The kinetics of formic acid oxidation (FAO) on Pd(111) in 0.1 mol/L H₂SO₄+0.1 mol/L HCOOH with and without addition of Na₂SO₄ is studied using cyclic voltammetry and potential step method, which is compared with that in 0.1 mol/L HClO₄. It is found that adsorbed sulfate has significant inhibition effect on FAO kinetics. After addition of 0.05 mol/L or 0.1 mol/L Na₂SO₄, FAO current in the negative-going scan is found to be significantly smaller than that at the same potential in the positive-going scan. We speculate that at potentials positive of the phase transition potential for the (SO₄⁺)ₙ−[(H₂O)ₙ−H⁺] or (SO₄⁺)ₙ−[Na⁺(H₂O)ₙ−H⁺] adlayer, the adlayer structure probably becomes denser and more stable with the increase of potential or with the addition of Na₂SO₄. The formation of connected adlayer network greatly enhance the stability of the adlayer, and the insertion of positive-charged H⁺ or Na⁺ into the adlayer network further reduces the electrostatic repulsion between partially charged sulfates. As a result, the destruction/desorption of compact sulfate adlayer becomes more difficult, which leaves much less free sites on the surface for FAO, and thus FAO kinetics at higher potentials and in the subsequent negative-going potential scan is significantly inhibited.

Key words: Formic acid oxidation, Pd(111) electrode, Sulfate adsorption, Anions effect

I. INTRODUCTION

Formic acid oxidation (FAO) on Pt group metal electrode is one of the simplest and most important model reactions in electrocatalysis. Understanding the FAO mechanism(s) and the factors which affect its oxidation kinetics is of great help in establishing the principles of electrocatalysis as well as developing highly efficient catalysts for the oxidation of small organic fuels in low temperature polymer electrolyte membrane fuel cells (PEMFCs) [1–5]. Pd is one of the best single metallic electrocatalysts toward FAO. At low temperature, FAO kinetics on Pd electrode is better than that on Pt electrode where the amount of CO₃ad formed on Pd is negligible, in contrast to the case with Pt [3, 6–9]. Systematic studies of FAO on single crystalline Pd(hkl) electrode reveal that at lower overpotentials (η≤0.5 V), Pd(111) has the highest FAO activity, while at higher overpotentials (η≥0.5 V), Pd(100) displays the highest FAO activity [7, 9]. However, the origin for such activity trend is not clear, and the exact mechanisms for FAO on Pd electrodes are still under debate [3, 8].

For many electrocatalytic reactions, strongly adsorbed anions on the catalysts surface usually induce a poisoning effect on the reaction kinetics [10]. Owing that sulfuric acid is a commonly used electrolyte in electrochemistry, the adsorption of (bi)sulfate on Pt group metals has been extensively studied. A recent study from Felic’s group revealed that in sulfuric acid containing solution, sulfate is the actual adsorbate on Pt(111) [11]. Electrochemical scanning tunneling microscopy (EC-STM) and Fourier-transform infrared spectroscopy (FTIRS) studies reveal that sulfate adsorbs with three of its O atoms bonding to the three neighboring atoms on Pt(111) and Pd(111) surfaces [12–16]. By monitoring the cyclic voltammograms (CVs) of Pd(111) in solutions with x mol/L H₂SO₄+0.1(1−x) mol/L Na₂SO₄ or with x mol/L H₂SO₄ (x=0.001−2) systematically, we find that the sulfate adsorption/desorption peak shifts positively with the increase of pH with a slope in the range of 10–30 mV/pH. Based on systematic analysis of these CVs, it is found that the pH- and solution composition-dependent shift of the onset potential for sulfate adsorption/desorption agrees well with that of the thermodynamic equilibrium potential for the following reactions (Lei, in preparation):

\[ \text{SO}_4^{2−} + H^+ + e^- = HSO_4^- \]  \hspace{1cm} (1)
\[ \text{SO}_4^{2−} + e^- = SO_4^{−} \]  \hspace{1cm} (2)

This confirms that the actual adsorbate on Pd(111) is also \text{SO}_4^{2−}. Since the pK₁ of H₂SO₄ is ca. −2, the standard thermodynamic equilibrium potential for the
latter reaction is ca. 0.12 V more positive than that for the former.

In addition, the adsorbed sulfate was reported to promote the FAO on Pt(111) in solutions with pH<5 [17, 18]. This promotion effect is attributed to the inference that sulfate adsorbate can tune the weakly adsorbed formate intermediate into a proper orientation to Pt surface, which facilitates fast breaking of C–H bond and consequently enhances FAO kinetics on Pt electrode [5, 17, 18]. In contrast, studies on Pd film bond and consequently enhances FAO kinetics on Pt surface, which facilitates fast breaking of C–H bond and consequently enhances FAO kinetics on Pt electrode [5, 17, 18]. However, no systematic comparison of the anions effect on FAO on well-defined single crystalline Pd electrodes is available so far. This may be partly due to the fact that Pt single crystal surfaces are more difficult to be prepared and to be kept in good condition [9]. In this work, we report the effect of sulfate adsorbate on FAO on Pd(111) electrode obtained by cyclic voltammetry and potential step methods. In contrast to the case with Pt(111), FAO current on Pd(111) electrode in 0.1 mol/L H$_2$SO$_4$ is found to be more than 5 times smaller than that in 0.1 mol/L HClO$_4$. The details of this inhibition behavior will be discussed.

II. EXPERIMENTS

Bead type Pd(111) electrode (ca. 3 mm in diameter) was prepared from Pd wire (0.8 mm in diameter, 99.99% purity, Tanaka Noble Metal Corp.) according to the Clavilier’s technique [20-22]. Before the electrochemical measurement, the Pd(111) electrode was annealed by inductive heating equipment (Easyheat 244, Ambrell Companies) at about 1300 °C in an argon atmosphere (99.9999%), cooled down for 1 min in a stream of argon, and then quenched in ultra-pure water which is in equilibrium with the same atmosphere. The electrode surface was protected with a deoxygenated water droplet to prevent contamination during the transfer to the electrochemical cell. A meniscus configuration between the Pd(111) surface and the electrolyte was formed while the potential was held at 0.5 V (vs. RHE).

A conventional two-compartment, three electrode glass cell was used for all the electrochemical measurements. An Ag/AgCl electrode and Pt foil electrode were used as reference electrode (RE) and counter electrode (CE), respectively. The electrode potentials were controlled by a potentiotstat (CHI660, Shanghai Chenhua). The Ag/AgCl electrode was placed in the 2nd compartment which was separated from the main cell body by glass frits, in order to avoid the contamination of the solution by the Cl$^-$ ions and by traces of dissolved Ag$^+$ leaked from the RE. The electrolyte solutions with 0.1 mol/L HClO$_4$ and 0.1 mol/L H$_2$SO$_4$+x mol/L Na$_2$SO$_4$ (x=0–0.1) with or without 0.1 mol/L HCOOH were prepared using concentrated H$_2$SO$_4$ (96%, Suprapure, Merck KGaA), Na$_2$SO$_4$ (>99.99%, Suprapure, Sigma Aldrich) or perchloric acid (70%, Suprapure, Sigma Aldrich), formic acid (ACS reagent ≥96%, Sigma), and ultra-pure water (18.2 MΩ-cm from Milli Q water system). The measured pH in 0.1 mol/L H$_2$SO$_4+$0.05 mol/L Na$_2$SO$_4$ or 0.1mol/L H$_2$SO$_4$+0.1 mol/L Na$_2$SO$_4$ are 1.06 and 1.12, which are slightly smaller than the theoretical values (ca. 1.16 and 1.39) predicted by the dissociation constant of sulfuric acid in the respective solution. This is probably due to the small errors in measuring the volume of sulfuric acid for preparing the solutions. Before each experiment, all solutions were purged with N$_2$ (99.999%, the Linde Group, China) for at least 20 min. Then the basic cyclic voltammogram (CV) for Pd(111) in each electrolyte was recorded. All experiments were carried out at room temperature (ca. 25 °C). For measuring the CVs and current transients for FAO, the rotation rate of the working electrode was controlled at 1000 r/min by a modulated rotator (Hokuto Denko Ltd.). The current displayed in the figures is normalized to the geometric surface area of the respective working electrode. All potentials in this work are quoted against the RHE according to the measured pH of the respective solutions.

III. RESULTS AND DISCUSSION

A. Effect of adsorbed sulfate on cyclic voltammograms of Pd(111)

FIG. 1 displays two representative cyclic voltammograms (CVs) of Pd(111) in 0.1 mol/L HClO$_4$ and 0.1 mol/L H$_2$SO$_4$ recorded at scan rate of 50 mV/s. The current due to hydrogen adsorption and desorption on Pd(111) in 0.1 mol/L H$_2$SO$_4$ is detectable at E<0.38 V, and gradually increases at more negative potentials. At potentials positive of hydrogen adsorption, there is a clear double layer charging region between 0.4 and 0.6 V. At around 0.7 V there is a pair of broad redox peaks which are assigned to water oxidation to the adsorption OH-species and the reductive desorption of OH$_{ad}$ [23].

In 0.1 mol/L H$_2$SO$_4$ hydrogen adsorption on Pd(111) starts around 0.32 V, this onset potential is ca. 60 mV, which is more negative than that in 0.1 mol/L HClO$_4$, as a result of the inhibition of H adsorption due to the strong adsorption of sulfate on Pd(111). The sharp cathodic peak at ca. 0.24 V (P1) is attributed to the desorption of sulfate, which is accompanied with the under potential deposition (UPD) of H onto Pd(111). The corresponding anodic peak (P1′), which marks the superposition of hydrogen desorption and sulfate adsorption appears at 0.28 V [22-24]. A pair of small redox peaks P2 (at 0.38 V) and P2′ (at 0.39 V) are also observed, which are attributed to a first order phase transition of the disordered sulfate adlayer into an ordered adlayer, composed by three different types of orientational do-
Cyclic voltammograms of a freshly prepared Pd(111) electrode in 0.1 mol/L HClO₄ (red line) and 0.1 mol/L H₂SO₄ (black line). Scan rate: 50 mV/s. Inset: the integrated charge in the positive- (solid line) and negative-going scan (dotted line) at E<0.5 V, line with square is the difference between the charge in 0.1 mol/L H₂SO₄ and 0.1 mol/L HClO₄.

The CVs given in FIG. 1 are in accordance with those reported previously [12, 22–24], confirming that the Pd(111) electrode we prepared was correctly oriented and is kept in good condition, and also the electrochemical system we used is clean. These results reveal that on Pd(111) the thermodynamic equilibrium potentials for under potential deposition of hydrogen and sulfate adsorption are in the same potential regime. As a result, hydrogen and sulfate compete for surface sites at these potentials.

The integrated charge (Qj) of the j-E curve for Pd(111) in 0.1 mol/L HClO₄ from 0.2 V to 0.45 V is 158 μC/cm² (corresponding to the stripping of ca. 0.7 monolayer (ML) of H₂) in the positive-going scan (inset in FIG. 1), which is ca. 35 μC/cm² smaller than that in the negative-going scan from 0.45 V to 0.2 V, this indicates that some H absorbed in the negative-going scan is not oxidized in the following positive-going scan at E up to 0.4 V. Qj of the j-E curve in 0.1 mol/L H₂SO₄ in the positive-going scan from 0.2 V to 0.5 V is 214 μC/cm², ca. 56 μC/cm² larger than that in 0.1 mol/L HClO₄. The difference agrees roughly with the charged needed for the formation of a (√3×√7) commensurate phase of sulfate adlayer with a coverage of ca. 0.2 ML (FIG. 2), where one electron is transferred from the precursor to the electrode during the adsorption [12–14].

In order to check how sulfate affects FAO, we have monitored the changes of the CV features with addition of Na₂SO₄ into the solution. FIG. 3 displays a set of representative CVs of Pd(111) electrode in solutions with 0.1 mol/L H₂SO₄ +x mol/L Na₂SO₄ (x=0, 0.05, 0.1) recorded at a scan rate of 10 mV/s, the measured pH of each solution is also indicated. The general shape of the CVs does not change with the addition of Na₂SO₄. With the increase of Na₂SO₄ concentration the peak position shows very small negative shift from 0.26 V to ca. 0.24 V, and the peak height at 0.24 V in the negative-going scan decreases slightly, while the magnitude of the current at more negative potentials increases slightly. This observation is similar to what have been reported on Pt(111), where a shift of the phase-transition spike toward lower potentials was found with the addition of Na₂SO₄ or Li₂SO₄ [29]. The change of CV features indicates that the Na⁺ cation would influence or participate in the formation of the sulfate adlayer, and the ordered (ensemble of rotational domains, patch-work like) adlayer is formed more easily and deformed more difficultly in the mixtures than in pure.
sulfuric acid.

**B. Cyclic voltammetric study on the effect of adsorbed sulfate on FAO at Pd(111)**

FIG. 4 displays the CVs for FAO on Pd(111) in 0.1 mol/L H$_2$SO$_4$ or 0.1 mol/L HClO$_4$. In 0.1 mol/L HClO$_4$, FAO current first increases with potential in the positive-going scan from 0.2 V to 0.52 V, then it decreases with potential from 0.52 V to 0.7 V. The Tafel slope for FAO on Pd(111) in the potential range from 0.2 V to 0.5 V is estimated to be in the range of 160–300 mV/dec. The value of the Tafel slope is significantly higher than 120 mV/dec, similar to our recent results for FAO on Pd film electrode [8]. This result indicates that there is counterweighing factor reducing the FAO kinetics with the increase of reaction overpotential under these conditions, which is superimposed with the increase of FAO kinetics with the reaction overpotential. The increase on the coverage of poisoning species such as bridge-bonded formate and bicarbonate with the increase of reaction potential is suggested to be responsible for that as supported by our recent ATR-FTIR data [8]. The decay of FAO current at $E>0.52$ V is attributed to the oxidation of Pd(111) surface at these potentials, which is also supported by the appearance of current wave for OH adsorption as supported by base CV given in FIG. 1 (red line). The $j$-$E$ features recorded in the negative-going scan from 0.7 V to 0.2 V is nearly the same as that in the positive-going scan except that the magnitude of the current is slightly smaller than that in the positive-going scan. Such behavior manifests that the surface conditions at the same potential are nearly the same in the positive- and negative-going scans, except that some surface sites (defects) may be preferentially blocked by O$_{ad}$ or FAO intermediates during the positive-going scan to 0.7 V.

The general feature for FAO on Pd(111) in 0.1 mol/L H$_2$SO$_4$ is similar to that in 0.1 mol/L HClO$_4$, except that (i) the current peak appears at ca. 0.35 V, which is ca. 0.17 V more negative than that in 0.1 mol/L HClO$_4$ and (ii) at $E<0.35$ V the magnitude of FAO current in 0.1 mol/L H$_2$SO$_4$ is ca. 1.8 times smaller than that in 0.1 mol/L HClO$_4$. The ratio of FAO current in 0.1 mol/L HClO$_4$ to that in 0.1 mol/L H$_2$SO$_4$ increases with potential at $E>0.35$ V, which reaches ca. 50 times at 0.57 V. The Tafel slope for FAO on Pd(111) in 0.1 mol/L H$_2$SO$_4$ in the potential range from 0.2 V to 0.35 V is ca. 135 mV/dec, which is slightly smaller than that in 0.1 mol/L HClO$_4$ in the same potential range. The onset potential for the decay of FAO current coincides roughly with the potential at which the phase transition to the ($\sqrt{3} \times \sqrt{7}$) superstructure sulfate adlayer occurs (FIG. 2).

In order to figure out the effect of sulfate adsorption on FAO kinetics on Pd(111), we have deliberately added 0.05 mol/L or 0.1 mol/L Na$_2$SO$_4$ into the 0.1 mol/L H$_2$SO$_4$+0.1 mol/L HCOOH solution, the corresponding CVs for FAO on Pd(111) in these solutions are displayed in FIG. 5. From FIG. 5 we can find that FAO current on Pd(111) in the positive-going scan in solutions with 0.1 mol/L H$_2$SO$_4$+x mol/L Na$_2$SO$_4$+0.1 mol/L HCOOH ($x=0, 0.05, 0.1$) is only slightly smaller than that with 0.1 mol/L H$_2$SO$_4$+0.1 mol/L HCOOH, which does not change much with adding Na$_2$SO$_4$ with concentration below 0.1 mol/L. However, in the negative-going scan, FAO current in solutions with 0.1 mol/L H$_2$SO$_4$+x mol/L Na$_2$SO$_4$+0.1 mol/L HCOOH is significantly smaller than that with 0.1 mol/L H$_2$SO$_4$+0.1 mol/L HCOOH. Furthermore, the higher the concentration of Na$_2$SO$_4$, the smaller the FAO current in the negative-going scan is. The ratio of FAO current in the positive-going to that in the negative-going scan is the highest around the current peak potential. At the current peak, the ratio of the peak FAO current in the cases with addition of 0.05 mol/L or 0.1 mol/L Na$_2$SO$_4$ to that without Na$_2$SO$_4$ decreases from 50% to 25%. All these observations indicate that a more compact sulfate adlayer is formed at higher potentials when there is no competitive adsorption of H$_2$O. This inference is also supported by previous studies based on Monte Carlo simulations. It is found that as the potential is further increased the different rotational domains that appear at potentials immediately above the sharp spike coarsen into structures with increasing long-range order, which is accompanied with a small increase of (bi)sulfate surface coverage [27, 28, 30, 31]. Once the compact adlayer is formed, its destruction/desorption only occurs at much more negative potentials (this is also supported by the
In order to further confirm this speculation, we have recorded CVs for FAO on Pd(111) in 0.1 mol/L H$_2$SO$_4$ $+$ $x$ mol/L Na$_2$SO$_4$ $+$ 0.1 mol/L HCOOH ($x$=0, 0.05, 0.1) by systematically varying the upper potential limit (FIG. 6). We find that the higher the upper potential limit applied, the smaller the Faradaic current for FAO in the negative-going scan is. When the upper potential limit is fixed at 0.45 V, the ratio of the peak FAO current in the cases with addition of Na$_2$SO$_4$ of 0.05 mol/L or 0.1 mol/L to that without Na$_2$SO$_4$ decreases from 20% to 30%, which are significantly smaller than the cases with upper potential limit set at 0.7 V. Furthermore, in the case of 0.1 mol/L H$_2$SO$_4$ $+$ 0.1 mol/L Na$_2$SO$_4$ $+$ 0.1 mol/L HCOOH, the current peak in the negative-going scan appears at ca. 0.34 V, which is ca. 20 mV more negative than that with 0, 0.05 mol/L Na$_2$SO$_4$ concentration (FIG. 6). All these findings lead us to the conclusion that a more compact adlayer is formed when the potential is scanned to potentials positive of the phase transition potential of the ($\sqrt{3}$×$\sqrt{7}$) sulfate adlayer. A more compact sulfate adlayer is formed with the addition of Na$_2$SO$_4$, as a result of the increase of the chemical potential (concentration) of HSO$_4^-$ and SO$_4^{2-}$ as well as the insertion of the cations as counterions into the specifically adsorbed sulfate adlayer. The latter may induce a stabilizing effect since it can decrease electrostatic repulsion between partially charged sulfates [32]. Besides, recent studies based on DFT simulation and in situ surface X-ray scattering reveal that with the increase of potential the mean distance between sulfate adlayer and the Pt(111) or Au(111) substrate would reduce [33–35], which may further stabilize the sulfate adlayer. The effects of cation size on the structure of the interfacial water could also contribute [29, 36]. Further studies are underway in order to figure out how the cations interact with (bi)sulfate adlayer.

C. Current transients of FAO on Pd(111)

The $j$-$E$ curves obtained by cyclic voltammetry include the dynamic change induced by both the change of electrode potential and the reaction time. In order to simplify the consideration, we also measured the current transients of HCOOH oxidation on a freshly prepared Pd(111) electrode in 0.1 mol/L HCOOH $+$ 0.1 mol/L HClO$_4$ and 0.1 mol/L H$_2$SO$_4$ with $x$ mol/L Na$_2$SO$_4$ ($x$=0, 0.05, 0.1). The potential was first held at 0.7 V for 5 s, then it was stepped to a reaction potential (in the range of 0.2–0.5 V) and held at that potential for ca. 20 s. The $j$-$t$ curves recorded are displayed in FIG. 7(a). For comparison, current transients for FAO on Pd(111) in 0.1 mol/L HCOOH $+$ 0.1 mol/L HClO$_4$ are given in FIG. 7(b). When the electrode potential was stepped from 0.7 V to 0.5 V, FAO current in 0.1 mol/L HCOOH $+$ 0.1 mol/L
$\text{H}_2\text{SO}_4$ reaches maximum immediately, and then it displays slight decay with reaction time. This phenomenon indicates that in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{H}_2\text{SO}_4$ the surface condition of Pd(111) can change quickly to accommodate its status respective to the applied reaction potentials. The slight decay is attributed to the accumulation of reaction intermediates/products such as bridge-bonded formate ($\text{HCOO}_\text{ad}$) and bicarbonate ($\text{HCO}_3^-\text{ad}$), as inferred from ATR-FTIRS studies of FAO on Pd film electrode under attenuated total reflection configuration [8].

When the electrode potential was stepped from 0.7 V to 0.45 V and 0.4 V, FAO current in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{H}_2\text{SO}_4$ also reaches maximum immediately, and then it remains unchanged with reaction time, which indicates that once the fixed potential was reached, the surface condition (adsorbate coverage, domain structure) would not change obviously with reaction time. When the potential was stepped to reaction potentials below 0.4 V, there is also a very small decrease with reaction time, indicating the slow loss of active sites with the reaction time. As similar to the $j$-$E$ curves recorded by CVs, FAO current in the current transients is maximum at ca. 0.35 V, it is smaller at both higher and lower potentials (FIG. 7). The first increase in FAO current with potential from 0.2 V to 0.35 V is explained by the increase of overpotential, which prevails the decrease of active sites due to sulfate adsorption. The decrease of FAO current at $E = 0.35$ V is explained by the fast drop of the amounts of active sites due to the formation of compacted adlayer which prevails the increase of reaction overpotential.

In contrast to the case in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{H}_2\text{SO}_4$, in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{H}_2\text{SO}_4$ the FAO current transients took slightly longer time (ca. 5 s) to reach the maximum after stepping the reaction potential from 0.7 V to lower potentials. After the current maximum was reached, the current also did not show obvious change with reaction time (FIG. 7(a)). This finding further supports that when step or scan from 0.7 V to lower potentials it takes longer time for the sulfate adlayer to reconstruct to a structure which fits the applied potential. Furthermore, the magnitude of the FAO current with 0.05 mol/L or 0.1 mol/L $\text{Na}_2\text{SO}_4$ is significantly smaller than that without $\text{Na}_2\text{SO}_4$. The fact that the higher $\text{Na}_2\text{SO}_4$ concentration, the smaller the FAO current is in good agreement with the $j$-$E$ curves measured in the negative-going scan by CV. Such deviation of FAO current is highest at 0.35 and 0.4 V, where the FAO current in $\text{Na}_2\text{SO}_4$ containing solution is just ca. 25% to 30% of that without $\text{Na}_2\text{SO}_4$ (FIG. 7 and FIG. 8), which also agrees with the results obtained by CVs (FIG. 5 and FIG. 6). All these results further support that a more compact adlayer is formed in $\text{Na}_2\text{SO}_4$ containing solution.

Compared to the case in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{H}_2\text{SO}_4$, in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{HClO}_4$, the initial FAO current on Pd(111) is significantly higher, but there is a significant decay of FAO current with reaction time. The former is explained by that more free sites on Pd(111) in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{HClO}_4$ are available right after stepping to each reaction potential compared to the case in 0.1 mol/L HCOOH$+0.1$ mol/L $\text{H}_2\text{SO}_4$. The significant decay of FAO current with reaction time is preliminarily explained by the poisoning of Pd(111) surface by the formation of bridge-bonded formate ($\text{HCOO}_\text{ad}$) and bicarbonate ($\text{HCO}_3^-\text{ad}$) during FAO as inferred from ATR-FTIRS studies of FAO on Pd film electrode [8]. This observation indicates that even in solutions containing no strongly adsorbed anions, Pd surface may still be poisoned by strongly adsorbed products, intermediate or side products. It is well confirmed that although CO$_\text{ad}$ cannot be easily formed on Pd during FAO, however, with elongated reaction, CO$_\text{ad}$ may be formed by the reduction of CO$_2$ produced by FAO [3].

**D. The structure of sulfate adlayer on Pd(111) and its impact on FAO kinetics**

Present results clearly confirm that adsorbed sulfate has an inhibition effect toward FAO on Pd(111), which is in contrast to the case for FAO on Pt(111) where a promotion effect of sulfate toward FAO is observed [17, 18]. This discrepancy can be well explained by 

![Current transients of HCOOH oxidation on Pd(111) electrode](image-url)
FIG. 8 (a) Current of HCOOH oxidation on Pd(111) electrode in 0.1 mol/L HCOOH+0.1 mol/L H₂SO₄ with x mol/L Na₂SO₄ (x=0, 0.05, 0.1) measured at 15 s after the potential step to the respective reaction potentials. (b) The current measured in Na₂SO₄ containing solution are normalized to the ones (j̄₀) in 0.1 mol/L HCOOH+0.1 mol/L H₂SO₄ under otherwise identical condition. Data obtained from the curves given in FIG. 7.

FIG. 8 (a) Current of HCOOH oxidation on Pd(111) electrode in 0.1 mol/L HCOOH+0.1 mol/L H₂SO₄ with x mol/L Na₂SO₄ (x=0, 0.05, 0.1) measured at 15 s after the potential step to the respective reaction potentials. (b) The current measured in Na₂SO₄ containing solution are normalized to the ones (j̄₀) in 0.1 mol/L HCOOH+0.1 mol/L H₂SO₄ under otherwise identical condition. Data obtained from the curves given in FIG. 7.

The much stronger covalent interaction between Pd(111) and the sulfate adsorbate than that for Pt(111), which is also supported by the differences between the CVs of Pt(111) and Pd(111) in 0.1 mol/L H₂SO₄ [17]. We find that the peak (or onset) potential for sulfate adsorption on Pd(111) is ca. 0.1 V (or 0.2 V) more negative than that on Pt(111) under otherwise identical condition, indicating that the binding energy of sulfate on Pd should be 0.1–0.2 eV stronger than that on Pt. The two times smaller FAO current and slightly smaller Tafel slope for FAO on Pd(111) in 0.1 mol/L H₂SO₄ in the potential range of 0.2–0.35 V (135 mV/dec, FIG. 4) than that in 0.1 mol/L HClO₄ in the same potential range are explained by significantly less free sites as well as slower potential-dependent changes of free sites due to higher coverage of sulfate adlayer formed at E<0.35 V.

The decrease of FAO current on Pd(111) when scanning the potential from 0.35 V to 0.7 V in solution with 0.1 mol/L HCOOH+0.1 mol/L H₂SO₄ may be due to the increase of sulfate coverage as suggested in previous IRAS results [16]. One most probable origin is the formation of more compact structure of the sulfate adlayer induced by the increase of electrode potential. EC-STM studies revealed that at 0.4 V (the potential just positive of the phase transition peak, 0.38–0.39 V, FIG. 1), sulfate adsorbs with some domains display well defined ordered (√3x√7) adlayer, among which one sulfate with three of its O atoms bonding to the three neighboring atoms on Pd(111) surfaces [12–16]. The coarsening into much bigger domains with further increase of potential could increase the long-range order of sulfate adlayer [27, 28, 30, 31]. Simulation of the STM images based on DFT revealed that in between the adsorbed sulfate chains, there is [([H₂O)ₙ-H₃O⁺] chains which are non-coplanar in the direction parallel to the electrode surface [14]. This [(H₂O)ₙ-H₃O⁺] would form hydrogen bonds with the oxygen atoms of the adsorbed sulfates. Besides, it would play a key role in stabilizing the large negative charge that otherwise would be present in the inner layer if the sulfate was adsorbed retaining its charge. The potential of zero charge for Pd(111) in 0.1 mol/L H₂SO₄ is ca. 0.25 V vs. RHE [23]. At higher potentials, the effect of stabilization is manifested and more rigid (SO₄[^*]_{ad})ₙ+[H₂O)ₙ-H₃O⁺] adlayer is formed [33–35], which reduces free sites available for FAO. It should be noticed that with present data, we cannot exclude whether during FAO, HCOO⁻ or HCO₃⁻ will be included in such an adlayer or not.

The further decrease of FAO current on Pd(111) after addition of Na₂SO₄ at higher potentials and in the subsequent negative-going scans into lower potential range is probably due to the formation of a rather more compact structure of sulfate adlayer, since at these potentials, reaction (2) will become thermodynamically allowed and Na⁺ cation will also interact with the adsorbed sulfates. Na⁺ cations are assumed to have an stabilizing effect to decrease electrostatic repulsion between partially charged sulphate molecules [32]. Higher potentials may lead (SO₄[^*]_{ad})ₙ+[Na⁺(H₂O)ₙ-H₃O⁺] adlayer to find its most energetically stable configuration, although as seen from the base CVs given in FIG. 2 where barely no sulfate adsorption current is observed. In addition to the well-known phase transition of disordered, mobile phase to ordered (√3x√7) superstructure at relatively lower potentials, the (√3x√7) superstructure may also be enhanced with the further increase of potential and addition of Na₂SO₄. Once a more compact adlayer is formed at higher potentials, its destruction or desorption is more difficult, and less free sites are left on the surface at high potentials. As a result, FAO current on Pd(111) in the negative-going scan is significantly smaller than that at the same potential in the positive-going scan. Further studies with scanning tunneling microscopy and FTIR and investigations in solutions containing other alkaline cations are underway to verify such speculations.

IV. CONCLUSION

Formic acid oxidation (FAO) on Pd(111) in HClO₄ and H₂SO₄ acid containing solution with and without addition of Na₂SO₄ has been studied using cyclic voltammetry and potential step methods. We found that (i) no obvious difference in FAO current between the positive-going and negative-going scan is seen in both 0.1 mol/L HClO₄ and 0.1 mol/L H₂SO₄. FAO in 0.1 mol/L H₂SO₄ has a current peak at ca. 0.36 V,
which is 160 mV more negative compared to that in 0.1 mol/L HClO₄, and the magnitude of the current in 0.1 mol/L H₂SO₄ is ca. 2–50 times smaller than that in 0.1 mol/L HClO₄ depending on the reaction potential; (ii) in 0.1 mol/L H₂SO₄ + x mol/L Na₂SO₄, however, the FAO current in the negative-going scan is significantly smaller than that at the same potential in the positive-going scan.

Our results reveal that adsorbed sulfate has a significant inhibition effect on the FAO kinetics. At potentials positive of the phase transition potential for the (SO₄²⁻)₅[B(H₂O)₆]H₂O⁺ adlayer, the adlayer structure probably becomes denser with the increase of potential and addition of Na₂SO₄, and the destruction /desorption of compact sulfate adlayer formed at higher potentials becomes more difficult. As a result, FAO kinetics on Pd(111) covered by such an adlayer is significantly inhibited. Present results reveal that, if one wants to study the pH effect on FAO using solutions with x mol/L H₂SO₄ + y mol/L Na₂SO₄ as supporting electrolyte to tune the solution pH, the surface coverage of the adsorbates and their adlayer structure on Pd(111) change sensitively to the solution composition and the applied potential, this will significantly affect the FAO kinetics. Hence, when studying the pH effect of FAO on Pd(111), careful analysis of the potential- and solution composition-dependent change of adlayer structure and coverage is necessary before the intrinsic pH effect can be deduced.

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