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Methanol and formic acid oxidation in zinc electrowinning under process conditions

M. Wesselmark · C. Lagergren · G. Lindbergh

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Abstract The possibility of using methanol or formic acid oxidation as the anode process in zinc electrowinning was examined. The activity for methanol and formic acid oxidation on Pt coated high surface area electrodes was investigated over 36 h, at a current density used in industry. The activity could be maintained at a constant potential level in a synthetic electrowinning electrolyte if the current was reversed for short periods. During the tests, the anode potential was, more than 1.2 V below the potential for the oxygen evolving lead anodes used in modern zinc electrowinning. The lowered anode potential would lead to a significant energy reduction. However, tests in industrial electrolyte resulted in a very low activity for both methanol and formic acid oxidation. The low activity was shown to be caused mainly by chloride impurities. A reduction of the chloride content below 10^{-5} M is needed in order to obtain sufficient activity for methanol oxidation on Pt for use in zinc electrowinning. Pt and PtRu electrodes were compared regarding their activity for methanol oxidation and the latter was shown to be more affected by chloride impurities. However, at a potential of 0.7 V vs NHE, with a chloride content of 10^{-4} M, formic acid oxidation on PtRu gives the highest current density.

Keywords Anode reaction · Zinc electrowinning · Formic acid · Methanol

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M. Wesselmark (✉) · C. Lagergren · G. Lindbergh
Department of Chemical Engineering and Technology, Applied Electrochemistry, Royal Institute of Technology, KTH, 100 44 Stockholm, Sweden
e-mail: maria.wesselmark@ket.kth.se

1 Introduction

Most of the world's zinc is produced in electrowinning processes. A major drawback in conventional zinc electrowinning is the high anodic potential, ~2 V vs NHE [1]. Today, oxygen is evolved on lead anodes with a high over potential, which results in considerable energy losses. Another disadvantage with these anodes is that lead can dissolve and contaminate the zinc product. Lead is also undesirable for health reasons. By using dimensionally stable anodes (DSA®) the over potential can be decreased. DSAs have a low over potential for oxygen evolution but are easily deactivated by manganese dioxide, which precipitates on the precious metal coating [2]. The manganese in zinc electrolyte comes to some extent from the ore but it may also be added as an oxidising agent in order to remove iron from the solution. The potential for the formation of manganese dioxide is very close to that for oxygen evolution and manganese dioxide will always be formed when oxygen is evolved.

Another possibility to substitute the lead anodes and lower the anode potential is to use oxidation of organic compounds. Veerecken et al. [3] were the first to suggest the usage of methanol oxidation as anode reaction in zinc electrowinning. In a patent from 1981, Vining et al. [4] present a method for electrowinning with methanol consuming anodes. To prevent poisoning of the platinum catalyst by carbon monoxide the current was periodically reversed. A research group in Japan solved the problem with carbon monoxide poisoning by exposing the electrodes to air for 1 h every 48th hour [5]. The best result, i.e. a low potential for a high current density during a long period of time, was obtained with a porous platinum ruthenium electrode developed by Watanabe et al. [6], to which methanol vapour was fed from the backside of the electrode. The cell was operating at 1250 Am^{-2} for 4 days with a constant potential of 0.5 V without poisoning of the catalyst. However, the use of this type of anode in electrowinning would demand a complete redesign of the electrode and cell.

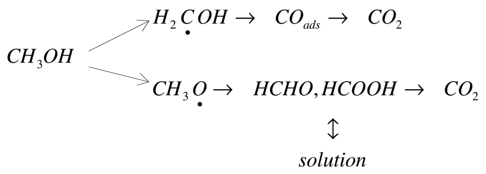
All these studies show the possibility of using methanol oxidation in zinc electrowinning, but none of the studies have used industrial electrolyte. However, Vereecken et al. did investigate the effect of different impurities present in the electrolyte [7]. Mn^{2+} had a minor impact on the reaction rate of methanol oxidation whereas the impact of Cl^- was large, even at low concentrations. Vereecken et al. used pre electrolysis to remove the chloride [7]. This method was tested in the present study but gave no satisfactory results.

Several groups have studied the effect of chloride on methanol oxidation, mainly on Pt [8–11]. The chloride ion adsorbs in a wide potential range and affects hydrogen adsorption as well as oxide formation on the platinum, which hinders adsorption of methanol as well as oxidation of CO to CO_2 [12–14].

Organic compounds, such as methanol and formic acid have been extensively studied for their use in fuel cells. Vielstich´s chapter in Encyclopedia of Electrochemistry [15] is an excellent review of the topic. Hamnett, Lamy and Wiekowski with co-workers have all undertaken interesting work concerning the mechanism of methanol oxidation [16–18]. The complete oxidation of methanol to form CO_2 is given in Eq. 1 [17].

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E^0 = 0.016\,V\,vs\,NHE \tag{1}$$

It is generally accepted that methanol oxidation can proceed via two different pathways, one via adsorbed CO and the other via the soluble species formaldehyde and formic acid. It has recently been suggested that the initial dehydrogenation step gives rise to different adsorbed species that determines through which pathway the methanol oxidation proceeds [19–22]. A simplified reaction scheme is presented in Eq. 2

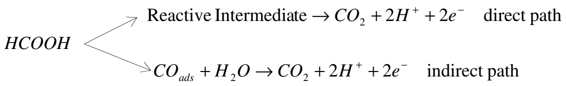


$$CH_3OH \begin{array}{l} \nearrow H_2\underset{\bullet}{C}OH \rightarrow CO_{ads} \rightarrow CO_2 \\ \searrow CH_3\underset{\bullet}{O} \rightarrow HCHO, HCOOH \rightarrow CO_2 \\ \qquad\qquad\qquad \updownarrow \\ \qquad\qquad\quad solution \end{array} \tag{2}$$

The best catalyst for adsorption and dehydrogenation of methanol is platinum. However, methanol oxidation on pure platinum is inhibited by strongly adsorbed carbon monoxide. By adding a second metal, like ruthenium, the oxidation rate can be increased significantly. The beneficial effect of ruthenium is mainly attributed to the ability of ruthenium to adsorb water at low potentials [23].

Formic acid oxidation has received a lot of attention both as intermediate in methanol oxidation and recently as fuel in fuel cells. The total reaction is given in Eq. 3 [22] and the more detailed dual pathway in Eq. 4.

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad E^0 = -0.25\,V\,vs\,NHE \tag{3}$$



$$HCOOH \begin{array}{l} \nearrow \text{Reactive Intermediate} \rightarrow CO_2 + 2H^+ + 2e^- \quad \text{direct path} \\ \searrow CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad \text{indirect path} \end{array} \tag{4}$$

The direct pathway is often considered as the dominating one on both Pt and PtRu catalysts, but the path via CO_{ads} becomes more important at higher potentials [19, 22, 24]. It has also been confirmed with spectroscopic methods that format (HCOO) is the most abundant intermediate on the surface [19, 22, 24–26].

The state-of-the-art catalyst for methanol oxidation in fuel cells is platinum ruthenium. PtRu is also one of the top candidate catalysts for formic acid oxidation but pure Pt and PtPd as well as Bi-modified Pt have shown good qualities for formic acid oxidation [27–30]. The environment and the operating potential in electrowinning differ in many aspects from the conditions in a fuel cell. PtRu is, for example, very sensitive to different electrochemical treatment and there would always be a risk to loose ruthenium from the surface since it is not possible to control the potential of a single anode in the electrowinning process. The operating anode potential will also most likely be much higher in electrowinning than it is in fuel cells. At higher potentials, CO is easily oxidized while the adsorption of methanol becomes more rate limiting [31, 32]. In this case, ruthenium worsens the performance of the catalyst through decreasing the surface available for adsorption. Platinum is therefore the primary choice of catalyst for methanol and formic acid oxidation in this study.

The aim of this study was to show a possible way of operating methanol and formic acid oxidizing electrodes in the industrial process before any optimization of the catalyst or the process were made. At Bolidens zinc plant in Kokkola, Finland, the electrolysis continues for 36 h before the cathodes are removed from the cell and the metal is harvested [33]. It could therefore be required that the anode should be able to maintain sufficient activity for methanol or formic acid oxidation during at least this time. In a previous study it was shown that the electrode was poisoned with time and needed to be reactivated [31]. If the electrodes were removed from the electrolyte, remaining in air for a longer period, the activity of the electrode was completely regained. This characteristic is essential for the life time of the electrode but it is not possible to use for reactivation during cell operation. The best method for reactivation during operation was periodic current reversal (PCR). The reversed current will result in a lower current efficiency but that will most likely be compensated by the reduced operating voltage. The PCR has also been shown to have no detrimental effect on the current efficiency or the zinc quality if the reversal fraction is no higher than 0.04 [34, 35].

2 Experimental

The electrodes used for longer studies at process current densities were of high surface area. The electrode material was a platinum coated titanium fiber structure, TySAR® (Electrosynthesis Co.Inc., USA.). A piece of 3 × 4 cm^2 of the electrode material was spot welded onto a titanium sheet of the same size with a titanium rod as current collector. Henceforth these high surface area electrodes will be referred to as Pt-TySAR® electrodes. The electrodes used in the rotating disc electrode (RDE) cell were made by Permascand AB. Titanium metal was coated with Pt and PtRu with a loading of 60 gm^{-2} and 5 gm^{-2}, respectively. Discs with an area of 1 cm^2 were punched out and placed into titanium holders suitable for an electrode rotator 616 from EG&G.

All chemicals were of analytical grade and water purified in a Millipore system was used. The synthetic sulphate electrolyte contained 160 gl^{-1} H_2SO_4. No zinc was added to the synthetic electrolyte since it has been shown to have little or no influence on the methanol oxidation [31]. All experiments were carried out in a thermostated three electrode glass cell. A PAR 273A potentiostat, EG & G Princeton, was used for all electrochemical measurements except for the potential sweeps in Fig 1, which were made with a Solartron 1286, Solartron Analytical. Tests were performed at 30°C and 40°C. The reference electrode was a Hg/Hg_2SO_4 electrode (R601 from Radiometer) with saturated K_2SO_4 at room temperature, 0.65 vs NHE, connected to a Luggin capillary. However, all potentials in this report are referred to the normal hydrogen electrode. A platinum basket was used as counter electrode. All tests were carried out with nitrogen bubbling through the solution to avoid any reactions with dissolved oxygen. The nitrogen bubbling also removes carbon dioxide formed in the anode process.

Longer studies at industrial current density were made galvanodynamically with cycles of oxidising and reducing currents. The current density used was 500 Am^{-2}, which is the current density used in industry. Cyclic sweeps were made before and after each test to control the status of the electrode.

The RDE was rotated with a constant rotation rate of 1500 rpm. The activity of the electrodes was studied with cyclic voltammetry. The Pt electrodes were swept between 0.02 V and 1.24 V vs NHE. The upper sweep limit for the PtRu electrodes was 0.7 V vs NHE to avoid irreversible oxidation of ruthenium, which can occur at higher potentials [36]. Even if the potential is kept below 0.7 V, ruthenium can dissolve in acidic solution with time and result in a more platinum-like surface [36]. The stability of the electrodes was studied during potentiostatic tests. Cyclic sweeps were made before each measurement until a constant voltammogram was obtained. This was done in order to clean the surface and activate the electrode. Only two sweeps were made on the PtRu coated titanium since its activity decreased for each sweep.

3 Results and discussion

3.1 Operating procedure in industrial process

To determine which current densities could be achieved with the Pt-TySAR® electrodes, potential sweeps were made in synthetic electrolyte with 1 M methanol and 1 M formic acid, respectively (Fig 1). The scan rate was 1 mVs^{-1}, which is close to steady state. Formic acid oxidation started at lower potentials than methanol oxidation and gave a higher current response in the whole potential sweep, except between 0.6 and 0.7 V vs NHE. The potential sweeps showed that the industrial current density of 500 Am^{-2} could be accomplished in an acceptable potential range. Cyclic voltammogram of the Pt-TySAR® electrode in sulphuric acid is also displayed in Fig. 1 to get an estimation of the active surface area of the electrode.

Examples of how the electrode could be operated with methanol or formic acid oxidation in the industrial process are presented in Fig. 2. In Fig. 2a and b, 1M methanol was used and a current density of 500 Am^{-2} was applied on the Pt-TySAR® electrode for 2 min and then 500 Am^{-2} was applied in the reversed direction for 5 s. During the reverse current, adsorbed species are believed to desorb and hydrogen evolves which cleans the surface from poisoning species. There is also a potential risk of CO_2 being adsorbed at the surface when the current is reversed. However, in this process the pH value is very low and CO_2 is unlikely to occur [37]. No CO_2 adsorption was observed in our experiments, but this could be an effect of the continuous nitrogen bubbling.

Figure 2a shows the average potential response for the anodic currents over 36 h. The average potential response

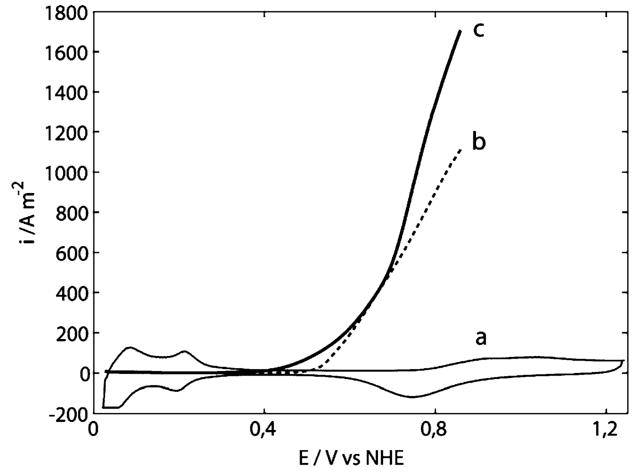


Fig. 1 Cyclic voltammetry on a Pt-TySAR® electrode at 40°C in (**a**) sulphuric acid at 100 mV/s, (**b**) 1 M methanol at 1 mV/s and (**c**) 1 M formic acid at 1 mV/s

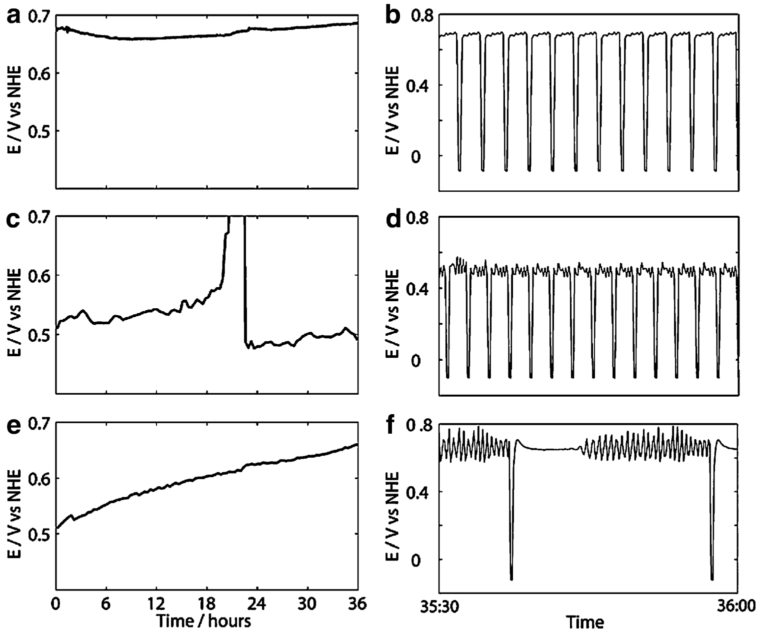
is given by the mean values of the potential response for each 2 min period of anodic current. The potential was slightly higher after 36 h than at the beginning of the period, which indicated that the reversed current did not reactivate the electrode completely. However, the methanol concentration was not held at a constant level and after 36 h more than half of the methanol must have been consumed. The increase in potential could therefore have been caused by the lowered methanol concentration. The last 30 min of the test are given in Fig. 2b and it can be seen that the potential increased during the forward current but started almost at the same value as in the previous cycle after the reducing current. It can also be seen in Fig. 2b, that during the reversed current the potential decreased to the level where hydrogen is evolved.

The optimal cycle time was found by starting with longer cycles and then decreasing the time of the cycle until only methanol oxidation and no oxygen evolution occurred during the 36 h test. However, the ratio of oxidizing current to reversed current and the length of the cycle could be optimised further.

The same cycling procedure was used for oxidation of formic acid. It can be seen in Fig. 2c that the potential was considerably lower than it was for methanol oxidation, but after 20 h the potential started to increase and oxygen started to evolve. The concentration used for the methanol oxidation, 1 M, was not enough for the oxidation of formic acid and the formic acid was consumed after 20 h. The cell was therefore refilled with 1 M formic acid. However, the increase in potential is not as large as expected, considering the decreasing formic acid concentration. Only half of the formic acid concentration should remain after 10 h, but when the formic acid was almost completely consumed, a rapid increase in potential was seen. The potential for formic acid oxidation varies more during one anodic period than it did for methanol, but there is no large increase in potential over the anodic period. The deactivation of the electrode was therefore assumed to be smaller with formic acid than with methanol oxidation. A longer cycling time could then be tested.

The result is presented in Fig. 2e where the electrolysis continued for 20 min before the current was reversed for 5 s. The formic acid concentration was 3M in this test instead of 1 M. No oxygen evolution occurs during the 36 h period but the increase in potential was higher than in

Fig. 2 Galvanodynamic test with PCR in 1 M methanol, 1 M and 3M formic acid at 500 Am^{-2} and 40°C. (**a**) 1 M methanol, PCR 2min/5s (**b**) the last 30 min enlarged. (**c**) 1M formic acid, PCR 2 min/5s (**d**) the last 30 min enlarged. (**e**) 3 M formic acid, PCR 20 min/10s (**f**) the last 30 min enlarged



the two previous tests. During 20 min of electrolysis the electrode may have been deactivated to a larger extent and 10 s of reversed current was not enough to reactivate the electrode completely. A longer period with reversed current could have reactivated the electrode better but a previous study showed that it might be necessary with both a reduction and an oxidation of the surface to regain the activity of the electrode completely [31]. The concentration of formic acid was not constant during this test and could also explain the increase in potential. However, most of the potential increase in 3 M formic acid (Fig. 2e) was probably caused by poisoning species, considering the small increase in potential in Fig. 2c, where the decrease in concentration was much higher.

3.2 Industrial electrolyte

To test the anode concept under conditions more similar to industry, the synthetic electrolyte was exchanged to industrial electrolyte from Bolidens zinc plant in Kokkola, Finland. The activity for methanol and formic acid was shown to be very low and had to be investigated further in detailed studies on rotating disc electrodes.

Potentiostatic experiments were performed with a platinum rotating disc electrode in industrial electrolyte and the current response is given in Fig. 3. The activity for both methanol and formic acid is reduced significantly in the industrial electrolyte immediately the potential is applied. The activity then continues to decrease until the surface is completely inactive for methanol and formic acid oxidation. The deterioration in industrial electrolyte is more pronounced for formic acid than for methanol. The cyclic voltammograms in Fig. 4 show the same trend. The starting potential for the oxidation reactions is the same in industrial and in synthetic electrolyte and it can be assumed that only the reaction rate and not the mechanism is affected in the industrial electrolyte. The low activity in the industrial electrolyte could be caused by adsorption of some impurity, blocking the active sites. However, the reaction mechanism of the two organic compounds is complex and further investigations are needed to find the cause of the low activity in industrial electrolyte.

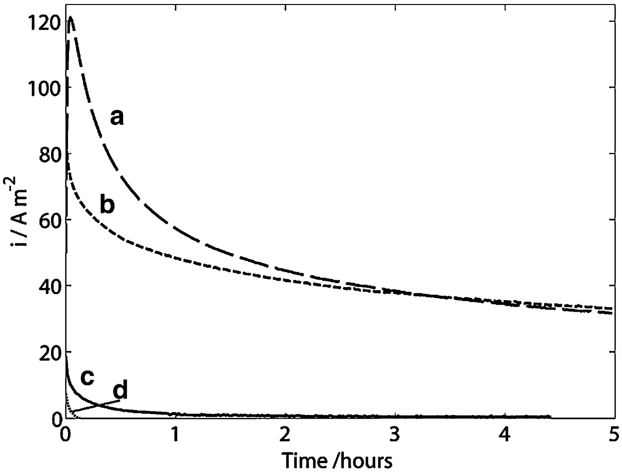


Fig. 3 Potentiostatic tests at 0.7 V in a RDE-cell with platinised titanium in synthetic elctrolyte with (**a**) 1 M formic acid and (**b**) 1 M methanol and in industrial electrolyte with (**c**) 1 M methanol and (**d**) 1 M formic acid. Temperature 30°C

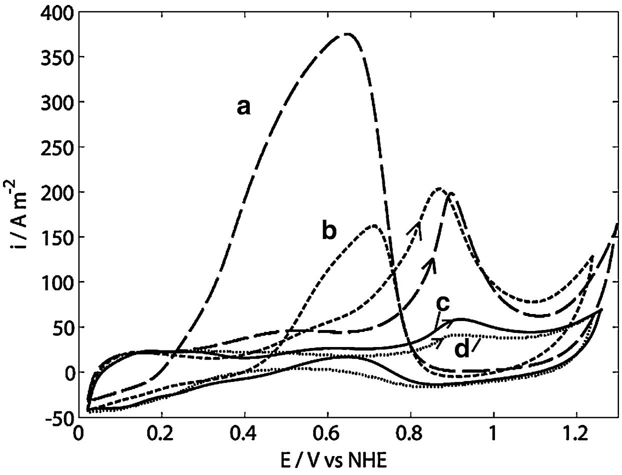


Fig. 4 Cyclic voltammetry on platinised titanium in a RDE-cell in synthetic electrolyte with (**a**) 1 M formic acid and (**b**) 1 M methanol and in industrial electrolyte with (**c**) 1 M methanol and (**d**) 1 M formic acid. Scan rate 100 mV/s and temperature 30°C

To get a picture of the surface reactions in industrial electrolyte, cyclic voltammograms were performed without addition of organic compounds. This was done on both Pt and PtRu to examine the difference between the two surfaces (Fig. 5). The voltammograms in industrial electrolyte were compared with voltammograms in synthetic electrolyte. In industrial electrolyte the hydrogen adsorption peaks disappear on platinum and the oxide formation is depressed. The oxide formation on PtRu was also decreased. Most likely, this is related to adsorption of impurities, hindering hydrogen adsorption and oxide formation as well as the adsorption of methanol and formic acid.

One of the impurities in industrial electrolyte is chloride, which is known to adsorb on platinum and poison the surface [7–11]. The effect of chloride on oxidation of methanol and formic acid was therefore examined. Initially, methanol oxidation was studied with cyclic voltammetry in synthetic electrolyte, to which the same amount of chloride was added as is found in the industrial electrolyte, i.e. 227 mg L^{-1}. The chloride was added in form of hydrochloric acid. The result is displayed in Fig. 6, where the cyclic voltammogram is compared with methanol oxidation in synthetic electrolyte and in industrial electrolyte. The dashed-dotted line, representing the

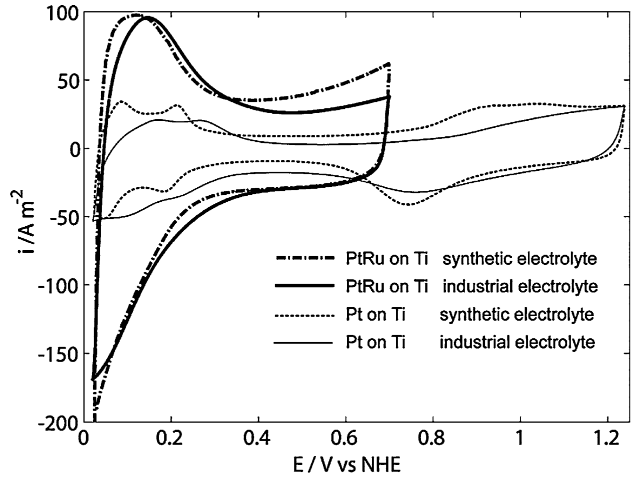


Fig. 5 Cyclic voltammetry on Pt and PtRu on titanium in synthetic and in industrial electrolyte. Temperature 30 °C and scan rate 100 mV/s

synthetic solution with chloride, gives a slightly higher current density than the solid line for industrial electrolyte. Potentiostatic experiments were also made in the same solutions as in Fig. 6 at 0.7 V vs NHE. The current response for methanol oxidation was identical in industrial and in chloride polluted synthetic electrolyte. So, by adding chloride to synthetic electrolyte the activity becomes almost as low as in industrial electrolyte. It could then be assumed that chloride is the main poisoning species, although other impurities also affect the surface for methanol oxidation to some extent. The effect of adding manganese and copper to the chloride polluted synthetic electrolyte was also studied since these elements can decrease the activity for methanol oxidation [3, 9]. No effect was seen when industrial concentrations of the two impurities was added to the electrolyte.

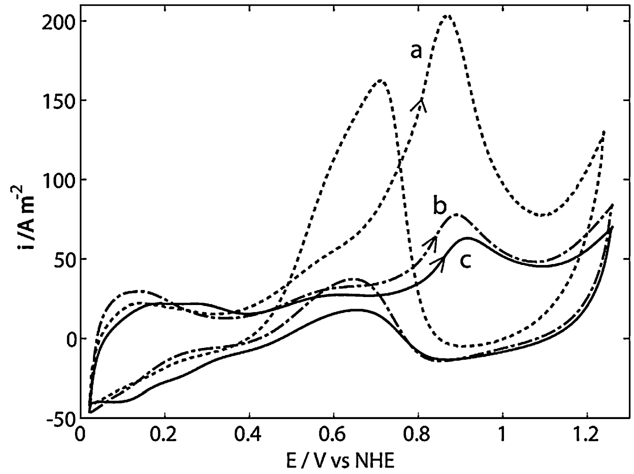


Fig. 6 Cyclic voltammetry on Pt on titanium in a RDE-cell with 1M methanol in (**a**) synthetic (**b**) chloride polluted synthetic and (**c**) industrial electrolyte. Temperature 30 °C and scan rate 100 mV/s

3.3 Effect of chloride

If methanol or formic acid oxidation is introduced as anode reaction in zinc electrowinning it is important to find out what levels of chloride is tolerable to achieve sufficient activity. Methanol oxidation experiments were therefore performed with different chloride concentrations on Pt rotating disc electrodes. The results can be seen in Figs. 7 and 8. The current density in Fig. 7 decreases with increasing chloride concentration. The current decays initially to different levels with the different chloride concentrations but all curves display a similar decay of current with time. Different chloride concentrations cover the surface to different extents, making the reaction surface smaller. A smaller active surface area results in a lower current density. Synthetic electrolyte polluted with 10^{-5} and 10^{-6} M chloride, curve b and a, give current responses of the same magnitude as that for pure synthetic electrolyte, but the slightly higher slopes indicate that deactivation may be faster with chloride impurities.

Experiments with different chloride concentrations were also made on a PtRu electrode to investigate if the PtRu surface behaved differently from the Pt surface (Fig. 8). In synthetic electrolyte, the PtRu electrode is initially more active towards methanol oxidation but decreases more rapidly than the Pt electrode, which is in accordance with previous measurements [31]. With the addition of chlorides to the synthetic electrolyte, it can be seen that the PtRu surface is much more sensitive to chloride impurities than the Pt surface. Even an addition of 10^{-6} M chloride results in a reduction in activity on PtRu and no methanol oxidation is observed with higher concentrations than 10^{-4} M chloride.

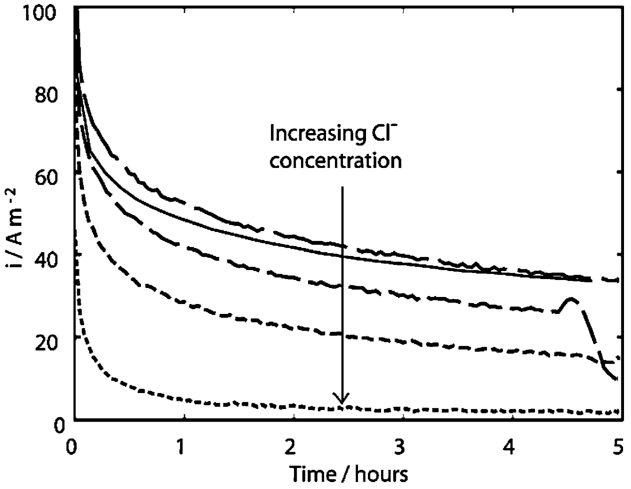


Fig. 7 Potentiostatic tests at 0.7 V in a RDE-cell on platinised titanium with 1M methanol and increasing chloride concentrations: 10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M and in pure synthetic electrolyte (—), temperature 30 °C

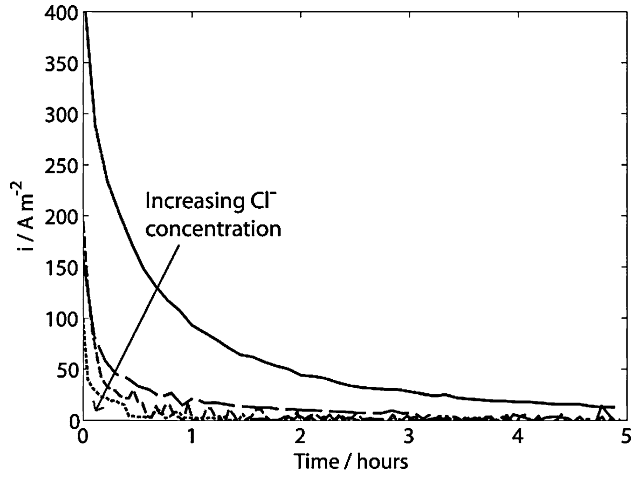


Fig. 8 Potentiostatic tests at 0.7 V in a RDE-cell on platinum ruthenium with 1M methanol and increasing chloride concentrations: 10^{-6} M, 10^{-5} M, 10^{-4} M and in pure synthetic electrolyte (—), temperature 30° C

There are several possible explanations for the sensitivity towards chloride impurities for methanol oxidation on PtRu. Chloride could adsorb more strongly on PtRu than on Pt, which would lead to a larger loss of active surface area. Different dominating pathways or rate determining steps on Pt and PtRu could also result in different behaviour towards chloride impurities. According to the literature and the results of this study, chloride most likely hinders adsorption of methanol, dehydrogenation of methanol, oxidation of CO_{ads} and readsorption of soluble intermediates but no definite explanation for the low activity on PtRu in comparison to Pt can be given. The impact of chlorides on methanol oxidation should be an important factor when evaluating the performance of direct methanol fuel cells. The fact that the influence of chlorides on methanol oxidation was different on Pt and PtRu merits further investigation from a mechanistic perspective.

PtRu had a high activity for formic acid oxidation and with a chloride content of 10^{-4} M PtRu displayed the best result during potentiostatic tests (Fig. 9). As mentioned in the introduction the direct pathway is believed to be dominant on both Pt and PtRu but the importance of the CO path increases on PtRu at higher potentials making the PtRu catalyst much more active towards formic acid oxidation than Pt [27, 28]. The first dehydrogenation step in methanol oxidation is also most likely more rate limiting on PtRu than on Pt at the higher potentials used in this study. This step does not exist in formic acid oxidation and may explain the higher activity of PtRu in comparison to Pt. Formic acid is believed to be able to adsorb and oxidize on Ru, which not is the case for methanol oxidation on Ru [27]. The initial high activity of PtRu is decreased by adding 10^{-4} M Cl$^-$, but is not decreased to the same level as for Pt. PtRu could in this sense be a good candidate for use as formic acid oxidizing anode in industrial electrowinning processes.

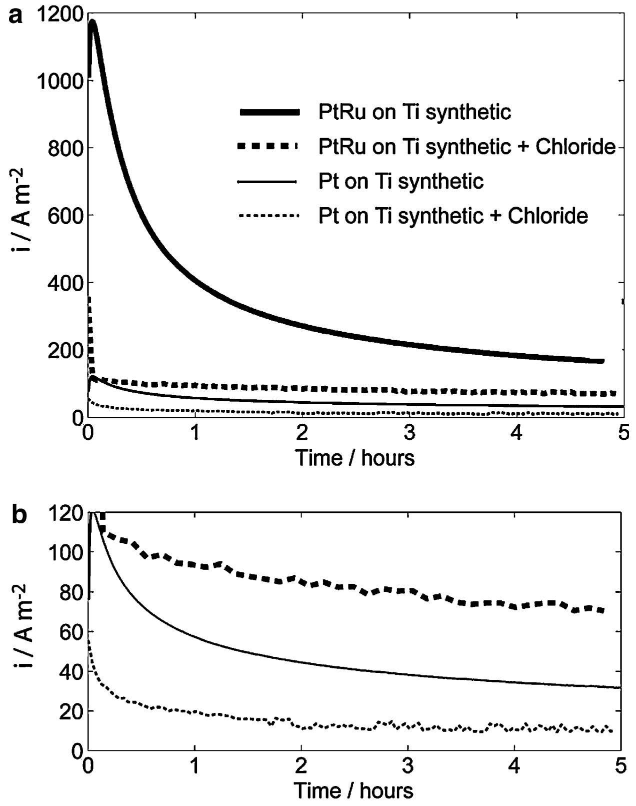


Fig. 9 (**a**) Potentiostatic tests in a RDE-cell with 1M formic acid at 0.7 V with PtRu and Pt on Ti in synthetic electrolyte and in synthetic electrolyte polluted with 10^{-4} M Cl$^-$, Temperature 30° C. (**b**) Enlargement of the three curves in the lower part in Fig. 9a

The results from the investigations of chloride impurities can be summarized in Fig. 10 where the current density after 2 h of the potentiostatic tests is displayed as a function of the chloride concentration. The current density decreases more rapidly on the PtRu electrode than on Pt with increasing chloride concentration. It is also striking how active PtRu is for formic acid oxidation even with an addition of 10^{-4} M Cl$^-$. However there are too few measurements made with formic acid oxidation to be able to draw reliable conclusions.

4 Conclusions

In this study an electrode and operating procedure for formic acid and methanol oxidising anodes were developed. Tests were also performed in industrial electrolyte and the effect of different impurities was examined.

The high surface area electrodes, Pt-TySAR®, were shown to be suitable as anodes in zinc electrowinning.

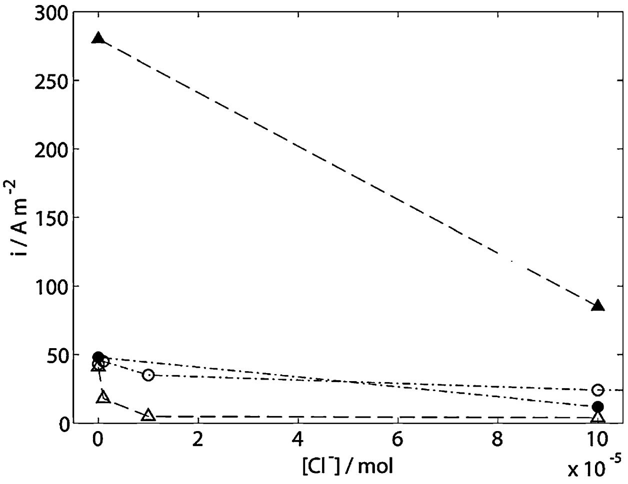


Fig. 10 Current density after 2 h of the potentiostatic tests as a function of chloride concentration for Pt on Ti in 1 M methanol (○), in 1 M formic acid (●) and for PtRu in 1 M methanol (△) and in 1 M formic acid (▲)

During 36 h, the potential was always below 0.7 V vs NHE during methanol oxidation with a periodically current reversal cycle (PCR) of 120 s/5 s. With formic acid oxidation the PCR cycle could be extended to 20 min/10 s and still give a potential below 0.7 V. The operating procedure is feasible in industry but could be further optimised.

The activity for formic acid and methanol oxidation was very low in industrial electrolyte. The major part of the activity reduction was caused by chloride impurities, blocking the active surface area.

Experiments with methanol oxidation on Pt on Ti and PtRu on Ti revealed a higher sensitivity for chlorides on PtRu on Ti. However, with 10^{-4} M Cl^{-}, formic acid oxidation on PtRu on Ti displayed the best result, i.e. a high current density during potentiostatic tests at the potential suitable for use in industry.

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