 22$ gN·m$^{-2}$·d$^{-1}$) is taken as a base for the calculation similar to the one presented in chapter 4, an anode surface area of 0.05 m$^2$·p$^{-1}$ and a reactor volume of only 0.5 L·p$^{-1}$ would be required. However, it has to be mentioned that the high removal rates were achieved with chlorine mediated oxidation which is critical due to the CBP formation. With direct oxidation, only an insignificantly higher ammonia removal rate (2.9 gN·m$^{-2}$·d$^{-1}$, chapter 4) was achieved compared to surface-based biological systems. The advantage of the high removal rates is therefore only given if chlorine mediated indirect oxidation is the main
reaction mechanism or if direct ammonia oxidation can be accelerated sufficiently by reducing the Nernstian diffusion layer.

Besides the removal rate, the energy consumption is a decisive performance indicator of a treatment process. The study in chapter 2 has shown that the specific energy demand for COD or ammonia removal in chlorine mediated electro-oxidation depended on the concentrations of COD and ammonia, respectively, the anode material, and the current density. In case of ammonia, however, the most important factor was the availability of active chlorine. Chloride oxidation was indispensable for ammonia removal and thus the specific energy demand of ammonia oxidation extremely increased if no chlorine was formed from chloride (Figure 6.1). The removal of ammonia via direct oxidation on graphite electrodes (chapter 4) resulted in a lower specific energy demand for ammonia oxidation than in chlorine mediated oxidation (Figure 6.1) even though the current efficiency was low (< 40%). Nevertheless, the specific energy consumption of around 40 Wh·gN⁻¹ was still an order of magnitude higher than in biological nitrogen removal (4 Wh·gN⁻¹, Maurer et al., 2003).

Thus, a trade-off exists between the electrode size needed for direct ammonia oxidation and the formation of CBPs as well as an elevated energy consumption for chlorine mediated ammonia oxidation. Consequently, improved electro-oxidation of ammonia either enhances the reaction rate of direct ammonia oxidation or increases the selectivity of indirect oxidation. Ideally, both these developments would go along with minimizing the overpotentials at the electrodes.

For COD removal, the lower specific energy demand with BDD compared to TDIROF resulted from the very high selectivity of the hydroxyl radicals for the oxidation of organic substances (chapter 2). The advantage of high COD concentrations for a low specific energy demand resulted mainly from high current efficiencies (initial \( CE_{COD} > 80\% \) in case of BDD and > 40\% in case of TDIROF) whereas the cell voltages (at applied current densities of 10 to 20 mA·cm⁻²) were of minor importance on both electrodes. At lower concentrations, the specific energy consumption for COD oxidation increased more strongly in function of an increasing current density due to the higher influence of the
needed cell voltages under these conditions. Hence, the current density should always be adapted to the current concentrations to achieve the most efficient treatment.

**Products of the Electro-Oxidation of Ammonia, Organics, and Chloride in Stored Urine**

The products of electro-oxidation of organic substances and ammonia are diverse (Panizza and Cerisola, 2009; Bunce and Bejan, 2011). Nevertheless, many substances can be considered intermediates and clearly dominating final products can be identified. Ammonia is primarily oxidized to molecular nitrogen (Michels et al., 2010) which was likely to be the main product in our experiments as well (chapters 2 and 4). This is a positive aspect for on-site urine treatment if the aim is to remove nitrogen to prevent the eutrophication of receiving waters or to reduce the nutrient load on existing treatment facilities. However, if the goal is to recover nutrients from urine, which would be a more sustainable way to deal with these resources, the complete oxidation to nitrate would be more desirable to prevent nitrogen losses. Such a process eventually could replace biological nitrification for complete nutrient recovery from urine (Udert and Wächter, 2012).

Organic substances are well known to be completely oxidized to $\text{CO}_2$ in electro-oxidation under mass transfer control (Kapałka et al., 2010) which was the case in our experiments as well. Nevertheless, intermediates are formed and their formation heavily depends on the type of anode material used (Comninellis, 1994). These intermediates are likely to act as precursors for the formation of OCBPs. It was shown in chapter 3 that the type of electrode had a significant influence on the OCBPs presumably due to the different intermediates that were formed. Therefore, the anode material is of outstanding importance for OCBP formation. Another important take home message from chapter 3 is that a good amount of the OCBPs were not intermediates but final by-products which were emitted via the off-gas of the electrolysis cell by electrochemical-stripping. This has to be prevented in on-site urine treatment either by mitigating OCBP formation during electro-oxidation or by an off-gas treatment.

Chlorate and perchlorate were other important by-products of chlorine mediated electro-oxidation. In fact, chlorate and perchlorate were the dominant products of chloride oxidation (chapter 3) and in that respect important for two reasons. Firstly, chlorate and perchlorate represent sinks for chloride which remove chlorine atoms from the mediating oxidation loop (Figure 1.3). This led to incomplete ammonia oxidation in some cases depending on the composition of urine (chapter 2). The mitigation of chlorate and perchlorate formation therefore would allow ammonia to be removed completely via fast mediated oxidation. Secondly, chlorate and perchlorate are toxic for aquatic environments and for humans (Srinivasan and Sorial, 2009; Urbansky, 2002) and must be removed from the treated urine if their formation cannot be prevented. Therefore, CBPs (chlorate, perchlorate and OCBPs) are a serious concern for the chlorine mediated electrolysis of source-separated urine and their mitigation must be further investigated.

In this thesis, nitrate formation was observed in most experiments regardless of the anode material used. Sometimes also substantial amounts were produced (Figure 6.2). However, the exact mechanism of nitrate formation remains elusive. At elevated current densities, nitrate formation could have resulted from breakpoint chlorination due to high
AC/ammonia-N ratios in the diffusion layer (Pressley et al., 1972). This would explain why nitrate formation ceased when no AC was produced from chloride anymore (chapter 2). By tendency, more nitrate was produced on BDD than on TDIROF anodes which might was a consequence of the strong oxidation power of the BDD anode. Nitrate, however, was also formed with direct oxidation on the graphite electrodes in synthetic urine (chapter 4). Thus, nitrate was formed via two pathways. In the experiments in chapter 2, it was further observed that nitrate was reduced at the steel cathode. The main reasons for the low nitrate yields therefore are the thermodynamically favored N₂ formation (Pressley et al., 1972, $E^\circ(N_2) = 92$ mV vs. SHE, whereas $E^\circ(NO_3^-) = 810$ mV vs. SHE) and the cathodic reduction of nitrate.

![Figure 6.2: Nitrate yields during galvanostatic electro-oxidation of men's and women's urine. The left panels show results for BDD. The right panels the results for TDIROF.](image)

References


Chapter 7

Outlook: Towards More Efficient Electrolysis of Urine

Thesis chapter:
Zöllig, H., Morgenroth, E., Udert, K.M.
How to Benefit from Chlorine Mediated Electro-Oxidation Despite the Formation of CBPs?

A possible pretreatment to mitigate CBP formation would be the selective removal of chloride by sequential evaporation (Wächter et al., 2015). However, it is not known yet how much chloride could be removed from stored urine with this process. By removing chloride, the formation of active chlorine could be minimized and thus the production of CBPs. Organic substances could still be removed with the BDD anode but the chlorine mediated removal of ammonia would be impeded (chapter 2). To remove the ammonia anyhow organic substance removal on BDD could be followed by direct ammonia oxidation on graphite anodes (chapter 4). Alternatively, the upstream elimination of the organic substances could at least limit the formation of OCBPs. This could be done in a biological reactor. The sludge age would have to be sufficiently low to prevent the growth of nitrifying bacteria or conditions in a biofilm system would have to be controlled such that heterotrophic bacteria can outcompete nitrifiers. The subsequent indirect oxidation would have to be optimized to achieve complete breakpoint chlorination for ammonia removal such that no residual chloramines would remain in the effluent (Kapałka et al., 2010).

The formation of CBPs might be acceptable if appropriate post-treatment processes can be provided. However, the primary goal must be preventing CBP formation. Post-treatment processes would have to include a treatment step for the off-gas of the electrolysis cells to eliminate OCBPs as well as for the processed urine to remove chlorate and perchlorate. The off-gas treatment could be adapted from the technologies that have been developed for OCBP removal from flue gas (Everaert and Baeyens, 2004). Technologies for on-site urine treatment might be the adsorption on activated carbon (Everaert et al., 2002) or catalytic oxidation although temperatures between 260 and 340 °C are needed (Everaert and Baeyens, 2004). However, the removal of chlorate and especially perchlorate might be more challenging (Srinivasan and Sorial, 2009). For on-site urine treatment, electro-reduction appears to be an attractive option because it could be integrated directly in an electrolytic process. Thereby, concomitant hydrogen production could additionally reduce perchlorate (Ye et al., 2012).

Selective Electro-Oxidation

The strategy of handling chlorine mediated electro-oxidation by engineering additional treatment steps can lead to complicated process combinations which are not particularly suitable for on-site urine treatment. Additionally, an even higher energy demand has to be expected. A more advisable approach is the development of new electrodes that are more selective for specific processes. Boggs and Botte (2010) found that Pt-Ir electrodes were the most active electrodes for direct ammonia oxidation in highly alkaline solutions reducing the overpotential to only 0.4 V which is considerably lower than what was found for graphite (1.4 V, chapter 4) or the TDIROF anode (1.3 V, Kapałka et al., 2011). The low overpotential and the highly alkaline media resulted in highly selective direct ammonia oxidation (CE > 90%) and yielded almost exclusively N\(_2\) in an ongoing process (Boggs and Botte, 2010; Bonnin et al., 2008). If this can also be achieved in urine, a much lower specific energy demand can be expected and the formation of CBPs could be prevented. However, in urine this has to go along with the development of an electrolysis
cell with improved hydraulic conditions to prevent a pH drop in the Nernstian diffusion layer (chapter 5).

For nitrogen recovery, complete oxidation to nitrate would be desirable. This requires a better understanding of the mechanisms leading to nitrate formation especially on other electrodes than Pt, for which some mechanisms for nitrate production have been suggested (Bunce and Bejan, 2011). Taking the mechanistic information for the oxidation on Pt anodes as a starting point it seems that nitrate formation through direct oxidation requires simultaneous splitting of water at elevated anode potentials to make reactive oxygen available. On Pt anodes it was found that hydroxylamine (NH$_2$OH) is likely to be an intermediate of nitrate formation according to equation (7.1) (Bunce and Bejan, 2011).

\[ \text{NH}_3, \text{H}_2\text{O} \rightarrow \cdots \rightarrow \text{NH}_2,\text{OH} \rightarrow \text{NH}_2\text{OH} \rightarrow \cdots \rightarrow \text{NO}_2^-, \text{NO}_3^- \] (7.1)

On Pt, the oxidation of NH$_2$OH results in NO$_2^-$, N$_2$O, and NO via intermediates of NH$_3$O$_{ads}$ and NO$_{ads}$ (Rosca et al., 2009). Furthermore, the work from Diaz et al. (2011) showed that nitrite is easily oxidized to nitrate. Therefore, further research on selective nitrate production should focus on understanding the formation of NH$_2$OH and its further selective oxidation to nitrite.

**Improving Mass Transport**

Besides the selectivity mass transfer is a major issue of direct electro-oxidation processes (chapter 4). For selective electro-oxidation processes, mass transport limited conditions are typically reached at higher overpotentials resulting in a limiting current density ($j_{lim}$, Hamann and Vielstich, 2007):

\[ j_{lim} = \frac{n \cdot F \cdot D \cdot c_{x,\infty}}{\delta_N} \] (7.2)

where $n$ [-] is the number of transferred electrons, $F$ [C·mol$^{-1}$] is the Faraday constant, $D$ [m$^2$·s$^{-1}$] is the diffusion coefficient, $c_{x,\infty}$ [mol·m$^{-3}$] is the concentration of the targeted compound $x$ in the bulk solution and $\delta_N$ [m] is the thickness of the Nernstian diffusion layer.

Equation (2) shows that under mass transport control, three parameters can still be influenced which are $D$, $c_{x,\infty}$ and $\delta_N$. The diffusion coefficient could be increased by increasing the working temperature. The $\delta_N$ can be influenced with the hydrodynamics at the electrode. At high flow velocities, $\delta_N$ is reduced leading to an increased $j_{lim}$. However, a trade-off between process velocity and energy investment is created in this way since forcing convection requires energy. A high $j_{lim}$ can also be achieved by keeping an elevated $c_{x,\infty}$. Therefore, good care needs to be taken not to dilute the urine and to work with cascades of electrolysis cells rather than in only one continuous flow stirred tank reactor.

An interesting idea for on-site urine treatment that goes into the direction of the above mentioned requirements is the integration of electrolysis cells directly into the pipes of the urine collection network especially in tall buildings. The potential energy of the urine coming from overlying floors could be used to induce high flow velocities in the electrolysis cells. Additionally, a pipe represents almost an ideal plug flow reactor. Thus, a cascade of electrolysis cells could easily be integrated into the pipes to be able to work at high concentrations at least in the upstream cells. The electrolysis cells could be
equipped with electrodes in a cylindrical shape such that the anodes take the function of the pipe wall with a high surface area and the cathodes could be a rod in the center of the pipe similar to the RenoCell (Chen, 2004). If larger electrode surfaces are needed cylindrical, bipolar electrodes could be placed between the central-rod-cathode and the pipe-wall-anode. For operation and maintenance it would be required that the pipes containing the electrolysis cells are easily accessible.

Long Term Studies in Real Applications

Once that selective and more energy efficient electro-oxidation processes have been identified their durability needs to be thoroughly assessed. Especially in fresh urine, there is a risk of scaling of the electrodes due to the precipitation of phosphate minerals induced by urea hydrolysis (Udert et al., 2003) although Ikematsu et al. (2007) proposed to inhibit the responsible enzyme (urease) by electrochemically produced chlorine. However, the changes of the chemical conditions in the Nernstian diffusion layer induced by the electrochemical reactions at the electrodes could cause additional scaling problems also in stored urine. This, however, will only become apparent in long term studies.

Other processes that could affect the persistence of electro-oxidation are biofouling and the poisoning of the electrode surface by non-reactive oxidation products. Poisoning of the electrode surface by $N_{ads}$ was observed on several electrode materials during direct ammonia oxidation (Bunce and Bejan, 2011; de Voys et al., 2001). This could still be an issue during long term operation of urine electrolysis on TDOIROF anodes even though it was demonstrated in chapter 5 that fast inhibition of direct ammonia oxidation resulted from a shift in local pH. Therefore, more long term experiments and pilot scale studies will be needed in the future.

References


Curriculum Vitae

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