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In situ time-resolved FTIRS study of adsorption and oxidation of ethylene glycol on Pt(100) electrode

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Abstract **Adsorption and oxidation of ethylene glycol (EG) on Pt(100) electrode were studied by *in situ* time-resolved FTIRS (TRFTIRS). The TRFTIR spectra recorded at 0.10 V illustrate that an IR band appears near 2050 cm^{-1} at t > 5 s, corresponding to linearly bonded CO formed in dissociative adsorption of EG. The TRFTIR results have confirmed also that CO species are distributed uniformly on Pt(100) surface. Another band appears near 2342 cm^{-1} at t > 70 s, associating with IR absorption of CO_2 produced in the direct oxidation of EG. With the increase of electrode potential, the direct oxidation of EG becomes gradually the main reaction. When the potential is above 0.40 V, the oxidation of EG occurs mainly via the reactive intermediates, i.e. species containing –COOH determined by *in situ* TRFTIRS.**

Keywords: ethylene glycol, Pt(100) electrode, dissociative adsorption and oxidation, *in situ* time-resolved FTIR spectroscopy.

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Metal single crystal planes provide model electrocatalysts of well-defined surface structure, and play an important role in fundamental studies of electrocatalysis. Ethylene glycol (EG) has attracted considerable interests in both basic studies and applications in direct fuel cells, since its complete oxidation transfers 10 electrons. In the strong acid environment of proton exchange membrane fuel cell (PEMFC), the sole stable and most active metal catalyst for the electro-oxidation of alcohols is platinum[1]. Extensive efforts have been devoted to investigating electrochemical adsorption and oxidation properties of EG on Pt electrodes with different surface structures[2—17]. The results demonstrated that the electrocatalytic oxidation of EG on Pt electrode occurred via a dual path reaction mechanism, and its oxidation includes a set of consecutive and parallel steps yielding several C1- and C2-products[4—6,9]. The oxidation route of EG proceeding without C—C bond cleavage in acidic solutions includes consecutive, two-electron transferring processes that yield some intermediates, such as glycolaldehyde, glyoxal, glycolic acid, glyoxylate and oxalic acids, and the final product is CO_2. In parallel to the above route, the dissociative adsorption of EG may occur due to the strong interaction between EG and Pt surface, resulting in formation of adsorbed CO species and other strongly bound adsorbates, which empoisons Pt surface and causes the so-called "self-poisoning" phenomenon. However, these studies were focused mainly on surface structure effects of Pt electrodes and on the reaction mechanism by determining intermediates and products involved in EG electrocatalytic oxidation using different methods, such as chromatography[9,12], *in situ* FTIR spectroscopy[2,3,6,10,12,13], and differential electrochemical mass spectroscopy[10], and the surface processes and kinetics of EG oxidation were less studied and needed to be further understood at a molecular level. In the present paper, the dissociative adsorption and oxidation of EG on Pt(100) surface are investigated by *in situ* time-resolved FTIR reflection spectroscopy, and new information of EG reaction kinetics was obtained.

1 Experimental

In situ time-resolved FTIR spectroscopy experiments were carried out on a Nexus 870 FTIR apparatus (Nicolet) equipped with a liquid nitrogen cooled MCT-A detector. 10 interferograms were collected and co-added into each spectrum of spectral resolution 16 cm^{-1}. The resulting spectrum is calculated as $\Delta R / R = \left(R_{E_2} - R_{E_1}\right) / R_{E_1}$, where R_{E_1} and R_{E_2} are single-beam spectra recorded at E_1 and E_2, respectively. A saturated calomel electrode (SCE) was used as reference electrode. Before each measurement the Pt(100) electrode was annealed in a hydrogen-oxygen flame, quenched with super pure water and transferred into electrochemical cell under protection of a droplet of pure water. The solutions were prepared using Millipore water (18.0 MΩ cm) provided from a Milli-Q Lab apparatus (Nihon Millipore), super pure H_2SO_4 and ethylene glycol of analytical grade (both from Shanghai Chemicals, Inc., China). All measurements were carried out at around 20℃.

2 Results and discussion

Our previous studies [18] illustrated that the average rate ($\bar{\upsilon}$) of dissociative adsorption of EG on Pt(100) electrode varies with adsorption potential E_{ad} following a volcano-type distribution. The maximum of $\bar{\upsilon}$ ($\bar{\upsilon}^{max}$) is located near 0.10 V. Taking E_{ad} = 0.10 V as a coteau, $\bar{\upsilon}$ declines no matter whether E_{ad} decreases or increases gradually. $\bar{\upsilon}$ tends towards zero when the adsorption potential is below –0.22 V or above 0.40 V.

In situ time-resolved FTIR spectra (TRFTIRS) obtained on Pt(100) electrode at E_2 = 0.10, 0.25, 0.40 and 0.90 V in 0.1 mol L^{-1} EG + 0.1 mol·L^{-1} H_2SO_4 solution are shown in Fig. 1(a)—(d). We can see from Fig. 1(a) that a negative going band near 2050 cm^{-1} starts to appear in the spectrum at t > 5 s, corresponding to linearly bonded CO

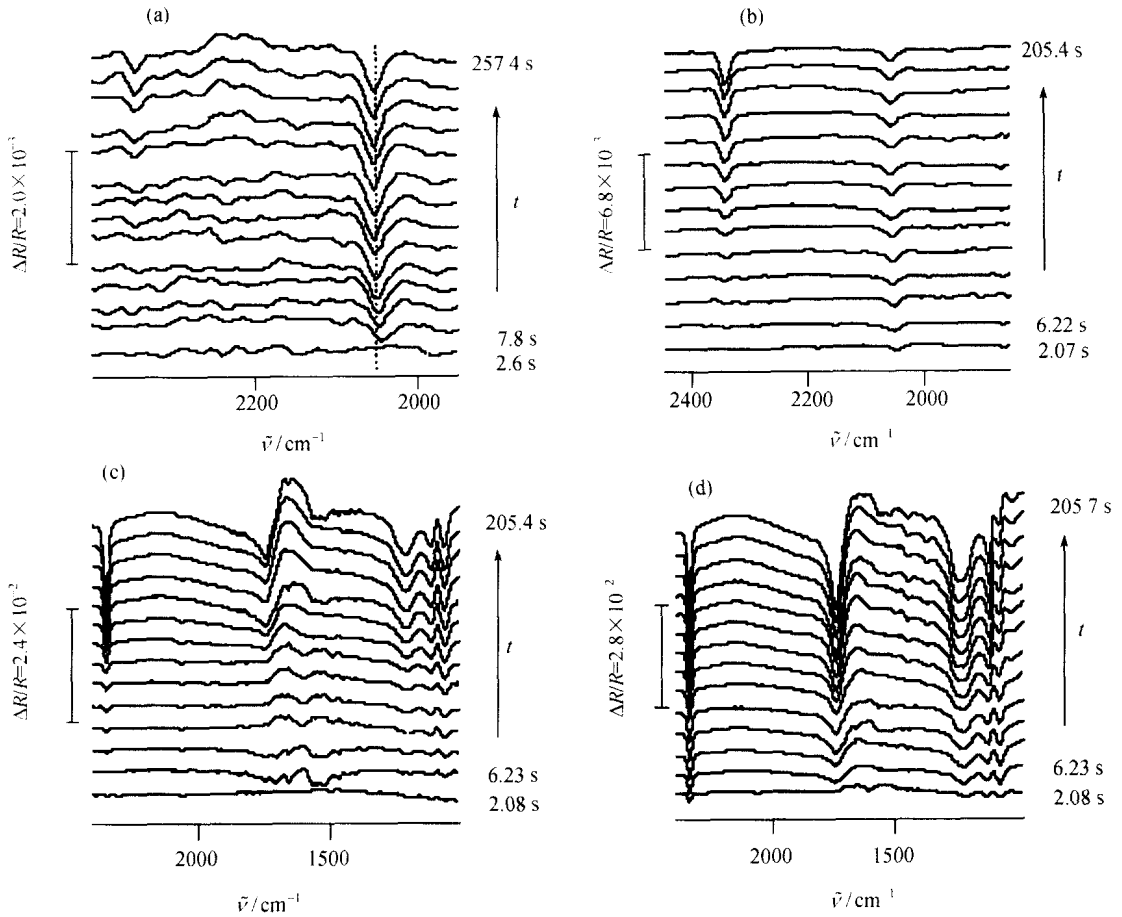

Fig. 1. *In situ* time-resolved FTIR spectra obtained for Pt(100) electrode in 0.1 mol·L^{-1} EG + 0.1 mol·L^{-1} H_2SO_4 solution with E_1 at –0.22 V and E_2 at (a) 0.10 V, (b) 0.25 V, (c) 0.40 V, (d) 0.90 V.

(CO_L) derived from dissociative adsorption of EG on Pt(100) electrode at E_2 = 0.10 V[2,3,6]. The intensity of the band increases progressively with time and attains almost a constant value at t > 100 s. The negative going monopolar band and its variation indicate that the dissociative adsorption of EG on Pt(100) electrode at E_1 =–0.22 V has not occurred (otherwise a bipolar band will appear), and CO_L species were formed exclusively at 0.10 V. The intensity of the band increases progressively with t, indicating that the quantity of CO_L increases gradually and it is accumulated on Pt(100) surface. The band center ($\tilde{\nu}_{CO_L}$) shifts positively with time from 2042 cm^{-1} (t = 7.8 s) to 2054 cm^{-1} (t = 257.4 s), which is apparently caused by the increase of CO_L coverage, and demonstrates that the CO_L species are distributed uniformly on Pt(100) surface without the formation of island. At the same time, a small negative going band near 2342 cm^{-1} appears when t > 70 s, corresponding to the asymmetry stretching of CO_2 that is the final product of EG direct oxidation[3−6]. The intensity of this band increases progressively with t. The appearance of CO_2 band indicates that EG can be directly oxidized at 0.10 V where is located the maximum value of $\bar{\upsilon}$ in its volcano-type distribution, and illustrates the competitive reaction with EG dissociative adsorption. Fig. 2(a) shows the variation of the integration intensity of CO_L and CO_2 bands with t on Pt(100) surface for E_2 = 0.10 V. We can see that the formation of CO_L on Pt(100) surface in EG dissociative adsorption is obviously more significant than the production of CO_2 species in EG direct oxidation.

In Fig. 1(b) (E_2 = 0.25 V), we can observe two similar IR bands, namely, CO_L band at about 2050 cm^{-1} and CO_2 band around 2342 cm^{-1}. The intensity of CO_L band still increases with increasing t and rapidly attains a stable constant value, and in the initial stage of reaction the band center ($\tilde{\nu}_{CO_L}$) also shifts positively with increasing t. In contrast to the results in Fig. 1(a), the CO_2 band appears in the initial stage of reaction, its intensity increases faster with increasing t than that of CO_L band. The variation of integration intensity of CO_L and CO_2 bands with t at this potential is shown in Fig. 2(b). We can see that in the recorded time window, the intensity of CO_2 band increases

linearly and quickly with increasing *t*, and the variation of CO_L band intensity with *t* is similar to that of E_2 = 0.10 V. We can see also that when *t* is larger than 60 s, the intensity of CO_2 band becomes stronger than that of the CO_L band.

When E_2 = 0.40 V (Fig. 1(c)), the number of IR bands is increased and all bands are negatively going. Except the CO_L and CO_2 bands, the assignment of other bands is as follows: the bands near 1740 and 1230 cm^{-1} may be attributed to IR absorption of –COOH groups[4]; the band near 1100 cm^{-1} can be assigned to the stretching vibration of SO_4^{2-} anions[19]; the band near 1059 cm^{-1} can be ascribed to C—O stretching of the primary alcohol[4]. Among these bands, the intensity of the —COOH and the CO_2 bands is gradually increased with increasing *t*, and is apparently larger than that measured at E_2 = 0.25 V. This may indicate that the rate of EG direct oxidation increases significantly at E_2 = 0.40 V, accordingly, the production of intermediates containing —COOH and CO_2 in EG oxidation on Pt(100) is fast at this potential. We can also see that the intensity of IR bands near 1100 and 1059 cm^{-1} is gradually increased with increasing *t*, which may be attributed to the consumption of H_2O in the thin-layer solution involved in EG oxidation. In addition, the CO_L band can be hardly observed in the spectra, which may be attributed to three aspects: (1) The rate of EG dissociative adsorption is very small at this potential[18]; (2) the adsorbed CO derived from EG dissociative adsorption can be oxidized, which decreases the possibility of CO_{ad} accumulation on Pt(100) surface; (3) the competition occurs between dissociative adsorption and direction oxidation of EG, the latter takes place via the reactive intermediates, i.e. species containing —COOH determined by *in situ* TRFTIRS. With further increase of sample potential E_2 (Fig. 1(d)), the intensity of the above IR bands is increased rapidly with increasing *t*, which can be clearly seen from *in situ* TRFTIR spectra of different E_2 but at the same reaction time (*t* = 60 s) shown in Fig. 3. From the variation of integration intensity of CO_2 band with *t* at E_2 = 0.75 V given in Fig. 2(c), we can see that when *t* is longer than 100 s, the quantity of CO_2 produced by EG oxidation approaches to a stable value. At this potential no CO_{ad} species can be detected by *in situ* TRFTIRS.

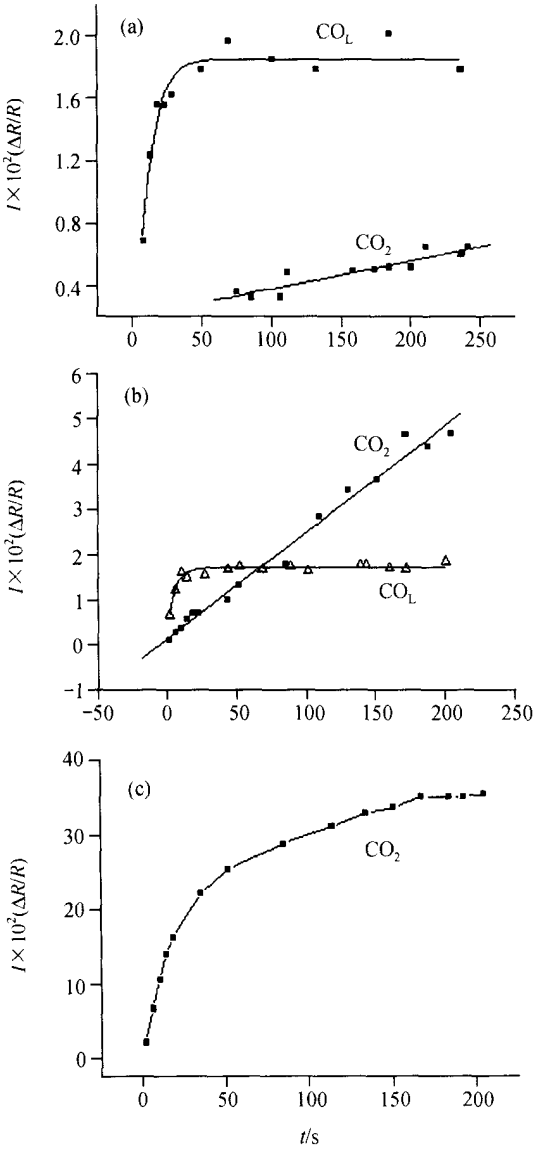

Fig. 2. Comparison of variation of integration intensity (*I*) of CO_L and CO_2 band versus reaction time *t*. (a) E_2 = 0.10 V; (b) E_2 = 0.25 V; (c) E_2 = 0.75 V.

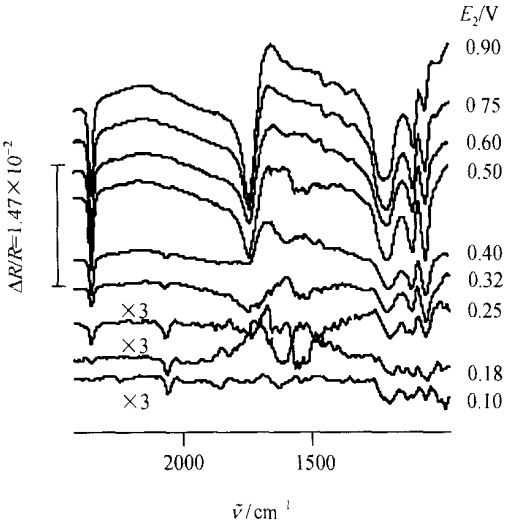

Fig. 3. *In situ* time-resolved FTIR Spectra recorded on Pt(100) electrode for reaction time *t* = 60 s in 0.1 mol·L^{-1} EG + 0.1 mol·L^{-1} H_2SO_4 solution with E_1 at –0.22 V and varying E_2 (0.10, 0.18, 0.25, 0.32, 0.40, 0.50, 0.60, 0.75, 0.90 V).

3 Conclusion

In the present paper, the adsorption and oxidation of ethylene glycol (EG) on Pt(100) electrode were studied by *in situ* time-resolved FTIRS. The results demonstrated that

a negative going band near 2050 cm^{-1} corresponding to linearly bonded CO (CO_L) formed mainly via dissociative adsorption of EG at E_2 = 0.10 V, and this band appears in the spectra at reaction time t > 5 s. The intensity of this band is increased progressively with increasing t. In the initial stage, the CO_L band center ($\tilde{\nu}_{CO_L}$) is blue-shifted with increasing t, indicating that the $\tilde{\nu}_{CO_L}$ changes with CO_L coverage, and implying that CO_L species are distributed uniformly on Pt(100) surface. In addition, a band near 2342 cm^{-1} appears in the spectra at t > 70 s, which is assigned to IR absorption of CO_2 species that are formed via direct oxidation of EG. With the increase of E_2, the direct oxidation of EG becomes gradually the main route of EG oxidation, and leads to the decrease of the rate of EG dissociative adsorption on Pt(100) surface. When E_2 > 0.40 V, all EG molecules reaching electrode surface can be oxidized directly into CO_2, and the oxidation of EG occurs mainly via the reactive intermediates that are the species containing –COOH determined by *in situ* TRFTIRS.

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