



# The kinetics of methanol oxidation at a Pt film electrode, a combined mass and infrared spectroscopic study



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## ABSTRACT

The methanol oxidation reaction (MOR) at a Pt film electrode was investigated by combined differential electrochemical mass spectrometry (DEMS) and electrochemical in-situ FTIR spectroscopy in an attenuated-total-reflection configuration (EC-ATR-FTIRS). The combination of DEMS and EC-ATR-FTIRS enables simultaneous measurement of the total amount of CO<sub>2</sub> generated by every methanol oxidation pathway and the amount of adsorbed CO that is oxidized to CO<sub>2</sub> via the indirect pathway. The kinetics of methanol dehydrogenation to CO and CO oxidation to CO<sub>2</sub> were analyzed based on the change of the IR signal of adsorbed CO by switching between <sup>12</sup>CH<sub>3</sub>OH and <sup>13</sup>CH<sub>3</sub>OH-containing solutions while maintaining constant potential. The rate constants of CO oxidation to CO<sub>2</sub> ( $k_{ox}$ ) were obtained from the decay of the IR band of the preadsorbed isotope, and the relative rates of the other two pathways of methanol oxidation were derived from  $k_{ox}$  and the CO<sub>2</sub> generation efficiency obtained by DEMS. The present results reveal that with the increase of the potential from 0.6 to 0.75 V, i) faradic current increases ca. 5 times while the current efficiency for CO<sub>2</sub> production decreases from 25% to 8%; ii) the contribution of CO<sub>ad</sub> pathway to CO<sub>2</sub> production decreases from 33% to 18%; iii) a significant amount of CO<sub>2</sub> is produced through the non-CO<sub>ad</sub> pathway, and even at potentials >0.6 V a significant amount of HCHO is produced.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) show great potential as energy devices for portable electronics and automobiles because of the high energy density and easy storage and transport of methanol [1–10]. However, the slow kinetics of the methanol oxidation reaction (MOR) remains one of the major challenges for DMFCs. In order to understand the mechanism and the key factors that limit MOR kinetics, extensive studies on MOR have been carried out. Pt is well-recognized as the best monometallic catalyst for MOR [11–31]. At a Pt electrode, methanol can either be completely oxidized to CO<sub>2</sub> or be incompletely oxidized to side-products such as HCHO, HCOOH and CO<sub>ad</sub> [17–19,24,25,27]. Vibrational spectroscopic studies demonstrate that CO<sub>ad</sub> is the most stable surface adsorbate among all other methanolic fragments, and it leads to the deactivation of the Pt surface at low potentials ( $E \leq 0.5$  V vs. RHE) and at temperatures below 60 °C [20,24,32].

A dual path mechanism, with a direct and an indirect path is proposed for the complete oxidation of methanol to CO<sub>2</sub>. The indirect path proceeds via the formation of CO<sub>ad</sub> through a series of dehydrogenation steps and subsequent CO<sub>ad</sub> oxidation to CO<sub>2</sub>, while the direct

path is believed to go either through non-CO<sub>ad</sub> adsorbates or through soluble side-products like HCHO or HCOOH [17–19]. Quantitative information on the different pathways in MOR kinetics is of great importance in determining the key factors that limit its reaction kinetics and understanding its structure-activity relationship [33–35]. However, the relative amount of CO<sub>2</sub> generated by each of the two pathways remains unknown. The current efficiency for CO<sub>2</sub> production from MOR has been quantitatively determined by differential electrochemical mass spectrometry (DEMS), but DEMS provides no information on the pathway by which CO<sub>2</sub> is produced from CH<sub>3</sub>OH [36,37]. The kinetics of methanol dehydrogenation to CO<sub>ad</sub> and CO<sub>ad</sub> oxidation have been obtained from electrochemical in-situ FTIR spectroscopic studies under an attenuated-total-reflection configuration (EC-ATR-FTIRS) [38].

In EC-ATR-FTIRS, the incident infrared light approaches (and the reflected IR light leaves) the thin film working electrode/electrolyte interface through an optical prism. Hence a thick electrolyte layer is possible, and rapid mass transfer to and from the electrode surface can therefore be ensured. The shallow penetration depth of the evanescent wave (typically a few hundred nanometers) ensures that only molecules adsorbed to the surface or near it will be detected [31,39]. Compared with the ATR mode, conventional infrared absorption spectroscopy (IRS) under an external reflection configuration has the advantage of being applicable to single crystal and polycrystalline

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electrodes, but it suffers from poor mass transfer and high ohmic resistance, as the electrode surface should be pushed very close ( $<10\ \mu\text{m}$ ) to the IR window to diminish IR absorption by the solvent. Such problems also happen in transmission-based IR measurement, as it requires the electrolyte channel at the electrode to be very narrow ( $<10\ \mu\text{m}$ ). Thus, EC-ATR-FTIRS is more appropriate for studying fast electrocatalytic reactions that involve fast mass transport, surface adsorption and desorption. However, EC-ATR-FTIRS cannot provide information on how much  $\text{CO}_2$  is produced during MOR. Combining EC-ATR-FTIRS with DEMS can overcome the limitations of the individual experiments [40–42] by providing quantitative information on the  $\text{CO}_2$  production rate and the contribution of the indirect,  $\text{CO}_{\text{ad}}$  pathways to the complete oxidation of methanol to  $\text{CO}_2$  under exactly the same reaction conditions.

In this paper we demonstrate the use of EC-ATR-FTIRS combined with DEMS to obtain the kinetics of methanol dehydrogenation to  $\text{CO}_{\text{ad}}$ ,  $\text{CO}_{\text{ad}}$  oxidation, and total  $\text{CO}_2$  production for the MOR under potentiostatic conditions. The kinetics of  $\text{CO}_{\text{ad}}$  oxidation were monitored using the isotopic tracer method, in which an adlayer of one CO isotope is prepared on the electrode by oxidation of isotopically-labeled  $\text{CH}_3\text{OH}$ , and the solution is switched between  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{12}\text{CH}_3\text{OH}$  and  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{13}\text{CH}_3\text{OH}$ , during the potentiostatic measurements, so that the IR signal of the  $\text{CO}_{\text{ad}}$  being desorbed has a different frequency from that of CO being adsorbed. We found that from 0.6 to 0.75 V, i) the faradaic current for methanol oxidation increases 5 times, while the current efficiency for  $\text{CO}_2$  production decreases from 25% to 8%; ii) the contribution of  $\text{CO}_{\text{ad}}$  pathway to  $\text{CO}_2$  production decreases from 33% to 18%. Mechanistic and kinetic implication of present results toward MOR will be discussed.

## 2. Experimental

Millipore Milli-Q water and sulfuric acid (suprapure, Merck) were used to prepare  $0.5\ \text{M}\ \text{H}_2\text{SO}_4$ , which was used as the supporting electrolyte. Before the calibration measurement for the  $\text{CO}_2$  mass signal, the supporting electrolyte was first purged with  $\text{N}_2$  (N5.0, Linde China) for 10 min and then bubbled with CO (N 4.7, Linde, China) for ca. 15 min. Then CO stripping was carried out by cyclic voltammetry and both the Faradaic current and the mass signal for  $\text{CO}_2$  are recorded as a function of applied potential.  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{12}\text{CH}_3\text{OH}$  and  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{13}\text{CH}_3\text{OH}$  were prepared using  $\text{CH}_3\text{OH}$  or  $^{13}\text{C}$ -labeled  $\text{CH}_3\text{OH}$  (99%, for analysis) from Sigma Aldrich. Before the measurements, both the supporting electrolyte and the methanol containing solution were purged with  $\text{N}_2$  for 15 min and continuously purged with  $\text{N}_2$  during the measurements.

A dual thin-layer spectro-electrochemical flow-cell made of Kel-F was used for the combined DEMS and EC-ATR-FTIRS measurements (Fig. 1) [7,41–44]. The electrochemical reaction, IR signal detection, and the subsequent mass sample introduction take place in two separate thin-layer compartments, respectively. Capillaries connect the solution inlet with the first compartment, the first compartment with the second compartment, and the second compartment with the solution outlet. Both of the thin-layer compartments are built by pressing the prism or the mass inlet membrane via a circular tightening gasket ( $\sim 100\ \mu\text{m}$  thick). The cell volume is ca.  $15\ \mu\text{l}$ . In the first compartment, the working electrode (WE) was a Pt thin film electrode with a thickness of ca. 50 nm, deposited on the flat reflecting face of a hemi-cylindrical Si prism by electroless plating, following a procedure described elsewhere. The active surface area of the film electrode was ca.  $3.7\ \text{cm}^2$ , as estimated from the charge for the oxidation of a saturated H adlayer formed in the potential region from 0.4 V to 0.05 V. Two separate counter electrodes (A Pt gauze and a Pt wire) were used as shown in Fig. 1, to collect the current separately and avoid oscillation. A reversible hydrogen electrode (RHE) placed outside of the cell was used as a reference electrode.

In the second compartment, the electrolyte was flowed past a porous Teflon membrane (Scimat,  $60\ \mu\text{m}$  thick, 50% porosity,  $0.2\ \mu\text{m}$  pore diameter), which was used to introduce the gaseous and volatile species into the MS for on-line detection. The PTFE membrane is supported on

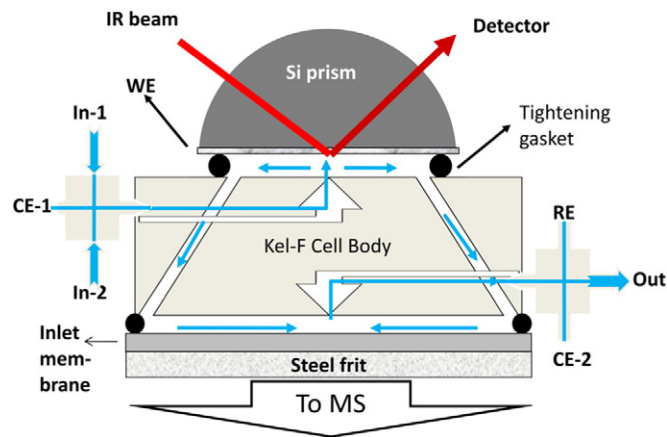


Fig. 1. Schematic illustration of the thin-layer flow-cell for combined DEMS and in situ ATR-FTIRS measurements. In-1 and In-2: two inlet ports for electrolyte; CE-1 and CE-2: ports for connecting two counter electrodes (a Pt gauze and a Pt wire); WE and RE: ports for connecting to the working and reference electrodes; Out: electrolyte outlet port. Arrows show the directions of the solution flow through the capillaries inside the cell.

porous steel frits. A radial laminar electrolyte flow over the working electrode can be achieved either by the hydrostatic pressure or a rotatory pump. The flow of electrolyte can prevent the accumulation of side-products near the electrode surface while minimizing the mass transport effect. A delay of ca. 1 s (depending on the solution flow rate) between the faradaic current signal and the mass spectrometric response occurs due to the electrolyte flow time from the first compartment to the second compartment. Such time delay can be treated by a translation of the time axis. No mass signal tailing was observed, as shown in the CO stripping result in Fig. 2. For more details about the flow cell and DEMS setup please also see Ref. [41,44].

The electrode surface was pre-cleaned by cycling in the potential region from 0.06 V to 1.3 V at a scan rate of 100 mV/s under a continuous flow of  $\text{N}_2$ -saturated  $0.5\ \text{M}\ \text{H}_2\text{SO}_4$  solution, until reproducible cyclic voltammograms were obtained. During the potentiostatic measurement, after the electrode potential was set to the respective reaction potential (0.6, 0.7 and 0.75 V) in the supporting electrolyte, the solution was switched to  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{13}\text{CH}_3\text{OH}$  for 2 min to adsorb  $^{13}\text{CO}$ . It was then switched to  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{12}\text{CH}_3\text{OH}$  to desorb  $^{13}\text{CO}$  and then back to  $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.1\ \text{M}\ ^{13}\text{CH}_3\text{OH}$  or vice versa. The faradaic current, the mass spectrometric signal of  $m/e = 44$  for  $^{12}\text{CO}_2$  and  $m/e = 45$  for  $^{13}\text{CO}_2$ , and the IR spectra in the range from 1000 to  $4000\ \text{cm}^{-1}$  were recorded simultaneously as a function of reaction time. The electrolyte flow rate was kept at  $50\ \mu\text{l/s}$  so the electrolyte in the cell (cell volume is ca.  $15\ \mu\text{l}$ ) was renewed about 3 times in 1 s.

The electrode potential was controlled using a potentiostat (CHI 760E, Shanghai ChenHua, China). The DEMS setup used in the present study was a HiddenHPR-40 DSA Bench Top-Membrane Inlet Gas Analysis System. Mass signals were collected at 20 point/s. The IR spectroscopic measurements were carried out using a Varian FTS-7000 spectrometer equipped with a Mercury Cadmium Telluride (MCT) detector. A spectrum taken at the corresponding reaction potential in the supporting electrolyte was used as a reference spectrum. All spectra were obtained with a resolution of  $4\ \text{cm}^{-1}$  and 1 spectrum/s. The spectra are presented in absorbance mode, i.e.,  $\log(R_0/R)$ , where  $R_0$  and  $R$  are the reflectance at reference and sample potential, respectively.

## 3. Results and discussion

### 3.1. Calibration of the $\text{CO}_2$ mass signal and the IR band intensity based on $\text{CO}_{\text{ad}}$ coverage

In order to get quantitative data for the  $\text{CO}_2$  production efficiency from methanol oxidation, the mass signal of  $\text{CO}_2$  detected has to be

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