



A method for kinetic study of methanol oxidation at Pt electrodes by electrochemical in situ infrared spectroscopy

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ABSTRACT

In this contribution, we describe a method to estimate the kinetics of the indirect pathway in methanol oxidation reaction (MOR) at Pt electrode by using electrochemical in situ infrared spectroscopy combined with a thin-layer flow cell. Based on a quantitative relationship between the coverage of adsorbed carbon monoxide (CO_{ad}) and its infrared band intensities determined experimentally, CO_{ad} coverages during MOR are estimated from the simultaneously recorded time-resolved IR measurements. By assuming that CO_{ad} oxidation goes through Langmuir–Hinshelwood mechanism, its rate constant is estimated in pure supporting electrolyte under otherwise identical condition. Based on the result, the rates of CO_{ad} formation and CO_{ad} oxidation during MOR are deduced from the CO_{ad} coverage–time curve. The methodology is exemplified with MOR on Pt electrode at +0.6 V (versus RHE) in 0.1 M HClO₄ with 2 M methanol. It is found that under forced-flow condition: (i) the maximum reaction rate for CO_{ad} oxidation is ca. 0.004 molecule site⁻¹ s⁻¹ which is 100 times smaller than the maximum rate for CO_{ad} formation from methanol dehydrogenation; (ii) with increase in CO_{ad} coverage from zero to 0.5 ML, the current efficiency of the indirect pathway for MOR increases and reaches ca. 17% under steady state. The general applicability of such a method is shortly discussed.

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1. Introduction

Extensive studies on the electro-oxidation of methanol have been carried out in the past decades, since methanol is believed to be one of the promising fuels for low temperature fuel cells [1–19]. Pt is found to be the best monometallic catalyst for methanol oxidation reaction (MOR) [1,3,20,21], and has been the most frequently used model electrocatalyst for the mechanistic and kinetic studies on MOR. At Pt electrode, methanol can be either completely oxidized to CO₂ or be oxidized incompletely to side-products such as HCHO, HCOOH and CO_{ad}, which are shown in a simplified reaction scheme in Fig. 1 [5–7,14,15,17]. For the complete oxidation of methanol to CO₂, a dual path mechanism with the direct pathway going through non-CO_{ad} adsorbates, while the indirect pathway proceeding via the formation of CO_{ad} and its subsequent oxidation, is proposed [5–7]. By monitoring the mass signal of CO₂ and methylformate using differential electrochemical mass spectrometry (DEMS), the production rate of CO₂ and HCOOH can be evaluated [14,15,22]. By subtracting the equivalent currents for CO₂ and HCOOH production from the total MOR current, the

amount of HCHO produced from MOR can also be estimated (Fig. 1). For the complete oxidation of methanol to CO₂, however, no quantitative information on the contribution of the direct and indirect pathway is available so far.

In a recent study by Chen et al. on HCOOH oxidation at Pt surface using the electrochemical in situ infrared spectroscopy under attenuated total reflection configuration (EC-ATR-FTIRS) coupled with a thin-layer flow cell, the rate of CO_{ad} formation under conditions where CO_{ad} oxidation rate is negligibly small (i.e., $\theta_{CO} \sim 0$) and the rates of both CO_{ad} formation and CO_{ad} oxidation under steady state where both rates equal each other are deduced [23], based on the time-resolved IR spectra recorded during potentiostatic HCOOH oxidation reaction and a linear relationship between CO_{ad} surface coverage and its IR band intensity [23–26]. The coupling of the EC-ATR-FTIRS with the flow cell largely eliminates the influence from the ill-defined mass transport as commonly encountered in stationary cells and from the re-adsorption and the subsequent reaction of side products (such as HCHO and HCOOH in MOR), this enables the kinetic analysis for complicated reactions such as MOR. However, procedure on how to carry out such quantitative analysis, especially under conditions when both CO_{ad} formation and CO_{ad} oxidation are active but with different reaction rates, has not been provided. As a consequence,

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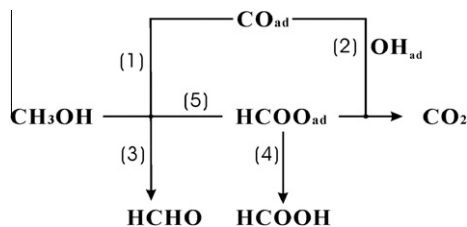


Fig. 1. A simplified reaction scheme for methanol oxidation at Pt electrode: (1) the pathway for CO_{ad} formation from methanol dehydrogenation; (2) the pathway for CO_{ad} oxidation to CO_2 through the indirect pathway; (3) the pathway leads to soluble HCHO production, (4) the pathway leads to soluble HCOOH production and (5) the formate pathway.

quantitative information about the effects of CO_{ad} coverage on the kinetics of the formation and oxidation of CO_{ad} during the electrocatalytic oxidation of C_1 molecules is not available so far.

In this paper, we describe in detail the procedure on how to derive the instantaneous rates of CO_{ad} formation and CO_{ad} oxidation as a function of reaction time (with any CO_{ad} coverage) during MOR by using EC-ATR-FTIRS, from which the current efficiency of the indirect pathway in MOR to CO_2 can be estimated. The paper is organized as following: firstly, the control experiments and the procedure for deriving the relationship of the CO_{ad} surface coverage with the IR band intensities of CO_{ad} species are described. Then, time-resolved infrared spectra and current transient recorded during MOR on Pt film electrode at +0.6 V (versus RHE) are presented, this potential was chosen since all possible pathways involved in MOR operate. Afterwards, the process on how to carry out kinetic analysis on MOR is exemplified by taking the time-resolved IR spectral data and chronoamperometric transients simultaneously recorded during MOR on Pt at +0.6 V. The mechanism/kinetics of MOR and general applicability of such a method are briefly discussed.

2. Experimental

The configuration of the thin-layer spectro-electrochemical flow-cell used in this study has been described in detail in Ref. [23]. The cell volume is ca. 15 μl . In order to minimize the effect of mass transport on the kinetic analysis, in the present study 2 M methanol was used and the flow rate of electrolyte was ca. 250 $\mu\text{l/s}$. This means that the electrolyte in the cell will be renewed every 60 ms, one can almost ignore the re-adsorption and oxidation of HCHO and HCOOH products [23,27,28]. A Pt thin film (thickness of 50 nm) chemically deposited on the flat face of a hemi-cylindrical Si prism [29] was used as working electrode (WE). The active surface area of the WE is ca. 4.8 cm^2 , as determined by the charge associated with oxidation of a monolayer of under-potential deposited H(upd-H) atoms (calculated from the integrated charge in the CV from 0.05 to 0.45 V) [30,31]. A reversible hydrogen electrode (RHE) was used as reference electrode (all the potentials in this paper are quoted against RHE) and the electrode potential was controlled by a potentiostat (PAR 273 A, Ametek, USA). Millipore Milli-Q water, ultrapure perchloric acid (Suprapure, Sigma-Aldrich), methanol (for analysis, Fluka) were used to prepare the solutions. Supporting electrolyte used in all measurements in this study was 0.1 M HClO_4 and constantly purged by N_2 (N_2 , 99.999%, Nanjing Special Gas Corp.). Before the measurements, continuous potential cycles in the potential region from +0.05 to +1.3 V at a scan rate of 0.05 V/s in 0.1 M HClO_4 were carried out to clean Pt thin film electrode until its cyclic voltammogram (CV) showed the characteristic feature of polycrystalline Pt electrode (Fig. 2, dotted line). All the experiments were carried out at room temperature (ca. 18 ± 2 °C).

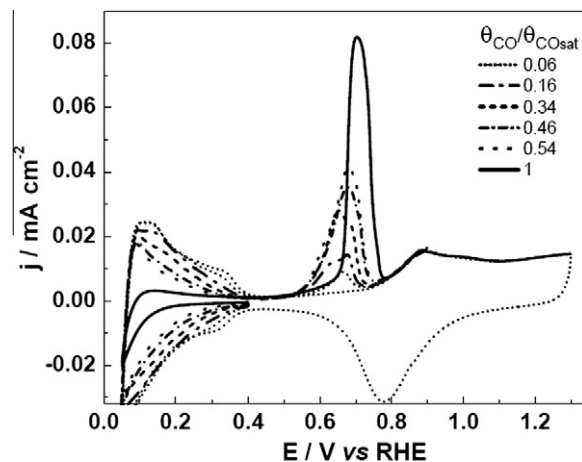


Fig. 2. Cyclic voltammograms of CO stripping at Pt electrode— in 0.1 M HClO_4 with various θ_{CO} (as denoted in the figure) formed either from the decomposition of 0.05 M CH_3OH in 0.1 M HClO_4 at 0.4 V or from direct adsorption of CO from CO saturated 0.1 M HClO_4 solution for different time duration, scan rate: 20 mV/s. The base CV is also shown as dotted line.

The quantitative relationship between the surface coverage and the IR band intensity of CO_{ad} in the low coverage regime ($\theta_{\text{CO}} < 0.5$ ML) is derived according to the following procedure. Firstly the electrode potential was held at +0.4 V in 0.1 M HClO_4 , then 0.1 M HClO_4 + 0.05 M CH_3OH was flowed through the cell and the IR spectra were recorded simultaneously. The reasons for using 0.05 M CH_3OH solution instead of CO saturated solution are: (i) direct adsorption of CO from bulk solution saturated with CO is too fast to accurately control of its surface coverage; (ii) and it is well confirmed that at $E < 0.65$ V, CO is the only stable adsorbate formed from methanol dehydrogenation at Pt surface [13,32], thus 0.05 M MeOH instead of CO was used to make sure that the rate of CO_{ad} formation from methanol dehydrogenation is relatively slow, so that CO_{ad} coverage can be easily controlled by switching the valve between the two electrolyte supplying bottles with and without methanol. After CO_{ad} with a desired coverage is formed from methanol dehydrogenation for a certain holding time at the potential (+0.4 V), the electrode potential was stepped to 0.05 V and the electrolyte was immediately switched back to 0.1 M HClO_4 . And the CO_{ad} coverage was determined by the subsequent cyclic voltammetric stripping after completely washing away the residual methanol in the cell by continuously flushing the cell with 0.1 M HClO_4 at +0.05 V. The further uptake of CO_{ad} at +0.05 V during the above potential step process is negligible, since methanol adsorption/dehydrogenation is largely hindered by the upd-H atoms [33] and the previously formed CO_{ad} at +0.4 V [13]. The corresponding IR spectra of CO_{ad} at different CO coverages are recorded during the methanol adsorption and subsequent CO stripping measurements. Since maximum CO_{ad} surface coverage achievable from methanol dehydrogenation is below 0.5 ML, the data points in the $\theta_{\text{CO}}-I_{\text{COL}}$ plot with $\theta_{\text{CO}} > 0.5$ ML are derived from direct adsorption of CO from CO saturated 0.1 M HClO_4 solution for various time duration.

Potentiostatic MOR was carried out as following. Firstly, the electrode potential was held at +0.6 V in 0.1 M HClO_4 , and a background infrared spectrum was recorded. After that the electrolyte supplying bottle was switched to 0.1 M HClO_4 + 2 M CH_3OH solution (pre-deaerated by N_2 for at least 10 min). After ca. 5 min of MOR at +0.6 V, the electrolyte supplying bottle was switched from methanol-containing solution back to the supporting electrolyte again. Meanwhile the cell is immediately washed with 0.1 M HClO_4 solution while the electrode potential was kept constant there for another 5 min to follow the CO_{ad} oxidation kinetics. The

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