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Coadsorption of Perchlorate and Bisulfate Ions with Tl Adatoms on Pt(111): A SNIFTERS Study

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In situ reflection infrared spectroscopy with electrochemical modulation has been used to investigate the coadsorption of anions for the system Tl_{ads}/Pt(111) in dilute sulfuric and perchloric acids. For the first time evidence of coadsorption of perchlorate induced by underpotentially deposited Tl atoms is reported. The spectroscopic data show that the platinum surface is covered by Tl adatoms and by perchlorate or bisulfate from $E = 0.4$ V up to the onset of the Tl stripping peak. The possible structures of the Tl−ClO_4 and Tl−HSO_4 adlayers at Pt(111) are discussed.

Introduction

The effects of anion adsorption on the underpotential deposition (upd) of metals is well documented in the literature.[1,2] In situ infrared spectroscopy was used in studies of upd metal coadsorption with CO on noble metals[3,4] and in nitrate reduction.[5] The effects of sulfate and bisulfate adsorption on gold for Cu upd were reported recently.[6] In an earlier paper[7] it was shown by cyclic voltammetry that specifically adsorbed anions cause pronounced effects on the upd of Tl^+ on Pt(111). In the present paper, vibrational spectroscopy has been used to study subtractively the coadsorption of nonadsorbing and moderately adsorbing anions during Tl upd. Although a preliminary note on anion adsorption on clean and Cu-modified Pt(111), and Rh-(111) electrodes by subtractively-normalized interfacial FTIR spectroscopy (SNIFTIRS) appeared recently,[8] the present study appears to be the first report of changes in the adsorption properties of these ions under the influence of a metal adlayer.

Experimental Section

The spectroelectrochemical cell and the optical path were described earlier.[9] The cell consisted of a ZnSe hemispherical window with its Teflon body pressed tightly against the flat surface of the window. By using this novel design, several enhancing effects are achieved including low first-surface reflection losses, reflection near the critical angle, and beam collimation.[10] A platinum wire (0.5 mm diameter, 7 cm in length) tied in a loop around the platinum electrode served as the counter electrode, and a Ag wire immersed in 0.01 M $AgClO_4$ + 0.1 M $HClO_4$ served as the reference electrode. All potentials were recalibrated to the reversible hydrogen scale by measuring the difference in potentials of the two reference electrodes after each spectral data acquisition, which was found to be 0.65 ± 0.01 V. The Mattson RS-1 spectrometer and Solartron 1286 potentiostat used were computer controlled using a program designed to set the potential of the working electrode alternatively to the sample or reference potential for the working electrode prior to spectral acquisition. The reference potential was constant and set near the onset of hydrogen evolution in

the supporting electrolyte. 4096 scans with 4 cm^{-1} resolution were coadded in cycles of 128 scans each. Parallel polarization of the IR light was used in all experiments. The spectra are presented as relative normalized reflectance, $-\Delta R/R$. No smoothing of the spectra was performed, and the spectra are offset for clarity in the presented figures.

The platinum single crystal (Metal Crystals and Oxides Ltd., Cambridge, England) with (111) surface orientation to within 0.2° of the surface normal axis was polished by diamond and alumina pastes with a final polishing using 0.05 μm alumina. The crystal was annealed in a hydrogen−air flame, cooled in a hydrogen stream, and subsequently transferred to the spectro-electrochemical cell while protected by a drop of ultrapure water. The cleanliness of the solution in the cell and the veracity of the crystal structure were checked using cyclic voltammetry before each experiment in which spectral data were acquired. After recording the voltammogram, the electrode was pushed against the flat side of the ZnSe hemisphere as described earlier.[10] The solutions were prepared with 18 MΩ nanopure water (Barnstead), ultrapure H_2SO_4 (Merck), ultrapure $HClO_4$ (Aldrich), and ACS grade Tl_2CO_3 (Fluka).

Results and Discussion

Cyclic voltammograms of Pt(111) in 0.1 M $HClO_4$, with and without Tl^+, and in 0.1 M $HClO_4$ + 1 mM H_2SO_4 with and without further addition of Tl^+ are presented in Figure 1. The curve for Pt(111) in perchloric acid is characteristic of this system and confirms the structure of the surface and the cleanliness of the system. With addition of 1 mM H_2SO_4, the so-called "butterfly" peak disappears in the potential region 0.6 < E < 0.9 V, and the well-known shape characteristic of Pt-(111) in sulfuric acid[11] is observed in the potential region 0.4 < E < 0.7 V. The nature of the latter peak in the above potential region has been the topic of considerable controversy.[11-14] In a recent study Faguy et al.[15] showed on the basis of SNIFTIRS experiments that a potential dependent band with an intensity maximum centered around 1250 cm^{-1} occurs in this potential region; this band is ascribed to the ν_4 asymmetric stretch of the bisulfate anion adsorbed on trigonal sites, or more precisely, to H_3O^+−SO_4^{2-} ion pairs. The present work supports

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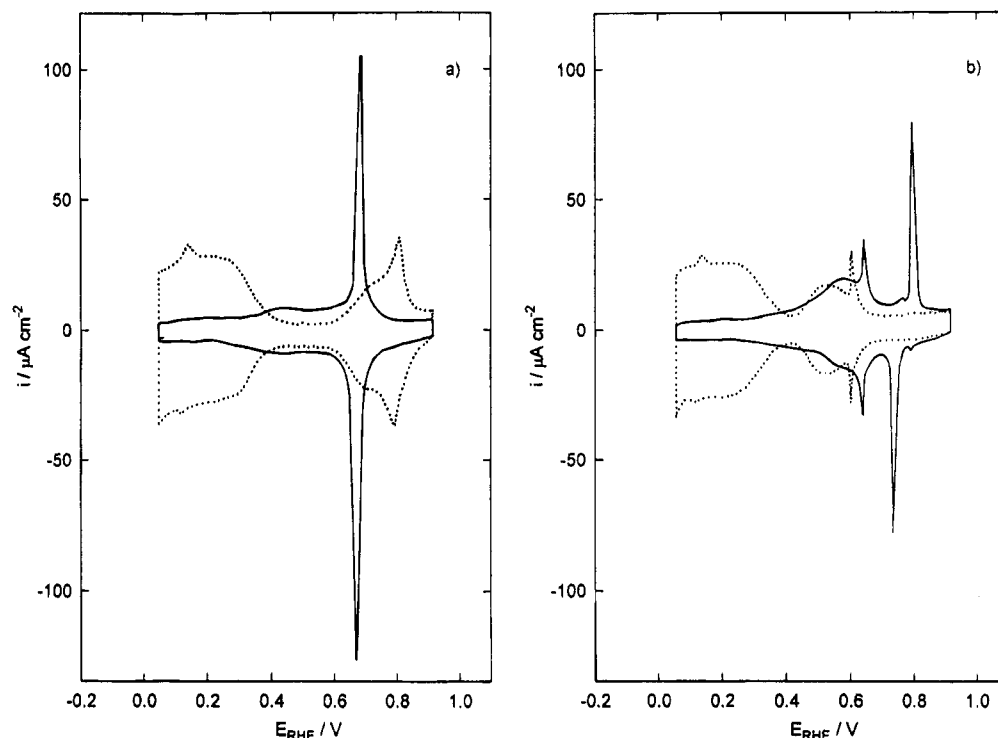Letters

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Figure 1. Cyclic voltammetry of Pt(111) in a solution containing: (a) 0.1 M HClO₄ (•••) and 0.1 M HClO₄ + 1 mM Tl⁺ (—), and (b) 0.1 M HClO₄ + 1 mM H₂SO₄ (•••), and 0.1 M HClO₄ + 1 mM H₂SO₄ + 1 mM Tl⁺ (—). Sweep rate 50 mV/s.

this conclusion and shows further that the bisulfate adsorption is affected by the presence of Tl adatoms formed by upd.

When Tl⁺ is added to the solution containing 0.1 M HClO₄ + 1 mM H₂SO₄, the hydrogen adsorption region in Figure 1a is completely suppressed, and the bisulfate adsorption is shifted by ~30 mV to more positive potentials. This phenomenon can be explained by assuming that anion adsorption occurs at the 3-fold symmetric hollow sites formed by the Tl adatoms. A close-packed hexagonal Tl adlayer[16] cannot accommodate anions at such a position. For adsorption to occur at these sites, Tl coverage must be low and the potential more positive. This conclusion is supported by the X-ray diffraction data which show the existence of the low coverage (√3 × √3) Tl adlayer in sulfuric acid solutions.[16]

The influence of the anion on Tl upd is evident from Figure 1. The Tl adsorption and desorption peaks in 0.1 M HClO₄ + 1 mM Tl⁺ are observed in Figure 1a at 0.68 V. When 1 mM H₂SO₄ is added to the solution, the Tl peaks are shifted to more positive potentials and appear at 0.79 V in the anodic and at 0.72 V in the cathodic scan, (Figure 1b).

The SNIFTIR spectra were first acquired in the supporting electrolytes, in the absence of Tl⁺. In the 0.1 M HClO₄ solution, only a broad band centered at 1100 cm⁻¹ is observed, which is ascribed to the triply degenerate ν_3 mode of the perchlorate anion.[17] When the potential is made more positive, the intensity of the band increases showing the accumulation of perchlorate anions in the double layer.[18] No apparent frequency shift of this band is observed. When 1 mM H₂SO₄ is added to the above solution, three positive going bands are observed at ~1250, 1100, and 940 cm⁻¹ (not shown), ascribed to the $\nu_4(HSO_4^-)$, $\nu_3(ClO_4^-)$, and $\nu_1(HSO_4^-)$ modes, respectively. The frequency of the bisulfate ν_4 band depends on potential and is initially seen at ~1200 cm⁻¹ at a potential of 0.4 V. It shifts to the blue as the potential is made more positive with a rate of ~100 cm⁻¹/V, in agreement with earlier results.[8,12,15]

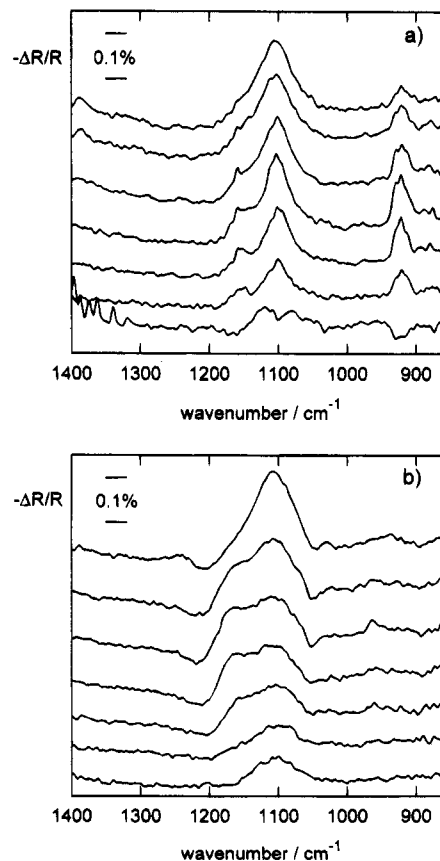Figure 2a shows spectra obtained in a solution containing 0.1 M HClO₄ + 1 mM Tl⁺. Besides the dominating perchlorate

Figure 2. SNIFTIR spectra of Pt(111) in (a) 0.1 M HClO₄ + 1 mM Tl⁺ and (b) 0.1 M HClO₄ + 1 mM H₂SO₄ + 1 mM Tl⁺ solutions as a function of electrode potential. Sample spectra were taken every 100 mV, starting at 0.3 V (bottom spectrum) to 0.9 V, with the background (reference) scan taken at 0.05 V. 4096 scans are coadded in 32 cycles of 128 scans each with 4 cm⁻¹ resolution and p polarized light. The spectra are offset vertically for clarity.

ν_3 stretch at 1100 cm⁻¹, two other peaks at 1160 and 921 cm⁻¹ are observed. As the potential is made more positive, the

intensity of $\nu_3(ClO_4^-)$ peak steadily increases with the potential. However, the intensity of the bands at 1160 and 921 cm^{-1} increases with positive shift of the potential until 0.6 V and then starts to decrease. At 0.68 V, the Tl stripping peak is seen on the cyclic voltammogram (Figure 1). Therefore, the bands at 1160 and 921 cm^{-1} appear to be related to the presence of the Tl adatoms on the electrode surface.

The SNIFTIR spectra of 0.1 M $HClO_4$ + 1 mM H_2SO_4 + 1 mM Tl$^+$ are shown in Figure 2b. Besides the ν_3 band due to perchlorate ions, a new band, centered at 1165 cm^{-1} appears. The band is hardly visible at 0.4 V but grows as the potential is made more positive, reaches a maximum value around 0.7 V, and then starts to decline. A comparison of Figure 2b with Figure 1 demonstrates the potential correlation of the SNIFTIRS band with the voltammetric stripping peak of Tl obtained in the same solution. On the other hand, the potential behavior of the ν_3 stretch of perchlorate band at 1100 cm^{-1} is identical with that in Figure 2a, that is, it steadily increases with the increase of potential. Surprisingly, however, the bisulfate bands at 1250 and 940 cm^{-1} are visible only at the most positive potential.

The spectral feature at 1165 cm^{-1} in Figure 2b cannot be ascribed to free sulfate, since the $\nu_3(SO_4^{2-})$ appears[17] at ~1100 cm^{-1}, and its frequency is found to be potential independent.[15,18] This band can also not be ascribed to the free bisulfate ion, since the potential behavior of the bisulfate ion adsorbed at the electrode surface is quite different.[15] The new band is tentatively ascribed to formation of an adsorbed Tl$^+$–HSO$_4^-$ ion pair. Similarly, the band at 1160 cm^{-1} in Figure 2a is ascribed to formation of Tl$^+$–ClO$_4^-$ ion pair. These observations are now discussed in more detail.

It is known that the symmetry of a free sulfate or perchlorate ion is T_d, where all S–O (Cl–O) bonds are equivalent.[17] In a bisulfate ion, one oxygen atom is bonded to hydrogen and the symmetry is lowered to C_{3v}. If bisulfate is coordinated to a metal ion through one or two of its three oxygen atoms, the symmetry is further lowered to C_s. Similarly, the symmetry of a ClO$_4^-$ ion is lowered to C_{3v} or C_{2v} when it coordinates to metal cations. Then, the triply degenerate $\nu_3(ClO_4^-)$ vibration at 1100 cm^{-1} is split, and two or three bands appear in the spectrum.[17] It is difficult to distinguish the symmetry of the adsorbed anions from the spectra shown in Figure 2 because the strong band at 1100 cm^{-1} due to the perchlorate ions which are accumulating in the double layer covers the whole frequency range from 1190 to 1040 cm^{-1}. An attempt was made to subtract this band from the spectra in Figure 2. To do so, a set of spectral data in the supporting electrolytes, 0.1 M $HClO_4$ and 0.1 M $HClO_4$ + 1 mM H_2SO_4 with the same sample and background potentials as those in Figure 2 but without Tl in the solution were subtracted from the spectra shown in Figure 2. Although this subtraction may be affected by a change in the pzc of Pt(111) in the solutions with and without Tl, it is assumed that this effect is small. However, the results presented in Figure 3 demonstrate clearly that there are features in the spectra which are not due to perchlorate ions electrostatically attracted into the double layer.

The difference spectra in Figure 3a provide more evidence that the T_d symmetry of ClO$_4^-$ ion is lost and that the remaining spectral features are more complex. Three peaks, resulting from the splitting of the triply degenerate ν_3 mode, centered at 1160, 1100, and 1035 cm^{-1} are observed, so that the actual symmetry of the adsorbed perchlorate appears to be C_{2v}. The additional peak at 921 cm^{-1} is attributed to the $\nu_1(ClO_4^-)$ band which becomes active due to the change in selection rules when the symmetry is lowered. In an earlier paper[19] it was shown that
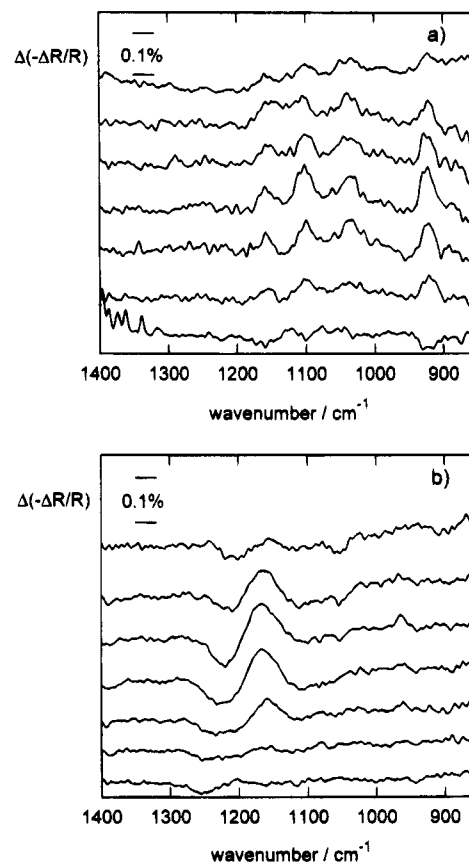

Figure 3. SNIFTIR spectra of Pt(111) in (a) 0.1 M $HClO_4$ + 1 mM Tl$^+$ and (b) 0.1 M $HClO_4$ + 1 mM H_2SO_4 + 1 mM Tl$^+$ solutions, after subtraction of (a) the perchlorate, or (b) the perchlorate and bisulfate double layer bands, as a function of electrode potential. Conditions identical to those in Figure 1.

the perchlorate band splits into three bands in alkali metal perchlorate–acetonitrile solutions due to ion pairing. The frequency difference between the most shifted components of the $\nu_3(ClO_4^-)$ band was found to be greater in Li$^+$ than in Na$^+$ solutions (66 compared to 42 cm^{-1} peak-to-peak); this observation was attributed to stronger ion pairing in the former solution due to the larger charge/radius ratio of the Li$^+$ ion.[19] It is interesting that the splitting of the perchlorate band in the present work is 125 cm^{-1} peak-to-peak, almost twice as large as in the LiClO$_4$/acetonitrile system. Such a large splitting cannot be explained by ion-pairing in the solution. It is more likely due to the coordination of perchlorate with Tl$^+$ adsorbed at the surface. Furthermore, since the symmetry of the perchlorate is lowered to C_{2v}, the ClO$_4^-$ is coordinated to either one Tl (unidentate) or two Tl atoms (bidentate).[17] Due to the high coverage by Tl upd atoms at the surface, the latter form seems more likely. A possible explanation would be that the Pt(111) surface is covered with Tl$^+$–ClO$_4^-$ ion pairs which interact with each other. This interpretation is also supported by the data presented in Figure 3b. If the splitting of the perchlorate ν_3 band is a result of coordination to an adsorbed Tl ion and then to another Tl$^+$ from the solution side, similar spectral features would be observed when H_2SO_4 is added to the system. In fact, this is not the case. Surprisingly, there is no apparent shift of the split ν_3 bands with potential. Only the intensity of the bands changes, in a way which is consistent with the changes in the Tl$^+$ coverage at the electrode surface (see Figure 1).

In contrast to the Tl$^+$–ClO$_4^-$ difference spectra shown in Figure 3a, only one band, centered at 1165 cm^{-1}, is observed after the addition of H_2SO_4 to the system (Figure 3b). The potential induced behavior of the intensity of the 1165 cm^{-1}
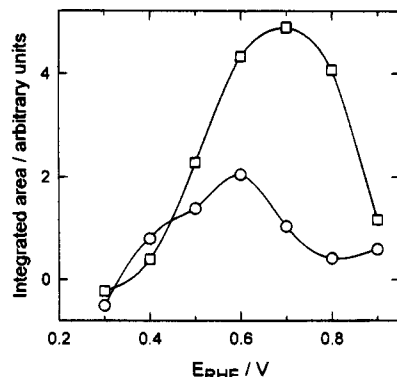
Figure 4. Dependence of integrated area on electrode potential for the bands shown in Figure 3; (O) perchlorate bands, (□) bisulfate bands.

band clearly follows the voltammetric profile (Figure 1), showing a maximum at 0.7 V. At this potential maximum coverage of bisulfate among the Tl^+ adatoms is obtained. As Figure 1 shows, the desorption of thallium commences at a potential of 0.75 V, and consequently for the spectra obtained with the sample potentials of 0.8 V the 1165 cm^{-1} band is less intense, and negligible at 0.9 V. The dramatic difference between the spectra given in Figure 3 also shows the strong affinity of the bisulfate ions towards the Pt(111) surface.

Additional evidence that the bands shown in Figure 3 correspond to the adsorbed perchlorate or bisulfate is found in Figure 4 where their integrated intensity is plotted against electrode potential. The maxima in these plots occur at the potential of the Tl^+ stripping peak in each solution (see Figure 1) where the surface coverage of thallium and coadsorbed ions is the highest.

Since the symmetry of sulfate ion is identical to that of perchlorate, coordination of sulfate to Tl_{ads} would lead to splitting of its triply degenerate ν_3 mode into two or three peaks.[17] However, this has not been observed.[20] On the other hand, in the case of bisulfate, splitting of its $\nu_1(A_1)$ mode cannot occur and only a frequency shift may be expected. Therefore, it is most likely that bisulfate form ion pairs with the thallium adatoms, which are adsorbed at the Pt(111) surface.

The exact position of the centers of bisulfate or perchlorate ions when they are coadsorbed with Tl ions on the surface cannot be deduced from the infrared spectra. However, the absence of the ν_4 asymmetric stretch for adsorbed bisulfate ion on Pt(111) indicates that Tl and the coadsorbed anions probably do not lie in the same plane. The ν_4 band (at ~1250 cm^{-1}) is only observed in Figure 2b after the potential of the Tl stripping peak. Although the SNIFTIRS technique cannot provide direct evidence of the adsorption of Tl, the splitting of the perchlorate ν_3 band (Figure 3a) demonstrates that perchlorate ions are adsorbed on the network of Tl adatoms, so that each perchlorate is probably coordinated to two Tl upd atoms. A similar conclusion, based on the equal charge of ClO_4^- and HSO_4^-

may be drawn for the surface network of Tl and bisulfate ions. The X-ray scattering study presently under way may provide more evidence on the Tl–sulfate interactions.[16]

In summary, the data presented clearly demonstrate the effects of underpotentially deposited thallium on the adsorption of anions at the interface. For the first time evidence of coadsorption of perchlorate induced by Tl adatoms at the electrode surface has been obtained by in situ infrared spectroelectrochemistry. The striking changes in the vibrational properties of the adsorbed perchlorate and bisulfate ions induced by Tl is noteworthy. Questions regarding the structure of the ionic species at other platinum crystals and at different pH's will be addressed in future work.

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