

Borate adsorption at Pt(111) in acidic medium

I. Specific adsorption

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Abstract The adsorption/desorption process of borate was studied at Pt(111) in acidic solution by cyclic voltammetry. A so-called butterfly wave in the cyclic voltammogram of Pt(111) in HClO₄ shifted to negative direction upon the addition of boric acid with the disappearance of its sharp spikes. The shift in potential was found to be -57 mV with a tenfold increase of boric acid concentration. This illustrates that this anomalous wave is due to borate adsorption/desorption by a one-electron transfer process. The borate adsorption/desorption wave was observed to shift by -63 mV/pH. At pH>3, the anomalous wave splits forming two separate waves, depending on the pH and the scan rate. The appearance of two waves is assigned to the change in the adsorption mode of borate or the participation of OH in the adsorption process.

Introduction

The specific adsorption of anions was extensively studied at Pt(111) electrodes firstly by Clavilier et al. [1, 2], using cyclic voltammetric technique. Anion adsorption was

clarified as a charge transfer reaction [3–5] with the help of CO displacement experiment.

The absence of the so-called anomalous wave in case of sulfate adsorption at Pt(111) was observed [6]. This result was confirmed later by Taguchi and Aramata [7]. Furthermore, sulfate adsorption was widely examined by various nonelectrochemical methods, such as scanning tunneling microscopy, Fourier transform infrared, and radiotracer techniques [5, 8–10]. On the other hand, both phosphate and acetate adsorption waves on Pt(111) were found to be pH-dependent [11–14].

The importance of borate electrochemistry arises from its presence as one of the main component of many electroplating baths. Many authors [15, 16] claim that boric acid was added to the electroplating baths as a buffering agent. Because the pK_{a1} value of boric acid is 9.14, its predominant form in acidic media up to pH 5 is the undissociated molecule. This indicates the absence of any buffering action of boric acid in this baths. It seems that the influence of boric acid on electrodeposition of Ni–Zn alloy is very complicated [17] and is not yet clear.

Because, in the authors' knowledge, specific adsorption of borate on Pt(111) has not yet been studied, the aim of this work is to study the borate adsorption by changing both the borate concentration and the pH value.

Experimental

The experiments were performed in a conventional three-electrode compartment cell with a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as counter electrode. The preparation of the Pt(111) electrode and cleaning of the electrode before each experiment was done according to the method of Clavilier et al. [1, 18]. The

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solutions were prepared from HClO_4 (Merck Suprapur), KClO_4 (Merck Proanalysis), and H_3BO_3 (Merck Suprapur) with Milli-Q-Water ($>18 \text{ M}\Omega$). The electrolytic solution was kept oxygen-free during the measurements by continuous bubbling of ultrapure Argon over the solution. The contact of working electrode with the solution took place by hanging meniscus technique. The coefficient of variation (CV) measurements were carried out at ambient temperature with potentiostat (Toho 2000) and function generator (Toho FG-01). The set up was connected to a personal computer for data acquisition and processing.

Results and discussion

Influence of boric acid concentration on the borate adsorption process

Figure 1 shows the cyclic voltammograms of Pt(111) in 0.1 M HClO_4 solutions in the absence and presence of different concentrations of boric acid. In boric acid-free solution, the voltammetric waves below ca. 0.1 V/SCE was assigned to the hydrogen adsorption/desorption process with coverage of $2/3$ of a monolayer. The so-called butterfly wave at $E > 0.26$ V/SCE is related to the OH adsorption/desorption process [19–21]. Addition of boric acid into the perchlorate solutions seems to have no influence on the total charge density of the voltammetric waves related either to hydrogen or anion adsorption. On the other hand, the originally observed butterfly wave is subjected to a potential shift to the negative direction with the disappearance of its sharp spikes in both anodic and cathodic directions. The shift to the negative direction

increases as the boric acid concentration increases. Similar behaviors were previously reported in acetate-containing [14] and phosphate-containing [11, 12] solutions. However, the potential shift observed is much less in the case of borate. This is may be due to the weakness of the adsorption capability of borate compared to the other anions. Accordingly, this may lead to the assumption of the presence of competitive adsorption between borate and hydroxyl ions. If this assumption is correct, this competition would be expected to depend on the pH of the solution. This assumption will be discussed in details in the next section. The shift of the peak potential as a function of boric acid concentration is illustrated in the inset of Fig. 1. From the slope of this figure, a shift to a negative potential direction by 57 mV for a tenfold increase of boric acid concentration is obtained. This indicates that this peak can be assigned as borate adsorption/desorption process via one-electron transfer reaction.

Influence of pH on the borate adsorption process

Figure 2 shows the pH-dependence of CVs in $10^{-3} \text{ M H}_3\text{BO}_3 + 0.1 \text{ M XClO}_4$ solutions (where X is H^+ and/or K^+) of pHs 1.23, 1.91, and 2.25. The solution pH value was governed by changing the HClO_4 concentration, while the total ionic strength was kept constant by the addition of KClO_4 . The peak position of borate adsorption shifted negatively by 63 mV/pH as shown in the inset of Fig. 2. Such pH dependence of the anion adsorption wave is also reported for perchlorate [20, 21] and phosphate [11] adsorption at Pt(111). These pH effects clarify that H^+ cations are involved in the adsorption/desorption process of borate at low pH value. The very low value of the first

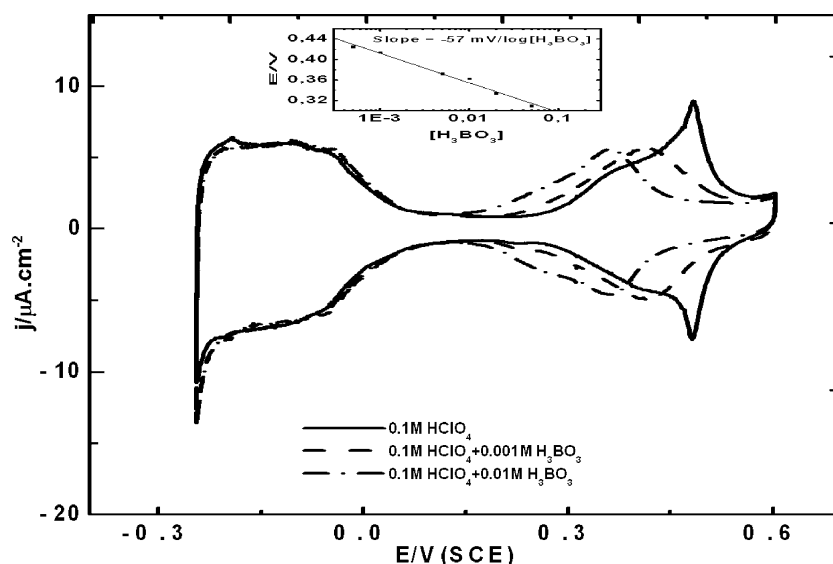


Fig. 1 Cyclic voltammograms of Pt (111) in 0.1 M HClO_4 in the absence and presence of different concentrations of H_3BO_3 at 5 mV/s. *Inset:* peak potential–boric acid concentration dependence at pH 1.23

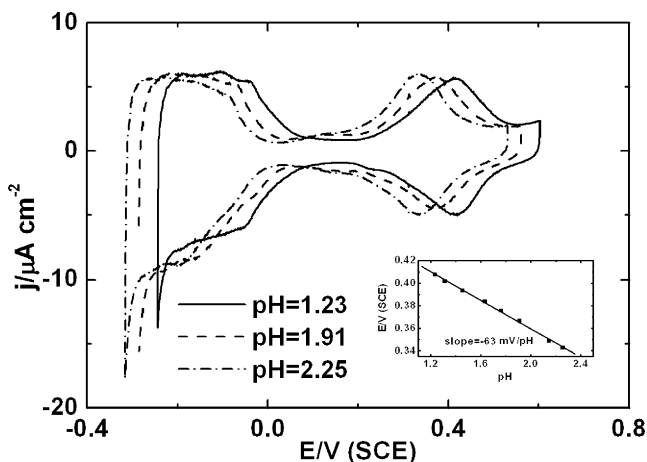
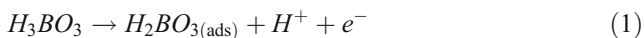


Fig. 2 The change of voltammograms of Pt(111) at 5 mV/s with pH increase in 10^{-3} M H_3BO_3 +0.1 M XClO_4 . $\text{X}=(\text{H}^++\text{K}^+)$. Inset: peak potential–pH relationship

dissociation constant of boric acid ($K_1=7.3\times 10^{-10}$) indicates that at $\text{pH}<5$, borate is in the form of H_3BO_3 , and therefore a reaction



is suggested.

At $\text{pH}>3$, the CV exhibits a splitting of the wave at a potential >0.0 V/SCE. This splitting is more pronounced in the negative direction as shown in Fig. 3. A simple possible explanation is that a new species starts to participate in the adsorption process at $\text{pH}>3$. However, this assumption can be excluded as the total charge under the anion adsorption wave was found to be identical to that one calculated from the voltammograms recorded at $\text{pH}<3$. This indicates that there is no formation of a new adsorption species. The other

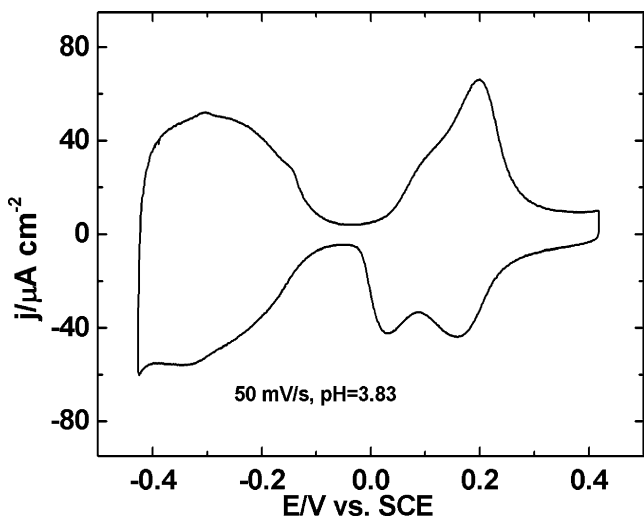


Fig. 3 Cyclic voltammogram of Pt (111) in 10^{-2} M H_3BO_3 +0.1 M XClO_4 . $\text{X}=(\text{H}^++\text{K}^+)$, $\text{pH}=3.83$, and scan rate=50 mV/s

possibility is the change in the adsorption mode as was proposed earlier [12]. A similar result was reported in the case of phosphate at different pH values that depended on the nature of the cations used [13]. Another interesting observation can be obtained from Fig. 4 where the CVs were recorded in borate-containing solution of $\text{pH}\approx 4.3$ at a different scan rate. As shown from this figure, at sweep rate=50 mV/s, two adsorption waves were observed instead of one at lower pH value. As the sweep rate decreases, these two waves merge together to form one broad peak. Such sweep rate dependences are unique in solutions with borate because it was not observed in the cases of phosphate solutions at $\text{pH}<4.6$ and of perchlorate and sulfate solutions at $\text{pH}<4$ [7]. Now, according to these results, a new question arises, which is: Is it really only one species that participates in this adsorption/desorption process even at lower pH value? Or is it possible that two species (likely to be OH and borate) are adsorbed together? If the last assumption is the favorable one, this may explain the splitting of the anion adsorption wave at higher pH value and also by changing the scan rate. The recombination of the two waves, again at slow sweep rate (5 mV/s), indicates that one of this species undergo a very low adsorption/desorption process compared to the other one. So, as the increase of the pH leads to the increase of the hydroxyl ions in the electrolyte, it seems that increasing the pH facilitate the adsorption of the OH on the Pt surface. This is in agreement with the recent results obtained at Pt(111) in NaOH solution, which show a shift of OH adsorption peak to lower potential value as the pH increases [22]. This possible assumption will be discussed further in the presence of the Zn upd process in borate-containing solution (El-Shafei and Aramata, submitted for publication).

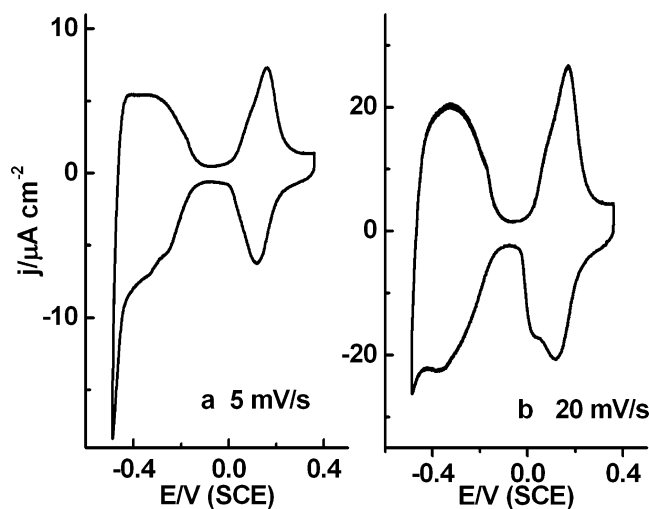


Fig. 4 Cyclic voltammograms at various sweep rates on Pt (111) in 10^{-2} M H_3BO_3 +0.1 M XClO_4 . $\text{X}=(\text{H}^++\text{K}^+)$ and $\text{pH}=4.3$

Conclusion

Borate adsorption/desorption waves appeared at Pt(111) upon the addition of H_3BO_3 to perchloric acid solution with the disappearance of the butterfly wave. The borate adsorption/desorption waves are being dependent on both borate concentration and pH by -57 and -63 mV per decade, respectively. This indicates the presence of borate adsorption on Pt(111) where the adsorption/desorption process is suggested as in Eq. 1.

The specific adsorption of H_3BO_3 was found to take place on Pt(111), which occurs at more positive potentials in comparison with that of the other oxoacids. This occurrence will be interpreted to be that the specific adsorption strength of H_3BO_3 is taken to be weak compared to that of phosphate but strong enough than OH adsorption in perchloric acid solution. The state of the adsorbed borate at the interface should be investigated in detail because borate forms polyacids by various configurations in bulk solution, being dependent on pH. When borate adsorbs according to Eq. 1, the two-dimensional structure of the adsorbed borate will be interesting to be clarified, which will be correlated with cations in solutions, as found in acetate [14] and phosphate [4] adsorption processes at high pHs. At higher pH values, the possibility of competition or the combination of both borate and OH adsorption cannot be excluded. This later point still needs further investigation.

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