Short communication

IR spectroscopy as a probe of bisulfate absorption at platinum electrodes under aqueous electrochemical conditions: elimination of bulk interference by using a thin layer flow cell

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INTRODUCTION

In recent years, several workers have examined the utility of IR spectroscopy to probe in situ the specific adsorption of electrolyte anions at metal electrodes [1–10]. There is interest in examining the behavior of electrolyte anions at metal electrodes to gain an insight into the structure of the electrical double layer and its effect on electrochemical reactivity. An early series of IR experiments aimed at probing electrolyte adsorption examined the interaction of sulfate and bisulfate at polycrystalline platinum electrodes under aqueous electrochemical conditions [3–6]. These studies explored electrolyte adsorption over a wide range of electrode potential and solution pH values. Potential-dependent alterations in the position of sulfate and bisulfate spectral features were observed and the vibrational bands were assigned to modes of adsorbed surface species on the basis of the perturbations observed [3–6]. More recent IR experiments examined bisulfate adsorption at Pt(111) over the double layer and hydrogen adsorption potential regions and reported bisulfate spectral perturbations similar to those observed in experiments that employed polycrystalline platinum [10].

Studies which aimed to define the practical analytical limits of the in situ IR technique have indicated the importance of considering the effect of potential-dependent alterations in the composition of the thin layer cavity on the appearance of the sulfate and bisulfate spectral features [7–9]. In the thin layer spectroelectro-

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chemical cells employed for the in situ IR measurements, the working electrode is positioned firmly against a window of IR transparent material, with the electrode–window distance being of the order of a few micrometers [1,11,12]. The entrapped solution layer is sufficiently thin that, for many species, transport between the thin layer cavity and the bulk solution is slow on the time scale of the IR experiment. As a consequence, the composition of the solution within the thin layer cavity is altered by changes in the electrode potential. IR studies aimed at probing anionic adsorption have noted conditions under which potential-dependent alterations in the pH value and ionic composition of the thin layer cavity are observed [2,7–9]. Spectral features associated with these solution species appear in potential-difference IR spectra and can make it difficult to discern features of species in the interfacial region. Indeed, these studies have refuted the validity of assigning IR bands to adsorbed sulfate and bisulfate, and have called for experiments which utilize a thin layer flow cell [13,14] which permits the solution in the thin layer cavity to be replenished continuously, thereby keeping the composition of the solution layer constant [9].

In this communication, we report the first IR spectra of bisulfate at a platinum electrode under aqueous electrochemical conditions obtained using a thin layer spectroelectrochemical flow cell, which allows direct control of the solution composition within the thin layer cavity by forcing solution through a small opening in the center of the IR transparent window [14]. The potential-difference IR spectra show alterations in the position and integrated intensity of the bisulfate band, which is consistent with the early studies which probed bisulfate adsorption at polycrystalline [3–6] and monocrystalline [10] platinum electrodes. The results of the present experiments indicate that spectra from earlier studies of bisulfate adsorption [3–6,10] contain important information regarding the composition and bonding of electrolyte anions at the interface.

EXPERIMENTAL

The experiments involve a spectroelectrochemical flow-through cell similar in design to one previously described by Roth and Weaver [14]. The cell window was a calcium fluoride trapezoid with a small (0.9 mm) hole drilled through the center (Solon Technologies, Solon, OH) into which a polyethylene tube was epoxied. The thin layer cavity was purged continuously with an electrolyte solution of 0.05 M H_2SO_4 (Baker Ultrex H_2SO_4 with Barnstead Nanopure water) at a flow rate of 0.4 ml min^{-1}. The working electrode was a polycrystalline platinum disk 6 mm in diameter sealed in a glass tube and polished with alumina (with particle sizes of 1.0, 0.3 and 0.05 μm) to a mirror finish. In the experiments, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode were used. The IR spectra were obtained using a Digilab FTS-40 IR spectrometer. A total of 1024 interferograms were collected at each potential and the potential was switched between the reference and sample every 64 scans. The reference potential was −0.25 V. All the potentials are reported with respect to the SCE.

RESULTS AND DISCUSSION

Figure 1 shows a cyclic voltammogram of the polycrystalline platinum electrode immersed in 0.05 M H_2SO_4 in the thin layer flow cell with the electrode positioned away from the IR window. The voltammograms were recorded just prior to collection of the spectral data. The potential-difference IR spectra obtained under constant flow conditions and under stagnant thin layer conditions are shown in Figs. 2 and 3 respectively. Consistent with earlier studies [3–6,10], a potential-dependent spectral feature is observed near 1200 cm^{-1} and is assigned to the asymmetric S–O stretching mode of adsorbed bisulfate. In the spectra obtained under flow conditions, the adsorbed bisulfate spectral features appear to be slightly narrower and are positioned at a higher energy level compared with the bisulfate spectral features obtained under stagnant thin layer conditions. These differences are more apparent when the spectra obtained under the two different conditions are plotted together, as shown in Fig. 4. The differences are attributed to potential-dependent alterations in the thin layer cavity electrolyte composition, which occurs under stagnant conditions, and demonstrates the spectral perturbations encountered when the composition of the thin layer cavity is not strictly maintained.
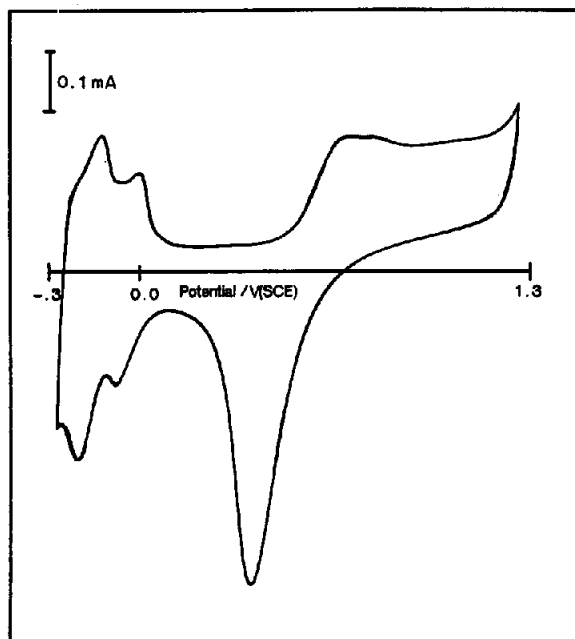

Fig. 1. Cyclic voltammogram of a polycrystalline platinum electrode immersed in 0.05 M H_2SO_4 just prior to collection of spectral data. A scan rate of 100 mV s^{-1} was employed.
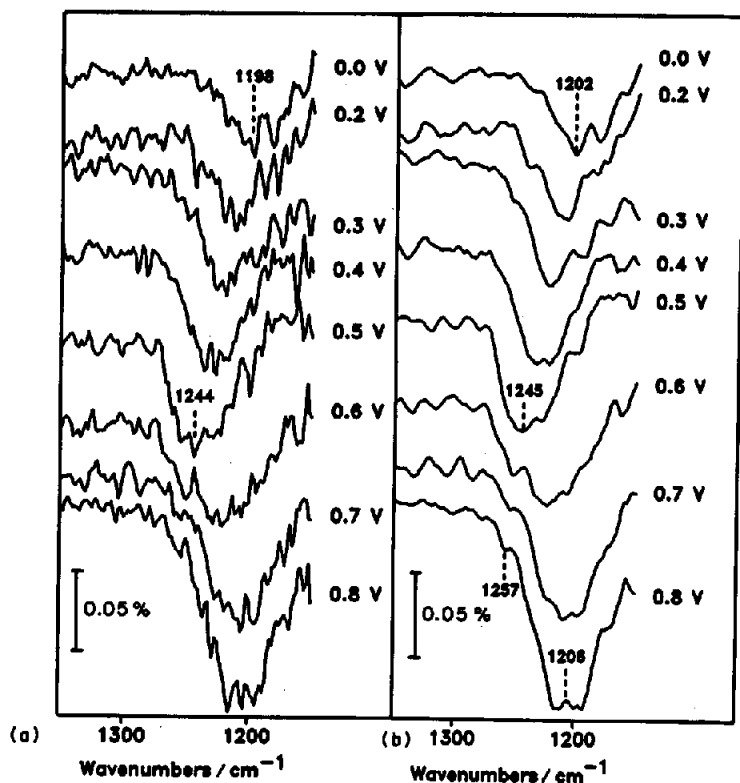
Fig. 2. Potential difference spectra of platinum in 0.05 M H_2SO_4 obtained with a flow rate of 0.4 ml min^{-1}. (a) unsmoothed spectra; (b) spectra shown in part (a) smoothed with an 11-point Savitsky–Golay function. The background spectrum was collected at −0.25 V. Spectra are displayed in units of $\Delta R/R$.

Figure 5 shows the potential dependence of the band position and integrated intensity for the spectra obtained with a constant electrolyte flow. At potentials between 0.0 and 0.5 V, the position of the bisulfate band compares favorably with the spectral features observed in studies which probed bisulfate adsorption from dilute sulfuric acid electrolyte solutions at polycrystalline and monocrystalline platinum [4,10] under stagnant thin layer conditions. In the present study, the position of the bisulfate band begins to shift back toward its bulk solution value at 0.6 V, coincident with the onset of surface oxidation. In earlier polycrystalline [4] and monocrystalline [10] studies, this shift commences at higher positive potentials. The tuning rate was determined to be 87 cm^{-1} V^{-1} in the present study, as compared with the values of 100 cm^{-1} V^{-1} and 108 cm^{-1} V^{-1} reported in earlier polycrystalline [4] and monocrystalline [10] bisulfate adsorption studies respectively.
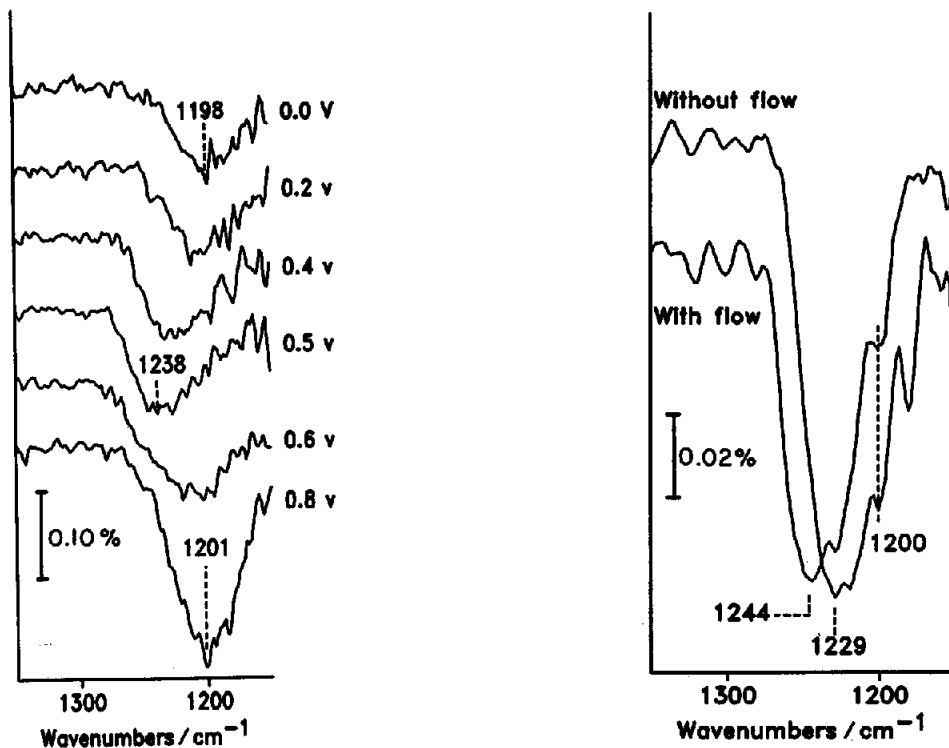
Fig. 3. Potential difference spectra of platinum in 0.05 M H_2SO_4, obtained under stagnant thin layer conditions. The background spectrum was collected at -0.25 V. Spectra are displayed in units of $\Delta R/R$.

Fig. 4. Potential difference spectra from Figs. 2 and 3 at $+0.4$V (smoothed using the 11-point Savitsky–Golay function).

The potential dependence of the integrated intensity of the bisulfate bands shown in Fig. 2 is qualitatively similar to findings reported in the earlier polycrystalline studies [4], increasing sharply at potentials corresponding to the onset of surface oxidation. Furthermore, in the experiments to examine the effect of the solution flow rate on the intensity of the bisulfate band at potentials in the oxide region, the band intensity was observed to remain constant for solution flow rates at and in excess of 0.4 ml min^{-1}. Studies aimed at defining the practical analytical limits of the in situ IR technique suggest that the increase in intensity of the anion bands at potentials in the oxide region can be attributed, in part, to the migration of anions into the thin layer cavity to compensate for the excess positive charge which accumulates when protons are formed during surface oxidation [2,7–9]. Charge compensation of this sort should not be required when a constant electrolyte flow rate is employed. At a flow rate of 0.4 ml min^{-1}, the average solution
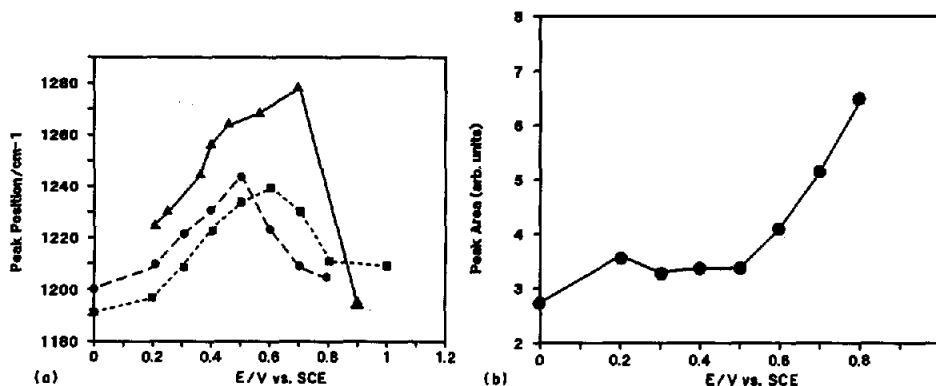
Fig. 5. Potential dependence of (a) the asymmetric S–O stretching frequency of the bisulfate band and (b) the integrated intensity of the bisulfate band. Full circles represent spectral features observed in the present work using data from Fig. 2(b). Full triangles represent spectral data obtained from ref. 10. Full squares represent spectral data obtained graphically, from ref. 4 and are for an electrolyte solution of 0.05 M H_2SO_4.

residence time within the thin-layer region is about 20 ms when an average thin–layer cavity thickness of 5 μm is assumed. This time period is significantly shorter than the time period over which the spectra are obtained (about 1 min.). Therefore, under the conditions employed, the composition of the thin layer solution is maintained. It is possible that the sharp increase in the bisulfate band intensity observed at potentials in the oxide region indicates alterations in the interfacial bisulfate, arising from compact and diffuse layer charging at oxidized platinum.

Spectral features attributable to adsorbed sulfate were also apparent in the present study; however, the signal-to-noise ratio in this spectral region was insufficient to make qualitative comparisons with the earlier findings. The earlier studies of sulfate and bisulfate adsorption at polycrystalline platinum utilized a platinum working electrode with a considerably larger surface area (25 mm in diameter) [3–6] compared with that of the working electrode employed in the present study. As a consequence, in the earlier polycrystalline studies, the integrated band intensity is larger and the signal-to-noise ratio is better compared with the spectra shown in Fig. 3. Experiments that utilize a larger surface area working electrode will be required to address questions concerning the potential-dependent alterations in the interfacial pH value proposed in the earlier polycrystalline sulfate–bisulfate adsorption experiments [4]. The application of the Savitsky–Golay function to generate smoothed spectra follows the procedure adapted in studies which probed bisulfate adsorption at Pt(111) [10].

Radiotracer techniques have demonstrated the potential dependence of bisulfate adsorption at platinum [15] and second harmonic generation experiments have provided additional evidence to support an adsorbed state of bisulfate at platinum

[16]. Hence, in situ IR techniques are expected to sample the adsorbed bisulfate layer and observe spectral features assignable to adsorbed species. In view of the spectral interferences associated with bulk solution alterations [2,7–9] and optical distortions [17], observing potential-dependent alterations in vibrational band position is an important criterion for assigning vibrational bands to modes of adsorbed species.

In summary, potential-dependent alterations in the spectral features of bisulfate adsorbed at platinum were observed under aqueous electrochemical conditions by using a spectroelectrochemical flow cell which eliminated potential-induced alterations in the composition of the thin layer cavity. The potential-dependent spectral features are consistent with those observed in earlier studies of sulfate and bisulfate adsorption at polycrystalline and monocrystalline platinum metal electrodes, which suggests that these early studies provide important insights into the interaction of bisulfate with platinum electrodes.

ACKNOWLEDGMENT

REFERENCES

1 A. Bewick and S. Pons, in R.J.H. Clark and R.E. Hester (Eds.), Advances in Infrared and Raman Spectroscopy; Vol. 12, Wiley, New York, 1985, Ch. 1.
2 D.S. Corrigan and M.J. Weaver, J. Electroanal. Chem., 239 (1988) 55.
3 K. Kunimatsu, M.G. Samant, H. Seki and M.R. Philpott, J. Electroanal. Chem., 243 (1988) 203.
4 K. Kunimatsu, M.G. Samant and H. Seki, J. Electroanal. Chem., 258 (1989) 163.
5 K. Kunimatsu, M.G. Samant and H. Seki, J. Electroanal. Chem., 272 (1990) 185.
6 M.G. Samant, K. Kunimatsu, H. Seki and M.R. Philpott, J. Electroanal. Chem., 280 (1990) 391.
7 I.T. Bae, X. Xing, E.B. Yeager and D.A. Scherson, Anal. Chem., 61 (1989) 1164.
8 I.T. Bae, D.A. Scherson and E.B. Yeager, Anal. Chem., 62 (1990) 45.
9 T. Iwasita and F.C. Nart, J. Electroanal. Chem., 295 (1990) 215.
10 P.W. Faguy, N. Markovic, R.R. Adzic, C.A. Fierro and E.B. Yeager, J. Electroanal. Chem, 289 (1990) 245.
11 H. Seki, K. Kunimatsu and W.G. Golden, Appl. Spectrosc. 39 (1985) 437.
    D. Popenoe, S.M. Stole and M.D. Porter, Appl. Spectrosc. 46 (1992) 79.
12 L-W.H. Leung and M.J. Weaver, J. Phys. Chem., 92 (1988) 4019.
13 J.O.M. Bockris and B. Yang. J. Electroanal. Chem., 252 (1988) 209.
    R.J. Nichols and A. Bewick. Electrochimica Acta. 333 (1988) 1691.
14 J.D. Roth and M.J. Weaver, Anal. Chem., 63 (1991) 1603;
    J. Electroanal. Chem., 307 (1991) 119.
15 G. Horanyi and A. Wieckowski, J. Electroanal. Chem., 294 (1990) 267.
16 D.J. Campbell and R.M. Corn, J. Phys. Chem., 92 (1988) 5796.
    M.L. Lynch, B.J. Barner, J.M. Lantz and R.M. Corn, J. Chim. Phys., 88 (1991) 1271.
17 R.P. Young and R.N. Jones, Chem. Rev., 71 (1971) 219.
    J.P. Hawranek, P. Neelakantan, R.P. Young and R.N. Jones, Spectrochim. Acta, 32A (1976) 85.
    P.P. Popanoe, S.M. Stole and M.D. Porter, Appl. Spectrosc., 46 (1992) 79.
    M.D. Porter, Anal. Chem., 60 (1988) 1143A.