

Preliminary note

Surface and electrochemical characterization of Pd cathodes after prolonged charging in LiOD + D₂O solutions *

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(Received 19 April 1990)

INTRODUCTION

One of the typical characteristics of the hydrogen evolution reaction is its extreme sensitivity to various impurities present in the solution. The related effects (irregular time variation of the overvoltage, anomalous Tafel slopes) are well known, not only from early fundamental work [1], but also from industrial practice [2].

We showed recently [3] that the contamination of a palladium cathode, polarized in LiOD + D₂O solution, with lead and more so with zinc, leads to the build-up of very large overvoltages for D₂ evolution. In the present communication we describe the results of surface analyses for a series of Pd electrodes used as cathodes in the D₂O electrolysis cells run for up to 34 days. These data may be relevant to the conditions of the experiments reported by Fleischmann et al. [4].

EXPERIMENTAL

All electrolyses and most of the current-overvoltage measurements were carried out in a cylindrical glass cell (Metrohm) containing 30 to 50 cm³ of solution. Palladium cathodes were cold-worked 10 × 10 × 0.5 mm 99.95% metal foils (Métalor). A large 99.95% platinum foil (Métalor) positioned around (and about 2 cm from) the central cathode served as counter-electrode. For comparison purposes two sorts of deuterium oxide were used: one from Fluka (99.8%) and the other from Paul Scherrer Institut (PSI) in Villigen (99.7%). The electrolytic solutions were prepared by addition of lithium metal (Fluka, 99%) or LiOH (Merck, 98%).

* Dedicated to Professor Robert Monnier on the occasion of his 85th birthday.

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Potentials were measured with respect to a deuterium ($D_2O + OD^- | D_2 | Pt-black$) reference electrode in the same solution and, thus, gave the overvoltage directly for each imposed value of current density. The measurements were performed by imposing, point-by-point increasing values of current (Amel Model 553 potentiostat). In most cases, overvoltages were recorded during 30 s and averaged over the final 20 s. For all measured overvoltage values the ohmic drop, between the reference electrode and the Pd cathode interface, was corrected by use of a current interrupter technique (Amel Model 568 function generator and Nicolet Model 3091 digital oscilloscope). The ohmic drop varied linearly with the current over the entire range of explored current densities. After each current interruption the solution was flushed with a stream of deuterium. Differing series of measurements were repeated in a two-compartment cell, to current densities of several mA/cm^2 , giving results very similar to those obtained in a one-compartment cell. The negligible effect of mixing of the evolved D_2 and O_2 so close to the electrodes in a cylindrical electrolysis cell having configuration analogous to that employed by Fleischmann et al. [4] has been confirmed recently [5].

The surface composition was analysed by X-ray photoelectron spectroscopy (XPS). The spectra were recorded with a VG Escalab 5 using $MgK\alpha$ radiation (1253.6 eV, Au 4f at 84.0 eV, 1.5 eV FWHM). The relative concentrations were determined from integrated peak heights after subtraction of a linear background and correction for analyser transmission $T(E)$ and mean free path λ by

$$T(E_k)\lambda(E_k) \sim E_k^{0.35}$$

and using theoretical cross sections [6]. Immediately after the electrolysis current was switched off, the samples were extracted from the cell, washed in doubly distilled water and dried in a desiccator before being transferred to the spectrometer.

The Li metal and D_2O used to prepare the solutions were analysed (at Analub, St Sulpice) for trace impurities by inductively coupled plasma (ICP) spectrometry (Beckman Spectra Span).

RESULTS

As reported in our previous communication [3], the prolonged charging of a palladium cathode in 0.1 M $LiOD + D_2O$ solution builds up a significant overvoltage. A typical example of such an increase is shown in Fig. 1, in which are compared the log $i-\eta$ plots for two Pd cathodes: the first (C) being charged for 220 h in an "as-prepared" solution and the second pre-charged for only 16 h in a "pre-electrolyzed" solution*. The abnormally large values of deuterium overvoltage, combined with unusually high Tafel slopes, as observed for electrode C, are

* The pre-electrolysis was carried out at $64 mA cm^{-2}$ for 220 h; because of the use of a platinum anode and of an one-compartment cell, this treatment brought about an increased platinum contamination with respect to an untreated solution.

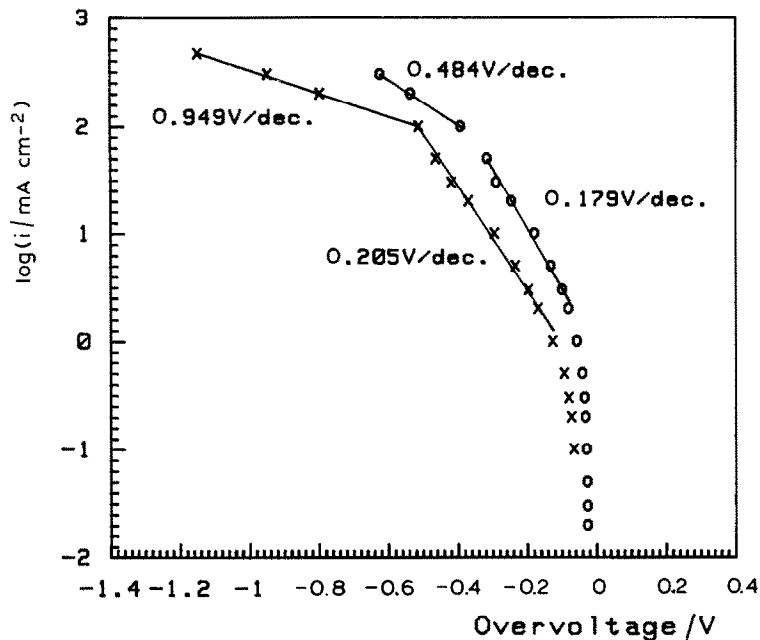


Fig. 1. Comparison of semilogarithmic current density–overvoltage plots for two Pd cathodes in 0.16 M LiOD + D₂O (sat. D₂) at 25°C. Curve a (×) refers to electrode C pre-charged for 220 h at 64 mA cm⁻² in a solution without pre-electrolysis, curve b (○) to an electrode pre-charged for 16 h at 64 mA cm⁻² in a pre-electrolyzed solution.

related to the impurities (in particular, some of them) accumulated in the outermost (1.5–2.0 nm) surface region of the palladium. There are significant differences both in the nature and the amounts of contaminants identified by XPS for samples E and C (Table 1). If we neglect the large concentrations of carbon and oxygen, the surface layer of electrode E (which was identical to that used to record curve b in Fig. 1), contained some sodium and platinum and traces of lead. Surface analysis of electrode C revealed that in addition to the increased amounts of platinum and lead two other species were present, viz., chromium and zinc.

As expected, lead and zinc, which both have low exchange currents for hydrogen evolution [7], markedly affect the overvoltage for the cathodic discharge of D₂O at the palladium. However, the effect by zinc has been found [3] to be much stronger than that of lead. In particular, zinc deposition onto the surface of palladium was shown to be responsible for the drastic change in the Tafel slope, that takes place at overvoltages greater than ca 0.5 V. Thus, electrode A, which exhibited even more zinc contamination than electrode C from Fig. 1, above 0.6 V, also showed a Tafel slope of ca. 2 V/dec. twice as high as that for C. The extent of the zinc effect on the deuterium overvoltage is illustrated in Fig. 2, which shows two successive polarization runs for a Pd electrode in 0.16 M LiOD + D₂O solution containing 10⁻⁶ M dm⁻³ of ZnO. It is noteworthy that the abrupt change in the $d\eta/d \log i$ slope,

TABLE 1

Results of XPS analyses of the Pd cathodes after prolonged electrolyses of D₂O. in. = initial concentrations; f. = final concentration

Elec- trode identi- fication	Electrode treatment	Solution	Relative concentrations (at.%) of the species detected in the outermost surface region of Pd													
			Pd	Pt	Cu	Pb	Cr (III)	Zn (II)	Ca (II)	Mg (II)	Na (I)	O	C			
A	for 220 h at 64 mA cm ⁻² then polarized up to 450 mA cm ⁻² then for 70 h at 64 mA cm ⁻²	in. 0.1 M LiOD ^a + D ₂ O (PSI) f. 0.16 M LiOD + D ₂ O	1.5	2.1	1.9	0.4	1.1	3.1							45.7	44.2
C	as electrode A	in. 0.1 M LiOD ^a + D ₂ O (F) f. 0.16 M LiOD + D ₂ O	0.8	3.5		0.9	2.2	1.2							46.4	45
E	for 16 h at 64 mA cm ⁻²	0.16 M LiOD ^a + D ₂ O (F) pre-electrolysis	12	1.2		0.3							5 ^e	41.5	40	
F	for 22 h at 128 mA cm ⁻²	0.16 M LiOD ^a + D ₂ O (F) pre-electrolysis	33.3	0.6		~0.1		1						50	15	
G2	for 16 h at 64 mA cm ⁻² then two polarization runs up to 300 mA cm ⁻² in the presence of ZnO	0.16 M LiOD ^a + D ₂ O (PSI) pre-electrolysis + 10 ⁻⁶ M ZnO ^c	12.8	13		1.1		4.1					3.2 ^e	40.6	25.2	
B2	for 34 days at 64 mA cm ⁻²	in. 0.1 M LiOD ^b + D ₂ O (PSI) f. 0.16 M LiOD + D ₂ O	0.4	4.7	2.7		4.5	2.1						64.1	21.5	
C2	for 25 days at 64 mA cm ⁻² then for 15 min at 450 mA cm ⁻²	in. 0.1 M LiOD ^b + D ₂ O (F) f. 0.16 M LiOD + D ₂ O	1.1	0.9			5.4	0.7	9.6	15.3				53.4	13.6	
K	for 13 days at 64 mA cm ⁻²	in. 0.28 M LiOD ^b + D ₂ O (F) f. 0.52 M LiOD + D ₂ O	^d				3.4		9.9					42.6	44.1	
L	for 17 days at 64 mA cm ⁻²	in. 0.1 M LiOD ^b + D ₂ O (PSI) f. 0.16 M LiOD + D ₂ O	^d	2.7			2.9	5.8						59.9	28.7	

^a prepared using LiOH.^b prepared using Li metal.^c ZnO added to the solution after the pre-charging for 16 h.^d absence of the Pd signal denotes thicker layer of impurities.^e presence of the Na signal requires further study.

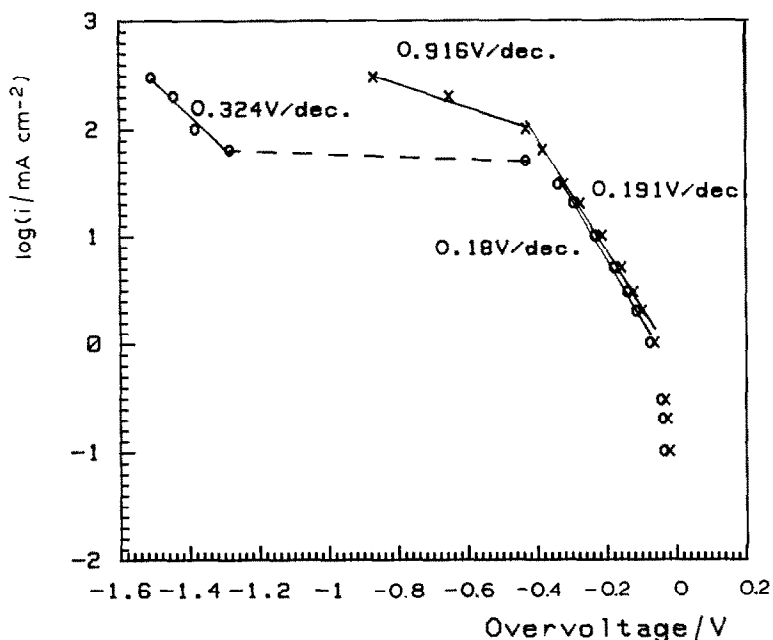


Fig. 2. Log i -overvoltage plots for a Pd electrode (G2) in 0.16 M LiOD + D₂O (D₂ sat.) solution containing an addition of 10^{-6} M dm⁻³ of ZnO. (×) First run; (○) second run (after 30 min at open circuit). Electrode pre-charged for 16 h at 64 mA cm⁻² in a pre-electrolyzed solution without ZnO.

observed in Fig. 2, is fairly consistent with the reversible potential of Zn deposition. XPS analysis, performed after the second polarization run in Fig. 2 and associated with a "jump" of the overvoltage from 0.4 to ca. 1.3 V, showed about 4 at.% of Zn(II) species to be present in the surface layer of electrode G2 (Table 1). The lead contamination of palladium has been shown [3] to exert a sort of co-operative effect with respect to zinc, changing the initial Tafel slope and so makes Zn deposition possible at relatively low current densities.

In view of their low exchange currents for hydrogen evolution, close to that of lead [7], both copper and chromium may also be expected to poison the catalytic activity of palladium for the reduction of D₂O. The two latter species (Cu and Cr), together with sodium and some calcium and magnesium were found in both kinds of heavy water used in our experiments (cf. Table 2). On the other hand, the concentrations of Zn and Pb species in both D₂O samples analysed by ICP spectrometry were lower than the corresponding detection limits (of 15 and 50 ppb, respectively). However, consistently larger amounts of Zn species, detected on the surface of Pd samples being polarized in the LiOD solutions made up from D₂O-PSI (see Table 1), indicate that its level of contamination with zinc is certainly higher than that for D₂O-Fluka. As regards the lead impurity, it could have originated from LiOH used to prepare a part of solutions.

TABLE 2
ICP analyses of D₂O and Li samples

Sample	Elements detected in the ICP spectra/ $\mu\text{g dm}^{-3}$							
	Cr	Cu	Zn	Pb	Ca	Mg	Sr	Na
D ₂ O (Fluka)	10	6	$\leq 15^c$	$\leq 50^c$				+
D ₂ O (PSI)	15	15	$\leq 15^c$	$\leq 50^c$	+ ^d		+	+
Li (Fluka) ^{a,b}					32	30	+	+

^a Analysed as 5M solution in triply distilled H₂O; results recalculated for 0.1 M Li⁺ solution.

^b Contained also Fe and traces of Al and Si.

^c Less than the detection limit of

^d + means: present in the spectrum; no quantitative analysis effected.

Platinum, coming from the dissolution of anodes in the LiOD + D₂O electrolysis cell, in principle, is expected to lower the overvoltage of deuterium evolution [8]. However, in the case of electrodes A and C, the presence of significant amounts of platinum in the surface layer apparently does not prevent poisoning of these electrodes by lead and zinc.

Prolonged electrolysis experiments performed in LiOD + D₂O solutions made up using lithium metal resulted in substantial changes in the nature and distribution of impurities at/in the surface of the Pd cathodes. In particular, the photoelectron spectra of electrodes C2 and K contained intense signals due to calcium and (in the former case) magnesium. The two latter species are typical major contaminants of metallic lithium; in our case, the concentration levels, determined by ICP analysis and recalculated for a 0.1 M Li⁺ solution, were close to 30 $\mu\text{g dm}^{-3}$ for both Ca and Mg (cf. Table 2). In our opinion, the incorporation of the latter species into the surface region of palladium is explained in terms of the precipitation of Ca(OH)₂, or Mg(OH)₂, owing to the local increase in pH close to the strongly polarized cathode, rather than by the electrodeposition of the corresponding metals. Interestingly, when a Pd cathode was charged in a more concentrated 0.28 M LiOD + D₂O solution its surface was covered predominantly by a Ca(OH)₂ deposit (electrode K, Table 1). A similar effect was also produced in 0.1 M LiOD + D₂O solution by a short excursion to high cathodic current densities (electrode C2, Table 1).

DISCUSSION

The results reported above clearly indicate that even relatively short electrolysis of LiOD + D₂O solution causes significant surface contamination of the Pd cathode. Of the impurities identified by XPS, zinc (originated from D₂O) causes a sharp increase in the D₂ overvoltage at palladium. The electrodeposition of Zn, which requires quite negative potentials, is favoured by large current densities and by the presence of impurities which increase the D₂ overvoltage; in contrast, it will be delayed by the incorporation of platinum into the surface region of palladium. If we assume the Zn(II) concentration in the solution to be in the range of 10⁻⁸ mol

dm^{-3} and the thickness of the diffusion layer of 5×10^{-3} cm consistent with an intense cathodic gas evolution we obtain the limiting current density of 4 nA cm^{-2} . This implies that conducting the electrolysis for ca 32 h would permit the formation of a monolayer of zinc. However, such completion of the Zn monolayer demands that the cell contains no less than 25 cm^3 of 10^{-7} M Zn(II) solution per square cm of the cathode surface area*. In the case of prolonged high current density electrolysis of LiOD/D₂O, the additions of fresh D₂O to the cell provide an extra source of impurities. For example, an electrolysis run at 0.5 A cm^{-2} for 30 days led to the decomposition of more than 120 cm^3 of D₂O, causing a large accumulation of the related impurities at the Pd surface.

The reported poisoning of palladium by zinc, causing D₂ overvoltages of more than 1.6 V (Fig. 2), opens the way to a series of secondary reactions, among which are: Li incorporation into both Pd [9] and Zn [10] and, possibly, the formation of ZnD₂ and LiD [3]. The two latter reactions are expected to be favoured by the strong supersaturation of the diffusion layer at the Pd cathode with D₂ gas [11]. LiD is, of course, unstable in water but might be preserved at the electrode surface under a protective layer of LiOD [3,12].

The results reported here show clearly that the distribution of the impurities at the Pd surface, which determines its long term electrochemical behaviour, may depend critically (i) on the origin of D₂O and Li(LiOD) used to prepare the solutions and (ii) on the actual electrolysis conditions including the current density and the ratio of the solution volume to the electrode (Pd and Pt) surface area. Of the impurities detected, zinc appears to be the key element since it modifies the cathodic behaviour of palladium strongly. The electrodeposition of Zn at the Pd cathode is influenced not only by the level of solution contamination and the current density but also by the competition between the high- and low-hydrogen-overvoltage impurities for the sites at the Pd surface. Calcium (and magnesium) seem to play a special role in forming (particularly at high current densities and in slightly more alkaline solutions) a precipitate of Ca(OH)₂(Mg(OH)₂). This, in turn, is expected to cause pronounced blocking of the electrode surface, resulting in a local build-up of strong electrical fields.

ACKNOWLEDGEMENT

Part of this work has been supported by the Swiss National Science Foundation.

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* This example reflects the conditions of some of our tests (see, in particular, electrode L, Table 1).

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