

The Adsorption and Oxidation of Isopropanol at Platinum Electrode in Alkaline Media*

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Abstract The adsorption and oxidation of isopropanol in alkaline media at platinum electrode have been investigated by using electrochemical quartz crystal microbalance (EQCM) and in situ FTIR spectroscopy. The results show that there is no self-poisoning in the electrooxidation of isopropanol in alkaline media. Though no poison species, such as CO, are evidenced by in situ FTIR spectroscopy, the adsorption of isopropanol or its dissociative products on Pt surface is suggested by EQCM data. The final product of isopropanol oxidation is only acetone under experimental condition, which suggests that the oxidation of isopropanol into acetone takes place via dehydrogenation step. The EQCM studies provide quantitative results of surface mass variation and have thrown new light in the elucidating isopropanol oxidation.

Keywords: Pt electrode, Electrooxidation, Isopropanol, In situ FTIR, EQCM, Alkaline media

The electrochemical oxidation of small organic molecules is of fundamental importance in electrocatalysis, and is also a key factor in the application of the oxidation as anodic process in direct fuel cells. Isopropanol is the smallest secondary alcohol molecule. Due to the particularity of the molecular structure, isopropanol is the only molecule among C₃ alcohol that fails to dissociate into CO at the surface of platinum electrodes in acidic media^[1,2]. This feature makes isopropanol suitable to be employed in fundamental studies, such as electrochemical reaction kinetics^[3-4] and the effects of molecular structure^[1]. The oxidation of isopropanol in acidic media on platinum single crystal and poly-crystalline electrode has been investigated extensively by using traditional electrochemical methods^[5,6], mass spectroscopy^[7], and in situ spectroscopy^[1-4].

In situ FTIR spectroscopy is a powerful tool for determining intermediates and products involved in the oxidation at molecular level^[8]. Since IR spectroscopy was introduced into the field of in situ electrochemical studies, numerous experiments using this technique have been carried out. It has been applied most frequently in the investigation of electrocatalysis in fuel cell applications. It is worth pointing out that nearly all investigations

mentioned above are carried out in acidic media.

In the last decade, the application of the quartz crystal microbalance (QCM) technique in an electrochemical cell, under potential control, led to the EQCM. The attractiveness of this approach is based on the high sensitivity of the quartz crystal resonator to mass change^[9]. Under favorable conditions, a typical EQCM can measure a mass change of 0.1~1 ng·cm⁻² at electrode/electrolyte interfaces, so has wide applications in the characterizations of the interfacial electrochemical processes such as the transport of ions and solvents during electrochemical reactions, detection of chemical and biochemical species, deposition of metals on surfaces and the growth of molecular layers.

Although a direct fuel cell based on alkaline electrolyte is more promising^[10], little attention has been paid to in situ IR spectroscopic and EQCM investigations of the oxidation of small organic molecules in alkaline media because of the progressive "carbonation" of the solution as a result of CO₂ retention^[11]. The aim of the study is to quantitatively investigate the electrochemical oxidation mechanism of isopropanol on Pt electrode in alkaline media at molecular level via in situ FTIR and EQCM. Besides, the results are compared with those of its ox-

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ation in acidic medium^[1] in order to elucidate the reaction mechanism of isopropanol in alkaline media.

1 Experiments

The in situ electrochemical FTIR experiments were carried out using a Nicolet 870 FTIR apparatus equipped with a Gopher IR source and a MCT-B detector cooled with liquid-nitrogen. The instrument was purged throughout the experiment with clean air free CO₂ and H₂O by a Balston 74-5301 clean air package. A CaF₂ disk was used as the IR window, and an IR cell of thin layer configuration between electrode and IR window was approached by pushing the electrode against the window during FTIR measurements. The incident infrared beam was aligned at about 60° to the normal of electrode surface. The multi-step FTIR spectroscopy (MSFTIRS) technique^[12] was applied for the investigation of isopropanol adsorption and oxidation, and the spectrum was reported as the relative change in reflectivity that is calculated as $R/R(E_s^i) = [R(E_s^i) - R(E_R)] / R(E_R)$, where $R(E_s^i)$ is the resulting spectrum of the *i*th sample potential E_s^i , $R(E_s^i)$ is the single beam spectrum acquired at E_s^i , and $R(E_R)$ is the single beam spectrum recorded at the reference potential E_R . In the difference spectra, the positive-going bands indicate that the IR adsorption at E_R is greater than that at E_s and the negative-going bands correspond to the greater IR absorption at E_s than that at E_R . For each spectrum 400 interferograms were collected at 16 cm⁻¹ resolution and coadded into each single-beam spectrum.

The EG&G PARC electrochemical device consisted of a model 263A potentiostat and a model QCA917 Seiko quartz crystal analyzer^[13], both controlled by M270 software, using an microcomputer. AT-cut quartz crystals with a fundamental frequency of 10 MHz were used as the working electrodes. Each crystal had 0.2 cm² circular area on each side, covered by a bimetallic layer consisting of a Ti substrate coated with a Pt surface. Electrochemical measurements were made in a compartment glass with 30 mL capacity. The cell had a special Teflon cover with holes designed to host the auxiliary and working electrodes and the degassing tubes. The Luggin compartment was connected directly to the cell's body.

The working electrode used in IR experiments was a Pt disk of ca. 5.0 mm diameter. It was polished with alumina powder of 1, 0.3 and 0.05 μm, cleaned in an ultrasonic bath, washed again with Milli-Q water. It was subjected finally to potential cycling in 0.1 mol · L⁻¹ H₂SO₄ between -0.25 and 1.2 V vs SCE at 50

mV · s⁻¹ until a stable voltammogram was achieved. This potential cycling was carried out as a pretreatment (electrochemical cleaning) in both cyclic voltammetry and IR experiments. The reference electrode was a saturated calomel electrode (SCE), separated from the cell by a bridge made of a stopcock with two ends containing the solution. The counter electrode was a Pt foil with a geometric area of 1 cm². All the glassware was cleaned before use by immersion in CrO₃+H₂SO₄ solution, followed by thorough rinsing in Milli-Q water.

The electrolytes were prepared with NaOH, isopropanol of analytical grade and water purified by Milli-pore s Milli-Q system. The solutions were deaerated by bubbling nitrogen gas of high purity. The experiments were carried out at around 20 °C, and under atmospheric pressure.

2 Results and Discussion

2.1 Cyclic voltammetric results

Small organic molecule oxidation in acidic media at Pt electrode generally contains self-poisoning phenomenon^[1], i.e. poison species is generated during the electrooxidation. However, even as preface stated, isopropanol is the only molecule among C₃ alcohol that does not dissociate into CO at the surface of platinum electrodes in acidic media. Fig.1 presents the cyclic voltammogram of isopropanol oxidation in alkaline media at an AT-cut quartz crystal Pt electrode. It is clear from Fig.1 that even in the potential region of hydrogen adsorption-desorption, isopropanol oxidation in the positive going potential sweep (PGPS) could take place immediately and produce two current peaks (I and II) at -0.56 and -0.31 V, which is similar to that of isopropanol oxidation in acidic media^[1]. The results imply that there is no self-poisoning in the reaction, which is in accordance

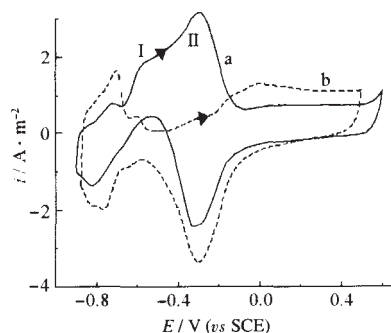


Fig.1 Cyclic voltammograms of Pt electrode in 0.1 mol · L⁻¹ CH₃CHOHCH₃+0.1 mol · L⁻¹ NaOH solution (a), 0.1 mol · L⁻¹ NaOH solution (b) sweep rate 50 mV · s⁻¹

with in situ FTIR results (section 2.2). According to Li et al.^[14], the oxidation state of the Pt surface plays a key role in the oxidation of alcohols, the oxidation of alcohols on a Pt electrode is controlled by the formation of surface oxides on the Pt electrode at different potentials. The dependence of the reaction process on the oxidation states of the platinum surface yielded similar features in the cyclic voltammogram for oxidation of different alcohols at a Pt electrode, so it is difficult to assign two current peaks in PGPS. The branch of the i - E curve in the negative going potential sweep (NGPS) is similar to that of other organic molecule oxidation^[1]: only one oxidation current peak appears at -0.51 V, but its magnitude is very small, and another negative current peak, which is caused by the reduction of surface oxides formed at higher potentials in PGPS, is observed at -0.31 V.

2.2 In situ FTIR results

Fig.2 presents a series of spectra obtained by fixing E_R at -0.90 V, which is in the potential region of hydrogen adsorption-desorption and is lower than the oxidation onset potential of isopropanol, and by varying E_S from -0.8 to 0.4 V.

When E_S is lower than the threshold oxidation potential of isopropanol (near -0.7 V, see Fig.1) there are no significant features in the spectrum, but when E_S is at -0.7 V, a negative going band situated at 1699 cm^{-1} appears immediately. This feature coincides roughly with the oxidation onset potential of isopropanol. These spectra have the following features.

(a) In the range from 2100 to 1800 cm^{-1} , no IR bands corresponding to adsorbed CO can be observed in Fig.2. This is a direct proof that isopropanol cannot dissociate into CO species during its interaction with the Pt surface, which is in accordance

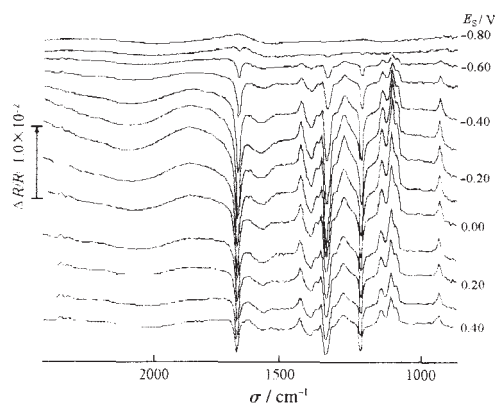


Fig.2 Difference spectra obtained with a Pt electrode in 0.1 $\text{mol} \cdot \text{L}^{-1}$ isopropanol + 0.1 $\text{mol} \cdot \text{L}^{-1}$ NaOH solution. The reference potential E_R was at -0.90 V, and the values of potential E_S for each spectrum are indicated in the figure.

with the observation from cyclic voltammogram of Pt electrode in Fig.1. The similar situation has been reported in its oxidation on both Pt polycrystalline and single crystal electrode in acidic media^[14]. In the isopropanol molecule, the OH group is connected to the second carbon atom of the chain, with a methyl at either side, so it may be too difficult for this carbon atom to approach the Pt surface for dissociation into CO.

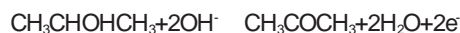
(b) A few positive going bands near 947 , 1127 , 1116 , 1166 , 1468 cm^{-1} denotes the decrease of isopropanol concentration in the thin layer during the oxidation of isopropanol at E_S .

(c) No negative going band corresponding to the CO_2 asymmetrical stretch at 2340 cm^{-1} appears in the spectrum until E_S is at 0.4 V, which indicates effectively that isopropanol is not oxidized into CO_2 under present conditions^[1]. This result differs from that reported in acid solutions, where isopropanol can easily be oxidized into CO_2 ^[1].

(d) In the fingerprint region a few negative going bands may be seen on the spectra^[1,15]. The bands near 1426 and 1369 cm^{-1} can be assigned to the symmetrical and asymmetrical deformation of C—H in the $-\text{COCH}_3$ group respectively; the band near 1238 cm^{-1} can be attributed to the stretching plus bending of the C—CO—C chain; the band near 1699 cm^{-1} can be assigned to the C=O stretching. It is worth pointing out that the intensity of these bands first increases steadily with the electrode potential to reach a maximum between -0.30 – 0.10 V, and then starts to decrease at more positive potentials.

(f) The baseline shift and the broad band which appears at 1600 cm^{-1} in the spectra of Fig.2 as the electrode potential increases could be related to changes in the concentration of H^+ and OH^- in the thin layer as the reaction proceeds^[16]. In fact, H^+ is produced as isopropanol is oxidized, giving rise to change in pH which may be compensated by diffusion of OH^- and H_2O into the thin layer.

The combination of the above features indicates that under the experimental conditions, the main reaction occurring at the electrode is the dehydrogenation of isopropanol to acetone, i.e.



2.3 EQCM results

Fig.3 shows the Δm variation in a solution containing 0.1 $\text{mol} \cdot \text{L}^{-1}$ $\text{CH}_3\text{CHOHCH}_3$ and 0.1 $\text{mol} \cdot \text{L}^{-1}$ NaOH measured with the AT-cut quartz crystal Pt electrode during the CV scanning. Nearly a constant value of Δm is maintained from -0.90 to -0.78 V in PGPS. Compared with the isopropanol free electrolyte,

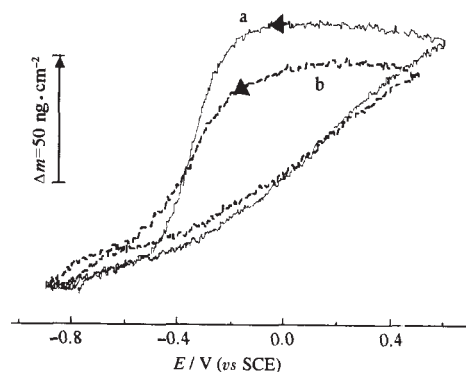


Fig.3 Δm variation of Pt electrode in $0.1 \text{ mol} \cdot \text{L}^{-1}$ $\text{CH}_3\text{CHOHCH}_3 + 0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution (a) and $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution (b) sweep rate $50 \text{ mV} \cdot \text{s}^{-1}$

where the Δm increased continuously in the same potential region, this result may imply that isopropanol or its adsorptive products are possibly adsorbed preferentially on the electrode surface in this potential region^[17-18]. Since no chemically adsorbed species are evidenced by in situ FTIR spectroscopy, this point cannot exclude the possibility of isopropanol and its dissociative adsorption on Pt surface, which indicates EQCM is a powerful tool for studying the interfacial electrochemical processes. From -0.4 V on, the Δm increases quickly, which is ascribed to the electrooxidation, re-adsorption of isopropanol and oxygen adsorption (or Pt surface oxidation). When E varies from -0.4 to 0.6 V , the Δm increases by $87.9 \text{ ng} \cdot \text{cm}^{-2}$. It is interesting to see that the Δm almost remains constant between 0.6 and -0.20 V in NGPS, then, it decreases quickly to joint the Δm curve recorded in the PGPS when electrode potential is swept below -0.20 V , implying that the Δm remains constant after one CV cycle.

3 Conclusions

The CV, EQCM and in situ FTIR spectroscopy are used to reveal the reaction mechanism of isopropanol oxidation in alkaline media on Pt electrode at a molecular level and quantitatively. The main conclusions can be drawn from the experimental results as follows: (1) there is no self-poisoning in the electrooxidation of isopropanol in alkaline media (2) Since no chemically adsorbed species, such as CO, are evidenced by in situ FTIR spectroscopy, the adsorption of isopropanol or its dissociative products on Pt

surface are suggested by EQCM data. (3) Isopropanol oxidation in PGPS could take place immediately even in the potential region of hydrogen adsorption-desorption, and two current peaks (I and II) at -0.56 and -0.31 V are detected. (4) The final product of isopropanol oxidation is only acetone under the experimental condition, it may therefore be suggested that the oxidation of isopropanol into acetone takes place via dehydrogenation step. (5) The EQCM studies provide quantitative results of surface mass variation and have thrown new light in the elucidating isopropanol oxidation.

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碱性介质中异丙醇在铂电极表面的吸附和电化学氧化*

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摘要 运用电化学循环伏安、原位 FTIR 反射光谱和石英晶体微天平(EQCM)等方法研究了碱性介质中异丙醇在 Pt 电极表面吸附和氧化行为. 结果表明: 碱性介质中异丙醇电氧化过程不存在自毒化现象. 虽然电化学原位 FTIR 反射光谱未能检测到 CO 等毒性物种, 但 EQCM 结果证明异丙醇或其解离产物吸附于铂电极上. 在实验条件下, 碱性介质中异丙醇在铂电极上氧化的最终产物只有丙酮, 预示着碱性介质中异丙醇通过脱氢步骤氧化成丙酮. EQCM 研究还从电极表面质量定量变化的角度提供了异丙醇吸附和电氧化反应机理的新数据.

关键词: Pt 电极, 电氧化, 异丙醇, 原位 FTIR, EQCM, 碱性介质

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