ABSTRACT

Electrochemical and Surface-enhanced Raman Studies of CO and Methanol Oxidation in the Presence of Sub-monolayer Co-adsorbed Sulfur

By Mathew Mattox

Electrooxidation of carbon monoxide (CO) and methanol on platinum are two important reactions in direct methanol fuel cells. The presence of coadsorbates often modifies the reaction significantly. In this thesis we report our studies on the effects of adsorbed sulfur on CO and methanol electrooxidation on Pt. Although adsorbed sulfur is often considered a surface poison, the cyclic voltammetric and chronoamperometric results show that the presence of a sub-monolayer of adsorbed sulfur promotes the aforementioned reactions. Surface-enhanced Raman spectroscopy, together with electrochemical results, was used to elucidate a possible mechanism of the enhancement effect.

Electrochemical and Surface-enhanced Raman Studies of CO and Methanol Oxidation in the Presence of Sub-monolayer Co-adsorbed Sulfur

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List of Abbreviations

S _{ads}	adsorbed sulfur
CO _{ads}	adsorbed carbon monoxide
SER	surface-enhanced Raman
H _{des}	hydrogen desorption / adsorbed hydrogen
H _{ads}	hydrogen adsorption
OH _{ads}	adsorbed hydroxide
cm ⁻¹	wavenumber
X _S	relative sulfur coverage
CV	cyclic voltammogram

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Chapter 1. Introduction

Hydrogen fuel cells are probably the most well-known type of fuel cells due to the fact that hydrogen is the most electroactive fuel for fuel cells and thus has the highest potential for fuel cell applications¹. However, the problem of safe and low weight on-board hydrogen storage has proven a difficult obstacle to overcome for hydrogen fuel cell development. Methanol is the most electroactive organic fuel for fuel cells¹. Methanol is an attractive fuel for portable small to intermediate load power sources powering small portable electronics such as laptops and cell phones due to the ease of storage and transportation of methanol¹. Much of the potential for fuel cells stems from the fact that chemical energy is directly converted to electrical energy which yields to high theoretical energy conversion efficiencies for fuel cells¹. Thermodynamic calculations show that the equilibrium theoretical anode potential for methanol oxidation is 0.016 V vs. SHE; however, experimentally methanol oxidation requires a large overpotential and is only oxidized at potentials above 0.5 V vs. SHE¹. Since the potential at which methanol oxidation occurs is essentially a measure of the kinetics of the methanol oxidation reaction it can be seen from a theoretical standpoint that there is much room for improvement in methanol oxidation kinetics. It is believed that this high overpotential is due to the removal of carbonaceous intermediates formed during the methanol oxidation process. In order to systematically improve the electrode kinetics of methanol oxidation, the complete elucidation of the reaction mechanism of methanol oxidation is necessary. Once the mechanism of methanol oxidation is determined, deliberate modifications to anode catalysts can be made to improve methanol oxidation kinetics, lowering the large overpotential for methanol oxidation that currently plagues fuel cell catalysis.

Direct methanol fuel cells generate electric current via the direct oxidation of methanol in an electrochemical environment. The anode and cathode are separated by an ion conducting membrane, typically Nafion, which is a perfluorocarbon sulfonic polymer membrane.^{1, 2} The oxidation of methanol takes place at the anode while the reduction of oxygen occurs at the cathode. The basic schematic for a direct methanol fuel cell is shown below in Figure 1.1.



Figure 1.1 Schematic of a direct methanol fuel cell. The shaded area indicates a polymer membrane and the black areas are either anode or cathode catalysts. The relevant cathode and anode reactions are shown.

Direct methanol fuel cells are hindered by several problems. The reaction kinetics of methanol oxidation at the anode surface is often too slow and requires expensive noble metal catalysts. Methanol crossover, methanol from the anode crossing the polymer membrane and oxidizing directly at the cathode can also inhibit fuel cell efficiency. The oxygen reduction reaction is also inhibited due to poor electrode kinetics. While methanol crossover and slow oxygen reduction reaction kinetics are important obstacles to the development of direct methanol fuel cells the rest of this thesis will only address the topic of anode catalyst research.

The widespread use of direct methanol fuel cells has been hindered by the need for expensive noble metal anode catalysts and propensity of these catalysts to poisoning. Catalyst poisoning is caused by strongly adsorbing species modifying the surface active sites either sterically or electronically. Most often intermediates from the oxidation of methanol, typically carbon monoxide or other small carbon containing molecules such as formic acid or formaldehyde, block access to the electrode surface active sites. Methanol oxidation can take place by one of two pathways either the direct oxidation of methanol or via an intermediate. The direct oxidation of methanol is shown below¹:

$$CH_3OH \rightarrow H_2O + CO_2$$
 $E^\circ = 0.016 \text{ V vs. SHE}$

Alternatively, methanol oxidation proceeds via the production of a strongly adsorbing intermediate. These intermediates can be CO, formaldehyde or formic acid. Shown below are two possible reaction pathways involving intermediates³:

$$CH_3OH \rightarrow (adsorbed intermediate) \rightarrow CO_{ads} \rightarrow CO_2$$

 $CH_3OH \rightarrow (other adsorbed intermediate) \rightarrow HCHO, HCOOH \rightarrow CO_2$

Again, in order to systematically study fuel cell anodes, the reaction involving CO as the intermediate will be studied even though removal of other carbonaceous intermediates is of importance to fuel cell development.

The most common catalyst found in direct methanol fuel cells is an alloy of platinum and ruthenium. Although the mechanism of methanol oxidation on Pt surfaces is widely debated, the mechanism of methanol oxidation is fairly well agreed upon for Pt-Ru catalysts. The reaction mechanism for methanol oxidation on Pt-Ru proceeds by the Langmuir-Hinshelwood mechanism of heterogeneous catalysis that is shown below⁴:

$$Ru + H_2O \rightarrow Ru - (OH)_{ads} + H^+ + e^{-1}$$

$$Pt-(CO)_{ads} + Ru-(OH)_{ads} \rightarrow Pt + Ru + H^+ + e^- + CO_2$$

Here, the adsorbed hydroxide must come into close proximity to the adsorbed carbon monoxide in order for the reaction to take place. Although Pt-Ru catalysts are well characterized as well as the best direct methanol fuel cell catalysts currently available, Pt-Ru catalysts are susceptible to poisoning. In order to further reduce the onset potential for methanol oxidation more research is needed in the field of anode catalysts.

Catalysts can be affected by the adsorption of foreign atoms that can significantly modify the chemical and physical properties of the metal surface, acting as a reaction promoter or reaction poison⁵⁻¹⁰. Adsorbed sulfur is commonly regarded as a catalyst poison. It is well agreed upon that sulfur can block surface sites on Pt as well as modify the electronic structure of the metal and is difficult to remove. Sulfur blocks the hydrogen adsorption and desorption reactions and suppresses PtO formation on Pt electrodes. However, some studies suggest that adsorbed sulfur acts as a catalyst. In the late 1960's, Binder et al^{11, 12} first reported that the electrooxidation of solution CO and formic acid on Raney Pt was promoted by sulfur. In the early 1970's, Louka¹³ observed that methanol oxidation on Pt was enhanced in the presence of adsorbed sulfur. In 1985, Watanabe and Motoo^{6, 10} discovered the phenomenon of enhanced CO oxidation by adsorbed atoms S, Se, and Te. However, their explanation of the observed pH dependence, specifically that H_3O^+ and OH⁻ species are not present at pH 7¹⁰, is lacking. Sulfur and CO were again in 1998 by Zaera¹⁴ on platinum single crystal surfaces using scanning tunneling microscopy highlighting subtle surface structure changes when sulfur is adsorbed onto the catalyst surface in the presence of CO. It has been hypothesized that island formation leads to enhanced CO oxidation, based on the notion that the periphery of the islands are the most reactive. However, isotopic labeling experiments suggest that this is not the sole reason for the enhanced CO electrooxidation due to adsorbed sulfur¹⁴. Additionally, these experiments were performed in ultra high vacuum and extrapolation of these results to electrochemical environments can be misleading. Sulfur enhanced electro-oxidation of CO has also been studied on platinum catalysts for proton exchange membrane fuel cells by Venkataraman⁹, who observed that H₂ oxidation occurred at lower potentials when platinum catalysts were synthesized with a small amount of Na₂S₂O₃ present. Enhanced CO and methanol electrooxidation in the presence of sulfur is not new. However, a clear explanation of this phenomenon is missing and given the importance of CO and methanol oxidation in fuel cell reactions a complete understanding of sulfur enhanced electrooxidation is needed.

Recent advancement in laser technology has re-invigorated the use and application of Raman spectroscopy as a vibrational probe. The rich vibrational spectra available with SERS including the metal-adsorbate stretching region of 150 cm⁻¹ -850 cm⁻¹, which is unavailable to IR, is well suited to identify intermediates and adsorbed species in the oxidation of methanol and CO. The combination of cyclic voltammetry, chronoamperometry, and surface-enhanced Raman spectroscopy was used to aid in the determination of a possible mechanism of sulfur-enhanced electrooxidation of carbon monoxide and methanol.

Chapter 2. Cyclic Voltammetry on Pt, Rh, Pd, Au with Co-adsorbed Sulfur

2.1 Introduction

Cyclic voltammetry is an electrochemical technique where potential is scanned in a triangular waveform and current output is monitored. The range of the potential scan is often referred to as the potential window and depends on a number of parameters, most notably: type of electrode, supporting electrolyte, and pH of the solution. The Randles-Sevcik equation (Equation 2.1) allows for one to calculate the predicted faradaic current response for a given system.

$$i_{p} = (2.69 \text{ x } 10^{5})n^{3/2} \text{AD}^{1/2} \text{Cv}^{1/2}$$
 (Equation 2.1)

Where i_p is the peak current, n is the number of electrons in the balanced reaction, A is the area of the electrode, D is the diffusion coefficient, C is the bulk concentration of the electroactive species, and v is the scan rate. The rate of change of potential is often referred to as the scan rate and is an important parameter in cyclic voltammetry since the charging current is directly proportional to scan rate. For a cyclic voltammetry experiment the high and low potentials are limited by the potential window, which is dependent upon the type of electrode material, the supporting electrolyte, and the potentials where faradaic reactions occur. The potential window for Pt in aqueous solutions is limited by the evolution of hydrogen (negative potentials) and oxygen evolution (positive potentials) assuming aqueous solutions are used. Since the majority of experiments for this thesis were performed on Pt, the potential window limiting reactions are as follows:

Hydrogen Evolution Reaction $2H^+ + 2e^- \rightarrow H_{2(g)}$ $E^\circ = 0.0 \text{ V vs SHE}$

Oxygen Evolution Reaction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\circ = 1.23 \text{ V vs. SHE}$ These reactions define the potential window region for which faradaic reactions can be observed in aqueous solution using a Pt working electrode. Faradaic reactions must occur between these potentials or the current output will be distorted by current generated from the oxygen evolution or hydrogen evolution reactions. Processes at the electrode surface are governed by the Nernst equation (Equation 2.2).

$$E = E^{\circ} - 0.0591/n \log Q \qquad (Equation 2.2)$$

Where E is equal to potential, E° is the standard potential of the reaction, n is the number of electrons in the balanced equation and Q is the reaction quotient. However, the Nernst potential is the theoretical value based on equilibrium considerations, in actuality, potentials can be affected by electrode kinetics. Slow electrode kinetics can force the potential further away from equilibrium potential. This difference between the actual potential where a reaction takes place and the equilibrium potential is called the overpotential. Experimentally, cyclic voltammetry involves scanning the potential of an electrode from an initial potential through high and low potentials while monitoring the current output. Cyclic voltammetry can be used to observe increases and decreases in the current density of reactions under examination as well as monitor changes in overpotentials under various conditions. The initial potential is often chosen as a potential where no faradaic processes occur. The high and low potentials are limited by the potential window of the electrochemical experiment. The final potential selection is often chosen to return the electrode to a useable condition for subsequent experiments.

2.2 Experimental Methods

2.2.1 Chemicals

Double distilled, 70% perchloric acid (HClO₄) was obtained from GFS Chemicals. Semiconductor grade (99.997%) carbon monoxide (CO) was obtained from Spectra gas. Sodium perchlorate (NaClO₄· 6 H₂0) was obtained from Fluka Laboratory Chemicals. Sodium hydroxide (NaOH), glacial acetic acid (CH₃COOH) and boric acid (H₃BO₃) were obtained from Fisher Scientific. Sodium hydrogenphosphate (Na₂HPO₄) and sodium dihydrogenphosphate (NaH₂PO₄) were obtained from Sigma-Aldrich. Sodium sulfide (Na₂S) was obtained from Fisher as sublimed sulfur and recrystallized in milli-Q water prior to use. All solutions were made with Milli-Q water 18.2 MΩ resistivity (Milli-Q A10, Millipore)

2.2.2 Cyclic Voltmammetry

All electrochemical experiments were performed on CHI instruments electrochemical analyzer model 600, 630, or 750 using a 2-compartment, 3-electrode setup. All potentials listed are versus Ag/AgCl reference electrode unless otherwise noted. The counter electrode was always a flame annealed Pt wire unless otherwise noted. Shown in Figure 2.1 is a diagram of a two compartment three electrode setup used. The two compartment three electrode cell was used in order to remove dissolved oxygen from the supporting electrolyte solution since dissolved oxygen influences the surface chemistry of Pt and limits the size of the potential window. By purging supporting electrolytes with inert gases such as Ar or N_2 , the potential window will not be affected much by dissolved oxygen. All two compartment three electrode cells were cleaned by soaking in concentrated H_2SO_4 overnight followed by soaking in water for at least one hour prior to use to remove any residual acid from the porous frit separating the two compartments.



Figure 2.1 Two electrode, three compartment cell configuration. Note the valve to the right of the gas inlet, this allows for gas to either purge through the solution or blanket the top of the solution and minimized the effects due to dissolved oxygen.

2.2.3 Electrode preparation

Although the use of well defined single crystal electrode surfaces is often preferred, polycrystalline electrodes were used primarily for this research for two reasons: fuel cell catalysts are predominately polycrystalline in nature and polycrystalline Pt electrodes are easy to prepare. The crystallographic nature of the catalyst surface does have an effect on the amount of poisoning that will occur and single crystal studies are very important that should not be ignored. Polycrystalline Pt electrodes were polished successively in 1.0, 0.3 and 0.05 micron micropolish and sonicated in milli-Q water (18.2 M Ω resistivity) for 10 minutes prior to analysis. The cleaned Pt electrodes were checked electrochemically for cleanliness prior to each experiment by scanning the potential from -0.25 V to 1.0 V. The outermost trace in Figure 2.3 shows the CV of a clean Pt electrode.

2.2.4 Experimental techniques

Cyclic voltammograms of polycrystalline Pt were performed in CO-saturated solutions prepared by purging previously deaerated solutions with CO for 5 minutes at constant potential of 0.0 V. To monitor adsorbed CO, cyclic voltammograms were observed in the same CO saturated solution described previously upon completion of the solution CO oxidation CV. The solution CO was removed by purging N₂ for 10 minutes at 0.0 V. The potential was held at 0.0 V to ensure that the adsorbed CO would remain on the Pt surface. Typically the supporting electrolyte concentrations were 0.1 M and the choice of supporting electrolyte was determined based on pH. pH 1 experiments were conducted in 0.1 M HClO₄ supporting electrolyte. pH 3 experiments were prepared by the acidification of 0.1 M NaClO₄ by dropwise addition of 0.1 M HClO₄. pH 5 experiments were conducted in an aqueous buffer solution containing 10 mM glacial acetic acid and 90 mM NaClO₄. pH 7 experiments were conducted in an aqueous buffer solution containing 5 mM NaH₂PO₄, 5 mM Na₂HPO₄ and 90 mM NaClO₄. pH 9 experiments were conducted in an aqueous buffer solution containing 10 mM boric acid and 90 mM NaClO₄. pH 12 experiments were conducted in 0.1 M NaOH. Sulfur was deposited in an aqueous solution consisting of 20 µM-2 mM Na₂S, 0.1 M NaClO₄ and 1 mM NaOH for 60 seconds at -0.6 V (vs. Ag/AgCl) depending on the desired sulfur coverage. The pH of supporting electrolyte solutions was measured using Mettler Toledo SevenEasy pH meter with Mettler-Toledo Inlab 413

electrode. The pH meter was calibrated with pH buffer solutions of 4.01, 7.00, 9.21, 10.01 available from Mettler-Toledo GmbH, Analytical CH-8603, Schwerzenbach, Switzerland.

2.2.5 Sulfur enhanced methanol electro-oxidation

Two cells containing 0.1 M HClO₄ were purged with N_2 gas for 10 minutes. In one cell CO was purged 5 minutes and a CV was taken, followed by purging N_2 . This was done to establish a clean electrode surface and later used to determine sulfur coverage. Only CO and N_2 were introduced into this cell to reduce the likelihood of contamination from residual methanol from previous experiments. The second cell contained 24mL of 0.1 M HClO₄, prior to the analysis 1 mL of methanol was added to the 0.1 M HClO₄ solution to obtain a methanol molarity of roughly 1 M. Upon deposition of sulfur onto the electrode the procedure was repeated.

2.3 Results

Previous studies of the electrocatalytic effect of sulfur adatoms on formic acid oxidation on polycrystalline platinum shows that sulfur ions S²⁻ actually form sulfur adatoms, abbreviated $S_{ads}^{15}_{BB}$. Sulfur adsorbs strongly to the Pt electrode surface as evidenced by the high potentials required to oxidize S_{ads} to SO_4^{2-} through a 6 electron process ^{7, 15, 16}. Shown below in Figure 2.2 is the oxidation of S_{ads} on polycrystalline Pt the arrows indicate the direction of change after each successive segment. Initially the $S_{ads} \rightarrow SO_4^{2-}$ peak is very large and begins at roughly 0.8 V, once the sulfur is oxidized the Pt \rightarrow PtO formation peak dominates at high potentials and begins roughly at 0.4 V. Simlarly the PtO \rightarrow Pt reduction peak increases after multiple segments. Initially the H_{des}/H_{ads} reaction which occurs at low potentials is blocked due to sulfur adsorption, once the sulfur is oxidized from the surface after the first couple scans the H_{des}/H_{ads} peaks increase. Note the scan rate was 100 mVs⁻¹ on a Pt electrode with sulfur deposited for 60 seconds in 0.1 M NaClO₄ / 1 mM NaOH/ 2 mM Na₂S.



Sulfur blocks the H_{des}/H_{ads} reaction seen at low potentials. Increasing the coverage of sulfur successively decreases the charge from the H_{des}/H_{ads} reaction and can be used to quantify the amount of S_{ads} coverage^{15, 17}. The hydrogen desorption charge can be easily integrated using the CHI software that is standard with the program. The sulfur coverage can be determined by Equation 2.3:

$$X_S = \frac{Q_H^0 - Q_H^S}{Q_H^0}$$
(Equation 2.3)

Where Q_{H}^{0} and Q_{H}^{s} are the H desorption charge from clean and sulfur-covered Pt surfaces, respectively and X_s is the sulfur coverage expressed as a decimal. Shown below in Figure 2.3 is how the H_{des} charge (potentials below 0 V) and PtO formation charge (potentials above 0.3 V) decrease when sulfur coverage increases. Current density was evaluated using the hydrogen desorption charge and assuming 210 μ C/cm² which is the charge required for desorption of a full monolayer of adsorbed hydrogen on Pt (111).



Figure 2.3 Cyclic voltammograms of Pt electrodes covered with various amounts of sulfur on 0.1M HClO₄. The X_S are from outermost trace to the innermost trace is 0, 0.24, 0.48, 0.63, 0.86 respectively. The arrows indicate scan direction.

Sulfur coverage can also be calculated by integrating the charge from the oxidation of adsorbed CO to CO_2 in a similar fashion as shown above by Equation 2.3. Additionally, sulfur coverage can be quantified by the method developed by Sung et al., by measuring the charge of the oxidation of sulfur to sulfate ion as given by Equation 2.4^{7, 18}.

$$\theta_S = \frac{Q_S}{6 \times Q_H^0}$$
(Equation 2.4)

Where the Q_S is the charge involved in the S_{ads} oxidation. Cyclic voltametric results show that S_{ads} calculations using Equation 2.4 are two to four times lower than the corresponding X_S. This indicates that S_{ads} blocks more than one H_{ads} . To further examine the S_{ads} blocking behavior, $Ru(NH_3)_6^{3+/2+}$ redox reaction was used to probe the electrochemically accessible area. In this case, the sulfur coverage was calculated using the charges involved in $Ru(NH_3)_6^{2+}$ oxidation on clean and S-covered Pt in a similar fashion to that shown in Equation 2.3 at the potentials used $Ru(NH_3)_6^{3+/2+}$ does not mediate any reactions with the adsorbed sulfur. The obtained sulfur coverage is three to four times smaller than that evaluated using Equation 2.3 at the highest attainable θ_{s} , further confirming that one S_{ads} blocks multiple H_{ads}. In the following Figures and discussion, X_S will be used instead of θ_S , to denote different sulfur amount on the surface for better comparison with the previous work. It can be seen from Figure 2.4 below that the sulfur coverage calculated using Equation 3 and H_{des}/H_{ads} charge and CO oxidation charge follow closely the unit slope. Therefore the X_S is the relative sulfur coverage, i.e. relative to the sulfur coverage at which Sads completely blocks the hydrogen adsorption (CO adsorption as well, vide *infra*). Additionally, for θ_S larger than a value at which the X_S cannot be used, the CO oxidation is completely blocked and is not useful for the purpose of the present work.



Figure 2.4 Comparison of the relative sulfur coverage obtained from the H desorption charge, $X_S(H)$, with that from the adsorbed CO oxidation charge, $X_S(CO)$, on the same sulfur covered Pt electrode. The dash trace shows a unit slope line as a guide to the eye.

Figure 2.5 shows cyclic voltammograms of solution CO oxidation on Pt covered with varying amounts of sulfur. The decrease in onset potential is largest with increasing sulfur coverage. It can be concluded from figure 2.5 that sulfur promotes solution CO oxidation to lower potentials with increasing sulfur coverage. The largest increase in onset potential occurs when the X_S is 0.86. The inset zooms in on the 0.0 V to 0.4 V portion of the potential window to further clarify the decrease in onset potential due to sulfur adsorption.

It can be seen from previous Figures that the presence of adsorbed sulfur reduces the CO oxidation current. CV's plotted as potential vs. current can be misleading since catalyst active sites that are blocked are assumed to not be available for CO oxidation. A more accurate description can be seen if one takes into account the current density which indicates that the sites that are available for CO oxidation are much more catalytically active in the presence of sulfur. Figure 2.6 shows the same CV's as presented in figure 2.5 but plotted in terms of current density. It is clear from Figure 2.6 that at high sulfur coverage, a large enhancement occurs.



Figure 2.5 Sulfur coverage dependence of solution CO oxidation. Anodic segments of cyclic voltammograms of solution CO oxidation on Pt electrodes covered with various amounts of sulfur recorded in CO-saturated 0.1 M HClO₄. The CV is plotted as potential vs. current. The inset is an enlargement of the onset potential region. The relative sulfur coverage, X_S are: solid: 0.86; dash: 0.63; dash-dotted: 0.24; dotted: 0. Scan rate: 0.1 Vs⁻¹. The arrow indicates the scan direction.



Figure 2.6 Anodic segments of the cyclic voltammogram of solution CO oxidation on Pt electrode covered with various amounts of sulfur recorded in CO-saturated 0.1 M HClO₄. The CV is plotted as potential vs. current density. The inset is an enlargement of the onset potential region. The relative sulfur coverage, X_S are: solid: 0.86; dash: 0.63; dash-dotted: 0.24; dotted: 0. Scan rate: 0.1 Vs⁻¹. The arrow indicates the scan direction.

To make a more quantitative assessment of the S_{ads} effect on the solution CO oxidation, the onset potential difference (ΔE), defined as the potential difference at a current equal to 5% of the CO oxidation peak current on the clean Pt surface, was measured and plotted as a function of the X_S (Figure 2.7). The ΔE increases sharply with the amount of sulfur on the surface and approaches a plateau near $X_S = 0.65$. This observation is similar to that reported by Watanabe and Motoo^{6, 10}. Since 1 sulfur atom can block many Pt sites, the X_S relative sulfur coverage of the sites available for hydrogen adsorption and desorption and CO oxidation, was used instead of θ which is actual surface coverage typically reported in single crystal and UHV studies.



Figure 2.7 Sulfur coverage dependence of the shift in onset potential for solution CO oxidation. The onset potential difference of solution CO oxidation on S-covered Pt plotted against the relative sulfur coverage. The dash curve serves as a guide to the eye.

The reduction in onset potential for solution CO electro-oxidation by adsorbed sulfur is slightly different for adsorbed CO. Large onset potentials over hundreds of mV like those seen for solution CO were not observed, rather small changes on the order of tens of mV changes in onset potential were observed and only under low sulfur coverages. Figure 2.8 shows a CV of adsorbed CO on polycrystalline Pt. Note that during the first segment H_{des} is completely blocked due to the strong adsorption of CO. However, in subsequent segments H_{des} is very clear indicating that the CO was oxidized off of the surface. The inset shows a more detailed look at the anodic CO oxidation section of the potential window.

Shown in Figure 2.9 is a CV of adsorbed CO with an X_S of 0.48. Now it can be seen that sulfur is inhibiting the oxidation of adsorbed CO and forcing the reaction to a more positive potential. The insert is a close up showing the extent of the onset potential for each segment at 0.4 V to 0.75 V.



Figure 2.8 Cyclic voltammogram of adsorbed CO oxidation where the relative sulfur coverage X_S is 0.09. Cyclic voltammograms of irreversibly adsorbed CO oxidation on clean (dash traces) and sulfur covered (solid traces) Pt electrodes in 0.1 M HClO₄. The insets are the enlargement of the peak section of the first anodic segment of the corresponding CVs, showing the peak potential shift of the adsorbed CO oxidation. Scan rate: 0.1 V s⁻¹.



Figure 2.9 Cyclic voltammogram of adsorbed CO oxidation where the relative sulfur coverage X_s is 0.48. Cyclic voltammogram of irreversibly adsorbed CO oxidation on clean (dash traces) and sulfur covered (solid traces) Pt electrodes in 0.1 M HClO₄. The inset is an enlargement of the peak section, 0.4 V – 0.75 V of the first anodic segment of the corresponding CV, zooming in on the peak potential shift of the adsorbed CO oxidation. Scan rate: 0.1 Vs⁻¹.

To determine if the sulfur effect is dependent on the nature of the metal surface other Ptgroup transition metals were examined. Au electrodes covered with Pt, Pd, and Rh thin films were studied, this was simply to remain consistent with our SERS experiments which required the use of thin films. The use of transition metal thin films deposited on Au is required for surface-enhanced Raman experiments and will be discussed in detail in chapter 4. When available bulk polycrystalline Pt electrodes were often used for cyclic voltammetry simply due to the ease of electrode preparation. However SERS considerations do not allow for the use of polycrystalline Pt electrodes. Following SERS protocols (described in more detail in chapter 4), Pd and Pt electrodes were prepared by electrochemically roughening gold electrodes, depositing 1 monolayer of Cu on the electrochemically roughened Au via Cu underpotential deposition immediately followed by redox replacement with platinum or palladium. Rh was deposited on the Au electrode directly by constant current deposition. Prior to preparation of thin film metal electrodes a CV of clean Au was taken. Contaminated Au electrodes often show anomalous peaks that are different from the AuO formation that occurs after 1 V and the AuO reduction that occurs at 0.9 V. Shown in Figure 2.10 are cyclic voltammograms of Pt, Pd, Rh and Au in acidic solution. It can be seen from Figure 2.10 A that sulfur, $X_S = 0.8$ shifts the onset potential for solution CO oxidation on Pt to more negative potentials by roughly 300 mV. Figure 2.10 B shows that solution CO oxidation is shifted to negative potentials on Rh in the presence of sulfur by roughly 500 mV. However adsorbed sulfur, $X_S = 0.8$ on Pd and Au exhibits no enhancement and actually inhibits oxidation of solution CO (Figure 2.10 C and D).



Figure 2.10 Comparison of Sulfur effect on solution CO oxidation for Pt, Pd, Rh, and Au electrodes. Cyclic voltammograms of CO oxidation on sulfur-modified (solid traces) and clean (dash traces) metal electrodes obtained in CO-saturated 0.1 M HClO₄. (A). Pt; (B). Rh; (C). Pd and (D). Au. The relative sulfur coverage, X_s , is around 0.8. The dotted traces in each panel are from the corresponding S-modified metals in N₂-purged 0.1 M HClO₄ for comparison. The arrows indicate the potential scan direction. Scan rate: 0.1 Vs⁻¹.



Figure 2.11 Cyclic voltammograms of methanol oxidation on clean (dotted trace) and S-covered (solid and dash traces) Pt electrodes obtained in 1 M MeOH + 0.1 M HClO₄, plotted in current. The X_S are: 0.1 for solid trace and 0.6 for dash trace. Scan rate: 0.1 Vs⁻¹

In addition to observed enhanced CO oxidation cyclic voltammetry data, methanol chronoamperometry experiments show that a pronounced increase in methanol electro-oxidation occurs when sulfur is present on the electrode surface. It is important to note that methanol oxidation current decreases at a much slower rate when sulfur is present this is shown in the normalized current time transients. Since adsorbed sulfur promotes the solution and adsorbed CO electrooxidation on Pt electrodes at certain sulfur coverages, it is of interest to examine how the adsorbed sulfur affects methanol electrooxidation. Figure 2.11 displays cyclic voltammograms of methanol oxidation on S-covered Pt electrodes with two different X_{S} (0.1 and 0.6). For the higher X_s, the CV is also plotted in the current density form (Figure 2.12). The current density was calculated using the surface area evaluated from the H desorption charge, which is the area available for H adsorption (presumably also for methanol adsorption), but not the sulfur-free area (vide supra). Interestingly, at low X_S (< 0.3) the presence of S_{ads} promotes methanol oxidation; both the current and current density are larger than the respective quantities on clean Pt. However, at high $X_S (> 0.75)$ both the current and current density are lower than those from the clean Pt surface, indicating S_{ads} blocks methanol oxidation. In the range of $0.3 < X_S < 0.75$, the absolute current is smaller than the corresponding clean surface, but the current density (with respect to the Pt area available for H adsorption) is higher. Loučka¹³ observed the decrease of absolute current, but increase of the current density of methanol oxidation on Pt electrodes modified with S_{ads} . In his work, only one X_S (0.65, which was taken as θ_S in the paper) was examined. The X_S falls in the range of $0.3 < X_S < 0.75$, consistent with the findings described above.

Figure 2.12 shows three cyclic voltammograms in 1 M methanol and 0.1 M HClO₄, the solid red trace shows a X_S of 0.1 which exhibits as slight decrease in onset potential of roughly 30 mV and an increase in current versus the dotted brown trace which is polycrystalline Pt with no sulfur added. This signifies that the kinetics of methanol oxidation are improved with the addition of a low sulfur coverage. Also shown is the commonly perceived notion that sulfur is a catalyst poison since at high sulfur coverage, $X_S = 0.6$ the onset potential is shifted far to the right and current output is suppressed versus polycrystalline Pt with no sulfur added. It is clear that low sulfur coverage catalyzes methanol electro-oxidation both in terms of decreasing onset potential and increasing current density over clean polycrystalline Pt.


Figure 2.12 Cyclic voltammograms of methanol oxidation on clean (dotted trace) and Scovered (solid and dash traces) Pt electrodes obtained in 1 M MeOH + 0.1 M HClO₄, plotted in current density. The X_S are: 0.1 for solid trace and 0.6 for dash trace. Scan rate: 0.1 Vs⁻¹ To better understand the mechanism of sulfur enhanced electro-oxidation of CO pH dependence studies were observed. Couto^{19, 20} studied the effect of pH on CO electrooxidation on polycrystalline Pt and the a similar protocol was used to study the pH dependence of sulfur enhanced CO electrooxidation. The pH's studied ranged from 1-12. It is hypothesized that pH dependent studies would lend support to the notion that the reaction mechanism for sulfur-enhanced CO electro-oxidation mechanism is similar to the Langmuir-Hinshelwood mechanism of CO oxidation observed on Pt-Ru involving adsorbed hydroxide species⁴. As shown above, the sulfur coverage enhancement effect levels off at X_S above 0.6, so all pH dependent studies were performed with X_S above 0.6. The pH dependence of sulfur enhanced solution CO oxidation was investigated by varying the pH of the solution and monitoring the shift in onset potential. 0.1 M supporting electrolytes and buffers with pH values of 1, 3, 5, 7, 9, and 12 were examined for solution CO oxidation on polycrystalline Pt electrodes with X_S higher than 0.6. All Figures are plotted in terms of current density.

Figure 2.13 is a cyclic voltammogram of solution CO oxidation in 0.1 M HClO₄ pH 1, the blue dashed trace is two segments of solution CO oxidation on polycrystalline Pt electrode and the red solid trace shows solution CO oxidation on sulfur covered ($X_s = 0.84$) polycrystalline Pt electrodes. The arrows indicate scan direction. It can be seen from Figure 2.13 that solution CO oxidation onset potential is roughly 300 mV more negative on sulfur covered Pt than on clean Pt. It should be noted that the oxidation of CO as well as hydrogen evolution and oxygen evolution reactions are all shifted to more negative potentials by roughly 60 mV per pH unit as pH increases. Figure 2.14 shows two CV segments of solution CO oxidation on clean Pt (blue dashed trace) and sulfur covered ($X_S = 0.71$ red solid trace) Pt electrodes. The supporting electrolyte was 0.1 M NaClO₄ acidified to pH 3. At pH 3 the shift in onset potential is less than that observed for pH 1, roughly 250 mV more negative with sulfur than on clean Pt. At pH 5 (Figure 2.15) the shape of solution CO CV with and without sulfur is roughly the same as the previous CVs. The onset potential is roughly the same as previous pH experiments as well. At pH 7 (Figure 2.16) the onset potential is not as pronounced as it is in acidic solutions, a trend of increasing pH and less enhancement of solution CO oxidation is apparent. The decreasing contribution of sulfur to solution CO is even more pronounced in Figure 2.17, pH 9. Here, the onset potential is considerably less than acidic solutions. From pH 9 to pH 12 (Figure 2.18) there

is little change in onset potential. There appears to be a leveling off of the sulfur enhancement effect. Since the potential window for Pt is solution dependent and shifts roughly 60 mV per pH unit change, a quantitative method for comparing cyclic voltammograms had to be established. The method involved once again assigning the onset potential, the lowest potential where oxidation begins as 5% of the peak height of CO oxidation on clean Pt. Figure 2.19 shows the ΔE for solution CO oxidation under changing pH conditions. The trend can be seen in Figure 2.19 that the sulfur effect is more pronounced in acidic solutions and dramatically decreases once the solution pH changes from acidic to neutral and continues to decrease with increasing pH until leveling off around pH 9. It is believed that sulfur provides adsorbed oxygenated species at the electrode surface, specifically adsorbed hydroxide. Since hydroxide is readily available in basic solution it is believed that the presence of adsorbed hydroxide due to sulfur is less pronounced.



Figure 2.13 Cyclic voltammogram of solution CO oxidation on polycrystalline Pt and S covered Pt electrodes at pH 1. CV of solution CO oxidation on polycrystalline Pt electrode (Blue dashed trace) and sulfur covered ($X_S = 0.84$) Pt electrode (Red solid trace) in 0.1 M HClO₄ pH 1 supporting electrolyte, scan rate 0.1 V s⁻¹. The arrows indicate scan direction.



Figure 2.14 Cyclic voltammogram of solution CO oxidation on polycrystalline Pt and S covered Pt electrodes at pH 3. CV of solution CO oxidation on polycrystalline Pt electrode (Blue dashed trace) and sulfur covered ($X_S = 0.71$) Pt electrode (Red solid trace) in 0.1 M NaClO₄ pH 3 supporting electrolyte, scan rate 0.1 V s⁻¹. The arrows indicate scan direction.



Figure 2.15 Cyclic voltammogram of solution CO oxidation on polycrystalline Pt and S covered Pt electrodes at pH 5. CV of solution CO oxidation on polycrystalline Pt electrode (Blue dashed trace) and sulfur covered ($X_S = 0.75$) Pt electrode (Red solid trace) in aqueous buffer solution containing 10 mM glacial acetic acid and 90 mM NaClO₄ at pH 5, scan rate 0.1 V s⁻¹. The arrows indicate scan direction.



Figure 2.16 Cyclic voltammogram of solution CO oxidation on polycrystalline Pt and sulfur covered Pt electrodes at pH 7. CV of solution CO oxidation on polycrystalline Pt electrode (Blue dashed trace) and sulfur covered ($X_s = 0.63$) Pt electrode (Red solid trace) in aqueous buffer solution containing 5 mM NaH₂PO₄, 5 mM Na₂HPO₄ and 90m NaClO₄ at pH 7, scan rate 0.1 V s⁻¹. The arrows indicate scan direction.



Figure 2.17 Cyclic voltammogram of solution CO oxidation on polycrystalline Pt and S covered Pt electrodes at pH 9. CV of solution CO oxidation on polycrystalline Pt electrode (Blue dashed trace) and sulfur covered ($X_S = 0.65$) Pt electrode (Red solid trace) in aqueous buffer solution containing 10 mM boric acid and 90 mM NaClO₄ at pH 9, scan rate 0.1 V s⁻¹. The arrows indicate scan direction.



Figure 2.18 Cyclic voltammogram of solution CO oxidation on polycrystalline Pt and S covered Pt electrodes at pH 12. CV of solution CO oxidation on polycrystalline Pt electrode (Blue dashed trace) and sulfur covered ($X_S = 0.61$) Pt electrode (Red solid trace) in 0.1 M NaOH at pH 12, scan rate 0.1 V s⁻¹. The arrows indicate scan direction.



Figure 2.19 Summary of pH dependence of the change in onset potential for solution CO. The average onset potential difference, defined as 5% of the peak current of the solution CO oxidation on clean Pt, on S-covered Pt electrodes as a function of solution pH. The dash curve serves only as a guide to the eye.

Previous studies on the reactivity of CO report that CO forms distinct islands on Pt and that the periphery of these islands are the most reactive towards CO Oxidation¹⁴. However, this is not believed to be the dominant contribution to the sulfur enhancement effect. Previous studies indicate that CO and sulfur form mutually repelling domains and can form separate islands on the electrode surface¹⁴. In order to determine if CO oxidation was catalyzed by sulfur through electronic and or mechanistic means and not by island formation, iodide and bromide were deposited onto the surface of Pt electrodes. It is the hypothesis that if island formation were the dominant contribution to the observed sulfur enhancement then a similar enhancement would occur when halides are adsorbed on Pt forming discreet CO and X, where X is I or Br, domains. However, iodine was shown to block CO oxidation completely (results not shown). Iodine was deposited at 0.4 V for 60 seconds in fresh 1 mM KI / 0.1 M NaClO₄. As a supplement to the iodine island formation experiment adsorbed bromine was examined as well with similar results (also not shown). Bromine was deposited at 0.4 V for 60 seconds in 1 mM KBr/0.1 M NaClO₄ and again no enhancement was observed. However, it cannot be ruled out that halide adsorption could exceed the range of sub-monolayer coverages obtained with sulfur. This work needs to be reexamined since iodide is known to form full monolayer coverage of catalytically active surfaces^{21, 22}.

2.4 Conclusions

There are a range of methods to calculate sulfur coverage and X_S was determined to be the best fit for these experiments due to the fact that sulfur blocks equally as many CO molecules as hydrogen atoms. Results for sulfur coverage experiments need to be presented in current density format since Pt atoms blocked by sulfur are not considered catalytically active. Enhanced solution CO oxidation occurs when sulfur is present and the onset potential decreases with increasing sulfur coverage up to about X_S of 0.6 before leveling off. Irreversibly adsorbed CO oxidation is also shifted to more negative potentials in the presence of sulfur, however this only occurs at low sulfur coverages, X_S of 0.09. In agreement with previous studies methanol oxidation was also enhanced due to the presence of adsorbed sulfur. In fact, both an increase in current and current density as well as a decrease in onset potential were observed for the oxidation of methanol at low sulfur coverage, X_S of 0.1. Studies of the sulfur effect on various Ptgroup transition metals prove that the chemical nature of the electrode surface is a key component in the sulfur enhancement effect. Rh and Pt exhibit enhanced solution CO oxidation in the presence of sulfur whereas solution CO oxidation on Pd and Au is inhibited by the presence of sulfur.

The pH dependence of the sulfur effect lends support to the hypothesis that hydroxide may be a key component in the reaction mechanism for the observed sulfur enhancement. This does not agree with previous studies which showed that the sulfur effect's largest enhancements occur in acidic and basic solutions and are smallest in neutral solutions. Adsorbed halide experiments suggest that island formation is not the dominant force behind the enhancement effect.

Chapter 3. Chronoamperometry on Pt with Co-adsorbed Sulfur

3.1 Introduction

Chronoamperometry is an electrochemical technique where the potential is held at a fixed value where no faradaic processes occur and is stepped to a potential where faradaic processes occur and current is monitored. Often this is called a potential step experiment and current is recorded as a function of time. The selection of the initial potential, step potential, and time are the variables in a potential step experiment. When the potential is stepped to a potential where faradaic processes occur a depletion of the analyte near the electrode surface occurs and the diffusion current is the limiting current, assuming the solution is unstirred. The limiting current is inversely proportional to the square root of time, $t^{-1/2}$. The diffusion limited current can be described by the Cottrell equation (Equation 3.1) shown below which was solved for the case of semi-infinite linear diffusion.

$$i_d(t) = nAFC^*(D/\pi t)^{1/2}$$
 (Equation 3.1)

Where, $i_d(t)$ is the diffusion limited current as a function of time, n is the number of electrons in the balanced chemical reaction, A is the area of the electrode, D is the diffusion coefficient of the electroactive species, C^{*} is the bulk concentration of the electroactive species in solution, and t is time. Chronoamperometry can be used to determine electrode areas, diffusion constants, and to monitor the diffusion limited current. Chronoamperometric experiments are carried out in unstirred solution. Once the potential is stepped to potentials where faradaic currents occur, the faradaic currents are obscured by large charging currents at short times, due to the double layer charging. In order to reduce the signal of charging currents background i-t transients, i.e. i-t transients with no faradiac reactions can be subtracted from i-t transients with faradiac reactions occurring.

3.2 Experimental methods

See chapter 2 for the instruments used, type of cells and procedure for introducing solution CO and adsorbed CO into the solution. Single potential step experiments were conducted in 0.1 M HClO₄ for solution CO and adsorbed CO experiments, sulfur was introduced to the system by holding at -0.6 V for 60 seconds in 2 mM Na₂S/ 0.1 M NaClO₄ / 1 mM NaOH. The initial and final potential are given for each Figure.

3.3 Results

To reveal the mechanism behind the catalytic effect of the S_{ads} on the CO oxidation, chronoamperometry was also employed. The experiments were all conducted in a singlepotential step fashion with an initial potential at 0.0 V and various final potentials. Both the solution and the adsorbed CO oxidation were examined. Since the catalytic effect for solution CO oxidation is most prominent at high X_S, we focus the chronoamperometric studies in this X_S region for now. Previous studies of the electrooxdation of CO on polycrystalline Pt using chronoamperometry suggest that a Langmuir-Hinshelwood mechanism is required for the oxidation of CO^{14, 19, 20}. Chronoamperometry was used to determine if sulfur enhanced CO oxidation involves a Langmuir-Hinshelwood mechanism as well. Figure 3.1 shows a pair of current-time transient plots obtained on clean (dash traces) and S-modified (solid traces) Pt electrodes. The X_S was fixed at 0.82. The initial potential was 0.0 V and the final potential was 0.40 V for solution CO and 0.45 V for adsorbed CO oxidation. The corresponding i-t transient obtained in 0.1 M HClO₄ was used as the background and subtracted from each plot. For the solution CO oxidation, consistent with the cyclic voltammetric results, the steady state current on S-covered Pt is much higher than that on clean Pt electrode, as long as the final potential was kept below the take-off potential (around 0.6 V) of the CO oxidation on clean Pt. The i-t plot for the final potential in the range of 0.35 V to 0.6 V has a very similar shape. Close inspection of Figure 3.1 reveals that the oxidation current decays faster on the S-covered Pt at a shorter time (< 2 s), but at a longer time, the current decays more rapidly on the clean Pt (Figure 3.2). This transition of current decay rate also occurs at other final potentials that are below the peak potential of CO oxidation on the clean surface. The above observations indicate that CO oxidation is more facile on the S-modified surface, leading to a larger current at lower

overpotentials. It should be pointed out that the chronoamperometric results are plotted in the current-time format. Given that for S-modified Pt, part of the surface is covered by S_{ads} and CO oxidation does not occur on these sites, the difference between S-covered and clean Pt electrodes will be even larger if the results were plotted in terms of current density (with respect to the Pt area available for CO adsorption).

For adsorbed CO oxidation, the current-time transient plot for S-covered Pt is drastically different from that of the clean Pt surface. On the clean Pt surface, the transient shows a current plateau at shorter times (< ~4 s) and followed by a current peak at about 6 seconds. The length of the plateau and the position of the peak current strongly depend on the final potential. The higher the final potential, the shorter the plateau, and the shorter time the peak appears. The plateau was attributed to the relaxation of the compact CO adlayer as a result of the oxidation of small amount of CO_{ads}. The appearance of the current peak can be explained by the Langmuir-Hinshelwood reaction mechanism. The presence of S_{ads} changes the shape of the i-t plot significantly. Neither the plateau nor the peak remains. The current decays monotonically shortly after the potential step. This observation is similar to that obtained from CO_{ads} oxidation on Pt(111) surface with the CO coverage below 0.3, which is reasonable since at this sulfur coverage (X_S = 0.82), the θ_{CO} is below 0.2 (*vide supra*).



Figure 3.1 Solution CO chronoamperometry: single potential step current-time transient plots for solution CO oxidation on Pt electrode obtained in CO-saturated 0.1 M HClO₄. Initial potential: 0.0 V; final potential: 0.40 V, Solid trace: S-covered Pt with $X_S = 0.82$. Dash trace: clean Pt. The inset shows the current-time transient in normalized current and at shorter time scale to demonstrate the current decay rate.



Figure 3.2 Current-Time Transients for Adsorbed CO Oxidation. Single potential step current-time transient plots for adsorbed CO oxidation on Pt electrodes obtained in CO-saturated and N₂-purged 0.1 M HClO₄. Initial potential: 0.0 V; final potential: 0.45 V. Solid red trace: S-covered Pt with $X_S = 0.82$. Dashed blue trace: clean Pt.

The X_S dependent S_{ads} promotion and poison effects on Pt are also evident in the chronoamperometric plots. Figures 3.3 and 3.4 show a pair of chronoamperometric plots of methanol oxidation on clean (dash traces) and S-covered (solid traces) Pt electrodes plotted as current vs. time and the insets are plotted as current density vs. time. The inset in each panel shows the transient plot in current density which is again calculated using Pt areas available to H adsorption. All of the transient plots were obtained by a single potential step method, with an initial potential of 0 V and final potential of 0.55 V. The X_S for the S-covered surface is 0.76 (Figure 3.3) and 0.10 (Figure 3.4). From Figure 3.4, it is clear that at low X_S, the S_{ads} slows down the decay of methanol oxidation current over time. For example, the methanol oxidation drops down to one half of its maximum rate at 0.55 V within 10 seconds on the clean Pt, while it takes about 70 seconds on the sulfur-covered surface. The similarity of the chronoamperometric curves suggests, however, the reaction pathway on the two surfaces might be the same. Chronoamperometric curves recorded at other potentials within the methanol oxidation peak are qualitatively the same at the same X_S. Consistent with the cyclic voltammetric results, at relatively high X_S, the diffusion limited methanol oxidation current on S-covered Pt is much smaller than that on the clean surface. The higher the X_S, the difference in diffusion limited current is very large and can be explained by sulfur blocking the surface active sites. However, the current density decay on the two surfaces is about the same at short times (< 30 s for X_S = 0.76). At a longer time, the current density at the S-covered Pt is higher, even if the X_S is nearly 1, suggesting the Pt sites available for hydrogen adsorption are more active to the reaction at longer times.



Figure 3.3 Current-time transients for methanol oxidation. Chronoamperometric curves of methanol oxidation on Scovered (red solid traces) and clean (blue dotted traces) Pt at 0.55 V in 1.0 M MeOH + 0.1 M HClO₄. Sulfur coverage, $X_S = 0.76$. The inset shows the corresponding curves plotted in current density with respect to the available Pt sites.



Figure 3.4 Current-time transients for methanol oxidation at low sulfur coverage. Chronoamperometric curves of methanol oxidation on S-covered (red solid traces) and clean (blue dotted traces) Pt at 0.55 V in 1.0 M MeOH + 0.1 M HClO₄. Sulfur coverage, X_s =0.10. The inset shows the corresponding curves plotted in current density with respect to the available Pt sites.

3.4 Conclusions

From the chronoamperometry data shown above it can be determined that the sulfur effect on CO and methanol oxidation is very robust, enhancing CO and methanol oxidation for the entire duration the experiments. In agreement with the literature, sulfur at high X_S acts as a catalyst poison for methanol oxidation, however, high X_S catalyzes solution CO oxidation. The reaction of solution CO oxidation is more facile on sulfur covered Pt than on Pt alone as oxidation current evidenced by the higher in chronoamperometric experiments. Chronoamperometric experiments confirm the coverage dependence of the sulfur enhancement effect for solution CO and methanol oxidation as shown where low sulfur coverage on Pt exhibits a larger oxidation current than higher sulfur coverage on Pt. Comparison of chronamperometric results with previous studies suggest that a similar Langmuir-Hinshelwood mechanism to that proposed for solution CO oxidation on Pt exists possibly involving the same intermediates and rate determining steps, namely,the coadsorption of OH_{ads} and CO_{ads}. In order to further confirm this mechanism spectroscopic studies are needed. In agreement with cyclic voltammetric studies chronoamperometric experiments confirm that adsorbed CO is inhibited by sulfur at higher X_S. This suggests that two different types of CO are present on the surface of the electrode, strongly adsorbed CO and weakly adsorbed CO which is in agreement with the findings of Markovic et al.²³

Chapter 4. Surface-Enhanced Raman Spectroscopy on Pt, Rh, Pd, and Au

4.1 Introduction

Typically, when light is scattered from a molecule the result is elastic scattering, where the incident wavelength is the same as the scattered wavelength. However, roughly one in 10⁶ photons will undergo inelastic scattering where the scattered wavelength is different from the incident wavelength. This inelastic photon scattering is called the Raman effect and is the basis for Raman spectroscopy. The energy difference between Raman scattered photons and incident photons is equal to a vibrational energy level, thus Raman spectroscopy yields vibrational information about a molecule. This phenomenon can be explained quantum mechanically when an electron is momentarily excited to a virtual state, a quantum mechanically forbidden state energetically between electronic states. Once the electron relaxes to a vibrational level in the ground state other than the initial ground state a difference in wavelength of light emitted will occur. The difference in incident wavelength and Raman scattered wavelength is called the Raman shift and has units of cm⁻¹, called wavenumbers.

Two types of Raman scattering can occur, Stokes and anti-Stokes. If the initial vibrational state is the ground vibrational state and the final vibrational state is a vibrationally excited state, the Raman scattering is said to be Stokes scattered. If the initial state is above the ground vibrational state and the final state is below the initial vibrational state, the Raman scattering is said to be anti-Stokes scattered. Considering the Boltzmann distribution of electrons it can be seen that Stokes scattered radiation will be more intense than Anti-Stokes scattered radiation. Shown in Figure 4.1 is an energy level diagram of the Raman scattering process showing both Stokes and anti-Stokes scattered light. It is convention in Raman spectroscopy to only show the Stokes scattered radiation.



Figure 4.1. Energy level diagram of Raman scattering process. The solid black lines indicate electronic states, the short solid lines indicate vibrational states and the dotted lines indicate a virtual state.

Since roughly only one in 10^6 incident photons will undergo Raman scattering, Raman intensities are inherently weak, often several orders of magnitude weaker than infrared intensities. Raman active modes of a molecule are due to changes in the polarizability of the molecule. Thus, heteroatomic molecules containing atoms with lone pairs such as pyridine and molecules with distributed π -electron clouds, such as carbon-carbon double bonds are strong Raman scatterers.

Interest in Raman spectroscopy increased after the discovery of surface enhanced Raman scattering in the late 1970's²⁴. Surface enhanced Raman scattering occurs on roughened metal surfaces typically coinage metals, with surface features on the order of 10-200 nm. A large local electromagnetic enhancement effect occurs when the incident wavelength is close to the plasmon excitation wavelength of the metal surface. Since the polarizability of a molecule is a function of the external electric field, large enhancements in the external electric field will yield higher Raman intensities. Surface enhanced Raman spectroscopy (SER) excludes the use of well-defined single crystal surfaces and requires roughened coinage metals, so SER is limited to certain applications. Using techniques designed by Weaver et al.²⁵⁻³³ SER active transition metal electrodes can be prepared. Since the SER effect only occurs near the metal surface, SER is a valuable technique for studying surface chemistry, specifically adsorbed atoms and molecules.

Since potential is a key factor in methanol and CO electrooxidation, potential dependent analysis of intermediates and coadsorbates is important. Since SER active transition metal thin films can be deposited on electrode surfaces the combination of SER and potential control allows for the monitoring changes in surface chemistry with respect to potential. The ability to use SER in electrochemical environment combined with the ability to probe the metal-adsorbate stretching and interadsorbate stretching frequencies make SER an excellent technique to study the sulfur enhanced electrooxidation of CO and methanol.

Shown in Figure 4.2 is a SER electrode preparation schematic. Initially polycrystalline Au is not rough enough to obtain meaningful SER data so the Au electrode is roughened electrochemically. Once a suitable roughness is obtained the Au electrode is placed in a Cu solution and one monolayer of copper is adsorbed onto the Au electrode surface. Since Cu is deposited below the potential for bulk copper deposition, only one monolayer of copper will form on the electrode surface. Once the copper is deposited on Au the electrode is placed in either a Pt or Pd solution where Cu is displaced by Pt or Pd by redox replacement at open circuit potential. Rh was deposited on electrochemically roughened Au by constant current deposition.

SERS Electrode Surface Preparation Scheme



Figure 4.2 Schematic electrode preparation for SERS active thin film electrodes. Shown is a schematic involving only the surface of the electrode. Step 1 involves the electrochemical roughening of Au to prepare a SERS active substrate, this takes place in 0.1 M KCl and involves cycling the potential of the electrode from -0.3 V to 1.2 V for 15 minutes. Step 2 involves the Cu underpotential deposition of 1 monolayer of Cu on Au. For Pd and Pt electrodes, the redox replacement of Cu with either Pd or Pt is shown in step 3.

SER is dependent on the excitation frequency of the laser. The setup for SER used thesis consists of a 785nm Raman laser with an objective for collecting backscattered light while the potential of the electrode was held constant throughout the collection process, typically spectra were collected over 60 seconds, since some spectra were collected over shorter time frames all SER data will be reported as counts per second (cps) unless otherwise noted. Often surface enhanced Raman spectra are plagued with "hot spots" where the subtle differences in surface structure create anomalously large electromagnetic enhancements. These anomalously large electromagnetic enhancements can lead to SER spectra that are not representative of the majority of the surface species. To combat this problem all SER experiments were repeated several times and Raman signals were collected at several spots for each electrode to ensure uniformity. Shown in Figure 4.3 is a schematic of the experimental setup for Raman spectroscopy experiments. The same two compartment three electrode electrochemical cells were used for potential dependent SER studies.

4.2 Experimental methods

To obtain surface enhanced Raman effect on Pt, the overlayer method was used.³⁴⁻³⁷ Briefly, a Au electrode was polished successively with 1.0 and 0.3 μ m Al₂O₃ powder on a polishing cloth and roughened by electrochemical oxidation-reduction cycles in 0.1 M KCl to obtain SERS activity as described by Gao et al.²⁵ Platinum thin films were electrodeposited on the SERS active Au surface by the redox replacement approach.²⁷ To ensure the Au surface is entirely covered by Pt, 2 to 3 redox replacement cycles were employed.²⁷ Raman spectra were collected with a micro-Raman probe (SpectraCode, West Lafayette, IN) equipped with a SpectraPro 300i triple grating monochromator (Acton Research, Acton, MA) and a liquid nitrogen cooled red-intensified back illumination CCD detector (Princeton Instruments, Trenton, NJ). The laser excitation at 785 nm was from a diode laser (Process Instruments, Salt Lake City, UT) coupled to optical fiber bundles and focused onto the sample with a long working distance 20x microscope objective (NA 0.42) to a 100 μ m spot. The Raman scattering light was collected in a back-scattering fashion with the same objective. The laser power at the sample was around 5 mW. The Raman shift axis was calibrated with a neon light. Typical spectrum acquisition time was 30 sec.



Figure 4.3 Schematic of Surface Enhanced Raman setup. Shown is the same two compartment three electrode as seen in Chapter 2. The electrode potential was controlled throughout the collection process. A 785 nm Raman laser was setup perpendicular to the electrode and backscattered light was detected at 180° from the electrode surface.

Au electrodes were polished successively in 1.0, 0.3, and 0.05 micron alumina micropolish slurry (Buehler) and sonicated in milli-Q water for at least 10 minutes to remove any residual alumina particles. The electrode was placed in 0.1 M KCl, and cycled from -0.3 V-1.3 V for 15 cycles (15 minutes) under potentiostat control using a Potentiostat/Galvanostat Model 273A from EG&G Princeton Applied Research. All potentials are with respect to Ag/AgCl reference electrodes. The counter electrode was a flame annealed Au wire. The method for deposition of Pt thin film on electrochemically roughened gold electrodes involves the underpotential deposition of Cu on Au first and followed by redox replacement with Pt. Once the Au electrode was electrochemically roughened Cu was deposited in 1 mM CuSO₄ / 0.1 M H₂SO₄ for 2 minutes at 0.0 V (vs. Ag/AgCl). The electrode was rinsed and immediately placed in deaerated 5 mM K₂PtCl₄ / 0.1 M HClO₄ for 4 minutes at open circuit potential. Care was taken to ensure that the 5 mM K₂PtCl₄/ 0.1 M HClO₄ solution was stored in a dark environment as it is photosensitive. This deposits 1 monolayer of Pt on Au and can be repeated multiple times to place multiple layers of Pt on Au. Substituting 5 mM PdCl₂ / 0.1 M HClO₄ for 5 mM K₂PtCl₄ / 0.1 M HClO₄ in the previously mentioned preparation of Pt thin films can be used to prepare Pd thin film electrodes. The method of preparation for Rh thin films on electrochemically roughened Au was slightly different than the preparation of Pt and Pd thin film electrodes. Once the Au electrode was electrochemically roughened Rh was deposited by constant current deposition in deaerated 5 mM RhCl₃/ 0.1 M HClO₄. Using galvanostat mode on the Potentiostat/Galvanostat Model 273A from EG&G Princeton Applied Research the current was held at 5 µA for 30 seconds.

4.3 Results

While SER spectra were collected over the range of 100 cm⁻¹ to 3000 cm⁻¹ the region of the metal-adsorbate stretching frequency (150-850 cm⁻¹) and carbon-oxygen (C-O) stretching frequency (1700-2100 cm⁻¹) regions were emphasized. Shown in Figure 4.4 are potential dependent SERS spectra in the C-O stretching frequency. Two peaks, one at 1865 cm⁻¹ and the other at 2076 cm⁻¹ can be assigned to C-O stretching for CO at bridge and atop sites respectively. For solution CO on Pt at -0.2 V the peaks are at 1865 cm⁻¹ and 2076 cm⁻¹. Once sulfur is introduced to the electrode, middle (green) trace, there is only a small redshift in solution CO

peak position when sulfur, $X_S = 0.85$ is present. The SER spectra for adsorbed CO, top (brown) trace, shows that there is a slight redshift in peak position for adsorbed CO in the presence of sulfur, $X_S = 0.85$. It can also be seen that the introduction of sulfur reduces band intensity, which can likely be attributed to sulfur physically blocking the Pt sites. Also of interest is the fact that the band intensity for atop and bridging CO is reduced by an equal amount when sulfur is present, indicating that sulfur blocks atop and bridging sites equally.

Shown in Figure 4.4 are potential dependent SERS spectra collected at -0.2 V in 0.1 M perchloric acid electrolyte. The bottom (red) trace shows the Pt-carbon CO stretching bands at 488 cm⁻¹ and 398 cm⁻¹ which can be assigned to atop and bridging sites, respectively. Once sulfur is added, $X_S = 0.85$ a broad peak at 310 cm⁻¹ appears due to the M-S stretch (green trace) and the Pt metal–carbon stretching frequency redshifts to 472 cm⁻¹. The stretching frequency for adsorbed CO is also redshifted in the presence of sulfur, $X_S = 0.85$, second trace from the top (brown trace). The top (yellow) trace is a SER spectra collected with only sulfur and no CO present in the solution, confirming that the broad peak at 310 cm⁻¹ is due to adsorbed sulfur.



Figure 4.4 SERS of C-O stretching frequency on Pt thin film electrode. Shown are the C-O stretching frequencies for bridge bound and atop bound CO on Pt. The bottom (red) trace is solution CO on Pt in 0.1 M HClO₄. The middle (green) trace is solution CO stretching in the presences of sulfur, $X_S = 0.85$ and the top (brown) trace shows adsorbed CO stretching frequency in the presence of sulfur, $X_S = 0.85$



Figure 4.5 SERS of Metal-Carbon Stretching frequency on Pt thin film electrode in 0.1 M HClO₄. Bottom trace, solution CO on Pt, 2^{nd} trace from bottom (green) trace solution CO with $X_S = 0.85$. 2^{nd} trace from top (brown) CO_{ads} with $X_S = 0.85$. Top (yellow) trace $X_S = 0.85$ with no CO present in solution.



Figure 4.6 SER spectra of metal-carbon stretching CO coverage dependence. Solution CO in 0.1 M HClO₄. $\theta_{CO} = 0.17$ (brown), 0.21 (blue) and 0.37 (red and green).



Figure 4.7 SERS Spectra for Metal-Sulfur Stretching Region for Rh, Pd, Pt, Au. SER spectra collected at 0.0 V for various sulfur covered Rh, Pt, Pd and Au. The dashed line serves as a guide to the eye dividing the spectra into two groups, those with metal-sulfur stretching frequencies above 300 cm^{-1} and those below 300 cm^{-1} .

It can be reasonable to assume that a mixed adlayer of sulfur would reduce CO coverage, therefore reducing the dipole coupling of CO which could be observed as changes in wavenumber for CO stretching frequencies. Shown in Figure 4.6 are SER spectra of CO adsorbed on Pt as a function of CO coverage. $\theta_{CO} = 0.17$ (brown), 0.21 (blue) and 0.37 (red and green). Two SER spectra are shown for the case of $\theta_{CO} = 0.37$ since the peak shifts slightly in the same experiment, however it should be noted that this shift is small, 2 cm⁻¹. The spectra were recorded in 0.1 M HClO₄ at 0.0 V. Of particular importance is the fact that the metal-carbon stretch changes very little with changing CO coverage. It can be concluded then that the observed 16cm⁻¹ shift in CO stretching at high X_s is mainly due to the adsorption of sulfur at the electrode surface and not due to a decrease in dynamic dipole coupling due to lower CO coverage.

Figure 4.7 shows the metal-sulfur stretch for Pd, Pt, Au, and Rh. Both Rh-S and Pt-S stretching frequencies lie above 300 cm⁻¹ whereas, Pd and Au both exhibit metal-sulfur stretching frequencies below 300 cm⁻¹. The two regions of interest are the above 300 cm⁻¹ region and below 300 cm⁻¹ region. Based on previous SERS studies on sulfided Au electrodes this observed shift in frequencies can be assigned to different adsorbed sulfur species present on the electrode surface, namely adsorbed thiol, SH_{ads} and adsorbed atomic sulfur, S_{ads}³⁸. The metal-sulfur stretching frequencies below 300 cm⁻¹ seen on Pd and Au are assigned to the adsorbed thiol stretch. The metal-sulfur stretch above 300 cm⁻¹ seen on Rh and Pt was assigned to the atomic sulfur stretch. Comparing Figure 4.7 and Figure 4.4 it can be seen that Pd and Au show no sulfur enhancement effect toward CO oxidation whereas Rh and Pt do exhibit this effect. It is believed that the nature of the adsorbed sulfur species is responsible for this observation.

4.4 Conclusions

SERS results indicate that the metal-CO bond weakens in the presence of sulfur. CO dependent SERS studies indicate that this is not due to the decrease in CO coverage, but due to the electronic effect of sulfur binding to the metal surface, thus altering the metal d-band occupancy. The largest changes in CO binding due to sulfur adsorption occur in the metal-adsorbate stretching frequency region where the Pt-CO stretching frequency was redshifted more

than 10 cm⁻¹ in the presence of sulfur. A small redshift in the C-O stretching frequency was observed in the C-O stretching region. It can be seen that the metal-sulfur stretch varies depending on the nature of the metal surface and that the SERS data suggest that Au and Pd are covered with an adsorbed thiol, whereas Pt and Rh are covered with atomic sulfur. These findings agree with previously reported electrochemistry experiments, see Chapters 2 and 3.
Chapter 5. Discussion and Conclusions

5.1 Discussion

The ultimate goal of the present research is to understand the catalytic effects of S_{ads} on the electrooxidation of carbon monoxide and methanol. We start with CO oxidation. The electrooxidation of CO on Pt has been extensively studied both theoretically and experimentally. It is generally accepted that the reaction proceeds through a Langmuir-Hinshelwood mechanism, which can be represented by the following reaction steps in an acidic medium:^{39, 40}

$$H_2O \leftrightarrow OH_{ads} + H^+ + e^-$$
(3)

$$CO_{ads} + OH_{ads} \rightarrow COOH_{ads}$$
 (4)

$$COOH_{ads} \rightarrow CO_2 + H^+ + e^-$$
(5)

The second step is generally considered as the rate determining process. The reaction rate is therefore proportional to both the CO and OH coverages. Depending on whether the CO_{ads} and OH_{ads} form a well mixed adlayer, there are two extreme cases – mean field approximation model and nucleation-and-growth kinetics.³⁹⁻⁴³ If the CO_{ads} and OH_{ads} form a well mixed layer or the diffusion of the CO_{ads} or OH_{ads} on the surface is faster than reaction (4), the reaction kinetics can well be described by the mean-field approximation. If the CO_{ads} diffusion is slow, the nucleation-and-growth approach is a better description. Through a series of studies on Pt(111) and its vicinity step surfaces, Lebedeva et al. concluded that CO_{ads} diffusion on Pt surfaces is fast, and the mean-field approximation is a better model for the system.^{39, 41, 42}

In the present case, the addition of sulfur on the Pt surface has several significant effects on the CO adsorption. From photoemission spectroscopic experiments and ab initio selfconsistent field calculations, it is found that S_{ads} decreases Pt 5d orbital occupancy significantly.⁴⁴ This will increase the CO 5 σ to Pt d donation and lower the extent of the metal d to CO 2 π * back donation, which affects the Pt-CO bonding.^{45, 46} More importantly, the repulsive interaction between CO and S weakens the CO-Pt bonding. In agreement with these, in ultra high vacuum environment, the thermal desorption spectroscopic (TDS) studies indeed show that CO desorbs at lower temperatures on S-covered Pt as compared to the clean surface.^{8, 47-50} The binding energy of CO adsorption on terminal sites was lowered by more than 30 kJ/mol.⁴⁸ In the present study, the SER spectra show that the coadsorbed S redshifts the Pt-CO stretching frequency by more than 15 cm⁻¹. The change of the Pt-CO stretching frequency, rather than the C-O stretching, is a direct indication of Pt-CO bonding change, as shown by density functional theory calculation.^{45, 46} The redshift of the Pt-CO stretching frequency therefore indicates the weakening of the Pt-CO bond. The weaker CO-Pt bonding facilitates the CO oxidation.

The results show that the S_{ads} enhancement for solution CO is very different from that for CO_{ads}. The SER spectra show that after removal of CO from solution, the intensity of vibrational bands from CO_{ads} decreases, which implies the loss of CO_{ads}. Weakly adsorbed CO is likely to be oxidized at more negative potentials. In other words, there are sites that are more active toward CO oxidation on the surface and these sites are created by the presence of S_{ads}. It is envisioned that the location of these more active sites is likely to be near the S_{ads}. The coadsorption of S and CO has been shown by using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) in the UHV to form segregated CO and S islands on Pt(111) due to the repulsive interaction between the two adsorbates.⁵¹⁻⁵⁴ At the boundary of the S islands, CO adsorption is likely to be weaker and these surface sites are likely to be responsible for the observed low overpotential of solution CO oxidation. In the presence of CO in solution, there is a continuous supply of CO to the more active sites. When solution CO is removed, weakly adsorbed CO desorbs, leaving the more active sites free of COads. The COads remaining on the surface perhaps do not diffuse to these more active sites or the diffusion is very slow due to the repulsion of the CO_{ads} and S_{ads} . Consistent with this picture, it has been shown in UHV that a trace amount (0.01 ML) of S_{ads} strongly suppresses the CO diffusion on Ni(110).⁵⁵

The observed v_{Pt-CO} blueshift on S-covered Pt upon removal of solution CO supports the notion that desorption of weakly adsorbed CO does occur, leaving behind more strongly bound

CO. Compared with the S-free surface, the v_{Pt-CO} obtained either with or without CO in solution is lower on the S-covered Pt with intermediate or lower X_S, suggesting that in addition to the weakening of the Pt-CO bond at sites next to the S_{ads}, on which the CO_{ads} desorb after the removal of the solution CO, S_{ads} reduces the overall Pt-CO bond strength. This observation suggests that S_{ads} has both short and long range effects on the Pt-CO bond. Although it is not clear why at the higher sulfur coverage (X_S = 0.85), the blueshift of v_{Pt-CO} is small after CO removal, it is possible that the strong redshift by the presence of S_{ads} overcompensates the blueshift.

The weakening of the Pt-CO bond is not sufficient to explain the observed results. From the photoemission spectroscopic experiments and ab initio calculations, it has also been shown that S_{ads} reduces the d band occupancy of Au and Pd.^{56, 57} In addition, CO adsorption on Pd is weakened by S_{ads}, as suggested by the TDS results.⁵⁸ However, the cyclic voltammetric results show that S_{ads} blocks solution CO oxidation on these metals. X-ray photoelectron spectroscopic studies revealed that the presence of Sads on Fe surfaces promotes the formation of surface hydroxide and suppresses the surface oxide formation.⁵⁹ It is possible that S_{ads} on Pt has a similar effect. The pH dependence of the onset potential difference (ΔE) for solution CO oxidation seems to support this hypothesis. At low pH, the presence of S_{ads} significantly reduces the overpotential for the formation of OH_{ads}, hence decreases CO oxidation potential. At higher pH, the OH_{ads} is readily available from the adsorption of OH⁻ and the S_{ads} effect on the OH_{ads} formation is much less significant, the CO oxidation is therefore less promoted by the presence of Sads. Sads may also facilitate the formation of OHads and inhibit formation of oxide on Rh, which also shows the S_{ads} catalytic effect. These effects may be absent on Pd and Au, which are more noble than Pt and Rh. Although more work is required to understand the metal dependence of the sulfur effect, it seems clear that both the promotion of OH_{ads} and the weakening of the Pt-CO bond play an important role in the enhancement of the CO oxidation by S_{ads}.

For the oxidation of irreversibly adsorbed CO, the presence of a small amount of S_{ads} (X_S < 0.3, roughly equivalent to $\theta_S = 0.1$) decreases the peak potential. However, if the X_S is higher, the peak potential is more positive. This may be understood in terms of the CO adlayer structure change with the presence of S_{ads} and the S_{ads} distribution. At low X_S, S_{ads} decorates in the CO

adlayer and forms an intermixed adlayer. The CO_{ads} does not need to travel a long distance to react with OH_{ads} and the diffusion of CO_{ads} is not significantly inhibited by S_{ads} as compared to when S_{ads} form islands at higher X_S ; therefore, the reaction is facile. At higher X_S , S_{ads} and CO_{ads} may form segregate islands, the CO_{ads} diffusion is significantly slowed down and the reaction is therefore retarded. However, in either case, energetically the CO adlayer is more reactive than the clean surface because the coadsorption of sulfur weakens the Pt-CO bond, but kinetically the CO surface diffusion rate determines where the current peak appears. This picture is consistent with the STM and LEED results from the UHV, which show the formation of segregate CO and S islands on Pt(111).⁵¹⁻⁵⁴

It has been reported that the presence of acetonitrile (< 0.01 M) in the electrolyte also promotes solution CO oxidation, but strongly inhibited adsorbed CO oxidation.⁶⁰ This observation was explained partly by the so-called "third-body" effect, in which the adsorbed acetonitrile blocks the surface sites that are less active for CO oxidation, leaving behind the more active sites.⁶⁰ While the "third body" effect can explain the weakening of the Pt-CO bond in the present case, it cannot account for the enhancement of CO oxidation. Had the more active sites been on the surface before S adsorption, solution CO oxidation current would be observable at low overpotentials on S-free Pt. In addition, adsorbed halides, which would have a third body effect similar to that of S_{ads}, inhibit solution CO oxidation, strongly against the third body effect being the main mechanism for the enhancement of solution CO oxidation by S_{ads}.⁶¹

Based on the SERS data, pH dependence of CO oxidation, and chronoamperometric results a mechanism of the oxidation of CO in the presence of co-adsorbed sulfur is proposed. Chronamperometric data suggest that the presence of adsorbed hydroxide is involved in the rate limiting step, showing in the mechanism below as step 2. SERS results indicate a surface species of sulfur vary depending on the metal and that the enhanced CO and methanol oxidation on Pt and Rh are metal dependent. While sulfur has been shown to alter the electronic state of the metal surface it is only believed to be part of the overall enhancement effect. The mechanism shown below is the proposed mechanism for sulfur enhanced CO oxidation.

$$Pt-S_{ads} + H_2O \rightarrow Pt-SH_{ads} + Pt-OH_{ads}$$
(1)

$$Pt-OH_{ads} + Pt-CO_{ads} \rightarrow CO_2 + H^+ + e^-$$
(2)

$$Pt-SH_{ads} \rightarrow Pt-S_{ads} + H^+ + e^-$$
(3)

.It should be noted that the same mechanism applies to Rh, however, Pd and Au are believed to have adsorbed thiol initially and thus step 1 does not occur on Pd and Au. The electronegativity of chemisorbed sulfur changes the electronic nature of the surface to reduce back donation from the Pt d-orbital to the CO π^* antibonding molecular orbital. However, it is not believed that this is the dominant effect, partly due to the fact that adsorbed anions, Cl⁻ and l⁻, which both have higher electronegativity than sulfur have not been shown to promote CO or methanol oxidation. Although it cannot be ruled out that the high coverage of Cl⁻ and l⁻ may sterically inhibit active sites. If electronic modification of the surface were the only cause of the sulfur enhancement effect the enhancement of CO oxidation would be equal at all pH values and clearly there is a pH dependence to the sulfur catalyzed electro-oxidation of CO. Since both CO and S_{ads} are mutually repelling adsorbates it might be logical to think about the fact that separate domains form and that the outer edges of these domains could be the most active toward CO electro-oxidation. SERS data indicates that two different types of adsorbed CO exists, strongly adsorbed CO as seen in adsorbed CO experiments and weakly adsorbed CO that is only present in CO saturated solution which is in agreement with the findings of Markovic et al.²³ It has been shown that CO binds preferentially at atop sites at low CO coverages typically below 0.30. CO is then equally distributed between atop sites and 2 fold bridging sites at higher CO coverages typically 0.50 and higher⁶². The SERS spectra for adsorbed CO stretching frequency change is much less than the stretching frequency change for solution CO. This is due to the fact that there are weakly bound CO molecules near the sulfur domains that are catalytically more active. When only adsorbed CO is on the surface these more active sites are unoccupied. This is supported electrochemically with the cyclic voltammetry data that shows the sulfur enhancement effect to be more prominent for solution CO that it is for adsorbed CO.

Methanol oxidation was studied by cyclic voltammetry. Cyclic voltammetric results show that at X_S smaller than about 0.3, the oxidation current is significantly larger on the S-modified Pt than that on the clean surface. Increasing the amount of sulfur to $X_S > 0.3$ on the surface reduces the oxidation current significantly. However, if the current is expressed in terms of per Pt site available for CO or H adsorption (presumably for the methanol adsorption too), the current density is larger than that on S-free surface, suggesting that the S_{ads}, in the coverage range of $X_S < 0.75$, catalyzes methanol oxidation. This enhanced activity likely arises from the increased reactivity of Pt toward COads oxidation when modified with Sads. Methanol oxidation involves dissociation of three C-H bonds before formation of CO.^{1, 17, 63, 64} The initial step of the reaction requires at least three Pt surface sites.⁶⁴ If the sulfur coverage is so high that the decrease of current caused by the lost of surface sites cannot be compensated by the increase of current arising from the more facile removal of the surface poisoning reaction intermediate, CO, the absolute current will be lower than the clean surface. This is similar to the methanol oxidation on Ru modified Pt at which the optimal Ru coverage (θ_{Ru}) is 0.1 to 0.2.⁶⁵⁻⁶⁷ As suggested by the higher current density on S-modified Pt, the surface sites available for methanol oxidation are still more active in removing CO. For $X_S > 0.75$, both the current and the current density are lower than the clean Pt, presumably because the available sites on S-modified Pt are less active for methanol dissociation or because of the ensemble effect.⁶⁴ The higher current density observed at the longer time (> 30 s) in the transient plot for $X_S > 0$. 75 can be understood in terms of the loss of active sites on clean Pt due to the formation of surface oxides which is largely inhibited on the S-covered surface at the potential examined.

An alternative explanation for the enhanced methanol oxidation could be the third body effect, in which the S_{ads} blocks certain sites and changes the reaction pathway so that the formation of CO_{ads} is inhibited.^{64, 68} While this possibility cannot be ruled out based on our observations, the S coverage dependence of the methanol oxidation current favors the argument of the enhanced CO oxidation.⁶⁴ In addition, surface-enhanced Raman spectra show that CO_{ads} is still formed on the S-modified Pt surface when it is in contact with methanol, indicating at least the formation of CO is not completely shut down.

5.2 Conclusions

Sulfur adlayer on Pt up to a coverage of about 0.33 can be obtained by holding the electrode potential at -0.6 V in dilute Na₂S solutions. The obtained S adlayer is stable in the potential range from -0.25 V to +0.8 V in 0.1 M HClO₄. The effect of S_{ads} on the carbon monoxide and methanol electrooxidation was examined. By using cyclic voltammetry and chronoamperometry, we have demonstrated that Pt electrodes modified with a small amount of sulfur can significantly increase the surface reactivity toward CO and methanol oxidation. For solution CO oxidation, the onset potential of the reaction shifts to the negative direction for more than 300 mV, and the extent of the potential shift increases with the sulfur coverage up to about 0.3. Similar CO oxidation potential shift was observed on Rh, but not on Pd or Au. For adsorbed CO, at low sulfur coverage ($X_S < 0.3$), the oxidation peak potential is about 40 mV negative to that of the corresponding clean Pt. However, at higher coverages, the peak potential is about 30 mV more positive. For methanol oxidation, the current is enhanced by nearly a factor of two when the Pt surface is modified with small amount of sulfur ($X_S < 0.3$), and suppressed significantly when the S_{ads} coverage is significantly higher ($X_S > 0.75$). The peak potential does not change much by the small amount of Sads. Based on surface-enhanced Raman spectra it is believed that the adsorption of sulfur weakens the overall Pt-CO bond, which is a long range effect. In addition, the Pt-CO bonding strength for CO_{ads} near the S_{ads} is reduced to an even larger extent; the adsorption becomes reversible - the CO_{ads} desorb after the removal of dissolved CO from the solution. This is probably a short range effect. The enhanced reactivity of the S-modified Pt toward CO and methanol oxidation is a result of several interplaying effects exerted by Sads. On one hand, the repulsive electrostatic interaction between CO and S, as well as the decrease of Pt d band occupancy by Sads, weakens the Pt-CO bond. On the other hand, Sads promotes the formation of OH_{ads} which is the oxidant for CO oxidation. As a result of enhanced CO oxidation, methanol oxidation was also enhanced with the presence of a small amount of sulfur. However, when the sulfur coverage is high, the surface site blocking effect is more significant than the catalytic effect, rendering a smaller oxidation current. A mechanism was proposed for the sulfur-enhanced electrooxidation of CO based on SERS, chronoamperometry and cyclic voltammetry. It is believed that sulfur aids in the removal of CO which explains the observed enhanced methanol oxidation.

5.3 Future work

Preliminary results suggest that the effect of sulfur on CO oxidation is very interesting on transition metals other than Pt. Shown below in Figure 5.1 are anodic segments from a cyclic voltammogram of solution CO oxidation on Pd thin film electrodes. It is interesting to note what appears to be a slight enhancement due to the presence of both low and high sulfur coverage, however, many more experiments are required to confirm this observation. Probing the metal-adsorbate stretching region it can be seen Figure 5.2, the corresponding SER data for the same electrodes shown in Figure 5.1, that the Pd-CO stretching frequency on clean Pd is at 374 cm⁻¹ and no shift in this frequency was observed in the presence of sulfur.⁶⁹ Since there is no observable redshift in Pd-CO stretching frequency it is doubtful that there is any substantial enhancement effect due to sulfur on Pd.

The case of sulfur enhancement on Rh is more interesting. Shown in Figure 5.2 are SER spectra for Rh and Rh with high and low sulfur coverage. The Rh-CO peak at 459 cm⁻¹ redshifts from 7 cm⁻¹ to 452 cm⁻¹ in the presence of sulfur, however, this redshift is only observed at high sulfur coverage⁷⁰. At low sulfur coverage, no shift in Rh-CO peak position was observed. The broad feature at 350 cm⁻¹ is assigned to the Rh-S stretching frequency. Further experiments are needed to confirm these observations and attention should be focused on both the metal-adsorbate and interadsorbate stretching frequencies. It is the author's opinion that the sulfur enhancement effect be researched more thoroughly for transition metals other than Pt. The cause of the metal dependence of this effect is unknown.



Figure 5.1 Anodic segments of solution CO oxidation on Pd thin film electrode. The blue dashed trace is clean Pt, solid green trace is with low sulfur coverage and the red dotted trace is with high sulfur coverage. The arrows indicate direction of the scan.



Figure 5.2 Potential dependent SER spectra of solution CO stretching on Pd with and without sulfur. Both blue and light blue traces are solution CO on Pd thin film electrode, as visible Pd-CO stretch is visible at 374 cm⁻¹ as well as a shoulder at 339 cm⁻¹. CO stretching on Pd with high sulfur coverage green trace shows a shoulder at 335 cm⁻¹ and a peak at 302 cm⁻¹. CO stretching on low Pd with low sulfur coverage is shown in red, shows peaks at 309 cm⁻¹, 335 cm⁻¹ and a shoulder at 370 cm⁻¹.



Figure 5.3 Potential dependent SER spectra for solution CO on Rh. All spectra were collected at 0 V. Shown in blue is solution CO on Rh, Rh-CO stretching is at 459 cm⁻¹ and a shoulder at 530 cm⁻¹. Shown in green is solution CO on Rh with high sulfur coverage, there is a Rh-CO stretch at 452 cm⁻¹ and a broad Rh-S peak centered at 350 cm⁻¹. Shown in red is solution CO on Rh with low sulfur coverage, peaks are 307 cm⁻¹ (unassigned but visible in all Rh SER spectra), Rh-CO stretch at 460 cm⁻¹ and Rh-O stretch at 531 cm⁻¹ are visible.



Figure 5.4 Anodic segments of cyclic voltammograms of solution CO oxidation on Rh thin film electrode in 0.1 M HClO_4 and 100 mVs^{-1} scan rate. Shown in blue dashed trace is solution CO oxidation on clean Rh. The solid green trace is solution CO oxidation on Rh with high sulfur coverage. The red dotted trace shows solution CO oxidation on Rh with low sulfur coverage.

Although the use of polycrystalline Pt in the present study hinders a more quantitative analysis of the adsorbed S effects on the reactions, a qualitative understanding of the S_{ads} catalytic effect is nonetheless achieved. It remains to examine how the catalytic effect depends on the surface crystal orientation. Due to the dependence of CO poisoning as the nature of the surface it is suggested that single crystal surfaces be examined to give more insight into the mechanism of sulfur enhanced electro-oxidation of CO and methanol. Previous work has shown that Pt(111) and Pt(110) behave very differently toward CO poisoning and it is believed that sulfur enhanced electro-oxidation will be surface sensitive. Thus, it is the author's opinion that further studies of sulfur enhanced electro-oxidation on single crystal surfaces should take place. These studies will not only shed light on the mechanism of the catalytic effect of Sads on the CO and methanol oxidation, but will also advance our understanding of the two important reactions in methanol fuel cell development. Due to the nature of the single crystal electrode surface no enhancement of Raman scattering will occur, thus SER spectroscopy cannot be used to examine the nature of the adsorbed species. In addition to the further investigation of sulfur-enhanced electro-oxidation on single crystal electrodes the study of the sulfur effect on microelectrode arrays with controlled particle size and spacing should be examined as well. It is unlikely that DMFC's will find any real-world applications if the cost remains high due to the requirement of expensive noble metal catalysts. It is logical to then try to reduce platinum loading by a reduction in the platinum particle size. Controlled spacing would allow for the maximum amount of catalyst particles using a minimum amount of noble metal. Results from different metal surfaces suggest that the catalytic effect is metal dependent, which is yet to be understood and could also yield some interesting results.

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