Preliminary note

Electrochemical incorporation of lithium into palladium from aprotic electrolytes

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INTRODUCTION

Among numerous questions raised by the recent paper of Fleischmann et al. [1], describing their heavy water electrolysis experiments, an important one concerns the specific influence of the cation of LiOD electrolyte on the behaviour of a palladium cathode. In fact, the reported observations of an excess heat generation in the latter experiments seem to be closely associated with the presence of Li^+ cations in the electrolyte [2]. One of the typical features of the prolonged electrolyses of a 0.1 M LiOD + D_2O solution between palladium cathodes and platinum anodes, mentioned by Fleischmann et al. [1], was the build-up of high cathodic overvoltages. This leads to an important question: what is the critical value of the electrode potential which would allow the incorporation of lithium into the PdD_x cathode [3]?

Lithium has been shown to alloy electrochemically, at ambient temperature, with a number of metals including the three noble metals, gold, silver and platinum [4]. In these electrolysis experiments, performed in a 1 M $LiClO_4$ + propylene carbonate solution, the formation of lithium alloys at Au, Ag and Pt cathodes was observed to start at potentials slightly more positive than ca. 0.4 V with respect to the Li^+/Li electrode.

The aim of the present study was to establish in which potential range the Li^+ cations undergo reduction at a palladium cathode and whether such a reaction is

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affected by the presence of deuterium in the palladium metal. In this note we describe cyclic voltammetric measurements performed in two different aprotic electrolytes: (i) a solution of 1 M $LiClO_4$ in a liquid solvent + propylene carbonate and (ii) a solid polymer electrolyte consisting of poly(ethylene oxide)–lithium perchlorate complex, $(PEO)_8LiClO_4$.

EXPERIMENTAL

Propylene carbonate (PC) (Merck) was vacuum distilled from molecular sieves. Anhydrous $LiClO_4$ (G. Fredrick Smith Co.) was dried at 120°C in a dynamic vacuum before use. A film of solid electrolyte, having a thickness of 300 to 500 μm, was prepared from high molar mass poly(ethylene oxide) (Jansen), molar mass 5×10^6 g, and $LiClO_4$ dissolved in acetonitrile (Fluka) which had been distilled from molecular sieves. The $LiClO_4$–PEO electrolyte with a O/Li ratio equal to 8 was formed and dried in an argon glove box (Jaram) (water content less than 1 ppm) [5].

The cell used for electrochemical measurements was a "sandwich" of a palladium disk (11 mm diameter, 1.5 mm thick), a glass filter paper (Ecole Française de Papeterie) soaked in $LiClO_4$ + PC electrolyte or a film of solid electrolyte, $LiClO_4$–PEO, and a 1 mm thick lithium foil (Lithcoa). A small (5 mm diameter) Li disk served as a reference electrode and a 16–11 mm diameter Li ring was used as the counter-electrode. The Pd disks were cut from a sheet obtained from a palladium ingot melted under argon; they were then polished with 0.3 μm alumina to a mirror finish. A stainless steel pressure reactor (Parr Instrument Company) was used to deuteride the Pd metal. The sample was activated by degassing the reactor and by subsequent deuterium absorption–desorption cycles at 150–175°C under a pressure of 15–20 bar. After several such cycles, the sample was charged by exposing it to deuterium at a pressure of 20 bar and a temperature of 175°C for about 60–90 min to get a final completely deuterided sample PdD_x ($x > 0.55$ corresponding to the β-phase).

The cells were assembled in the dry box and maintained (within a sealed glass vessel) either in an argon atmosphere at 25°C, when the $LiClO_4$ + PC electrolyte was used, or under vacuum at 80°C for the solid $LiClO_4$–PEO electrolyte cell. Cyclic voltammetric measurements were conducted using a Tacussel type 40-1X potentiostat, driven by a Servovit control system, and a Sefram TGM 101 recorder. X-ray diffraction patterns were recorded to characterize the various samples, namely pure, deuterided and Li-incorporated palladium on a Philips diffractometer with Ni-filtered Cu K_α radiation. All these measurements were carried out at room temperature.

RESULTS AND DISCUSSION

A cyclic voltammogram (the first cycle) of a PdD_x electrode in 1 M $LiClO_4$ + PC solution is given in Fig. 1. No appreciable cathodic current flows until ca. 1.8 V
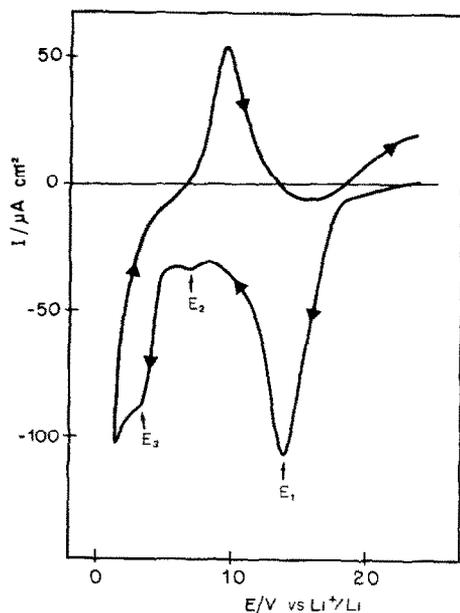
Fig. 1. Cyclic voltammogram (the first scan) of a deuterided palladium (PdD_x) electrode in 1 M $LiClO_4$ + PC at 25°C. Potential sweep rate $v = 100$ mV/min.

versus the Li^+/Li electrode, where the first reduction peak begins, reaching a maximum at $E_1 \approx 1.4$ V. It is followed by a less marked peak at $E_2 \approx 0.7$ V and a third one (appearing as a shoulder) at $E_3 \approx 0.34$ V. When the negative sweep was pursued close to the potential of the Li^+/Li electrode, it resulted in a strong rise of the current corresponding to a reversible deposition of the lithium metal.

The occurrence of three distinct reduction peaks at potentials positive with respect to $E(Li^+/Li)$ is indicative of the formation of Pd–Li alloys with lithium activity, a_{Li}, much lower than 1. Palladium is known to form a series of inter-metallic compounds with lithium and, on the Pd-rich side of the phase diagram, a Pd + Li solid solution [6,7]. The latter is isotypic with pure Pd up to ca. 6 at.% Li content.

Additional experiments performed with a 1 μm thick palladium foil, also charged with D_2 gas prior to the voltammetric measurements in 1 M $LiClO_4$ + PC, allowed us to estimate the amount of lithium incorporated into the PdD_x cathode in the region of the first reduction peak. The area of this peak, which was shifted to still more positive potentials ($E_1' \approx 1.6$ V) with respect to that in Fig. 1, was equivalent to a mean Li content in Pd of about 1 at.%.

It seems plausible that Pd and especially PdD_x might be able to intercalate at least such a small amount of lithium, in the interstitial sites of the fcc lattice, as they do in the case of much larger amounts of H^+ or D^+ ions. This would explain the occurrence of the first reduction peak at such a positive potential and also its
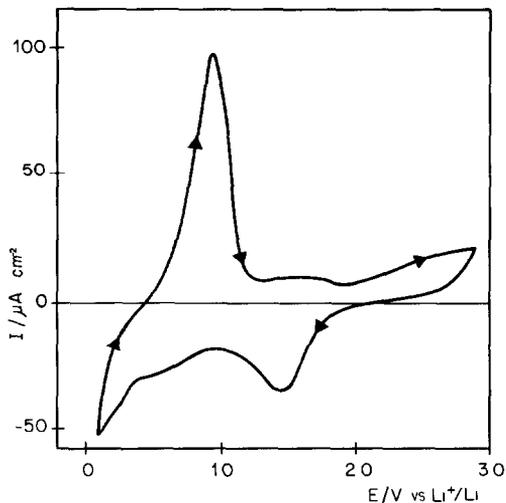
Fig. 2. Eighth voltammetric cycle recorded for a Pd electrode in 1 M $LiClO_4 + PC$. 25° C; $v = 800$ mV/min.

relatively high intensity. In view of a significant lattice expansion associated with the formation of a $PdD_{0.55}$ β-phase, corresponding to a volume increase of about 11% with respect to pure Pd, one would expect PdD_x to be more particularly "hospitable" towards lithium. As a matter of fact, the reduction peak at $E_1 \approx 1.4$ V, obtained with the PdD_x electrode, was 20–30% larger than the analogous peak for the non-deuterided Pd electrode. However, the positions of these peaks were practically identical as were also the main features of the whole voltammograms for both kinds of electrode.

During continuous cycling inside the potential limits shown in Fig. 1, the voltammograms of deuterided and non-deuterided electrodes underwent similar changes which, in particular, consisted in a progressive decrease of the cathodic peak at $E_1 \approx 1.4$ V. This is seen clearly in Fig. 2 which shows, as an example, the eighth voltammetric cycle recorded for the non-deuterided Pd electrode in 1 M $LiClO_4$ + PC. The relatively large intensity of the main anodic peak at ca. 0.9 V is probably due to slow rearrangements taking place in the Pd lattice. Although, during some cycles, distinct anodic features could be observed at ca. 1.7 and 2.3 V, complete reoxidation of the incorporated lithium required much more positive potentials. Extending the potential scan up to 3.3–3.4 V, which resulted in a strong increase of the anodic current, allowed us to regain on the reverse sweep the original height of the reduction peak at $E_1 \approx 1.4$ V. However, such a positive potential limit was normally avoided during continuous cycling as it coincided with a partial oxidation of the electrolyte.

The above results, regarding the incorporation of lithium into palladium at quite positive potentials, were confirmed by experiments performed in the presence of the
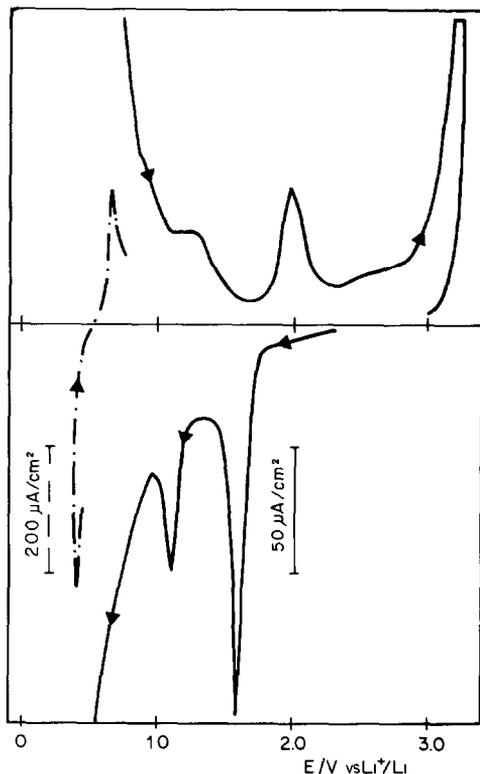
Fig. 3. Cyclic voltammogram (the first cycle) for a Pd electrode in $(PEO)_8LiClO_4$ at $80\,^{\circ}$C. $v = 100$ mV/min.

solid polymer electrolyte $(PEO)_8LiClO_4$. The first negative scan (Fig. 3) of a non-deuterided Pd electrode shows a sequence of three well-defined peaks with the maxima at ca. 1.58, 1.1 and 0.4 V. Contrary to the case of the 1 M $LiClO_4 + PC$ solution, all three stages of the incorporation of Li into Pd from the $(PEO)_8LiClO_4$ electrolyte are apparently quasi-reversible. This change in behaviour is most likely due to a higher lithium diffusion rate in the Pd lattice at $80\,^{\circ}$C, the temperature at which the polymer electrolyte has to be operated. Still, among the three anodic peaks visible on the reverse sweep in Fig. 3, having maxima at ca 0.64, 1.26 and 1.98 V, it is the latter one which is shifted the most with respect to its cathodic equivalent.

The Pd and PdD_x electrodes were also submitted to prolonged (40 h) cathodic polarization at a constant potential of 0.7 V vs. the Li^+/Li electrode in 1 M $LiClO_4 + PC$ and then analysed by X-ray diffraction. As expected for a Pd + Li alloy containing less than 6 at.% of Li, the incorporation of lithium into a palladium electrode did not produce significant changes in the X-ray peak positions. The observed cell dimensions were: $a = 0.3891$ nm for pure Pd; $a = 0.3887$ nm for the

Li-incorporated sample. The decrease in the unit cell parameter value is in accordance with the values obtained for solid solutions of Li with Pd [7]. In addition, considerable alterations in the peak intensities were seen. The X-ray diffraction pattern of a deuterided sample was typical of PdD_x (β-phase; $x > 0.55$): $a = 0.4027$ nm in agreement with the literature [6]. However, after Li intercalation the sample showed a mixture of phases, namely PdD_x and Li-incorporated Pd. Probably, the deuterium atoms in PdD_x may be replaced to some extent by Li atoms.

CONCLUSIONS

We have demonstrated that electrochemical incorporation of Li into Pd starts at potentials as positive as ca. 1.8 V versus the Li^+/Li electrode. Three distinct stages of lithium incorporation, preceding the deposition of pure Li metal, have been identified by cyclic voltammetric measurements using two different aprotic electrolytes. In view of these results, the incorporation of lithium into a palladium electrode, polarized cathodically in a $LiOD + D_2O$ solution, appears as a not unlikely process [3]. A rough estimate indicates that the equilibrium potential of the D_2O/D_2, OD^- electrode in a 0.1 M $LiOD + D_2O$ solution should be about 2.35 V more positive than that of the Li^+/Li electrode. This would mean that overvoltages in the range of 0.6 V (which seem to be reached easily when high current densities are imposed on the PdD_x cathode [1]), may already lead to a simultaneous reduction of D_2O molecules and an incorporation of Li^+ ions. At such potentials, the discharge of Li^+ cations should be favoured by a negative charge of the PdD_x cathode. Because of the slowness of the Li diffusion inside the Pd lattice, the main effect one may expect after electrolysis for a few hours, is the formation of a Pd + Li alloy in the surface region (some μm deep) of the Pd cathode. It is interesting to note, in this connection, that a Pd + 1 at.% Li alloy already exhibits marked changes in electrochemical behaviour with respect to pure Pd [8].

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