

# Complete Quantitative Online Analysis of Methanol Electrooxidation Products via Electron Impact and Electrospray Ionization Mass Spectrometry

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**ABSTRACT:** We report on a novel approach for complete quantitative online product analysis in electrocatalytic reactions, combining electron impact ionization mass spectrometry (EI-MS) and electrospray ionization mass spectrometry (ESI-MS) for simultaneous detection of both volatile and nonvolatile reaction products. The potential of this method is demonstrated using continuous methanol oxidation in a flow cell. The overall reaction rate was followed via the Faradaic current; CO<sub>2</sub> formation was monitored mass



spectrometrically via a membrane inlet system, and formaldehyde and formic acid were detected by ESI-MS after a derivatization–extraction–separation procedure introduced recently (Zhao, W.; Jusys, Z.; Behm, R. J. Anal. Chem. 2010, 82, 2472–2479) providing quantitative data on the product distribution. In a more general sense, this approach is applicable for a wide range of reactions at the solid–liquid interface or in liquid phase.

The oxidative conversion of organic fuels into electric energy in direct oxidation fuel cells such as direct methanol fuel cells (DMFCs) or direct ethanol fuel cells (DEFCs) is a promising route in sustainable energy concepts, with potential applications in various areas.<sup>1,2</sup> A major problem in the realization of these technologies is the fact that these reactions may lead to a number of volatile and nonvolatile incomplete oxidation reaction intermediates, in addition to the stable final product CO<sub>2</sub>. Part of these products is highly toxic, such as formaldehyde or acetaldehyde, and therefore, the formation of these side products should be minimized. In addition, their formation lowers the efficiency of the energy conversion process significantly. Therefore, the complete, quantitative analysis of the reaction products in these electrocatalytic reactions, possibly online during the reaction, has been a key issue in electrochemistry over the last decades.

A common method used for such kind of analysis, differential electrochemical mass spectrometry (DEMS),<sup>3–5</sup> has been highly successful for the identification and quantitative product analysis in "simple" reactions such as CO oxidation, involving few and highly volatile products only,<sup>3</sup> but is quickly limited in its applicability for more complex reactions, due to the low volatility of some reaction products and their fragmentation upon electron impact ionization. Recently, DEMS has been coupled with an additional detection electrode, allowing one to detect also reactive nonvolatile species, though one cannot distinguish between different species.<sup>6</sup> Analysis by chromatographic,<sup>7</sup> spectroscopic,<sup>8–10</sup> and analytical techniques,<sup>11–13</sup> where these restrictions are absent, was either applicable only for part of the reaction products or could not be used online, for real time analysis.

In the present contribution, we describe a novel approach for the complete quantitative real time online analysis of continuous methanol oxidation in a flow cell, involving the combination of electrospray ionization mass spectrometry (ESI-MS) for the analysis of nonvolatile (ESI-MS) and electron impact mass spectrometry (EI-MS) for volatile reaction products.

ESI-MS is an excellent technique for the direct detection of complex liquid phase products of electrochemical reactions,<sup>14,15</sup> since the soft ionization mode avoids fragmentation of the product molecules. Its application for fuel cell related electrocatalysis research, however, was not possible so far due to the high acidity of the supporting electrolyte (ion suppression and instrument corrosion) and due to the adsorption/reaction of the nonaqueous solvents commonly used for electrochemical ESI-MS with the noble metal electrodes. In addition, aldehydes (one of the products in the oxidation of alcohols) have a very low ionization probability in ESI-MS. Recently, we developed a system for continuous derivatization-extraction, which allowed us to extract organic molecules into a mineral acid free organic phase and applied it for the quantitative detection of formic acid and formaldehyde in a highly acidic supporting electrolyte by ESI-MS.<sup>16</sup> In that case, the analyte was offline collected in separate methanol electrochemical oxidation experiments and later injected into the online derivatization-extraction-separation system to be detected by ESI-MS. In the present study, we went a decisive step forward, connecting this setup with an electrochemical cell for online analysis of the methanol oxidation products, during continuous reaction, and combining it with EI-MS via a membrane inlet. In previous DEMS experiments, the formation of formic acid was followed by the production of methylformate, and formaldehyde formation was calculated assuming

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**Figure 1.** Schematic drawing of the combined setup for online analysis of gaseous and nonvolatile reaction products, using electron impact ionization mass spectrometry via a membrane inlet in a thin-layer electrochemical (EC) flow cell and electrospray ionization mass spectrometry for the simultaneous quantitative detection of the methanol electrooxidation products in a single experiment.

that formaldehyde, formic acid, and  $\rm CO_2$  are the only reaction products. Though plausible, the latter assumption has never been proven quantitatively in an online experiment.<sup>18–20</sup> In the present study, we established a combination of the two methods (DEMS and ESI-MS) for the quantitative online analysis of both gas phase and liquid phase products in a continuous electrocatalytic reaction,<sup>17</sup> giving direct quantitative access to the volatile and soluble reaction products of the methanol oxidation reaction.

## EXPERIMENTAL SECTION

Continuous electrooxidation of methanol at different constant potentials was performed over a commercial carbon-supported Pt/C catalyst (E-Tek, Inc.) in methanol containing sulfuric acid solution, which was fed into a dual thin-layer electrochemical flow cell. A schematic drawing of the combined setup for the online quantitative analysis of the methanol electrooxidation reaction products, employing a combination of EI-MS and ESI-MS for simultaneous detection of both volatile and nonvolatile species, is depicted in Figure 1. The flow cell was interfaced to an EI-MS setup via a membrane inlet system. The outlet of the flow cell was linked to the analyte pretreatment system for sequential derivatization-extraction-separation of nonvolatile components, which in turn was connected to the ESI-MS. In this configuration, the overall methanol oxidation reaction rate was monitored via the Faradaic current, and CO<sub>2</sub> formation was followed by EI-MS via the membrane inlet system, while formaldehyde and formic acid were both detected after online extraction into an immiscible organic phase by ESI-MS.

**Electrode Preparation and Electrochemical Measurements.** The thin-film Pt/Vulcan (E-TEK, Inc.) electrode was prepared on a mirror-polished glassy carbon disk (Sigradur G, Hochtemperatur Werkstoffe GmbH, Germany) by sequential pipetting/drying of 20  $\mu$ L of an aqueous Pt/Vulcan (20 wt % Pt) suspension and aqueous Nafion solution,<sup>19,20</sup> resulting in a catalyst film of 6 mm in diameter with a platinum loading of 28  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>. The electrode was mounted in the thin-layer DEMS flow cell,<sup>21</sup> so that the catalyst film was exposed to the solution within a centered circular tightener (inner diameter of 6 mm, ca. 50  $\mu$ m thick), forming a thin electrolyte layer of ca. 5  $\mu$ L of volume on the electrode. Two Pt counter electrodes interconnected via the external resistance were used. A saturated calomel electrode (SCE) connected to the outlet of the DEMS cell by a Teflon capillary served as reference electrode. All potentials, however, are quoted against that of the reversible hydrogen electrode (RHE).

Deaerated electrolyte (0.1 M methanol in 0.5 M sulfuric acid) was introduced into the thin-layer electrochemical (EC, Figure 1) flow cell using a gastight glass syringe (Harward Apparatus) operated by a syringe pump (see Figure 1). The electrolyte and products formed at the electrode were transported to the second thin-layer compartment, which is interfaced to the mass spectrometer via a porous membrane (Scimat, 60  $\mu$ m thick, 50% porosity, 0.2  $\mu$ m pore diameter).<sup>21</sup>

**Quantitative Detection of Volatile Reaction Products via EI-MS.** The online mass spectrometry setup for gaseous/ volatile product analysis was described in detail elsewhere.<sup>19,20</sup> It consists of a differentially pumped two-chamber system with a Balzers QMS 112 quadrupole mass spectrometer, a Pine Instruments potentiostat, and a computerized data acquisition system.

For the quantitative detection of carbon dioxide, the mass spectrometer setup was calibrated in separate experiments via potential-step electro-oxidation of formic acid, using the same flow rate to ensure an identical collection efficiency of the membrane inlet in the calibration experiments. The sensitivity factor K\* was determined in these calibration experiments as the ratio of mass spectrometric current (charge), multiplied by two (number of electrons in oxidation of formic acid molecule to  $CO_2$ ), and the Faradaic current (charge). Using the same proportionality, the ion current (charge) was converted into partial current for methanol oxidation to  $CO_2$  by accounting for a release of six electrons per one molecule.

Quantitative Detection of Nonvolatile Reaction Products via ESI-MS. The out-flowing electrolyte at the outlet of the cell is mixed in a T connector (Upchurch Scientific) with a saturated 2,4-DNPH solution in 0.5 M sulfuric acid, which is delivered from a separate syringe pump, for the derivatization of formaldehyde to form 2,4-dinitrophenyl hydrazone in a subsequent capillary.<sup>19</sup> After derivatization, the streams of the aqueous reaction mixture and an organic extraction phase (isobutylacetate) are guided against each other to meet in the next T connector. Due to the immiscibility of the phases and their equal flow rates (0.05 mL min<sup>-1</sup>), small and rather regular separate segments of the individual phases are formed and pass through a Teflon capillary (see magnified sketch in Figure 1). This enables an efficient extraction (ca.  $25\%^{19}$ ) of the organic molecules from the aqueous phase into the organic phase at the liquid–liquid phase interface due to the high ratio of the contact area between the phases and their volume. (Note that the esterification reaction of methanol and formic acid occurs in acid solution, with an equilibrium concentration of the resulting methylformate of ~10% of that of formic acid. During extraction, the hydrolysis of the ester prevails, allowing the ester to decompose and thus to extract formic acid into the organic phase.)

Separation of the two phases is achieved in a third Tconnector. After extraction and phase separation, only a mineral acid-free organic phase is guided via a capillary to the injection needle of the ESI-MS. The potentiostat, syringe pumps, and other peripheral devices are connected to the power lines via an isolation transformer (Tufvassons).

The flow rates of both inlet and derivatization syringes (0.05 mL min<sup>-1</sup>) are controlled by a common multisyringe pump (Harward PHD 2000), whereas the organic phase for extraction (isobutylacetate) and the mobile phase (pure water) are driven by separate syringe pumps (Harward 11Plus) at flow rates of 0.1 and 0.2 mL min<sup>-1</sup>, respectively (for details, see ref 16). Special care was taken to avoid possible back-diffusion of the analyte from the derivatization loop back into the cell via the outflow capillary, by optimizing the diameter and the length of the outflow and derivatization capillaries. (Note that the calibration was performed using the same flow cell with a bare glassy carbon substrate at an open-circuit and the same capillary network as for the measurements.) For the ESI-MS measurements, the electrospray ionization mass spectrometer (Varian, Inc., model 1200 L) was used in the negative ion mode (detector voltage, 1 kV; needle voltage, -4.5 kV; needle current, ca.  $-17 \ \mu\text{A}$ ; the ESI chamber at 50 °C and the nebulizing gas at 350 °C (20 psi)), since (i) both analyte molecules, formic acid and the derivatized product of formaldehyde (2,4-dinitrophenyl hydrazone), have functional groups that readily lose a proton and since (ii) this allows one to avoid oxidation of the analyte during the electrospray process possible at the positive ion mode. These settings were used both in the experiments and in calibration measurements, in which the mixtures of methanol with formaldehyde and formic acid at known concentrations were analyzed after passing via the same derivatization-extraction-separation network. This way, we can avoid that possible electrochemical reaction in the ESI source, such as the reduction of dinitrophenyl-hydrazone in the negative ion ESI mode, affecting the quantification of the reaction products. The analyte was periodically injected manually into the ESI-MS employing a Rheodyne 6-port valve, first sampling an aliquot (5  $\mu$ L) from the continuously flowing organic phase into the sample loop and then injecting these 5  $\mu$ L of the analyte from the sample loop into the continuously flowing mobile phase (pure water). The Rheodyne 6-port valve and the connection to the PEEK capillary leading to the ESI source were electrically grounded. The choice of water as mobile phase was based on the low resulting background signal, significantly lower than, e.g., that observed for acetonitrile or water-methanol mixtures, and its immiscibility with the organic phase (isobutyl acetate). Because of the considerable loss of reaction products during extraction and derivatization processes, addition of acetonitrile to the mobile phase to reduce the water induced ion

suppression is not favorable since it further reduces the analyte concentration, especially when the methanol oxidation reaction is performed at low potential with low product concentrations. The mass spectrometric m/z 45 signal was monitored for formic acid detection, and 2,4-dinitrophenyl hydrazone was detected at the m/z 208.7 signal (single ion mode). The presence of sulfuric acid in the organic phase was routinely checked at m/z 97. The signals were quantified by integrating the area of the corresponding mass spectrometric peaks using the software provided by Varian Inc..

## RESULTS AND DISCUSSION

Figure 2a,b presents the Faradaic current (a) and the mass spectrometric (b) m/z 44 ion current transients upon stepping the working electrode potential from 0.06 to 0.65 V<sub>RHE</sub> (vs the Reversible Hydrogen Electrode, RHE) for 10 min and then stepping back to the initial potential. Figure 2c,d depicts the corresponding ESI-MS time responses for the mass signals of



**Figure 2.** Simultaneously measured response upon stepping the working electrode potential from 0.06 V (at 1 min) to 0.65 V (RHE) for 10 min and back to the initial potential. Faradaic current (a); m/z 44 ion current (b) transients; time response for the mass spectrometric signals of formic acid at m/z 45 (c); and derivatized formaldehyde at m/z 208.7 (d). Pt/C catalyst loading: 28  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>; solution: 0.1 M methanol in 0.5 M sulfuric acid; room temperature.

formic acid at m/z 45 (c) and derivatized formaldehyde (d) at m/z 208.7. The CO<sub>2</sub> ion current exhibits a 12–13 s delay in the response of the reaction products due to the time required for transporting the electrolyte into the second compartment of the thin-layer cell containing the membrane inlet.

For the ESI-MS signals, the time delay is significantly longer, with around 7 min until the reaction products reach the ESI-MS and an additional few minutes until the signals reach stable values. This time delay (7 min) reflects the residence time in the derivatization and extraction capillaries and the subsequent time required for the analyte in the organic phase to reach the ESI-MS ionization chamber. Steady-state values are reached around 12 min after the initial potential step and remain constant for ca. 5 min for a potential step duration of 10 min. The product concentrations were determined from the averaged peak intensities during these 5 min by standard calibration (see ref 15). At the reverse potential step, back to the initial value, the time required for the ESI-MS signals to reach the background level is slightly longer (Figure 2b), which we attribute to a combination of slow diffusive release of trapped product molecules from small gaps in the interconnects between the capillaries and release of residual product molecules in the ESI chamber.<sup>16</sup> The considerable time for the signal to reach its steady-state value ( $\sim 5$  min, see Figure 2c,d) is caused by a diffusive broadening of the initial step profile in the product concentration during the transport from the flow cell to the 6-port valve. To be compatible with the ESI-MS intensities and to correct for the small decrease in the Faradaic current and m/z 44 ion current signals during the 10 min at elevated potential, we used average values, averaged over these 10 min.

Analogous experiments were performed for a number of different constant electrode potentials between 0.45 and 1.0  $V_{RHE}$ , holding the respective potential for 10 min each time. After that, the potential was stepped back to 0.06  $V_{RHE}$  and held there for at least 10 min to return to the background intensities of the ESI-MS signals. For lower and higher potentials the methanol electrooxidation rates are rather low, with conversions below the detection limits.<sup>16</sup> Furthermore, at potentials above 1.0  $V_{RHE}$ , electrooxidation of the carbon support to CO<sub>2</sub> contributes increasingly to the apparent product distribution. The results obtained for the activity and product distribution in the methanol oxidation reaction at different electrode potentials, in the above potential window, are summarized in Figure 3.

Figure 3a displays the measured (net) Faradaic current, the partial currents for CO<sub>2</sub>, formic acid, and formaldehyde formation, and the sum of the partial currents during potentiostatic oxidation of methanol over the Pt/C catalyst at the different potentials. The partial currents were determined by converting the corresponding mass spectrometric signals into Faradaic currents using appropriate calibration constants (see Experimental Section) and the number of electrons for the formation of CO<sub>2</sub>, formic acid, and formaldehyde molecule of 6, 4, or 2 electrons per molecule, respectively. Both the overall and partial reaction currents show that measurable methanol oxidation starts at about 0.5 V<sub>RHE</sub>, passes through a maximum at ca. 0.7  $V_{RHE}$ , and decays to negligible rates at ca. 1.0  $V_{RHE}$ . The low methanol oxidation rates at lower potentials are due to surface poisoning of the catalyst by CO<sub>ad</sub>, which results from the dissociative adsorption of methanol, whereas at high potentials oxygen/OH adsorption and Pt oxide formation increasingly inhibit the reaction.<sup>18</sup> Considering the tacit



**Figure 3.** Activity and selectivity of the methanol electrooxidation reaction over a Pt/C catalyst at different constant electrode potentials. (a) Measured (net) Faradaic current, partial currents for methanol oxidation to the corresponding products (see figure), and the sum of the partial reaction currents; b) formation rates (in nanomoles per second) for the individual reaction products and the total methanol oxidation rate (methanol consumption).

assumption in previous studies that the only products during continuous methanol oxidation are  $CO_2$ , formaldehyde, and formic acid,<sup>20</sup> it is important to note that the sum of partial currents agrees perfectly with the measured Faradaic net current (Figure 3a). This also confirms the validity of the previous assumption that only these three products are formed during methanol electrooxidation and also the correctness of the quantitative evaluation procedure employed in this work.

The current efficiencies for methanol oxidation products in the potential region from 0.65 to 0.80 V<sub>RHE</sub> are 70  $\pm$  5% for CO<sub>2</sub>, 10  $\pm$  1% for formic acid, and 20  $\pm$  2% for formaldehyde, respectively. The data of Figure 3a agree well with previous data obtained on a similar catalyst for methanol oxidation in potentiodynamic measurements<sup>20</sup> and in constant potential oxidation at 0.6 V<sub>RHE</sub> at different catalyst loadings,<sup>19</sup> employing online DEMS with a membrane inlet. In those measurements, the production of formaldehyde was not measured directly but calculated from the difference of the measured Faradaic current and the sum of the partial currents for CO<sub>2</sub> and formic acid formation. In that case, we had to assume that only these three components are formed during reaction, which can be proven in the present measurements. The absolute steady-state rates for the formation of the different methanol oxidation products at different constant potentials, at present catalyst loading and flow rate, are shown in Figure 3b. In the same potential region, from 0.65 to 0.80 V<sub>RHE</sub>, CO<sub>2</sub> formation accounts for about half of the overall reaction products, while methanol conversion to formic acid and formaldehyde is only a quarter of the overall amount (or half of that for CO<sub>2</sub> formation), with product yields of  $53 \pm 5\%$  for CO<sub>2</sub>,  $23 \pm 2\%$  for formic acid, and  $24 \pm 2\%$  for formaldehyde formation.

Ongoing work on the product analysis of a much more complex reaction, on the continuous oxidation of ethylene glycol (ethylene glycol fuel cells<sup>22</sup>) with a large number of incomplete oxidation products, underlines the potential of this analysis scheme for studies of fuel cell relevant organic molecule oxidation reactions. In addition to applications in energy related electrocatalysis, this approach is applicable for product analysis of various other reactions at the solid–liquid interface and equally for analysis of homogeneous reactions in a liquid phase, as well as for the detection and quantitative analysis of gaseous/volatile and liquid phase species for the environmental issues.

## CONCLUSIONS

In conclusion, we have presented a novel approach for online analysis of the reaction products in continuous electrocatalytic reactions such as organic molecule oxidation, which allows for the first time to quantitatively detect all reaction products, in this case of the methanol oxidation reaction, simultaneously. It combines electron impact ionization mass spectrometry, via a membrane inlet system, for detection of gaseous reaction products, and electrospray ionization mass spectrometry for simultaneous quantitative detection of nonvolatile reaction products. The potential of that method was demonstrated for continuous methanol oxidation over a carbon supported Pt/C catalyst. The sum of the partial currents for CO<sub>2</sub>, formic acid, and formaldehyde formation was found to agree perfectly with the measured Faradaic current, confirming the previous assumption that these are the only products formed during continuous methanol electrooxidation. The current efficiencies and product yields were determined at different potentials between 0.45 and 1.0  $V_{RHE}$ , revealing that in the range of highest activities (0.65-0.80 V<sub>RHE</sub>) CO<sub>2</sub> formation prevails with about 50% product yield, while formaldehyde and formic acid formation each contribute about 25%. The potential of this analysis approach for energy related electrocatalysis and product detection in liquid phase reactions, both at the solid-liquid interface and in the homogeneous liquids, was outlined.

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#### Notes

The authors declare no competing financial interest.

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