

# The effect of surface species on the rate of H sorption into nanostructured Pd

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**Studies of the hydrogen region of nanostructured H<sub>1</sub>-e Pd films in 1 M sulfuric acid in the presence of crystal violet, or when small amounts of Pt are deposited on to the surface, show that the adsorption of hydrogen onto the metal surface is suppressed but that at the same time the kinetics of absorption of hydrogen into the Pd to form the β-hydride are significantly enhanced suggesting that the strongly adsorbed hydrogen on the Pd surface acts as a blocking layer for absorption of hydrogen into the Pd lattice.**

## 1. Introduction

Mesoporous metals with regular nanoarchitectures can be prepared using chemical or electrochemical reduction of a metal salt dissolved in the aqueous domains of a lyotropic liquid crystalline phase.<sup>1,2</sup> In this approach the metal is formed from the lyotropic liquid crystalline phase of a non-ionic surfactant formed from a high concentration of surfactant (typically between 30 and 60 wt.%) and an aqueous solution of the appropriate metal salt. The resulting metals are “casts” of the particular lyotropic phase used so that it is possible to produce mesoporous metals with different pore topologies and with different pore and wall thicknesses depending on the choice of surfactant and template solution composition.<sup>1</sup> Following the original work on the electrochemical deposition of mesoporous platinum films,<sup>1,3–5</sup> this approach has been extended to the deposition of several other metals including cobalt,<sup>6</sup> nickel,<sup>7</sup> tin,<sup>8</sup> rhodium<sup>9</sup> and palladium.<sup>10</sup>

The electrochemistry of Pd differs significantly from that of Pt because Pd is able to absorb large quantities of hydrogen forming Pd α- and β-hydride phases.<sup>11</sup> In previous studies<sup>10</sup> we were therefore particularly interested in the effects of the nanostructure of the Pd on this process. In Pd films deposited from the H<sub>1</sub> hexagonal lyotropic liquid crystalline phase of C<sub>16</sub>EO<sub>8</sub> or Brij56<sup>®</sup> the Pd walls between the pores are only a few nanometres thick. Consequently the diffusion of hydrogen atoms into Pd bulk is not the rate-limiting step. This allows us to distinguish between the adsorbed and absorbed hydrogen in the voltammetry of these H<sub>1</sub>-e Pd films (here we use the term H<sub>1</sub>-e to denote the metal electrochemically deposited from the H<sub>1</sub> lyotropic liquid crystalline phase and having the corresponding regular nanoporous structure). Upon addition of crystal violet to the solution the Pd surface is blocked and the H-adsorption is suppressed.<sup>12</sup>

In this paper we present results showing the effects of crystal violet and sub-monolayer coverages of Pt on the voltammetry of H<sub>1</sub>-e Pd films in acid solution. We compare the voltammetric peaks associated with the formation and oxidation of the β-hydride phase and the formation and stripping of adsorbed

hydrogen with and without either crystal violet or Pt present. We show that in when either crystal violet or Pt is present on the H<sub>1</sub>-e Pd surface the adsorption of hydrogen is suppressed and at the same time the kinetics for formation of the β-hydride phase are significantly enhanced.

## 2. Experimental

Hydrochloric acid (AnalaR BDH), sulfuric acid (AnalaR BDH), ammonium tetrachloropalladate (premin-99.998% Alfa Aesar), hydrogen hexachloroplatinate (IV) hydrate (99.9% Aldrich), Brij56<sup>®</sup> (Aldrich), crystal violet (Aldrich), octaethyleneglycol monohexadecyl ether (C<sub>16</sub>EO<sub>8</sub>, Fluka), and heptane (99%, Lancaster) were all used as received. All aqueous solutions were freshly prepared using reagent-grade water (18 MΩ cm) from a Whatman “Stillplus” system coupled to a Whatman RO 50. All glassware were soaked overnight in a 3% Decon/deionized water solution and washed thoroughly at least three times with deionized water prior to use.

All electrochemical experiments were carried out using an EG&G Model 263A potentiostat/galvanostat with a large area platinum gauze counter electrode and either a homemade saturated mercury sulfate (SMSE) or saturated calomel electrode (SCE) reference electrode. The counter electrode was a large area platinum gauze. The SMSE was used to avoid chloride contamination of the sulfuric acid electrolyte solution used in the studies of the nanostructured metal electrodes and all potentials are reported with respect to this reference electrode (potentials with respect to SMSE are shifted 0.45 V negatively of the corresponding potential vs. SCE). The reference electrode was used in conjunction with a luggin capillary and stored in a saturated potassium sulfate solution when not in use.

The phase of the lyotropic liquid crystalline plating mixtures was confirmed by polarized light microscopy using an Olympus BH-2 polarized light microscope equipped with a Linkam TMS90 heating stage and temperature control unit. Phases were assigned on the basis of their characteristic optical textures.<sup>13</sup>

The H<sub>1</sub>-e Pd films were freshly prepared before each electrochemical experiment by electrochemical deposition on to gold disc electrodes (area 0.0079 m<sup>2</sup>) formed by sealing 1 ± 0.1 mm diameter gold wire in glass. Immediately before use, the gold disc electrodes were freshly polished using silicon carbide paper (Cc 1200, English Abrasives) and then alumina/water slurries (Buehler) starting with a particle size of 25 μm and ending with a particle size of 0.3 μm. H<sub>1</sub>-e Pd films were deposited from a solution containing 12 wt.% (NH<sub>4</sub>)PdCl<sub>4</sub>, 47 wt.% C<sub>16</sub>EO<sub>8</sub> or Brij56<sup>®</sup>, 39 wt.% water and 2 wt.% heptane at 25 °C. These conditions correspond to the hexagonal (H<sub>1</sub>) lyotropic phase for both mixtures as determined by studies of the phase diagram for the system. These deposition mixtures are highly viscous and must be prepared with care to ensure a uniform

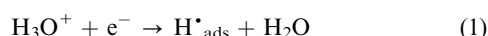
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composition. After all of the components were mixed, the mixture was heated and stirred to ensure homogeneity and then cooled before use. Pd was deposited from the liquid crystalline plating mixture at 0.1 V. After deposition the H<sub>1</sub>-e metal films were rinsed in purified water to remove the adherent surfactant mixture.

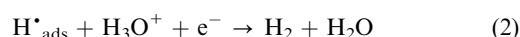
Electrochemical measurements on the H<sub>1</sub>-e Pd films were carried out at room temperature (18–23 °C) in 1 M H<sub>2</sub>SO<sub>4</sub>. Before each experiment the solution was sparged for 10–15 min with a stream of highly purified argon gas to displace dissolved oxygen. The electrochemical active surface areas of the H<sub>1</sub>-e Pd films were estimated by integrating the charge passed in the surface oxide stripping reaction recorded in 1 M sulfuric acid following the procedure suggested by Rand and Woods.<sup>14</sup> Small amounts of Pt were deposited onto the H<sub>1</sub>-e Pd surface from an aqueous solution containing 25 mM H<sub>2</sub>PtCl<sub>6</sub> and 1 M HCl. The surface coverages were calculated from the charge passed to deposit the Pt and the surface areas of the H<sub>1</sub>-e Pd films determined from the voltammetry.

### 3. Results and discussion

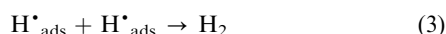
The hydrogen electrode reaction at transition metal electrodes can take place in alkaline as well as in acid media by a multistep sequence which can be described as the Volmer–Heyrovsky–Tafel mechanism.<sup>15–19</sup> The first step in its process is the formation of adsorbed hydrogen on the metal surface from the discharge of H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup> (Volmer reaction).



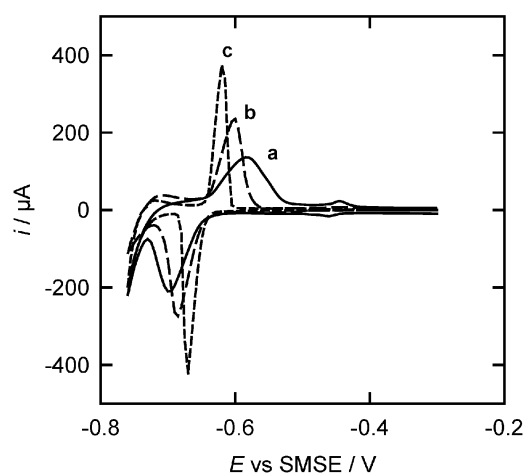
where H<sup>\*</sup><sub>ads</sub> is an adsorbed hydrogen at the metal surface. This is followed by either an electrochemical step (Heyrovsky reaction)



or by a chemical step (Tafel reaction)



For Pd electrodes this picture is complicated by the absorption of hydrogen atoms into the bulk of the metal to form the Pd hydride phases. There is no clear consensus in the literature about the mechanism by which the hydrogen enters the metal.<sup>16,17–19</sup> In particular it is not clear whether adsorbed hydrogen atoms formed in the Volmer reaction are intermediates in the process or not. It has been suggested that a sub-surface layer of sorbed hydrogen may be involved.<sup>15,19–22</sup>

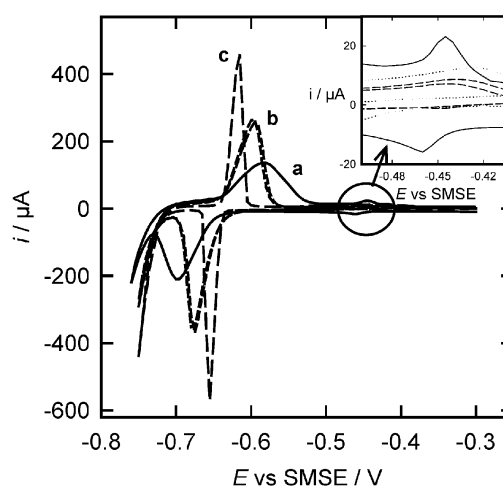


**Fig. 1** Set of cyclic voltammograms of H<sub>1</sub>-e Pd (200 nm thick, deposition charge 3.5 mC, deposited from the Brij56<sup>®</sup> plating bath) deposited on a gold disc electrode (area 0.0079 cm<sup>2</sup>) recorded at 10 mV s<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> (a) without crystal violet, (b) in the presence of 0.5 mM, and (c) 1 mM crystal violet.

Fig. 1a) shows the cyclic voltammetry of a freshly prepared H<sub>1</sub>-e Pd film recorded at 10 mV s<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> without crystal violet added to the solution. The voltammogram shows two well separated voltammetric features associated to the formation of adsorbed and absorbed hydrogen. The pair of peaks at -0.46 V on the cathodic and at -0.445 V vs. SMSE on the anodic scan correspond to the formation and stripping of adsorbed hydrogen on the Pd surface. The larger pair of peaks at -0.7 V on the cathodic scan and at -0.58 V vs. SMSE on the anodic scan correspond to the entry of hydrogen into the bulk of the metal to form the β-hydride and its oxidation on the return sweep.<sup>10</sup> Curves (b) and (c) in the same figure show the effect of 0.5 and 1 mM crystal violet on the voltammetry. The first striking difference to the voltammetry shown in (a) is the absence of the peaks for adsorbed hydrogen onto Pd. From previous studies it is well known that crystal violet adsorbs onto the Pd surface and blocks hydrogen adsorption.<sup>10,12</sup> Thus our results show that the crystal violet is able to diffuse into the pores of the nanostructure and adsorb to the walls of the pores within the Pd film even though it is quite large (diameter ~1.4 nm) compared to the diameter of the pores themselves (diameter 3 nm).

From comparison of the three voltammograms we can also see that the crystal violet has a significant effect on the voltammetry associated with the formation of the β-hydride phase. As the concentration of crystal violet increases the separation of the pair of peaks associated with the β-hydride phase decreases (from 110 to 50 mV), the peaks become sharper (the peak width changes from 70 to 25 mV) and the peak height increases. Nevertheless the charge associated with the peaks and the mid-peak potential (0.65 V vs. SMSE) remain unchanged. These changes indicate that the thermodynamics of the reaction are unchanged but that the kinetics of the reaction are significantly accelerated by the adsorbed crystal violet. A similar, but less dramatic, effect was observed by Baldauf and Kolb in their experiments on thin (5 ML) epitaxial layers of Pd deposited on Au(111) single crystals.<sup>12</sup>

An almost identical effect can be produced by the deposition of small amounts of Pt onto the H<sub>1</sub>-e Pd surface. Fig. 2 shows a set of cyclic voltammograms recorded at 10 mV s<sup>-1</sup> in 1 M sulfuric acid for H<sub>1</sub>-e Pd electrodes with different amounts of Pt deposited on the surface. As the surface coverage of Pt



**Fig. 2** Set of cyclic voltammograms at 10 mV s<sup>-1</sup> in 1 M sulfuric acid of Pt deposited from the aqueous solution containing 25 mM H<sub>2</sub>PtCl<sub>6</sub> and 1 M HCl onto H<sub>1</sub>-e Pd with increasing number of Pt atoms covering the Pd surface. H<sub>1</sub>-e Pd (a) was initially deposited onto a (0.0079 cm<sup>2</sup>) gold disc electrode (3.5 mC total deposition charge). In curve (b) 1 Pt atom and in curve (c) 3 Pt atoms are for every 10 Pd atoms. This corresponds to a Pt coverage on the Pd surface of 0.1 and 0.3 monolayers.

increases from zero to 0.3 ML the voltammetric peaks associated with the  $\beta$ -hydride become narrower (going from 70 to 20 mV) and the peak separation decreases (from 113 to 37 mV) whereas the charge under the peaks and the midpeak potential (0.64 V vs. SMSE) is unchanged. At the same time voltammetric peaks associated with the hydrogen adsorption decrease (see inset) showing that the adsorption of hydrogen on the Pd surface is blocked by the presence of the Pt. Inspection of the voltammograms recorded with 1 mM crystal violet or 0.3 ML Pt present show that in both cases the voltammetry is limited by the uncompensated solution resistance within the pores of 36  $\Omega$ . This is supported by the results of studies at different sweep rates (not shown).

There is, however, one significant difference between the results in Figs. 1 and 2. In the case of crystal violet (Fig. 1) the current for the evolution of hydrogen at the extreme cathodic limit of the sweep is unchanged by the addition of 1 mM crystal violet to the solution. In contrast the presence of 0.3 ML of Pt on the electrode surface (Fig. 2) more than doubles the hydrogen evolution current at the cathodic limit of the sweep. This indicates that the presence of Pt on the surface has the expected catalytic effect on hydrogen evolution.

Although the effects of poisons on the rate of hydrogen absorption into metals, including Pd, are well known there is no clear consensus on the mechanism of this effect. The different models suggested in the literature have been discussed by Conway and Jerkiewicz.<sup>15</sup> Beck *et al.* have suggested that the poisons interfere with the H atom recombination step (reaction 3) in the cathodic evolution of H<sub>2</sub>.<sup>23</sup> According to this model the presence of the poison reduces the number of active sites for hydrogen adsorption on the Pd surface and, as a consequence, the rate of H<sub>2</sub> evolution is decreased. As a result the rate of formation of absorbed hydrogen from the adsorbed hydrogen intermediate,

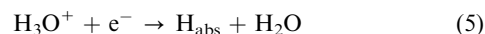


is increased. This model is not consistent with our experimental results; in the case of crystal violet we see no change in the rate of hydrogen evolution, in the case of Pt we see a significant increase in the rate of hydrogen evolution: in neither case do we see the decrease in the rate of hydrogen evolution posited by Beck *et al.*<sup>23</sup>

Conway and Jerkiewicz<sup>15</sup> propose an alternative explanation. They suggest that the adsorption of the poison at the electrode surface decreases the coverage of adsorbed hydrogen but increases the chemical potential of the adsorbed hydrogen. As a result, and based on a consideration of the shapes of the free energy curves for the reactions of hydrogen evolution and absorption,<sup>24</sup> one can explain why the poison increases the rate of absorption of hydrogen into the metal. In this model the formation of the absorbed hydrogen is assumed to occur through an adsorbed intermediate. However there is no direct experimental evidence in the literature for this. Our results (Fig. 1) clearly show that adsorption of hydrogen on H<sub>1</sub>-e Pd occurs at a potential which is 200 mV less negative than the absorption process (formation of upd hydrogen). The formation of adsorbed hydrogen from the adsorbed form is a chemical reaction; it is not driven by the applied potential. Therefore the strongly adsorbed upd hydrogen formed at around -0.45 V vs. SMSE cannot be an intermediate in formation of the absorbed hydrogen because the reaction is strongly thermodynamically unfavourable. Equally the intermediate cannot be the overpotential adsorbed (opd) hydrogen intermediate on the path to hydrogen evolution discussed by Jerkiewicz<sup>19</sup> because formation of the  $\beta$ -hydride phase occurs at a potential 46 mV anodic of hydrogen evolution.<sup>10</sup> Of course it is possible that there is a third adsorbed hydrogen intermediate which is a much less stable than the upd adsorbed hydrogen species and which is distinct from the opd adsorbed species which is an intermediate in the hydrogen

evolution reaction but there is no evidence for this from our experiments.

We therefore suggest, in the absence of clear evidence for an adsorbed intermediate, that the hydrogen absorption reaction occurs in a single step<sup>15</sup>



The effects of crystal violet and low coverages of Pt can then be explained in terms of a blocking of the surface by the adsorbed hydrogen which acts as a barrier to (rather than intermediate in) the formation of absorbed hydrogen. Once this barrier layer is removed by in presence of a poison such as crystal violet or by the presence of a sub-monolayer coverage of Pt reaction (5) can proceed at a much faster rate.

Whatever the explanation, the practical result is that for H<sub>1</sub>-e Pd electrodes the rates of absorption and desorption of hydrogen into the metal can be significantly enhanced by adding crystal violet or by deposition a small amount of Pt onto the surface. For these nanostructured films, because the walls of the Pd nanostructure are so thin diffusion of hydrogen through the Pd is not rate limiting, and the overall kinetics of the process become limited by the interfacial kinetics for the formation of the absorbed hydrogen in 1 M H<sub>2</sub>SO<sub>4</sub>. Upon addition of crystal violet or Pt the rate of the interfacial reaction is significantly increased until ultimately the rate becomes limited by the resistance of the electrolyte solution.

#### 4. Conclusion

In this paper we have shown that the high surface area of the H<sub>1</sub>-e Pd films allows us to clearly separate the upd of hydrogen on the electrode surface from the formation of the  $\alpha$  and  $\beta$ -hydride phases and hydrogen evolution. Our results show that when crystal violet is added to the bulk solution it is adsorbed onto the Pd surface. In the presence of crystal violet the formation of upd hydrogen is blocked and yet the rate of hydrogen absorption into the metal is significantly increased while the rate of hydrogen evolution is unchanged. We also find that modification of the H<sub>1</sub>-e Pd surface by a sub-monolayer coverage of Pt blocks the formation of upd hydrogen and again enhances the rate of absorption of hydrogen into the metal although in this case the rate of hydrogen evolution is increased.

Based on our results we suggest that the strongly adsorbed upd hydrogen acts as a barrier to absorption of hydrogen into the metal which occurs either in a single direct step or through an adsorbed hydrogen intermediate which is neither the strongly adsorbed upd hydrogen nor the opd hydrogen intermediate in the hydrogen evolution reaction.

Whatever the mechanism, our results show that absorption of hydrogen into H<sub>1</sub>-e Pd in the presence of either crystal violet or sub-monolayer coverage of Pt is so fast that it becomes iR drop limited in our experiments in 2 M H<sub>2</sub>SO<sub>4</sub>.

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