

***In situ* Surface-Enhanced Raman Scattering Spectroscopic Study of Sulfur Adsorption on Polycrystalline Platinum Electrode Surface**

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Abstract: The paper reports the first *in situ* surface enhanced Raman scattering (SERS) spectro-electrochemistry study of sulfur adsorption and electro-oxidation on highly roughened polycrystalline Pt surface in both acidic and basic supporting electrolytes. The SERS spectra were taken at a constant electrode potential after accumulative electro-oxidation CVs of the Pt electrode with pre-adsorbed sulfur species and at different electrode potentials that were varied stepwise of the Pt electrode immersed in sulfur-containing electrolytes without pre-adsorbed sulfur species. In both cases, a dominant vibrational band at 299 cm⁻¹ in acidic electrolyte but at 310 cm⁻¹ in basic electrolyte was observed, which was assigned to the Pt—S stretching vibration. The Pt—S bond appeared quite strong as evidenced by the total blockage of the Pt surface for hydrogen adsorption and the need of multiple electro-oxidation CVs to completely remove the adsorbed sulfur. Additionally, a small amount of poly sulfur species (S₈ or other types) as represented by a minor peak at 470 cm⁻¹ was also observed in the acidic but not in the basic electrolyte. These poly sulfur species only bound to the Pt surface weakly and could be removed easily. This work yielded important information on sulfur adsorption and electro-oxidation on roughened, polycrystalline platinum surfaces and demonstrated the applicability and usefulness of the *in situ* SERS spectroelectrochemistry in investigating the chemistry of sulfur adsorption/poisoning on platinum surfaces.

Key words: platinum; sulfur; Raman spectroscopy

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1 Introduction

Platinum (Pt) is an important electrode material and catalyst used in fuel cells^[1]. When the fuels, such as hydrogen, methanol, formic acid or other small organic molecules, are made from earthly-bound, sulfur (S) containing coal, crude oil or natural gas, they carry inevitably trace amount of sulfur that can be readily bound to Pt and poison the catalytic surface. Therefore, understanding the chemical nature of inter-

action between S and Pt is of fundamental importance to unravel S-poisoning mechanism by which novel S-tolerant materials may be designed and developed for practical fuel cell applications^[2-3].

Among the available *in situ* spectroelectrochemical methods, *in situ* surface enhanced Raman scattering (SERS) spectroscopy is unique in terms of detection sensitivity on the SERS enabling metals (Ag, Au, or Cu)^[4-6] and accessibility to low-frequency vi-

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brational modes of molecules of which the latter is particularly important for interrogating surface metal-adsorbate, including metal-S bonds^[7]. Although Pt is usually not considered a good SERS enabling metal, Tian et al. has nonetheless demonstrated recently that by roughening polycrystalline Pt it was possible to observe good quality SERS spectra of the adsorbed pyridine^[8-11]. In this paper, we report that the same method can be applied to investigate the Pt—S bond of the adsorbed S species on the Pt surface.

2 Experimental

A commercial platinum rod electrode (Bioanalytical, 2 mm²) was used as the working electrode. The Pt electrode was first roughened by square wave oxidation-reduction cycles (SWORC) method devised by Tian et al.^[10] that consisted of subjecting the Pt electrode to square wave cycling that had a frequency of 500 Hz and upper and lower switching potentials at 2.4 V and -0.25 V respectively in a supporting electrolyte of 0.5 mol · L⁻¹ H₂SO₄ for 20 min. The electrode was then held at -0.25 V until the electro-reduction of the surface was completed before being immersed in a 0.01 mol · L⁻¹ Na₂S solution for 30 min to deposit the S species. The S-adsorbed Pt electrode was finally washed with milli-Q water (18.2 MΩ) to remove non-chemisorbed S species and incorporated into the *in situ* electrochemical (EC) cell for SERS measurements.

The details of the *in situ* EC SERS cell were reported previously^[9]. It consisted of a cylindrical Teflon cell body with the Pt working electrode inserted from below and a top quartz window covering the top. The counter (a Pt wire looped around the working electrode) and reference (Ag/AgCl, 1 mol · L⁻¹) electrodes were introduced into the cell through the side holes on the cylindrical cell body.

SERS spectra were obtained using a confocal microprobe Raman system (Renishaw RM1000) equipped with a deep depletions CCD peltier cooled down to -70 °C. The microscope attachment is based

on an Olympus BH2-UMA system and uses a 50x-long working-length objective (8 mm) so that the objective will not be in contact with the electrolyte. A holographic notch filter was used to filter the exciting line and two selective holographic gratings (1200 g/mm and 2400 g/mm) were employed depending the spectral resolution required. The exciting wavelength was 785 nm from a Renishaw Ar ion laser with a max power of 27 mW and a spot of ca. 3 μm on the surface. The slit and pinhole in experiment were 100 and 400 μm, respectively. A CHI660 electrochemistry station was employed for potential control. All the chemicals used were of analytical reagent grade, and the solutions were prepared using milli-Q water.

3 Results and Discussions

The cyclic voltammograms (CVs) of the pre-roughened and roughened Pt electrodes in 0.5 mol · L⁻¹ H₂SO₄ are shown in Fig. 1. The hydrogen adsorption and desorption and Pt oxidation and reduction peaks are in excellent agreement with the known literature values/peak positions for a clean polycrystalline Pt surface, ensuring the good quality of the initial state of the experiment. By using the hydrogen desorption charges, we estimated that the roughening process increased the electrochemical active surface area by about 200 times^[12].

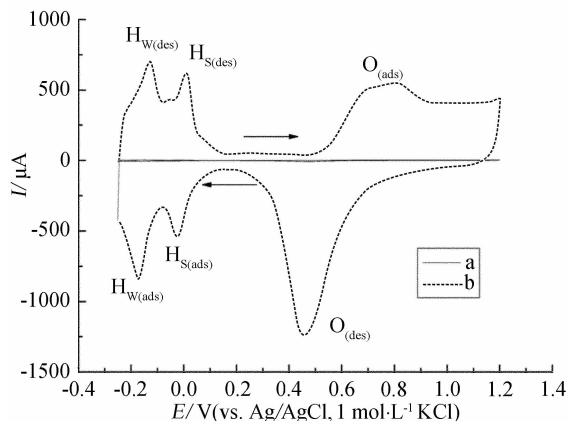


Fig. 1 Cyclic voltammograms of the Pt working electrode a. before roughening; b. after roughening in 0.5 mol · L⁻¹ H₂SO₄

The *in situ* SERS spectra ($\Delta R = R - R_f$ where R_f is the reference spectrum) recorded for the roughened bare Pt electrode in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ held at different potentials are shown in Fig. 2, with the spectrum at 0.2 V as reference. A band that centered first at 470 cm^{-1} and then at 570 cm^{-1} started appearing at 0.6 V whose intensity became stronger as the electrode potential moved to more positive potentials. Based on the CVs in Fig. 1, we assign the band centered at 470 cm^{-1} for the Pt—OH like species and that centered at 570 cm^{-1} to the Pt—O_x like species^[9,13-14].

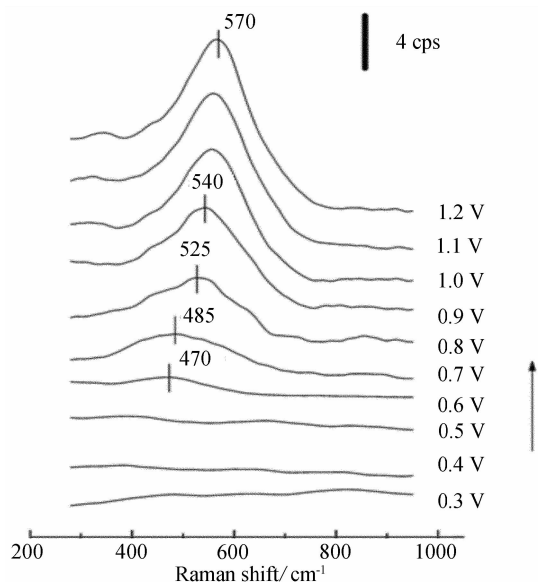


Fig. 2 The *in situ* SERS spectra recorded on roughened Pt electrode in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ at different potentials

Fig. 3 presents the first 13 CVs of the S-pre-adsorbed Pt electrode in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$, which is the concentration of supporting electrolyte that will be used hereafter for literature comparisons and for reducing Raman signal from SO_4^{2-} . The 1st cycle showed in Fig. 3a (black curve) was scanned from the open circuit potential (OCP, 0.35 V) to -0.25 V and to 0.2 V but the ensuing CVs were all full cycles (0.2 V to 1.2 V to -0.25 V to 0.2 V). The lack of any hydrogen adsorption/desorption current in the 1st cycle indicates that the Pt electrode surface

was completely blocked initially by the adsorbed S species. Even though the anodic current increased dramatically after 0.7 V in the 2nd cycle implying the electro-oxidation of the adsorbed S, the hydrogen adsorption/desorption was still completely suppressed (Fig. 3b, curve b). But the adsorbed S species were gradually electro-oxidized away thereafter as the number of the consecutive CV increased. The CV eventually stabilized after the 9th cycles indicating a complete electro-oxidation of the adsorbed S species. However, the stabilized CV shows clear differences as compared to the initial CV (Fig. 1) evidencing that the S adsorption-electrooxidation cycle changed to certain extent the surface morphology of the Pt electrode.

In situ Raman spectra were recorded at the OCP (0.35 V) and at 0.2 V after the 1st, 2nd, 3rd, and 13th cycles (the electrode potential was held at 0.2 V after each cycle) and these spectra are presented in Fig. 4. As can be seen, the spectrum recorded at the OCP before any potential cycles (Fig. 4a) shows a dominant peak at 299 cm^{-1} , a small peak at 470 cm^{-1} , and an even smaller peak at 220 cm^{-1} . The spectrum recorded after the 1st potential cycle (Fig. 4b) is identical to the previous one, which is expected since no adsorbed S was electro-oxidized. After the 2nd CV cycle, the peaks at 470 cm^{-1} and 220 cm^{-1} disappeared completely and the main peak became broadened and shifted slightly to high frequency, but with little change in peak integral. The latter is consistent with the EC observation that the hydrogen adsorption/desorption was still completely blocked after the 2nd cycle, i. e., few adsorbed S species were physically removed. We conjecture that the oxidation current observed in the 2nd CV was probably associated with the oxidation of adsorbed S species from an anionic state to a neutral state without physically removing the species from the Pt surface. This hypothesis is currently being investigated by the on-going research in our lab. However, the spectrum recorded after the 3rd CV cycle does show a clear decrease in the peak ampli-

tude, suggesting that the physical removing of the adsorbed S species started. Indeed, the EC data also show that the Pt surface sites started being unblocked for hydrogen adsorption/desorption after the 3rd CV. Finally, the spectrum recorded after the 13th CV cycle shows no peaks, which is consistent with a complete electro-oxidation of the adsorbed S as suggested by the corresponding EC data.

Since it is clear from the S electro-oxidation CVs in Fig. 3 that the adsorbed S species persisted on the Pt electrode surface until at least the 7th CV cycle, we thus assign the peak at 299 cm⁻¹ to the Pt—S bond vibrational band^[15]. Available literature values and assignments^[7,15-16] suggest that the peaks at 220 cm⁻¹ and 470 cm⁻¹ can be assigned to trace S₈ species and/or other kinds of poly sulfur species respectively that only bound to the Pt surface weakly and could thus be removed easily. Since the peak amplitude at 220 cm⁻¹ is so tiny, we will not discuss it anymore but focus only on the peak at 470 cm⁻¹ as a representative peak for poly sulfur species.

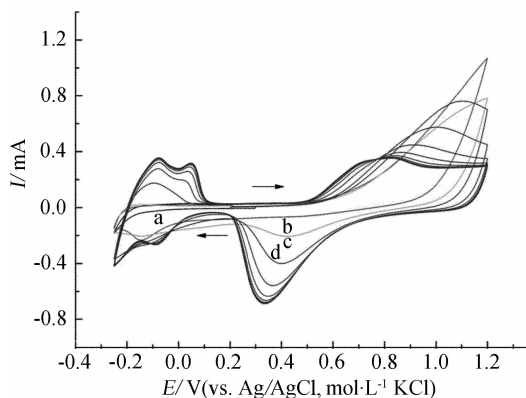


Fig. 3 Cyclic voltammograms for S deposited Pt electrode in 0.1 mol · L⁻¹ H₂SO₄ in different cycles
a. 1st cycle; b. 2nd cycle; c. 3rd cycle; d. 4th ~ 13th cycles

The S adsorption on the Pt electrode was further investigated by the *in situ* SERS spectroscopy in 0.1 mol · L⁻¹ H₂SO₄ containing 2 mmol · L⁻¹ H₂S. Fig. 5 shows the SERS spectra recorded under potential control in the aforementioned solution. These spectra were obtained by changing the electrode potential stepwise

from the OCP (0.35 V) to -0.25 V, then to 1.2 V in negative direction. As can be seen from these spectra, the same spectral features as those in Fig. 4 were observed, indicating that the final products of S adsorption is independent of the source of S species. Again, we assign the peak at 300 cm⁻¹ to the Pt-S bond vibrational band whose amplitude started decreasing after 0.8 V even with the presence of S species in the solution. This indicates that beyond this electrode potential, the electro-oxidation of the adsorbed S species was faster than their adsorption. Additionally, the S species represented by the vibrational band 470 cm⁻¹ show interesting behavior as a function of the step electrode potential. In cathodic potential step direction from the OCP, the peak at 470 cm⁻¹ disappeared at -0.2 V while the main peak at 297 cm⁻¹ stayed on. In anodic potential step direction from -0.25 V, the peak at 470 cm⁻¹ reappeared at 0.2 V whose amplitude increased until 0.5 V but decreased thereafter and disappeared again at 0.9 V. As to the main peak at 297 cm⁻¹, its amplitude dropped significantly at 1.0 V and at the same time a band at 570 cm⁻¹ associated with the Pt—O formation started appearing. The depletion of the adsorbed S species continued onwards until most of them were removed at 1.1 V. Altogether, these observations indicate that (1) the poly sulfur species had a weaker binding to the Pt surface than the single sulfur did and were not stable at both negative and positive ends (-0.25 V and 1.2 V respective) of the electrode potentials, (2) the S adsorption prevented the formation of the Pt—OH species and thus delayed the oxidation of Pt surface.

In order to study the effect of pH on the S adsorption on the Pt electrode surface, we also carried out the similar *in situ* SERS measurements as discussed above but in a basic solution. Fig. 6 shows the first 13 CV cycles of the S pre-adsorbed Pt electrode in a 0.1 mol · L⁻¹ NaOH solution. The overall shape evolution of these CVs is very similar to that observed in the acid solution (Fig. 2) but the potential region was shifted to -0.9 V to 0.5 V (vs. Ag/AgCl, 1

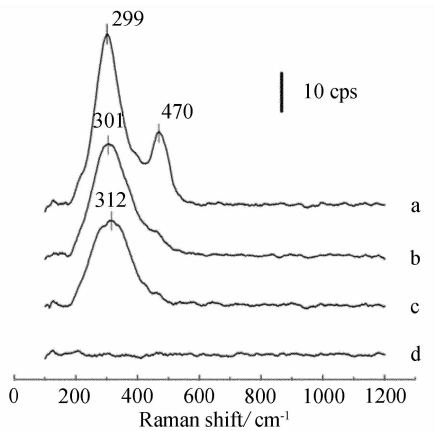


Fig. 4 The SERS spectra obtained on S-adsorbed Pt electrode in 0.1 mol · L⁻¹ H₂SO₄ after CV treatment at 0.05 V · s⁻¹ with different cycles
a. at the OCP, after; b. the 1st cycle; c. the 2nd cycle; d. the 3rd cycle; e. the 13th cycle, the spectra were recorded by holding the electrode potential at 0.2 V after the given CV cycles

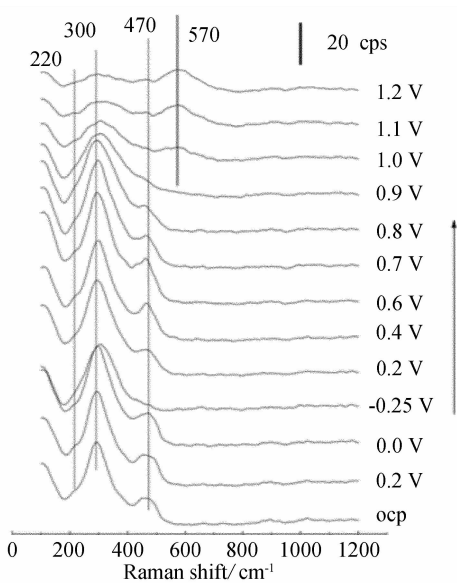


Fig. 5 The *in situ* SERS spectra of the Pt electrode recorded at different electrode potential in 0.1 mol · L⁻¹ H₂SO₄ containing 2 mmol · L⁻¹ H₂S the spectrum recorded at 0.2 V in 0.1 mol · L⁻¹ H₂SO₄ without H₂S was used as the reference spectrum

mol · L⁻¹ KCl). Initially, the Pt electrode surface was completely blocked by the adsorbed S species as indicated by the 1st potential scan that first went cathodically to -0.9 V then anodically to -0.4 V that the hydrogen adsorption/desorption was completely suppressed. However, according the CV data, the un-

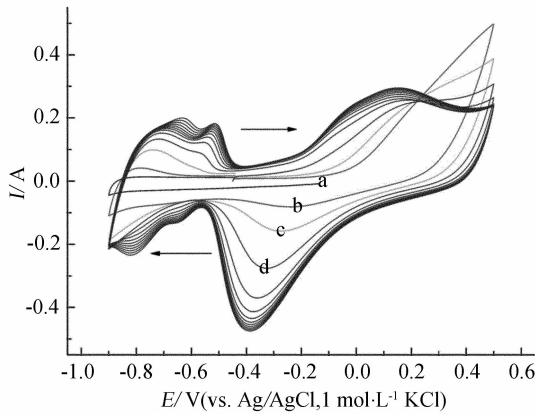


Fig. 6 Cyclic voltammograms for S pre-adsorbed Pt electrode in 0.1 mol · L⁻¹ NaOH with different cycles
a. the 1st cycle; b. the 2nd cycle; c. the 3rd cycle; d. the 4th ~ 13th cycles

blocking of the S-blocked Pt sites had already started happening during the 2nd CV which was earlier than that in the acidic solution. The depletion of the adsorbed S species continued onwards until a complete depletion was achieved as indicated by the 13th CV (Fig. 6).

The *in situ* SERS spectra were again recorded at the OCP (-0.1 V) and at -0.4 V after the 1st, 2nd, 3rd, and 13th cycles, as shown in Fig. 7. A peak at 310 cm⁻¹ was observed at the OCP (-0.1 V), which we assign to the Pt—S bond vibrational band in the basic solution, though it was blue shifted from the peak frequency (299 cm⁻¹) observed in the acidic solution. An identical spectrum was obtained after the 1st CV. This is what would be expected since no electro-oxidation happened during the 1st CV. A clear decrease in the peak amplitude was observed for the spectrum recorded after the 2nd CV, which was earlier than that in the acidic solution but in agreement with the EC data obtained in the basic solution (vide supra and Fig. 6). This confirmed that it was easier to electro-oxidize the adsorbed S species in the basic than in the acidic solution. No peaks were observed after the 13th CV, as expected from the EC data since all adsorbed S species were electro-oxidized from the Pt electrode surface. Additionally, no poly sulfur species were observed on the Pt electrode surface in the basic solution, in agreement with the observations made in the acidic solution that the poly sulfur species were

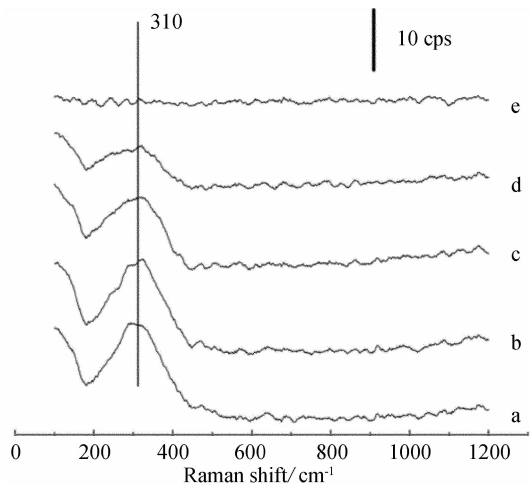


Fig. 7 The *in situ* SERS spectra of S pre-adsorbed Pt electrode in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH after different CV treatments at $0.05 \text{ V} \cdot \text{s}^{-1}$ with different cycles a. the OCP (-0.1 V) and -0.4 V after; b. the 1st cycle; c. the 2nd cycle; d. the 3rd cycle; e. the 13th cycle, the spectrum recorded at -0.4 V without S adsorption was used as the reference spectrum

much less stable on the Pt electrode surface than the Pt—S species.

In situ SERS spectra were also recorded stepwise at different potentials in a $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution containing $2 \text{ mmol} \cdot \text{L}^{-1}$ Na_2S that provided a continuous source of sulfur for S adsorption while the SERS spectra were taken. The stepwise potential went first cathodically from the OCP (-0.1 V) to -0.9 V then anodically to 0.5 V . The spectrum recorded at -0.4 V in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH without Na_2S was used as the reference spectrum. These spectra were shown in Fig. 8. As in the case of the Pt electrode with pre-adsorbed S species, a peak at 310 cm^{-1} was observed at the OCP (-0.1 V) which we assign to the Pt—S bond vibrational band. The amplitude of this peak was rather invariant between -0.9 V and -0.1 V , implying the stability of the Pt—S species over the corresponding potential region. The amplitude at 310 cm^{-1} started decreasing at 0.0 V and onwards anodically. At the same time, a shoulder showed up at 260 cm^{-1} that became a small peak as the signal at 310 cm^{-1} disappeared gradually and persisted up to 0.5 V . No poly sulfur species were observed over the whole potential range

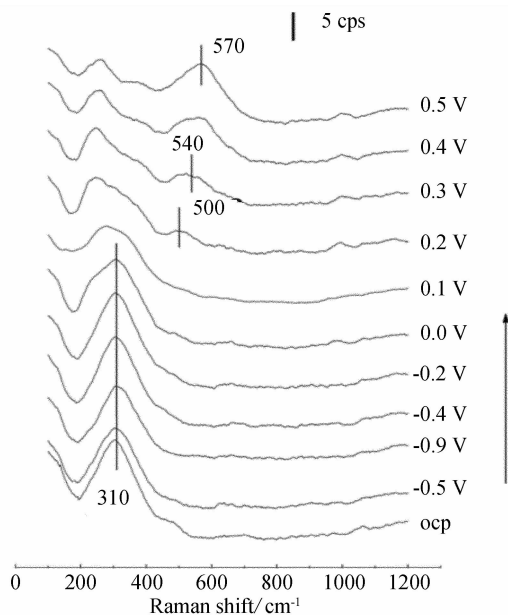


Fig. 8 The *in situ* SERS spectra recorded on the Pt electrode in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH containing $2 \text{ mmol} \cdot \text{L}^{-1}$ Na_2S at different potentials the spectrum recorded at -0.4 V in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH without Na_2S was used as the reference spectrum

but a signal at 500 cm^{-1} appeared at 0.2 V which we assign to Pt—OH based on the CV profile. At 0.3 V , a signal at 540 cm^{-1} showed up and grown stronger onwards anodically, which can be reasonably assigned to the formation of Pt—O_x species.

4 Conclusions

We have reported in this paper an *in situ* SERS investigation of sulfur adsorption on polycrystalline Pt electrode surface in both acidic and basic supporting electrolytes that (a) contained no sulfur source but with sulfur pre-adsorbed Pt electrode or (b) contained sulfur source but with no pre-adsorbed S on the Pt electrode. It was observed that the S adsorption and electro-oxidation on roughened polycrystalline Pt surface could be followed *in situ* by SERS spectroelectrochemistry. The SERS spectra were taken at a constant electrode potential (0.2 V) after accumulative CVs under condition (a) but at different electrode potentials that were varied stepwise under situation (b). In both cases, a dominant vibrational band at 299 cm^{-1} was observed in acidic electrolyte and was assigned to

the Pt—S stretching vibration. The Pt—S bond appeared quite strong as evidenced by blocking all the Pt surface sites for hydrogen adsorption, and needing multiple CVs to remove completely the adsorbed S. Additionally, a small amount of poly sulfur species (S_8 or other types) as represented by a minor peak at 470 cm^{-1} was also observed. These poly sulfur species only bound to the Pt surface weakly and could be removed easily. In the basic electrolyte, A major peak at 310 cm^{-1} was also observed in both (a) and (b) conditions and was assigned to the Pt—S bond stretching. In contrast to the acidic solution, no poly sulfur species were observed. Additionally, the Pt—S species appeared to be more readily electro-oxidized. In summary, this work yielded important information on sulfur adsorption and electro-oxidation on roughened, polycrystalline platinum surfaces and demonstrated the applicability and usefulness of the *in situ* SERS spectroelectrochemistry in investigating the chemistry of sulfur adsorption/poisoning on platinum surfaces.

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多晶铂电极表面硫吸附物种的原位表面增强拉曼光谱研究

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摘要: 本工作首次报道了在酸性或碱性电解质中高粗糙度多晶铂电极表面硫物种的吸附、电氧化过程的原位表面增强拉曼光谱研究. 分别在两种情况下采集了粗糙铂电极的表面增强拉曼光谱:(a)循环伏安处理后控制一定电位(0.2 V)下;(b)逐步控制不同电位. 酸性电解质条件下,两种情况均观察到位于 300 cm^{-1} 的 Pt—S 振动. Pt—S 键较强,阻止了氢在铂电极表面的吸附,需多次循环伏安处理才能完全将表面吸附的硫去除. 同时还观察到位于 470 cm^{-1} 处的少量多聚 S 物种(S_8 或者其他类型). 这些多聚 S 物种仅仅微弱地键合在铂电极的表面,可以容易地除去. 在碱性电解质中,同样也在(a)和(b)情况下观察到位于 310 cm^{-1} 的 Pt—S 振动吸收. 本工作获得了有关硫在粗糙多晶铂电极表面吸附和电氧化重要信息,证明了原位表面增强拉曼光谱在研究铂表面的适用性.

关键词: 铂; 硫; 拉曼光谱