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Effects of catalyst poisons on UPD and OPD H coverage at H_2-evolving cathodes in relation to H sorption into the metals

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Abstract

In a previous paper we have directed attention to the apparently anomalous situation that at H_2 evolving cathodes, e.g. Fe, steels, Ti, chemisorption of catalyst poisons such as S or As-containing compounds much enhance the rate or extent of H sorption into such metals yet they diminish the coverage by adsorbed H that is the intermediate in the H_2-evolution reaction (HER) and the source of the sorbed H. In new work presented in this paper, the effects of competitive chemisorption of thiourea, cysteine, diethanolsulphide and As-species on the underpotential deposition (UPD) of H, i.e. below the H_2/H^+, reversible potential, and on the extra overpotential-deposited (OPD) H associated with the mechanism of the HER, are quantitatively evaluated at Pt and Pd by means of cyclic voltammetry, steady-state polarization measurements and potential-step transients. H transfer rates through Fe-membrane bielectrodes are increased 10-fold by the presence of 31 p.p.m. As in the charging solution. Since H coverage is substantially reduced by the As, and H diffusion is a bulk process, this enhancement must be due to a kinetic effect in the interfacial of H transfer into the metal.

Keywords: Chemisorption; Cathodes; Catalysis

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1. Introduction

An outstanding problem connected with electrochemical sorption of H into transition-metal cathodes is that strongly adsorbing catalyst poisons, such as S- and As- containing compounds, substantially enhance the rate of sorption of electrogenerated H into such electrodes yet they largely block the metal surfaces for H adsorption, so that steady-state H-coverages are diminished in a major way. Explanations that have been tendered [1] for this effect are quite controversial. Previously, Conway and Jerkiewicz [2] demonstrated that the enhancement effect could only arise for thermodynamic reasons if the chemical potential of adsorbed H was raised by the co-adsorbed poison through 2-d lateral interaction effects.

In the present paper we examine the effects of co-adsorbed S- and As-containing catalyst poisons on the cathodic H_2 evolution kinetics and the extent of H adsorption at Pt and Pd. Also, the effect of the poisons and changing the proton (H) source from alkaline water to the melt KF.2HF, both at 85 °C, on the apparent values of the H diffusion constant in the metal is examined in relation to identification of the rate-controlling process in electrochemical H sorption and diffusion.

2. Experimental

2.1. Briefly, the methodologies employed in this work were as follows

Effects of thiourea, cysteine, diethanolsulphide and As (as As_2O_3 dissolved into the supporting electrolyte solution) on (a) the underpotential deposition (UPD) of H at Pt and (b) cathodic kinetics of the H_2 evolution reaction (HER) at Pt, were studied. In the case of thiourea and As-species, the competitive adsorption behavior of the poisons vis à vis H was determined from cyclic voltammetry at Pt electrodes in the H UPD range of potentials (0.05 to 0.35 V versus RHE).

In other experiments on the kinetics of the overall HER, ‘‘iR’’ -corrected Tafel relations were determined at Pt in the absence and presence of poisons and the potential-relaxation method [3] was employed to evaluate changes of coverage by overpotentially-deposited (OPD) H, the chemisorbed intermediate in the HER.

Electrochemical H-transfer experiments were conducted

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at Fe, as a membrane bi-electrode, from aq. 0.5M NaOH and from a KF.2HF melt, both at 358 K, in order to investigate the effect of proton source at the H-injection side on the derived apparent H-diffusion constants, *D*, in the metal cathode materials.

Two methods were employed to determine (apparent) *D* values: (a) the $t_{1/2}$ method, [4,5] in which the time required for a cathodic H-sorption transient current to reach half of its final steady-state value at a membrane bi-electrode was determined; and (b) computer simulation of the whole sorption transient to obtain a non-linear, least-squares best-fit curve which thus corresponds to the desired *D* value. Both procedures are based on the following equation for the ratio of the time-dependent sorption current, i_t, to that in the limit in the steady-state ($t \rightarrow \infty$, $i = i_\infty$):

$$\frac{i}{i\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{n=\infty} \frac{(-1)^n}{2n+1} \exp\left[-\frac{\pi^2 (2n+1)^2 Dt}{4L^2} \right] \qquad (1)$$

where *n* is a series of integer values in the summation involved in Eq. (1) and *L* is the path-length for semi-infinite diffusion through the metal-host membrane. Eq. (1) usually converges after a small number of terms have been taken in the summation.

Returning to procedure (a), when $i_t / i_\infty = 1/2$, Eq. (1) leads to $t_{1/2} = 0.379\ L^2/D$ from which *D* is determined. Procedure (b) finds the best-fit value of *D* required to represent the experimental sorption transient according to Eq. (1).

The effect of As(III) species on the transfer and apparent diffusion behavior of H was thus evaluated.

Complementarily, a series of experiments were conducted on the effect of thiourea on the cathodic sorption of H into, and the anodic desorption out of, a thin Pd membrane electrode. Galvanostatic charging and discharging, together with single-cycle voltammetry, were the experimental procedures employed (see Fig. 7 later).

Apart from the deliberate additions of poison species, all experiments were done under the conditions we have previously developed [6] for “high-purity” interfacial and electrode-kinetic measurements.

3. Results and discussion

3.1. Competitive isotherms for blocking of UPD of H at Pt by As species and thiourea

The competitive blocking of UPD of H in the potential range 0.05 to ca 0.35 V (RHE) can be accurately determined by slow cyclic voltammetry (25 mV s^{-1}) as shown in Fig. 1 for thiourea. This diagram shows the current–response profiles for underpotential deposition and desorption of H electrosorbed in the process $H_2O + e + Pt \rightarrow Pt/H + OH^-$, i.e. below the H_2/H_2O reversible potential in 0.5 mol dm^{-3} aq. H_2SO_4, with progressively added thiourea at concentrations 0 and 5×10^{-8} to 1×10^{-4}M. The resulting series of curves demonstrate progressive competitive blocking of Pt sites by thiourea that are otherwise available for H chemisorption up to a monolayer near a potential of 0.05 V, RHE. The two maxima correspond to distinguishable principal states of chemisorption of H at two main crystallographic orientations of exposed Pt micro-grains at the electrode surface as found first in the work of Will and Knorr [7].

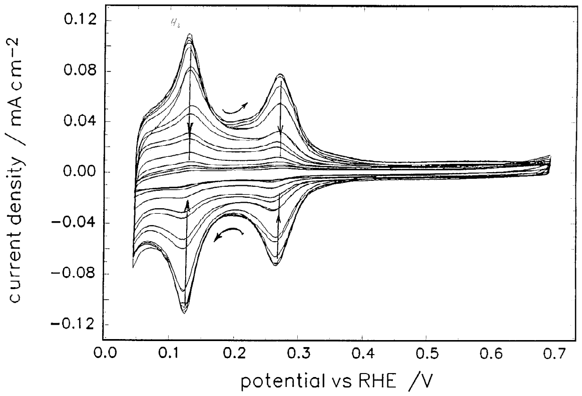

Fig. 1. Cyclic voltammograms of UPD H at polycrystalline Pt at 298 K in 0.5 mol dm^{-3} $H_2SO_4 + x$ mol dm^{-3} thiourea: 5×10^8 mol $dm^{-3} < x < 1\times10^{-4}$ mol dm^{-3}, scan rate 25 mV sec^{-1}. Arrows show directions of decrease of anodic and cathodic current responses corresponding to progressive increases of thiourea concentration and diminution of Pt sites available for H electrosorption.

By evaluation of the charges for H adsorption or desorption by integration of the current versus potential (≡ time) profiles in the usual way, the coverages by H as a function of potential and thiourea concentration can be evaluated. From these data the adsorption isotherm of thiourea is derived as shown in Fig. 2, together with isotherms for cysteine and cysteine hydrochloride at Pt, similarly derived. Cysteine has the strongest H-blocking effect and θ_H is reduced to near zero by a concentration

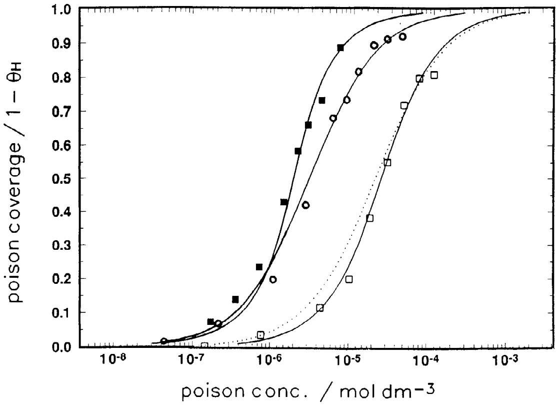

Fig. 2. Coverages of UPD H as a function of poison concentration in 0.5 mol dm^{-3} H_2SO_4 on Pt. (o) thiourea; (■) cysteine; (□) cysteine (HCl); (—— or · · ·) indicate Langmuir or Frumkin isotherm behaviour. Data from curves such as in Fig. 1.

around 10^{-4} mol dm^{-3}. At polycrystalline Pt (Fig. 1) thiourea in 0.5 mol dm^{-3} H_2SO_4 blocks the two main distinguishable H adsorption states (at 0.12 and 0.26 V, RHE) to almost the same relative extent with increasing concentration. As (present initially as AsO_2^- ions) is more selectively adsorbed over the first H peak at 0.26 V, RHE, in 2 mol dm^{-3} KOH solution.

3.2. Blocking of adsorption of the OPD H intermediate in the HER in relation to Tafel plots

In order to relate the effects of adsorption of the poisons (P) to the kinetics of the HER the coverages, θ_P, by the respective poisons as a function of overpotential η are required. They cannot be directly determined, e.g. by cyclic voltammetry as in the case of UPD H coverages. 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 being continuously bubbled around the Pt electrode and, because small surface area electrodes were used, little H_2 had been evolved, thus minimizing interference with the θ_P determinations by H_2 reoxidation currents. This procedure enabled evaluation of θ_P, from $\Delta\theta_H$, when P had been initially preadsorbed from a given concentration in a separate solution. The method had been validated by separate experiments in which no poison had been adsorbed. In this ex situ type of experiment no further poison adsorption could take place during the Tafel polarization runs. This technique was also found to be applicable to in situ experiments, when rates of adsorption of poisons already in solution were sufficiently slow that θ_P did not change during its evaluation in the H UPD region.

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 above after steady-state cathodic polarization at each potential had been attained in the Tafel curve measurements. As η was increased, θ_H was found to increase semi-logarithmically with η, with a slope of −81 mV per decade (inset Fig. 3), due to progressive desorption of thiourea with increasing η. Placing this value in Eq. (2) below for $d \ln \theta_H / d\eta$, a Tafel slope of −48 mV per decade results, similar to the experimental value of −41 mV per decade (Fig. 3). Correspondingly a calculated Tafel plot can be constructed and compared with the experimental behaviour as in Fig. 3.

3.3. Electrode-kinetical aspects of the poison effects on the HER

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_o) and Tafel slope

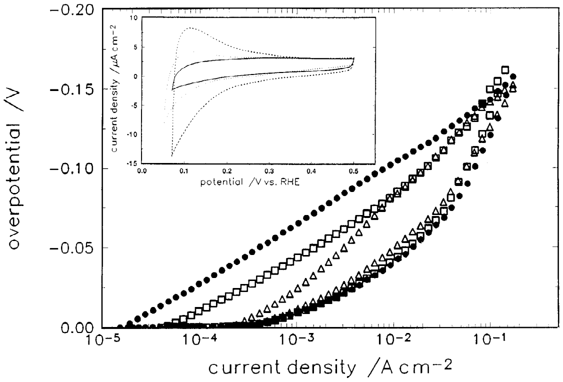

Fig. 3. Tafel plots of the HER showing ascending and descending polarizations for the HER at polycrystalline Pt in 0.5 mol dm^{-3} aq. H_2SO_4 at 298 K taken after ex situ adsorption (•) thiourea; (□) cysteine; (Δ) DES; *Inset*; Cyclic voltammograms taken before the cathodic polarizations shown. (———) thiourea; (····) cysteine; (—–) DES, scan rate 50 mV s^{-1}.

(b) values. Especially the latter can be indicative of the effects of the poisons on the potential dependence of θ_H and thus [8] on the mechanism of the overall HER. The Tafel slope, b, for the HER under conditions when the coverage by OPD H is appreciable and potential-dependent is given [8] by

$$b^{-1} = \frac{d \ln \theta_H}{d\eta} + \frac{\beta F}{RT} \tag{2}$$

where β is the barrier symmetry factor for electron transfer ($\beta \simeq 0.5$) in the electrochemical type of H-desorption step in the HER viz. $MH_{ads} + H_3O^+ + e \rightarrow M + H_2 + H_2O$.

At active, clean Pt surfaces, the IR-corrected Tafel relations are curved (Fig. 4) indicating involvement of the recombinative ($2MH_{ads} \rightarrow 2M + 2H_2$) mechanism, (the curvature is not due to diffusion control as was shown by rotating-disc electrode measurements). However, when thiourea is present in the electrolyte, a linear region is

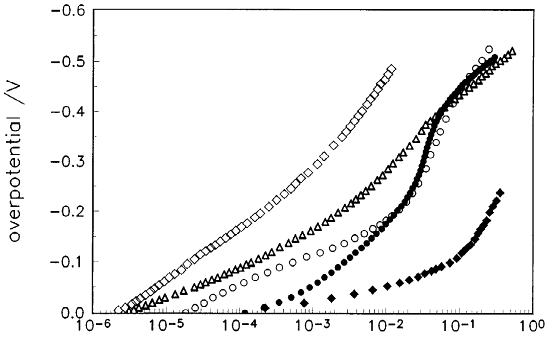

Fig. 4. IR-corrected Tafel plots for the HER in various supporting electrolytes with addition of 5×10^{-3} mol dm^{-3} thiourea: (◊) 2 mol dm^{-3} H_2SO_4; (Δ) 0.5 mol dm^{-3} H_2SO_4; (O) 0.5 mol dm^{-3} NaOH; The corresponding poison-free behaviour is shown by (•) for 0.5 mol dm^{-3} NaOH and by (♦) for 2 mol dm^{-3} and 0.5 mol dm^{-3} aq. H_2SO_4.

observed over several decades of current-density (Fig. 4) having b near -60 mV. Such a value is difficult to account for conventionally (cf. Eq. (1) and Ref. 4) through any of the usual steps in the HER 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, the coverage by which is dependent on η over the range of the observed Tafel plot.

The effects of thiourea at a H_2-evolving cathode are complicated by its electrocatalytic reduction through either or both of the following surface reactions. Alternative steps are as follows, one involving OPD H:

$$\mathrm{M-thiourea_{(ads)}+4M-H_{(ads)}\Rightarrow H_2S+H_2C(NH_2)_2+M} \tag{3}$$

and the other an electrochemical step involving proton discharge:

$$\mathrm{M-thiourea_{(ads)}+4H_3O^+ + 4e^- \Rightarrow H_2S+H_2C(NH_2)_2 + 4H_2O} \tag{4}$$

Elsewhere we have examined whether 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, taking account of electrochemical hydrogenation of thiourea [9,10]. A kinetic analysis in terms of fitted rate-constants for the electrochemical discharge and desorption steps of the HER, and reaction 4, enables θ_H and the Tafel η versus log i relation to be calculated from $i=F(\nu_1+\nu_2)+4F\nu_4$.

On the basis of the above approach, the experimental $i(\eta)$ behaviour for thiourea adsorption and hydrogenation in 0.5 mol dm^{-3} H_2SO_4, occurring during the HER, was fitted using a non-linear least squares calculation as in Fig. 5 for which the rate constants required for a good fit were evaluated. ν_1, ν_2, ν_3 and ν_4 in Fig. 5 are the component velocities of the discharge and the two desorption steps in the HER, and ν_4 refers to reaction 3. The resulting relative coverage versus potential relationships for both thiourea and the OPD H are shown in Fig. 6.

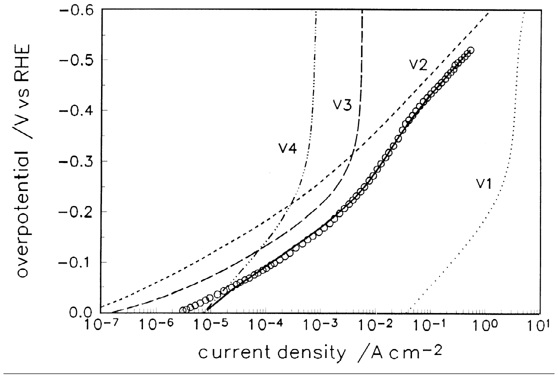

Fig. 5. Tafel plots for the HER and EHR in 0.5 mol dm^{-3} H_2SO_4+ 5.110^{-3} mol dm^{-3} thiourea. (o) experimental data; (-) best-fit line; the broken lines represent the contributions of each of the reaction steps; (ν_1, ν_2 and ν_3) for the HER; (ν_4) for the EHR.

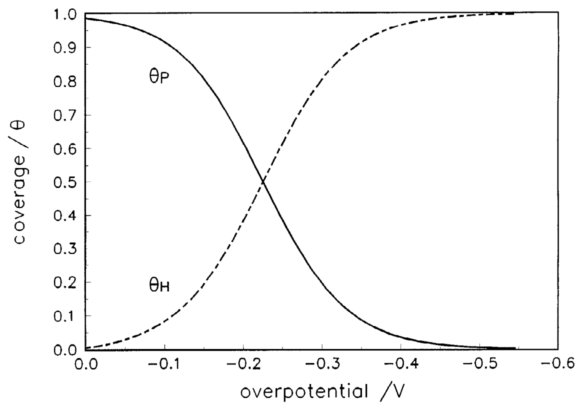

Fig. 6. Coverage versus overpotential calculated from the rate constants determined from the kinetic fitting of the experimental data in Fig. 5.

3.4. *Effect of thiourea on H sorption and desorption at Pd*

Here we return to the general topic of effects of poisons on H sorption. Experiments were conducted on H sorption and desorption at a Pd cathode in the presence and absence of thiourea.

Fig. 7 (inset) shows a linear (anodic) potential scan of H desorption current from Pd following cathodic charging at 67 mV versus RHE for 10 min in (a) clean, poison-free 0.5 mol dm^{-3} H_2SO_4 solution and (b) after charging in the same solution but discharging from the solution made from 1×10^{-3} mol dm^{-3} in thiourea. The same charge for H desorption is recovered (90 μC) as for the clean solution but only over a much more positive potential range, 0.8 to 1.6 V. Thus anodic desorption of H is completely inhibited so long as thiourea remains on the surface. Correspondingly, the main curves in Fig. 7 shows the H oxidative

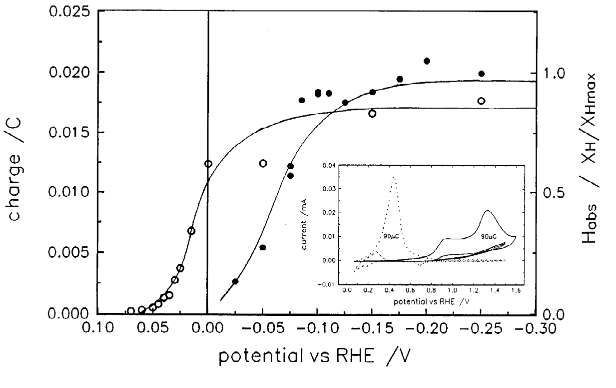

Fig. 7. The quantity of H absorbed into a Pd cathode as a function of cathodic charging potential in 0.5 mol dm^{-3} H_2SO_4 (o) 0.0 mol dm^{-3} thiourea; (•) 4.2×10^{-4} mol dm^{-3} thiourea; *Inset*; cyclic voltammograms of H_{abs} oxidation after charging in 0.5 mol dm^{-3} $H_2SO_4+1\times10^{-3}$ mol dm^{-3} thiourea. Total desorption charge is 90 μC in each case.

desorption charges for H previously sorbed into Pd at various potentials in the range 0.07 V to −0.25 V, as a function of those potentials, in the presence and absence of thiourea. Evidently, for the former conditions, significant H sorption begins only when charging potentials more negative than ca. 0.00 V versus RHE are applied, i.e. when OPD H is appearing.

3.5. As effects on H sorption rates into Pd and Fe

In these experiments, rates of sorption of H into Fe membrane bielectrodes were determined by the classical method of anodic desorption of H from the transfer side following cathodic H injection pulses. The Fe membranes were Pd-coated on the transfer side to avoid corrosion or passivation. H transfer rates and apparent diffusion constants, *D*, were determined by the ‘‘half-time’’ for the rise of the transient, as described earlier.

The H permeation current, i_a, into Fe is enhanced by a factor of 2 to 2.5 times (Fig. 8) at a cathodic charging current-density of -0.1 mA cm^{-2} and by about 10 times at a charging rates of -1 mA cm^{-2}.

For transfer through Fe from the KF.2HF melt and from 0.2 mol dm^{-3} NAOH, each at 358 K and in the absence of a poison, the derived *D* values were $2.3 \pm 0.3 \times 10^{-4}$ cm^2 s^{-1} and $2.7 \pm 0.3 \times 10^{-4}$ cm^2 s^{-1}, respectively, i.e. there is little dependence on the proton source at the given temperature, as is to be expected. The *D* datum for the KF.2HF melt corresponds to the diffusion coefficient values that are determined for H as steady-state diffusional transfer is approached at appreciable cathodic current-densities as shown in the upper curve in Fig. 9. Literature values for the diffusion coefficient of H in Fe deposited from aqueous solutions are available for a temperature of 298 K [4] and depend appreciably on the conditions of preparation of the Fe sample, values being in the range 8×10^{-5} to 1.2×10^{-5} s^{-1}. Our values are somewhat larger, due to the higher temperature (358 K) at which experiments were conducted.

Fig. 9 shows the apparent diffusion constants for H permeation in to the Fe electrode, derived by an analysis of the permeation transients, as a function of cathodic charging current in the absence and presence of As (As_2O_3) dissolved in the solution at a concentration of 31 ppm. Since the process of migration of H within the Fe electrode cannot be influenced by externally absorbed poison, the difference between the upper and lower curves of Fig. 9 must originate from a *surface* electrochemical effect of the As on the kinetics and mechanism of the step of interphasial discharge and transfer of H.

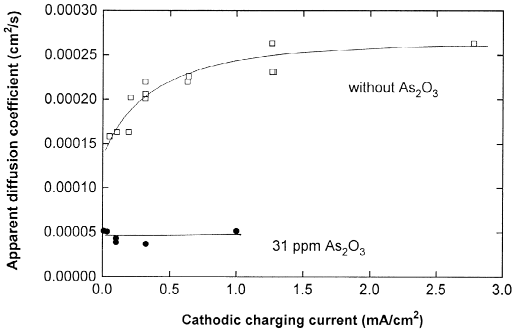

Fig. 9. Effect of 31 ppm As (as As_2O_3) on H permeation and transport in Fe from KF.2HF melt 85 °C, calculated as values of the apparent diffusion constant.

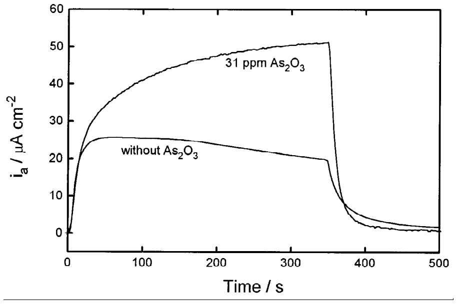

Fig. 8. Permeation current, i_a, for a 0.5 mm Fe membrane charged at -0.1 mA cm^{-2}, with and without the presence of As_2O_3 in KF.2HF melt at 85 °C.

Because competitive adsorption by As-, or S- compounds, substantially diminish θ_H, it must be concluded that the enhancement is due to change of mechanism of H entry across the metal interface, due to either: (a) the influence of the P species on the H transfer across the very first layer of metal atoms in the ‘‘skin’’ of the electrode into the bulk lattice, or (b) by a change from H-atom transfer (then blocked by P) to direct injection of much smaller protons into the lattice in a way that may be analogous to injection of Li^+ cations directly from a solvated state into layer–lattice structures such as TiS_2 or MoS_2. Thermodynamic effects [2,11,12] do not adequately explain the behaviour. H transfer in mechanism (a) could be influenced by a change of surface potential (χ) and associated field due to chemisorption of the poison; $\Delta\chi$ changes due to the presence of adsorbates can be large (~0.5 V). Correspondingly, the local electronegativities of surface metal atoms will generally be diminished by adsorption of an electro-donative poison.

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