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Adsorption and electrochemical oxidation of small sulfur-containing anions on Pt electrodes in organic media

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ABSTRACT

Acetic acid is an important organic solvent for the chemical industry, for example, in catalytic hydrogenation and for electro-synthesis reactions generally. In this work, the adsorption and electrochemical oxidation of several sulfur-containing anions (S^{2-} , $S_2O_4^{2-}$, $S_2O_5^{2-}$ and SO_3^{2-}) over Pt electrodes in a mixture of sulfuric acid/acetic acid was investigated by cyclic voltammetry. Electrochemical oxidation provides a means of regenerating Pt catalysts and the sulfur-containing anions studied are examples of species that might be produced under synthetic conditions or could be present as impurities in industrial feedstock. In order to determine the oxidation reaction mechanism and its surface-structure sensitivity, Pt polycrystalline and single-crystal electrodes are implemented in this study. It is found that the oxidation of the sulfur-containing species on Pt polycrystalline electrode takes place at higher potentials in comparison to the same reactions in aqueous media. This is attributed to the low coverage of surface oxide, due to the low concentration of water and the adsorption of acetate at the surface. Experiments on the Pt basal planes and stepped surfaces reveal a strong surface-structure dependence for the oxidation of all the sulfur-containing species. These results provide valuable information that will aid the engineering of nanocatalysts with specific crystalline structure less prone to contamination during catalytic process in mixtures of sulfuric/acetic acid.

INTRODUCTION

Electrochemical processes in organic media continue to attract considerable interest, not least due to major technological applications, such as Li-ion batteries,^[1] the electroplating of metals in ionic liquids and eutectic solvents^[2] and new electrosynthetic pathways for fine chemicals.^[3] Among other attributes, the use of organic solvents can prove advantageous when the solubility of the reactants or products is poor in aqueous media^[4] or where reagents are susceptible to oxidation or hydrolysis by water.^[5] Despite the large number of reports on electrochemical processes in organic solvents,^[6] there are relatively few studies that provide an exhaustive understanding of the role adsorbed species or the effect of electrode surface structure on reactivity and selectivity of processes in such media. A close approximation to understand the role of the surface structure on the adsorption of organic molecules is therefore to examine previous works on the oxidation/reduction of organic molecules in aqueous media.^[7]

Acetic acid is commonly used as a protic organic solvent for non-aqueous electrochemistry because of the good solubility of certain organic substances in this medium, the wide electrochemical window (up to 4 V)^[1a] and low cost. Previous studies have shown that the adsorption of acetic acid at both polycrystalline and single-crystal Pt electrodes in aqueous media was reversible.^[8] On the other hand, acetic acid together with sulfuric acid is used for (non-electrochemical) catalytic hydrogenation reactions, which require a strongly acidic environment,^[9] for example the catalytic hydrogenation of compounds with unsaturated carbon-nitrogen bonds,^[9b, 10] e.g. imines (RC=NR), oximes (RCH=NOH) and nitriles (RC≡N).^[10] The hydrogenation of these compounds results in saturated amines, either as intermediates or products, which can adsorb on the Pt surface. The presence of a strong acid in solution, such as sulfuric acid, promotes amine protonation, resulting in the formation of R-NH₃⁺.

While supported Pt nanoparticles exhibit good reactivity under mild reaction conditions, these catalysts show rapid deactivation, for example due to feedstock impurities.^[11] Very little is known about the poisoning species or the reactive sites that are inhibited during catalytic synthetic chemical reactions, and new insight on this aspect of catalysis may aid the development of efficient protocols for catalyst recovery. Given the increasing interest in (electro)chemical synthesis in organic solvents^[3a, 4a, 12] and the lack of knowledge of poisoning by sulfur-containing species, this work aims at establishing structure-activity relationships for the adsorption and electro-oxidation of different sulfur-containing species at polycrystalline and single-crystal Pt electrodes in mixed solutions of sulfuric and acetic acid. While these findings are of particular relevance for industrial Pt-catalyzed hydrogenation reactions, it will also give insights in other metal-sulfur systems, such as the Li-S batteries and MoS catalysts.^[13] The relevance of these findings for industrially relevant Pt-catalyzed hydrogenation reactions is briefly discussed.

RESULTS AND DISCUSSION

Electrochemical characterization of polycrystalline Pt

Prior to the characterization of the polycrystalline platinum electrode with adsorbed sulfur-containing species, the bare (clean) electrode was studied in the sulfuric-acetic acid solution. While a number of investigations have shown that the adsorption of acetic acid (acetate ions) at low concentrations is a reversible process,^[8a, 8b, 8e] characterization of Pt electrodes using acetic acid as an electrolyte has not been reported. Fig. 1 shows the voltammetric profiles at Pt polycrystalline electrodes recorded in a 2 M solution of sulfuric acid in acetic acid (red line) and 2 M solution of sulfuric acid in water (black line). Comparison of the voltammetric profiles reveals significant differences across the entire potential window, associated with the specific adsorption of particular anions and the relative

availability of protons and hydroxyl ions. In the potential region between 0.0 – 0.4 V, features associated with the hydrogen adsorption/desorption (H_{ads}/H_{des}) are affected by the presence of acetic acid. While the features present certain similarities, the H_{ads}/H_{des} peaks in aqueous solution are sharper and more reversible than those in the acetic acid. These sharp peaks measured in aqueous sulfuric acid are associated with the competitive co-adsorption of hydrogen and (bi)sulfate anions on the surface.^[14] Conversely, in acetic acid, the presence of a mixed layer of hydrogen, (bi)sulfate and acetic acid/acetate is expected.^[8e] It can be noticed that the adsorption/desorption process of protons in the sulfuric/acetic acid mixture is affected by the electrolyte resistance caused by the low concentration of water.

Interestingly, at higher potentials, the voltammetric features associated with the oxidation/reduction of the Pt surface are significantly smaller in acetic acid compared to the aqueous media. These decreased (and almost absent) current peaks are largely due to the low concentration of water in the electrolyte, which is required to form a surface oxide. As concentrated H_2SO_4 is typically supplied as a 96 % solution (with the remaining 4 % mostly comprising of water), the presence of water in small concentrations (~0.5 M) cannot be avoided. In addition, both acetic and sulfuric acid are highly hygroscopic. On the other hand, the adsorption of acetate anions at these positive potentials can also cause a decrease of Pt oxidation/reduction.^[8b-8c] Heinen *et al.* have used *in-situ* attenuated total reflection configuration (ATR-FTIRS) to study the adsorption of acetic acid at polycrystalline Pt surfaces and found that acetic acid was adsorbed at potentials between 0.1 V and 1.3 V versus RHE. The high adsorption strength of acetate leads to the positive shift of potentials for platinum hydroxyl adsorption and oxidation.

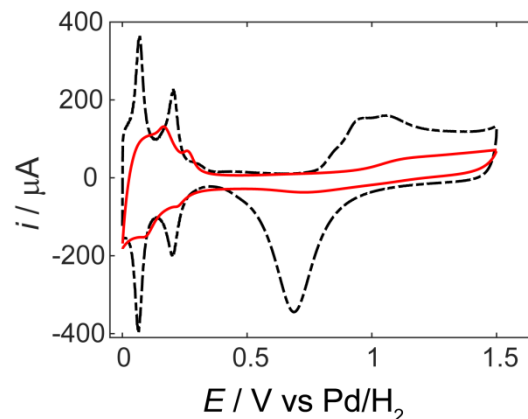


Fig. 1. Voltammetric profiles of polycrystalline Pt foil electrodes in 2 M H₂SO₄ aqueous solution (dotted-dash line) and in 2 M sulfuric acid in acetic acid (red line). Scan rate, ν = 500 mV s⁻¹.

Electrochemical characterization of polycrystalline Pt electrodes modified by sulfur-containing species

The Pt electrodes modified with four different sulfur species (Na₂S, Na₂S₂O₄, Na₂S₂O₅ and Na₂SO₃) were investigated in the 2 M sulfuric acid in acetic acid solution. Fig. 2 shows the current-voltage response during 50 consecutive cycles of the potential of the surface-modified electrodes to illustrate the electrode regeneration process during the oxidation/reduction cycles. The extent to which the electrochemically active surface area was recovered during the oxidation and reduction cycles was calculated using the charge associated to the hydrogen desorption charge (Q_H) and the charge associated to the sulfur oxidation (Q_S) for each cycle and is shown in supporting information (Fig. S2).

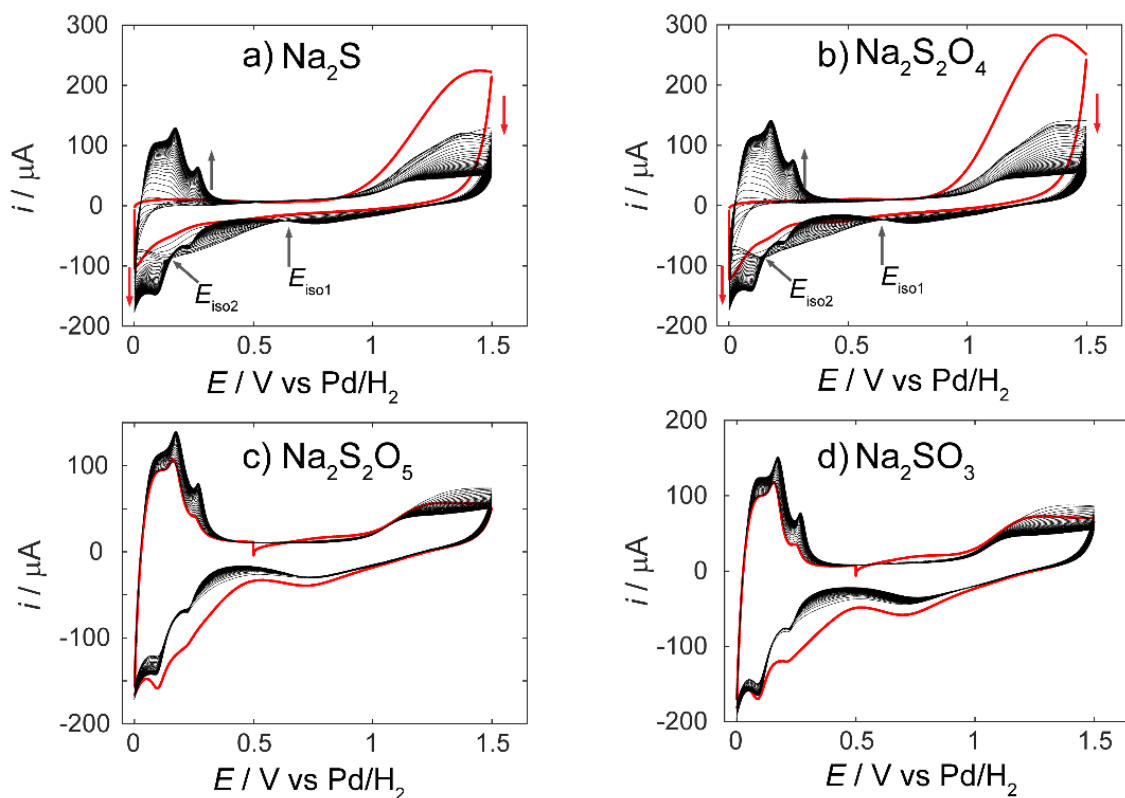


Figure 2. Consecutive cyclic voltammograms of Pt electrodes after surface modification in (a) Na_2S and (b) $\text{Na}_2\text{S}_2\text{O}_4$, (c) $\text{Na}_2\text{S}_2\text{O}_5$ and (d) Na_2SO_3 solutions as described in the experimental section. In each case, the first voltammogram recorded at a fresh S_{ads} modified Pt electrode is shown a red line. The black lines correspond to the consecutive cycles during the regeneration process (direction indicated in part a). All CVs were recorded in 2 M H_2SO_4 in acetic acid. Scan rate: $\nu = 500 \text{ mV s}^{-1}$.

It can be seen in Fig. 2 that platinum electrodes modified with Na_2S and $\text{Na}_2\text{S}_2\text{O}_4$ are strongly poisoned, as evidenced by the complete suppression of the $\text{H}_{\text{des}}/\text{H}_{\text{ads}}$ features. On the other hand, Pt electrodes modified with $\text{Na}_2\text{S}_2\text{O}_5$ and Na_2SO_3 solutions showed a much weaker poisoning effect.

Regarding the regeneration process, Fig. 2a and Fig. 2b also show that the electrodes modified with Na_2S and $\text{Na}_2\text{S}_2\text{O}_4$ required multiple oxidation/reduction cycles to recover the characteristic features of a clean Pt electrode. These results are comparable with previous results for the oxidation of sulfur containing species at platinum electrodes in aqueous

media.^[15] However, in contrast to the studies in aqueous media, the onset potential for the oxidation of S_{ads} appears at more positive potential, ca. ~ 0.95 V, and the number of cycles required for a “complete” regeneration of the electrode is significantly larger. In fact, it was found that in the acetic acid electrolyte, the S_{ads} monolayer cannot be efficiently removed by oxidation cycling with a potential limit of 1.2 V versus Pd/H₂ (Supporting Information, Fig.S1). Therefore, a higher potential limit, 1.50 V vs Pd/H₂, was used. This effect can be attributed to the lower coverage of OH species available at the Pt surface, due to strongly adsorbed acetate/acetic acid at high potentials and the low concentration of water in the electrolyte.

Our previous work in aqueous solution suggested that the final oxidation product from S_{ads} is (bi)sulfate, which readily desorbs from the surface.^[15] In acetic acid, however, the oxidation of sulfur-containing species is evidently more complicated. Whereas the charge associated with the oxidation process at positive potentials decreases monotonically, the cathodic scan of the voltammetric profiles in Fig. 2a-2b shows more complex behaviour. Two isopotential points were observed at 0.63 V (E_{iso1}) and 0.16 V (E_{iso2}). At $E > 0.63$ V, the charge associated to the reduction of Pt oxide reduction gradually increases as the cycle number increases. At $E < 0.63$ V, the CV profile shows a broad peak first and the current of this peak increases up to the 8th cycle, when it then starts to decrease and a new peak appears at $E < 0.16$ V. Nevertheless, we can intuitively associate these peaks to partial adsorption/hydrogenation of intermediate species from the oxidation of the S_{ads} . Alternatively, the broad feature might be associated with the reduction of trace oxygen in the electrolyte. Successive potential cycling leads to complete oxidation of these intermediates to the final product, likely (bi)sulfate, which can be desorbed from the platinum electrode.

The voltammetric profiles of the Pt electrodes modified by $\text{Na}_2\text{S}_2\text{O}_5$ and Na_2SO_3 show a different electrochemical response compared to those modified with Na_2S and $\text{Na}_2\text{S}_2\text{O}_4$. The first important difference to notice is the absence of a large oxidation peak at high potentials. On the other hand, in the first cycle of the negative scan, a reduction feature appears right after the oxide reduction feature at approx. 0.45 V. This feature is extended and overlaps with the H_{ads} process. Interestingly, this feature disappears in the second cycle and, in fact, the voltammetric profiles resemble the blank CV (for the clean electrode surface) in the absence of any adsorbed species. This suggests that $\text{S}_2\text{O}_5^{2-}$ and SO_3^{2-} have only a subtle poisoning effect and most of the sulfur-containing species can be removed within a single voltammetric sweep, and subsequent potential cycling only has a minor effect on the voltammetric profile.

Electrochemical characterization of surface modified platinum single-crystal electrodes in acetic acid media

To gain further insights on the surface-structure dependence of sulfur adsorption and electro-oxidation, voltammetric experiments were performed on Pt single-crystal electrodes with well-defined surface structure. These surfaces include three basal planes, Pt(100), Pt(111) and Pt(110) and two stepped surfaces vicinal to Pt(111), namely Pt(755)=Pt[6(111)×(100)] and Pt(775)=[6(111)×(110)]. As in the case of the polycrystalline electrode, the blank voltammograms of the basal planes were characterized in a 2 M solution of sulfuric acid in acetic acid. The CV profiles and their analysis can be found in the supporting information (Fig. S3).

After investigating the electrochemical response of the clean platinum surfaces, the electrodes were modified in a 0.1 M Na_2S solution, as described in the experimental section. Fig. 3 shows the oxidative stripping of a monolayer of S_{ads} on the different Pt single-crystal

electrodes. Three important characteristics are observed. Firstly, a total suppression of the current in the $H_{\text{ads}}/H_{\text{des}}$ region was found on all surfaces, indicating a complete blocking of the Pt sites. Secondly, there is a strong surface-structure dependence of the oxidation of S_{ads} . Lastly, small but clear reduction features (~ 0.4 V) were observed in the cathodic scan, after oxidation of adsorbed sulfur species. These features do not relate to hydrogen adsorption, but indicate the presence of a strongly adsorbed intermediate species, as we will discuss below.

Examining the surface structure-dependence of the S_{ads} oxidation in more detail (Fig. 3), the voltammetric profile of the Pt (111) surface, marked as curve a, shows the onset of S_{ads} oxidation at ~ 0.85 V, with a broad peak centred at 1.08 V. On the other hand, the Pt(100) surface (curve c) shows a sharp oxidation peak at a more positive potential, i.e. 1.24 V. Interestingly, the voltammetric profile of the Pt(755), which contains (111) terraces and (100) step sites, shows two oxidation features that coincides with the contributions of the oxidation of S_{ads} on the (111) and (100) sites. In Fig. 3, the voltammetric profile of the Pt(110) surface (curve e) shows a broad oxidation peak in the potential region of 0.8 – 1.4 V. Similar to the voltammogram of Pt(755), the voltammetric profile of Pt(775) shows contributions at low potentials of the oxidation of sulfur adsorbed on (111) sites, and at slightly more positive potentials associated to the oxidation of sulfur on the Pt(110) sites.

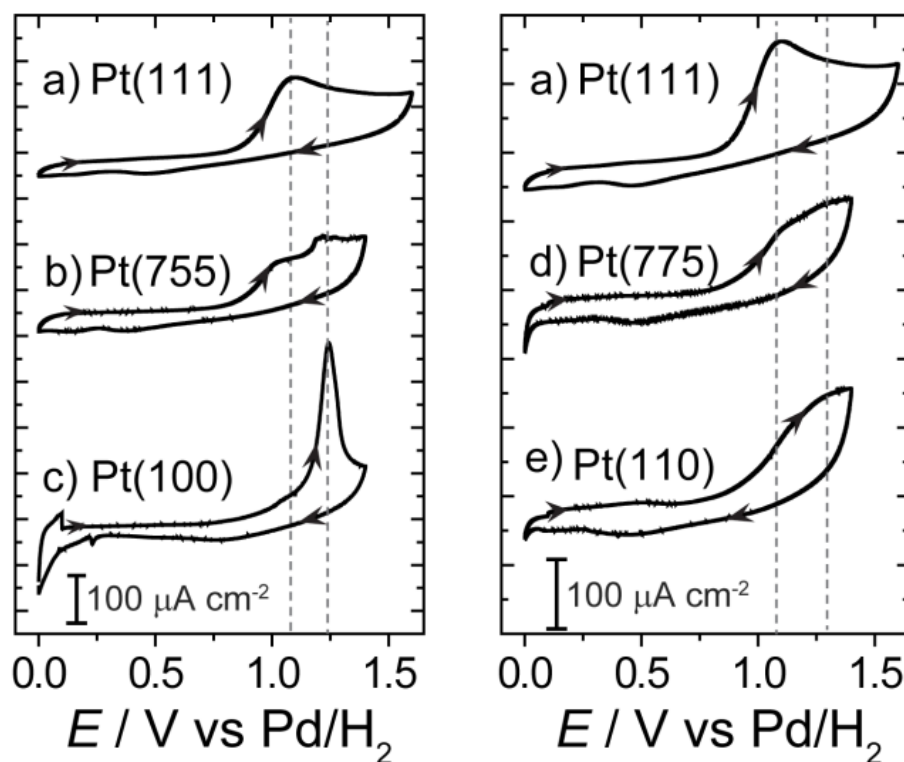


Figure 3. Voltammetric profiles for a) Pt (111), b) Pt(755), c) Pt(100), d) Pt(775) and e) Pt(110) single-crystal electrodes modified by Na_2S . Electrolyte: 2 M H_2SO_4 in acetic acid. Scan rate $\nu = 50 \text{ mVs}^{-1}$. Arrows indicate the scan direction.

Fig. 4 shows the first three consecutive scans of the oxidation of a monolayer of S_{ads} on Pt(111), Pt(100), Pt(110), Pt(755) and Pt (775) surfaces. It can be seen that the current for S_{ads} oxidation is highest in the first scan on all surfaces, similar to the results obtained on polycrystalline electrodes. However, despite considerable oxidation of the initial sulfur species in the first scan, the recovery of the $\text{H}_{\text{des}}/\text{H}_{\text{ads}}$ region lags, indicating the presence of strongly bound (intermediate) species. Among the surfaces studied herein, Pt(100) and Pt(110) show the quickest recovery towards the response for an unmodified surface, upon potential cycling. For these two surfaces, the voltammetric feature for hydrogen desorption can be observed in the second anodic scan in the potential region of 0 – 0.25 V. This feature is clear

on the third scan for Pt(111) surface, while for the Pt(755) and Pt (775) surfaces, there was little recovery after three voltammetric cycles in the potential range studied here.

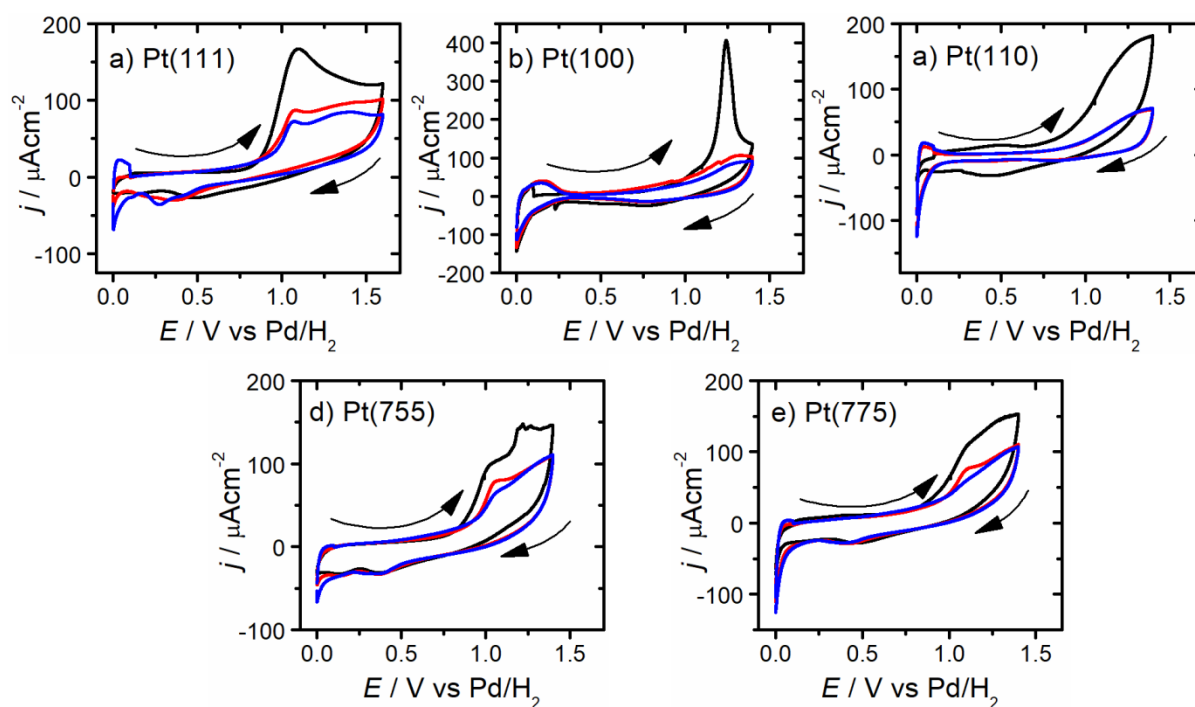


Figure 4. a-e) Voltammetric profiles for Pt single-crystal electrodes modified by Na₂S. In each figure, the black, red and blue line corresponds to the first, second and third scan, respectively. Electrolyte: 2 M H₂SO₄ in acetic acid. Scan rate $\nu = 50 \text{ mV s}^{-1}$.

To gain further insights into the possible reaction mechanism of the oxidation of S_{ads} at the surface of the electrodes, and the likely reaction intermediates, we also modified the five single-crystal surfaces with K₂SO₃, as described in the experimental methods. Fig. 5 shows the voltammetric profiles of these electrodes after modification in the sulfuric-acetic acid solution.

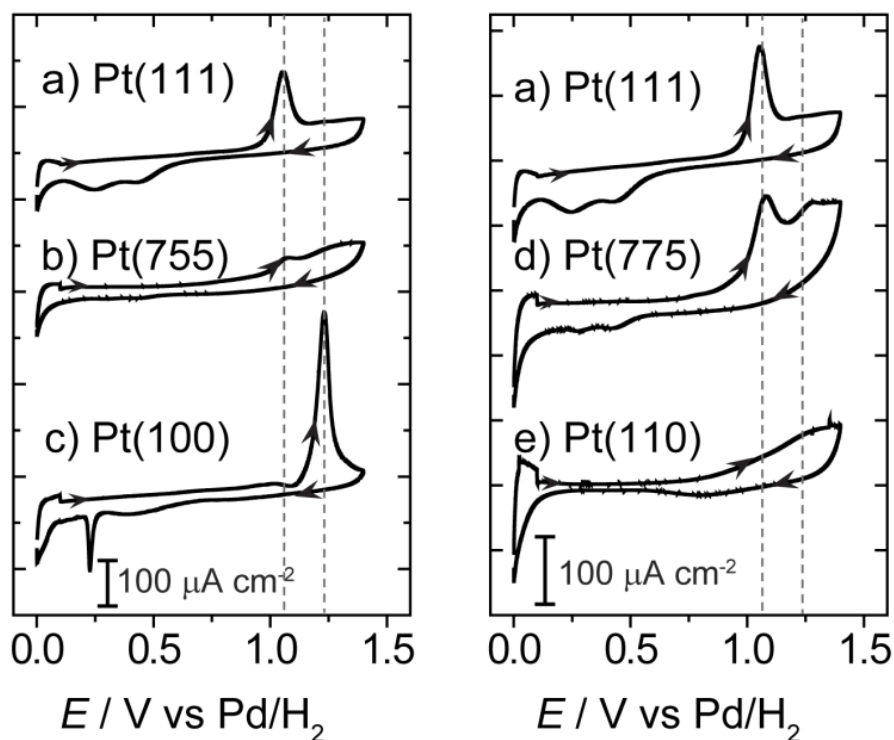


Figure 5. Voltammetric profiles for a) Pt (111), b) Pt(755), c) Pt(100), d) Pt(775) and e) Pt(110) single-crystal electrodes modified by K_2SO_3 . Electrolyte: 2 M H_2SO_4 in acetic acid. Scan rate $\nu = 50 \text{ mVs}^{-1}$.

As in the case of Na_2S modification, the voltammetric profiles in Fig. 5 show that at all surfaces, the H_{ads}/H_{des} features is suppressed, indicating complete blocking of Pt sites. Closer inspection reveals a different surface-structure dependence of the S_{ads} oxidation for Na_2SO_3 modified electrodes. First, the Pt (111) surface shows a well-defined peak centred at 1.1 V, which is significantly different to the broad peak observed when the surface was modified with Na_2S (Fig. 3, curve a). Moreover, the voltammetric profile for Pt(100) surface shows a sharp oxidation peak at approximately 1.23 V. Although the peak potentials are similar to those observed at the Na_2S modified electrodes, the peak shape is significantly different. Pt(100) modified with K_2SO_3 shows a sharp reduction peak at 0.23 V in the cathodic sweep. This feature only appears after oxidizing S_{ads} on Pt(100) surface and might relate to a reaction intermediate, which binds strongly to the surface. Alternatively, it could

also point towards competitive adsorption between acetic acid and sulfate on this surface. We propose that upon oxidation of $\text{SO}_{3,\text{ads}}$, the reaction product, i.e. SO_4^{2-} , remains adsorbed, forming a compact layer on the surface at sufficiently positive potentials. In the negative scan, the reductive desorption of this compact layer takes place and it is replaced by the adsorption of acetic acid, which gives rise to a sharp peak at 0.23 V. This behaviour is not visible in the blank voltammogram, where a mixture of acetate and sulfate is present on the surface (rather than a compact sulfate layer). Conversely, starting from a sulfur poisoned surface (i.e., no acetate on the surface), oxidation of the S_{ads} produces sulfate which remains strongly adsorbed on the surface at high potentials, blocking acetate adsorption. Only when the potential is sufficiently low, is the sulfate adsorption sufficiently weakened to allow displacement by acetate. This type of reductive desorption behaviour has been previously reported to be surface structure dependent for similar anion replacement.^[16]

In the case of the Pt(755) ([6(111)×(100)]) surface, which has both (111) and (100) geometry, the oxidation peak shows a major oxidation charge contribution from (111) and a minor yet still noticeable charge contribution from (100). In contrast to Pt(111) and Pt(100), the voltammetric profile for Pt (110) shows a broad oxidation wave in the potential region of 0.85 – 1.4 V. The voltammetric profile of the Pt(775) surface (Pt[6(111)×(100)]) shows a well-defined peak of the oxidation of adsorbed species on the (111) terrace sites and at slightly more positive potentials associated to the oxidation of sulfur on the Pt(110) step sites.

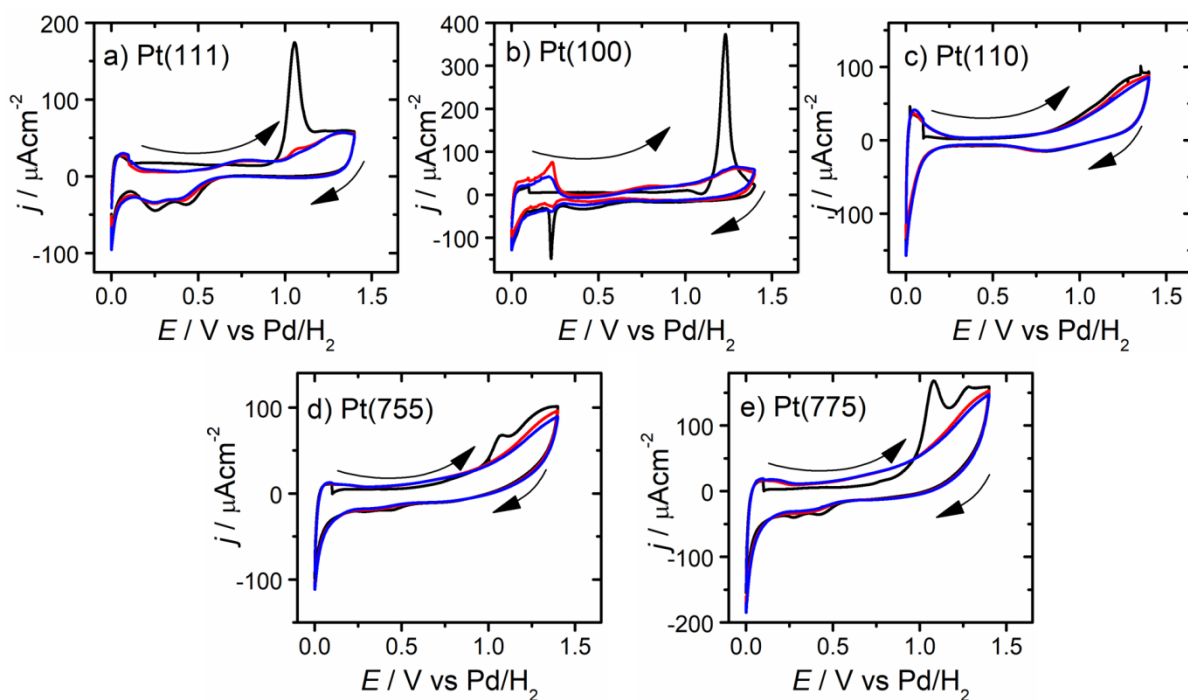


Figure 6. a-e) Voltammetric profiles for Pt single-crystal electrodes modified by K_2SO_3 . In each figure, the black, red and blue lines correspond to the first, second and third scan respectively. Electrolyte: 2 M H_2SO_4 in acetic acid. Scan rate $v = 50 \text{ mV s}^{-1}$.

When consecutive voltammetric cycles are recorded at a Pt surface modified by K_2SO_3 (Fig. 6), the profiles show a much faster recovery of the surface in comparison with those in Fig. 4, in which the electrodes were modified by Na_2S . Fig. 6 also shows that among the five electrode surfaces studied, Pt(110) surface shows fastest recovery, followed by the Pt(100) and Pt(111) surfaces. In the case of the Pt(110) and Pt(111) surfaces, almost all the adsorbed species are desorbed/oxidized in the first anodic sweep. For Pt(100), the sharp peak in the cathodic sweep at 0.23 V decreases dramatically after the first cycle, which also indicates that the oxidation product, tentatively assigned as adsorbed (bi)sulfate, is formed in the first scan, and a minimal amount is formed in the second and third scans.

Combining the results described above, we can propose a general mechanism of the reactivity of platinum electrodes in a sulfuric/acetic acid electrolyte, both with and without

adsorbed sulfur species. In the absence of adsorbed sulfur species (i.e. control voltammograms), the voltammetric profiles are similar to those for an aqueous electrolyte with a strongly coordinating anion (acetate). The adsorption strength of acetate is higher than that of (bi)sulfate, and acetate adsorption occurs over a wide potential range. Thus, within the voltammetric window explored in this study, it is reasonable to consider that the platinum surface in the sulfuric/acetate electrolyte is covered with a coordinating layer of acetate ions.

GENERAL DISCUSSION AND CONCLUSIONS

We have studied the adsorption and electrochemical oxidation of sulfur species at platinum electrodes in a sulfuric acid/acetic acid solution, in the search for a clearer understanding of the passivation of platinum catalyst surfaces during the hydrogenation of organic compounds in this medium. It was found that Na_2S , $\text{Na}_2\text{S}_2\text{O}_4$, Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_5$ strongly adsorbed on Pt surfaces under the studied conditions, resulting in a blocking of the surface sites. The recovery of the reactive sites can be achieved by consecutive electrochemical potential cycle in the potential range of 0 – 1.5 V vs Pd/H₂. We suggest the recovery of the electrode is activated by the formation of surface oxides which occurs at higher overpotentials to those observed in aqueous media for the recovery of poisoned Pt electrodes.

It was also found that the oxidation of the monolayer of the sulfur species is surface-structure dependent. Pt(111) showed the lowest overpotential for oxidation of the sulfur species while Pt(110) showed the largest overpotential. Using platinum stepped surfaces Pt(111), Pt(100), Pt(110), Pt(755)–Pt[6(111)x(100)] and Pt(775)–Pt[6(111)x(110)], we found that the oxidation of the sulfur species takes place on both terrace and step sites different adsorption sites suggesting the low diffusion of the sulfur on the surface. From these results,

we can also conclude that sulfur species adsorbed on terrace sites of both geometries (111) and (100) are more readily oxidised than those adsorbed on surface defects (steps) which required higher overpotentials and more successive cycles.

Based on our observation of the potential dependence of the oxidation of the different sulfur species, a simplified schematic mechanism is proposed and shown in Fig. 7. The oxidation of adsorbed sulfur species takes place at potentials higher than 1.0 V, accompanied by the formation of platinum oxide on the surface. As a result, different adsorbed intermediates species such as SO, SO₂ and SO₃ can be formed on the surface. This oxidation process, and its rate, is limited by the coverage of oxides species on the platinum surface, which, in turn, depends on the applied potential. Since the OH availability is low due to the low concentration of water, several oxidation steps (potential cycles) might be required to facilitate oxidation. Further oxidation of SO₃, in the same potential range, results in the formation of (bi)sulfate species which remain adsorbed at positive potentials but desorbed at sufficient less positive potentials.

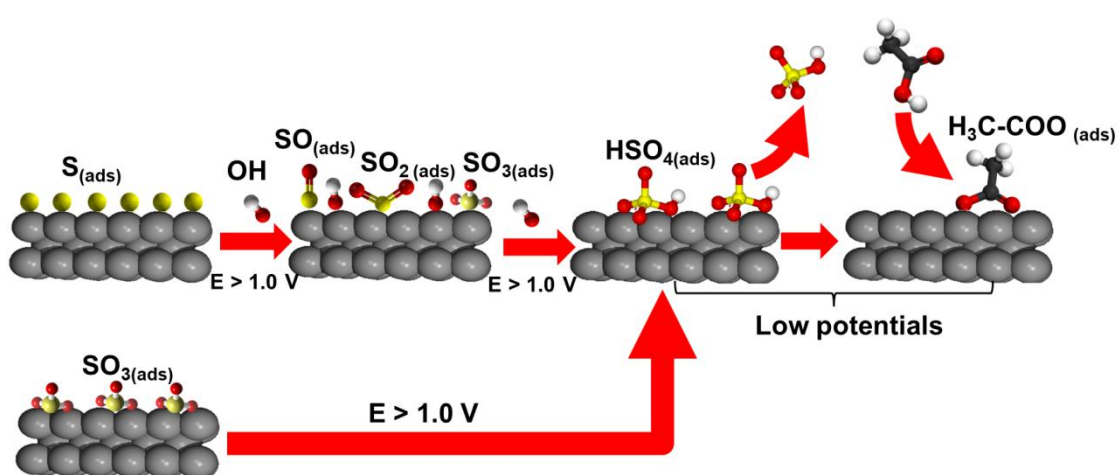


Figure 7. Schematic representation of the proposed mechanism of the oxidation of the sulfur species on platinum surfaces in sulphuric/acetic acid electrolytes.

These findings imply that the Pt catalyst which would be most resistant to poisoning would contain (111) domains and a low step density, providing a guideline for the rational design of catalysts. In addition, electrochemical protocols or oxidation/reduction cycles can be used to treat catalysts in a post-mortem fashion, and reactivate the platinum active sites.

EXPERIMENTAL SECTION

Chemicals and Materials.

Glacial acetic acid (> 99 %, Fisher Chemicals or ≥ 99.85 % VWR, Chemicals), sulfuric acid (96% Suprapur®, Merck), $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (≥ 99.99 %, Sigma-Aldrich), $\text{Na}_2\text{S}_2\text{O}_4$ (~85.0 %, Sigma-Aldrich), $\text{Na}_2\text{S}_2\text{O}_5$ (≥ 93 %, Fisher Chemicals), and Na_2SO_3 (ACS reagent, anhydrous, ≥ 98.0 %, Sigma-Aldrich) were used. All the experiments were performed in a freshly prepared solution of 2 M sulfuric acid in acetic acid.

Electrochemical measurements.

Two electrochemical systems were used in this work. The first system compromised the use of Pt foils (> 99.95 %, 0.125 mm thickness; Advent Research Materials) as working electrodes (electrochemical specific surface area 0.62 cm^2). Prior to each measurement, the foils were flame annealed followed by cooling in ultra-pure water and drying by nitrogen flow. Cyclic voltammetry (CV) measurements of Pt foil electrodes were carried out in a three-electrode configuration, using a PalmSens potentiostat (EmStat). A Pt foil (99.99 %, MaTeck or Alfa Aesar) was used as the counter electrode and a palladium (Pd) wire saturated with adsorbed hydrogen (Pd/H₂) was used as reference electrode.

In the second system, a range of Pt bead-type single-crystal electrodes (icryst, Jülich, Germany) with surface orientations of Pt(111), Pt(100), Pt(110), Pt(755)–Pt[6(111)x(100)]

and Pt(775)–Pt[6(111)x(110)] were used as working electrodes. Before each measurement, Pt single-crystal electrodes were flame annealed by a butane torch for approx. 1 minute, and cooled down in a H₂/Ar atmosphere (ca. 1:3 in volume). It has been shown that this procedure leads to surface topographies reasonably close to the nominal ones.^[16c, 17] The electrochemical measurements on the single-crystal electrodes were carried out in a 2-compartment cell using an Autolab PGSTAT12 potentiostat. A Pd/H₂ reference electrode was connected via a Luggin capillary. For cleaning purposes, all glassware was soak in an acidic solution of K₂MnO₄ overnight. After removal from the K₂MnO₄ solution, the glassware was further cleaned with a diluted solution of piranha (1 mL H₂SO₄ and 3 mL H₂O₂ in 1 L water). The cleaning process was follow by rinsing the glassware with a copious amount of ultra-pure water. Before adding the working solution the cell was rinsed with acetic acid.

All reported potentials in this work are against the Pd/H₂ electrode. Unless otherwise indicated, all electrochemical measurements were carried out in solution deaerated by N₂ or Ar prior to electrochemical studies.

Surface modification of the Pt electrodes with sulfur-containing species.

The platinum electrodes were modified by immersion at open circuit potential conditions in freshly prepared aqueous solution, containing 0.1 M of a particular sulfur species mentioned above. Given the difference in the electrochemical surface area and to ensure the maximum coverage of the electrode, the immersion time was 5 minutes for Pt foils and 1 minute for the single-crystal electrodes.^[15] After surface modification, the Pt electrodes were rinsed with abundant ultra-pure water to remove any non-strongly adsorbed sulfur species and dried in a N₂ or Ar atmosphere prior to its immersion at controlled potential in the electrochemical cells.

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KEY WORDS: Platinum electrode, single-crystal Pt surfaces, sulfur poison, electro-oxidation, acetic acid

ASSOCIATED CONTENT

Supporting Information

S1. Potential limit effect on sulfur oxidation.

S2. Charge analysis.

S3. Blank voltammetric profiles of Pt(111) and Pt(100) electrode in acetic acid.

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Author Contributions

Experiments on polycrystalline electrodes were performed by C.-H. C.

Experiments on single crystal electrodes were performed by P.R.

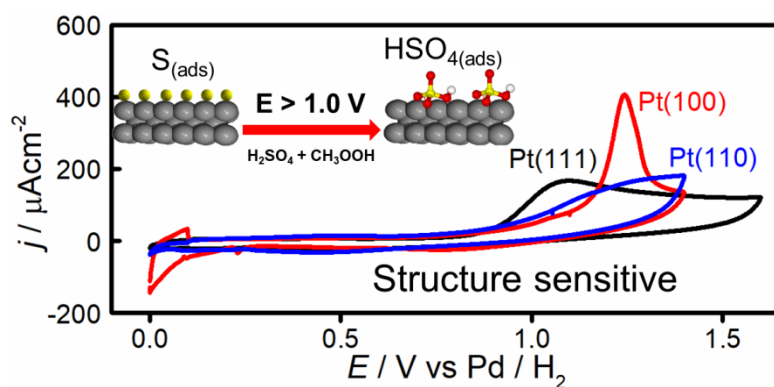
All the authors contribute equally in the analysis of the results, discussion, writing and revision of the manuscript.

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Electrochemical recovery. Electrochemical oxidation provides a means to eliminate surface sulfur-poisoning species such as (S^{2-} , $S_2O_4^{2-}$, $S_2O_5^{2-}$ and SO_3^{2-}) from the surface of Pt catalysts. Pt single-crystal electrodes revealed surface-structure sensitivity of the electro-oxidation of the adsorbed sulfur species.