HYDROGEN SULFIDE KINETICS ON PEM FUEL CELL ELECTRODES

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A concise mechanism for the poisoning kinetics of hydrogen sulfide (H$_2$S) on composite solid polymer electrolyte Pt (SPE-Pt) electrode is presented. The simplified version of the mechanism is validated experimentally by charge balances and theoretically by a model, which predicts the oxidation current as a function of the applied potential. H$_2$S dissociatively adsorbs onto SPE-Pt electrode as linear and bridge bonded sulfur (S) species and, under favorable potentials, undergoes electro-oxidation to sulfur and then to sulfur dioxide (SO$_2$). A fraction of the adsorbed S species remains as ‘hard-to-oxidize’ adsorbents and causes irreversible loss of catalytic activity. Deactivation of bridge sites occurs first followed by the loss of linear sites.

INTRODUCTION

Though extensive research had been done on the issue of CO poisoning in polymer electrolyte membrane (PEM) fuel cells, there is much less in the literature on H$_2$S poisoning. Uribe et al showed that the poisoning effect due to H$_2$S is cumulative and irreversible (1). According to them, after H$_2$S poisoning, total recovery with neat hydrogen was not possible and a partial recovery was possible by a potential scan between 0 and 1.4 V vs. dynamic hydrogen electrode (DHE). Mohtadi et al found that the degree of recovery of a PEM fuel cell anode poisoned by H$_2$S depended on the degree of oxidation of two surface species observed in the cyclic voltammogram (2). Further they reported that the increase in Pt loading increased the partial recovery both with neat hydrogen and by a potential scan. Loučka, the first to study the kinetics of H$_2$S adsorption and oxidation on single crystal platinum electrodes in aqueous phase at 25 ºC, found that H$_2$S became completely dehydrogenated on adsorption and that the hydrogen thus formed became anodically oxidized at positive electrode potentials (3). Also, the charges for oxidation of adsorbed sulfur were too high to account for the oxidation of a mere monolayer of adsorbed sulfur. This was explained by the formation of a poorly reducible oxide on the electrode and not due to the presence of multiple layers of adsorbed sulfur atoms. Further, according to Loučka, complete removal by oxidation of adsorbed sulfur could not be attained by holding the poisoned Pt electrode at 1.6 V vs. DHE unless the degree of S coverage on the electrode was very low. Complete oxidation was reached only by periodic polarization to such positive potentials. Loučka proposed the following mechanism,

$$Pt - S + 3H_2O \rightleftharpoons SO_3 + 6H^+ + 6e^- + Pt$$

[1]
Najdekar et al attributed the formation of the poorly reducible oxide to the sulfidation of Pt electrode (4). They attributed the large oxidation peak in the 1.25-1.42V potential window to the oxidation of platinum. They compared the oxidation and the reduction charges of each cycle of the cyclic voltammogram and postulated that platinum oxide reacted with sulfur released at the electrode surface with the regeneration of sulfide. Using potentiodynamic oxidation at elevated temperatures (i.e. >60 °C), Contractor et al demonstrated the presence of two forms of chemisorbed sulfur distinguished by the number of platinum sites occupied per sulfur atom (5). Based on electrons per site (e.p.s.) calculations, they attributed the first peak to the oxidation of linear-bonded sulfur and the second peak to the oxidation of bridge-bonded sulfur. Pitara et al also confirmed this presence of two forms of chemisorbed sulfur (6). They reported that the adsorption of sulfur was sensitive to the nature of the platinum surface. While, one sulfur atom covered one Pt atom when H₂S was adsorbed on a smooth Pt atom in zero valence state, the charge of the adsorbed sulfur depended on the degree of its coverage on a rough platinum surface, ranging between 1.5 and 2 at low coverage to 1 at higher coverage. In another study, they showed that the sulfur species adsorbed on the surface of the platinum were likely to be composed of sulfur and sulfides (7).

Farooque et al studied the oxidation of H₂S on a rotating tripolar wiper-blade electrode in the low potential region [0-0.45V vs. SHE, (8)] and in the tafel region [0.45-1.4V vs. SHE, (9)] and reported that at lower oxidation potentials, the anodic oxidation of H₂S followed a two-electron process to yield elemental sulfur, protons and electrons. Using likelihood approach, a statistical tool to validate the most likely model from a set of contending models, they were able to prove that the low potential oxidation of H₂S most likely followed the mechanism given below,

\[ \text{Pt} - S + 4H_2O \leftrightarrow SO_4^{2-} + 8H^+ + 6e^- + \text{Pt} \]  \[\text{[2]}\]

The chemical reactions 3 and 4 were faster than the electrochemical reactions 5 and 6. This confirmed the two-electron oxidation mechanism put forward by Loucka. Also, they reported that the oxidation of H₂S at higher potentials yielded colloidal sulfur. In their experiment, the wiper-blade electrode system continuously cleaned the surface by piperidine (a selective solvent for sulfur) to remove the colloidal sulfur formed. Since the electrode was always clean for further H₂S adsorption and oxidation, sulfur was the main product both in the lower and at the higher oxidation potentials.

H₂S poisoning studies have also been done for a variety of fuel cell systems. Uribe et al and Mohtadi et al studied the H₂S poisoning effects in a PEM fuel cell system. Chin et al investigated the poisoning effect of H₂S on the anodic oxidation of hydrogen on Pt in a 94 wt% phosphoric acid electrolyte fuel cell over a temperature range of 25 – 170 °C (10). They reported that the extent of H₂S poisoning decreased with increasing temperature and increased with increasing electrode potential. Further, at sufficiently high anodic potentials, a layer of adsorbed elemental sulfur was found to form on the
electrode surface, which suppressed the formation of platinum oxide at the oxygen adsorption potentials. According to Kawase et al, who studied the effect of H₂S on molten carbonate fuel cells, large voltage losses occurred after the cell was exposed to 5 ppm H₂S (11). They attributed this to the formation of SO₄²⁻ and S²⁻ on the nickel electrode.

Paál et al investigated gas phase H₂S adsorption on platinum in the presence of H₂ (12). They were able to identify the presence of sulfide and sulfate species on the poisoned surface using XPS. Also, studies by Mathieu et al on gas phase chemisorption of H₂S on Pt showed that H₂S adsorbed dissociatively on Pt and the dissociation lead to adsorbed sulfur and gaseous hydrogen (13). While investigating the effects of sulfur poisoning on platinum supported on alumina, Chang et al found that the adsorbed sulfur induced Pt agglomeration by weakening the metal-support interaction and caused migration of Pt clusters in the process (14). Their observation was based on the size of Pt clusters measured before and after H₂S exposure (15).

Donini et al described an electrochemical process for decomposing H₂S to produce hydrogen and sulfur (16). They used a divided electrolytic cell and a mixture of H₂S and volatile basic solution as the electrolyte to produce a polysulfide solution at the anode compartment. The polysulfide solution was then distilled to produce elemental sulfur. They later extended this invention to produce sulfur directly in a gas phase electrolysis process, where H₂S is oxidized at high potentials in a composite solid polymer electrolyte (CSPE)-Pt anode at elevated temperatures [>120 ºC, (17)].

More recently, Wang et al developed an amperometric H₂S sensor based on its electrochemical oxidation route on a CSPE-Pt electrode (18). They found that the electro-oxidation products of H₂S depended on the local electrode potential at the time of adsorption. Using XPS, they found that the main oxidation product was elemental sulfur at lower potentials and SO₄²⁻ at higher oxidation potentials. They reported that even at higher potentials, the elemental sulfur was difficult to remove from the surface of the electrode. This finding agrees with that of Loucka, Najdekar et al and Contractor et al. Further, they tested the durability of their H₂S sensor and reported that the deposition of elemental sulfur on the CSPE-Pt electrode was the main factor affecting the life of the sensor (19). However, they reported that the tolerance levels of a CSPE-Pt electrode were significantly better than that of planar Pt electrodes and they attributed this to the highly porous nature of the former and hence to the increased surface area.

Following conclusions could be derived based on the above observations in the literature on the kinetics of H₂S adsorption and oxidation, both in liquid phase [planar (3-9) and CSPE-Pt (16) electrodes] and in gas phase [planar (10-16) and CSPE-Pt (1, 2, 17-19) electrodes],

a. H₂S adsorption on Pt is dissociative producing elemental sulfur and hydrogen. The hydrogen thus formed undergoes oxidation at positive electrode potentials.

b. The sulfur thus formed strongly adsorbs to Pt. The adsorption results in linear-bonded sulfur species, Pt-S, and bridge-bonded sulfur species, (Pt)₂-S. The nature of adsorption is a strong function of temperature.

c. The Pt-S or (Pt)₂-S thus formed undergoes further oxidation at high electrode-potentials to yield SO₂, SO₃ or SO₄²⁻.

d. It takes several potential scans to completely clean the surface off of H₂S, S and their oxidation products.

e. In the process of H₂S and S adsorption and oxidation, a small percentage of the active catalyst sites are irreversibly lost due to the formation of an adsorbate that is difficult to oxidize or an oxide that is difficult to reduce.
f. Some of the explanations for the irreversible loss due to H₂S poisoning include sulfur induced Pt agglomeration, formation of platinum sulfides and oxides that are difficult to reduce and the migration of Pt clusters due to loss in the metal-support interaction.

Based on the above observations, a comprehensive list of reactions H₂S, as linear and bridge bonded species, can undergo on a CSPE-Pt electrode,

\[
Pt + H_2S \leftrightarrow Pt - H_2S_{ads} \quad [7]
\]

\[
Pt - H_2S_{ads} \leftrightarrow Pt - SH_{ads} + H^+ + e^- \quad [8]
\]

\[
Pt - SH_{ads} \leftrightarrow Pt - S_{ads} + H^+ + e^- \quad [9]
\]

\[
Pt - S_{ads} + 2H_2O \leftrightarrow SO_2 + 4H^+4e^- + Pt \quad [10]
\]

\[
2Pt + H_2S \leftrightarrow (Pt)_2 - H_2S_{ads} \quad [11]
\]

\[
2Pt - H_2S_{ads} \leftrightarrow (Pt)_2 - SH_{ads} + H^+ + e^- \quad [12]
\]

\[
2Pt - SH_{ads} \leftrightarrow (Pt)_2 - S_{ads} + H^+ + e^- \quad [13]
\]

\[
2Pt - S_{ads} + 2H_2O \leftrightarrow SO_2 + 4H^+4e^- + (Pt)_2 \quad [14]
\]

Where reactions 7 and 11 represent adsorption and desorption of H₂S on Pt surface, and reactions 8, 9, 12 and 13 represent the oxidation of the adsorbed H₂S resulting in sulfur adsorption. Reactions 10 and 14 represent the oxidation of adsorbed sulfur to SO₂. One of the main objectives of this article was to probe the multiple peaks obtained during the CV for the distribution of linear and bridge bonded S on the CSPE-Pt surface. Further charge balances are made to quantify the exact amount to different species formed during the electro-oxidation of H₂S adsorbed on the surface of the CSPE-Pt electrode.

**EXPERIMENTAL**

**Fuel Cell**

Pt catalyst ink with 75 wt% catalyst and 25 wt% Nafion® (dry solids content) was prepared with commercially available 40.2 wt% Pt on Vulcan XC-72 catalyst (E-TEK De Nora North America, NJ) and Perfluorosulfonic acid-PTFE copolymer (5% w/v, Alfa Aesar, MA). Isopropyl alcohol (99% v/v, VWR Scientific Products) was used as the thinning solvent. The ink was mixed properly for at least 8 hours. ELAT® electrodes (E-TEK De Nora North America, NJ) coated with a hydrophobic mixture of carbon and Teflon® on one side were used as gas diffusion layers (GDL). The GDLs were cut into 10 cm² pieces. Catalyst ink was then sprayed onto the GDLs, air dried for ½ hour and then dried at 110 °C for 10 minutes in vacuum to evaporate any remaining solvent. The process was repeated until the target loading (0.5 mg/cm²) was achieved. The active area of the electrodes was 10 cm². Both the anode and the cathode side had a loading of 0.5 mg/cm² of Pt. The catalyzed GDLs were then bonded to a pretreated Nafion® 112 membrane by hot pressing at 140 °C for two minutes at 500 psig to make a membrane electrode assembly (MEA). The MEA was assembled into a fuel cell with single channel serpentine flow field plates bought from Fuel Cell Technologies. The cell was incubated at 343K and atmospheric pressure for at least 8 hours with 0.25 standard liters per minute
(SLM) H₂ (UHP Hydrogen, Air products) and 0.18 SLM O₂ (UHP Oxygen, Air Products) on the anode and cathode side respectively. The temperature of the anode and the cathode humidity bottles were 80 °C and 70 °C respectively such that gases flowing through were fully humidified. Current - Voltage (VI) performance curves were recorded after incubation and compared with a baseline VI performance curve to confirm that the fuel cell is working properly.

Cyclic Voltammetry & Electrochemical Area

For initial characterization of the MEA, the cell was cooled down to 25 °C. N₂ at 0.10 SLM was fed through the anode side (henceforth called as the working electrode, WE) and H₂ at 0.05 SLM was fed through the cathode side of an open circuited cell. H₂ flowing over Pt/C acted as a dynamic hydrogen electrode (DHE) and hence all the potentials reported here are with reference to this electrode. The open circuit potential was monitored while it decayed from the typical H₂/O₂ potential (~1.0 V vs. DHE) to the characteristic N₂/H₂ potential of ~0.085 V vs. DHE. N₂ flow was then switched to a flow of 476 ppm CO in N₂ with a total flow rate of 0.10 SLM for 300 seconds. This exposure and the resulting adsorption were found earlier to result in the maximum surface coverage of CO on Pt. N₂ flow was then restored to purge out CO present in the bulk of the flow channels. The cell was held at a constant potential of 50 mV for 25 seconds, which was followed by cyclic voltammetry (CV) at a scan rate of 20 mV/s from 50 to 1150 mV and back to 50 mV vs. DHE. Experiments were conducted using a M263A potentiostat/galvanostat in conjunction with ECHEM software made by EG&G (Princeton Applied Research). The area under the CO oxidation peak, Q.CO, in the potential window 600 – 850 mV relative to the background current was used to calculate the amount of CO oxidized, which is then used to calculate the maximum active electrochemical area, Q.max. The voltammogram obtained from a CO covered electrode was baseline corrected and the two convoluted peaks were deconvoluted with a bimodal Gaussian distribution using commercially available Tablecurve2D® made by Systat®. The resulting fit was always with a R² greater than 0.98 and the deconvolution parameters were estimated for a 95% confidence interval. The bimodal Gaussian distribution equations, the deconvolution procedure and associated fitting parameters were discussed elsewhere (20).

Adsorption

While the cell was still at 25 °C, N₂ flow on the WE was switched to a flow of 50 ppm H₂S in N₂ for 600 seconds. The total flow rate of this mixture was 0.10 SLM. This exposure and the resulting adsorption were found earlier to result in the maximum surface coverage of H₂S on Pt. N₂ flow was then restored to purge out H₂S present in the bulk of the tubing and flow channels. The cell was then held at a constant potential of 50 mV for 25 seconds followed by cyclic voltammetry (CV) at a scan rate of 5 mV/s from 50 to 1400 mV and back to 50 mV vs. DHE. The CV scans were repeated until no further oxidation peaks were noticed - i.e. until a CV cycle overlapped with a baseline CV corresponding to a clean electrode. This experiment was repeated with conditioned fresh MEAs at eleven other temperatures in the 30-110 °C window.

Sequential adsorption & performance measurements

After a cell with a fresh MEA was conditioned at 70 °C and characterized for its true electrochemical area at 25 °C, it was taken back to 70 °C for sequential adsorption & performance measurements. The adsorption experiment like the one described before was
done at 70 °C followed by a H₂/O₂ performance measurement. The cell was then cooled to 25 °C for ECA measurement using CO adsorption. This constituted one cycle. Such cycles were repeated until the cell lost more than half of its original active electrochemical area.

**ELECTRO-KINETIC MODEL**

An electro-kinetic model is presented in conjunction with the data as a proof for the existence of one kind of reaction taking place on two kinds of adsorption sites, i.e. bridge and linear. This model assumes the following:

a. Mass transport of Pt sites and/or the adsorbed species were ignored.
b. Isothermal conditions exist and reaction heat was ignored.
c. Pt sites were assumed not to dissolve, migrate or ripen under the influence of the applied potential for the duration of the experiment. Though the applied potential routinely exceeded the equilibrium potential for Pt dissolution (~1.0V vs. DHE), this was a valid assumption because of the duration of the applied potential, which was of the order of few minutes as opposed to the time constant for Pt dissolution and migration which is at least two orders of magnitude higher. We confirmed this by repeatedly scanning the electrode (50-1400 mV, 5 mV/s) while observing ECA loss at regular intervals. No significant ECA loss was observed after 100 cycles.
d. Only the catalyst sites (Pt) participated in the reaction; the support (carbon) did not contribute to the oxidation current. We verified this by exposing H₂S to an uncatalyzed MEA followed by a potential scan at the rate of 5mV/s in the 50-1400mV vs. DHE window. No oxidation peaks and unusually high currents were observed.
e. Desorption of adsorbed species and the diffusion back to the bulk were ignored because our previous experiments (20) suggested that desorption times were at least three orders of magnitude greater than those of adsorption. Further, the cell thickness (thickness of the porous electrode, \(l\)) was smaller than the diffusion layer thickness (if there was diffusion of desorbed H₂S within the pores), that is, \(l << \sqrt{2D_{H₂S}t}\) for the given experimental time \(t\).
f. N₂ flow in the bulk did not affect the kinetics of the adsorbed species
g. The concentration of the adsorbed species and Pt sites were assumed to be uniform \([C(x, t) = C(t)\) and \(C_m(x, t) = C_m(t)\) for \(0 \leq x \leq l\)]
h. The degree to which adsorption equilibrium was attained before the start of the CV is assumed to be completely shifted towards adsorption, that is, no desorption was assumed to take place prior to and during the experiment.
i. Except for the surface coverage, the state of the electrode was assumed to be the same for all the experiments (CVs) when they were initiated.
j. No further adsorption was assumed to take place immediately after the initiation and during the CV experiment.
k. The oxidation products (CO₂, SO₂ etc.) formed during the experiment were assumed to be carried away by N₂ flowing in the bulk and that they do not affect the kinetics of the electro-oxidation reaction, that is, no lateral interactions occurred between the adsorbed species and the oxidation products.

Equations for two scenarios are presented – one where multiple electro-oxidation reactions occur on one kind of sites and the other where one type of reaction occurs on different types of sites.
One kind of sites, multiple reactions

If H$_2$S adsorbs onto the Pt sites and under the influence of an applied potential $E$ undergoes multiple electro-oxidation reactions, $1, 2, ......, n$, the concentration of the sites can be expressed as,

$$
C = C^0 e^{− \frac{ART \left( \frac{k_1}{\alpha_1} + \frac{k_2}{\alpha_2} + ... + \frac{k_n}{\alpha_n} \right)}{VF \nu}}
$$

where $C^0$ is the initial concentration of Pt sites and $k_n$ is the rate constant for the $n^{th}$ electro-oxidation reaction which can be expressed as,

$$
k_n = k_n^0 e^{− \alpha_n F \left( E_n^0 - E \right)} \frac{RT}{n}
$$

where $\alpha_n$ is the transfer coefficient and $E_n^0$ is the equilibrium potential vs. DHE corresponding to the $n^{th}$ electro-oxidation reaction and $E$ is the applied potential vs. DHE.

The oxidation current from this reaction is,

$$
i_n = N_n FAC k_n
$$

where $N_n$ is the number of electrons transferred. The peak current, which occurs at $E_n^0 = E$ is given by,

$$
i_n^P = N_n FAC^0 e^{− \frac{ART \left( \frac{k_1^0}{\alpha_1} + \frac{k_2^0}{\alpha_2} + ... + \frac{k_n^0}{\alpha_n} \right)}{VF \nu}} k_n^0
$$

The total current due to the oxidation of all adsorbed species is the summation of individual currents,

$$
i = \sum_{n} i_n
$$

One reaction, multiple sites

If H$_2$S adsorbs onto the different kinds of Pt sites and under the influence of an applied potential $E$, undergoes one reaction pathway, the concentration of the of Pt sites of the $m^{th}$ kind can be expressed as,
\[ C_m = C_m^0 e^{-\frac{ARTk}{VF\nu\alpha}} \]  

where \( C_m^0 \) is initial concentration of the Pt sites of the \( m^{th} \) kind and \( k \) is the rate constant of the lone electro-oxidation reaction expressed as,

\[ k = k^0 e^{\left(-\frac{\alpha F(E^0 - E)}{RT}\right)} \]  

where \( E^0 \) is the equilibrium potential vs. DHE. The oxidation current from this reaction is,

\[ i_m = NFAC_m k \]  

where \( N \) is the number of electrons transferred in the reaction. The peak current, which occurs at \( E^0 = E \) is given by,

\[ i_m^p = NFAC_m^0 e^{\left(-\frac{ARTk^0}{VF\nu\alpha}\right)} k^0 \]  

The peak potential [obtained by differentiating equation 22 and setting the result to zero] occurs at,

\[ E_m^p = E^0 - \frac{RT}{\alpha F} \ln \left(\frac{VF\nu\alpha}{ARTk^0}\right) \]  

The total current due to the oxidation of adsorbed species on all the sites is the summation of individual currents,

\[ i = \sum_m i_m \]  

RESULTS AND DISCUSSION

Figure 1 shows the first cycles of cyclic voltammograms obtained on a SPE-Pt electrode exposed to 50 ppm H2S in N2 for different temperatures. Data from higher temperature show two oxidation peaks corresponding to oxidation of species from two different types of sites. Though multiple potential sweeps were required to completely oxidize the adsorbed S from the SPE-Pt surface, the number of cycles decreased with temperature. At 110 °C, only one such potential sweep was required to completely oxidize all of the adsorbed S species. Further, the peak potential, \( E_p \), for S oxidation decreased with temperature. This was found to be the case for similar studies done on
single crystal Pt in aqueous solutions (4). It is possible to estimate parameters such as $k^0$, $C^0_l$ and $C^0_b$ based on the peak current and peak potential values and such an attempt is presented elsewhere (21).

These oxidation curves were baseline-corrected, that is, the second cycle from the CV data was subtracted from the first cycle. For low temperature CV data where multiple scans were required to completely oxidize the adsorbed S to SO₂, subsequent cycles were baseline-corrected and added to the first baseline-corrected cyclic voltammogram, that is in general, $(n+1)^{th}$ cycle would be subtracted from the $n^{th}$ cycle and the resulting data would be added to the first cycle. The area under each of the resulting baseline-corrected curves was deconvoluted using a bimodal Gaussian distribution. The area under the first peak contributes to oxidation charge $Q_1$ and the area under the second peak contributes to oxidation charge $Q_2$.

Figure 2 shows the data vs. model of a baseline corrected CV obtained from an adsorption experiment at 110 °C. Parameters used for data prediction are given in table 1. The principal aim of this model was to prove that one type of reaction occurs on two types of sites. It is not hard to see that in the first case, where multiple reactions occur on one type of sites, the concentration of sites, defined by (1), decays with the applied potential as a single profile. Since the oxidation current is proportional to the concentration of sites, the current profiles for each of the reaction should have the same shape and fall on top of each other. Though each of the current profiles should have different peak currents, as defined by equation 18, they have the same peak potential. This type of behavior contradicts data, which clearly exhibits distinct peaks, indicating different energies of oxidation.

Figure 3 shows the number of electrons transferred per site (e. p. s) for different temperatures calculated from cyclic voltammogram data. $Q_1$ and $Q_2$ represent the oxidation charges of peaks I and II respectively. $(2Q_1+Q_2)/Q_{\text{max}}$ gives number of electrons transferred per site (e. p. s) if charge from peak I correspond to oxidation of bridge bonded species and charge from peak II correspond to oxidation of linearly bonded species. $(Q_1+2Q_2)/Q_{\text{max}}$ gives the e. p. s if charge from peak I correspond to oxidation of linearly bonded species and charge from peak II correspond to oxidation of bridge bonded species. $Q_{\text{max}}$ is the charge obtained from a fresh electrode corresponding to an EPS = 1. $Q_{\text{max}}$ was calculated from CO adsorption and stripping at 298 K, where adsorption was assumed to go to saturation (20). The number of electrons transferred per site was uniform ~6 for the case where the first peak was a result of bridge oxidation and the second, linear oxidation. The e. p. s was non-uniform for the other case. This concludes our discussion on mechanism validation, both theoretical and experimental.

Figure 4 shows the result of sequential adsorption and performance measurements at 70 °C. These baseline-corrected CVs were the result of CO adsorption and stripping experiments done at 25 °C on a fresh electrode and on electrodes with irreversible loss of catalytic activity induced by three and eight cycles of sequential H₂S adsorption and stripping at 70 °C. The amplitude of peak I decrease with increasing number of cycles, while the amplitude of peak II remains unchanged. Since peak II corresponds to oxidation due to bridge bonded species, the number of bridge sites decrease with increasing exposure to H₂S. It is interesting to note that H₂/O₂ performance curves at 70 °C on a fresh electrode and on an electrode after ten cycles of sequential H₂S adsorption and stripping, as shown in figure 5, exhibit little or no change. However, there are subtle changes in the performance both in the kinetic region (figure 6) as well as in the IR region (figure 7). The performance in the IR region corresponds to the trend of
sites lost. However, there is a slight increase in the performance in the kinetic region for cycle 4, where most of the bridge sites were lost and very little linear sites were lost. This is in accordance with the literature in that H\textsubscript{2} oxidation reaction is more facile on linear sites than on bridge sites.

**CONCLUSION**

A concise mechanism is presented for the kinetics of hydrogen sulfide on a CSPE-Pt electrode. This mechanism is validated experimentally by charge balances and theoretically by a model, which predicts the oxidation current as a function of the applied potential. A fraction of the adsorbed S species remains as ‘hard-to-oxidize’ adsorbents and causes irreversible loss of catalytic activity. This sulfur induced poisoning deactivates bridge sites first followed by linear sites.

**NOMENCLATURE**

\[ A \] projected area of the porous electrode, cm\textsuperscript{2}  
\[ C \] total concentration of catalyst sites, mol/cm\textsuperscript{3}  
\[ C^0 \] initial concentration of total catalyst sites, mol/cm\textsuperscript{3}  
\[ C_m^0 \] initial concentration of catalyst sites of \(m\text{th}\) kind, mol/cm\textsuperscript{3}  
\[ D_{H_2S} \] diffusion coefficient of H\textsubscript{2}S in N\textsubscript{2}, cm\textsuperscript{2}/s  
\[ E \] applied potential, V  
\[ E^0 \] thermodynamic equilibrium potential vs. DHE, V  
\[ E_m^0 \] thermodynamic equilibrium potential vs. DHE for the \(m\text{th}\) electro-oxidation reaction, V  
\[ E_m^p \] peak potential corresponding to the electro-oxidation reaction occurring at sites of \(m\text{th}\) kind, V  
\[ e.p.s \] number of electrons transferred per Pt site  
\[ F \] Faraday’s constant, 96,487 C/equiv.  
\[ i \] total electro-oxidation current, A  
\[ i_m \] electro-oxidation current from sites of \(m\text{th}\) kind, A  
\[ i_n \] electro-oxidation current from \(n\text{th}\) reaction, A  
\[ i_m^p \] peak current corresponding to the electro-oxidation reaction occurring at sites of \(m\text{th}\) kind, A  
\[ i_n^p \] peak current corresponding to the \(n\text{th}\) electro-oxidation reaction, A  
\[ k_n \] electro-oxidation rate constant of \(n\text{th}\) reaction, cm/s  
\[ k^0 \] equilibrium electro-oxidation rate constant, cm/s
\( k_{n}^{0} \) equilibrium electro-oxidation rate constant of \( n^{th} \) reaction, cm/s

\( l \) thickness of the porous electrode, cm

\( N \) number of electrons transferred

\( N_{n} \) number of electrons transferred in the \( n^{th} \) electro-oxidation reaction

\( Q_{l} \) oxidation charge from peak I of a CV done on H\(_{2}\)S adsorbed electrode, mC

\( Q_{2} \) oxidation charge from peak II of a CV done on H\(_{2}\)S adsorbed electrode, mC

\( Q_{CO}^{b} \) oxidation charge from peak I of a CV done on CO adsorbed electrode, mC

\( Q_{CO}^{l} \) oxidation charge from peak II of a CV done on CO adsorbed electrode, mC

\( Q_{\text{max}} \) maximum oxidation charge calculated from a CV done on a CO adsorbed electrode, corresponding to an e.p.s = 1, mC

\( R \) universal gas constant, 8.314 J/(mol K)

\( t \) time, s

\( T \) temperature, K

\( V \) volume of the porous electrode, cm\(^3\)

\( x \) distance coordinate in the X direction, cm

**Greek**

\( \alpha \) transfer coefficient

\( \alpha_{n} \) transfer coefficient of \( n^{th} \) electro-oxidation reaction

\( \nu \) sweep rate, V/s

**Subscript**

1 peak I

2 peak II

\( CO \) carbon monoxide

\( n \) \( n^{th} \) electro-oxidation reaction

\( m \) catalyst site of \( m^{th} \) kind

**Superscript**

0 initial condition or standard state

\( b \) bridge sites

\( l \) linear sites

\( p \) peak
FIGURE 1. Cyclic voltamgrams obtained from a 40% Pt supported on Vulcan XC-72R after exposure to 50 ppm H₂S in N₂ for 600s at 298 K (■), 318 K (○), 343 K (●), 353 K (▲), 373 K (●) and 383 K (○). Both adsorption and cyclic voltammetry were conducted at these temperatures. CVs were conducted in N₂ 30s after the gas supply was changed from H₂S in N₂ to N₂. All CVs were recorded at a scan rate of 5 mV s⁻¹.
FIGURE 2. Data (peak I: -O-, peak II: -O- ) vs. model (solid line) of a baseline corrected CV obtained from a 40% Pt supported on Vulcan XC-72R after exposure to 50 ppm H₂S in N₂ for 600s at 383 K. Peaks I & II correspond to currents, respectively, due to the oxidation of bridge and linear bonded S species. Parameters used for data prediction are given in Table 1.
FIGURE 3. Electrons transferred per site (e. p. s) for different temperatures calculated from cyclic voltammogram data. \(Q_1\) and \(Q_2\) represent the oxidation charges of peaks I and II respectively. \((2Q_1+Q_2)/Q_{\text{max}}\) gives number of electrons transferred per site (e. p. s) if charge from peak I correspond to oxidation of bridge bonded species and charge from peak II correspond to oxidation of linearly bonded species. \((Q_1+2Q_2)/Q_{\text{max}}\) gives the e. p. s if charge from peak I correspond to oxidation of linearly bonded species and charge from peak II correspond to oxidation of bridge bonded species. \(Q_{\text{max}}\) is the charge obtained from a fresh electrode corresponding to an EPS = 1.
FIGURE 4. Baseline corrected voltammograms obtained from a 40% Pt supported on Vulcan XC-72R after exposure to 0.1 SLM flow of 50 ppm CO in N₂ for 300 s at 298 K. CO adsorption and cyclic voltammetry were conducted at 298 K. These CVs were obtained on a fresh electrode (•), after three cycles (●) and after eight cycles (△) of H₂S adsorption and oxidation at 343 K. All CVs were recorded at a scan rate of 20 mV s⁻¹.
FIGURE 5. H₂/O₂ polarization curves at 343 K and 1 atm pressure for a fresh electrode (-O-) and after ten cycles (-●-) of H₂S adsorption and oxidation.
FIGURE 6. Kinetic region of H₂/O₂ polarization curves at 343 K and 1 atm pressure for a fresh electrode (○) and after two (△), four (□) and ten cycles (●) of H₂S adsorption and oxidation.
FIGURE 7. IR region of H$_2$/O$_2$ polarization curves at 343 K and 1 atm pressure for a fresh electrode (-O-) and after two (-▲-), four (-□-) and ten cycles (-●-) of H$_2$S adsorption and oxidation.
FIGURE 8. The loss of linear (peak II, □-) and bridge (peak I, ●-) sites as a result of H₂S adsorption and oxidation cycles.

TABLE I. List of parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value, units</th>
<th>Reference/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10 cm²</td>
<td>Measured</td>
</tr>
<tr>
<td>C₉₀</td>
<td>2.542 x 10⁻⁵ mol cm⁻³</td>
<td>Estimated</td>
</tr>
<tr>
<td>C₁₀</td>
<td>7.208 x 10⁻⁶ mol cm⁻³</td>
<td>Estimated</td>
</tr>
<tr>
<td>E₉₀</td>
<td>0.9 V vs. SHE*</td>
<td>(5)</td>
</tr>
<tr>
<td>E₁₀</td>
<td>1.1 V vs. SHE*</td>
<td>(5)</td>
</tr>
<tr>
<td>l</td>
<td>10⁻³ cm</td>
<td>Assumed</td>
</tr>
<tr>
<td>k₉₀</td>
<td>5.985 x 10⁻⁹ cm s⁻¹</td>
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</tr>
<tr>
<td>k₁₀</td>
<td>2.638 x 10⁻¹⁰ cm s⁻¹</td>
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</tr>
<tr>
<td>N</td>
<td>6 mole e⁻/mole H₂S</td>
<td>Estimated</td>
</tr>
<tr>
<td>T</td>
<td>383 K</td>
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</tr>
<tr>
<td>α</td>
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</tr>
<tr>
<td>v</td>
<td>0.005 V s⁻¹</td>
<td>Measured</td>
</tr>
</tbody>
</table>

* SHE – Standard Hydrogen Electrode
ACKNOWLEDGMENTS

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REFERENCES