

Preliminary note

On the behavior of Pd deposited in the presence of evolving deuterium

S. Szpak and P.A. Mosier-Boss

Naval Ocean Systems Center, San Diego, CA 92152-5000 (USA)

J.J. Smith

Department of Energy, Washington, DC 20545 (USA)

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INTRODUCTION

Recently, Fleischmann et al. [1] reported that nuclear events can occur when deuterium is electrochemically compressed within the Pd–lattice. These events were reported to produce excess enthalpy, tritium, and neutrons. The exact nature of these events and the conditions leading to their initiation are poorly understood. In fact, the existence of such events is questioned by many [2]. The present position among those investigating this problem [3] is as follows: enthalpy production is a non–steady state process whose rate depends on the nature of the electrode material; however, the observed steady state production arises from an averaging of small perturbations. Nuclear events are believed to occur on the electrode surface as well as within the electrode interior.

This note reports on an alternative experimental approach to produce conditions favorable to the observation of this extraordinary behavior by exploiting the Pd/D codeposition. The approach, because an ever expanding electrode surface is created, assures the existence of non–steady state conditions as well as simplifies the cell geometry by eliminating the need for uniform current distribution on the cathode and, more importantly, eliminates long charging times effectively. Three sets of preliminary experimental results are presented here, i.e., the production of excess enthalpy, the production of tritium and the presence of some form of radiation. Due to the preliminary nature of this communication, the data are considered qualitative.

EXPERIMENTAL

A glass cell was provided with a bubbler, filled with heavy water to isolate the cell interior and, yet, allow the escape of gases generated in the course of codeposition. Two types of working electrodes were constructed. The first, Fig. 1, illustrates the arrangement for excess enthalpy measurements. Here, a copper foil, ca 4.0 cm² in area and 0.02 cm thick, attached to a glass tube, served as the cathode. A copper–constantin thermocouple, T₁, was inserted into this tube and cemented to the dry portion of the copper foil. A second, identical thermocouple, T₂, located half–way between the cathode and the Pt foil auxiliary electrode, measured the electrolyte temperature. The codeposition occurred from a solution of 0.05 M PdCl₂ (Aldrich) and 0.3 M LiCl (Mallinckrodt) dissolved in a 99.9% pure

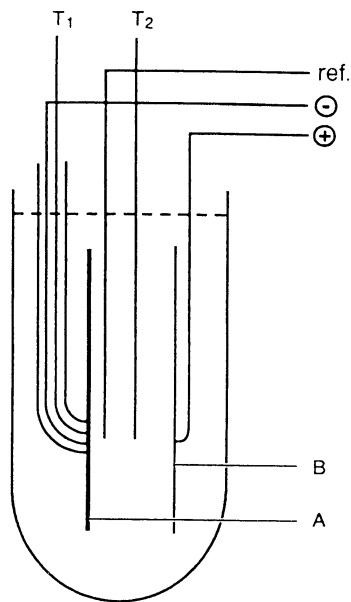


Fig. 1. Experimental cell. (A) Working electrode (B) counter electrode (ref.) reference electrode (T₁) thermocouple attached to working electrode (T₂) thermocouple in solution.

D₂O (Merck) under potentiostatic control (AMEL model 553). A potential of -0.8 to -2.0 V, measured against either Ag/AgCl or the Pd wire (D-charged to the $\alpha \rightarrow \beta$ transition) reference electrodes in the same solution, was applied. The cell voltage and current were monitored using a Hewlett-Packard model 7132A chart recorder. The temperature of the Cu-foil and solution were monitored using an OMEGA model 411A trendicator.

A second cell, shown in Fig. 2, was designed to detect radiation emanating during the codeposition. In this arrangement, photographic film, which was encased in light-tight and solution-impermeable envelopes, is placed in close proximity to the screen electrode.

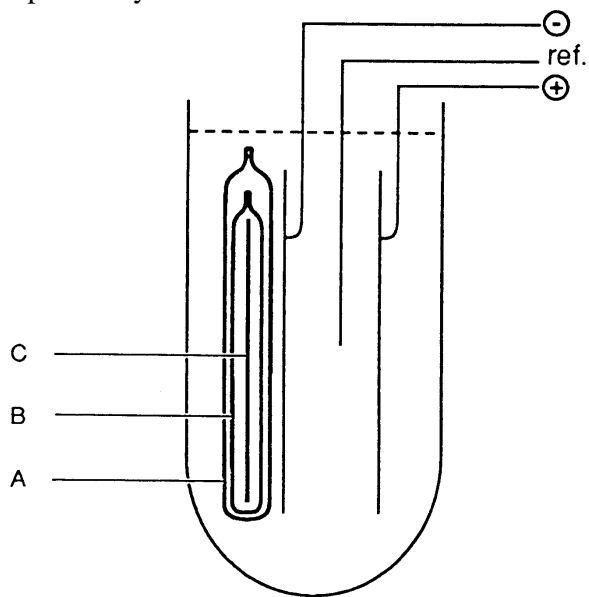


Fig. 2. Electrolytic cell for radiation detection. (A) Solution-impermeable envelope (B) light-tight envelope (C) photographic film.

RESULTS AND DISCUSSION

In the course of codeposition of Pd from D₂O electrolytes, the temperature of the working electrode, T₁, was always greater by 2–4°C than that measured in the electrolyte, T₂, Fig. 3. This indicates that the heat source is located at or within the Pd/D deposit. A suggestion that T₁ > T₂ can be explained by increased resistivity of the D₂-gas film on the electrode surface [4] is rejected on several grounds: first, a vigorous evolution of gases on both electrodes is known to promote efficient heat transfer; second, formation of a gas film is prevented by deuterium absorption and evolution; third and most important, the steep temperature rise of the cathode, indicated by ΔT in the insert Fig. 3, which was observed upon termination of flow of the cell current. Crude energy balance determinations were made periodically during each run: an excess enthalpy production between 10 and 40% was observed. Control experiments involving codeposition from light water showed a fundamental difference in the behavior observed between the Pd/D codeposition from heavy and Pd/H from light water. In the latter case, temperatures T₁ and T₂ were equal and no temperature rise was noted upon termination of the current flow.

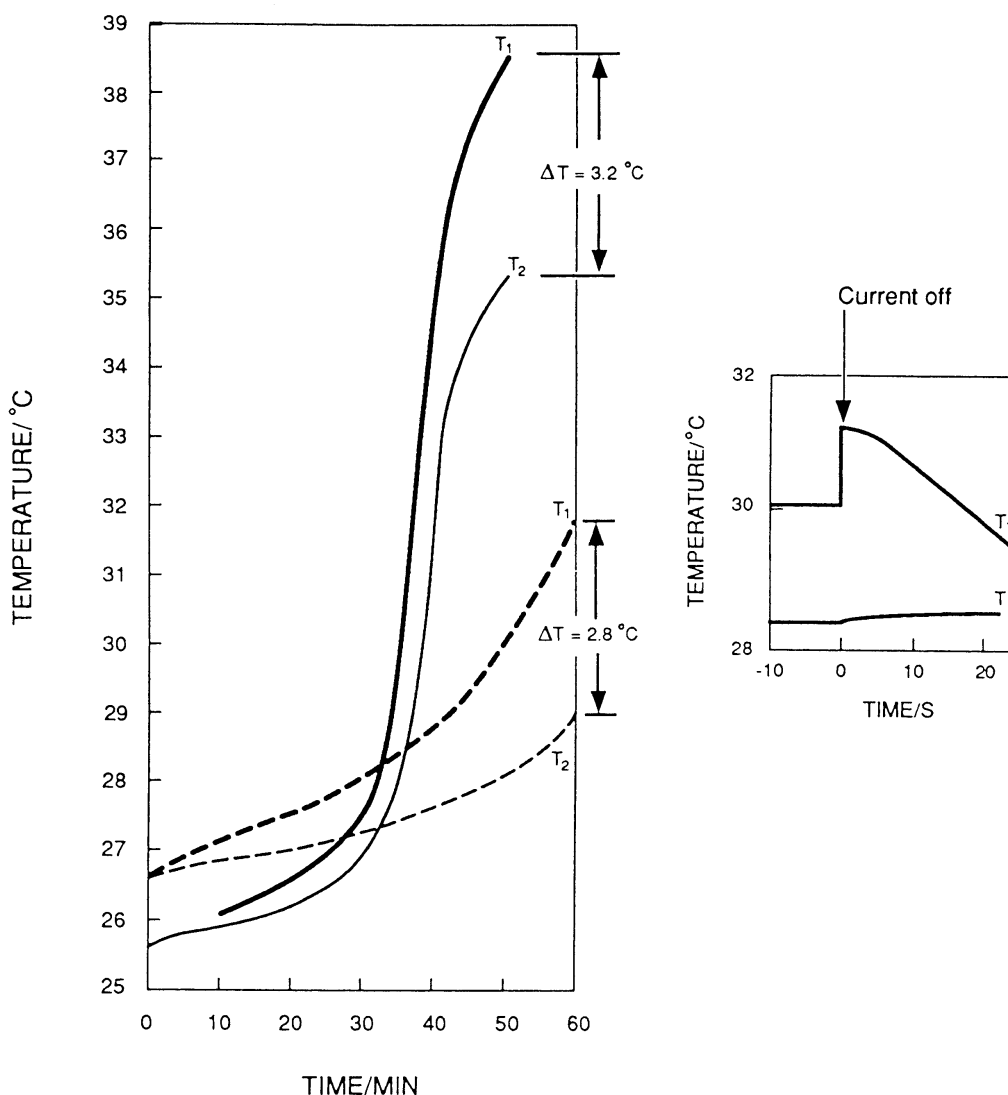


Fig. 3. Electrode/cell temperature evolution for two experiments. Thermocouple identification as in Fig. 1. Insert: jump in electrode temperature upon termination of current flow.

An example of a more accurate estimate of excess enthalpy production is illustrated in Fig. 4. To minimize heat losses, the electrochemical cell was immersed in a water bath whose temperature was kept equal, within 0.3 K, to that of the cell interior. The energy balance, however, did not include the latent heat of vaporization and the heat carried out by the evolving gases, i.e., in reality, the excess enthalpy production was somewhat greater than reported in Fig. 4. The production of excess enthalpy required 0.25×10^4 J and occurred after ca. 20 min of charging. No correlation between the variation in the cell current and potential, the temperature difference, $\Delta T = T_1 - T_2$, and the excess enthalpy production was attempted (further details will be published at a later time).

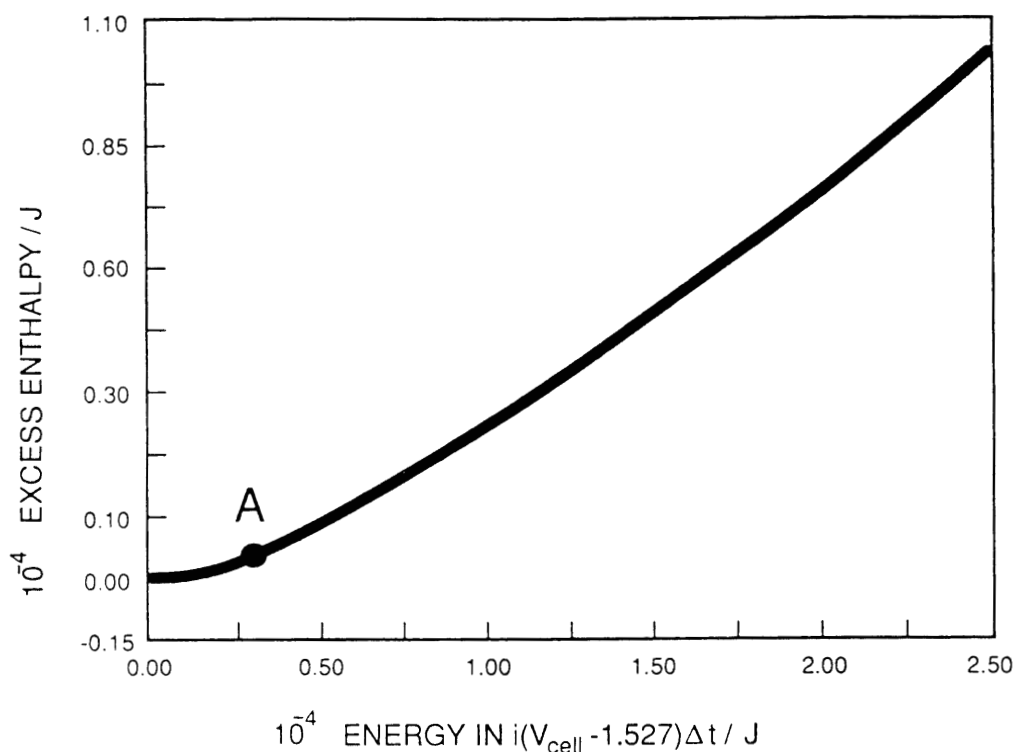


Fig. 4. Excess enthalpy production. Working electrode: Ni screen temperature gradient between cell interior and water bath not greater than 0.3 K. Point A: energy input needed to generate excess heat, 0.25×10^4 J time elapsed: ca. 20 min.

The analysis of spent electrolyte for tritium concentration showed an order of magnitude increase over that initially present in fresh electrolyte. In particular, the analysis of electrolytes from eight different runs showed the ^3H concentration within the range 230–270 disintegrations per min per cm^3 , compared to 30 in fresh electrolyte. It is noteworthy that this ca. ten-fold enrichment of tritium occurred after 10 to 16 h of electrolysis. This enrichment of tritium cannot be attributed to any external factors because (i) no electrolyte was added in the course of electrolysis and (ii) the cell interior was separated from the outside by a trap filled with heavy water. Appropriate precautions were taken to eliminate the interference of chemi-luminescence. The control experiments produced no tritium.

Evidence of the radiation emanating from the negative electrode is presented in Fig. 5. The developed photographic film (Kodak) shows areas exposed to the radiative flux and those partially blocked by the Ni screen electrode. The interaction between the radiative flux and this particular film suggests that the source is a low energy radiation, likely soft X-rays. What appears to be a double or triple exposure is most likely due to slight displacement of the film with respect to the electrode that occurred in the course of the 12 h codeposition. It is noted that the radiograph shown in Fig. 5 was

obtained under conditions vastly different from those reported recently [5,6], i.e., during the Pd/D codeposition rather than from Pd electrodes examined after successful completion of excess enthalpy generation. No radiation was observed in the control experiment. within the range 230—270 disintegrations per min per cm³, compared to 30 in fresh electrolyte. It is noteworthy that this ca. ten-fold enrichment of tritium occurred after 10 to 16 h of electrolysis. This enrichment of tritium cannot be attributed to any external factors because (i) no electrolyte was added in the course of electrolysis and (ii) the cell interior was separated from the outside by a trap filled with heavy water. Appropriate precautions were taken to eliminate the interference of chemiluminescence. The control experiments produced no tritium.

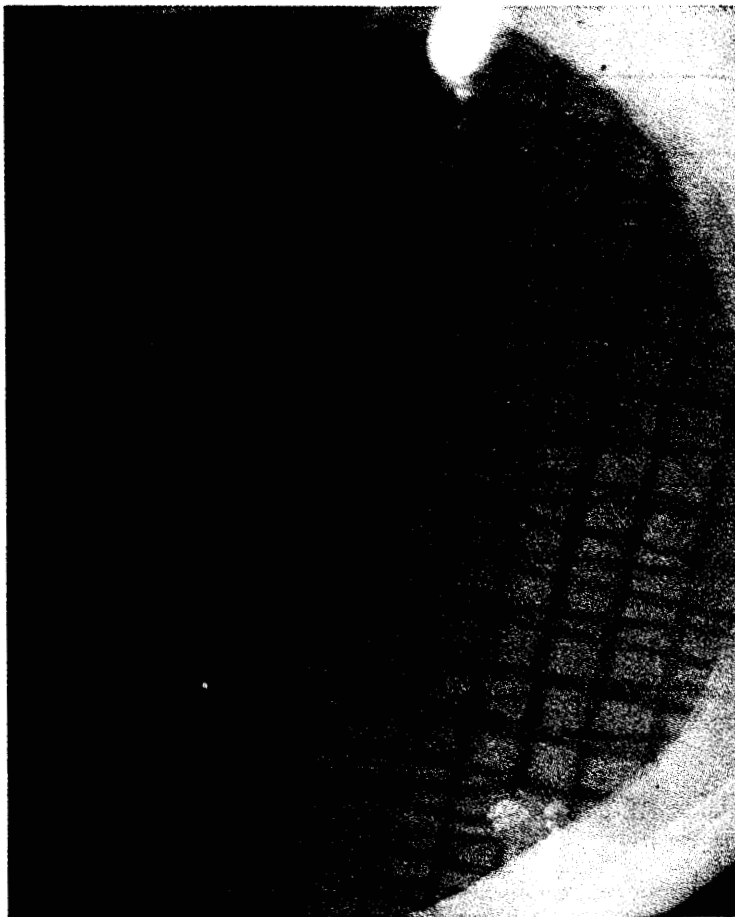


Fig. 5. Record of radiation emanating during Pd/D codeposition.

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