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Short communication

The effect of ultrasound on the electrochemical loading of hydrogen in palladium

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1. Introduction

Although the application of ultrasound for the control and modulation of various chemical processes is a subject of continued interest [1], there is surprisingly little discussion in the recent literature of the effects of ultrasound on fundamental electrochemical processes. In early systematic studies of the hydrogen evolution reaction under acidic conditions [2,3], it was observed that, on a platinum electrode, the overvoltage for hydrogen evolution decreased by up to 30 mV on the application of ultrasound, and that this decrease was largely independent of current density in the approximate range 1–100mA cm^{-2}, i.e. the Tafel slope was largely unaffected under these conditions. On removal of the ultrasound, the original polarization was regained only on continued electrolysis for up to 1 h. These results refer to electrolytes which had been pre-electrolysed for 10 to 20 h. With more extensive pre-electrolysis (36 h), the results were generally similar; however, the polarization decrease on the application of ultrasound was smaller (by a factor of two) under comparable conditions, and the original polarization was recovered rapidly on cessation of irradiation. On the application of ultrasound to a nickel electrode evolving hydrogen, the same general phenomenon was observed, i.e. a decrease in overvoltage without a significant change in Tafel slope [3]. For these experiments, the acoustic frequency was 300 kHz and the acoustic intensity was estimated to be approximately 1 W cm^{-2} of electrode area.

In attempting to explain these observations, two principal mechanisms were proposed [2,3]. The first involves the stripping of adsorbed impurities on irradiation with ultrasound, leading to an increase in the number of sites available for occupancy by surface adsorbed hydrogen atoms. The second effect, less important than the first although nonetheless operative, was thought to be the reduction in the degree of supersaturation of dissolved molecular hydrogen in the immediate vicinity of the electrode surface, due to micro-agitation associated with bubbles undergoing cavitation. Both these effects were predicted to lead to a decrease in polarization at constant current without affecting the Tafel slope [2].

For a cathodically polarized palladium electrode in an aqueous electrolyte, in addition to gaseous hydrogen evolution, the absorption of hydrogen will occur, as has been discussed extensively [4]. As the archetypal metal–hydrogen system, the properties of relatively highly-loaded compositions in the palladium–hydrogen system (i.e. values of the H/Pd atomic ratio in excess of 0.8) are of considerable interest [5]; in particular, the achievement of such loadings by electrochemical means is a subject which has received renewed attention recently [6,7].

In the hydrogen evolution reaction, surface adsorbed hydrogen atoms are generally acknowledged to be the key intermediate species. For a palladium cathode, at a given electrochemical current, net absorption (in a single-phase region) will proceed to a maximum extent determined by the chemical potential of the surface adsorbed hydrogen [8]. While this quantity may not be expected to be entirely uniform over the surface of an electrode, changes in the steady-state average hydrogen loading with varying experimental conditions will reflect changes in the (average)

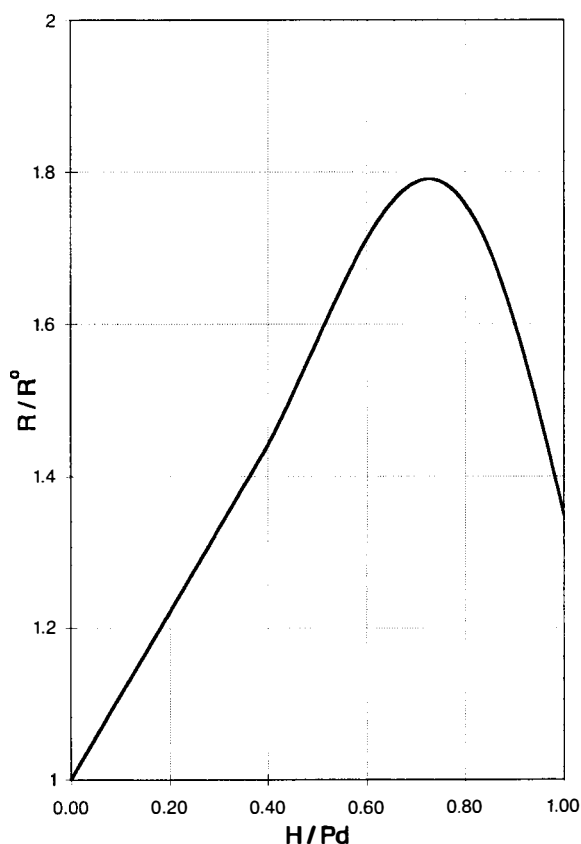* Corresponding author.
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Fig. 1. Variation of resistance with loading for the Pd–H system at 298 K. $R°$ is the resistance at $H/Pd = 0$.

surface chemical potential. The in situ average loading of a palladium cathode is most conveniently determined from a measurement of its four-point resistance, as has been discussed previously [6,7]. The correlation between resistance and loading employed in this work is shown in Fig. 1.

In this work, some preliminary results concerning the effect of ultrasonic irradiation on the hydrogen loading of palladium in β-phase PdH are reported. In addition to providing data concerning the interaction of ultrasound with a metal–hydrogen system, these results may be used more particularly to infer the effect of irradiation on the chemical potential of surface adsorbed hydrogen for a palladium electrode which is evolving hydrogen under cathodic polarization.

2. Experimental

The electrochemical cell used here was of a similar design to that employed previously [6]. The working volume of the cell consisted of a vertically-mounted quartz tube 2.5 cm in diameter and 17.5 cm high. A cylindrical cage (approximately 7.5 cm high and 2.5 cm in diameter) was constructed of quartz rods, held together with PTFE discs, and located at the bottom of the cell container. A platinum wire (0.5 mm diameter, 1 m long) was wound on

the outside of this cage and served as the anode. The cylindrical palladium (or platinum) cathode was mounted vertically in the centre of the cage. The cell, otherwise sealed, was connected, via a gas vent, to a bubbler.

Both acidic and basic aqueous electrolytes were employed. Approximately 45 cm³ of electrolyte was used; as the cells were run 'open', resulting in solvent loss by electrolysis, periodic water additions were made. In some experiments, the electrolyte temperature was monitored directly using an Omega K-type thermocouple, encased in Teflon tubing, and placed in the cell electrolyte.

Cylindrical palladium cathodes, 1 mm diameter and 3 cm long, were made from wire supplied by Engelhard (Part No. 44613; purity unknown). Pretreatment of the cathodes involved degreasing in trichloroethylene, then acetone then methanol and finally isopropanol before annealing for 3 h at 800°C, followed by slow cooling, in vacuo. PTFE sheathed platinum lead wires were spot-welded to the ends of each cathode (for current supply and four-point resistance measurement), which was then etched for 20–30 s in aqua regia, rinsed in water and tissue dried before placing in the cell. Cylindrical Engelhard platinum cathodes, 1 mm diameter and 3 cm long, were also prepared with the same pretreatment process described above, but without the annealing stage.

For the preliminary work reported here, experiments were performed with the cells suspended in a 345 W Branson B8200-4 ultrasonic bath operating at 20 kHz. An auxiliary Neslab CFT-75 refrigerated recirculator was used to maintain the bath temperature at 20 ± 1°C both with and without ultrasound generation. The length of the quartz cell casing was such that the location of the cathode within the bath could be varied; the experiments reported here were carried out with the cell sitting on the bottom of the bath. It was not possible to obtain a firm estimate of the acoustic power supplied to a given cell, although it is unlikely to be more than a few watts, given the relative volumes of the cell and the bath. Typically, two independent cells were operated simultaneously in the ultrasonic bath.

An automated data collection system was employed. A typical set-up involved an Apple Macintosh IIsi computer and an IOTech MacSCS1488 bus controller for data storage and experiment control with Keithley models 706 scanner and 195A digital multimeter for cell voltage and current measurement. Electrochemical power was supplied using an HP 66000A MPS mainframe containing two DC HP66105A (0–20 V) power modules. Axial cathode resistance was measured using a separate Tecrad DMO-350 digital micro-ohmmeter for each operating cell.

3. Results

Representative results from three experiments, denoted I, II and III, involving three different palladium cathodes
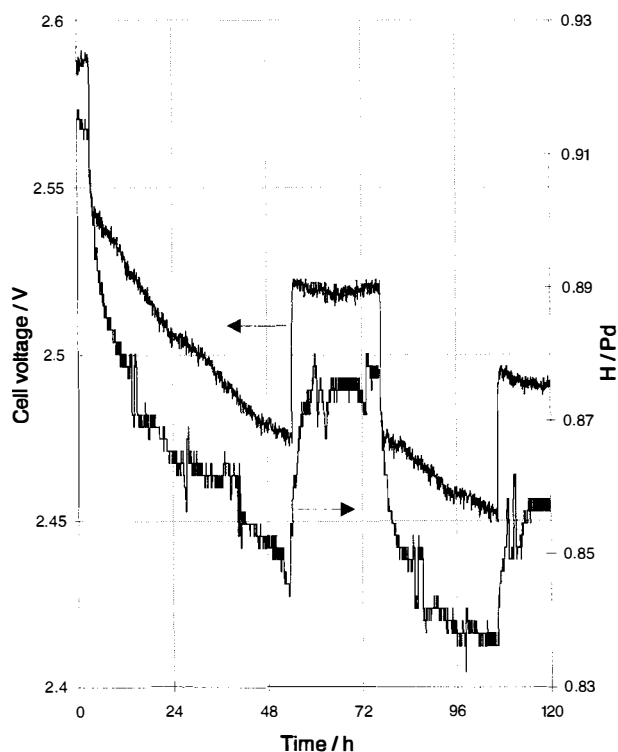
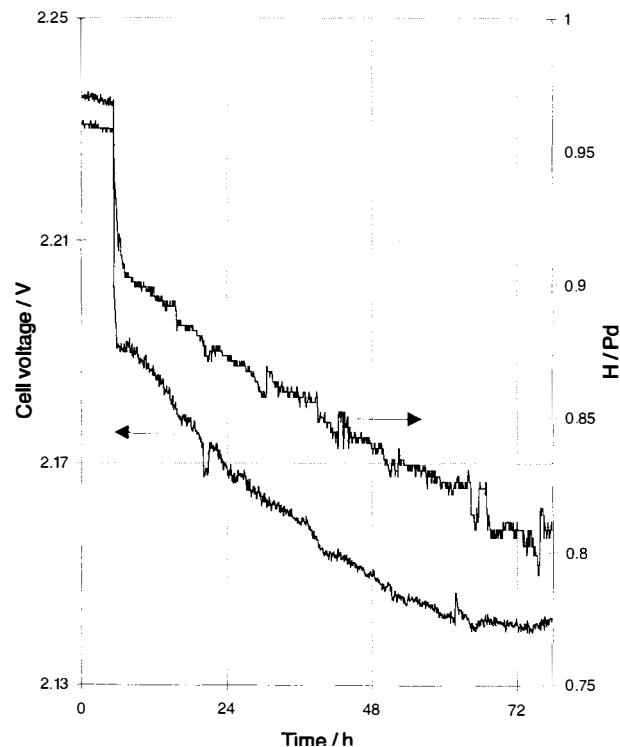Fig. 2. Variation of cell voltage and loading with time for experiment I.

Fig. 3. Variation of cell voltage and loading with time for experiment II.

are shown in Figs. 2–4 respectively. A chronology of events for each experiment is shown in Table 1. Each cathode was loaded initially in the absence of ultrasound; these data are not shown in Figs. 2–4.

The primary consequence of the application of ultrasound to a well-loaded, cathodically polarized palladium electrode is a decrease in loading; a concomitant, and closely parallel, decrease in the measured cell voltage is also observed. Reference to Fig. 2 reveals that, on removal of the irradiation, at 54.3 and 106.6 h, reloading occurs, but not to the original extent; in order to reload an electrode more completely, a brief period of exposure to anodic current (in the absence of irradiation) is usually necessary. Qualitatively similar results were obtained for both acidic and basic electrolytes.

On irradiation, at least two processes, with widely differing time constants, may be identified. The first involves a relatively rapid (on the order of 1 h) drop in both loading and cell voltage (note: although we interpret a change in the measured cathode resistance as a change in loading, temperature effects may also be important during this first phase, as discussed further below). While the magnitude of the loading decrease is variable, that of the voltage decrease is more-or-less constant (30–50 mV), and independent of current density, in the experiments performed here. Following these changes is an extended period during which the loading decreases slowly, with a parallel cell voltage decrease, leading to a new steady-state after a variable time period of several tens of hours. The variability of this time period is well illustrated by compar-

Table 1
Experiment chronology

Experiment	Cathode	Electrolyte	Current density/ mA cm^{-2}	Time/h	Action taken
I	Pd	1 M LiOH	104	3.3	Ultrasound on
				54.3	Ultrasound off
				76.8	Ultrasound on
				106.6	Ultrasound off
II	Pd	1 M H$_2$SO$_4$	52	5.4	Ultrasound on
III	Pd	1 M LiOH	52	6.8	Ultrasound on
IV	Pt	1 M H$_2$SO$_4$	52	22.8	Ultrasound on
				74.1	Ultrasound off

ison of the data in Figs. 3 and 4. Although the total loading decrease during given periods of sonication is not strictly reproducible, the final loading on extended sonication is typically in the range $0.75 < H/Pd < 0.8$, regardless of the initial loading. It is of interest to note that, on removal of the ultrasound, reloading is completed typically within less than 10 h (Fig. 2).

The results of irradiation of a platinum cathode maintained at $52\,mA\,cm^{-2}$, experiment IV, are shown in Fig. 5. On irradiation, there is a relatively rapid drop in cell voltage (in the range 30–50 mV), which is recovered equally rapidly when the ultrasound is removed. In addition, the cell voltage decreases significantly during the intermediate period, in a manner similar to that found for palladium. At lower current densities (about $10\,mA\,cm^{-2}$), this latter decrease is absent, although the initial, relatively rapid, decrease on initial irradiation is still present. For a platinum cathode, the variation of cathode resistance during irradiation may be used to calculate the variation of cathode temperature, using the known temperature coefficient of resistance of platinum under these conditions $(0.0039\,K^{-1})$. For experiment IV, the calculated temperature change is shown in Fig. 5. In general, temperature changes measured by this method were about 5°C for the experiments carried out here; similar temperature changes were also measured in the electrolytes of cells which contained thermocouples.

Finally, it may be remarked that, on sonication of a virgin palladium sample in the absence of electrochemical current, no change in resistance was observed which could
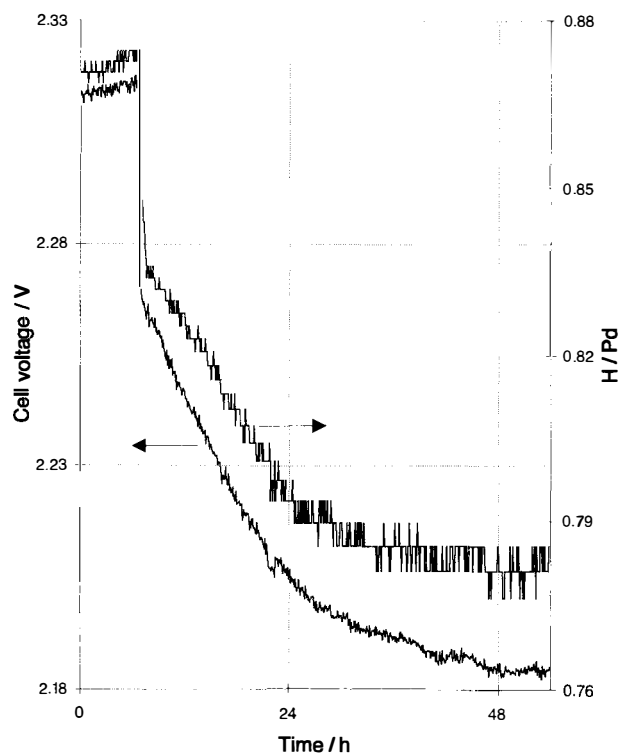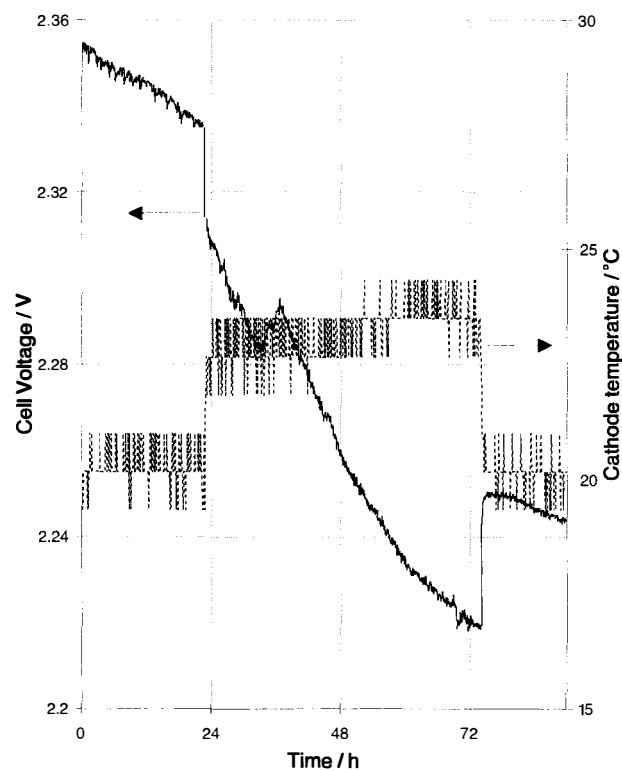

Fig. 5. Variation of cell voltage and cathode temperature with time for experiment IV.

not be ascribed to the (small) temperature change within the cell.

4. Discussion

Having achieved a given hydrogen loading in palladium at a certain cathodic current, the application of ultrasound causes both the loading, and the measured cell voltage to decrease. On removal of the irradiation, a (partial) recovery of these quantities is observed. The magnitudes of the observed effects, both in terms of resistance and voltage changes, as well as the time taken to achieve them, are variable. In agreement with conclusions reached earlier [2], these effects, in the well temperature-controlled system employed here, are thought to be too large to be entirely due to the relatively small temperature increase in the cell which results from irradiation.

Considering first the changes in cell voltage, although the cathode potential was not measured (with respect to a standard hydrogen reference electrode) in the experiments reported here, the cell design employed ensures that most of the total cell polarization resides at the cathode, for the cathodic current densities of interest. (The electrolyte resistance is approximately $1\,\Omega$ and the ratio of cathode/anode surface areas is 1:16). Thus, concerning the relatively rapid 30–50 mV cell voltage change associated with the application and removal of ultrasound to both palladium and

Fig. 4. Variation of cell voltage and loading with time for experiment III.

platinum cathodes, we are able to identify (at least a significant fraction of) this change with the overvoltage change observed previously for platinum alone [2,3]. Reference to the data in Fig. 5 reveals that the effects of temperature changes on the cell voltage and the cathode resistance (and, hence, the apparent loading) will be important only during this initial phase of sonication. The cell voltage decrease observed for palladium (and platinum at higher current densities) on prolonged irradiation, is significantly larger (and slower) than that observed previously.

On moving between steady-states, the changes of hydrogen loading in palladium observed on irradiation reflect changes in the average chemical potential of surface adsorbed hydrogen atoms. Thus, on prolonged irradiation, the observed decrease in loading corresponds to a decrease in this chemical potential. On removal of the ultrasound, the chemical potential increases and the palladium reloads (on the normal time scale expected for a (bulk) diffusion-limited loading process), the cell voltage having adjusted more rapidly. At constant current, a change in the chemical potential of adsorbed hydrogen will contribute directly to a change in overvoltage [9–11]. Thus, the closely parallel behaviour of the loading and the cell voltage adds support to the contention that changes in the latter largely reflect changes in the cathode overvoltage. As a point of reference, we note that, on loading from $H/Pd = 0.7$ to $H/Pd \approx 1$, the contribution of the hydrogen chemical potential to the total cathode overvoltage will increase by approximately 300 mV at room temperature [6,12]. This figure may be compared with the cell voltage changes observed here for somewhat lower loading changes.

Although, based on the results of the preliminary experiments described here, we are unable to provide a thorough explanation for the phenomena observed, we are inclined to assign a critical rôle to be played by certain (unidentified) surface-adsorbed species (other than hydrogen). It is recognized that, in order to achieve hydrogen loadings in palladium in excess of approximately 0.8 at room temperature using aqueous electrochemistry, a 'clean' (or 'catalytically active') cathode surface is inadequate (see, for example, Ref. [13]). In contrast, high surface chemical potentials, and hence high loadings, may be obtained by the use (deliberate or otherwise) of certain inhibitors (or 'surface poisons') which, it is suggested, tend to impede the recombination of adsorbed hydrogen atoms [9,10,14–17]. Although no deliberate additions of agents designed to affect the mechanism of the hydrogen evolution reaction were made in the experiments described here, the relatively high hydrogen loadings obtained prior to irradiation serve to indicate their presence. In view of the well-known utility of ultrasound for stripping surfaces of adsorbed species, we associate (at least) the major part of the loading (and closely associated cell voltage) decrease observed on irradiation with the removal of species which act to raise the chemical potential of the adsorbed hydrogen. The suggestion that it is a critical agent, rather than just adsorbed

hydrogen itself, which is removed from the surface, is supported by the observation that the original cathode loading is not recovered on cessation of irradiation (as pointed out above, in order to reload an electrode more completely, a brief period of exposure to anodic current (in the absence of irradiation) is usually necessary). In any case, regardless of the requirement for a critical agent or its mode of operation, it is clear that the surface states necessary for the attainment of high loadings do not re-form completely on removal of ultrasound, at the particular current densities employed here.

Although, in the absence of the identification of a critical agent, the foregoing discussion can only be offered at the present time as a guide for further study, it is worth pointing out that extensive surface contamination has been reported for palladium electrodes cathodically polarized in aqueous solutions (for example, see Refs. [18,19]). Furthermore, despite undertaking the usual precautions necessary for contaminant control in electrochemical experiments, it was felt necessary to explain prior results obtained for the irradiation of platinum electrodes partially in terms of the removal of (unspecified) surface species [2,3]. Finally, it perhaps should be emphasized that the allocation of a critical rôle to be played by agents which are introduced adventitiously into the system is not inconsistent with the observation of elements of irreproducibility in these experiments, in particular with respect to the magnitudes of the changes in loading and cell voltage.

Acknowledgements

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