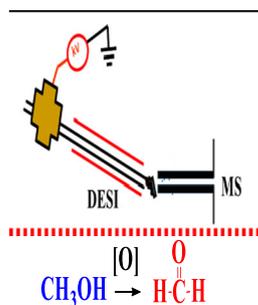


Online Monitoring of Methanol Electro-Oxidation Reactions by Ambient Mass Spectrometry

Si Cheng,¹ Qiuhua Wu,^{1,2} Howard D. Dewald,¹ Hao Chen¹

¹Center for Intelligent Chemical Instrumentation, Department of Chemistry and Biochemistry, Edison Biotechnology Institute, Ohio University, Athens, OH 45701, USA

²College of Sciences, Agricultural University of Hebei, Baoding, Hebei 071001, China



Abstract. Online detection of methanol electro-oxidation reaction products [e.g., formaldehyde (HCHO)] by mass spectrometry (MS) is challenging, owing to the high salt content and extreme pH of the electrolyte solution as well as the difficulty in ionizing the reaction products. Herein we present an online ambient mass spectrometric approach for analyzing HCHO generated from methanol electro-oxidation, taking the advantage of high salt tolerance of desorption electrospray ionization mass spectrometry (DESI-MS). It was found that HCHO can be detected as $\text{PhNHNH}^+=\text{CH}_2$ (m/z 121) by DESI after online derivatization with PhNHNH_2 . With this approach, the analysis of HCHO from methanol electro-oxidation by MS was carried out not only in acidic condition but also in alkaline media for the first time.

Efficiencies of different electrodes for methanol oxidation at different pHs were also evaluated. Our results show that Au electrode produces more HCHO than Pt-based electrodes at alkaline pH, while the latter have higher yields at acidic solution. The presented methodology would be of great value for elucidating fuel cell reaction mechanisms and for screening ideal fuel cell electrode materials.

Keywords: Methanol electro-oxidation, Fuel cell, Electrochemistry, Mass spectrometry, Desorption electrospray ionization

Received: 19 March 2016/Revised: 25 May 2016/Accepted: 10 July 2016/Published Online: 25 August 2016

Introduction

A fuel cell is an electrochemical device in which the chemical energy stored in fuel is converted directly to electrical energy through an electro-catalytic process. With the ever-increasing demand for environmentally friendly energy sources, fuel cells are considered as a promising energy technology. Currently, numerous research efforts are underway to improve the performance of fuel cells, including development of inexpensive catalysts [1, 2]. The strengths of direct methanol fuel cells (DMFCs) are efficient fuel utilization, high energy-dense, yet reasonably stable liquid fuel under all environmental conditions. Indeed, the energy density of methanol is an order

of magnitude greater than even highly compressed hydrogen, and 15 times higher than lithium-ion batteries.

The DMFCs rely on the oxidation of methanol on a catalyst layer to form carbon dioxide. However, the electro-oxidation of methanol often results in a variety of incomplete oxidation products, such as formaldehyde (HCHO), formic acid (HCOOH), methylformate (HCOOCH₃), carbon monoxide (CO), etc. [3, 4]. These byproducts can deactivate expensive cell catalysts and thus the fuel cell itself. Many analytical techniques, such as infrared spectroscopy [5], fluorescence spectroscopy [6], and electrochemistry [7], were employed to monitor the products resulting from the methanol electrochemical oxidation reaction but they lack detection specificity. Mass spectrometry (MS) can serve as a powerful detector for electrochemical reactions with high sensitivity and selectivity since MS can provide molecular weight and structural information for redox reaction products or intermediates. Online coupling of electrochemistry (EC) with MS has a history of over 40 y [8–16]. In the past, differential electrochemical mass spectrometry (DEMS) was adopted to monitor fuel cell reactions; however, it

Electronic supplementary material The online version of this article (doi:10.1007/s13361-016-1450-9) contains supplementary material, which is available to authorized users.

Correspondence to: Howard D. Dewald; e-mail: dewald@ohio.edu, Hao Chen; e-mail: chenh2@ohio.edu

only can detect volatile and small molecules, such as CO₂ and CO [17, 18], and is blind to byproducts, such as HCHO, that cannot easily penetrate the membrane separating the electrochemical cell and the mass spectrometer vacuum chamber. Recent efforts were made to detect HCHO using electrospray ionization mass spectrometry (ESI) after extraction of methanol electro-oxidation products for removing the corrosive and nonvolatile sulfuric acid that was used as electrolyte [4, 19]. Although the method employed an elegant extraction strategy, it involved complicated sample transfer processes, and the extraction yield was not high (ca. 25%) [4, 19]. Furthermore, the previous mass spectrometric studies mainly focused on monitoring methanol electrochemical oxidation in acid media, not in alkaline solution. As alkaline pH offers higher stability to fuel cell materials than acidic pH [20], electrolysis of methanol in alkaline solution is receiving increased attention. Therefore, there is a need for the development of a mass spectrometric approach that is fast, highly selective, and sensitive to measure cell reaction products such as HCHO, at both acidic and alkaline pHs [7].

In order to tackle this challenging problem, our strategy is to use ambient mass spectrometry [21], such as desorption electrospray ionization mass spectrometry (DESI-MS) [22], for the monitoring of HCHO from methanol electro-oxidation. DESI is an important ionization method in the MS field, and it has been introduced to provide direct ionization of analytes with little or no sample preparation. Besides analyzing solid samples from surfaces [21, 23–31], DESI has been extended to directly ionize liquid samples, ranging from small organics to high-mass proteins, in our and other laboratories [9–11, 13, 14, 32–45]. In this study, using DESI-MS to monitor HCHO generated from methanol electro-oxidation has several advantages: (1) compared with DEMS, the detection is convenient and performed at ambient conditions rather than in vacuum; (2) there is no requirement to separate the small potential applied to the electrochemical cell from the high voltage used for DESI spray, which is in contrast to the traditional EC/MS configuration using an ESI interface. Therefore, the instrumentation involved in this method for coupling the electrochemical cell with MS is simplified; (3) DESI is highly tolerant to inorganic salt electrolytes, which is important to the HCHO detection in the presence of the high salt-content solution resulting from acid/base neutralization of sulfuric acid or KOH used for methanol electro-oxidation. The high concentration of salts is known to suppress signal for ESI ionization [46]. We demonstrate that our DESI-MS is a rapid method that can be used for online detection and quantification of HCHO generated from methanol electro-oxidation at both acidic and alkaline media, with no need of sample extraction. In addition, the amount of HCHO generated from different electrodes was evaluated and compared, providing a novel platform for future electrolytic catalyst screening.

Experimental

Materials

HPLC-grade isopropanol, HPLC-grade acetonitrile, phenylhydrazine, Nafion 117 solution (5% in a mixture of low aliphatic alcohols and water), methanol, methanol-d₁, methanol-d₄, methanol-¹³C, and formaldehyde-¹³C solution were purchased from Sigma Aldrich. Sodium hydroxide and potassium hydroxide were purchased from Fisher Chemicals, Fair Lawn, NJ, USA and used without further purification. Pt/C nanoparticle (50/50 wt%) was purchased from E-TEK Inc., Somerset, NJ, USA. The deionized water used for sample preparation was obtained using a Nanopure Diamond Barnstead purification system (Barnstead International, Duquaque, IA, USA).

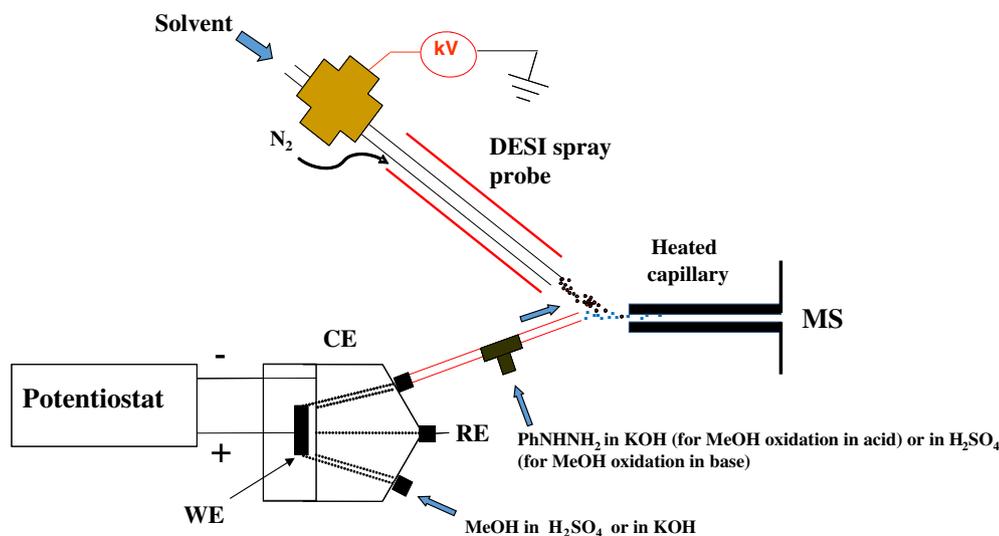
Preparation of Pt/C Electrode

Pt/C suspension was prepared by mixing and sonicating 8 mg Pt/C powder, 4 mL of deionized water, 1 mL of isopropanol, and 20 μ L of Nafion 117 solution before use, following the published procedure [7]. To prepare the thin-film working electrode, 10 μ L of Pt/C suspension was pipetted and then dried on an Au disc electrode (i.d. 8 mm).

Online EC/DESI-MS Apparatus

A home-built DESI apparatus (Scheme 1) for coupling an electrochemical cell with a Thermo Finnigan LCQ DECA MAX ion trap mass spectrometer (San Jose, CA, USA) was used. The electrochemical Reactor Cell was equipped with a working electrode (WE), a counter electrode (carbon-loaded PTFE), and a reference electrode (HyREF, a pseudo reference electrode). In our experiment, different working electrodes including a Pt disc electrode (i.d. 8 mm), an Au disc electrode (i.d. 8 mm), and a Pt/C (50% wt) disc electrode were used to evaluate the performance of different electrodes in producing HCHO from electro-oxidation of methanol. A Roxy potentiostat (Antec BV, Zoeterwoude, Netherlands) was used to apply potential to the cell for triggering methanol oxidation when the methanol sample flowed through the cell. Sample solutions were prepared in methanol/water containing 0.1 M sulfuric acid or 0.1 M KOH as electrolyte and infused into the cell by a syringe pump for electrolysis at a flow rate of 5 μ L/min. The products from the cell underwent online derivatization with 20 mM phenylhydrazine introduced via a Tee mixer. The derivatized reaction products were subsequently monitored by online DESI-MS.

DESI ionization occurs via interaction of sample with charged microdroplets from the DESI spray; the resulting ions were detected by the mass spectrometer. The DESI spray probe was aimed at the sample capillary tip and kept 1–2 cm away from the mass spectrometer inlet. The positive ion mode was used for HCHO detection, the DESI spray solvent used was ACN/H₂O/1% HOAc at an injection flow rate of 10 μ L/min, and the nitrogen gas pressure for DESI spray was set to 160 psi. For detection of HCHO generated from methanol oxidation in



Scheme 1. Apparatus for online DESI-MS monitoring of methanol electro-oxidation in a thin-layer electrochemical flow cell

sulfuric acid, the derivatizing reagent used was 20 mM phenylhydrazine in 0.18 M NaOH solution infused at an injection flow rate of 5 $\mu\text{L}/\text{min}$. The final pH of the solution after derivatization was around 2, which was beneficial to the derivatization reaction. For detection of HCHO generated from methanol oxidation in 0.1 M KOH, the derivatizing reagent used was 20 mM phenylhydrazine in 0.06 M sulfuric acid solution, which was infused at an injection flow rate of 5 $\mu\text{L}/\text{min}$.

For quantification of HCHO, a formaldehyde- ^{13}C solution serving as an internal standard was introduced from another Tee mixer to mix with the electrolyzed methanol sample solution (see apparatus shown in Figure 4S, Supporting Information) prior to derivatization with phenylhydrazine. The derivatized reaction products were monitored online by DESI-MS.

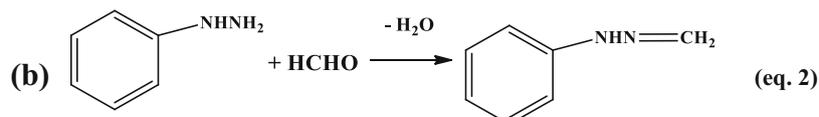
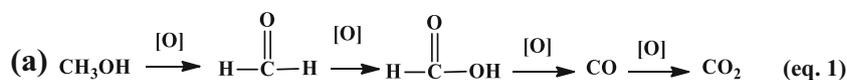
Results and Discussion

Monitoring Methanol Electro-Oxidation in Acidic Conditions

Equation 1 of Scheme 2 shows the possible oxidation process for methanol in which incomplete oxidation first produces HCHO, which can be further oxidized into HCOOH, CO,

and finally CO_2 [47, 48]. As the oxidation products emerge from the cell, HCHO can be derivatized with phenylhydrazine PhNHNH_2 (Equation 2, Scheme 2) [4]. The resulting hydrazone product $\text{PhNHN}=\text{CH}_2$ can be ionized as the protonated phenylhydrazone of m/z 121 by DESI for MS detection.

In our experiment, a Pt disc WE (i.d. 8 mm) was chosen first for testing. A solution containing 0.5 M methanol in 0.1 M sulfuric acid was introduced to the cell as the sample solution. For detecting HCHO, phenylhydrazine was introduced for HCHO derivatization. In addition, NaOH was also doped in the phenylhydrazine solution for neutralizing most of the sulfuric acid matrix (to ca. pH 2) as sulfuric acid is highly corrosive to instruments. As shown in Fig. 1a, when sample and derivatizing reagent were introduced with no potential applied to the cell, no phenylhydrazone product from HCHO derivatization reaction was detected. When a 2.0 V potential was applied to the cell, the peak of $\text{PhNHNH}^+=\text{CH}_2$ at m/z 121 arose (Fig. 1b). This indicates that the methanol oxidation in the cell produces incomplete oxidation product HCHO, which can be detected by DESI-MS. Upon collision-induced dissociation (CID), the ion of m/z 121 gave rise to fragment ions m/z 93 and 94 by loss of $\text{CH}_2\text{N}^\cdot$ and HCN, respectively, confirming its structure. Furthermore,



Scheme 2. Reactions showing (a) the proposed methanol electro-oxidation process, (b) the derivatization reaction of HCHO with PhNHNH_2

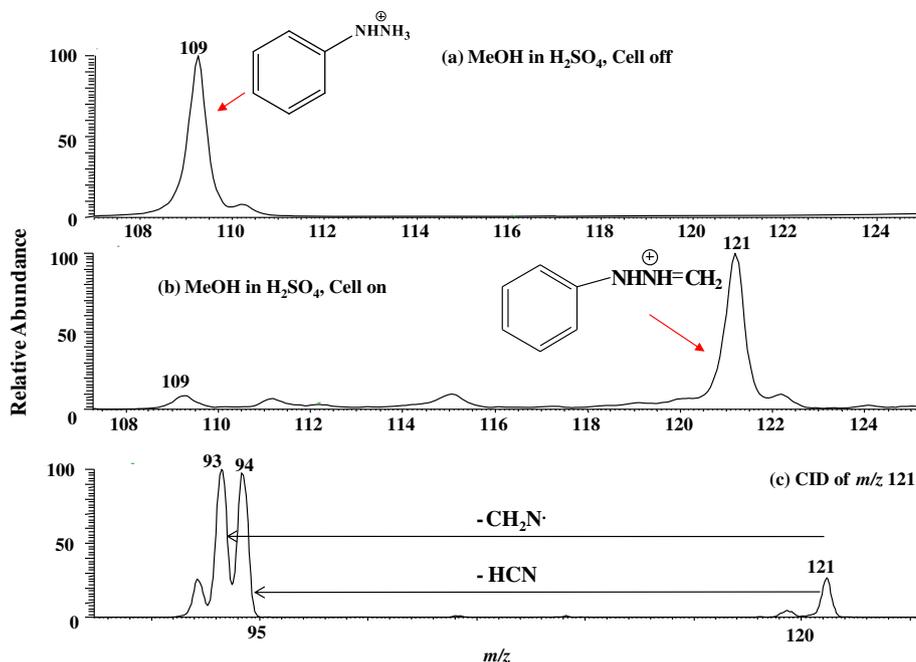


Fig. 1. DESI-MS spectra acquired when a solution of 0.5 M methanol in water containing 0.1 M sulfuric acid flowed through the fuel cell using the Pt electrode with an applied potential of (a) 0.0 V and (b) 2.0 V; (c) CID MS/MS spectrum of the product ion $\text{PhNHNH}^+=\text{CH}_2$ (m/z 121)

when methanol- ^{13}C was used to replace CH_3OH , the product ion $\text{PhNHNH}^+=^{13}\text{CH}_2$ of m/z 122 was observed with 1 Da mass shift (Figure 1S, Supporting Information), consistent with the product peak assignment. CID of m/z 122 shows the fragment ions m/z 93 and 94 by losses of $^{13}\text{CH}_2\text{N}^+$ and H^{13}CN , respectively, consistent with the assignment above. When CH_3OH was replaced by CD_3OD , the corresponding product ion $\text{PhNHNH}^+=\text{CD}_2$ of m/z 123 was also detected (Figure 2S, Supporting Information). Again, CID of m/z of 123 yields the fragment ions m/z 93 and 95 by loss of CD_2N^+ and DCN , respectively, further confirming the ion structure. In comparison to the previous reports of HCHO detection from methanol electrochemical oxidation in 0.1 M sulfuric acid using ESI-MS [4, 19], our method does not involve extra extraction steps. Therefore, the instrumentation is simplified and the analysis is faster.

In our experiment, the resulting sample solution contains high salt (ca. 50 mM Na_2SO_4), which could suppress ion signal for detection by traditional spray ionization methods. Indeed, when traditional ESI-MS was used for ionizing the sample solution, the protonated phenylhydrazine was hardly detected (Figure 3S-a, Supporting Information). In contrast, the peak was clearly observed by DESI (Fig. 1b) under similar experimental conditions, suggesting the high salt tolerance of DESI [37]. The absolute intensity of the peak of m/z 121 in ESI-MS spectrum (4500, manufacturer arbitrary unit) was much lower than that in the DESI-MS spectrum acquired on the same day using the same experimental conditions (4,400,000, manufacturer arbitrary unit, Figure 3S-b in Supporting Information). In this case, the time interval is about 1 min between the MS

detection of the HCHO signal and the start of the cell electrolysis, which is much shorter than 7 min time delay reported in the previous ESI-MS study [4, 19], owing to the need for extra extraction process.

Monitoring Methanol Electro-Oxidation in Alkaline Solution

Our DESI-MS also allows the monitoring of methanol electro-oxidation in an alkaline condition. To date, a majority of the work related to direct methanol fuel cells was conducted in acidic media while a few studies of methanol oxidation in alkaline solutions were reported [49–51]. There are several advantages of oxidizing methanol electrochemically at alkaline pH. First, it was shown that the methanol oxidation yield is higher in alkaline solution compared with that in acid media [49–51]. Second, better oxygen reduction kinetics in alkaline solution than in acidic environment was also found [20]. Third, an alkaline fuel cell provides a wide selection of possible electrocatalysts [20]. Owing to these existing advantages, it is necessary to develop an analytical method for monitoring methanol electro-oxidation in alkaline solution as well.

Figure 2 shows the result of the methanol oxidation in the alkaline condition; 0.5 M MeOH in 0.1 M KOH was introduced into the flow cell at a flow rate of 5 $\mu\text{L}/\text{min}$. Phenylhydrazine in 0.06 M sulfuric acid was introduced to derivatize the electrochemically generated HCHO (sulfuric acid was added to neutralize the medium to approximately pH 2). Without a potential applied on the cell, no protonated phenylhydrazine was observed (Fig. 2a). When a 2.0 V

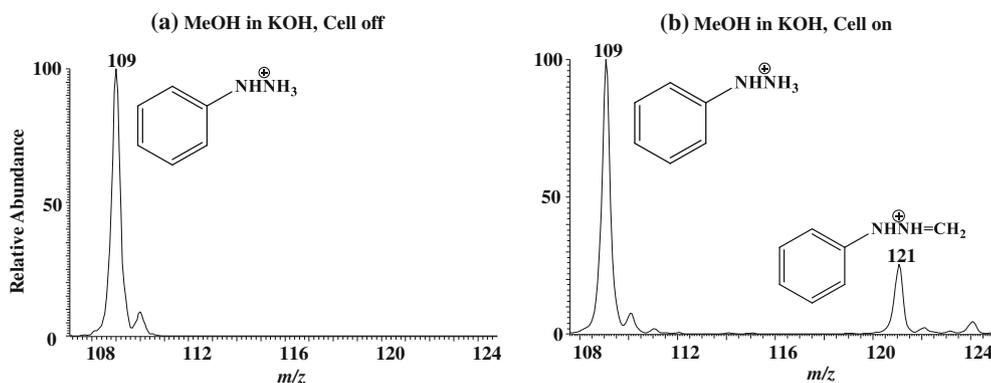


Fig. 2. DESI-MS spectra acquired when a solution of 0.5 M methanol in water containing 0.1 M KOH flowed through the fuel cell using the Pt electrode with an applied potential of (a) 0 V and (b) 2 V

potential was applied to the cell, a peak at m/z 121 corresponding to the protonated phenylhydrazone was clearly seen, indicating the formation of HCHO (Fig. 2b).

After successfully detecting HCHO from methanol electro-oxidation in alkaline pH, we also tested the detection of acetaldehyde from ethanol electro-oxidation in alkaline pH. It was proposed that $C_2H_5O^-$ is the reactive form of ethanol in alkaline solution and it is adsorbed to form ethoxy on the Pt surface. The adsorbed ethoxy then is oxidized to acetaldehyde [52]. Indeed, in our experiment, the acetaldehyde could be detected. Figure 3 shows the result of the ethanol oxidation in the alkaline condition; 0.5 M EtOH in 0.1 M KOH was introduced into the flow cell at a flow rate of 5 μ L/min. Phenylhydrazine in 0.06 M sulfuric acid was introduced to derivatize the electrochemically generated CH_3CHO . Without a potential applied to the cell, no derivatized product was observed (Fig. 3a).

When the cell was applied with a 2.5 V potential, a peak at m/z 135 corresponding to the protonated derivatization product was observed, indicating the formation of CH_3CHO (Fig. 3b). Upon CID, the ion of m/z 135 gave rise to fragment ions m/z 93, 94, 108, and 118 by loss of $CH_3CH=N^+$ and CH_3CN , $CH_2=CH^+$ and NH_3 respectively, confirming its structure. To the best of our knowledge, this result represents the detection of alcohol oxidation products at alkaline pH by MS for the first time.

Performance of Different Electrodes in Acidic and Alkaline Conditions

After identifying HCHO from electrochemical oxidation of methanol using Pt electrode in both acidic and alkaline conditions, other electrodes such as Au electrode and Pt/C (50/50) were also employed for comparison. The purpose of such an

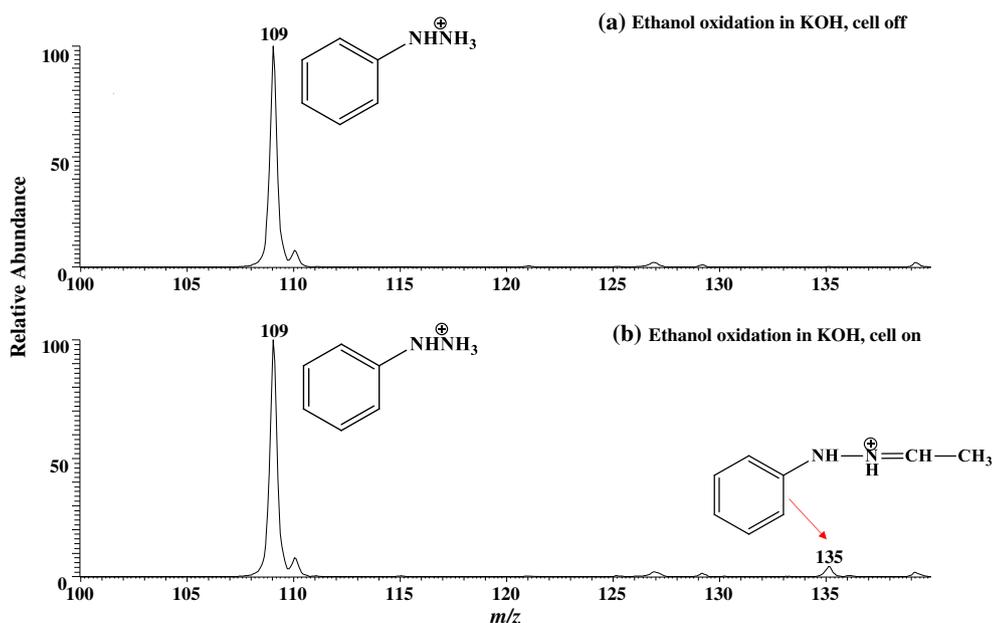


Fig. 3. DESI-MS spectra acquired when a solution of 0.5 M ethanol in water containing 0.1 M KOH flowed through the fuel cell using the Pt electrode with an applied potential of (a) 0 V and (b) 2.5 V

experiment is to evaluate the electrocatalytic performance of different electrodes for converting methanol into formaldehyde.

For quantification of HCHO generated from methanol electro-oxidation on different electrodes, a formaldehyde- ^{13}C solution was used as internal standard. For example, under acidic oxidation condition, 0.5 M MeOH in 0.1 M sulfuric acid was infused to the flow cell for electrolysis at 3 $\mu\text{L}/\text{min}$. 1.0 mM formaldehyde- ^{13}C in 0.1 M sulfuric acid was introduced via a Tee mixer at 3 $\mu\text{L}/\text{min}$ to mix with the oxidized methanol as it exited from the cell. The mixed solution was derivatized using phenylhydrazine in 0.18 M NaOH that was introduced via another Tee mixer at 6 $\mu\text{L}/\text{min}$. In this case, the electrochemically generated HCHO and the internal standard H^{13}CHO were detected at m/z 121 and 122, respectively. The amount of HCHO generated can be calculated based on the peak height ratio of m/z 121 to m/z 122 and the known quantity of the internal standard, in consideration that two formaldehyde products would have a similar ionization efficiency because of structural similarity. The method was also used for quantifying methanol electro-oxidation in alkaline solution (detailed procedure is described in SI).

Figure 4a shows the HCHO yields from three different electrodes under acidic condition. In general, the yields are very low (<1%). It is likely that an excess amount of methanol was used and the residence time for methanol in this electrochemical flow cell was short (ca. 5 s based on the flow rate and

the dead volume of the thin layer flow cell of 0.5 μL). Also, another possible factor for low oxidation yield is a result of the small electrode surface (the i.d. of the electrode disc used is only 8 mm). Indeed, when the concentration of the injected methanol was lowered to 0.1 M, a higher yield (4.4%) was obtained. Although the yield is low, the success of HCHO detection by DESI-MS reveals the high sensitivity of our method. For industrial fuel cells, the yield would be significantly higher because of the use of a larger electrode and longer electrolysis time [4, 53]. We would expect a good utility of our DESI-MS for real world analysis.

It can be seen from Fig. 4 that different electrodes have different yields. The Au electrode has the lowest yield for the formation of HCHO among three electrodes, whereas the oxidation efficiency of Pt and Pt/C (50/50) electrodes are comparable. This result is in line with a previous report that Au electrode is usually considered as a poor catalyst toward methanol oxidation in acidic condition [54]. It is probably because Au has relatively weaker chemisorption of methanol in acid than Pt or Pt-based catalysts [55]. Figure 4b shows the quantitative analysis result for methanol oxidation at alkaline pH. Interestingly, the yield of HCHO for MeOH oxidation for Au electrode is higher in alkaline solution than that in acidic condition, whereas Pt and Pt/C electrodes have relatively poorer yields of HCHO compared with those in acidic conditions, which is in line with the previous report [56]. It is likely that the Au electrode in the alkaline environment is strongly covered with

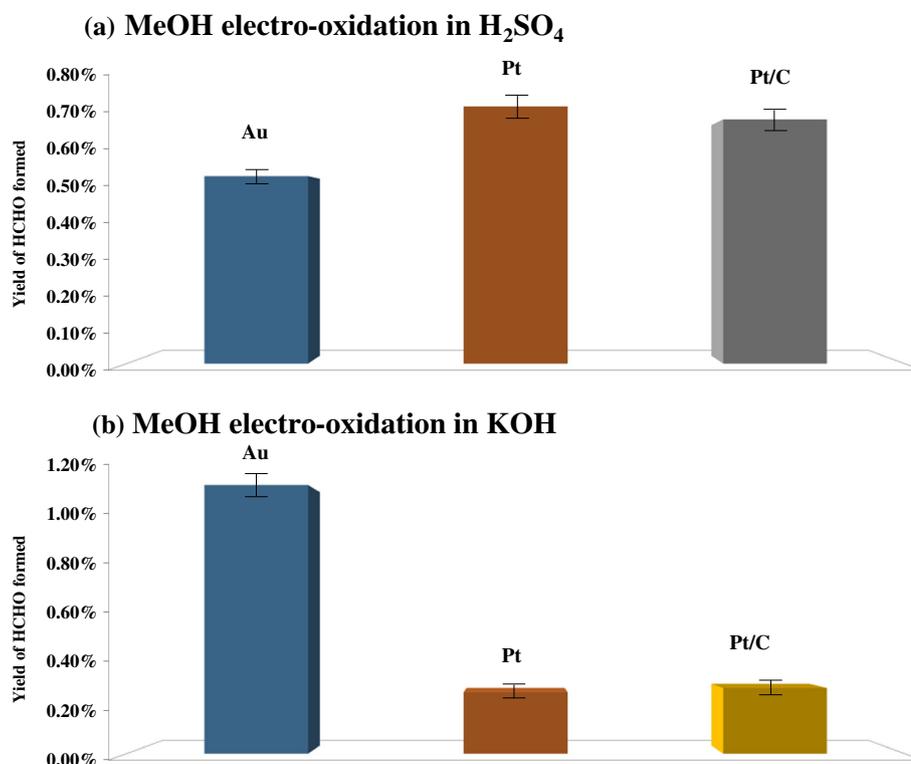


Fig. 4. Yields of HCHO generated from methanol electro-oxidation using different electrodes: (a) Au, Pt, and Pt/C (50/50) in acidic condition; (b) Au, Pt, and Pt/C (50/50) in alkaline condition

chemisorbed and partially hydrated OH^- ions. The adsorbed OH^- can be oxidized to form MOH (where the M means Au here), and MOH is oxidized further to produce MO [57]. The generation of the gold oxide [58] is an important property of Au electrodes, which plays a key role in enhancing the catalytic activity in alkaline solution [59]. These results shown above suggest that our findings for electrode oxidation efficiency are in good agreement with previous literature reports.

Conclusions

Analysis of HCHO generated from the methanol electro-oxidation reaction is traditionally difficult, and this study presents an ambient DESI-MS approach to tackle this challenge, for the first time. Our DESI-MS method is fast, has high salt tolerance, and involves simple instrumentation, which can be applicable for HCHO analysis from methanol electro-oxidation in both acidic and basic conditions. Conversion yields by different electrodes were evaluated and the results showed that platinum-based catalysts produced more HCHO in acidic condition than the Au catalyst, while the latter offered a higher yield over the platinum group catalysts in alkaline condition. The presented methodology would be valuable for elucidating fuel cell reaction mechanisms and for screening ideal fuel cell electrode materials.

A patent application was filed for the preliminary study of this work [60].

Acknowledgments

Q.W. thanks the Program of Study Abroad for Young Teachers by Agricultural University of Hebei. This work is supported by NSF Career (CHE-1149367), NSF IDBR (CHE-1455554), and Ohio University Technology Seed Fund (GR0017495.01.05).

References

1. Leuthold, L.A., Mandscheff, J.F., Fathi, M., Giroud, C., Augsburg, M., Varesio, E., Hopfgartner, G.: Desorption electrospray ionization mass spectrometry: direct toxicological screening and analysis of illicit ecstasy tablets. *Rapid Commun. Mass Spectrom.* **20**, 103–110 (2006)
2. Paul, D.R., Robeson, L.M.: Polymer nanotechnology: nanocomposites. *Polymer* **49**, 3187–3204 (2008)
3. Ota, K.I., Nakagawa, Y., Takahashi, M.: Reaction products of anodic oxidation of methanol in sulfuric acid solution. *J. Electroanal. Chem.* **179**, 179–184 (1984)
4. Zhao, W., Jusys, Z., Behm, R.J.: Quantitative online analysis of liquid-phase products of methanol oxidation in aqueous sulfuric acid solutions using electrospray ionization mass spectrometry. *Anal. Chem.* **82**, 2472–2479 (2010)
5. Iwasita-Vielstich, T.: Advances in Electrochemical Science and Engineering. **1**(3), 127–170 (2008)
6. Childers, C.L., Huang, H., Korzeniewski, C.: Formaldehyde yields from methanol electrochemical oxidation on carbon-supported platinum catalysts. *Langmuir* **15**, 786–789 (1999)
7. Wang, H., Rus, E., Abruña, H.D.: New double-band-electrode channel flow differential electrochemical mass spectrometry cell: application for detecting product formation during methanol electrooxidation. *Anal. Chem.* **82**, 4319–4324 (2010)
8. Liu, P., Lanekoff, I.T., Laskin, J., Dewald, H.D., Chen, H.: Study of electrochemical reactions using nanospray desorption electrospray ionization mass spectrometry. *Anal. Chem.* **84**, 5737–5743 (2012)
9. Bruckenstein, S., Gadde, R.R.: Use of a porous electrode for in situ mass spectrometric determination of volatile electrode reaction products. *J. Am. Chem. Soc.* **93**, 793–794 (1971)
10. Hambitzer, G., Heitbaum, J.: Electrochemical thermospray mass spectrometry. *Anal. Chem.* **58**, 1067–1070 (1986)
11. Diehl, G., Liesener, A., Karst, U.: Liquid chromatography with post-column electrochemical treatment and mass spectrometric detection of non-polar compounds. *Analyst* **126**, 288–290 (2001)
12. Bartmess, J.E., Phillips, L.R.: Electrochemically assisted fast atom bombardment mass spectrometry. *Anal. Chem.* **59**, 2012–2014 (1987)
13. Regino, M.C.S., Brajter-Toth, A.: An electrochemical cell for on-line electrochemistry/mass spectrometry. *Anal. Chem.* **69**, 5067–5072 (1997)
14. Kertesz, V., Van Berkel, G.J.: Surface-assisted reduction of aniline oligomers, N-phenyl-1,4-phenylenediamine and thionin in atmospheric pressure chemical ionization and atmospheric pressure photoionization. *J. Am. Soc. Mass Spectrom.* **13**, 109–117 (2002)
15. Zhou, F.M., Van Berkel, G.J.: Electrochemistry combined online with electrospray mass spectrometry. *Anal. Chem.* **67**, 3643–3649 (1995)
16. Brown, T.A., Chen, H., Zare, R.N.: Identification of fleeting electrochemical reaction intermediates using desorption electrospray ionization mass spectrometry. *J. Am. Chem. Soc.* **137**, 7274–7277 (2015)
17. Wolter, O., Heitbaum, J.: Differential electrochemical mass spectroscopy (DEMS)—a new method for the study of electrode processes. *Ber. Bunsenges. Phys. Chem.* **88**, 2–6 (1984)
18. Jusys, Z., Massong, H., Baltruschat, H.: A new approach for simultaneous DEMS and EQCM: electro-oxidation of adsorbed CO on Pt and Pt–Ru. *J. Electrochem. Soc.* **146**, 1093–1098 (1999)
19. Zhao, W., Jusys, Z., Behm, R.J.: Complete quantitative online analysis of methanol electrooxidation products via electron impact and electrospray ionization mass spectrometry. *Anal. Chem.* **84**, 5479–5483 (2012)
20. Verma, A., Basu, S.: Direct use of alcohols and sodium borohydride as fuel in an alkaline fuel cell. *J. Power Sources* **145**, 282–285 (2005)
21. Cooks, R.G., Ouyang, Z., Takats, Z., Wiseman, J.M.: Ambient mass spectrometry. *Science*, **311**, 1566–1570 (2006)
22. Takáts, Z., Wiseman, J.M., Gologan, B., Cooks, R.G.: Mass spectrometry sampling under ambient conditions with desorption electrospray ionization. *Science* **306**, 471–473 (2004)
23. Chen, H., Talaty, N., Takáts, Z., Cooks, G.R.: Desorption electrospray ionization mass spectrometry for high-throughput analysis of pharmaceutical samples in the ambient environment. *Anal. Chem.* **77**, 6915–6927 (2005)
24. Weston, D.J., Bateman, R., Wilson, I.D., Wood, T.R., Creaser, C.S.: Direct analysis of pharmaceutical drug formulations using ion mobility spectrometry/quadrupole-time-of-flight mass spectrometry combined with desorption electrospray ionization. *Anal. Chem.* **77**, 7572–7580 (2005)
25. Williams, J.P., Scrivens, J.H.: Rapid accurate mass desorption electrospray ionisation tandem mass spectrometry of pharmaceutical samples. *Rapid Commun. Mass Spectrom.* **19**, 3643–3650 (2005)
26. Shin, Y.-S., Drolet, B., Mayer, R., Dolence, K., Basile, F.: Desorption electrospray ionization-mass spectrometry of proteins. *Anal. Chem.* **79**, 3514–3518 (2007)
27. Jackson, A.U., Werner, S.R., Talaty, N., Song, Y., Campbell, K., Cooks, R.G.: Targeted metabolomic analysis of *Escherichia coli* by desorption electrospray ionization and extractive electrospray ionization mass spectrometry. *Anal. Biochem.* **375**, 272–281 (2008)
28. Talaty, N., Takats, Z., Cooks, R.G.: Rapid in situ detection of alkaloids in plant tissue under ambient conditions using desorption electrospray ionization. *Analyst* **130**, 1624–1633 (2005)
29. Wiseman, J.M., Ifa, D.R., Song, Q., Cooks, R.G.: Tissue imaging at atmospheric pressure using desorption electrospray ionization (DESI) mass spectrometry. *Angew. Chem. Int. Ed.* **45**, 7188 (2006)
30. Badu-Tawiah, A., Bland, C., Campbell, D.L., Cooks, R.G.: Non-aqueous spray solvents and solubility effects in desorption electrospray ionization. *J. Am. Soc. Mass Spectrom.* **21**, 572–579 (2010)
31. Zhang, S., Shin, Y.-S., Mayer, R., Basile, F.: On-probe pyrolysis desorption electrospray ionization (DESI) mass spectrometry for the analysis of non-volatile pyrolysis products. *J. Anal. Appl. Pyrol.* **80**, 353–359 (2007)
32. Miao, Z., Chen, H.: Proceedings of 56th ASMS Conference on Mass and Allied Topics. Denver, CO, June 1–5 (2008)
33. Chipuk, J.E., Brodbelt, J.S.: Transmission mode desorption electrospray ionization. *J. Am. Soc. Mass Spectrom.* **19**, 1612–1620 (2008)

34. Ma, X., Zhao, M., Lin, Z., Zhang, S., Yang, C., Zhang, X.: Versatile platform employing desorption electrospray ionization mass spectrometry for high-throughput analysis. *Anal. Chem.* **80**, 6131 (2008)
35. Ferguson, C.N., Benchaar, S.A., Miao, Z., Loo, J.A., Chen, H.: Direct ionization of large proteins and protein complexes by desorption electrospray ionization-mass spectrometry. *Anal. Chem.* **83**, 6468–6473 (2011)
36. Liu, Y., Miao, Z., Lakshmanan, R., Loo, R.R.O., Loo, J.A., Chen, H.: Signal and charge enhancement for protein analysis by liquid chromatography-mass spectrometry with desorption electrospray ionization. *Int. J. Mass Spectrom.* **325/327**, 161–166 (2012)
37. Miao, Z., Chen, H.: Direct analysis of liquid samples by desorption electrospray ionization-mass spectrometry (DESI-MS). *J. Am. Soc. Mass Spectrom.* **20**, 10–19 (2009)
38. Miao, Z., Chen, H., Liu, P., Liu, Y.: Development of submillisecond time-resolved mass spectrometry using desorption electrospray ionization. *Anal. Chem.* **83**, 3994–3997 (2011)
39. Miao, Z., Wu, S., Chen, H.: The study of protein conformation in solution via direct sampling by desorption electrospray ionization mass spectrometry. *J. Am. Soc. Mass Spectrom.* **21**, 1730–1736 (2010)
40. Sun, X., Miao, Z., Yuan, Z., Harrington, P.D.B., Colla, J., Chen, H.: Coupling of single droplet micro-extraction with desorption electrospray ionization-mass spectrometry. *Int. J. Mass Spectrom.* **301**, 102–108 (2011)
41. Basile, F., Zhang, S., Kandar, S.K., Lu, L.: Mass spectrometry characterization of the thermal decomposition/digestion (TDD) at cysteine in peptides and proteins in the condensed phase. *J. Am. Soc. Mass Spectrom.* **22**, 1926–1940 (2011)
42. Zhang, Y., Yuan, Z., Dewald, H.D., Chen, H.: Coupling of liquid chromatography with mass spectrometry by desorption electrospray ionization (DESI). *Chem. Commun.* **47**, 4171–4173 (2011)
43. Cai, Y., Adams, D., Chen, H.: A new splitting method for both analytical and preparative LC/MS. *J. Am. Soc. Mass Spectrom.* **25**, 286–292 (2014)
44. Cai, Y., Liu, Y., Helmy, R., Chen, H.: Coupling of ultrafast LC with mass spectrometry by DESI. *J. Am. Soc. Mass Spectrom.* **25**, 1820–1823 (2014)
45. Zheng, Q., Zhang, H., Tong, L., Wu, S., Chen, H.: Cross-linking electrochemical mass spectrometry for probing protein three-dimensional structures. *Anal. Chem.* **86**, 8983–8991 (2014)
46. King, R., Bonfiglio, R., Fernandez-Metzler, C., Miller-Stein, C., Olah, T.: Mechanistic investigation of ionization suppression in electrospray ionization. *J. Am. Soc. Mass Spectrom.* **11**, 942–950 (2000)
47. Iwasita, T.: Electrocatalysis of methanol oxidation. *Electrochim. Acta* **47**, 3663–3674 (2002)
48. Lamy, C., Coutanceau, C.: Electrocatalysis of alcohol oxidation reactions at platinum group metals. *Royal. Soc. Chem.* **1**, 1–70 (2012)
49. Hao Yu, E., Scott, K., Reeve, R.W.: A study of the anodic oxidation of methanol on Pt in alkaline solutions. *J. Electroanal. Chem.* **547**, 17–24 (2003)
50. Schmidt, T.J., Ross, P.N., Markovic, N.M.: Temperature-dependent surface electrochemistry on Pt single crystals in alkaline electrolyte: part 1. CO oxidation. *J. Phys. Chem. B* **105**, 12082–12086 (2001)
51. Shi-Gang, S., Ai-Cheng, C.: In situ FTIRS features during oxygen adsorption and carbon monoxide oxidation at a platinum electrode in dilute alkaline solutions. *J. Electroanal. Chem.* **323**, 319–328 (1992)
52. Lai, S.C.S., Kleijn, S.E.F., Öztürk, F.T.Z., van Rees Vellinga, V.C., Koning, J., Rodriguez, P.: Effects of electrolyte pH and composition on the ethanol electro-oxidation reaction. *Catal. Today* **154**, 92–104 (2010)
53. Korzeniewski, C., Childers, C.L.: Formaldehyde yields from methanol electrochemical oxidation on platinum. *J. Phys. Chem. B* **102**, 489–492 (1998)
54. Hammer, B., Norskov, J.K.: Why gold is the noblest of all the metals. *Nature* **376**, 238–240 (1995)
55. Hamnett, A.: Mechanism and electrocatalysis in the direct methanol fuel cell. *Catal. Today* **38**, 445–457 (1997)
56. Buck, R.P., Griffith, L.R.: Voltammetric and chronopotentiometric study of the anodic oxidation of methanol, formaldehyde, and formic acid. *J. Electrochem. Soc.* **109**, 1005–1013 (1962)
57. Chen, A., Lipkowski, J.: Electrochemical and spectroscopic studies of hydroxide adsorption at the Au(111) electrode. *J. Phys. Chem. B* **103**, 682–691 (1999)
58. Zhang, J., Liu, P., Ma, H., Ding, Y.: Nanostructured porous gold for methanol electro-oxidation. *J. Phys. Chem. C* **111**, 10382–10388 (2007)
59. Burke, L.D., Nugent, P.F.: The electrochemistry of gold: II. the electrocatalytic behaviour of the metal in aqueous media. *Gold Bull.* **31**, 39–50 (2008)
60. Chen, H., Pan, N., Dewald, H.: Online monitoring of fuel cell reactions by desorption electrospray mass spectrometry (2012) Patent Applic. WO2014074699, Pending