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Electrochemical Measurements on Palladium Cathodes in LiOD/D$_2$O Solutions related to the «Cold Fusion Experiments»

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Abstract: The current-voltage behaviour of palladium electrodes, polarized in an electrolysis cell filled up with a diluted solution of lithium deuteroxide in heavy water, is shown to be strongly influenced by the impurities co-depositing at the cathode. Among the impurities, identified on the surface of palladium at the end of the electrolyses, lead and especially zinc cause the shift of the electrode potential making possible lithium deposition and lithium deuteride formation. Some expected interactions of these compounds are discussed.

Strange behaviour of palladium cathodes, submitted to prolonged charging with deuterium in an electrolytic cell containing a relatively diluted (0.1 M) solution of LiOD in heavy water, reported by *Fleischmann, Pons,* and *Hawkins* [1], is still the subject of vigorous controversy [2–6]. In spite of all the uncertainties, it appears quite clearly that rare electrolysis experiments which have up to now led to an «excess heat generation» were conducted at high cathodic current densities exceeding 50 mA/cm^2 [7,8]. The analysis of possible anomalies occurring in the behaviour of the palladium electrodes polarized with such large cathodic currents in 0.1 M LiOD/D$_2$O solution requires first of all the knowledge of the actual relation between the current density and the electrode potential.

In the present note we report first series of such deuterium overvoltage measurements performed on Pd cathodes electrolytically pre-charged into the β-palladium/deuterium phase.

Experimental

For comparison purposes two sorts of D$_2$O 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%).

The cathodic current-overvoltage measurements were carried out in a cylindrical glass cell (Metrohm) containing ca. 30 cm^3 of 0.16 M LiOD/D$_2$O electrolyte saturated with deuterium. Palladium cathodes were 10 × 10 × 0.5 mm cold worked 99.95% metal foils (Métalor). A large 99.95% platinum foil (Métalor) positioned around the central cathode served as counter-electrode. Potentials were measured with respect to a deuterium (D$_2$O/D$_2$, OD$^\ominus$, Pt black) reference electrode in the same solution and, thus, gave directly the overvoltage 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 over 30 s and averaged over final 20 s. For all measured overvoltage values the ohmic drop, between the reference electrode and the Pd cathode interface, was corrected using 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. Various series of measurements were repeated in a two-compartment cell, up to current densities of several mA/cm^2, leading to the results closely similar to those obtained in the one compartment cell. Negligible effect of mixing of the evolved D$_2$ and O$_2$, close to the electrodes, in a cylindrical electrolysis cell having configuration analogous to that employed by *Fleischmann* et al. [1] has been confirmed recently [9].

Results and Discussion

Fig. 1 shows typical cathodic current *(i)* versus overvoltage (η) plots for palladium electrodes pre-charged for 8 days at a current density of 60 mA/cm^2. The principal electrochemical reactions occurring at the Pd cathodes may be summarized as follows:

$$\mathrm{Pd} + \mathrm{D_2O} + x\mathrm{e}^\ominus \rightarrow \mathrm{PdD}_x + x\mathrm{OD}^\ominus \qquad (1)$$

(reaction (1) is essentially completed during the pre-charging period)

$$\mathrm{PdD}_x + \mathrm{D_2O} + \mathrm{e}^\ominus \rightarrow \mathrm{PdD}_x\text{–}\mathrm{D}_{ad} + \mathrm{OD}^\ominus \qquad (2)$$

$$\mathrm{PdD}_x\text{–}\mathrm{D}_{ad} + \mathrm{D_2O} + \mathrm{e}^\ominus \rightarrow \mathrm{PdD}_x + \mathrm{D_2} + \mathrm{OD}^\ominus \qquad (3)$$

or

$$2\,\mathrm{PdD}_x\text{–}\mathrm{D}_{ad} \rightarrow 2\,\mathrm{PdD}_x + \mathrm{D_2} \qquad (4)$$

For overvoltages exceeding ca. 0.08–0.1 V, for which the contribution arising from the partial anodic current becomes negligible, linear η–log i Tafel plots are observed. Initial slopes b are slightly higher than 0.2 V/dec. but at overvoltages of 0.5–0.6 V they rise drastically to reach ca. 1 V/dec., respectively 2 V/dec. Anomalous Tafel slopes (i.e. b higher than ca. 0.18 V/dec.) are frequently associated with poisoning of

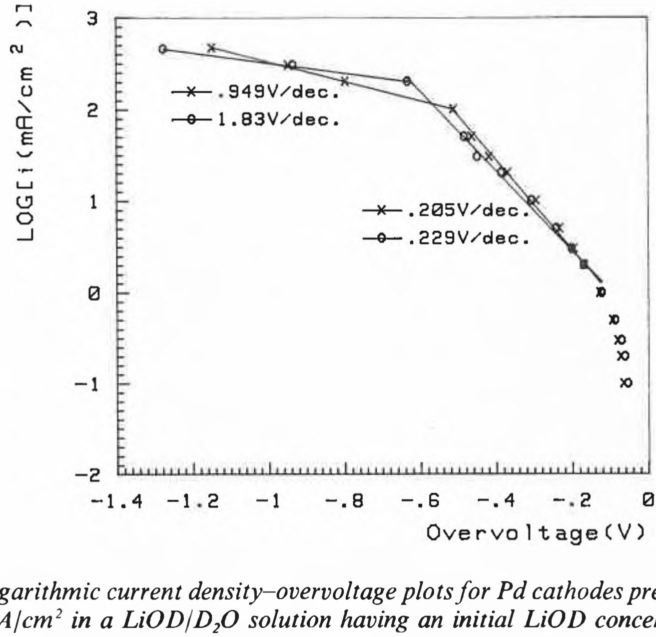

Fig. 1. Semilogarithmic current density–overvoltage plots for Pd cathodes pre-charged for 8 days at 60 mA/cm^2 in a LiOD/D$_2$O solution having an initial LiOD concentration of 0.1 mol/dm^3. Measurements performed in 0.16 M LiOD/D$_2$O (sat. D$_2$) at 25°C. Crosses refer to D$_2$O (Fluka), circles to D$_2$O (PSI); the latter electrode revealed Zn contamination two times larger than the former one.

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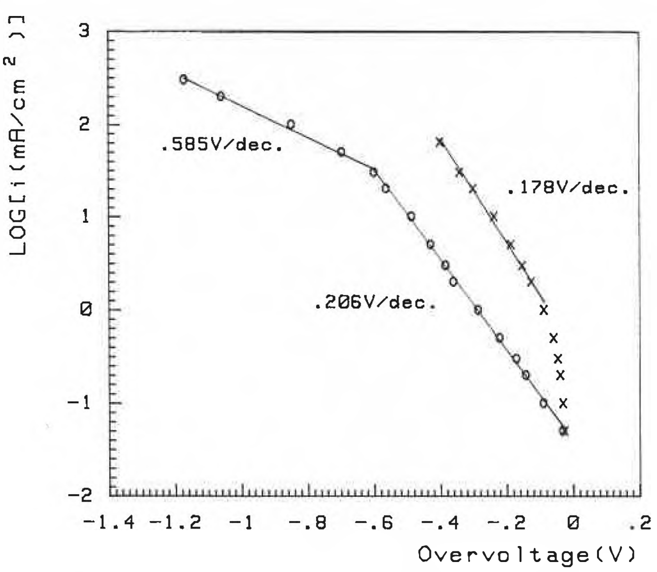

Fig. 2. Effect of poisoning by Pb (circles) on η–log i characteristics of Pd cathodes in 0.16 M *LiOD/D$_2$O (sat. D$_2$) at 25°C. Electrode pre-charged for 16 h at 64 mA/cm^2 in a pre-electrolyzed solution.*

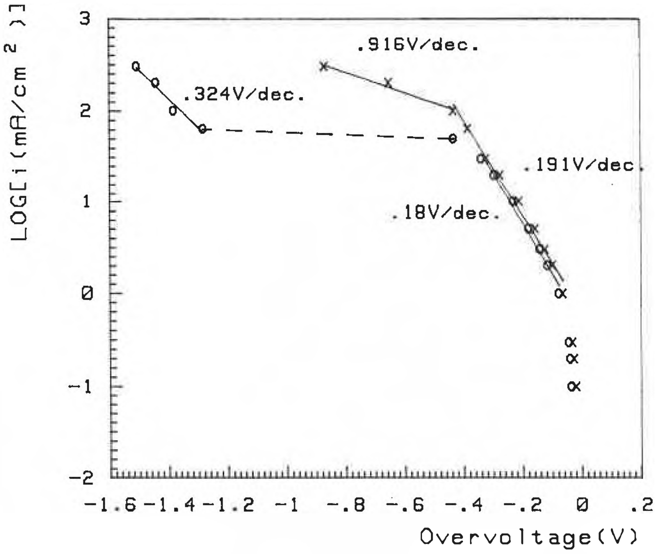

Fig. 3. η–log i relationship for a Pd cathode in 0.16 M *LiOD/D$_2$O (sat. D$_2$) solution containing 10^{-6}* M *ZnO addition. Crosses: first run; circles: second run (after 30 min at open circuit). Electrode pre-charged for 16 h at 64 mA/cm^2 in a pre-electrolyzed solution.*

the electrode by the impurities present in the solution. It is well known, since at least 40 years, that certain impurities, at concentrations as low as 10^{-10} mol/dm^3, may already affect the rate of hydrogen evolution reaction[10]. The effects of this kind are, consequently, to be expected in the case of Pd electrodes subjected to a sustained charging in LiOD/D$_2$O solution. As a matter of fact, X-ray photoelectron spectroscopic (XPS) analyses of the Pd electrodes used for the polarization experiments represented in Fig. 1, which will be described in a forthcoming paper (but see also Ref.[11]), have revealed as principal metallic impurities platinum (arising from the oxidation of the counter-electrode[12]), zinc and lead (originating in the solution). Whilst Pt ist a good catalyst of hydrogen evolution (but see Ref.[12]) this is not at all the case of Zn and Pb.

The effect of poisoning palladium by lead is quite apparent when one compares the η–log *i* relationships in Fig. 2. Prior to the polarization measurements, the Pd electrode had been pre-charged for 16 h at 64 mA/cm^2 in LiOD/D$_2$O solution purified by prolonged pre-electrolysis. The η versus *i* measurements performed under such conditions led to well reproducible Tafel slopes of ca. 0.18 V/dec. After the surface of that electrode has been contaminated with less than one monolayer of lead, a sensible increase of overvoltages (of ca. 0.2–0.3V) was observed during the following polarization measurements.

However, much more important modifications of the η versus *i* characteristic were produced by addition to LiOD/D$_2$O solution of 10^{-6} mol/dm^3 of ZnO (cf. Fig. 3). In particular, the second polarization run in Fig. 3 shows a drastical increase of the overvoltage. It is to be mentioned that the observed change of the Tafel slope (cf. also Fig. 1) coincides quite well with the reversible potential of zinc deposition from $ZnO_2^{2\ominus}$ solution of pH 13. The zinc accumulation at the electrode surface actually leads to a pronounced inhibition of the D$_2$ evolution favouring possibly PbD$_2$ and ZnD$_2$[13] formation and Li deposition[14].

The hydride formation should be particularly favoured by the strong supersaturation of the layer adjacent to the cathode with D$_2$ (in the case of high-current-density hydrogen evolution at a platinum cathode *Shibata*[15] determined local H$_2$ concentration equivalent to ca. 160 bar).

On the other hand, lithium deposition at the electrode surface may eventually lead to a series of reactions including alloying with zinc and palladium and, possibly, LiD formation. The possibility for lithium to enter into a direct contact with palladium will depend on the thickness of the zinc layer formed on the electrode surface and, so, on the amount of zinc present in the solution. A small amount of Zn (about a monolyaer) is probably necessary to allow Li deposition, thicker layers will slow down its interaction with Pd. Is it only a coincidence that some solutions employed recently in LiOD/D$_2$O electrolysis experiments[8] contained a small addition of NaCN, a strong complexing agent of zinc?

LiH has been reported to form during lithium deposition on a gold cathode from acetonitrile solutions containing water[16] (according to the suggested model, LiH would be preserved under a protective layer of LiOH). The question arises, however, whether similar mechanism may be applicable to the case of high-current-density charging of the palladium cathode in LiOD/D$_2$O solution. In particular, is the concentration polarization, occuring under such conditions, sufficiently strong to allow the stabilization of a LiOD film at the outermost electrode surface? (the solubility of LiOH in water is in the range of 5 mol/dm^3). The intended formation of LiD at the cathode of a Pd/LiOD/D$_2$O/Pt electrolysis cell might put into a direct contact the ionic deuteride (LiD), consisting of Li$^\oplus$ and D$^\ominus$ species, with the metallic PdD$_x$ including positively charged D$^\oplus$. In addition to its interactions with PdD$_x$ and also ZnD$_2$, LiD will obviously react in contact with water ($\Delta H = -132$ kJ/mol) and, at increased temperatures, with silicates (glass). Under certain conditions, both of these reactions become explosive.

At last, one has to mention another, largely investigated, property of LiD – that of undergoing, in the presence of strong electric fields, nuclear ^{7}Li(d, n)2α (and why not ^{6}Li(d)2α?) reactions (so-called «exploding» (Li + LiD) wires[17]). Yet, it remains to establish whether a correlation exists between the latter reactions and the experimental observations on the Pd/LiOD/D_2O/Pt electrolysis cells.

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