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pH effect on acetate adsorption at Pt(111) electrode

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ABSTRACT

pH effect on thermodynamics and kinetics of acetate adsorption on the Pt(111) electrode in solutions is studied over a wide pH range (from 1 to 13) by cyclic voltammetry and electrochemical impedance spectroscopy. With increasing solution pH i) from pH = 1.1 to 4.7, the peak potential for acetate adsorption shifts slightly from 0.39 V_{RHE} to 0.46 V_{RHE}, ii) from pH = 4.7 to 10.2 it shifts by ca. 56 mV/pH unit; iii) the adsorption isotherm for acetate adsorption does not show obvious changes, but the adsorption kinetics become slower with pH changing from 1.1, 4.7 to 7.6. The positive shift in the acetate adsorption peak with pH (on the RHE scale) can be explained by the pH-dependence of the thermodynamic equilibrium potential for acetate adsorption with either acetic acid or acetate anions as the precursor. The faster acetate adsorption kinetics in acid than in alkaline solution are attributed to a reduced activation barrier, owing to the formation of hydrated H^+ upon CH_3COOH deprotonation to adsorbed acetate.

1. Introduction

The change of solution pH significantly affects the kinetics of many electrocatalytic reactions for energy conversion systems, such as formic acid oxidation (FAO), hydrogen evolution/oxidation reaction and so on [1–8]. Such effects are frequently explained by invoking pH-induced change of surface adsorption. However, the pH-induced changes of other parameters, such as reactant precursors, the energy of formation of the active complex, availability of active sites and so on, may also be very important [5,6]. Hence, systematic studies of the pH effect on the adsorption behavior of potential adsorbates are necessary to quantify its role in related reaction kinetics.

It is well documented that the onset potential (on the scale of reversible hydrogen electrode, RHE) for the adsorption of anions such as halides [9], sulfate [10], and phosphate [11] shifts positively. On a Pt electrode, specifically, it roughly shifts from the hydrogen adsorption region, at very low (acidic) pH, to the hydroxyl (OH) adsorption region, at very high (alkaline) pH. Based on such phenomena, it is concluded that the adsorption of anions (in general) on Pt becomes weaker at higher pH values [9,11]. The increase of the potential of zero charge (pzc, on the RHE scale) [8] or the increase in the surface electronic population of the d-band on Pt(111) [9] with pH has been suggested to play an important role in this. Such speculations may be applied for adsorbates which are anions, when electrostatic interaction between the adsorbate and the electrode is dominant.

Among all possible adsorbates, studying the pH effect on acetate adsorption is of special significance: i) acetate usually adsorbs on the metal electrode through a bridge-bonded configuration with the two oxygen atoms in its carboxyl groups attached to the two neighboring metal atoms, its precursor before the adsorption is either CH_3COO^- or CH_3COOH, which is much simpler than the more complicated sulfate or phosphate systems. This simplifies the analysis and discussion. ii) Acetate adsorption remains a typical model system for studying the adsorption of organic acids, which are usually the reaction intermediates formed during the oxidation of small organic molecules. Especially, since the adsorption configuration and potential regime for formate and acetate are similar, while acetate cannot be further oxidized, studying acetate adsorption may greatly help to reveal the adsorption behavior of formate on Pt, and consequently help to understand the origins for the Volcano-type pH dependence of FAO activity on Pt, which are under hot debate recently [2–5].

In acidic solution, acetate adsorption on Pt(111) occurs in the double layer potential region, which is superimposed with the adsorption of H [12,13]. Aramata et al. has examined the pH effect on acetate adsorption on Pt(111) in acid. They found that the main peak for acetate adsorption shifts 60 mV_{SHE}/pH in solutions with $pH < 2$, while it does not shift (in SHE scale) with the increase of pH in solutions with $5 < pH < 6$. They found that the Langmuir adsorption isotherm is a good model for acetate adsorption at low coverage [14]. This is also supported by DFT simulation [15]. In contrast, our recent study reveals that the Frumkin adsorption isotherm fits better for acetate adsorption on Pt(111) in acid, and there is weak repulsion between adsorbed

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acetate with a Frumkin factor of ca. 2, even at low coverage [13]. In alkaline solutions, no systematic studies on acetate adsorption on Pt have been reported so far. In this work, we report our work on the effect of pH on acetate adsorption in solutions with pH ranging from 1 to 13. It is found that, with increasing solution pH from 1.1 to 10.2, the onset and peak potentials for acetate adsorption shift positively, while the kinetics for acetate adsorption decrease. The positive shift in acetate adsorption potential is well explained by the pH-dependence of the thermodynamic equilibrium potential and the barrier for acetate adsorption with either acetic acid or acetate anions as the precursor, i.e., if the adsorption pathway goes through as $HA \rightarrow H^+ + A_{ad} + e^-$, the equilibrium potential will shift negatively with a ratio of 60 mV/pH in SHE scale. If the adsorption pathway goes through as $A^- \rightarrow A_{ad} + e^-$, the equilibrium potential will be pH independent in SHE scale. Possible origins for the slower kinetics for acetate adsorption are also discussed.

2. Experimental

The preparation and characterization of the Pt(111) electrode, as well as the three electrode cell setup were described in detail in reference [16]. Electrolyte solutions with 0.1 M $HClO_4$ + 10 mM CH_3COOH + x M NaOH (x = 0–0.21), whose pH values are in the range from 1 to 13, were prepared using perchloric acid (96%), acetic acid (CH_3COOH, 98%), NaOH (99.99%), suprapure grade from Sigma–Aldrich co and Ultra-pure water (18.2 MΩ cm). All electrochemical measurements were done under hanging-meniscus configuration. All solutions were purged with N_2 (99.999%) for about 15 min before each experiment. The impedance of acetate adsorption on Pt(111) at its peak potential in solution with pH = 1.1, 4.7, and 7.6 were measured with an AC amplitude of 5 mV in the frequency range of 10^4 Hz to 0.1 Hz. All potentials are quoted against the RHE.

3. Results and discussion

Fig. 1b displays a set of cyclic voltammograms (CVs) recorded in 0.1 M $HClO_4$ + 10 mM CH_3COOH + x M NaOH (x = 0–0.21) solutions with different pH values ranging from 1.1 to 12.8. For comparison, the base CVs for the same Pt(111) electrode in 0.1 M $HClO_4$ and NaOH are included in Fig. 1a. Comparing to the base CV for Pt(111) in 0.1 M $HClO_4$, in acetate-containing solution with pH = 1.1, a new current wave appears in the potential region from 0.35 V to 0.7 V with a peak at ca. 0.39 V (RHE). The cathodic current wave recorded in the negative-going potential scan mirrors the anodic wave in the same potential regime. These peaks are assigned to the adsorption/desorption of bridge-bonded acetate on Pt(111), as confirmed by previous infrared spectroscopic studies [17,18]. At E > 0.60 V, the decrease in the anodic current with potential is in contrast to the current wave for OH_{ad} adsorption in acetate-free solution, suggesting that OH_{ad} adsorption is inhibited by adsorbed acetate formed at lower potentials. As a result, the adsorption of acetate leads to the disappearance of the characteristic OH adsorption/desorption on Pt(111) in $HClO_4$ around 0.7 V to 0.95 V [12].

With the increasing solution pH from 1.1 to 4.7, the current peak for acetate adsorption/desorption shifts from 0.39 V to 0.46 V. With the increase of the pH from 4.7 to 10.2, the peak position shifts 56 mV per pH unit, this trend is in agreement with previous observation by Aramata (note in his work, the potential is with respect to the SCE scale) [14]. In acetate-containing solution with pH 12.8 (Fig. 1b), the CV is similar to that in 0.1 M NaOH. This confirms that acetate cannot adsorb on Pt(111), due to the competition of OH_{ad} adsorption. This is supported by previous infrared spectroscopic results [19].

The integrated charge for acetate adsorption on Pt(111) as a function of electrode potential in solutions with different pH values is displayed Fig. 2b. The values are estimated from the CVs given in Fig. 1b.

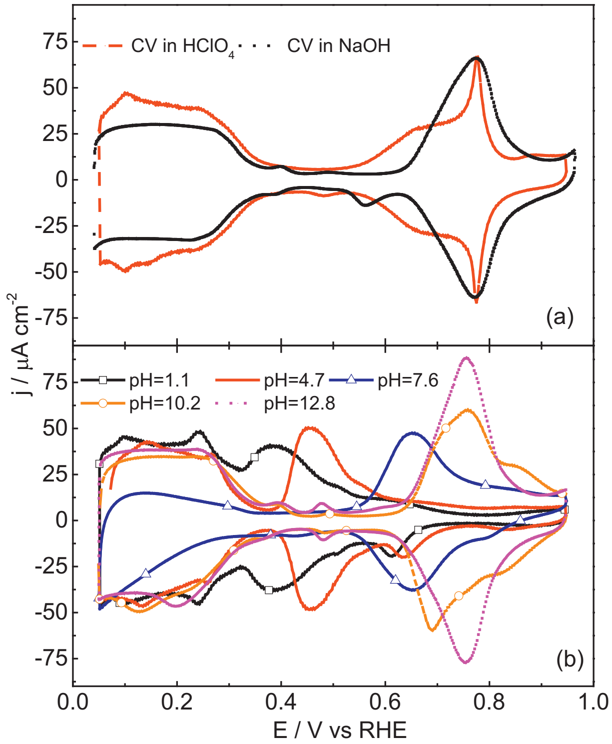

Fig. 1. Cyclic voltammograms of Pt(111) electrode in solutions of (a) 0.1 M $HClO_4$ and 0.1 M NaOH and (b) 0.1 M $HClO_4$ + 10 mM CH_3COOH + x M NaOH (x = 0–0.21) with different pH ranging from 1.1 to 12.8. Scan rate: 50 mV/s.

From Fig. 2b we see that although the onset potential for acetate adsorption shifts positively with increasing solution pH, the slope of the Q~E curve is roughly the same for solutions with different pH, which is similar to the case for sulfate adsorption on Pt(111) [10]. This is different from the case of halide adsorption, where the gradient of Γ versus potential becomes shallower as pH increases, as a result of the weakened anion-surface interaction as pH increases [9]. The absence of pH effect on the Q ~ E gradient for acetate adsorption further supports that the acetic components adsorbed on the Pt surface have the same configuration and intermolecular interaction in solution with different pH.

Fig. 2(c) shows a set of admittance plots recorded at the peak potential for acetate adsorption on Pt(111) in 0.1 M $HClO_4$ + 10 mM CH_3COOH + x M NaOH solutions with pH = 1.1, 4.7, and 7.6. The admittance values recorded for acetate adsorption are 236, 88 and 59 mS cm^{-2} in solutions of pH = 1.1, 4.7 and 7.6, respectively. The fact that the resistance for acetate adsorption becomes larger with increasing of pH reveals that the kinetics for acetate adsorption become slower at higher pH.

In the following, we will provide a self-consistent explanation for both the pH-induced shift of the onset potential for acetate adsorption, as well as the change of acetate adsorption kinetics. Acetic acid is a weak acid, and its dissociative reaction always occurs simultaneously with acetate adsorption:

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+ \quad (1)$$

The kinetics for both forward and backward reactions in Eq. (1) are very fast. The concentrations of CH_3COOH and CH_3COO^- in the bulk solutions are estimated based on the following equations:

$$a_{CH_3COOH} = \frac{c_0 \cdot 10^{pKa-pH}}{1 + 10^{pKa-pH}} \quad (2)$$

$$a_{CH_3COO^-} = \frac{c_0}{1 + 10^{pKa-pH}} \quad (3)$$