

RELIABLE PROCEDURE FOR THE INITIATION
OF THE
FLEISCHMANN-PONS EFFECT

S. Szpak, * *P.A. Mosier-Boss* * and *J.J. Smith* **
* Naval Ocean Systems Center, San Diego, CA 92152-5000
** Department of Energy, Washington, DC 20585

Abstract

Statistics on the initiation of the Fleischmann-Pons effect are rather poor. Reports presented at the First Annual Conference on Cold Fusion have indicated that, at best, only *ca* 1/10 of all attempts were successful in either producing excess enthalpy or yielding products associated with nuclear reactions. Here, we show that the Fleischmann-Pons effect can be reproducibly and rapidly initiated by employing electrodes prepared by electrodeposition from Pd^{2+} salts in the presence of evolving deuterium. The effectiveness of this procedure is examined in terms of tritium production.

1.0 Introduction.

On 23 March 1989, the TV audience, worldwide, learned that substantial amounts of energy can be generated by nuclear events in an electrochemical cell(1). Of many attempts to reproduce reported results, few succeeded and often irreproducibly. Reasons for a low success rate are not known. A generally held opinion is as follows: the Fleischmann - Pons (F.-P.) effect is a threshold phenomenon of a non-steady state character. It is believed that a number of conditions must be met to "switch-on" an electrode with the degree of loading being of paramount importance. The electrode loading, in turn, is governed by processes occurring within the electrode/electrolyte interphase(2). It is generally believed that the F.-P. effect is caused by non-steady state processes which appear as steady-state because of an averaging of small perturbations. The nature of these perturbations is not known but, most likely, they can be expressed in terms of localised gradients of the chemical potential.

In this communication, we report on an experimental procedure to initiate the F.-P. effect, *viz.*, the Pd/D co-deposition(3). This approach takes advantage of the existence of localised, time dependent gradients generated by an ever expanding electrode surface, *i.e.*, one that is created under non-steady state conditions. More importantly, it eliminates long charging times. In what follows, we describe the procedure required, provide the evidence for the occurrence of nuclear events *via* tritium production, discuss the morphology of the electrodeposited palladium as well as examine some of the structural aspects of the Pd electrode prepared by co-deposition.

2.0 The Pd electrode.

Palladium is very unique in its ability to absorb large quantities of hydrogen isotopes. Basic considerations of the electrochemical charging of the *Pd* rods have led to a model in which the interphase region plays a dominant role and the elementary processes govern the transport into the bulk. In particular, we adapted a model where the interphase is not an autonomous entity, *i.e.*, its structure as well as the operating driving forces are determined by participating processes occurring in the bulk phases in contact with each other. In addition to purely electrochemical considerations, the operating forces are subject to mechanical constraints arising from lattice expansion following the absorption of the interstitial, nH ; $n=1,2,3$. This model assumes a position independent surface coverage of the reactive species - a rather unrealistic assumption, as demonstrated by the existence of a region in which there is preferred penetration of nH .

Regions of preferred penetration can be displayed using the Nomarski optics where very small dimensional changes can be observed and recorded on a video tape. An example of the changes of the electrode surface obtained by electronically subtracted images recorded on the tape, are shown in Fig. 1. Evidently, even within a single grain, there are preferred sites of absorption. Clearly, an assumption of uniform surface coverage of the *Pd* rod cannot be justified in modeling exercises. An even more serious deficiency is the employment of the simplest interphase when, in fact, a supercharged region exists as indicated by the X - ray diffraction spectra.

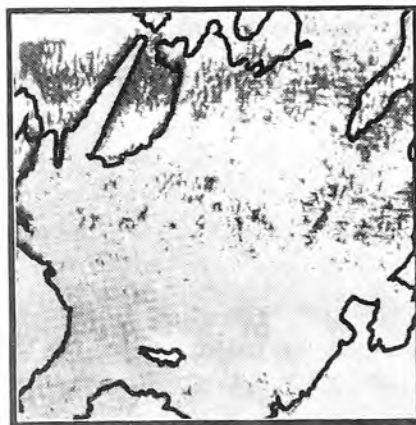


Fig. 1 - Evolution of surface morphology after 2 min. charging. Subtracted image is shown; individual grain is outlined

2.2 In situ X-ray diffraction spectrometry

The diffraction spectrum for the palladium foil immersed in an electrolyte at the rest potential is shown in Fig. 2. After two hours of charging at 1.5 V cathodic overpotential, while the electrode appearance has not changed, its structure has, namely, the formation of β -*PdD* is in evidence (peaks at 39.048° and 42.245° ; 2θ), Fig. 2b. With prolonged charging, the silvery color of metallic palladium has changed to black and, after 24 hours of charging, the recorded spectrum was that of the β -*PdD* phase only. With continued charging at somewhat higher overpotentials, a broadening of peaks is observed with no shift in their location, *i.e.*, indicating the presence of a supercharged layer. It is of interest to note that, upon termination of the current flow, escape of large quantities of absorbed deuterium occurs.

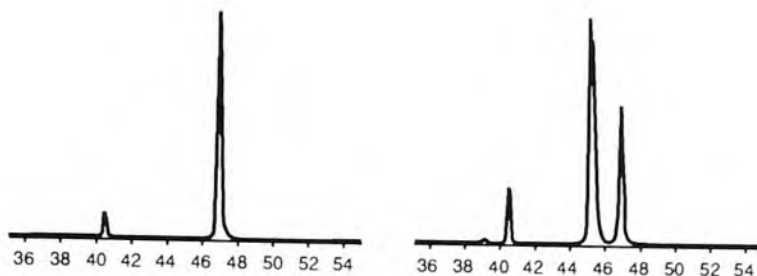


Fig. 2 - Progress in electrode loading by *in situ* X - ray diffraction.
left - electrode at rest potential; right - after charging for 3 hrs at $\eta = 1.5$ V

2.3 Preparation of Pd electrode by process of co-deposition.

Based on the above discussion, a rational approach to construct a Pd electrode suitable for rapid initiation of the F.-P. effect is by electrodeposition of palladium in the presence of evolving deuterium(3). In practice this can be done by deposition from a nearly saturated solution of $PdCl_2$, (approx. 0.05 M), in D_2O containing 0.3 N $LiCl$. The rate of deposition is potentiostatically controlled with the cell potential selected so as to promote vigorous deuterium evolution. Our present practice has been to begin the electrodeposition at a cathodic overpotential of 0.8 V and gradually increasing it to ca 3.0 V. The preferred substrate is a copper foil, although nickel has also been used. The evolving deuterium is co-deposited with Pd forming the β phase or, perhaps, containing even higher deuterium content. The Pd samples, electrodeposited in the presence of evolving deuterium were characterized by X - ray photoelectron microscopy. Resulting spectra were those of extremely pure palladium without traces of Pt, Ag, Rh, Si, Cl, i.e., elements that could have been deposited in the course of electrolysis(4).

3.0 Tritium production

One way to demonstrate the initiation of the F.-P. effect is *via* the tritium enrichment in the electrolyte phase. In an open system and in the absence of nuclear events, the time rate of change of the tritium concentration arises from two sources, *viz.*, the isotopic enrichment and the addition of the tritium containing heavy water needed to maintain a constant electrolyte volume. Typical progress in the codeposition and the onset of tritium production, together with the applied overpotentials, is illustrated in Fig. 3. According to these results, the codeposition process is completed within the first

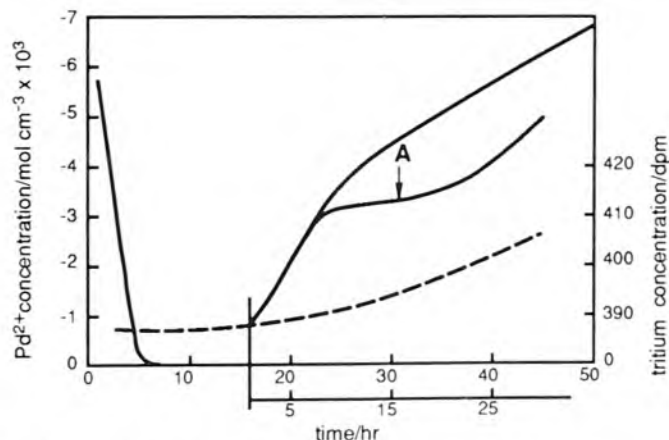


Fig. 3 - Early period in the co-deposition process.
Left - Pd^{2+} concentration as a function of time; right - 3H as a function of time; point A indicates addition of $SC(NH_2)_2$; dashed line - calculated isotopic enrichment

six to eight hours. The onset of tritium production, measured as an increase in dpm in the electrolyte phase, occurs somewhat later, *e.g.*, within hours after completion of co-deposition. The difference between the calculated enrichment, lower curve, and measured tritium concentration in the electrolyte phase indicates tritium production during the process of electrolysis.

3.1 Tritium distribution: electrolyte/electrode/gas phase.

Nuclear events producing tritium can occur at one or more locations, *viz.*, at the electrode surface, within the interphase or within the bulk electrode. Our experimental evidence seems to rule out the existence of dendrite assisted processes. Consequently, we adopt the view that these events occur within the *Pd* lattice, inclusive of the metal side of the interphase region. The location of the nuclear events might have a bearing on the distribution of tritium.

Examples of tritium production in cells employing *Pd* electrodes prepared by co-deposition during the electrolysis of D_2O containing dissolved $LiCl$ and Li_2SO_4 (0.3 N) are shown in Fig. 4. The increase in tritium concentration in the electrolyte phase is far greater than that due to the isotopic effect. The same applies to the composition of the gas phase. Most of the tritium generated by the electrochemical compression of deuterium appears to enter the gaseous phase. A cursory examination reveals that the rate of generation is not constant. We cannot ascertain, at this time, whether the change in the rate of production is smooth, or occurs in bursts as in cells using a conventional electrode design.

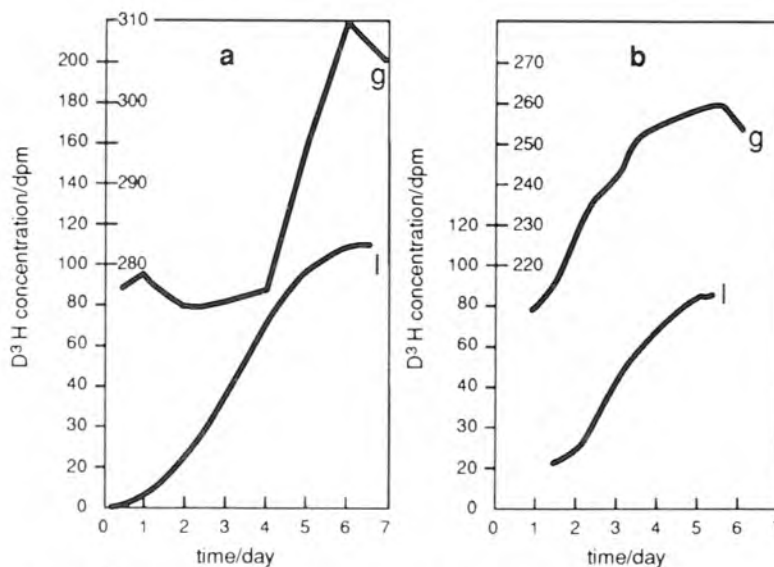


Fig. 4 - Distribution of 3H generated by electrochemical compression of 2H .

Electrolyte: a - 0.3 N $LiCl$ in 2H_2O b - 0.3 N Li_2SO_4 in 2H_2O ; l - electrolyte phase, g - gas phase

4.0 Electrode: its structure and behavior

The reproducibility of the F.-P. effect in cells employing electrodes prepared by the co-deposition process may be attributed to their morphology and purity. The growth form of the electrodeposited *Pd* is affected by processes occurring within the ever-changing interphase, primarily by the surface processes and mass transport. It can be assumed that the electrocrystallization of palladium in the presence of evolving deuterium must accommodate as well as be affected by the presence of deuterium.

The SEM photograph is typical of a three-dimensional nucleation. The co-deposited palladium consists of submicron spherical particles, Fig. 5. Such a morphology provides a large surface to volume ratio and, if a porous structure can be maintained, substantial amounts of deuterium can be absorbed. The remarkable feature of the deposit is its relatively high mechanical strength which can

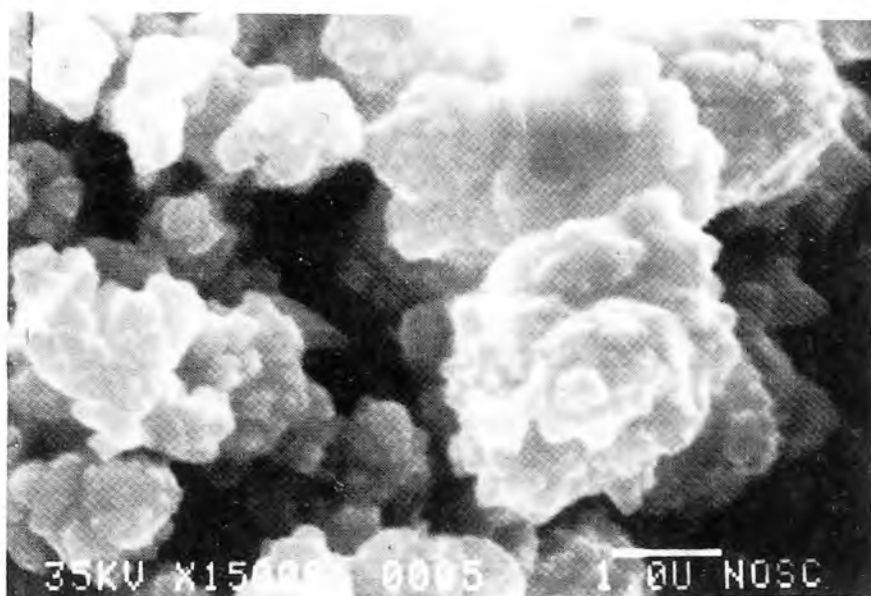


Fig. 5 - SEM photograph of co-deposited *Pd*

be attributed to the fact that the palladium is saturated with deuterium while being deposited so that further lattice expansion is not necessary. Dandapani and Fleischmann(5) concluded that the slow step is the discharge of D_3O^+ ions in acid solutions and D_2O molecules in alkaline electrolytes, *i.e.*, the charge transfer reaction is followed by a rapid absorption and $\alpha \rightarrow \beta$ phase transformation, followed by a rapid recombination, when the electrode charging has been completed. By charging we mean an accumulation of deuterium on the electrode surface, within the interphase, and within the bulk. Transport of deuterium in the bulk is by diffusion and governed by the time-dependent concentration at the plane separating the interphase from the bulk. Whether or not the electrode charging is controlled by the interphase or the bulk depends on the rate constants of the elementary processes involved in the charge transfer, and to a much lesser degree, by the thickness of the electrode(2).

4.0 Conclusions

(i) Predictions based on the modeling of the electrochemical charging of *Pd* rods are not reliable because of the lack of relevant input data and the existence of preferred absorption sites. Specification of surface coverage and electrode active areas is questionable.

(ii) At least three periods in the course of electrode charging can be identified. First, initially the β phase is dispersed throughout the *Pd* metallic phase. (The absence of the α phase indicates a rapid $\alpha \rightarrow \beta$ phase transition.) Second, total conversion to the β phase can be recognized by viewing the color of the electrode surface. (Transition from silvery to black). Third, a supercharged layer is formed. (When the β -*Pd* phase is further charged at high overpotentials).

(iii) Electrodes prepared by the co-deposition process reliably initiate the F.-P. effect, at least in terms of tritium production.

References

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