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Determination of Isotherm for Acetate and Formate Adsorption at Pt(111) Electrode by Fast Scan Voltammetry

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Fast scan voltammetry is an efficient tool to distinguish oxidative/reductive adsorption/desorption from that for bulk reaction. In this work, we provide a methodology that the isotherm of oxidative/reductive adsorption desorption processes at electrode surface can be obtained using just one solution with relatively low reactant concentration, by taking the advantage of varying the potential scan rate (relative of the diffusion rate) to tune the adsorption rate and proper mathematic treatment. The methodology is demonstrated by taking acetate adsorption at Pt(111) in acidic solution as an example. The possibility for extension of this method toward mechanistic studies of complicated electrocatalytic reactions is also given.

Key words: Adsorption, Desorption, Pt(111), Acetate anion, Formate anion

I. INTRODUCTION

In parallel with the electrocatalytic reactions at the electrode surface, adsorption and desorption of species such as water, cations, anions, as well as the decomposed fragments from the reactants or solvent always occur. Electrocatalytic reactions are often affected by such adsorbates to various extents through changing the electronic properties of the catalysts surface, blocking the surface active sites, changing the double layer structure and so on. Knowledge of adsorbate coverage, the adsorption state (configuration and domain structure), as well as the kinetics for their adsorption and desorption are of great help in unraveling their effects on related reactions. In this work, we will focus on deducing the adsorption isotherm for stably adsorbed fragments formed by electrochemical decomposition of reactants, *i.e.*, where charge transfer is accompanied.

In systems that no other faradaic reactions occur simultaneously with the adsorption/desorption processes, the adsorption isotherm can be inferred from the charge involved in such processes using conventional electrochemical measurements (*e.g.* cyclic voltammetry). However, for most electrocatalytic systems, the charge involved for fragment adsorption/desorption are usually much smaller than that for its bulk oxidation. In order that the adsorbate coverage derived from cyclic voltammetry is as accurate as possible, fast scan rate (typically $\geq$10 V/s) together with relative low reactant concentration is used in order to eliminate the current contributed from electrode reaction [1−3].

Due to faster consumption by adsorption and relatively slower compensation by diffusion (especially in solutions with low reactants concentration), the concentration of reactant at electrode surface may be much smaller than that in the bulk solutions. In addition to correctly deducing the charge involved in the adsorption, accurately evaluating the concentration of reactant near the electrode surface is also crucial to correctly derive the adsorption isotherm. Furthermore, to obtain the adsorption isotherm at any specific potentials, usually a number of cyclic voltammogram (CV) curves in a series of solutions with relatively low reactants' concentrations but expanding a wide range has to be recorded at relatively slow potential scan rate (typically $\leq$10 mV/s, in order to make sure that the concentration of reactant near the electrode surface is exactly the same as that in bulk solution). This is similar to the case for deriving the adsorption isotherm in gas phase studies, where reactants' pressure is systematically varied).

In this work, we will provide a novel and simple method, by which the adsorption isotherm can be obtained using just one kind of solution with low reactant's concentration. This is realized by taking the advantage of varying the potential scan rate to tune the adsorption rate (relative to the diffusion rate) and proper mathematic treatment of the measured faradaic current to obtain the concentration of reactant at the electrode surface at different scan rates. Acetate adsorption at Pt(111) electrode is taken as a model system to demonstrate this methodology. The possibility for extension of this method for mechanistic studies of complicated electrocatalytic reactions is also discussed.

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II. EXPERIMENTS

The electrolyte solutions with 0.1 mol/L $HClO_4$+ 1 mmol/L CH_3COOH or with 0.1 mol/L $HClO_4$+ x mmol/L HCOOH (x=0, 0.2, 0.4, 0.5, 1.0, and 2.0 mmol/L) were prepared using perchloric acid (70%, Suprapure, Sigma-Aldrich), acetic acid, or formic acid (Suprapure, Sigma-Aldrich), and ultra-pure water (18.2 MΩ, from Milli Q water system). Low acetic acid concentration is used in order that acetate coverage at fixed potentials can be easily tuned by changing the potential scan rate. Very low formic acid concentrations are used to make sure that when determining the coverage of formate using fast voltammetry, the contribution of the current from oxidation of formic acid molecules diffuses from the bulk is negligible [4].

The working electrode (WE) Pt (111) was prepared from small bead, obtained by melting and subsequent slow crystallization of a platinum wire of 0.8 mm in diameter (99.99%, Tanaka Noble Metal Corp.) according to Clavilier's technique [5]. Prior to any experiment, the working electrodes were annealed for about 10 s in a H_2-air flame, cooled down in a reductive atmosphere (H_2+N_2), and quenched in ultra-pure water in equilibrium with this atmosphere. The electrode surface was protected with a water droplet to prevent the contamination of the surface during the transfer to the electrochemical cell. A meniscus configuration was maintained between the Pt(111) surface and the electrolyte during all measurements.

A conventional two-compartment, three electrode glass cell was used for all the electrochemical measurements. A reversible hydrogen electrode (RHE) and Pt foil are used as reference electrode (RE) and counter electrode (CE), respectively. The electrode potentials were controlled by a potentiostat (CHI 660, Shanghai Chenhua). All potentials in the work are quoted against the RHE. The Ohmic drop was compensated by the instruments in all cases. All the measurements were carried out at room temperature. Before each experiments, all solutions was purged with N_2 (99.999%, the Linde Group, China) for at least 20 min. Then the base CV was recorded to make sure that the CV show well-documented features for Pt(111) electrode. Base CV for Pt(111) electrode recorded in 0.1 mol/L $HClO_4$ at a scan rate of 50 mV/s is recorded to check whether the homemade Pt(111) is well ordered and the cell system used for the work is clean or not.

CVs in solutions with 0.1 mol/L $HClO_4$+1.0 mmol/L CH_3COOH have been recorded at potential scan rates of 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 V/s. CVs for formic acid oxidation in solutions with different formic acid concentration have been recorded at potential scan rate of 50 mV/s and those for formate adsorption were recorded at 10 V/s. It should be noticed that because of the existence of uncompensated Ohmic resistance (R), as well as relatively high double layer capacitance (C) with working electrode of typical diameter of 2−3 mm or even larger as used, CVs recorded at scan rate above 50 V/s is largely distorted.

III. RESULTS AND DISCUSSION

A. Theoretical background

Rodes *et al.*'s FTIR measurement revealed that at Pt(111) acetate adsorbed in bridge-bonded configuration, with its two oxygen atoms bonding to two neighboring Pt atoms, and its C−C bond parallelled to surface normal [6]. Fukuda *et al.* revealed that using cyclic voltammetry at lower acetate coverage, acetate adsorption followed Langmuir type adsorption isotherm, while at higher coverage, there are repulsive interactions among adsorbed acetate [2]. Recent DFT calculation suggested Langmuir-type adsorption isotherm explained well the cyclic voltammetric behavior for acetate adsorption. Since the dissociation equilibrium constant for acetic acid was on the order of 10^{-5}, the adsorption of acetate at Pt in solutions with pH=1 can be expressed as [2, 7]:

$$HA \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A_{ad} + H^+ + e^- \tag{1}$$

The intrinsic rate for the adsorption is found to be very fast [2] the potential dependence of the rate constants, k_a and k_d, can be expressed by the Butler-Volmer equation:

$$k_a = k_a^0 \exp\left(\frac{\beta FE}{RT}\right) \tag{2}$$

$$k_d = k_d^0 \exp\left[\frac{-(1-\beta)FE}{RT}\right] \tag{3}$$

where β is the electron transfer coefficient and E is the applied potential. F is the Faraday constant, R is the gas constant, T is the temperature. Assuming that acetate adsorption at Pt(111) follows Frumkin type adsorption isotherm, under equilibrium we have the adsorption and desorption rate equals:

$$\frac{\theta}{\theta_{max}-\theta}\exp(g\theta) = K^0 c^s \exp\left(\frac{\eta F}{RT}\right) \tag{4}$$

where θ is the adsorbate coverage, θ_{max} is the maximum coverage achievable at Pt(111) surface, and g is the Frumkin factor, which reflects the effect of the interaction among adsorbate on the adsorption and desorption rates. If g>0, the adsorbates interaction is repulsive. If g=0, the isotherm approaches the Langmuir-type adsorption isotherm.

Except adsorption in the form of acetate, acetic acid is found not to oxidize at Pt electrodes at all, furthermore, the adsorbed acetate cannot also be further oxidized at Pt electrode [8, 9]. This means that acetate adsorption is the only charge transfer process. For such

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system, in order to obtain the adsorption isotherm at any specific potentials by just recording j-E curves in a single solution with low concentration of acetic acid, one may systematically vary the potential scan rates. Under such circumstance, the surface coverage of adsorbate at any potential $\theta(E)$ during the LSP from the onset for its adsorption up to the potential, where its saturation coverage is reached, can be easily determined by the charge involved in its adsorption.

On the other hand, one should keep in mind that in voltammetric studies using relative fast potential scan rate in stationary solutions with low reactant concentration, the concentration of reactant at electrode surface ($c^{\rm s}$) may be much smaller than that in the bulk solutions due to faster consumption by adsorption and relatively slower compensation by diffusion. Under such circumstance, since the intrinsic rate for acetate adsorption/desorption is rapid [2], it can still be assumed that the adsorbed species is always in equilibrium with the reactant at the electrode surface [10]. Since adsorption is the only process which consumes reactant, we have

$$D\frac{\partial c^{\rm s}}{\partial t}=\frac{\partial \theta}{\partial t} \tag{5}$$

where D is the diffusion coefficient of reactants. The concentration of reactant at the electrode surface can be obtained by a convolutive transformation of the experimentally measured adsorption current ($j_{\rm ad}(t)$) [10]

$$c^{\rm s}(E\,(t))=c^{\rm b}-\sqrt{\pi D}\int_0^t\frac{j_{\rm ad}(\tau)}{nF}\sqrt{t-\tau}{\rm d}\tau \tag{6}$$

The adsorption current can be derived from the measured current after correcting the double layer charging recorded in solutions free of adsorption processes in the same potential region. With the knowledge of $c^{\rm s}$ and θ at any adsorption potentials, the corresponding adsorption isotherm can be easily derived.

B. Experimental results on acetate adsorption at Pt(111) electrode

Base CV for Pt(111) electrode recorded in 0.1 mol/L $HClO_4$ at a scan rate of 50 mV/s is given in Fig.1, where two well separated potential regions are observed, *i.e.*, the hydrogen underpotential adsorption/desorption (HUPD) region (0.05 V$<E<$0.4 V) and the so-called "butterfly" region (0.55 V$<E<$0.9 V) with a sharp peak at 0.8 V. The "butterfly" feature in perchloric acid solution is associated with the adsorption of $OH_{\rm ad}$ from water and its desorption. These features are exactly the same as those reported in Refs.[11−13], confirming that the homemade Pt(111) is well ordered and the cell system used for the study is clean.

A representative cyclic voltammogram of Pt electrode in 0.1 mol/L $HClO_4$+1.0 mmol/L CH_3COOH at potential scan rate of 50 mV/s is shown in Fig.1. From the

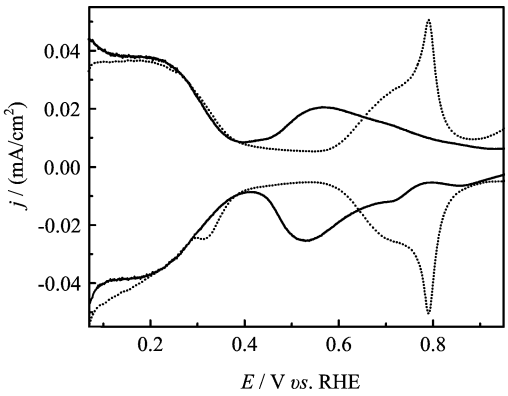

FIG. 1 Cyclic voltammograms of Pt electrode in 0.1 mol/L $HClO_4$ (dotted line) and 0.1 mol/L $HClO_4$+1 mmol/L CH_3COOH (solid line) at a scan rate of 50 mV/s.

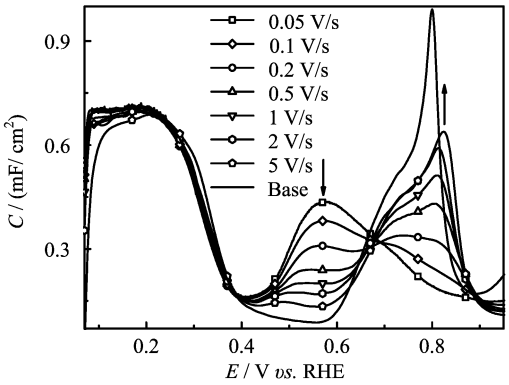

FIG. 2 Cyclic voltammograms of the Pt(111) in 0.1 mol/L $HClO_4$+1.0 mmol/L CH_3COOH at various scan rates.

curve, it is seen that an additional peak in the potential region from 0.4 V to 0.85 V appears, the current reaches a maximum at ca. 0.57 V. The current wave in the potential region from 0.4 V to 0.57 V can be attributed to acetate adsorption as well confirmed by infrared spectroscopic studies [6]. At $E>$0.57 V, the anodic current decreases with positive shift in electrode potential, which is attributed to the co-adsorption of both acetate and $OH_{\rm ad}$. The decrease in the anodic current with potential in the region of $E>$0.57 V is just in contrast to the corresponding current wave for $OH_{\rm ad}$ adsorption in acetate free solutions, suggesting that $OH_{\rm ad}$ adsorption is inhibited by adsorbed acetate formed at lower potentials.

With increase in the potential scan rate, the current peak at ca. 0.57 V turns into a broad plateau from 0.45 V to 0.6 V, this is clearly seen from the C-E curve as given in Fig.2. C is just derived from dividing the current by the corresponding potential scan rate, *i.e.*, $C=j/v$. This is explained by the fact that the adsorption is mainly controlled by the diffusion due to the low CH_3COOH concentration in the solution (1.0 mmol/L) used for examination. On the other hand, it is seen that the current wave at $E>$0.67 V increases with potential

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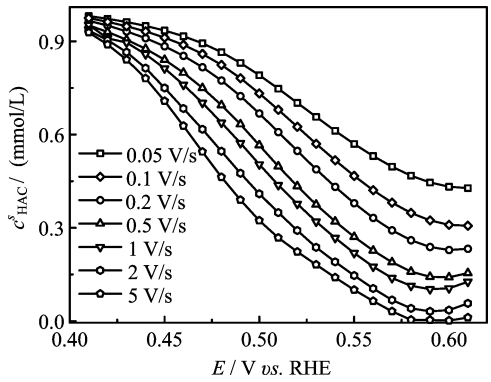

FIG. 3 Concentration of CH_3COOH near Pt(111) electrode surface as a function of electrode potential at various scan rates.

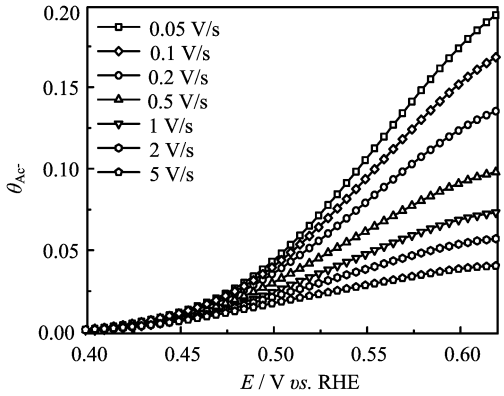

FIG. 4 Acetate coverage θ_{Ac^-} at Pt(111) electrode surface as a function of electrode potential at various scan rates.

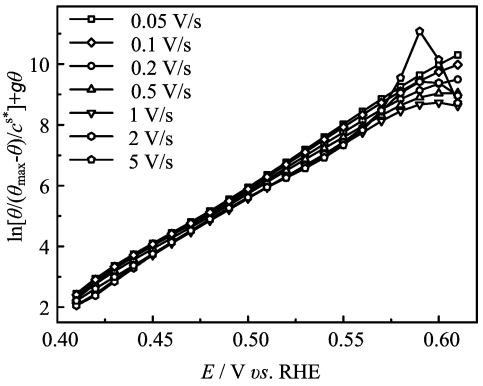

FIG. 5 Plots of $\ln[\theta/(\theta_{max}-\theta)/c^{s*}]+g\theta$ as a function of electrode potential.

scan rate. This is due to the fact that the faster the scan rate, the less acetate is adsorbed at lower potentials and more free sites are available for the competitive adsorption of OH_{ad} at higher potentials. Note the amount of water near the electrode surface is ca. 55 mol/L, OH_{ad} adsorption will only be limited by available free sites rather than by water diffusion.

From the C-E curve given in Fig.2 and Eq.(6), we can easily determine the $c^s(E)$. The change of c^s as functions of electrode potential at various potential scan rates are plotted in Fig.3. From Fig.3, it is clearly seen that at the same potential c^s decreases with increase in potential scan rate, and at the same potential scan rate c^s decreases with positive shift in electrode potential from 0.4 V to 0.6 V as expected from the faster comsumption of acetic acid near the electrode surface due to acetate adsorption and the relatively slower compensation by acetic acid diffusion. The faradaic current in the potential region from 0.4 V to 0.6 V mainly comes from acetate adsorption, since no other electrochemical processes occur in this potential range. The adsorption current is derived from the total measured current after correcting the double layer charging current recorded in acetate free solution in the same potential regime and under the same potential scan rate. With that, the acetate coverage at any potentials in this potential regime can be determined and given in Fig.4. From Fig.4, it is seen that under fixed potential scan rate acetate coverage increases with electrode potential, while at the same potential, acetate coverage decreases with increase in potential scan rate, as similar to the potential and scan rate dependence for the concentration of acetic acid at Pt(111) surface.

By putting the $c^s(E)$ and $\theta(E)$ at corresponding potential derived from LSP at different potential scan rate into Eq.(4), the value of g was found to be ca. 2. By plotting $\ln[\theta/(\theta_{max}\text{-}\theta)/c^{s*}]+g\theta$ as a function of electrode potential (Fig.5), defining that $c^{s*}=c^s/1$ mol in order to remove the units in the denominator, we found that all the plots from the data recorded at different potential scan rate display linear behavior with a slope of 38.7 V^{-1} (just equals coefficient F/RT, see Eq.(4)), and which superimposes well with each other. This confirms that throughout the regime with the coverage of adsorbed acetate from zero to saturate (ca. 0.3 ML, the repulsion of CH_3 groups among adsorbed bridged acetate renders that its saturation coverage is lower than 0.5 ML), acetate adsorption follows well the Frumkin-type adsorption isotherm. The relative small value for g suggests that there is very weak repulsion between adsorbed acetate species. The good linearity of the $\ln[\theta/(\theta_{max}-\theta)/c^{s*}]+g\theta$ versus E plots and the well superimposition of these plots from the data recorded at different potential scan rate also confirm that for adsorption/desorption processes whose kinetics is very fast, one can use fast scan rate as high as 5 V/s or above to derive the adsorption isotherm, but has to pay attention that under such conditions the concentration of reactant near electrode surface may not be the same as that in bulk solution. This is crucial for deriving the adsorption isotherm of fragments from reactants which accompanying with simultaneous bulk oxidation.

The results can be summarized as: in systems just with oxidative/reductive adsorption/desorption at

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metal electrodes, the adsorption isotherm of such process can be derived by using cyclic voltammetry in just one kind of solution with relatively low reactant's concentration, by taking the advantage of using potential scan rate (relative of the diffusion rate) to tune the adsorption rate and proper mathematic treatment. This is of advantage over most previous studies of the same purpose, which have to be done in solutions with various reactants concentrations. For the cases where the adsorption/desorption processes are very fast, our results confirmed that the isotherm determined using fast potential scan rate is comparable to that using slow scan rate (where adsorption equilibrium is reached), provided that the concentration of reactants near the electrode surface during the fast scan adsorption process is correctly evaluated.

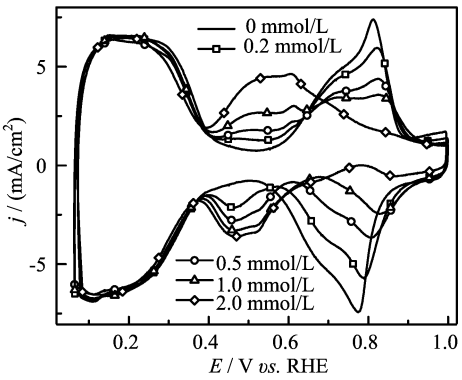

FIG. 6 Cyclic voltammograms of Pt(111) electrode in 0.1 mol/L $HClO_4$+x mmol/L HCOOH at 10 V/s, (x=0, 0.2, 0.5, 1.0, and 2.0 mmol/L).

C. Derivation of formate adsorption isotherm during HCOOH oxidation at Pt(111) electrode

Most electrocatalytic reactions involve two or more electrons transfer, and during electrocatalytic reactions several possible reaction pathways with different reaction intermediates may occur simultaneously. Under such conditions, there is subtle intercorrelation between the adsorbate coverage, reactant surface concentration, applied potential, and the faradic current. Correctly evaluating the relationship between reaction current and the adsorbed intermediates is crucial to deduce the role of such intermediates in the electrocatalytic reactions. Under such conditions, adsorbate coverage is better to be determined using spectroscopic techniques such as electrochemical *in situ* infrared spectroscopy. However, for many cases, the IR signal of adsorbate may not be strong enough to allow an accurate quantification. In this section, we will take formate adsorption during formic acid oxidation at Pt(111) electrode as an example, to demonstrate how to deduce formate adsorption isotherm using fast scan voltammetry.

Formic acid oxidation at Pt electrode is one of the most important model reactions in electrocatalysis. It was proposed that this reaction proceeds via "dual path" mechanisms with a "direct" and an "indirect" pathway [14, 15]:

$$\mathrm{HCOOH} \rightarrow \text{Active intermediate} \rightarrow \mathrm{CO_2}$$
$$\mathrm{HCOOH} \rightarrow \text{Poison intermediate } (\mathrm{CO_{ad}}) \dashrightarrow \mathrm{CO_2}$$

It is well accepted that the indirect pathway proceeds via the initial dehydration of HCOOH to CO_{ad}, which is then oxidized to CO_2 [14−16], and its contribution to the total current for formic acid oxidation is negligible [17]. In the direct pathway, COOH [18] and HCOO [19] have both been proposed as reaction intermediates. However, only bridge-bonded formate ($HCOO_B$) has been well confirmed by electrochemical *in situ* infrared spectroscopic studies under attenuated total reflection configuration (EC-ATR-FTIRS) [19−25]. By now, it is still under hot debate whether formate is just the reaction intermediate for the direct pathway. Obviously, correctly evaluating the relationship between reaction current and the adsorption behavior of formate is crucial to deduce the role for formate in the electrocatalytic oxidation of formic acid.

It is well known that the adsorption of CO at Pt is much stronger than that for formate, in order to derive formate adsorption isotherm during formic acid oxidation, we have to reduce the effect of CO adsorption and the contribution of current from formic acid oxidation to that of formate adsorption. To this end, we decided to use Pt(111) as working electrode, with very low HCOOH concentration (0.2 mmol/L to 2.0 mmol/L), and potential scan rate of 10 V/s. It is well confirmed that at Pt(111), CO_{ad} formation rate from HCOOH is negligibly slow. With low HCOOH concentration and potential scan rate of 10 V/s, the effect of HCOOH oxidation on deriving formate adsorption current can be largely eliminated, and the effect for CO_{ad} poisoning can be further suppressed since the channel for CO_{ad} formation is much slower than that for the direct pathway [26]. It should be noticed that, because of the resistance between the working electrode and Luggin cappilary, as well as relatively high double layer capacitance with working electrode of typical diameter of 2−3 mm used in the present work, CVs recorded scan rate above 50 V/s is largely distorted. When deriving formate adsorption isotherm at fixed potentials, we have to fix the potential scan rate at 10 V/s and systematically varying the concentration of formic acid.

Figure 6 shows the CVs for Pt(111) in 0.1 mol/L $HClO_4$+x mmol/L HCOOH (x=0−2.0 mmol/L) recorded at potential scan rate of 10 V/s. A broad current wave is observed between ca. 0.38 and 0.7 V, and increases with HCOOH concentrations, while the current peak around 0.8 V corresponding to OH_{ad} adsorption/desorption decreases. The anodic current wave from 0.38 V to 0.7 V has been assigned to the adsorption

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of HCOOB [4] as in accordance with EC-ATR-FTIRS results at Pt polycrystalline electrodes [17, 27]. Since the current wave at potentials higher than 0.6 V may include the contribution from OH_{ad} adsorption, our following analysis on formate adsorption isotherm will focus on the data recorded in the positive-going potential scan from 0.4 V to 0.6 V where the effects of other adsorbate such as OH_{ad} and CO_{ad} are negligible.

Since the current for formate adsorption is much higher than the current for formic acid oxidation at potential scan rate of 10 V/s in solutions with formic acid concentration below 2 mmol/L, the faradaic current can be considered solely from formate adsorption. Similar to the case for acetate adsorption, for formate adsorption from formic acid, $c^{s}(E)$ of formic acid can be obtained by the measured faradic current density ($j(t)$) and Eq.(6) [10] (Fig.7(a)). And the surface coverage of formate at any potential can be derived by simply integrating the charge involved for formate adsorption (Fig.7(b)). Using Eq.(4), g was found to be at 1.4. By plotting $\ln[\theta/(\theta_{max}-\theta)/c^{s*}]+g\theta$ verus E, a linear relationship was found. The slope value is around 38.7 V^{-1} and all such plots from the data recorded in solutions with different HCOOH concentration superimpose well with each other (Fig.8), as similar to the case for acetate adsorption from acetic acid. This confirms that formate adsorption also follows Frumkin-type adsorption isotherm, and the g factor is just 1.4, which is slightly smaller than that of 2 for acetate, indicating that the repulsion between adsorbed formate species is rather weak.

Since the intrinsic rate for formate adsorption/desorption is very fast, the surface coverage of formate ($\theta_{formate}$) should be always in equilibrium with the concentration of formic acid near Pt(111) surface (c^{s}) [1, 4, 17, 27−29]. Hence, if we know the adsorption isotherm for formate adsorption/desorption, and the concentration of formic acid near the electrode surface, the relationship between formic acid oxidation current with formate surface coverage at any potential scan rate can be easily determined. After careful analysis formic acid oxidation current and formate coverage relationship, we find that formate is not the reactive intermediate for formic acid oxidation at all, the details of such analysis will be reported elsewhere.

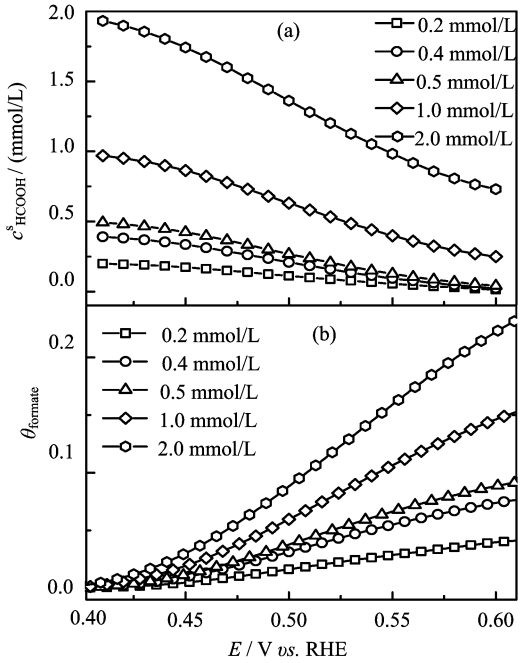

FIG. 7 Surface concentration of HCOOH (a) and formate coverage (b) at Pt(111) electrode during cyclic votammetric studies on formic acid oxidation in solutions with different bulk HCOOH concentrations at 10 V/s.

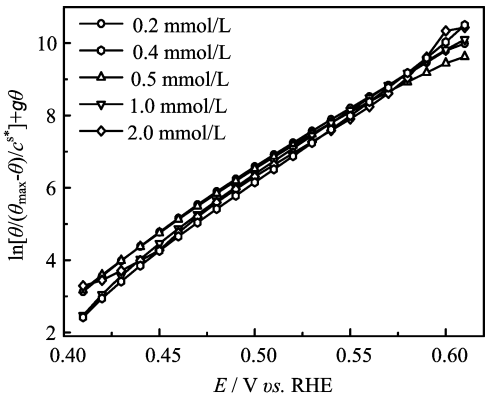

FIG. 8 Plots of $\ln[\theta/(\theta_{max}-\theta)/c^{s*}]+g\theta$ as a function of electrode potential with data from solutions with various concentration of HCOOH.

IV. CONCLUSION

Methodology for deriving the adsorption isotherm for anions and reaction intermediates using cyclic voltammetry has been discussed in detail by taking the adsorption behavior of acetate and formate at Pt(111) electrode as model systems. For the cases just with electrochemical adsorption, such as acetate adsorption, our studies reveal that the adsorption isotherm can be obtained using just one kind of solution with low reactant concentration, by taking the advantage of using potential scan rate (relative of the diffusion rate) to tune the adsorption rate and proper mathematic treatment. For studies of complicated electrocalytic reactions involving multiple pathways which occur in parallel with stable intermediate adsorption, one may use fast scan voltammetry accompanying with systematically varying the concentration of reactants. Crucial issues for correct derivation of the adsorption isotherm have been discussed in detail. We believe the strategy and methodology used in this work will be of great help for future mechanistic studies on complicated reactions [30].

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V. ACKNOWLEDGMENTS

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