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The effect of an external electric field on surface morphology of co-deposited Pd/D films

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Abstract

The polarized Pd/D electrode undergoes significant morphological changes when exposed to an external electric field. These changes range from minor, e.g. re-orientation and/or separation of weakly connected globules, through forms that result from a combined action of the field as well as that connected with the evolution of gaseous deuterium, to shapes that require substantial energy expenditure. ©2005 Elsevier B.V. All rights reserved.

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1. Introduction

A prolonged electrolysis of H₂O/D₂O, with the H₂/D₂ evolution taking place on solid Pd electrodes, produces substantial morphological changes in their surfaces [1]. They reported the following characteristic features: (i) the starting etch morphology affects the development of specific surface morphologies, e.g. the formation of “parallel rows of sharply edged ridges”, (ii) an intergranular uplifting of “structured” relative to “unstructured” grains and (iii) the PdD_x–D₂O system is more reactive than the PdH_x–H₂O system. Features (i) and (ii) indicate that, near the surface, a permanent deformation of the electrode material has occurred. The origin of change in surface morphology was not discussed in detail.

The starting point in our discussion is an observation that any solid undergoes permanent shape change when the internal forces exceed the elastic limits. In general, three types of forces can be identified as acting during the deformation of a solid, viz. (i) internal forces, i.e.

those forces that obey Newton’s law, (ii) applied (or external) forces, and (iii) capillary forces. The capillary forces (forces that act between the internal and surface molecules, or between solid boundary and the molecules of surrounding fluid) can be classified as either internal or external forces. When surface forces are non-uniformly distributed, they act as external forces [2].

If, in fact, capillary forces are involved in producing shape changes, then they can be magnified by placing the operating cell in an electrostatic field. In what follows, we examine the response of the Pd/D film, prepared by co-deposition [3], i.e. by simultaneous reduction of Pd²⁺ and D⁺/D₂O ions/molecules to an external electric field. The discussion is qualitative, because a complete determination of the deformation involves the solution of equations of the theory of elasticity with well defined boundary conditions. Because of the very complex nature of this system, this cannot be done even if drastic simplifications are invoked. In agreement with Rolison and Trzaskoma [1] observation, we found also that the Pd/D₂O system is more reactive than the Pd/H₂O system and, for this reason, only the behavior of the former is presented.

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2. Experimental

In an attempt to confirm the premise that surface forces initiate and, to a degree, govern the evolution of new structures during the electrolysis of D_2O , we followed the experimental protocol as described in Section 2.1.

2.1. Experimental protocol

An operating PdD// D_2O , 0.3 M LiCl//Pt cell was placed in an electrostatic field generated by a parallel plate capacitor where the field strength was maintained and controlled by setting the potential difference at a specified level. The cell geometry is shown in Fig. 1. The PdD electrode was prepared by the Pd electrodeposition onto an Au foil from a solution of 0.03 M $PdCl_2$ + 0.3 M LiCl dissolved in D_2O . The electrodeposition was under galvanostatic control with the current

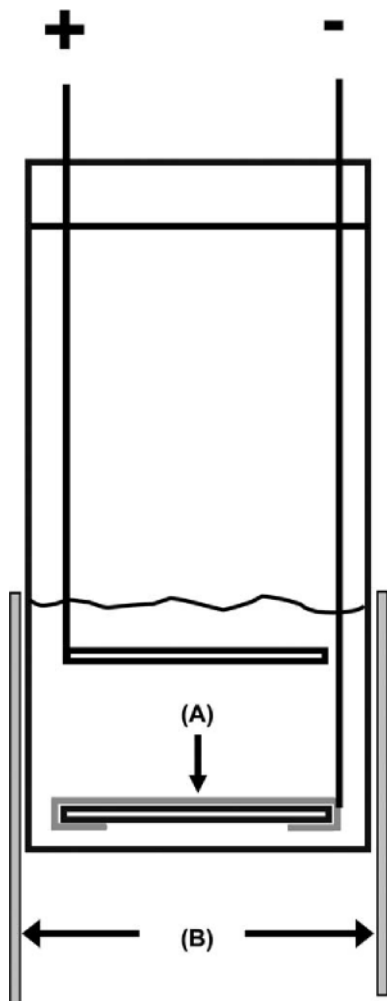


Fig. 1. Electrochemical cell. A– Au foil, B– copper plate (volume of electric field greater than volume of electrolyte).

density profile as follows: 1.0 $mAcm^{-2}$ for 8 h, 3 $mAcm^{-2}$ for 8 h and at 5.0 $mAcm^{-2}$ until all Pd^{2+} ions were reduced, i.e. when, by visual inspection, the solution becomes colorless. Upon completion of the Pd deposition, the cell current was increased to a value needed to maintain a visible gas evolution (usually 30– 50 $mAcm^{-2}$) for the next 2–3 h followed by the cell placement in an electric field (2500– 3000 Vcm^{-1}) with the cell current increased to about 100 $mAcm^{-2}$ for the next 48 h or longer. It is noteworthy that, after the co-deposition is completed, the cauliflower structure [4] is not affected by the applied current density. However, during the co-deposition low current densities are required to prevent the formation of powdery deposits.

3. Effect of an electric field

The variety of forms/structures resulting from the exposure to an electrostatic field (vide infra) strongly suggest that they arise from the co-operative and/or competitive interaction between cell components, relevant processes and their driving forces. Thus, to provide a rational interpretation one must: (i) consider the interaction of the field with the system and, in particular, with a conductor, liquid dielectric and the relationship between the surface forces and the bulk response (background information), (ii) define the system and its initial conditions (i.e. conditions just before the cell placement in an electric field), (iii) examine the effect of the field on the operation of individual components of the electrochemical cell.

3.1. Background information

To facilitate the identification of the dominant processes responsible for the change in both the surface morphology and the bulk structure, we review the interactions between the electrostatic field and the elements of an operating electrochemical cell. In particular, we include thermodynamic considerations, interactions with conductors, liquid dielectrics and the laws governing the bulk response to the surface forces.

3.1.1. Thermodynamic considerations

The energy transferred into molecules by stationary electric fields of less than $10^4 Vcm^{-1}$ is small compared with the energies of chemical bonds. Consequently, from a thermodynamic point of view, the electric field is regarded as a new variable [5,6]. Its effect is included in the $\sum_i l_i \delta L_i$ term of the infinitesimal change in the internal energy

$$\delta U = T\delta S + \sum_i l_i \delta L_i + \sum_j \mu_j \delta n_j \quad (1)$$

where l_i and L_i are the work coefficients and work coordinates (other symbols have their usual meaning). In

the electrolyte phase, this term reads: $-p\delta V + \mathbf{E}\delta(\mathbf{P}V)$, where the work coefficient is the electric field strength \mathbf{E} , and the conjugate work co-ordinate, $\mathbf{P}V$, is the product of the electric polarization, \mathbf{P} , and volume V , while for the electrified interphase additional terms must be added. An extensive treatment of the thermodynamics of electrified interfaces can be found in [7] and references therein.

The thermodynamics of a solid system is analogous to that of a liquid with 6 quantities, $V_0\varepsilon_i$, replacing volume, V (the quantity, $V_0\varepsilon_i$ is a product of reference volume and the strain component; the associate intensive parameter is the stress component). Thus, the fundamental equation of a solid system is $U = U(S, V_0\varepsilon_1, \dots, V_0\varepsilon_6, n_j)$. In particular, internal forces are associated with the strain just as the pressure is associated with the volume in a liquid system [5].

3.1.2. Conductors

Of interest here are the following effects: (a) introduction of an uncharged conductor into the field reduces the total energy of the field, (b) an uncharged conductor located outside the field is attracted towards the field, (c) a conductor, charged or uncharged, when placed in an electric field, cannot remain in stable equilibrium and (d) a “negative force” acts on the surface of a conductor [2, pp. 7, 31]. Consequently, if this conductor is constrained then it will suffer shape change, either reversible or permanent, depending upon the conditions at the surface and the time interval involved.

3.1.3. Liquid dielectric

While a conductor, when placed in an electric field always suffers “negative pressure”, a dielectric may either expand or contract, i.e. it may experience either negative or positive pressure. For the detailed discussion consult [2, p. 54].

3.1.4. Forces acting on the contact surface: shape change

The relationship between the surface forces and the bulk response (the Gauss theorem) is given by

$$\int \operatorname{div} \mathbf{A} \, d\tau = \oint A_n \, d\sigma, \quad (2)$$

where the div operator derives a vector from tensor. The left side term is the algebraic sum of all sources/sinks continuously distributed over the volume element. The right side defines the outflow, if positive and the inflow, if negative. Eq. (2) indicates that forces acting on any finite volume in a body can be reduced to forces applied to the surface of that volume and vice versa [8]. Consequently, it follows that the shape change at constant volume is associated with material motion due to internal forces acting on the surface. Thus, the deformation will be determined by the distribution of surface forces, while the rate of deformation by their magnitude.

However, internal stresses can be present without the presence of external loads, e.g. due to inhomogeneities, imperfections, etc, a likely situation in co-deposited films and the continuous evolution of deuterium. Thus, the change in shape and the degree of deformation depends on the distribution of the surface forces and indirectly through structural changes caused by these forces or other reactions.

3.2. The Pd/D–D₂O system: initial conditions

An operating cell is viewed as a system consisting of three subsystems, viz. the electrolyte, the interphase and the bulk Pd/D. The interphase itself is an assembly of non-autonomous layers defined by van Rysselberghe [9]. The electrolyte, an ionic conductor, is treated as a dielectric with added extraneous charges (positive and negative ions). The Pd/D system is considered a conductor containing, in addition to free electrons also mobile positive particles, the D⁺ species.

Just before the application of an external electric field all intensive state variables were constant in time, i.e. all irreversible processes inside the system occur continuously (there is a continuous exchange between the system and surroundings). The processes involved are: reduction of D⁺/D₂O ions/molecules and evolution of D₂. The mechanism of these reactions is not important except to say that all operating driving forces remain constant in time.

3.3. Effect of electric field

By placing an operating electrochemical cell, a part of the field energy is transferred to the cell. In particular, the electrostatic field affects each individual subsystems, viz. electrolyte, interphase and bulk electrode, in a different way. Moreover, the action may be either direct or indirect; in the latter case, it affects a process which is not directly connected with the presence of the electrical charge.

3.3.1. The electrolyte phase

The electrolyte phase contains mobile positive and negative ions distributed in a manner that assures charge neutrality (except at boundaries). It is known that an ion in contact with water is solvated, which means that the central ion is surrounded by an oppositively charged ionic cloud. When subjected to an external electric field, each ion is acted upon with a net force representing the difference between the accelerating force arising from the applied field and the opposing forces, viz. (i) the electrophoretic contribution associated with the structure of the moving entity (i.e. the central ion is accelerated in one direction while its ionic cloud in another), and (ii) the force connected with the relaxation of the ionic cloud [10].

3.3.2. Interphase

To reiterate, the interphase is an assembly of non-autonomous layers defined by the set of processes:

$D^+_{(r)} + e^-_{(r)} \rightarrow D_{(ad)} \rightarrow D_{(ab)} \rightarrow D^+_{(l)} + e^-_{(l)} \rightarrow D^+_{(m)}$. The positive and negative charges present in the interphase (the $D^+_{(r)}$, $D^+_{(l)}$, $e^-_{(r)}$, $e^-_{(l)}$ species) are mobile with the degree of mobility depending upon local conditions. When subjected to the applied field, the response is similar to that of the electrolyte phase, i.e. separation and drift of charged particles and an analog to mixing by time/ space dependent adsorption of deuterium.

Evidently, the interaction between the applied field and the forces acting at the surface during the reduction of D^+ ions (D_2O molecules) is primarily responsible for the observed changes in surface morphology illustrated in Figs. 3–7. The basis for this conclusion is the Gauss theorem, Eq. (2), and the structure of the interphase arising from the participating processes, inclusive of transport processes [9]. The bulk response arising from the Gauss theorem depends on the degree of change in the internal energy which, in turn, depends on the work of deformation, i.e. on the product of the strain component, $V_0\varepsilon$ and its conjugate stress component, σ .

3.3.3. Bulk Pd/D

Any charges on a conductor must be located at its surface. Charged mobile species, viz. D^+ , are also present in the bulk Pd/D material. In general, they will not be affected by an external field, since no field can exist there. However, in the present case, they might be affected by the field generated by the flow of cell current, i.e. the electrodiffusion of D^+ might occur.

4. Results and interpretation

The application of an external electrostatic field substantially changes the structure of the PdD deposits. This is illustrated in a series of SEM photographs taken from a number of runs. We selected examples of various structures to emphasize the complexity of the system as well as to indicate the impossibility of a quantitative analysis. The selected examples include minor deformation of the original structure shown in Fig. 2, definitive shape change, unusual structures, to a deformation associated with, what appears to be, a catastrophic event.

4.1. Reference morphology

In the absence of an external field, the structure of the deposits consists of globules, 3–7 μm in diameter, arranged in short columns, Fig. 2. Each of the individual globules is an aggregate of much smaller, almost spherical units, having diameters in a sub-micron range (micro-globules). The structure is uniform throughout the electrode and does not change with time or with the current density after the completion of co-deposition.

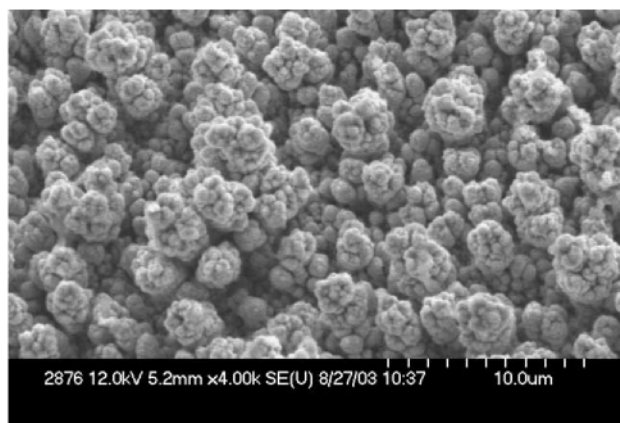


Fig. 2. SEM of co-deposited PdD film.

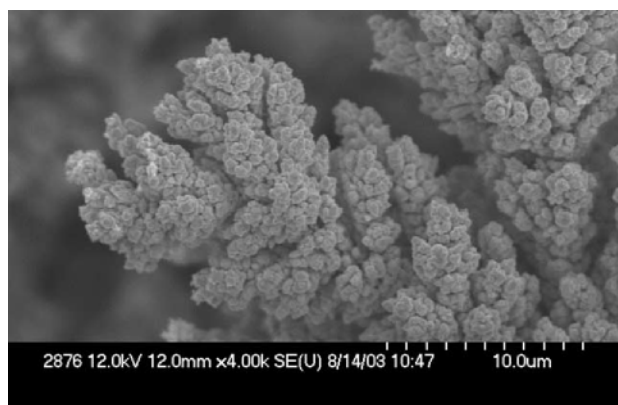


Fig. 3. SEM of the PdD film shortly after exposure to electric field.

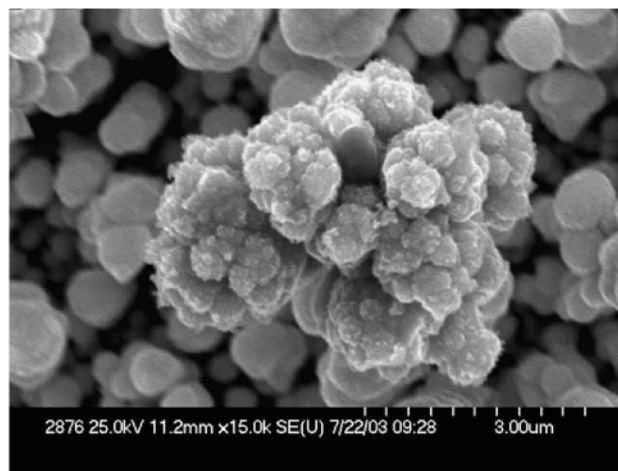


Fig. 4. SEM of the PdD film showing separation of globules and "smoothing" of their surface.

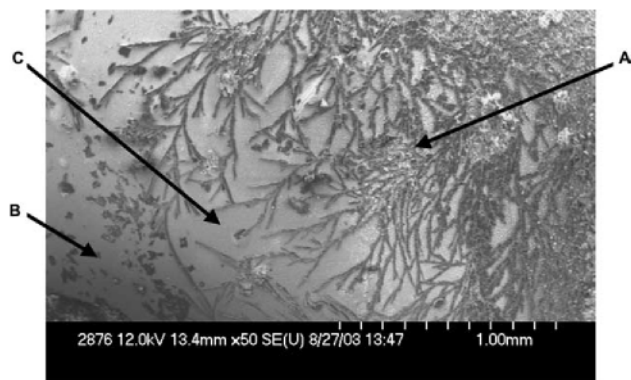


Fig. 5. Formation of branches (fractals) by the free floating micro-globules guided by local field.

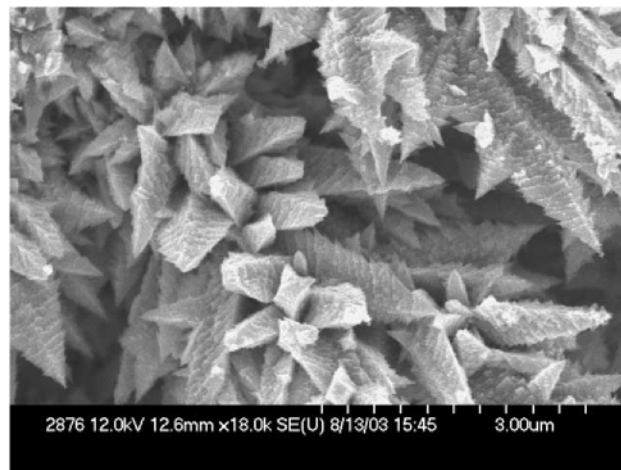


Fig. 6. Dendritic growth due to the action of the cell current on micro-globules immobilized in tight pores.

4.2. Re-orientation: globules separation

The first noticeable effect, after placing the cell in an electric field, is the “swelling” of the co-deposited PdD material followed by a displacement toward the negative plate of the capacitor. These visual observations suggest that (i) the swelling arises from an interaction of the constrained porous structure with an external field, (ii) the displacement toward the negative plate indicates weakening of the mechanical constraints and assigns a positive charge to the structural elements of the porous

structure of the PdD material. The re-orientation of globules position without substantial change in their size or appearance is shown in Fig. 3. We note that such re-orientation is associated with an increase in volume thus it would appear as “swelling” of the original structure. Indeed, this swelling is observed within minutes after engaging the electrostatic field.

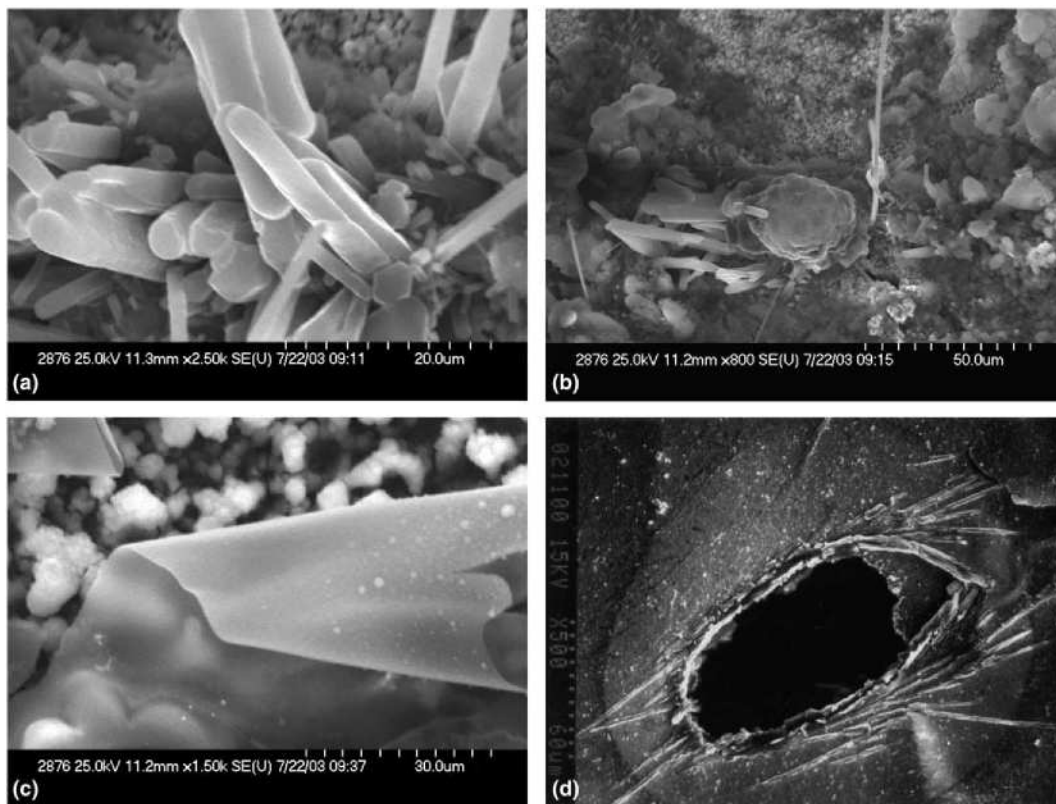


Fig. 7. Examples of the shape change requiring substantial energy expenditure. (a) Formation of circular and square rods, (b) a boulder with an extended wire, (c) a folded thin film, (d) a crater.

Another example of the disintegration of the PdD structure is shown in Fig. 4. This figure illustrates the breaking of the bonds holding together individual globules. The breaking of bonding and the separation of globules may be due to action of electrical forces alone or may be due to combined action of electric and mechanical forces arising from the bulk material response to the changing magnitude of surface forces (cf the Gauss theorem).

4.3. Effect of current distribution

A different set of processes appears to be responsible for the structural changes, viz. (i) the formation of branches (fractals), Fig. 5, and (ii) the production of dendritic growth, Fig. 6. In what follows, we argue that these two very different forms may have a common origin, namely that they are the result of a combined action of the current flow through a porous structure, the presence of evolving deuterium and the electric field on the separated micro-globules suspended in the electrolyte and restricted by the porous structure.

The observed morphological and structural changes occur during the reduction of D^+/D_2O ions/molecules at porous electrode. Thus, at least three factors should be considered: (i) the external field, (ii) the distribution of the cell current and (iii) the presence of gaseous deuterium within the confines of the structure. Since the depth of current penetration (for a given electrode kinetics, current density, etc) into the electrode depends on pore size and assuming that all factors are involved, a different response to the field are expected at different sites of the PdD material.

At sites of a relatively large pore size, the microglobules are acted upon by two factors, the electric field and the convective flow due to mixing by the evolving deuterium. The electric field redistributes the surface charges while the evolving gas brings micro-globules in contact with each other. Viewing Fig. 5, we identify three areas having distinct features: area A with high density of branches and unattached micro-globules, a sparsely populated by micro-globules, area B, and area C where unattached micro-globules are absent and where branches (fractals) are well defined. The latter indicates that the growth of branches is by addition of micro-globules leading to an apparent reversal of the action of an electric field (cf. Section 4.2 and Fig. 4).

Entirely different situation exists in small pore sizes; the pore wall may be covered by gaseous deuterium and thus shifting the cell current deeper into the porous structure. If a micro-globule is placed in the current path, and, if the potential drop over the length of the micro-globule in the electrolyte is greater than the sum of the anodic and cathodic overpotentials needed to dissolve Pd and deposit the Pd^{2+} ions, then dendritic growth is possible, as demonstrated in [11].

4.4. Unexplained shapes

While the morphologies shown in Fig. 3–6 can be accounted for on the basis of information assembled in Section 3.1, those in Fig. 7 suggest that additional factors are involved in producing the observed shape changes. Of the great variety of forms, we selected those illustrating the re-shaping of the spherical globules into (i) rods (circular and square), Fig. 7(a), (ii) long wire, Fig. 7(b), (iii) folded thin film, Fig. 7(c), and (iv) a crater, Fig. 7(d), the latter suggesting the presence of a violent event.

5. Closing remarks

In order to change the shape of a solid (at constant volume) energy must be supplied. This requirement raises a number of questions, among them: (i) how much energy is needed to produce the observed changes in both, original surface morphology and/or structure; (ii) is there enough energy available; (iii) what is the energy transfer path; (iv) at what rate the energy should be transferred to the solid to account for the observed changes.

- (i) Energy requirement. A minimum of the energy expenditure is required to produce changes illustrated in Figs. 3–6. However, the changes shown in Figs. 7(a)–(d), cannot be produced by the action of electric forces alone. Considerable work is needed to account for the variety of shapes. It appears that the process of shape change is driven by energy transferred from the electrostatic field and directed by the field.
- (ii) Energy of the electrostatic field. Total energy of an electrostatic field is proportional to the field strength which, in turn, is proportional to the voltage difference between the plates of the condenser. Consequently, as long as the voltage between plates is maintained at the same level, the energy supply is unlimited.
- (iii) Energy transfer path. Two energy transfer paths operate during the experimental run, viz. transfer from the field and that associated with the electrochemical process, principally due to absorption of deuterium. Work in progress is directed to the assessment of their contribution.

Parenthetically, nothing substantial can be gained (in terms of understanding) by conducting a set of parallel experiments involving “light” water. In contrast, a comparison with “light” water is essential when evaluating excess enthalpy generation (the Fleischmann–Pons effect) [12]. Here, a cursory examination of the response of the PdH–H₂O system showed essentially the same

behavior as the PdD–D₂O system, i.e. the swelling of the cathode material as well as its leaning toward the negative capacitor plate. Qualitatively, under the same conditions, the PdH–H₂ system shows fewer shape changes and the absence of the distinct features such as those illustrated in Fig. 7.

In conclusion, we recall a quote by Rolison et al. [13] “...the surface and near–surface characterization of electrolytically prepared PdD_x system requires great care and attention, but with the reward of unusual results.”

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