Electrochemical decomposition of choline chloride based ionic liquid analogues

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Received 31st March 2009, Accepted 28th May 2009
First published as an Advance Article on the web 17th June 2009
DOI: 10.1039/b906318h

Ionic liquids are studied intensively for electrochemical applications and more specifically for the electrodeposition of metals. In this paper the electrochemical stability of a deep-eutectic solvent based on choline chloride and ethylene glycol is studied over longer periods of electrolysis. The formation of several decomposition products such as 2-methyl-1,3-dioxolane was observed. Possible mechanisms for the formation of these products are given: some products involve a reaction at either the anode or the cathode, while others can be explained by consecutive reactions of reaction products formed at both electrodes. A range of chlorinated products like chloromethane, dichloromethane and chloroform could be detected as well. This is remarkable as evolution of chlorine gas at the anode is not observed. The formation of the chlorinated products is ascribed to the existence of the Cl_3^- ion in the solution. The presence of the Cl_3^- ion was observed photometrically. The presence of chlorinated products gives rise to a larger environmental impact and higher risks for health and safety, and it questions the "greenness" of these ionic liquid analogues. To reduce the decomposition of the solvent, water and easily oxidizable acids were added as 'sacrificial agents'. Their influence on the formation of 2-methyl-1,3-dioxolane was quantified. However, the addition of the sacrificial agents did not improve the stability of the solvent. Addition of formic acid reduced the formation of 2-methyl-1,3-dioxolane but chlorinated products could still be detected. Water reduced the formation of chlorinated products.

Introduction

The use of ionic liquids as an electrolyte for electrochemical reactions has received a lot of attention during the last few decades. A variety of different industrial applications of ionic liquids has been developed.[1] These electrolytes are being studied for application in batteries,[2] dye-sensitized solar cells,[3] electrochemical capacitors,[4] membrane additives for fuel cells,[2] electro-deposition of reactive metals[5] and nanomaterials,[6] electro-polishing,[7] electroplating,[8] and in metal extraction processes.[9]

The non-volatility, the good solvent properties, the excellent thermal, chemical and electrochemical stability and the tunability[10–13] of ionic liquids make them attractive as electrolytes.[14] These properties are only general and do not apply for all ionic liquids.[15] The physical and chemical properties of ionic liquids depend strongly on the combination of cation and anion used.[1]

For electrochemical applications, ionic liquids with a wide electrochemical window, low viscosity and high electric conductivity are being sought. Just as in the case of molten salts, the ionic liquid acts both as a solvent and electrolyte. Obviously, the energy consumption is much lower when using low melting ionic liquids.

Electrolytes for application in electrodeposition should have a high resistance against electrochemical reduction and oxidation.

However, oxidation and to a lesser extent reduction of the solvent will occur during electrodeposition. Oxidation of the solvent at the anode is inevitable when insoluble anodes are used. These are often necessary because soluble anodes are not available or give too many problems (*e.g.*, formation of oxide layers, Sn^{IV}, poor current distribution, polymers *etc.*). When the efficiency of the metal electrodeposition is lower than 100%, the organic constituents of the ionic liquid can be involved in reductions at the cathode as well.

Many reports exist on the electrochemical stability of ionic liquids at several electrode materials (platinum, glassy carbon and graphite).[14,16,17] The reported data are difficult to compare, as the reference systems are different and not always electrochemically well-defined (quasi reference electrodes such as platinum and silver wires are often used). Electrochemical windows of ionic liquids up to 6 V have been reported,[14] but these data result from rather short cyclic voltammetry experiments. Opposed to such short experiments, different reaction products can be found when longer electrolysis experiments are performed. Similarly, differences appear between reported upper limits of decomposition temperature dependent on the methodologies used and the interpretation of data.[18]

Thermo gravimetrical analysis gives rise to overestimation of the thermal stability of ionic liquids as Kosmulski *et al.*[19]

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reported. In these analyses the temperature is increased gradually (for example at a rate of 5 °C min^{-1}) until a certain weight loss of the sample. This value is taken as the degradation temperature (T_d). When a lower temperature than T_d is applied over a longer period a noticeable weight loss may be observed as well. Depending on the time of exposure, the maximum operating temperature can be 150 to 235 °C lower than the degradation temperatures found with TGA scans.[20–21]

Some possible causes of disagreement between reported data on the electrochemical stability of ionic liquids can be: (1) the slow and complex decomposition reactions at both anode and cathode; (2) whether or not a protective atmosphere above the electrolyte is applied; (3) the purity of the ionic liquid; for large scale applications, lower purities of the components will be used; it has already been demonstrated that the presence of impurities in the ionic liquid gives rise to differences in stability[22–24] and properties[25–26] of the ionic liquid; (4) differences in the chemical or structural nature of the electrodes giving rise to different reaction paths.

The electrodeposition of metals in aqueous solutions often shows a current efficiency less than 100% for the metal reduction. The side-reaction at the cathode is the reduction of water to hydrogen gas (equation 1). At the anode the oxidation reaction may be the dissolution of the anode in the case of soluble anodes, whereas with insoluble anodes water is oxidized to oxygen gas (equation 2).

$$4\ H_2O + 4\ e^- \rightarrow 4\ OH^- + 2\ H_2 \qquad (1)$$

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \qquad (2)$$

Only a few studies have been carried out on the cathode and anode reactions during metal depositions in ionic liquids. The same is true for investigations on how to avoid deterioration of the ionic liquid at the electrodes. Some literature can be found about the electrochemical decomposition of organic compounds in ionic liquids, its mechanisms and the products formed at the electrodes. Kumai *et al.*[27] investigated the decomposition of electrolyte in an AA-size Li/MoS_2 cell and found that ethylene carbonate and propylene carbonate decompose to ethylene and propylene respectively at the cathode. Kroon *et al.*[28] investigated the decomposition mechanism and products of the ionic liquids 1,1-butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium tetrafluoroborate on the cathode by quantum chemical calculations and verified these results by experiments. The 1,1-butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide undergoes three different decomposition routes according to the calculations and leads to the presence of methylpyrrolidine, octanes, octenes, 2-butanol, dimethyl-amine and butylpyrrolidine.

Many studies are devoted to the electrodeposition in ionic liquids. The focus is mainly on the cathodic process while the replenishment and the anodic reactions are not part of the study.

In this paper the decomposition reactions at the anode and cathode of the deep eutectic solvent[29] Ethaline200 are investigated during electrolysis over longer periods. Ethaline200 is composed of a 1:2 mixture (molar ratio) of choline chloride and ethylene glycol[29c] and as such is constituted of a choline cation and a complex anion of Cl^- and the H-bond donor ethylene glycol.[29d]

Some plausible decomposition routes and the quantification of the formation of 2-methyl-1,3-dioxolane were investigated. A possible remedy for the decomposition of the ionic liquid analogue by addition of sacrificial products is suggested.

Methods and materials

Reagents and solutions

$ZnCl_2$ (> 98%, Acros), ethylene glycol (> 99%, Chemlab), oxalic acid (Merck for synthesis), phthalic acid (99%, Acros), acetic acid (99–100%, Merck), formic acid (98–100%, Merck) and 2-methyl-1,3-dioxolane (98%, Alfa Aesar) were used as received.

Choline chloride solution (78 wt%) was obtained as a bulk product from Taminco (Ghent, Belgium). This solution was dried during one week in an oven at 70 °C and subsequently placed in a desiccator to allow cooling down and crystallizing while avoiding uptake of water by hygroscopicity of choline chloride. Ethaline200, an eutectic mixture of ethylene glycol and choline chloride in a molar ratio 1:2, was prepared as described previously.[30]

Seven 1.5 liter solutions were prepared:

(1) Pure Ethaline200;
(2) 1 M $ZnCl_2$ in Ethaline200;
(3) 0.5 M oxalic acid + 0.5 M $ZnCl_2$ in Ethaline200;
(4) 0.5 M phthalic acid + 0.5 M $ZnCl_2$ in Ethaline200;
(5) 10 wt% water + 0.5 M $ZnCl_2$ in Ethaline200;
(6) 1 M formic acid + 0.5 M $ZnCl_2$ in Ethaline200;
(7) 1 M acetic acid + 0.5 M $ZnCl_2$ in Ethaline200.

Electrolysis in a non-divided cell

A dimensional stabilised anode of RuO_2/IrO_2 coated titanium (RuO_2/IrO_2-DSA) (MAGNETO special anodes) and a brass cathode of 1.5 dm^2 were immersed in a 500 ml solution. The tests were carried out at room temperature.

A DC-power supply (Elektro-automatic 7030–050 0–30 V and 0–5 A) was used to set the current at a constant value. A sample of the solution was taken after 0, 6 and 192 hours.

For the pure Ethaline200 and the 1 M $ZnCl_2$ in Ethaline200 a constant current of 1.0 A was applied. The experiment with the 1 M $ZnCl_2$ in Ethaline200 had to be done at 70 °C to prevent crystallization. For this reason the subsequent solutions contained no more than 0.5 M $ZnCl_2$.

For these solutions the current was kept constant at 0.9 A as this resulted in better adhering depositions.

Electrolysis in a divided cell

A second set-up was constructed in order to enable sampling of the solution at the anode and cathode separately. A glass beaker was filled with 900 ml of solution. The anode was a RuO_2/IrO_2-DSA and the cathode was a stainless steel rod with a diameter of 1 cm which was immersed in the solution for 12 cm. Between cathode and anode an open transparent tube was placed as to separate as much as possible the liquids in both compartments. At the top of the transparent tube, a rubber stopper was placed. Samples of the solution around the cathode could be taken *via* a glass tube, which was forced through a perforation in this stopper. In this experiment the current was kept constant for 6 hours. Then, a sample was taken in both the anode and cathode compartment.

When performing the electrolysis on a pure Ethaline200 solution the current was kept constant at 3.0 A. As this led to a rather high current density at the cathode, the current (DC-power supply (Agilent E3620A 0–25 V and 0–1 A)) was reduced to 0.2 A for all other solutions; thus the current density was 0.5 A/dm^2 which allows homogeneous depositions of zinc and zinc alloys in choline chloride based deep-eutectic solvents.[31]

All experiments were carried out at room temperature. The only exception was the electrolysis of the solution with 1 M $ZnCl_2$ in Ethaline200 which was performed at 70 °C in order to prevent crystallization of $ZnCl_2$.

Headspace GC-MS analysis

The progress of the electrochemical decomposition was monitored by headspace GC-MS (TurboMatrix 40 Headspace Sampler (Perkin-Elmer), Clarus 600 (Perkin-Elmer) gas chromatograph and Clarus 600T (Perkin-Elmer) mass spectrometer) with a Elite-Wax column. The vials (Perkin-Elmer 20 ml) were filled with 5.00 ml of analyte.

Headspace program: oven temperature 80 °C, needle temperature 70 °C, transfer temperature 110 °C, injection time 0.02 min, pressure time 1 min, withdrawal time 0.5 min and thermostatization time 10 min. GC program: oven inlet 180 °C, split flow 10, start temperature 30 °C, hold 5 min, step 10 °C/min to 225 °C and hold 5 min. MS program: from 0 to 29.5 min scan all masses between 16 and 300. Scan time 0.15 s and inter scan delay 0.05.

For qualification a Wiley and NIST library for the mass spectra were used.

Quantification of 2-methyl-1,3-dioxolane

For the quantification of 2-methyl-1,3-dioxolane the following modifications to the programs were made:

Headspace: thermostatization time 20 min, needle temperature 100 °C, transfer temperature 120 °C and injection time 0.1 min.

GC: oven inlet 130 °C.

MS: scan all masses between 40 and 300, scan time 0.31 s and inter scan delay 0.09.

Four solutions were analysed by GC-MS with the above described modifications: a blank solution containing only 0.5 M $ZnCl_2$ in Ethaline200 and three standards containing 3.52; 7.04 and 35.24 mg/l 2-methyl-1,3-dioxolane, respectively.

Formation of chlorine gas

Electrolysis was performed on an Ethaline200 solution in an undivided cell while air was bubbled through the solution at the anode. The applied current was 0.5 A and the potential 4.5 V with two DSA-anodes at the side and a brass cathode in the middle. The gasses were directed to a washing bottle containing a 1 M NaOH solution in order to collect the eventually released chlorine gas. Every hour two samples of the NaOH solution were taken. After 5 hours the test was stopped and all collected samples were titrated with a 0.100 M $Na_2S_2O_3$ solution after addition of acidic KI to determine the concentration of hypochlorite ions in solution.

Reaction of Ethaline with chlorine gas

Chlorine gas was prepared by reaction of NaOCl with HCl and bubbled through Ethaline200 after which the unreacted chlorine gas was absorbed in a 1 M NaOH solution. After the chlorine gas had passed through the Ethaline200 solution, a sample was taken from this solution for GC-MS analysis.

The test was repeated with a longer exposure to the chlorine gas in order to perform UV-Vis measurements (Varian Cary300 UV-Vis) on the Ethaline200.

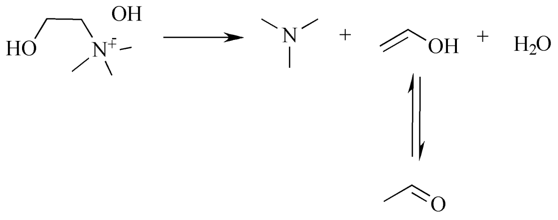
Results and discussion

All GC-MS analyses show the presence of water and ethylene glycol. This was expected, since ethylene glycol is one of the constituents of the ionic liquid analogue. Furthermore, as the experiments were performed under ambient conditions, water uptake of the ionic liquid analogue from the atmosphere could not be avoided. In some of the starting solutions a negligible amount of 2-methyl-1,3-dioxolane (maximum 3 mg/l) was already present.

Electrolysis in a non-divided cell

At the start of the experiment with pure Ethaline200 in a non-divided cell vigorous gas formation was observed at the cathode. It is reported earlier that the gas contains 88% H_2.[32] At the anode no visual reaction was observed. After 6 hours, the liquid had turned slightly yellow. The GC-MS analysis of the Ethaline200 solution after 6 hours of electrolysis indicated the presence of acetaldehyde, ethanol, trimethylamine, methylene chloride, dichloromethane, chlorofom, 2-methyl-1,3-dioxolane and ethylene glycol (Fig. 1). After 192 hours of electrolysis no additional compounds were detected.

The presence of trimethylamine (small peak around 1.50) in the chromatograms can be explained by a Hoffman elimination (Scheme 1) of choline base (= choline hydroxide).



Scheme 1 Hoffman elimination of choline hydroxide.

The instability and decomposition of choline base is well known.[33] Choline base is formed at the cathode where the concentration of OH^- is high because of the reduction of water (equation 1).

A second scheme involves the decomposition of choline by formation of a choline radical at the cathode. The choline radical (formed by the addition of an electron at the cathode) decomposes to trimethylamine and an ethanol radical or to dimethylaminoethanol and a methyl radical (Scheme 2).

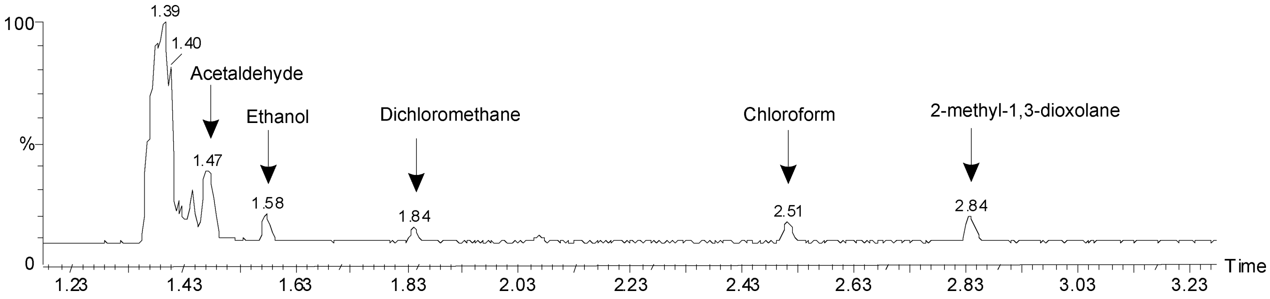
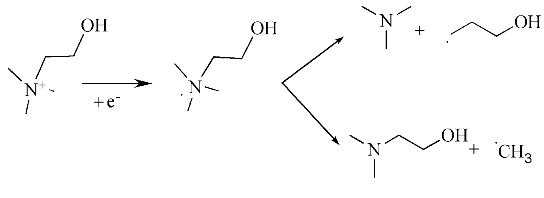


Fig. 1 Chromatogram of Ethaline200 solution after 6 hours of electrolysis



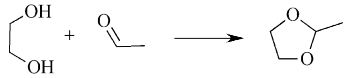
Scheme 2 Possible decompositions of choline cation at the cathode.

A similar mechanism was suggested to explain the formation of methyl-pyrrolidine as a decomposition product of the ionic liquid 1,1-butyl-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide.[28] The formation of a methyl radical explains the presence of chloromethane in the chromatogram. CH_3Cl is formed by recombination of the methyl radical with chlorine formed at the anode (see later). Chloromethane can react further with chlorine to form dichloromethane and chloroform, which are detected as well. Chloroform and dichloromethane were confirmed by the retention times of small additions of these products to pure Ethaline200.

In the Ethaline200 solution containing 1 M $ZnCl_2$ acetaldehyde, dioxolane, 2-methyl-1,3-dioxolane, ethylene glycol and 2-chloro-methyl-1,3-dioxolane were found at the anode. At the cathode no impurities were found, indicating the yield of Zn-deposition is nearly 100%. In aqueous electrolytes zinc anodes are used and no major breakdown of the solvent is expected. Zinc can be deposited from alkaline cyanide containing electrolytes but also from non-cyanide contaning zincate or acidic electrolytes.[34]

At the anode no reaction of choline chloride is expected as oxidation of quaternary ammonium compounds, with the nitrogen lone pair of electrons unavailable, does not occur within the potential range obtainable even in very inert solvents such as acetonitrile.[35]

The formation of 2-methyl-1,3-dioxolane can be explained by reaction of acetaldehyde with ethylene glycol with formation of a cyclic acetal (Scheme 3). The presence of acetaldehyde in the solution after electrolysis over longer intervals can be proven easily with a qualitative test based on Tollen's reagent.[36] The acetaldehyde originates from choline hydroxide (Scheme 1).



Scheme 3 Formation of 2-methyl-1,3-dioxolane by reaction of ethylene glycol with acetaldehyde.

Acetal formation is common and is used for instance for recycling of ethylene glycol from aqueous solutions[37] or as a protective group for diols or carbonyl groups in organic synthesis.[38–40]

In a blank analysis of the starting products (ethylene glycol and choline chloride) no appreciable amounts of chloroform and dichloromethane were detected. As both starting products of Ethaline200 are pure, the small amount of 2-methyl-1,3-dioxolane in some of the blank samples can also be explained by the Hoffman elimination of trace choline hydroxide present, giving rise to a small amount of acetaldehyde which leads to 2-methyl-1,3-dioxolane in the presence of ethylene glycol. Only a small amount can be formed as no OH^- is generated yet.

The GC-MS analysis of the Ethaline200 solution with 1 M $ZnCl_2$ after 6 hours of electrolysis indicated the presence of acetaldehyde, chloro-acetaldehyde, dioxolane, 2-methyl-1,3-dioxolane, ethylene glycol and 2-chloromethyl-1,3-dioxolane (Fig. 2). No chloroform, ethanol or dichloromethane were detected. This is not surprising as the cathode now involves mainly the reduction of zinc ions rather than the reduction of

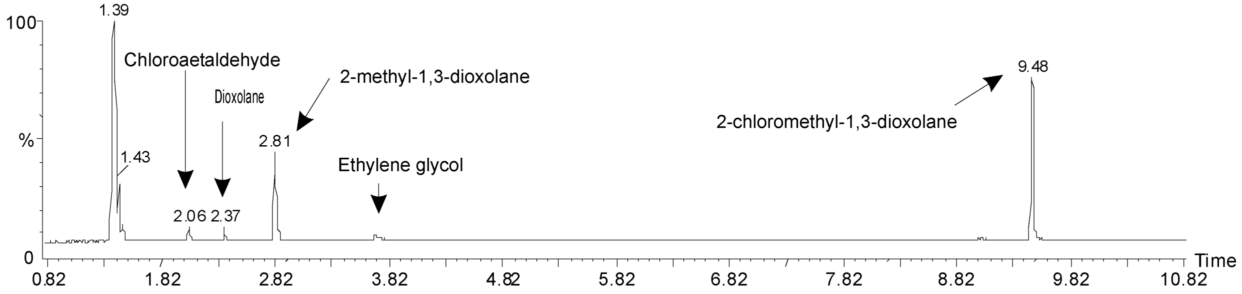


Fig. 2 Chromatogram of Ethaline200 with 1 M ZnCl2 solution after 6 hours of electrolysis.

the solvent. Thus the formation of trimethylamine, ethanol and methyl radicals do not occur. This solution coloured strongly yellow after 6 hours, different from the electrolysis of pure Ethaline200 where the solution remained nearly colourless.

After 192 hours of electrolysis of this solution, no chloroacetaldehyde was detected. Some other products were formed but could not be identified with certainty. The presence of ethanol was shown.

Addition of sacrificial products in a non-divided cell

While the reduction of metal at the cathode occurs at a current efficiency near 100% (therefore $ZnCl_2$ was always added in these experiments), the anodic reaction still leads to conversion of the organic components when insoluble anodes are used. The latter is required when soluble anodes cannot be used, which is often true for electrodepositions in ionic liquids. Oxalic acid, phthalic acid, acetic acid, formic acid or water were added as sacrificial agents to the solution. The aim was to prevent the oxidation of Ethaline200 at the anode by preferential oxidation of the sacrificial products. If possible complete oxidation to carbon dioxide is preferred (reactions 3–6).

$$\text{HOOC-COOH} \rightarrow 2\,\text{CO}_2 + 2\text{H}^+ + 2\,\text{e}^- \tag{3}$$

$$\text{C}_6\text{H}_4(\text{COOH})_2 + 12\,\text{H}_2\text{O} \rightarrow 8\,\text{CO}_2 + 30\,\text{H}^+ + 30\,\text{e}^- \tag{4}$$

$$\text{HCOOH} \rightarrow \text{CO}_2 + 2\,\text{H}^+ + 2\,\text{e}^- \tag{5}$$

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow 2\,\text{CO}_2 + 8\,\text{H}^+ + 8\,\text{e}^- \tag{6}$$

The oxidation of water is given in equation 2. The addition of water can seem contradictory as ionic liquids often offer specific advantages just because of the absence of water. However, the presence of water does not always diminish the beneficial properties found in ionic liquids. Therefore, for applications where small quantities of water are allowed, addition of water is a good alternative to other sacrificial agents. However the addition of water is not always possible like in applications for depositions of reactive metals such as aluminium.

When adding oxalic acid as a sacrificial agent, gas evolution was observed at the cathode and a white foam was formed on top of the solution after 2 hours of electrolysis. After 22 hours the foam had disappeared. No colour changes were observed until the experiment was stopped. After 6 hours, 2-methyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane were detected with GC-MS. At the end of the experiment 2-chloromethyl-1,3-dioxolane was detected as well.

When phthalic acid was added as a sacrificial agent, vigorous gas evolution was observed at the cathode. After 24 hours the solution turned yellow. The colour intensity increased till 48 hours and decreased later on. At the end of the experiment the solution was still light yellow. GC-MS analysis indicated the presence of 2-methyl-1,3-dioxolane, 2-chloromethyl-1,3-dioxolane and 1,2-ethanediol monoacetate after 6 hours. At the end of the experiment 2,2-dimethyl-1,3-dioxolane was detected as well.

When water was added to the ionic liquid analogue, gas production was observed at the cathode. No colour change of the solution was observed during the experiment (168 hours). GC-MS analysis indicated the presence of 2-methyl-1,3-dioxolane and 2-chloromethyl-1,3-dioxolane after 6 hours. After 168 hours 2,2-dimethyl-1,3-dioxolane and acetic acid were detected as well in the solution.

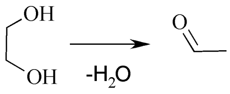
When adding formic acid as a sacrificial agent, gas formation occurred at the cathode. To a lesser extent gas formation was observed at the anode. After 8 hours the solution turned light yellow. After 24 hours the formation of gas at the cathode diminished. At the end of the experiment, the solution was still colourless. GC-MS analysis indicated the presence of 2-methyl-1,3-dioxolane and 2-chloromethyl-1,3-dioxolane. The concentration increased with increasing electrolysis time.

When adding acetic acid as a sacrificial agent, vigorous gas formation was observed at the cathode. Again some minor gas formation was observed at the anode. No remarkable colour changes were observed. GC-MS analysis indicated the formation of 1,2-ethanediol diacetate, ethanediol monoacetate, 2-methyl-1,3-dioxolane, 2-chloromethyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane. The concentration of these side-products increased over time (6, 24, 48 and 168 hours of electrolysis), except for the concentration of acetic acid where the detected amount diminished.

The addition of sacrificial products leads in most cases to even more deterioration products. Products such as 2,2-dimethyl-1,3-dioxolane and 1,2-ethanediol monoacetate were only detected when sacrificial agents are added. Only when formic acid is added no additional products are formed.

Electrolysis in a divided cell

GC-MS analysis of the Ethaline200 solution in the separated anode and cathode compartment shows the formation of 2-methyl-1,3-dioxolane, acetaldehyde and only a small amount of chloroform at the anode and trimethylamine at the cathode. Dichloromethane was not detected. Both solutions were still colourless after the electrolysis experiment. The absence of dichloromethane, in comparison with the undivided cell, can be explained as the methyl radical is generated at the cathode and the chlorine radical at the anode. As these electrodes are divided in this case these radicals do not react. As anode and cathode are divided, the formation of acetaldehyde cannot be explained through the reaction of Scheme 1 as this occurs at the cathode and the 2-methyl-1,3-dioxolane is formed at the anode. Thus at the anode the acetaldehyde can be formed by a dehydration of ethylene glycol.[41] Dehydration of ethylene glycol has been reported earlier in sulfuric acid media as an alternative route for the formation of 2-methyl-1,3-dioxolane.[42] This route explains why formation of 2-methyl-1,3-dioxolane is found even more in the anode compartment, where the formation of the unstable choline base is unlikely. This reaction is shown in Scheme 4.



Scheme 4 Dehydration of ethylene glycol to acetaldehyde.

In the Ethaline200 solution containing 1 M $ZnCl_2$ at the anode acetaldehyde, dioxolane, 2-methyl-1,3-dioxolane, ethylene glycol and 2-chloromethyl-1,3-dioxolane were found. At the cathode no impurities were found, indicating the yield of Zn-deposition is nearly 100%. The products at the anode are all due to oxidation of ethylene glycol or chloride which is not surprising because at the anode no reaction of choline chloride is expected as quaternary ammonium compounds do not oxidize easily.[35]

Addition of sacrificial products in a divided cell

Also in these experiments all solutions contained $ZnCl_2$.

When oxalic acid was added, after 2 hours the solution in the anode compartment turned yellow and on top of the cathode compartment a white foam formed. At the cathode gas formation was observed. At the anode gas formation was observed as well, but to a lesser extent. After 4 hours, in the cathode compartment, crystals were formed throughout the solution. This is possibly due to crystallization of $ZnCl_2$. The experiment in the divided cell was stopped after 14 hours because the solution in the cathode compartment was solidified completely by the crystals. When the tube that separates anode and cathode compartment was lifted out of the solution and the liquid mixed thoroughly, the crystals dissolved again. It can be stated the solution returns to the initial state before electrolysis; a slight difference was that the liquid stayed yellowish. GC-MS analysis indicated the formation of 2,2-dimethyl-1,3-dioxolane in both compartments.

When phthalic acid was added, no colour changes were noticed after 4 hours electrolysis and vigorous gas evolution was observed at the cathode. After 48 hours still no colour changes could be observed but the cathode compartment contained a lot of foam and crystals were formed at cathode and anode. GC-MS analysis of the solutions after 6 hours electrolysis indicated the formation of 2-chloromethyl-1,3-dioxolane and 1,2-ethanediol monoacetate at the anode. After 48 hours electrolysis, at the anode 2,2-dimethyl-1,3-dioxolane and 2-chloromethyl-1,3-dioxolane were detected and at the cathode some 1,2-propanediol and 2-methyl-1,3-dioxolane were detected.

When water was added purposely as a sacrificial agent, gas evolution was observed at the cathode and the solution in the cathodic compartment turned turbid and had a white-grey colour after 2 hours. GC-MS analysis indicated no deterioration products were formed at the cathode compartment after 6 hours of electrolysis. At the anode only 2-methyl-1,3-dioxolane was detected.

The addition of formic acid also lead to gas formation at the cathode. At the anode less gas formation was observed. After three hours the cathode compartment turned turbid and white-grey. At the bottom of the anode compartment the solution was yellow. After 4 hours the whole anode compartment turned yellow. After 8 hours the top layer in the anode compartment was dark yellow and the cathode compartment was less turbid. After 24 hours the experiment was stopped and samples were taken from both compartments. The anode solution was yellow and the cathode solution turbid white-grey. When the solutions of both compartments were mixed, the solution turned colourless again and even zinc particles on the bottom of the beaker that had fallen from the cathode, dissolved again slowly. GC-MS analysis indicated the presence of 2-methyl-1,3-dioxolane and 2-hydroxymethyl-1,3-dioxolane in both compartments whereas 2,2-dimethyl-1,3-dioxolane was only found in the anolyte.

When acetic acid was added as a sacrificial agent, there was gas formation at the cathode. To a lesser extent gas formation was observed at the anode. No remarkable colour changes were observed. After 6 hours no side-products were formed at the cathode. In the solution of the anode compartment, besides 2-methyl-1,3-dioxolane, formation of 1,2-ethanediol diacetate and ethanediol monoacetate was detected.

In the divided experiments additional deterioration products were formed as well and most of these products were formed at the anode. When water was used as a sacrificial agent only 2-methyl-1,3-dioxolane was found as deterioration product. Other products were not present, indicating that only ethylene glycol and water were oxidized, no chlorinated products could be found in these solutions although some were detected in the undivided experiment.

Chlorination

A remarkable observation during the aforementioned experiments was the formation of chlorinated side-products (*e.g.* chloro-acetaldehyde, 2-chloromethyl-1,3-dioxolane, chloromethane, dichloromethane, chloroform). The reaction of the solvent with chlorine gas formed at the anode could give a plausible explanation, but the formation of chlorine gas at the anode was not observed visually nor was the smell of chlorine gas observed.

Of course, a large concentration of chloride is present in the ionic liquid analogue because of the use of choline chloride and $ZnCl_2$. The oxidation of chloride to chlorine gas at the anode can thus be expected. In agreement with our observations, Chmielarz[32] did not report the detection of chlorine gas during the electrolysis of Ethaline200 among the gaseous components analysed with GC-MS (mainly H_2 (88 vol%) and dioxolanes were observed). It can be argued the chlorine formed reacts at a fast rate with the solvent and thus has no time to escape from the solution. This was tested in an electrolysis experiment where air was bubbled over the anode in a Ethaline200 solution in order to improve the release of chlorine out of the ionic liquid and to minimize in this way the reaction time with the organic components. The gas was passed over a NaOH solution in order to absorb chlorine gas that was possibly released but no chlorine could be detected in these samples. It can be concluded that the formation and release of chlorine gas is not likely.

The chlorination of organic constituents of the ionic liquid can be explained by the presence of a Cl_3^--ion which still reacts as an oxidant but remains in the solution. The formation of the Cl_3^--ion has been reported in chloroaluminate ionic liquids where the complex anodic behaviour of chloride was investigated.[43] The Cl_3^- remained in the ionic liquid. Sun *et al.*[44] also did not report chlorine gas evolution in electrolysis experiments over longer periods in $[BMIM]PF_6$ containing a high concentration of [BMIM]Cl. The UV-Vis photometric analysis indicates the direct oxidation to Cl_2 and Cl_3^- which are both dissolved in $[BMIM]PF_6$.

The detection of Cl_2 and Cl_3^- in other ionic liquids suggests these products might be formed as well during electrolysis of Ethaline200. The possibility that chlorine gas reacts with Ethaline200 was tested in an experiment where chlorine gas, formed by addition of HCl to a NaOCl solution, is bubbled through an Ethaline200 solution. A GC-MS analysis of the ionic liquid analogue after three hours contact with Cl_2 gas did not indicate the formation of any chlorinated compounds, so it is concluded that chlorine gas does not react with the organic constituents of Ethaline200.

With a higher amount of chlorine gas, the Ethaline200 turned yellow during the experiment as did the NaOH solution in the wash bottle. The Ethaline200 became colourless after the experiment was ended (probably the excess chlorine was released slowly from the solution). The GC-MS indicated the formation of only a small amount of 2-chloromethyl-1,3-dioxolane. It can be concluded that the predominant form of oxidized chloride is Cl_3^- and not Cl_2.

The stability of the Cl_3^- leads to an extended time of residence of Cl_2 in solution and can thus explain the formation of chlorinated products during electrolysis over longer periods.

The Cl_3^- is a sufficient strong oxidant to oxidize hydroxyl containing species.[43] The presence of Cl_3^- was further indicated by UV-Vis (Fig. 3). As can be seen in this figure, the maximum absorbance is found at 240 nm which corresponds well with values reported elsewhere[44] in other ionic liquids.

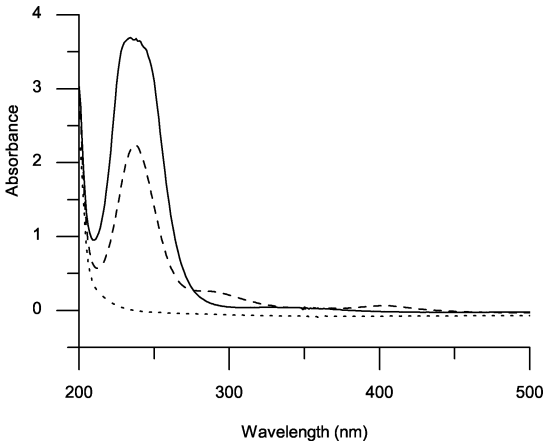


Fig. 3 UV-Vis spectra of pure Ethaline200 (.......), Ethaline200 with chlorine gas bubbled through (—) and Ethaline200 after electrolyses from the anode compartment (-----).

Quantification

The formation of 2-methyl-1,3-dioxolane during electrolysis of Ethaline200 was quantified by addition of 2-methyl-1,3-dioxolane to the ionic liquid analogue before the start of the electrolysis. The peak area in the chromatogram increased proportionally (Fig. 4). In all samples with 2-methyl-1,3- dioxolane addition the amount of 2,2-dimethyl-1,3-dioxolane found in the chromatogram was higher compared to the blank solution. No other components were detected. The results of the analysis can be found in Fig. 4.

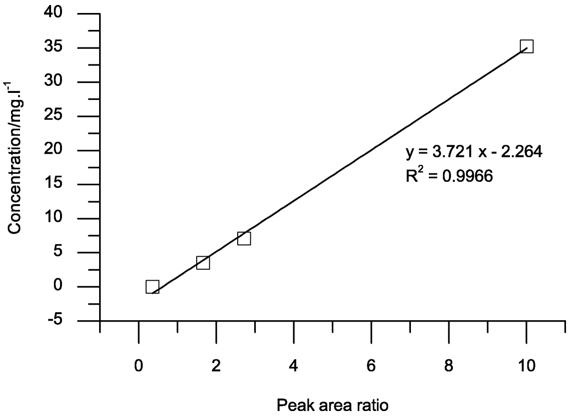


Fig. 4 Concentration of 2-methyl-1,3-dioxolane *versus* peak area ratio between 2-methyl-1,3-dioxolane and ethylene glycol

Some of the samples were selected and the amount of 2-methyl-1,3-dioxolane quantified. The results of this quantification can be found in Table 1. As can be seen in this table, the concentration of 2-methyl-1,3-dioxolane is largest in the solution where water was added. When formic acid was added, no major differences could be observed between the four solutions, indicating that formic acid hinders the formation of 2-methyl-1,3-dioxolane or is oxidized more easily.

Conclusions

Although choline chloride based ionic liquid analogues are cheap and several electrochemical processes are ready for large

Table 1 Concentration of 2-methyl-1,3-dioxolane in the different solutions

Sacrificial product added	Sample taken	Concentration (mg/l)
Acetic acid	Blank	n.d.
	Div. cell at the anode after 6 hours	4
	Div. cell at the cathode after 6 hours	n.d.
	From the undivided cell after 6 hours	16
Oxalic acid	Blank	3
	Div. cell at the anode after 6 hours	22
	Div. cell at the cathode after 6 hours	n.d.
	From the undivided cell after 6 hours	19
Formic acid	Blank	2
	Div. cell at the anode after 6 hours	4
	Div. cell at the cathode after 6 hours	4
	From the undivided cell after 6 hours	2
Water	Div. cell at the anode after 6 hours	95
	Div. cell at the cathode after 6 hours	n.d.
	From the undivided cell after 6 hours	69

n.d.: not detected.

scale operations, the decomposition of the organic constituents at the electrodes over longer periods of electrolysis hinders a breakthrough.

The decomposition is an important economic issue as the lifetime of the solutions is reduced and specific recycling strategies are required in order to remove the decomposition products. Moreover, the conversion of the organic constituents holds a risk for the formation of volatile or toxic products and an uncertain state of the solution at any moment. When promoted as 'green' alternatives for classic solvents, disposal of used ionic liquids should at least be compatible with biodegradation techniques. With the formation of an entire range of products, this is uncertain. Especially chlorinated products, even when the release of chlorine gas is not observed, are a concern.

When a sustainable longevity of the solutions is targeted in processes over longer periods, there is no other way than avoiding the decomposition. Therefore, in electrodeposition processes soluble anodes should be preferred. Unfortunately, these are not always available or give rise to other problems. Another solution is the addition of 'sacrificial agents' *i.e.* components that oxidize preferentially at the anode, thereby protecting the solution. Most of the tested sacrificial products in this study do not reduce the deterioration of the ionic liquid analogue. However, the experiments in a divided cell show the addition of water hinders the formation of chlorinated products but the conversion of the organic components *e.g.* of ethylene glycol to 2-methyl-1,3-dioxolane, remains. Formic acid inhibits the formation of 2-methyl-1,3-dioxolane. However, the efficiency of the zinc deposition at the cathode reduces as the deposited zinc dissolves accompanied by hydrogen gas formation and deterioration of the solvent *via* other routes remains.

Still, there exist possibilities to avoid decomposition in electrochemical processes. Closed loop processes, where cathode and anode reactions do not involve decomposition of the ionic liquids should be searched for. Further investigation is required to prevent the breakdown of the ionic liquid during electrolysis over longer periods either by addition of other sacrificial products or by using soluble anodes. In the latter case it is not impossible organic conversions still occur in side-reactions. If conversion of the ionic liquid, stemming from the organic reactions at the electrodes, cannot be avoided, online processes have to be considered in order to extract the conversion products and to recycle the ionic liquid.

Acknowledgements

The authors would like to thank the EU under framework programme 6 for funding this work through the IONMET project (www.ionmet.eu).

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