



# Quantification of formaldehyde production during alkaline methanol electrooxidation

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## ABSTRACT

The alkaline methanol electrooxidation reaction (MOR) in alkaline direct methanol fuel cells is still very little understood with regard to its electrochemical behavior. Theoretically, when using a rotating disk (RDE) as working electrode, the limiting current from an electrochemical reaction increases with the rotation rate as described by Levich. Contrary to this principle, the current resulting from the alkaline MOR does not increase, but decreases with rotation rate. In this work, we investigate the reason for this phenomenon using the method described by Nash and modified by Belman to quantify formaldehyde, a reaction intermediate of the alkaline methanol electrooxidation. The amount of formaldehyde is in direct relation to the rotation rate, proving that the current density loss can originate from an intensified removal of formaldehyde into the bulk solution. We analyse the influence of the electrolyte and methanol concentration on the formation of formaldehyde in order to investigate which conditions support the complete oxidation pathway and suppress the incomplete oxidation to formaldehyde. The concentration ratio as well as the absolute concentrations are of great importance for the pathways taking place. A low electrolyte concentration leads to an increase of the formaldehyde but decreasing the methanol concentration results in an absence of formaldehyde in the bulk solution.

## 1. Introduction

The alkaline direct methanol fuel cell (ADMFC) features some important advantages compared to the acidic version *e.g.* improved reaction kinetics for both anode and cathode reactions [1–4]. But the progress of the ADMFC is limited by different factors. Among others, the achievement of a steady-state is difficult. In our previous work, we showed that the stability of the system components is highly affected by various parameters, *e.g.* the degradation of the components in alkaline electrolyte hinders the stationary state of the system [5].

Using the rotating disk electrode (RDE) as working electrode in a three electrode system is typically a very powerful tool to investigate reaction kinetics. The Levich equation (Eq. (1)) enables the determination of the diffusion coefficient or the number of involved electrons from the electrochemical reaction by plotting the limiting current *versus* the square root of the rotation rate [6]. According to the Levich equation a linear slope results from the application given that the current is not controlled completely by kinetics:

$$i_L = 0.62 nFAD^{2/3} \nu^{-1/6} \omega^{1/2} c_0 = B_L \omega^{1/2} \quad (1)$$

with the Levich current  $i_L$  (A), the number of transferred electrons  $n$ , the Faraday constant  $F$  (C/mol), the electrode area  $A$  (cm<sup>2</sup>), the diffusion coefficient  $D$  (cm<sup>2</sup>/s), the angular rotation rate of the electrode  $\omega$  (rad/s), the kinematic viscosity  $\nu$  (cm<sup>2</sup>/s) and the reactant concentration  $c$  (mol/cm<sup>3</sup>).

RDE measurements, dynamic as well as stationary, of the alkaline methanol electrooxidation show a divergent behavior from the Levich equation. The current diminishes with increasing rotation rate [7–9]. In contrast to the behavior in alkaline electrolytes, the methanol electrooxidation in acid solutions follows the Levich equation, yielding higher current densities with increasing rotation rates [10,11]. Under the assumption that the recorded current is either diffusion or mixed kinetic-diffusion controlled, a possible explanation for the different behavior of the alkaline methanol oxidation reaction in contrast to acidic media could be that the reaction intermediates are weaker adsorbed in alkaline solution leading to an increased desorption rate in relative terms [12]. After desorption, the molecules can either re-adsorb or diffuse into the bulk solution. Fischer et al. described these possibilities for H<sub>2</sub>O<sub>2</sub> as reaction intermediate during oxygen reduction reaction [13]. A higher rotation rate could favor diffusion of intermediates into the

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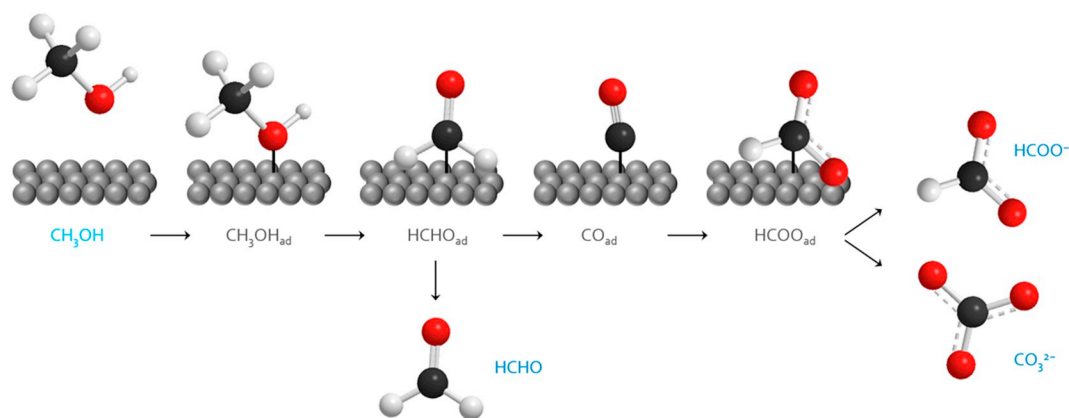
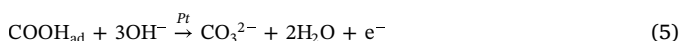
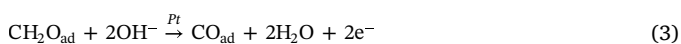
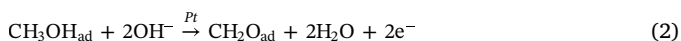


Fig. 1. Simplified reaction mechanism of the alkaline methanol electrooxidation.

solution reducing re-adsorption and further reaction.

Based on the mechanism scheme postulated by Beden et al. and supplemented by different research groups (Fig. 1), formaldehyde could be the relevant reaction intermediate [7,8,14,15]. Eqs. (2)–(5) describe the simplified reaction steps of the alkaline methanol oxidation. It proceeds via dehydration [16]. By the cleavage of two hydrogen atoms, formaldehyde is formed on the catalyst surface. Formaldehyde can desorb from the catalyst surface and diffuse into the bulk solution. Since there is equilibrium between desorption and adsorption, a share of the formaldehyde will adsorb again and be available for further reaction. We assume that parts of the formaldehyde diffuse further into the solution, leading to a loss of 4 electrons per molecule due to incomplete oxidation of methanol. This process might be promoted by the rotation rate and thereby responsible for the deviance of the expected behavior. To investigate the relation between the current loss and the increasing rotation rate, we analyse the amount of formaldehyde in the bulk solution. In addition to the rotational study, we vary the electrolyte and methanol concentration to examine their contribution to the formaldehyde production in the bulk solution.



For the formaldehyde quantification, we use the Hantzsch reaction with subsequent fluorescence analysis to quantify the amount of formaldehyde in an aqueous solution. This method, called the Nash method, is widely used to determine formaldehyde concentrations in biological materials as urine, saliva, respiratory air or waters by combining the conversion of formaldehyde to diacetyldihydropyridine, a fluorescence active species, with its detection by fluorescence spectroscopy [17–22]. Formaldehyde condenses with acetylacetone in the presence of an ammonium acetate buffer, according to the Hantzsch reaction, to 3,5-diacetyl-1,4-dihydropyridin (DDL) (Fig. 2) [23]. DDL is fluorescence active and shows a band at 510 nm. The peak area can be associated to the amount of DDL and thereby to the amount of formaldehyde, since formaldehyde is in equimolar quantities to the formed DDL and possesses the same concentration. In combination with electrochemical studies, HPLC method is widely used to detect formaldehyde since this technique enables the parallel detection of different substances [24,25]. But it is necessary to have an appropriate column and method to separate the resulting signals. The Nash analysis also requires an external calibration, but it can be achieved with less effort simplifying the formaldehyde analysis. Other research groups have already tested the Nash method in combination with

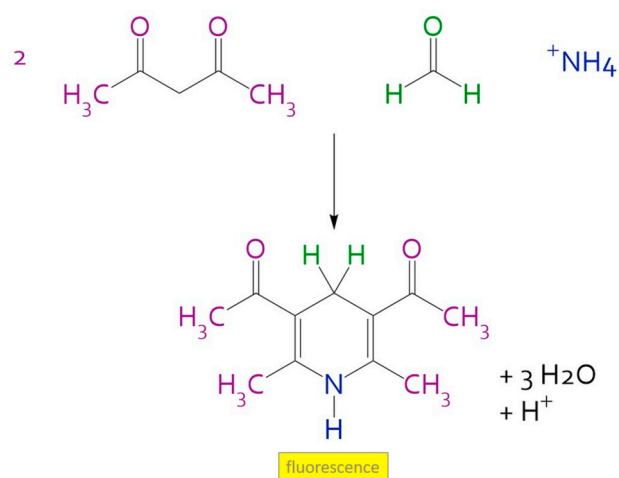


Fig. 2. Hantzsch reaction between acetylacetone and formaldehyde in presence of ammonia to DDL.

electrochemical measurements in the field of methanol oxidation in acidic media or in the field of photocatalysis [26–29]. Our intention was to test the method in combination with the methanol oxidation in alkaline media to investigate the formaldehyde concentration in the bulk solution.

## 2. Experimental section

### 2.1. Electrochemical measurements

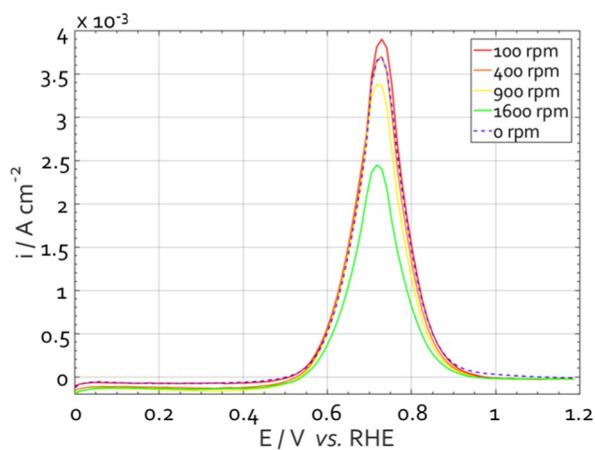
Electrochemical measurements were performed with a three electrode cell setup using a smooth platinum rotating disk electrode as working electrode ( $A = 0.196 \text{ cm}^2$ , Pine Instruments). The RDE was attached to a modulated speed rotator (Pine Instruments) to control the rotation rate. The counter electrode consisted of a platinum wire, and a reversible hydrogen electrode (RHE) from Gaskatel was used as reference electrode. All potentials in this work are referred to the RHE. All electrochemical experiments were performed at room temperature ( $25^\circ\text{C} \pm 0.5^\circ\text{C}$ ). The solutions were prepared from sodium hydroxide (Carl Roth GmbH, 98%, p.a.), methanol (VWR, HPLC grade) and Milli-Q water ( $R = 18.2 \text{ M}\Omega \text{ cm}$ ). The total electrolyte volume was 15 mL, the results are referred to the actual volume. The potential was controlled by a Zennium X potentiostat (Zahner Elektrik GmbH). The chronoamperometric (CA) measurements were all held at a constant potential of 0.71 V vs. RHE over 3600 s. The electrode was electrochemically cleaned prior to each measurement by cycling between 0.0 V and 1.2 V for 200 cycles with a scan rate of  $100 \text{ mV s}^{-1}$ .

## 2.2. Formaldehyde quantification by Nash method

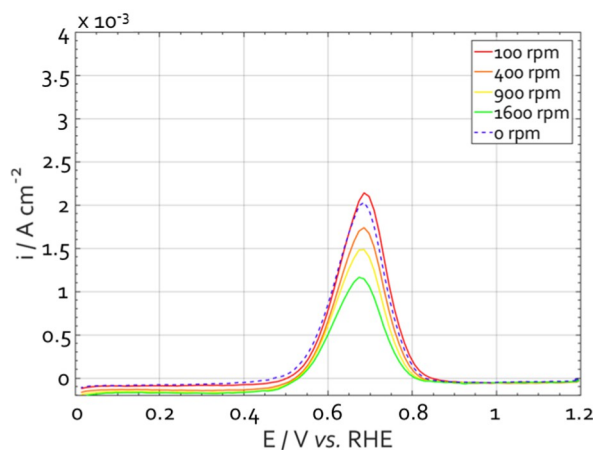
The samples for the Nash method were taken after defined times of 300 s, 900 s and 3600 s. The sampling consisted of two samples of 300  $\mu\text{L}$  each, taken from the reaction volume of 15 mL. The volume change due to the sample taking is considered in the calculation of the amount of substance. The samples were mixed with 600  $\mu\text{L}$  Nash solution, a combination of 0.02 M acetylacetone (Carl Roth GmbH, 98% for synthesis), 0.05 acetic acid (Carl Roth, 100%, p.a.) and 2.0 M ammonium acetate (Carl Roth, 97%, p.a.). The reaction was allowed to take place for about 12 h under light exclusion to ensure a complete reaction from formaldehyde to diacetyldihydrolutidine. Afterwards, a 250  $\mu\text{L}$  portion of the mixture was used for the investigation with the fluorescence spectroscopy. The excitation wavelength was 405 nm with a slit opening for the lamp of 20 nm and a photomultiplier voltage of 400 V. Blank samples of all pure solutions and their combinations without electrochemical treatment were taken in order to calculate a baseline for the DDL detection.

## 3. Results and discussion

Fig. 3 shows the forward and backward scan from dynamic CV measurements of an alkaline methanol solution on a smooth platinum catalyst with different rotation rates. The presented curves are obtained by rotations between 0 rpm and 1600 rpm. The recorded current from the alkaline methanol electrooxidation at a certain potential does not



(a) Forward scan (0.0 V  $\rightarrow$  1.2 V)



(b) Backward scan (1.2 V  $\rightarrow$  0.0 V)

Fig. 3. CV curves of a 0.5 M MeOH + 0.5 M NaOH solution on a platinum catalyst at room temperature with varied rotation rates of the RDE working electrode. Scan rate: 20  $\text{mV s}^{-1}$ .

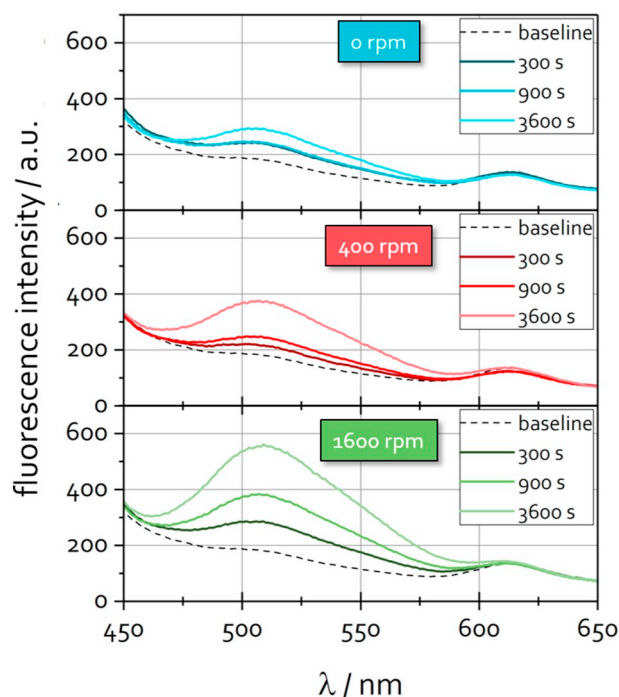


Fig. 4. Fluorescence spectra showing the DDL band at 510 nm. The samples are taken at different times during a CA measurement at 0.71 V vs. RHE in an alkaline methanol solution (both 0.5 M) on a platinum RDE at room temperature.

follow the Levich equation. After an initial increase of the current from 0 rpm to 100 rpm, the peak maximum decreases continuously with increasing rotation rate. This effect is observable for both the forward and backward scans.

### 3.1. Quantification of formaldehyde concentration in dependence on the rotation rate

We investigate the formaldehyde concentration during the methanol electrooxidation from stationary chronoamperometry (CA) measurements with changing rotation rates. The potential was held constant at 0.71 V vs. RHE which corresponds to the potential where the maximum current was recorded. Samples were taken from the bulk solution after three time intervals (300 s, 900 s and 3600 s) and mixed with the Nash solution. The associated fluorescence spectra of the formed DDL are presented in Fig. 4. The fluorescence band at 510 nm belongs to DDL so the integration of the peak area at 510 nm provides the formaldehyde concentration with respect to a calibration curve and the reaction volume. All measurements show a continuous increase of the formaldehyde concentration with reaction time (Fig. 5a). The slope depends strongly on the rotation rate. The increase is strongest at the highest adjusted rotation of 1600 rpm, demonstrating a strong effect of the rotation rate on the amount of detectable formaldehyde. A higher rotation rate leads to a higher amount of formaldehyde in the bulk solution. Fig. 5b shows the corresponding CA curves for the three different rotation rates. All three curves present a strong current density decay over time. The highest current density values are reached with the lowest rotation rate in accordance to the performed CV measurements. The results of these measurements verify the negative influence of the rotation rate on the reaction process. The behavior can be explained by the stronger removal of desorbed formaldehyde into the bulk solution at higher rotation rates preventing further reaction. As a result the complete methanol electrooxidation to  $\text{CO}_2$  or  $\text{CO}_3^{2-}$ , respectively, is minimized.

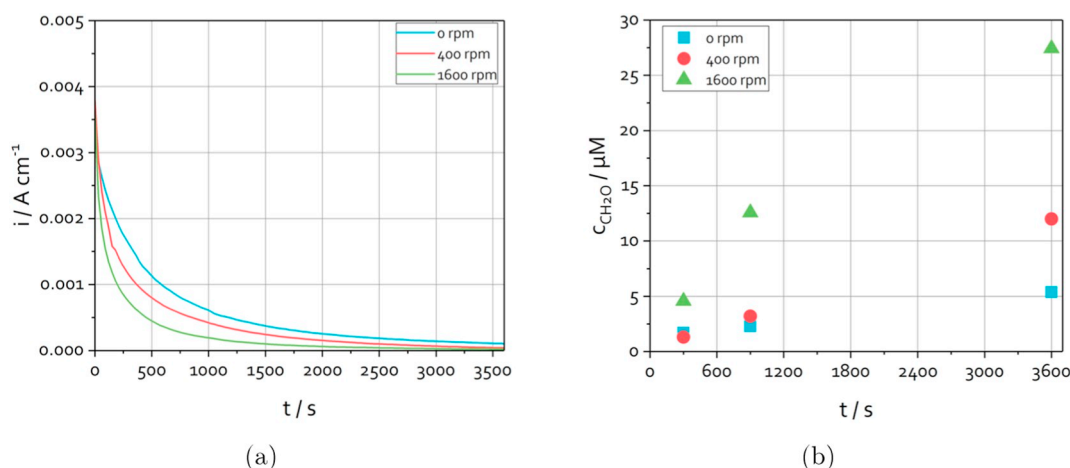


Fig. 5. CA measurement of a 0.5 M NaOH containing methanol solution (0.5 M) at 0.71 V vs. RHE on a platinum catalyst at room temperature for various rotation rates. a) CA curves. b) And corresponding formaldehyde concentration evolution calculated from fluorescence spectra of DDL.

### 3.2. Analysis of the formaldehyde concentration in dependence on reactant concentration

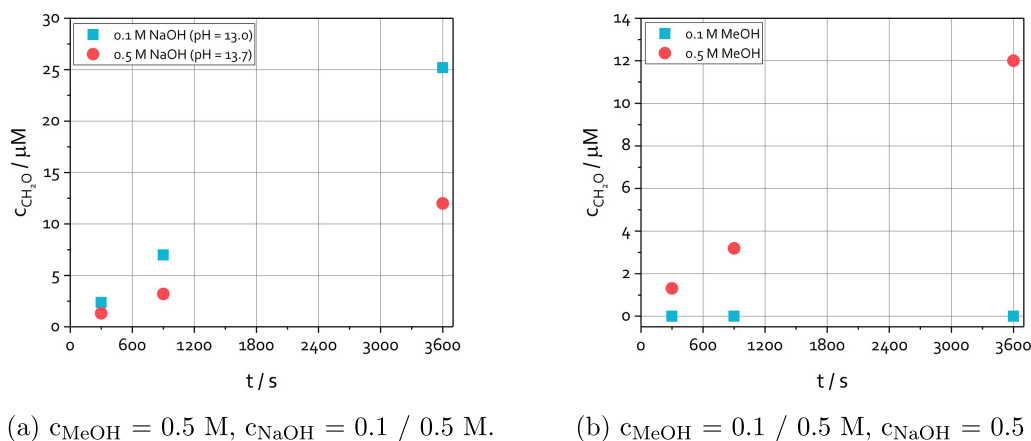
In addition to the analysis of the formaldehyde concentration in terms of the rotation dependence, the Nash method can also be used to determine the influence of other parameters on the preferred reaction pathway. In the following section, the impact of electrolyte and methanol concentration are analyzed. Fig. 6a presents the formaldehyde concentration recorded during CA measurements for two electrolyte concentrations, 0.5 M (pH: 13.7) and 0.1 M NaOH (pH: 13.0). The amount of formaldehyde approximately doubles as the electrolyte concentration is reduced from 0.5 M to 0.1 M NaOH. Thus, a low NaOH concentration favors the formaldehyde reaction pathway. A possible explanation is the lack of hydroxide ions on the catalyst surface, either because the concentration of  $\text{OH}^-$ -ions is too low or the adsorbed methanol molecules block too many free catalyst sites. The hydroxide ions are essential for the oxidation processes. 8  $\text{OH}^-$ -ions are necessary for the complete oxidation of methanol to  $\text{CO}_3^{2-}$ . The lack of  $\text{OH}_{\text{ads}}$  leads to a slower oxidation of formaldehyde facilitating the desorption of formaldehyde into the bulk solution.

Besides the electrolyte concentration, the influence of methanol concentration on the formation of formaldehyde is also investigated by reducing the methanol concentration to 0.1 M. The values for the formaldehyde concentration plotted against the reaction time can be found in Fig. 6b. The DDL band in the fluorescence spectra of the 0.1 M MeOH solution does not differ from the curves of the blank sample at any time,

resulting in a non-detection of formaldehyde. Hence, the decrease of the methanol concentration shifts the reaction pathway toward the complete oxidation pathway of methanol to  $\text{CO}_3^{2-}$ . The low MeOH concentration enables higher hydroxide concentrations at the surface, which facilitates the oxidation of all adsorbed formaldehyde and thereby decreases the amount of desorbed formaldehyde staying in the bulk solution. Alternatively to the reaction *via* directly chemisorbed intermediates on the catalyst surface, a water assisted reaction pathway may exist [30]. Iwasita et al. showed that formic acid as intermediate from alcohol oxidation in acid is bound to the catalyst surface *via* a water molecule and thus possesses a weaker bond [31]. Accordingly, assuming this also applies to formaldehyde, a higher methanol concentration would result in a higher formaldehyde concentration, both on the catalyst surface and in the bulk solution. In conclusion, it can be stated that the ratio between methanol and hydroxide concentration and the absolute concentrations have a decisive influence on the complete methanol oxidation rate.

### 3.3. Calculation of the charge from formaldehyde production

In this section, we evaluate which proportion of the total electrode charge results from the formaldehyde pathway (1). The charge resulting from formaldehyde formation is calculated by Faraday's law (Eq. (6)) using concentrations obtained by Nash results. Possible side reactions of formaldehyde except from the methanol electrooxidation path are neglected in the calculation. For example, formaldehyde could



(a)  $c_{\text{MeOH}} = 0.5 \text{ M}$ ,  $c_{\text{NaOH}} = 0.1 / 0.5 \text{ M}$ .

(b)  $c_{\text{MeOH}} = 0.1 / 0.5 \text{ M}$ ,  $c_{\text{NaOH}} = 0.5 \text{ M}$ .

Fig. 6. Impact of electrolyte (left) and methanol concentration (right) on the formaldehyde concentration during the alkaline methanol oxidation at a constant potential of 0.71 V vs. RHE on a platinum catalyst at room temperature with a scan rate of 400 rpm.

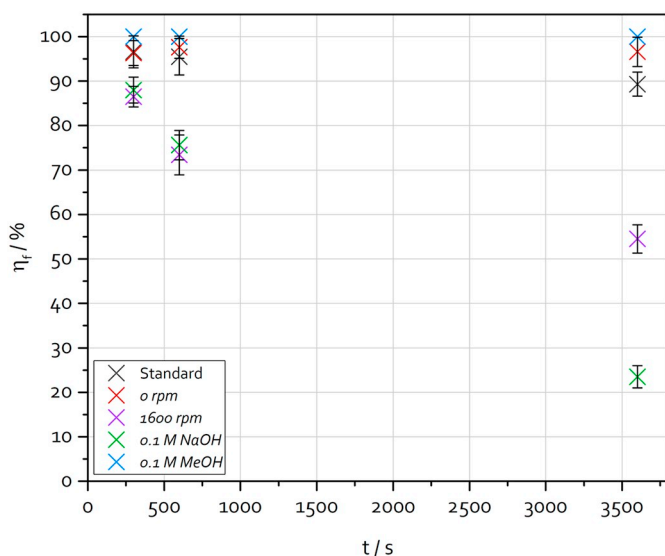


Fig. 7. Faradaic efficiencies ( $\eta_f$ ) of complete methanol electrooxidation during a CA measurement at 0.71 V over time. Standard refers to a 0.5 M MeOH + 0.5 M NaOH solution measured with a rotation rate of 400 rpm. The italic values describe the parameter changed in the measurement. The values for 0.1 M MeOH (blue) are without error bars because no formaldehyde could be detected resulting in a efficiency of 100%, assuming that formaldehyde is the only source of current loss and carbonate the only product of the alkaline MOR. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

disproportionate to formate and methanol according to Cannizzaro-type reaction [32]. Such a reaction would lead to an underestimation of the amount of produced formaldehyde.

$$Q_{\text{CH}_2\text{O}}(t) = n \cdot z \cdot F = c_{\text{CH}_2\text{O}} \cdot V \cdot 2 \cdot F \quad (6)$$

$$Q_{\text{tot}} = \int_{t_0}^t I(t) dt \quad (7)$$

$Q$  is the charge,  $n$  is the amount of substance,  $z$  is the number of electrons (which is 2 for formation of formaldehyde) and  $F$  is the Faraday constant. The integration of the current-time curve (Fig. 5b) gives the total charge at any time (Eq. (7)). The assumption is made, that the total charge is equivalent to the charge from  $\text{CH}_2\text{O}$  and  $\text{CO}_3^{2-}$  production. From these charge values, the Faraday efficiency in relation to the complete methanol oxidation can be calculated by Eq. (8), provided, that desorption of formaldehyde represents the only source for loss of charge. Other intermediates or products like formate are not taken into account at this stage to simplify the complex mechanism of the alkaline MOR.

$$\eta_f = 1 - \frac{Q_{\text{CH}_2\text{O}}}{Q_{\text{tot}}} \quad (8)$$

Fig. 7 shows the calculated Faraday efficiency values over time. Since the oxidation of methanol to formaldehyde is connected with a loss of electrons compared to the complete oxidation, the efficiencies are reduced by the incomplete oxidation to formaldehyde. The recorded current is lower at higher rotations rates while the formaldehyde concentration in the bulk solution increases. Hence, the percentage of the charge based on formaldehyde formation increases with the rotation rate. In the present system, half of the charge originates from the oxidation of methanol to formaldehyde after 3600 s with a rotation rate of 1600 rpm. With a rotation rate of 400 rpm the Faraday efficiency rises to 89.3% and, if the rotation is off, a further increase occurs to 96.6%.

The reduction of the hydroxide concentration (rotation of 400 rpm) leads to an enormous increase of the amount of formaldehyde in the bulk and thereby to a reduction of the Faraday efficiency of the

complete methanol oxidation. After 3600 s, less than one-third of the charge is based on complete methanol oxidation ( $\eta_f = 23.5\%$ ). Considering side reactions like the base-catalyzed Cannizzaro-type reaction of formaldehyde, this reaction would further reduce the contribution of the complete oxidation path to the recorded charge resulting in an even lower faradaic efficiency. In addition, the disproportion of formaldehyde might explain the pH dependent differences in the amount of formaldehyde. A higher pH value facilitates this reaction and thereby reduces the amount of formaldehyde in the solution. Lowering the methanol concentration from 0.5 M to 0.1 M results in no-detection of formaldehyde. So the formed formaldehyde seems to have been further oxidized to carbonate, whereas a low  $\text{OH}^-$  ion concentration promotes the pathway stopping at formaldehyde due to minimized re-adsorption.

#### 4. Conclusions

The combination of electrochemical measurements of alkaline methanol electrooxidation with the Nash method for the determination of the formaldehyde concentration has been demonstrated to be a valuable analytical method for the investigation of the reaction mechanism and its dependence on certain parameters. The analysis of the formaldehyde production during methanol electrooxidation with a fixed potential and different rotation rates shows that the increased amount of formaldehyde in the bulk is in direct relation to the rotation rate, giving an explanation for the deviating behavior from the RDE theory and Levich equation. Furthermore, the influence of the reactant concentrations on formaldehyde production is studied. A reduction of the electrolyte concentration leads to an increase of formaldehyde production, whereas the reduction of the methanol concentration suppresses the production of formaldehyde. The  $\text{OH}^-$ -ion availability is an important variable influencing the product distribution. Under certain conditions, the alkaline methanol electrooxidation follows the incomplete oxidation pathway to formaldehyde nearly completely. These results emphasize the importance and influence of the right concentration ratios and absolute concentrations for the alkaline methanol electrooxidation.

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#### References

- [1] A. Tripkovic, K. Popovic, B. Grgur, B. Blizanac, P. Ross, Methanol electrooxidation on supported Pt and PtRu catalysts in acid and alkaline solutions, *Electrochim. Acta* 47 (2002) 3707–3714.
- [2] B. Blizanac, P. Ross, N. Markovic, Oxygen electroreduction on Ag(1 1 1): the pH effect, *Electrochim. Acta* 52 (2007) 2264–2271.
- [3] E. Antolini, E. Gonzalez, Alkaline direct alcohol fuel cells, *J. Power Sources* 195 (2010) 3431–3450.
- [4] J. Prabhuram, R. Manoharan, Investigation of methanol oxidation on unsupported platinum electrodes in strong alkali and strong acid, *J. Power Sources* 74 (1998) 54–61.
- [5] T. Haisch, F. Kubannek, S. Baranton, C. Coutanceau, U. Krewer, The influence of adsorbed substances on alkaline methanol electro-oxidation, *Electrochim. Acta* 295 (2018) 278–285.
- [6] B. Levich, The theory of concentration polarisation, *Discuss. Faraday Soc.* 1 (1947) 37–49.
- [7] B. Beden, C. Lamy, A. Bewick, K. Kunimatsu, Electrosorption of methanol on a platinum electrode. IR spectroscopic evidence for adsorbed CO species, *J. Electroanal. Chem. Interfacial Electrochem.* 121 (1981) 343–347.
- [8] J.R. Hayes, D. Zeller, C. Friesen, The influence of platinum surface morphology on the electrooxidation of methanol in alkaline solutions, *ECS Trans.* 13 (2008) 41–54.
- [9] J.A. Vega, S. Smith, W.E. Mustain, Hydrogen and methanol oxidation reaction in hydroxide and carbonate alkaline media, *J. Electrochem. Soc.* 158 (2011)

- B349–B354.
- [10] G. Hou, J. Prakash, Rotating rate dependency of methanol oxidation on a smooth polycrystalline platinum surface, *ECS Trans.* 1 (2006) 27–33.
- [11] G. Hou, J. Parrondo, V. Ramani, J. Prakash, Kinetic and mechanistic investigation of methanol oxidation on a smooth polycrystalline Pt surface, *J. Electrochem. Soc.* 161 (2014) F252–F258.
- [12] E.H. Yu, K. Scott, R.W. Reeve, A study of the anodic oxidation of methanol on Pt in alkaline solutions, *J. Electroanal. Chem.* 547 (2003) 17–24.
- [13] A. Schneider, L. Colmenares, Y.E. Seidel, Z. Jusys, B. Wickman, B. Kasemo, R.J. Behm, Transport effects in the oxygen reduction reaction on nanostructured, planar glassy carbon supported Pt/GC model electrodes, *Phys. Chem. Chem. Phys.* 10 (2008) 1931–1943.
- [14] T. Biegler, D. Rand, R. Woods, Limiting oxygen coverage on platinized platinum; relevance to determination of real platinum area by hydrogen adsorption, *J. Electroanal. Chem. Interfacial Electrochem.* 29 (1971) 269–277.
- [15] A. Tripković, K. Popović, J. Momčilović, D. Dražić, Kinetic and mechanistic study of methanol oxidation on a Pt (100) surface in alkaline media, *J. Electroanal. Chem.* 448 (1998) 173–181.
- [16] A. Tripković, K. Popović, J. Momčilović, D. Dražić, Kinetic and mechanistic study of methanol oxidation on a Pt (111) surface in alkaline media, *J. Electroanal. Chem.* 418 (1996) 9–20.
- [17] T. Nash, The colorimetric estimation of formaldehyde by means of the Hantzsch reaction, *Biochem. J.* 55 (1953) 416.
- [18] S. Belman, The fluorimetric determination of formaldehyde, *Anal. Chim. Acta* 29 (1963) 120–126.
- [19] T. Rozylo, A. Zabinska, E. Tyihak, I. Rozylo-Kalinowska, The possibility of quantitative OPLC measurement of levels of formaldehyde in human saliva, *J. Planar Chromatogr.–Mod. TLC* 13 (2000) 394–396.
- [20] H.Y. Peter, C. Cauglin, K.L. Wempe, D. Gubisne-Haberle, A novel sensitive high-performance liquid chromatography/electrochemical procedure for measuring formaldehyde produced from oxidative deamination of methylamine and in biological samples, *Anal. Biochem.* 318 (2003) 285–290.
- [21] U. Riess, U. Tegtbur, C. Fauck, F. Fuhrmann, D. Markewitz, T. Salthammer, Experimental setup and analytical methods for the non-invasive determination of volatile organic compounds, formaldehyde and NOx in exhaled human breath, *Anal. Chim. Acta* 669 (2010) 53–62.
- [22] Q. Li, M. Oshima, S. Motomizu, Flow-injection spectrofluorometric determination of trace amounts of formaldehyde in water after derivatization with acetooacetanilide, *Talanta* 72 (2007) 1675–1680.
- [23] H. Stauffer, J. Bourquin, The spectrophotometric determination of formaldehyde in whole smoke/Eine spektralphotometrische Methode zur Bestimmung von Formaldehyd im Vollauch von Zigaretten, *Contrib. Tob. Res.* 6 (1971) 21–26.
- [24] S.R. Chowdhury, S. Ghosh, S.K. Bhattacharya, Improved catalysis of green-synthesized Pd-Ag alloy-nanoparticles for anodic oxidation of methanol in alkali, *Electrochim. Acta* 225 (2017) 310–321.
- [25] T. Su, R. He, *Methods in Determination of Formaldehyde*, Springer Netherlands, Dordrecht, 2017, pp. 271–295.
- [26] C.L. Childers, H. Huang, C. Korzeniewski, Formaldehyde yields from methanol electrochemical oxidation on carbon-supported platinum catalysts, *Langmuir* 15 (1999) 786–789.
- [27] J. Melcher, S. Feroz, D. Bahnemann, Comparing photocatalytic activities of commercially available iron-doped and iron-undoped aerioxide TiO<sub>2</sub>P25 powders, *J. Mater. Sci.* 52 (2017) 6341–6348.
- [28] C. Haisch, J. Schneider, M. Fleisch, H. Gutzmann, T. Klassen, D. Bahnemann, Cold sprayed WO<sub>3</sub> and TiO<sub>2</sub> electrodes for photoelectrochemical water and methanol oxidation in renewable energy applications, *Dalton Trans.* 46 (2017) 12811–12823.
- [29] C. Günemann, C. Haisch, M. Fleisch, J. Schneider, A.V. Emeline, D. Bahnemann, Insights into different photocatalytic oxidation activities of anatase, brookite, and rutile single-crystal facets, *ACS Catal.* 9 (2019) 1001–1012.
- [30] A. Capon, R. Parsons, The oxidation of formic acid at noble metal electrodes part III. Intermediates and mechanism on platinum electrodes, *J. Electroanal. Chem.* 45 (1973) 205–231.
- [31] T. Iwasita, R. Dalbeck, E. Pastor, X. Xia, Progress in the study of electrocatalytic reactions of organic species, *Electrochim. Acta* 39 (1994) 1817–1823.
- [32] Y.Y. Birdja, M.T.M. Koper, The importance of Cannizzaro-type reactions during electrocatalytic reduction of carbon dioxide, *J. Am. Chem. Soc.* 139 (2017) 2030–2034.