

Competitive effects of S-containing catalyst poisons on the UPD of H in relation to H₂ evolution kinetics and OPD of H at Pt

John H. Barber and Brian E. Conway*

Chemistry Department, University of Ottawa, 10 Marie Curie St., Ottawa, Ontario, Canada K1N 6N5

The competitive adsorption of catalyst poisons and adsorbed H is of interest in relation to their effects in promoting H absorption into transition metals. The capacity of three sulfur-containing compounds, thiourea, L-cysteine and 2,2-diethanolsulfide (DES), to block H adsorption at Pt electrodes in both the underpotential deposition (UPD) and overpotential deposition (OPD) regions is studied. Differences in the rates of adsorption (cysteine and DES < thiourea) and the reactivity of these molecules (thiourea > cysteine and DES) are shown to play important roles in the extent to which the poison, P, can block the UPD of H and modify the Tafel relationship for the hydrogen evolution reaction (HER). The relative H blocking, due to poison coverage, θ_p , is measured by means of cyclic voltammetry and potential-relaxation transient experiments. Measurements of rates of the HER as a function of overpotential are also made utilizing steady-state techniques. It is shown that, for θ_p of cysteine and DES < 0.9, inclusion of a constant site-blockage term is sufficient to account for the observed kinetic behaviour. In the presence of adsorbed thiourea, and virtually complete initial coverages of cysteine and DES, *i.e.* before any H₂ evolution takes place, θ_p varies with potential according to an isotherm determined by the kinetics of hydrogenation and/or desorption of the poison.

The sorption of H into transition metals under cathodic polarization in aqueous solutions and in wet corrosion¹ is a topic of major interest in electrochemical surface science and in the materials science of metals. This H-sorption process is well known to be promoted by catalyst poisons (P) such as As- and S-containing compounds that are strongly chemisorbed at the metal. The mechanism(s) of the promotion effect is (are) poorly understood and quite controversial.^{2,3} They must, however, be intimately connected with steps in the HER and the involvement of chemisorbed H in that process.

An important aspect of electrocatalysis of the HER at a variety of metals, as characterized by the 'volcano relation' observed between exchange current densities and heats of adsorption of H, was identified by Parsons in 1958;⁴ it is the standard Gibbs energy of adsorption of H which determines the relative two-dimensional fractions of unoccupied ($1 - \theta_H$) and occupied (θ_H) electrocatalyst surface sites, giving a maximum in the volcano curve when $\theta_H \approx 1 - \theta_H \approx 1/2$, in the simplest case. Competitive adsorption of a poison substantially diminishes θ_H in relation to its value in the absence of P at a given electrode potential.

The study of poisoning of catalyst surfaces played an important and historical role in elucidation of the phenomenon of heterogeneous catalysis through the discovery that minuscule quantities of poisons could have a large effect on the rates of heterogeneous reactions, a result that led to the concept of 'active centres'.⁵⁻⁷ Similar low-level effects of poisons were demonstrated in electrocatalysis of the HER.⁸

Several aspects of the mechanism of cathodic H sorption into metals were reviewed by Subramanian,³ together with some discussion of suggestions that had been made previously,⁹⁻¹² as explanations of the promoting effect of chemisorbed catalyst poisons on H sorption at electrodes and also in wet corrosion (presumably through similar mechanisms to those at cathodes). The previous explanations took, however, no account of the diminution of coverage of cathode surfaces by H due to competitive adsorption of the poisons and some suggestions, *e.g.* that M-H bond strengths were increased owing to the poison; that formation of gaseous hydrides (H₂S, AsH₃) or of 'colloidal' particles were the origin of the effect or that poisons interfered with H atom recombination, leading

supposedly to increasing probability of H entry, seem physically unrealistic.³ In recent studies of S adsorption at Pt electrodes,¹³⁻¹⁷ Marcus and Protopopoff¹⁸ gave an ingenious treatment of site-blocking by poisons in relation to H adsorption and absorption which is further examined in the present paper.

In previous papers^{2,19} we have discussed the apparently anomalous situation that at H₂-evolving cathodes, *e.g.* Fe, steel, Ti, chemisorption of catalyst poisons such as S-containing compounds greatly enhances the rate or extent of H sorption into metals yet they diminish the coverage by adsorbed H, which is the intermediate in the H₂-evolution reaction, and presumably the source of H that is absorbed.

In new work presented in this paper, the effects of competitive chemisorption of thiourea, cysteine and DES on the UPD of H, *i.e.* below the H₂/H⁺ reversible potential, and on the behaviour of the extra OPD H involved in the mechanism of the HER, are quantitatively evaluated at Pt by means of cyclic voltammetry, steady-state polarization measurements, potential-relaxation transients and electrochemical impedance spectroscopy (EIS). The results provide the quantitative basis required for further understanding of effects of poisons on H coverage, thence H absorption. The interpretation of these results will also be applied to some preliminary results concerning the effect of thiourea adsorption on the sorption of H into Pd.

It has been shown^{2,19} theoretically that changes of the H coverage alone, brought about by chemisorption of the poisons, cannot account for promotion of H sorption; such effects as lateral surface-dipole interactions and communal electronic effects in the surface plasma must be invoked.

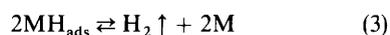
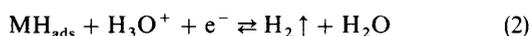
State and coverage by adsorbed H in relation to UPD and HER mechanisms

The state of chemisorbed H on transition-metal and metal-alloy electrodes is important as it is the intermediate in the HER and the source of H which becomes electrochemically sorbed into metals. The reactivity of this intermediate is dependent on the metal-to-hydrogen bond energy which is, in turn, dependent on the metal, the surface coverage of the H

intermediate⁴ and the presence of other adsorbed species on the electrode surface (adsorbed poisons, anions or foreign metals). These adsorbed species can affect the chemisorption of H by three mechanisms: (i) by site blocking (general or selective); (ii) through lateral interactions between the adsorbed species and (iii) by changes in the work function by electron donation or acceptance by the adspecies.

For the HER the effect of these adspecies (poisons) is generally to decrease the coverage of adsorbed H and the rate of the HER, and will depend on the type of association of the poison with the metal surface and the operative mechanism of the HER at the given metal and/or the range of potentials in which the electrode is polarized. The adsorbed poison can, however, become desorbed during strong cathodic or anodic polarization with the extent of desorption being dependent on the polarization potential, the surface coverage by the poison prior to the polarization and the electrochemical reactivity of the poison. When desorption takes place at cathodic overpotentials, modifications must be made in the kinetic equations for the HER since potential-dependent coverage [eqn. (I)] of surface sites by the poison will cause variation in the OPD H coverage and hence in the Tafel slope.

The possible steps in the HER and H-adsorption and -absorption processes are well known:²⁰



The kinetics of the overall process have been thoroughly studied both theoretically²⁰ and experimentally.^{21,22} It is known that Tafel slopes (*b*) for rate-controlling desorption steps (2) or (3) are less than $RT/\beta F$ ($\beta \approx 0.5$) when the coverage by the adsorbed H intermediate is $\ll 1$ and thence potential dependent. A generalized relationship involving the overpotential, η , is:

$$b^{-1} = \frac{d \ln \theta_H}{d\eta} + \frac{\beta F}{RT} \quad (I)$$

Experimental

Poisons studied

Three S-containing poisons, thiourea, cysteine and DES, were chosen in order to examine the effect of different electronic and chemical environments of the sulfur atom which lead to different surface chemical reactivities and adsorptive affinities at Pt. Each poison was either preadsorbed at the Pt electrode from a separate 0.1 mol dm⁻³ solution and then transferred to the electrochemical cell (*ex situ* adsorption) or added into the supporting electrolyte in the cell to give a known concentration (*in situ* adsorption).

Electrochemical measurements and data acquisition

Tafel-type current *vs.* potential relations were recorded using either a Hokuto 501 potentiostat/galvanostat, controlled by an HP 9000 series computer, or a computer-controlled PAR Verostat. All potentials were measured against a reversible hydrogen electrode in the same supporting electrolyte as that in the working electrode compartment but without the presence of poison, being separated from that compartment by a solution-sealed stopcock in the usual way. Experiments were conducted at 298 K. Corrections for the *IR* drop between the Luggin capillary of the reference electrode, and the working electrode were made by means of ac resistance or current interruption methods.

The working electrodes were small Pt poly-oriented spheroids having known surface areas between 0.01 and 0.005 cm², enabling small currents to be used, thus avoiding significant build-up of any products of reaction of the poison in the working electrode compartment. The EIS measurements were made using a small rotating-disc electrode (0.05 cm⁻²) (Pine Instrument Co.) to promote uniform mass transport to the working electrode. Ultra-clean conditions were employed as described previously,²³ including potential cycling of the Pt electrode between 0.05 and 1.5 V to ensure a clean initial surface. Cyclic voltammograms were recorded on a digital oscilloscope. Potential-relaxation data obtained following interruption of previously adjusted constant currents were collected digitally using the oscilloscope and processed, as described previously.^{24,25} EIS results were collected using a Solartron 1286 potentiostat/galvanostat coupled with a Solartron 1255 FRA.

In order to relate the effects of adsorption of the poisons to the kinetics of the HER the coverages, θ_P , by the respective poisons as a function of overpotential, η , are required. This information was provided by use of a new procedure in which, during evaluation of η as a function of current density at Pt, the potential was switched in a fast transient to the H UPD range within which a cyclic voltammogram was immediately recorded giving θ_H . Argon was continuously bubbled around the Pt electrode and, because small surface area electrodes were used, little H₂ was evolved, thus minimizing interference with the θ_P determinations by H₂ oxidation currents. This procedure enabled evaluation of θ_P , from $\Delta\theta_H$, when P had been initially preadsorbed and was validated by separate experiments in which no poison had been adsorbed. In the *ex situ* type of experiment no further poison adsorption could take place. This technique was also applicable to *in situ* experiments, when rates of adsorption of poisons were sufficiently slow that θ_P did not change during its evaluation in the H UPD region.

Solutions and gases

All solutions were prepared using 18.2 MΩ Milli-Q water. Thiourea and cysteine were doubly recrystallized and DES, 99+ % purity, was used without further purification. For electrolytes, very high-purity sulfuric acid (Sea Star Chemicals) and BDH Aristar grade sodium hydroxide were used without further purification. Argon and hydrogen gases for bubbling in the cell compartments were purified as described previously.²³

Results and Discussion

Adsorption of the poisons at the Pt electrode

The adsorption of the poisons leads to: (a) diminution of coverage by underpotentially deposited H and (b) changes in the kinetics of the HER and associated diminution of coverage by the OPD H and, additionally, (c) enhancement of sorption of H into the cathode at certain transition metals.

In a number of experiments, addition of the poison was made to an initially poison-free solution. This results in the desorption of previously adsorbed H (UPD-H and OPD-H), and anions, the amount being dependent on the electrode potential during poison adsorption, as shown over the H UPD region by the voltammograms in Fig. 1 for thiourea. In the UPD potential range, the anodic H desorption effect²⁶ is observed, *i.e.* at a constant potential, H is desorbed in a recordable anodic current (charge) transient. The coverage by the poisons on Pt, thus determined, is concentration and time dependent. The process of adsorption of P can be written, for conditions where P adsorption is competitive with that of H, as follows, where $\theta_{H(P)}$, $< \theta_H$, is the H coverage in the presence of P and $(1 - \theta_H, \theta_H)$ represents the initial state of free sites

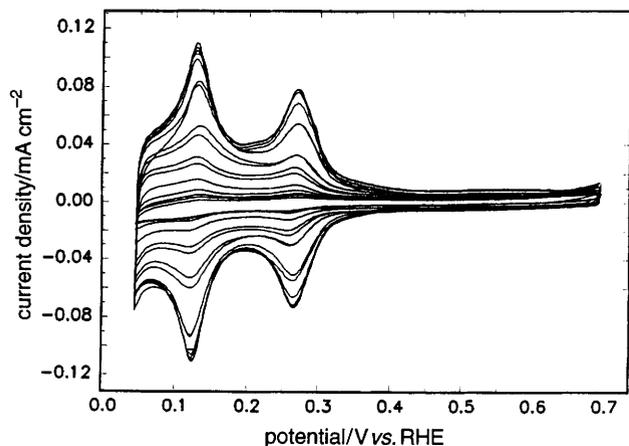
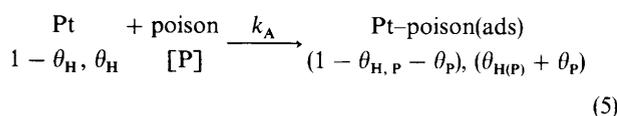


Fig. 1 Cyclic voltammograms of UPD H in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ - $x \text{ mol dm}^{-3}$ thiourea: $5 \times 10^{-8} < x/\text{mol dm}^{-3} < 1 \times 10^{-4}$, scan rate 50 mV s^{-1}

and the H coverage on the electrode when $\theta_p = 0$:



The variation in θ_p expressed as $\Delta\theta_H$ at a constant adsorption time but for various P concentrations is shown for cysteine and thiourea in Fig. 2. The maximum blocking of UPD H that thiourea produces on Pt in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ reaches *ca.* 99%. Owing to the complications from time and concentration factors when the poisons are present in the electrolyte, the preferred procedure, mentioned above, was adopted, in which the poisons were first separately adsorbed, *ex situ*, from an initial solution, 0.1 mol dm^{-3} in concentration, for adsorption times of 10 min for thiourea and 1 h for cysteine and DES; the electrode was then transferred to the test cell in which kinetic and coverage experiments were conducted. For thiourea the time allowed for adsorption had little effect past the 1 min value. Cyclic voltammograms (inset Fig. 3) were taken subsequently to this prior adsorption and indicate that, for thiourea preadsorbed under the conditions employed, the coverage by UPD H becomes almost zero but for cysteine and DES, the blockage of UPD H is incomplete. Adsorption times greater than 4–5 h were needed for a ‘complete’ film to be formed but θ_p s of 80–90% were attained quickly. These differences probably result from specific configurational surface-

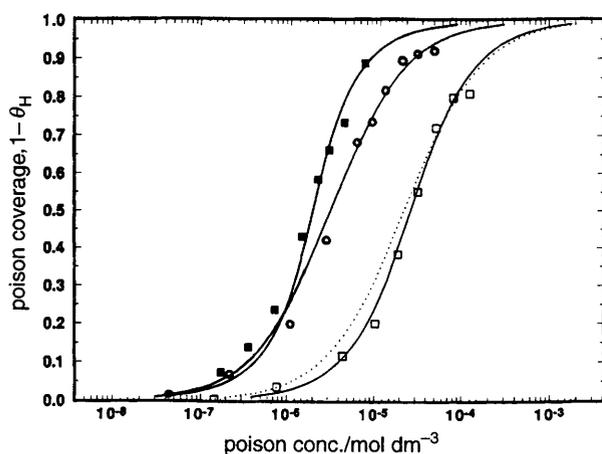


Fig. 2 Coverage of UPD H as a function of poison concentration in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ on Pt. (○) Thiourea; (■) cysteine; (□) cysteine (HCl); (---) or (—) indicate Langmuir or Frumkin isothermal behaviour.

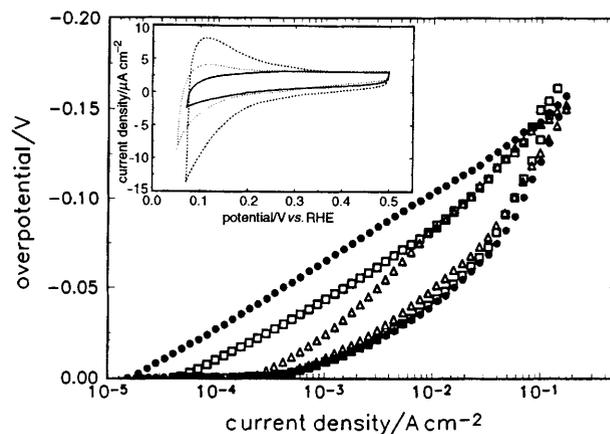


Fig. 3 Tafel plots of the HER showing ascending and descending polarizations taken after *ex situ* adsorption: (●) thiourea; (□) cysteine; (Δ) DES. Inset: cyclic voltammograms taken before the cathodic polarizations shown. (—) Thiourea; (···) cysteine; (---) DES, scan rate 50 mV s^{-1} .

bonding requirements^{14,15} similar to those for self-assembled monolayers.²⁷

All the voltammetric responses for preadsorbed poisons were found to be stable over 100s of cycles in the UPD H region, demonstrating a state of virtually constant poison coverage.

Poison effects on the steady-state polarization behaviour of the HER at Pt electrodes bearing preadsorbed poison films

The steady-state cathodic polarization measurements on the HER in the presence of thiourea, cysteine and DES reflect the effects of the relative values of poison coverage determined in the UPD H region, *viz.* $i(\text{thiourea}) < i(\text{cysteine}) < i(\text{DES})$, as shown in Fig. 3.

The Tafel relations were recorded for a series of increasing, and then subsequently decreasing, overpotentials up to, or down from, *ca.* -0.2 V . The resulting currents were always larger on the ‘descending’ than on the ‘ascending’ curve, due to irreversibility of the changes of θ_p with potential. Thus the poison becomes progressively desorbed with increasing η allowing a greater fraction of free sites to be available for H accommodation in the HER. However, at each point along the Tafel curves, an apparent steady state had been reached in the timescale of the measurements, *ca.* 1 min.

Quantitative measurements of H blocking by thiourea, as a function of η for the HER, were made by determining the charge for UPD of H, by the procedure described earlier, after steady-state cathodic polarization at each potential had been attained. As η was increased, θ_H was found to increase semi-logarithmically with η , with a slope of $-81 \text{ mV decade}^{-1}$ (inset Fig. 4). Placing this value in eqn. (I) for $d(\ln \theta_H)/d\eta$ a Tafel slope of $-48 \text{ mV decade}^{-1}$ results, similar to the experimental value of $-41 \text{ mV decade}^{-1}$ (Fig. 4). Correspondingly, a calculated Tafel plot can be constructed and compared with the experimental behaviour as in Fig. 4.

Analysis of the HER kinetics at Pt with the poison present in the electrolyte

Thiourea. The effects of poisons on the kinetics and mechanisms of the HER should be considered in relation to both the changes in exchange current density (i_0) and Tafel slope values. Especially the latter can be indicative of the effects of the poisons on the potential dependence of θ_H [eqn. (I)], and on the mechanism of the overall HER.

At active, clean Pt electrode surfaces, the *IR*-corrected Tafel relations are curved (Fig. 5) indicating^{21,24} involvement of the recombinative mechanism, step (3) (the curvature is not due to

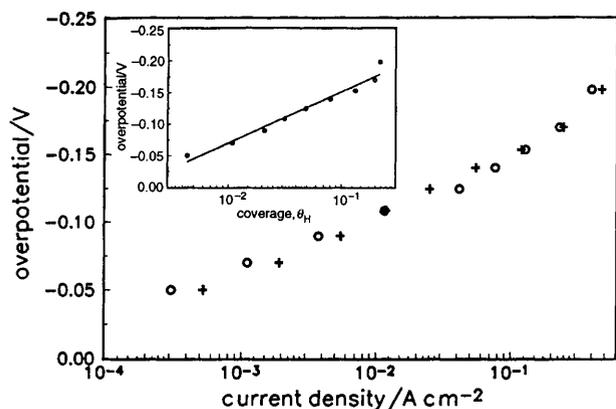


Fig. 4 Experimental (O) and simulated (+) Tafel plots of the HER after *ex situ* adsorption of thiourea. Inset: measured UPD H coverages at each corresponding overpotential in the main figure (slope = -81 mV).

diffusion control, as shown by rotating-disc electrode measurements). However, when thiourea is present in the electrolyte, a linear region is observed over several decades of current density (Fig. 6) having a Tafel slope near -60 mV. Such a value is difficult to account for conventionally [*cf.* eqn. (I)] through any of the steps (1) to (3) except with an unrealistic value of β . However, the -60 mV slope could be accounted for through a progressively changing coverage (θ_p) of the poison, as for the *ex situ* results, or a product of its reduction, *e.g.* H_2S , that is dependent on η over the range of the observed Tafel plot. Corrections of Tafel curves for

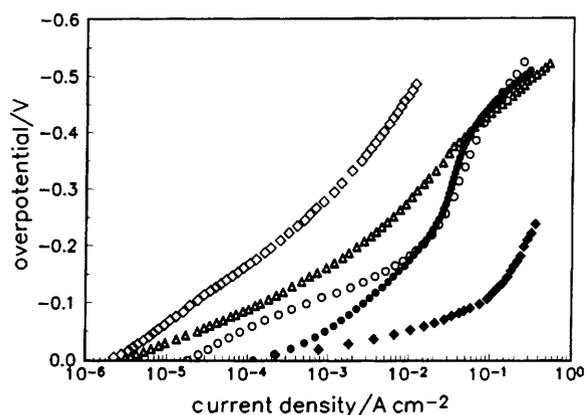


Fig. 5 Tafel plots for the HER in various supporting electrolytes plus $5 \times 10^{-3} \text{ mol dm}^{-3}$ thiourea. (\diamond) $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; (Δ) $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; (\circ) $0.5 \text{ mol dm}^{-3} \text{ NaOH}$; the corresponding 'clean' behaviour in (\bullet) $0.5 \text{ mol dm}^{-3} \text{ NaOH}$ and (\blacklozenge) 2 mol dm^{-3} and $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.

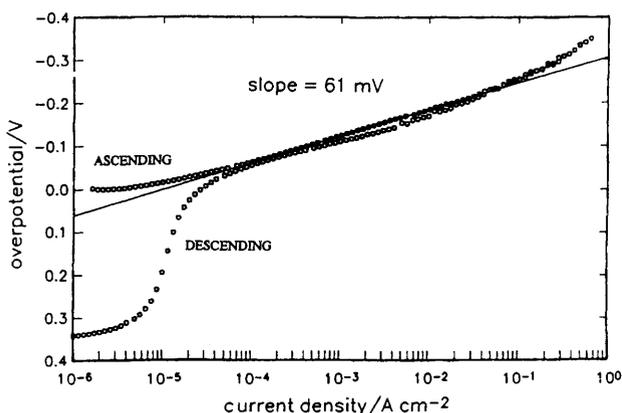
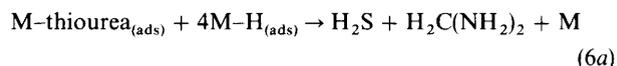


Fig. 6 Tafel plot of the HER in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ - $1.3 \times 10^{-4} \text{ mol dm}^{-3}$ thiourea, demonstrating the -60 mV Tafel slope and the 0.35 H_2S rest potential

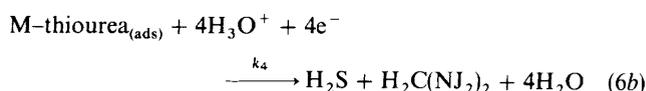
changes in θ_p with overpotential have been applied by several authors^{28,29} to account for Tafel slopes numerically $< -118 \text{ mV}$ when thiourea is adsorbed on Hg.

Thiourea and its selenium analogue have been the poisons of choice in a number of previous studies on hydrogen absorption³⁰⁻³² and corrosion inhibition.³³ The C=S bond is reactive in both reduction and oxidation³⁴ of thiourea. Reduction takes place during the HER at Pt to produce (at -50 mV *vs.* RHE) H_2S , PtS, PtS₂ and traces of colloidal sulfur^{35,36} on the Pt surface.† However, thiourea is not reduced in the UPD H region, contrary to N=O and C=C groups which observably react^{37,38} with the UPD H species.

The reduction of thiourea [eqn. (6a) and (6b)] has a pronounced effect on the kinetics of the HER which cannot be explained by site blockage alone. Alternative steps are as follows, one involving chemisorbed OPD H:



and the other an electrochemical step involving proton discharge:



Neutral or protonated methylenediamine and H_2S are the products, the latter being also a strong poison. Elimination of NH_3 from methylenediamine would give $\text{CH}_2=\text{NH}$ (the N analogue of formaldehyde), the structure of which has been considered in the literature.³⁹ The H_2S produced in (6a) or (6b) could remain adsorbed, especially as it would arise directly from the centre, C=S, by which thiourea is adsorbed. However, because the solution was being bubbled with H_2 , any free H_2S would tend to be expelled.

We now examine if the kinetic behaviour of the HER in the presence of thiourea can be attributed to the potential dependence of θ_p , which determines the maximum attainable coverages by H. Literature on the electrochemical hydrogenation reaction (EHR) of nitro compounds and unsaturated hydrocarbons^{37,40,41} suggests that at UPD potentials, a mixed mechanism of catalytic and electrochemical hydrogenation is operative, *viz.* eqn. (6a) and (6b) for the reaction of thiourea. At overpotentials in the HER region, the electrochemical mechanism is predominant,⁴¹ *i.e.* eqn. (6b) for thiourea. Therefore, accepting eqn. (6b) as the mechanism of hydrogenation of thiourea we can write:

$$\frac{d\theta_p}{dt} = 0 = v_A - v_4 \quad (II)$$

where, for process (6b)

$$v_4 = k_4[\text{H}_3\text{O}^+]^4\theta_p \exp(-\eta\beta F/RT) \quad (III)$$

and

$$\theta_p = \frac{k_A}{k_A + k_4 \exp(-\beta F/RT)} \quad (IV)$$

The effect of this potential dependence of θ_p in eqn. (IV) on the kinetics of the HER follows by writing the rate equations for the steps in the HER with the inclusion of θ_p ; thus‡

† PtS, PtS₂ and colloidal sulfur may not be direct products of thiourea reduction, but can result from the interaction of the resulting H_2S with the Pt surface.

‡ We recognize that, in a more sophisticated analysis, some dependence of k values on θ_p , due to lateral H-P interaction effects, could be included. However, comparison (see Table 1) of its fitted rate constants for the HER at a poison-free surface indicate that such interaction effects are not important or may have been engulfed into the fixed parameters defining the poison reaction.

$$v_1 = k_1(1 - \theta_H - \theta_P)\exp(-\eta\beta F/RT) - k_{-1}\theta_H \exp[(1 - \beta)\eta F/RT] \quad (\text{V})$$

$$= k'_1(1 - \theta_H - \theta_P) - k'_{-1}\theta_H \quad (\text{Va})$$

$$v_2 = k_2\theta_H \exp(-\eta\beta F/RT) = k'_2\theta \quad (\text{VI})$$

and

$$v_3 = k_3(\theta_H)^2 \quad (\text{VII})$$

The steady-state value of θ_H can then be determined using eqn. (V)–(VII) and eqn. (IV), giving

$$\theta_H + \frac{-(k'_1 + k'_{-1} + k'_2)}{4k_3} \frac{\sqrt{[(k'_1 + k'_{-1} + k'_2)^2 - 8k'_1(1 - \theta_P)k_3]}}{4k_3} \quad (\text{VIII})$$

The Tafel behaviour, η vs. $\log i$, can then be calculated from

$$i = F(v_1 + v_2) + 4Fv_4 \quad (\text{IX})$$

On the basis of the above approach, the experimental $i(\eta)$ behaviour for thiourea hydrogenation in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, occurring during the HER, was fitted using a non-linear least-squares calculation, as shown in Fig. 7, for which the rate constants required for a good fit are given in Table 1. The resulting relative coverage vs. potential relationships for both thiourea and the OPD H are shown in Fig. 8. Evidently this treatment gives a good account of the observed poisoning effect of thiourea [or derived H_2S , eqn. (6a) or (6b)] on the kinetics of the HER. The rate constants in Table 1 for the HER kinetics are all in good respective agreement with those found in the literature²⁵ for the HER on a clean Pt cathode. The rate constants for the EHR, k_A and k_4 , are for the step of adsorption of the poison [eqn. (5)], and for the coupled hydrogenation/desorption step [eqn. (6b)]. The value of k_A derived from the fitting of the experimental kinetic results obtained at the rotated electrode (2500 rpm) is 3–4 orders of magnitude lower than the calculated value for mass transfer of the thiourea to the rotating sphere. This indicates clearly that the EHR, proceeding through an adsorbed intermediate, is not diffusion controlled.

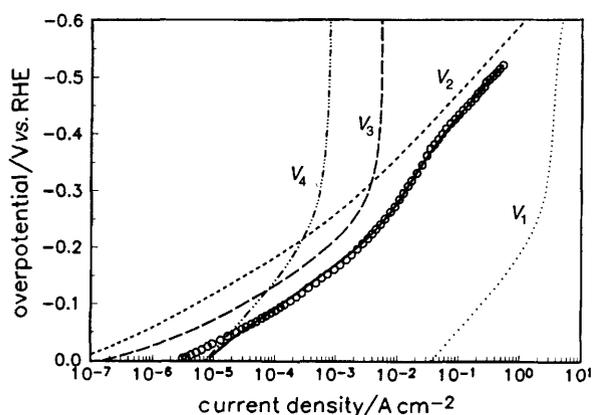


Fig. 7 Tafel plot for the HER and EHR in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ – $5.1 \times 10^{-3} \text{ mol dm}^{-3}$ thiourea. (○) Experimental data; (—) best fit line; the broken lines represent the contributions of each of the reaction steps; (v_1 , v_2 and v_3) for the HER; (v_4) for the EHR.

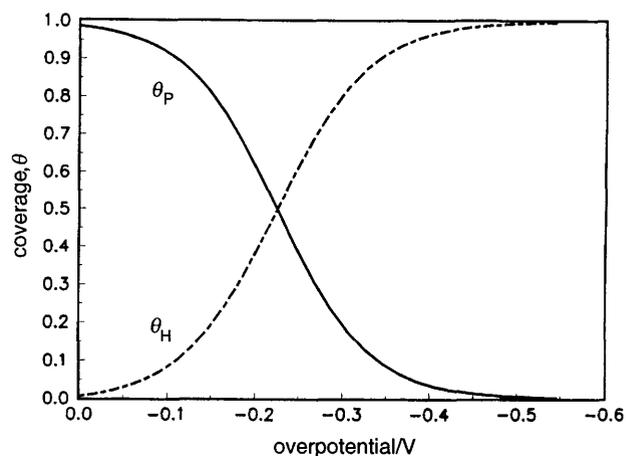


Fig. 8 Coverage vs. overpotential calculated from the rate constant determined from the fitting of the experimental data in Fig. 6, as listed in Table 1

Another factor which must be addressed for the case of thiourea is its acid–base properties; its protonation constant is $\text{p}K = 1.44$.⁴² Fig. 5 demonstrates the effect that has on the behaviour of the HER in three different electrolytes: $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $0.5 \text{ mol dm}^{-3} \text{ NaOH}$, having pH values of -0.30 , 0.292 and 11.7 , respectively. In $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ the fraction of thiourea protonated is ca. 10–20%. The polarization behaviour for this case indicates that the coverage by thiourea does not change with potential and the adsorption of the protonated species is likely to be enhanced at higher overpotentials. In $0.5 \text{ mol dm}^{-3} \text{ NaOH}$, on the other hand, where thiourea is not protonated, we observe at overpotentials $< -100 \text{ mV } i(\eta)$ behaviour similar to that in the absence of the poison indicating complete desorption of thiourea from the active sites for the HER (i.e. equivalent OPD H coverages). Using $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ the fraction protonated is 2–4%. It is seen (Fig. 5) that the behaviour when $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ is used is intermediate between that in $0.5 \text{ mol dm}^{-3} \text{ NaOH}$ (unprotonated) and $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (15% protonated), which provides some evidence that, in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, a mixture of both species could cover the surface. For thiourea in aq. HCl, for Hg as the substrate, it was proposed²⁸ that the adsorbed protonated species acted as a catalytic centre for rapid H_2 discharge. On Pt the HER on the bare substrate occurs at a faster rate than discharge from the adsorbed protonated species; the latter therefore only plays the role of a site blocker at Pt. In summary then, it appears that the protonated form, being able to remain on the surface up to elevated cathodic overpotentials, is a more effective poison than the neutral form, which becomes desorbed with increasing overpotential.

In order to obtain a better understanding of the role of thiourea coverage on the kinetic parameters in the HER, experimental conditions were set so that the coverage did not change with potential. This was achieved by first applying a cleaning cycle in the oxide region followed by an adsorption step in the double-layer potential region which produced a defined surface coverage for each point on the polarization curve; also the time of polarization was restricted so that hydrogenation and desorption would not significantly take place. In this way a family of Tafel-type measurements could

Table 1 Rate constants ($\text{mol cm}^{-2} \text{ s}^{-1}$) for thiourea hydrogenation in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$

k_1	k_{-1}	k_2	k_3	k_A	k_4
$(3.82 \pm 0.01) \times 10^{-7}$	$(5.1 \pm 50) \times 10^{-7}$	$(1.03 \pm 0.004) \times 10^{-10}$	$(5.65 \pm 0.03) \times 10^{-8}$	$(1.4 \pm 0.3) \times 10^{-9}$	$(2.0 \pm 0.6) \times 10^{-11}$

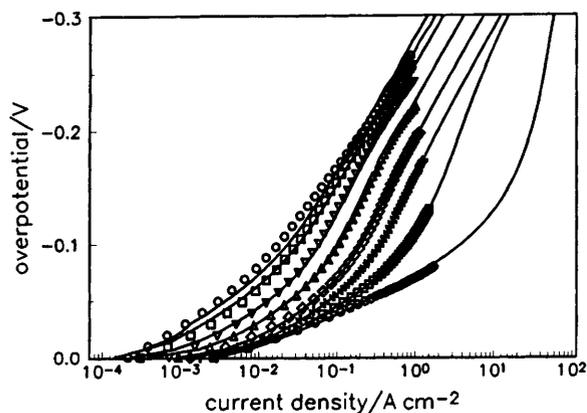


Fig. 9 Tafel plots and best-fit lines for the HER with stable coverages of thiourea (see text). Thiourea conc. = 2×10^{-7} – 4×10^{-6} mol dm^{-3} .

be collected, Fig. 9, which corresponded to a series of surface coverages by thiourea, under these conditions constant with overpotential. Fig. 9 also shows the results from the fitting of the kinetic equations for the HER, in the absence of EHR, to each curve. For the fitting, it was not necessary for θ_p to be specifically included, since it was absorbed into the rate constants, being almost constant with respect to potential. Comparing the fitted rate constants for the different steps with the surface coverages determined by means of cyclic voltammetry in the UPD H region [Fig. 10(a) and (b)], the rate constants for the alternative rate-limiting steps [eqn. (2) and (3)] are found to have direct relationships with θ_H while, for the electrochemical H adsorption/desorption, step (1), the rate constant values seem independent of coverage.

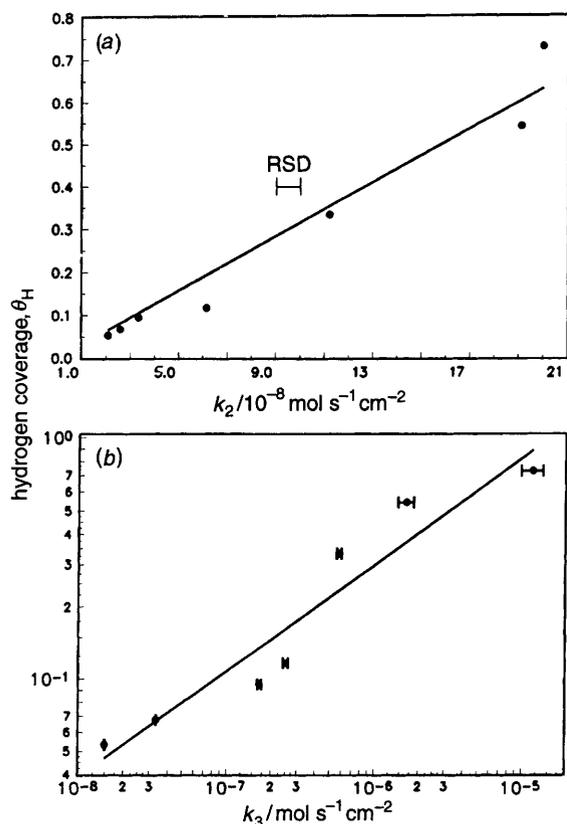


Fig. 10 (a) UPD H coverage vs. rate constant for step (2) in the HER mechanism. (b) UPD H coverage vs. rate constant for step (3) in the HER mechanism (slope = 2.2). Rate constants obtained from fitting of the data in Fig. 9.

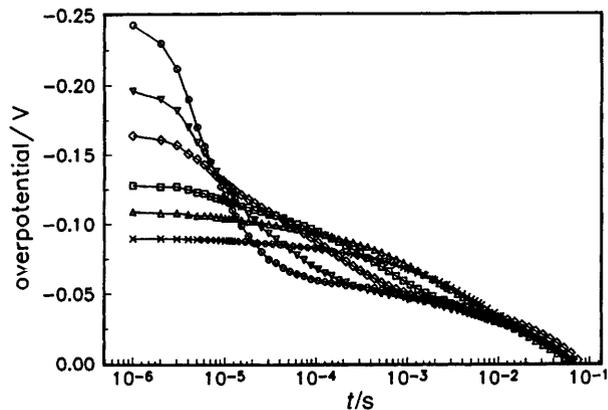


Fig. 11 Potential-relaxation transients taken in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ – $1.4 \times 10^{-4} \text{ mol dm}^{-3}$ cysteine at current densities (\times) 2.5×10^{-3} , (Δ) 6.3×10^{-3} , (\square) 2.5×10^{-2} , (\diamond) 8.8×10^{-2} , (∇) 2.5×10^{-1} and (\circ) $8.8 \times 10^{-1} \text{ A cm}^{-2}$. Lines are drawn for clarity.

Cysteine and DES

Cysteine is a common amino acid with a thiol group which has a chemistry intermediate between that of the C=S group in thiourea and the C–S–C group in DES. Cysteine also will carry a positive charge on its NH_2 group in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The charged nature of the cysteine species could give rise to some double-layer effects, but these are probably much weaker than the effect of site blockage. At shorter adsorption times, *i.e.* for less than complete poison coverages, the forward and reverse scans of overpotential were similar, which indicates only a minor dependence of poison coverage on η . If sufficient time is given, *ca.* 16–24 h, cysteine and DES produce films which virtually eliminate UPD of H. A dependence of θ_p , for cysteine and DES, on η is observed when $\theta_p \approx 1$ (full coverage) initially, before any H_2 has evolved; this is similar to the behaviour with thiourea but in that case the dependence was seen regardless of the initial surface coverage.

In order to explore this behaviour a series of potential-relaxation transients (Fig. 11) were recorded corresponding to various initial overpotentials, on an electrode covered fully with a cysteine film. Note that similar trends were observed using thiourea and DES on Pt in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and also on a Pd substrate with an adsorbed thiourea film. Numerical simulations were undertaken (Fig. 12) using the parameters given in Table 2 but non-linear least-squares fitting of the experimental data was unsuccessful owing to the anomalous potential dependence, $d\eta/d(\log t) \neq 118 \text{ mV}$, of the process of double-layer capacitance relaxation which would result when either of the normal two-step HER mechanisms

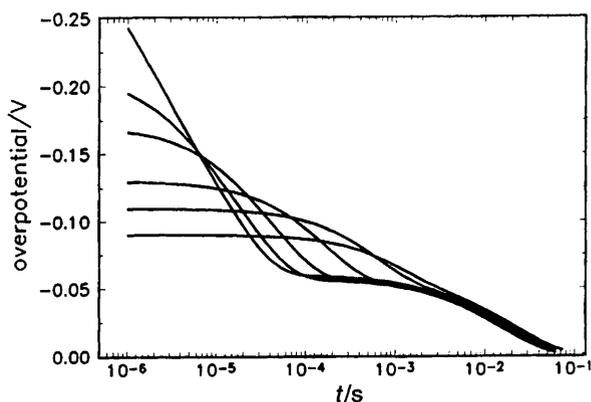


Fig. 12 Simulated potential-relaxation curves using the rate constants given in Table 2 and initial potentials corresponding to those of the experimental data from Fig. 11

Table 2 Parameters used for numerical simulation of potential relaxation curves

$C_{dl}/\mu\text{F cm}^{-2}$	$q_1/\mu\text{C cm}^{-2}$	θ_p
84	8.7×10^{-4}	0.94
74	9.7×10^{-4}	0.89
42	1.25×10^{-3}	0.8
20	2.0×10^{-3}	0.68
19	2.1×10^{-3}	0.41
19	3.24×10^{-3}	0.045

$k_1 = 4.7 \times 10^{-7}$, $k_{-1} = 9.35 \times 10^{-7}$, $k_2 = 4.6 \times 10^{-8}$ and $k_3 = 6.6 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$.

are operative.⁴³ This anomalous behaviour may arise from a charge-transfer reaction occurring between the poison and the Pt substrate during the double-layer relaxation. Although a good fit could not be achieved, the simulation illustrates how the effect of the potential dependence of θ_p on the HER kinetics accounts for the salient features of the experimental results. A correlation was achieved between the simulated and experimental results, by taking constant 'chemical', potential-independent rate constants; other potential-dependent terms were the C_{dl} (double-layer capacitance), q_1 (charge for full H coverage in the presence of P) and θ_p (poison coverage). These three parameters are not independent and, as expected, q_1 decreases with increasing θ_p , and the increase in C_{dl} may also be accounted for by a decrease in the separation of the charges across the interface, especially if charge is held by the poison itself.

In order to deal with the possibility that θ_p may change during the potential-relaxation process, we have studied the impedance behaviour (Fig. 13), over a frequency range between 300 kHz and 0.1 Hz, for the HER in the presence of low concentrations of cysteine and thiourea (incomplete coverages). Three dispersion processes were observed which can be assigned to the relaxation of C_{dl} , the OPD H pseudocapacitance through the charge-transfer impedance, and a pseudoinductance for the relaxation of θ_p . This is consistent with the two-adsorbate (H and P) model we have used and also with theoretical investigations on similar systems by Zoltowski⁴⁴ and by Bai and Conway⁴⁵⁻⁴⁷ which indicate that such inductive behaviour arises when the coverage of one of the adsorbates (here P) decreases with potential. Recognizing that the relaxation of θ_p is associated with the third time constant (*i.e.* the inductive semicircle) we can evaluate semi-quantitatively the relaxation time of θ_p . For thiourea the relaxation process occurs at frequencies < 1 Hz and for cysteine < 0.1 Hz. This indicates that θ_p will be stable within the time frame of the potential-relaxation process, *i.e.* times < 0.1 s, and validates the approach of using constant θ_p terms when simulating each potential-relaxation transient.

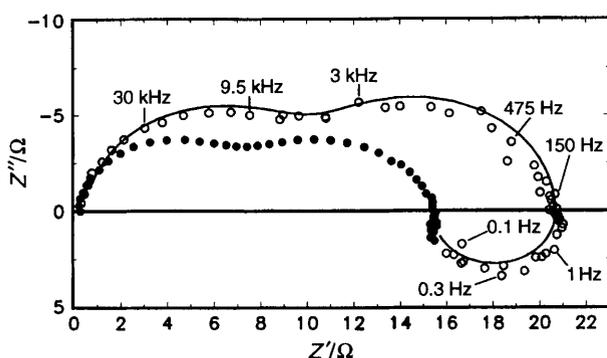


Fig. 13 Complex plane plot taken at $\eta = -125$ mV in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ – $5 \times 10^{-6} \text{ mol dm}^{-3}$ (●) cysteine and (○) thiourea; (—) best fit to the equivalent circuit given by Zoltowski⁴⁴ for a two-adsorbate system

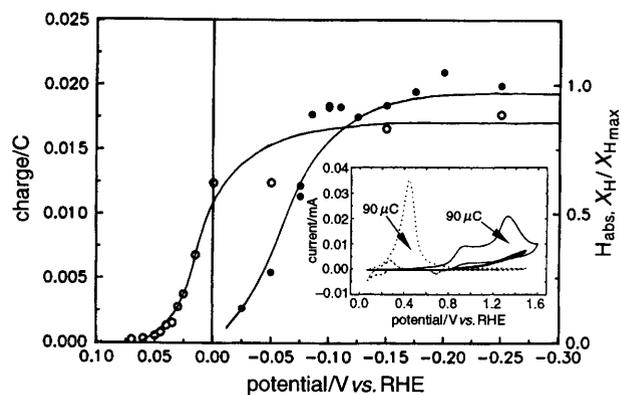


Fig. 14 Quantity of H absorbed into a Pd cathode as a function of cathodic charging potential in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; (●) 0.0 and (○) $4.2 \times 10^{-4} \text{ mol dm}^{-3}$ thiourea. Inset; cyclic voltammograms of H_{abs} oxidation after charging in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; discharged in (···) $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and (—) $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ – $1 \times 10^{-3} \text{ mol dm}^{-3}$ thiourea. Total desorption charge = $90 \mu\text{C}$ in each case.

Effects of thiourea on H sorption and desorption at Pd

Here, we return to the general topic of effects of poison on H sorption. Experiments were conducted on H sorption and desorption at a Pd cathode in the presence and absence of thiourea. As seen earlier, the effects of this poison at Pt on changes of UPD and OPD H coverage were determined. At Pd, such experiments are not possible owing to the swamping effects of charges associated with H sorption or desorption.

Fig. 14 (inset) shows a linear (anodic) potential scan of H desorption from Pd following cathodic charging at 67 mV vs. RHE for 10 min in (a) clean, poison-free $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution and (b) after charging in the same solution but then discharged after the addition of thiourea to give a resulting concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$. The same charge for H desorption is recovered ($90 \mu\text{C}$) as for the clean solution, but only over a much more positive potential range, 0.8 to 1.6 V , in fact where oxidative desorption of thiourea takes place. Thus anodic desorption of H is completely inhibited so long as thiourea remains on the surface. Correspondingly, the main curves in Fig. 14 show the H oxidative desorption charges for H previously sorbed into Pd at various potentials, in the range 0.07 to -0.25 V , as a function of those potentials, in the presence and absence of thiourea. Evidently, for the former condition, significant H sorption begins only when charging potentials more negative than *ca.* 0.00 V vs. RHE are applied, *i.e.* when OPD H is appearing. Note, however, that limiting H desorption charges are approached in both cases as increasing cathodic polarization is applied.

Thermodynamic discussion of bases for enhancement of H sorption by poison

At a recent conference¹⁹ we examined whether the presence of P at coverage θ_p , together with co-coverage θ_H by H, could raise the chemical potential of adsorbed H in such a way as to lead to enhanced H absorption into the electrode. The chemical potentials of H in the absence (μ_H) and in the presence ($\mu_{H(P)}$) of P are, for Langmuir adsorption,

$$\mu_H = \mu_H^0 + RT \ln \left(\frac{\theta_H}{(1 - \theta_H)} \right)$$

and

$$\mu_{H(P)} = \mu_{H(P)}^0 + RT \ln \left(\frac{\theta_{H(P)}}{(1 - \theta_{H(P)} - \theta_P)} \right) \quad (\text{X})$$

where $\theta_{H(P)}$ is normally $< \theta_H$ at a given potential.

However, considering kinetically the steps (1) and (2) in the HER mechanism, it is readily found, for steady-state conditions, that

$$\frac{\theta_{\text{H}}}{(1 - \theta_{\text{H}})} = \frac{(\bar{k}_1 + \bar{k}_{-2})}{(\bar{k}_{-1} + \bar{k}_2)} = \bar{K}_{\text{H}} \text{ (say)} \quad (\text{XI})$$

for $\theta_{\text{P}} = 0$ and also

$$\frac{\theta_{\text{H}}}{(1 - \theta_{\text{H(P)}} - \theta_{\text{P}})} = \frac{(\bar{k}_1 + \bar{k}_{-2})}{(\bar{k}_{-1} + \bar{k}_2)} = \bar{K}_{\text{H(P)}} \text{ (say), for } \theta_{\text{P}} > 0 \quad (\text{XII})$$

where \bar{k} s are the electrochemical rate constants for the indicated steps. Evidently then $\bar{K}_{\text{H}} = \bar{K}_{\text{H(P)}}$, so the presence of P in altering the 'configurational' term in μ does not change or increase the chemical potential of H. Hence, only when there are lateral (repulsive) interactions between H and P can P influence the 'driving force' for H sorption, from adsorbed H, into a metal electrode. Physically this could arise from dipole-dipole interactions and related surface electron-density changes determined by the difference of electronegativities of P and the substrate metal.

An original approach to the above problem was suggested by Marcus and Protopopoff^{17,18} who proposed that the effective coverage by H in the presence of P should be a normalized value, τ , defined as $\theta_{\text{H}}/\theta_{\text{H,s}}$ where $\theta_{\text{H,s}}$ is the local saturation value for H on the sites remaining unblocked (i.e. $1 - \theta_{\text{P}}$) by adsorption of P (occupying 1 H site per P). On this basis, the local chemical potential of Hs amongst Ps in terms of τ , would be

$$\mu_{\text{H}(\tau)} = \mu_{\text{H}(\tau)}^0 + RT \ln \frac{\tau}{(1 - \tau)} \quad (\text{XIII})$$

$$= \mu_{\text{H}(\tau)}^0 + RT \ln \frac{\theta_{\text{H}}/(1 - \theta_{\text{P}})}{1 - \theta_{\text{H}}/(1 - \theta_{\text{P}})} \quad (\text{XIV})$$

Rearrangements give

$$\mu_{\text{H}(\tau)} = \mu_{\text{H}(\tau)}^0 + RT \ln \frac{\theta_{\text{H}}}{(1 - \theta_{\text{H}} - \theta_{\text{P}})} \quad (\text{XV})$$

which turns out to be equivalent to eqn. (X) which, as shown above, does not lead to a difference between μ_{H} in the absence and presence of P, unless interaction effects are significant. Thus, a thermodynamic basis for enhanced sorption of H into metals by co-adsorption of poisons can be sought only through consideration of electrostatic pairwise or communal interactions between H and P.

Conclusions

1. Experimental procedures based on cyclic voltammetry, potential-step transients and potential-relaxation measurements at Pt have enabled the competitive adsorption of three S-containing catalyst poisons *vis à vis* H to be quantitatively evaluated. At Pt, both the UPD and the OPD of H are substantially blocked by the three poisons studied, the effects being strongest with thiourea. Measurements of the blocking of adsorption of the UPD of H by thiourea, cysteine and DES enable competitive adsorption isotherms for the three poisons to be constructed.

2. Thiourea can, however, undergo reductive desorption that makes its coverage dependent on overpotential, resulting in a Tafel relation for the HER having an unusual slope value of *ca.* -60 mV. Cysteine and DES suffer desorption only from high surface coverages and consequently this effect is smaller than with thiourea.

3. At sufficiently low pH, thiourea is protonated, resulting then in a diminished potential dependence of its adsorption.

4. Theoretical considerations show that co-coverage of electrode surfaces with P and H does not lead to change in the chemical potential of H (μ_{H}) and hence cannot provide a thermodynamic basis for the enhancement of H absorption into cathodes. Only when interaction effects are included in the μ_{H} function can such an enhancement effect arise. Similarly, a treatment of the chemical potential of H in terms of a reduced surface coverage fraction, based on fractional occupancy of the free sites left after some extent of poisoning, θ_{P} , also cannot lead to an increase of μ_{H} . Thus poisoning effects do not modify μ_{H} when only the 'configurational' component is considered.

5. Preliminary studies on the effects of thiourea on H absorption at Pd show that H absorption is inhibited at low cathode potentials and that which is sorbed can only become desorbed at more positive potentials than when no poison is present.

Financial support from OGS is gratefully acknowledged by J. B. as is support from the Natural Science and Engineering Research Council of Canada for this research.

References

- R. N. Iyer, I. Takeuchi, M. Zamanzadeh and H. W. Pickering, *Corrosion*, 1990, **46**, 360; see also O. Vosikovskiy, M. Marecek and D. J. Ross, *Int. J. Pressure Vessels Piping*, 1983, **13**, 197.
- B. E. Conway and G. Jerkiewicz, *J. Electroanal. Chem.*, 1993, **357**, 47.
- P. K. Subramanian, in *Comprehensive Treatise on Electrochemistry*, ed. J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White, Plenum, New York, 1980, vol. 4, p. 11.
- R. Parsons, *Trans. Faraday Soc.*, 1958, **34**, 1053.
- H. S. Taylor, *J. Phys. Chem.*, 1926, **30**, 145.
- H. S. Taylor, *Proc. R. Soc., London, Ser. A*, 1925, **108**, 105.
- G. M. Schwab, *Catalysis*, Macmillan, London, 1937, p. 280.
- J. O'M. Bockris and B. E. Conway, *Trans. Faraday Soc.*, 1949, **45**, 989.
- K. E. Shuler and K. J. Laidler, *J. Chem. Phys.*, 1949, **17**, 212.
- S. M. Belaglazov and M. I. Polukarov, *Zh. Prikl. Chim. Mosk.*, 1960, **33**, 389.
- V. P. Alikin, *Uchen. Zap. Perm. Gos. Univ.*, 1961, **19**, 3.
- U. R. Evans, *The Corrosion and Oxidation of Metals*, in *Scientific Principles and Practical Application*, Arnold, London, 1961, p. 397.
- E. Protopopoff and P. Marcus, *J. Electrochem. Soc.*, 1988, **135**, 3073.
- E. Protopopoff and P. Marcus, *Surf. Sci.*, 1985, **161**, 533.
- E. Protopopoff and P. Marcus, *Surf. Sci.*, 1986, **169**, L237.
- P. Marcus and E. Protopopoff, *C. R. Acad. Sci. Paris t.*, 1989, **308**, 1685.
- P. Marcus and E. Protopopoff, *J. Chim. Phys.*, 1991, **88**, 1423.
- P. Marcus and E. Protopopoff, *C. R. Acad. Sci., Paris*, 1989, **308**, 1127.
- G. Jerkiewicz, J. J. Borodzinski, W. Chrzanowski and B. E. Conway, *J. Electrochem. Soc.*, 1995, **142**, 3755; G. Jerkiewicz, J. J. Borodzinski, W. Chrzanowski and B. E. Conway, in *Proc. Symp. Electrochemistry and Materials Science of Cathodic Hydrogen Absorption and Adsorption*, The Electrochemical Society, Pennington, NJ, 1995, vol. 94-21, p. 44.
- J. O'M. Bockris and H. Mauser, *Can. J. Chem.*, 1959, **37**, 475.
- B. E. Conway and L. Bai, *J. Electroanal. Chem.*, 1986, **198**, 149.
- B. E. Conway and B. V. Tilak, *Adv. Catal.*, 1992, **38**, 1.
- H. Angerstein-Kozłowska, in *Comprehensive Treatise on Electrochemistry*, ed. J. O'M. Bockris, B. E. Conway and S. Sarangapani, Plenum, New York, 1984, vol. 9, p. 15.
- B. E. Conway and L. Bai, *Electrochim. Acta*, 1986, **31**, 1013.
- L. Bai, D. A. Harrington and B. E. Conway, *Electrochim. Acta*, 1987, **32**, 1713.
- B. MacDougall, B. E. Conway and H. Kozłowska, *J. Electroanal. Chem.*, 1971, **32**, 15.
- K. D. Truong and P. A. Rowntree, *J. Phys. Chem.*, in the press.
- E. Dayalan and R. Narayan, *J. Electroanal. Chem.*, 1984, **179**, 167.
- N. Mauree and L. Gierst, *Collect. Czech. Chem. Commun.*, 1971, **36**, 389.
- B. Baranski and M. Smialowski, *J. Phys. Chem. Solids*, 1959, **12**, 206.

- 31 Z. Syklarska-Smialowski and M. Smialowski, *J. Electrochem. Soc.*, 1963, **110**, 444.
- 32 M. D. Archer and N. C. Grant, *Proc. R. Soc. London, Ser. A*, 1984, **395**, 165.
- 33 K. Pillai and R. Narayan, *J. Electrochem. Soc.*, 1978, **125**, 1393.
- 34 V. P. Vasil'ev, V. I. Shorokhova, A. V. Katrovtseva and G. S. Lamakina, *Electrokhimiya*, 1983, **19**, 453.
- 35 A. A. Sutyagina, N. I. Il'chenko, M. N. Semenenko and G. D. Vovchenko, *Electrokhimiya*, 1979, **15**, 1094.
- 36 A. A. Sutyagina, I. L. Volchkova and M. N. Semenenko, *Russ. J. Phys. Chem.*, 1989, **63**, 714.
- 37 Y. B. Vassiliev, V. S. Bagotzky, O. A. Khazova, T. N. Yastrebova and T. A. Sergeeva, *Electrochim. Acta*, 1981, **26**, 563.
- 38 H. Ebert, R. Parsons, G. Ritzoulis and T. Van der Noot, *J. Electroanal. Chem.*, 1989, **264**, 181.
- 39 A. Streitwieser and C. H. Heathcock, *Introduction to Organic Chemistry*, MacMillan, New York, 1976, p. 13.
- 40 G. A. Bogdanovsky, G. P. Khomchenko and A. I. Shylgin, *Catalytic Reactions in Liquid Phase*, Alma-Ata, Acad. Sci. Kayakh SSR, 1963, p. 276.
- 41 G. A. Bogdanovsky and G. D. Vovchenko, *Kinet. Katal.*, 1969, **10**, 923; *Electrokhimiya*, 1970, **6**, 318.
- 42 V. P. Vasil'ev, V. I. Shorokhova, N. K. Grechina and L. V. Katrovtseva, *Russ. J. Inorg. Chem.*, 1978, **23**, 1274.
- 43 D. A. Harrington and B. E. Conway, *J. Electroanal. Chem.*, 1987, **221**, 1.
- 44 P. Zoltowski, *J. Electroanal. Chem.*, 1988, **240**, 53.
- 45 L. Bai and B. E. Conway, *Electrochim. Acta*, 1993, **38**, 1803.
- 46 L. Bai and B. E. Conway, *J. Electrochem. Soc.*, 1991 **138**, 2897.
- 47 L. Bai and B. E. Conway, *J. Electrochem. Soc.*, 1990, **137**, 3737.

Paper 6/02448C; Received 9th April, 1996