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***In situ* measurement of the deuterium (hydrogen) charging of a palladium electrode during electrolysis by energy dispersive x-ray diffraction**

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A method to determine the concentration of deuterium inside a palladium cathode during the electrolysis of LiOD-heavy water solution is described. This method is based on the measurement of the host metal lattice parameter which is linearly related to the concentration in a wide range. A hard-x-ray beam which is able to cross two glass walls and few centimeters of water solutions without suffering a strong attenuation has been used. The measurement of the lattice parameter is performed *in situ*, during the electrolysis, by using energy dispersive x-ray diffraction. The sample volume illuminated by the x-ray beam is limited to a small region close to the surface and depends on the incident photon energy. In principle, this allows one to study the dynamics of the charging process and to determine the concentration profile in the range from few up to tens of micrometers. The deuterium concentration, determined by this method, was then checked by degassing the cathode in a known volume and was always found in a very good agreement, showing that the charging was uniform for the whole sample. © 1995 American Institute of Physics.

I. INTRODUCTION

The palladium hydride is one of the most investigated examples of the metal-hydrogen system both from the structural and the thermodynamical point of view. However, a wide range of phenomena, which are not well understood, still exists, mostly in the high-concentration region of H in Pd. The literature available in the high range of concentration is quite scarce because of the difficulty in obtaining suitable and reproducible samples. Usually the hydrogen (H) or deuterium (D) charging is determined at the end of the experiment by weighting or degassing the sample or by an anodic discharge measuring the total charge. However, to better understand the palladium hydride system would be very useful to know the exact concentration of H(D) in the sample during the experiment. Unfortunately, very few examples of the atomic ratio determination during the charging procedure¹⁻⁵ exist. In this paper we will show that x-ray diffraction can be usefully employed to determine the charging of a palladium cathode during the electrolysis. Our reported data will mainly deal with the deuterium-palladium system but an extension to the hydrogen case is trivial.

Many physical parameters depend on the concentration of deuterium in the D/Pd binary system. Electrical resistance increases almost linearly with respect to the concentration in a wide range before reaching a maximum at the ratio of about 0.8.⁶ The measurement of this parameter has been used to monitor the status of charging of the sample.² However, it has been shown⁷ that the insertion of hydrogen in palladium can cause an ordering of the structure of the host metal similar to an annealing procedure, leading to a different resistance value of the sample after degassing with respect to the initial value.

One of the most employed methods to charge deuterium (or hydrogen) is the electrochemical one, but resistance measurements, performed during the electrolysis, can be strongly

affected by the noise generated by the electric field of the electrolytic current itself. Thus this kind of measurement can only show the variation of the D/Pd ratio and indicate if the actual value is bigger or smaller than 0.8. At this value the derivative of the resistance with respect to the hydrogen content changes sign.

The insertion of deuterium (or hydrogen) atoms in a metal lattice causes an expansion of the periodic structure of the host metal. The increase of the unit-cell volume depends only on the D(H)/metal ratio and is the same for many materials.⁸ Deuterium expands the lattice about 5% more than hydrogen. The dependence of the lattice parameter of palladium in the α and β phases versus the concentration of hydrogen or deuterium has been largely studied, but there are very few data for concentration higher than the lower boundary of the β phase at room temperature. Schriber and Morosin⁹ measured the relation between the lattice parameter of the β phase and the H or D concentration at 77 K. They showed that this relation is linear up to an atomic concentration of about 0.9. By assuming that the thermal expansion of the system is the same as pure palladium, the following relation between the deuterium concentration and the lattice parameter is obtained at room temperature:

$$c = -23.502 + 59.904a, \quad (1)$$

where c is the concentration of D in atomic ratio with respect to Pd, and a is the lattice parameter in nanometer units.

The lattice parameter is generally measured by using the diffraction of an opportune wave caused by the crystal periodical structure. Either x rays or neutrons or electrons can be employed for this purpose, but they all present technical problems when performing an *in situ* measurement during the electrolysis because of the large absorption cross section of the water solution and of the container vessel which have to be crossed by the beam. The use of a hard-x-ray white

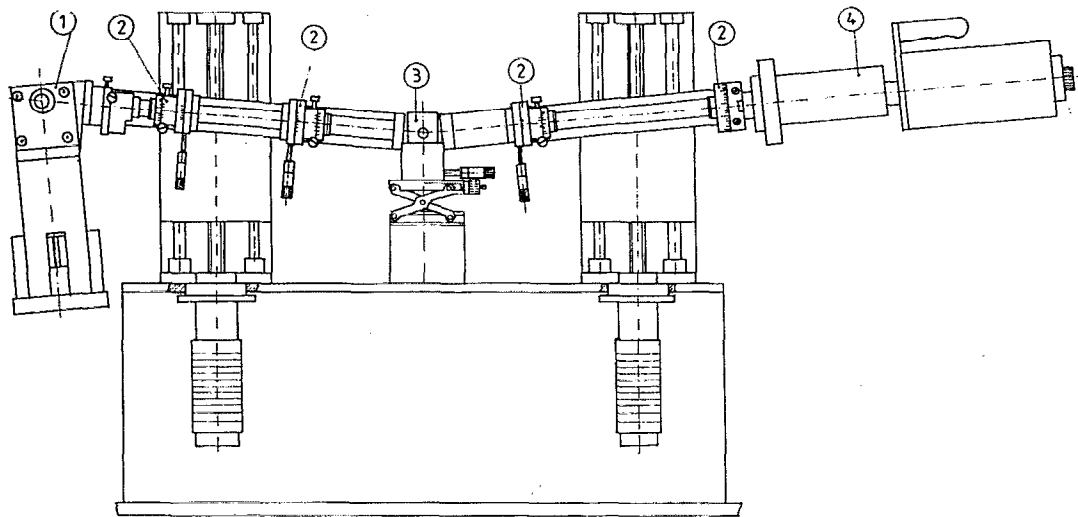


FIG. 1. Schematic layout of the energy dispersive diffractometer: (1) Tungsten or chromium x-ray tube, (2) collimating slits, (3) sample position, and (4) solid-state energy dispersive detector. All the components are mounted on two arms driven by linear actuators. The tangent of the angle is read by two linear encoders.

beam, which overcomes these problems, and of an energy dispersive detector allows one to measure the intensity of the diffracted beam from the surface of a palladium cathode during electrolysis. In this way we are able to determine the lattice parameter and by Eq. (1) the D/Pd ratio, *in situ*, during the electrolysis.

II. THEORY

In an x-ray-diffraction experiment an incident radiation of wave vector \mathbf{k}_0 is used ($|\mathbf{k}_0| = 2\pi/\lambda$, where λ is the wavelength of the incident radiation) and the intensity of the radiation diffused by the sample, with wave vector \mathbf{k}_1 , is measured as a function of the scattering vector \mathbf{q} :

$$\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_0, \quad (2a)$$

$$|\mathbf{q}| = q = (4\pi/\lambda) \sin(\vartheta), \quad (2b)$$

where 2ϑ is the angle between the \mathbf{k}_1 and \mathbf{k}_0 wave vectors. In general the measured intensity depends on the magnitude and on the orientation of \mathbf{q} with respect to the sample, but, for an ideal polycrystalline material, we can average along all the possible orientations of the grains and the diffused intensity is only a function of the magnitude q .

From Eq. (2) it is evident that we can measure the intensity either by varying the scattering angle ϑ at fixed incident energy, or as a function of the incident wavelength but keeping fixed ϑ . The first method is the most widely employed. The incident radiation is in general the K_α emission line of an opportune material (typically copper, $\lambda = 0.154$ nm). The diffused radiation is measured as a function of the diffraction angle by a scintillation counter. In the other method, which we have employed in the present measurements, a white beam is used and the diffused radiation is recorded by an energy dispersive detector.

In this case the energy dispersive method has two major advantages:

- (a) the incident energies are, in general, high enough for

allowing x rays to cross the cell walls and the electrolyte solution without suffering a strong attenuation;

- (b) the incident and outgoing beam directions are fixed with respect to the sample container, making the design of the cell very simple.

In the case of an ideal polycrystalline material having a simple cubic structure, as in palladium, the diffraction pattern shows peaks whose positions are defined by¹⁰

$$q = (2\pi/a) \sqrt{h^2 + k^2 + l^2}, \quad (3)$$

where a is the lattice parameter and h , k , and l are the Miller indices. The analysis of the peaks intensity allows one to determine the atomic positions inside the unit cell while the width of the peaks is related to the domain dimensions.

When we use the energy dispersive technique, it is more convenient to rewrite Eq. (3), by using Eq. (2), in order to make more evident the relation between the lattice parameter and the wavelength position of the peaks, as

$$\lambda = [2a \sin(\vartheta)] / \sqrt{h^2 + k^2 + l^2}, \quad (4a)$$

or as a function of the photon energy [remembering $E(\text{keV}) = 1.2398/\lambda(\text{nm})$]:

$$E = (2\pi \sqrt{h^2 + k^2 + l^2}) / [10.136a \sin(\vartheta)], \quad (4b)$$

where the lattice parameter a is in nanometers.

By an opportune choice of the scattering angle, a series of peaks will appear in the measured spectra. Since the penetration of a photon inside a material depends on its energy, different peaks also correspond to different sample depths and this can, in principle, allow one to determine the concentration profile.

III. EXPERIMENTAL APPARATUS

Our objective is to measure the lattice parameter of the palladium during the electrolysis by measuring the diffracted intensity of an x-ray beam as a function of the magnitude q

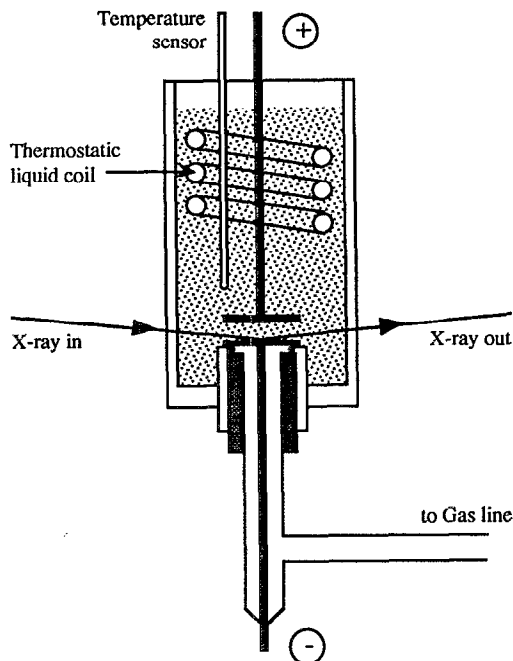


FIG. 2. Schematic layout of the electrolysis cell used to perform *in situ* x-ray diffraction from the surface of the palladium cathode. The electrolyte solution was a 0.1 M LiOD in heavy water solution. The cell temperature was kept constant by a thermostatic liquid circulating in a coil and monitored by a *K* thermocouple. The back side of the cathode was free in a gas line to measure the outcoming gas flux.

of the exchanged momentum. We have used a white incident beam and an energy dispersive solid-state detector. The drawing of the instrument is shown in Fig. 1. The device was specially designed to measure x-ray reflectivity from liquid surfaces; then the scattering plane is vertical.¹¹ Moreover, because the maximum angles of the incident and diffracted beams with respect to the horizontal plane are 40°, this instrument can also work as a diffractometer. The machine is mechanically very simple. It has two optical benches pivoting around a single central axis. The x-ray tube is mounted on one arm while the detector is on the other one. The rotation axis is at the sample position. The white incident beam is produced by a standard tube and, as anode material, we have successfully employed either tungsten or chromium. The useful energy range is from 12 keV just above the last *l* line of tungsten, to 55 keV. The two benches are moved by two linear actuators driven by step motors and the tangent of the two angles is read by two linear encoders. Both the minimum step movement and the resolution of the encoders are 1 μm, leading to a minimum angle increment and reproducibility of 0.0004°. The incident and diffracted beams are collimated by four slits made of tungsten 2 mm thick.

The detection of the x rays is performed by an EG&G acquisition system consisting of a planar HPGe solid-state detector (6 mm in diameter) and of a 92X Spectrum Master which performs the amplification, the analog-to-digital conversion, and the multichannel analysis. The system is connected to a personal computer running the Maestro software to visualize and to record the data. The energy resolution is about 1% in all the used range. This is the term which domi-

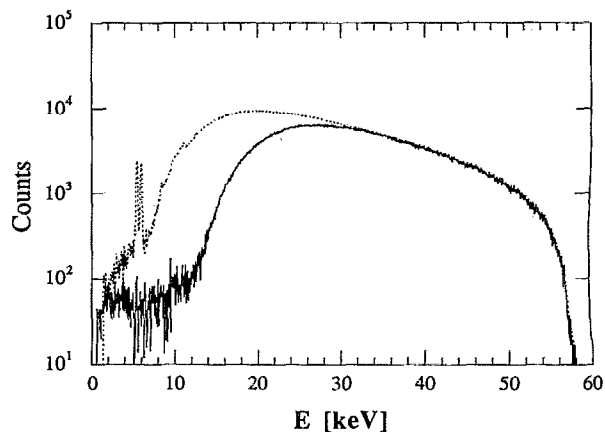


FIG. 3. White incident x-ray beam produced by a chromium tube (dashed line) and after going through the electrolytic cell (solid line). 3 cm of solution and two cell walls completely attenuate the beam for energies lower than 15 keV.

nates the instrumental resolution function. The maximum counting rate is about 10 kc/s.

To perform the necessary data reduction we first need to correct for the transport function of the detector. Due to the characteristic of a Ge solid-state detector, we have, for an incident x-ray photon of energy E_0 , a finite probability of counting it at an energy $(E_0 - E_\alpha)$ or $(E_0 - E_\beta)$, where E_α and E_β are the energies of the Ge- k_α and Ge- k_β transitions. This phenomena leads to a distortion of the measured spectra and to the appearance of peak echoes which we need to correct for. We measured this probability function as a function of the x-ray photon energy by measuring the intensity of the echoes of a diffraction peak of a silicon single crystal as a function of the scattering angle. We are then able to numerically remove this signal from the experimental data.

The experiments have been carried out using palladium plates (12 mm in diameter) as anode and cathode materials. The samples were previously annealed to remove oxygen from their surfaces. A diagram of the cell is shown in Fig. 2. We have used the same cell geometry of other experiments described elsewhere¹² and here we only point out that the electrolysis is performed in only one side of the cathode while the other is free in a gas environment where we can measure the outcoming gas flux, which is related to the α - β phase transition of a Pd membrane.¹³ The electrolyte was a 0.1 M solution of LiOD in heavy water. The distance between the two electrodes is 3 mm and the angles of the incident and diffracted beams with respect to the horizontal are 6°. In Fig. 3 we show the white incident beam and the beam transmitted by 3 cm of solution and two vessel glass walls as a function of the photon energy. This completely attenuates the beam for an energy lower than about 15 keV. Because of the horizontal geometry, gas bubbles can remain trapped between the electrodes, increasing the resistance of the cell and distorting the electrical field. We then mounted a small pump to make a forced flux of solution between the electrodes and this was enough to overcome the problem.

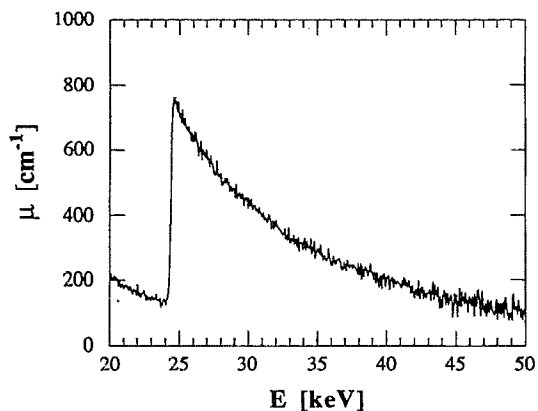


FIG. 4. Linear absorption coefficient μ of x-rays in palladium as a function of photon energy measured using a $25\ \mu\text{m}$ thick foil. The sharp change of μ at $24.35\ \text{keV}$ is due to the atomic absorption edge k of palladium.

IV. RESULTS

In Sec. II we showed that the energy position of a Bragg peak depends on the angle of scattering ϑ [Eq. (4b)]. Pure palladium has a face-centered-cubic structure with a lattice parameter of $0.38907\ \text{nm}$.¹⁴ We choose a scattering angle of 6° so that the lowest-order peak, which has a structure factor different from 0 [the (111)], occurs at an energy of $26.40\ \text{keV}$. This energy is just above the k -absorption edge of palladium which is at $24.35\ \text{keV}$. Moreover, because the maximum useful energy of the spectra is $55\ \text{keV}$, we can observe all the peaks up to the (222) in a single measurement.

The penetration of x rays into a sample is a complicated function of the photon energy and of the chemical composition and density of the sample itself. As it is shown in Fig. 2, we have measured the x-ray diffraction in a reflection geometry. Bragg peaks occur at different energies and, because the attenuation length is a function of the x-ray energy, they are due to the scattering from different sample depths. To determine the scattering volume with respect to the photon energy, we determined the linear absorption coefficient $\mu(E)$ by measuring the transmission of a $25\ \mu\text{m}$ thick foil of palladium (Fig. 4). Then considering the angle of incidence, the (111) peak, which is at about $26\ \text{keV}$, is due to the scattering of only the first $1.5\ \mu\text{m}$ of the sample, while in the case of the last visible peak, the (222), x-rays penetrate about $10\ \mu\text{m}$. By observing the shifts of different peaks we can, in principle, determine the deuterium concentration profile versus the distance from the surface.

To determine the deuterium charging we need to observe the variation of the lattice parameter of the palladium. Then a preliminary diffraction measurement of the sample inside the cell before starting the electrolysis is necessary to determine the exact angle of scattering, by inverting Eq. (3). In Fig. 5 we report one of these measurements where we can clearly observe the Bragg peaks and the fluorescence lines, whose positions do not depend on the concentration of deuterium. They are then essential to monitor the stability of the acquisition electronics system.

As an example we describe an experiment performed on a palladium¹⁵ cathode $1\ \text{mm}$ thick and $12\ \text{mm}$ in diameter.

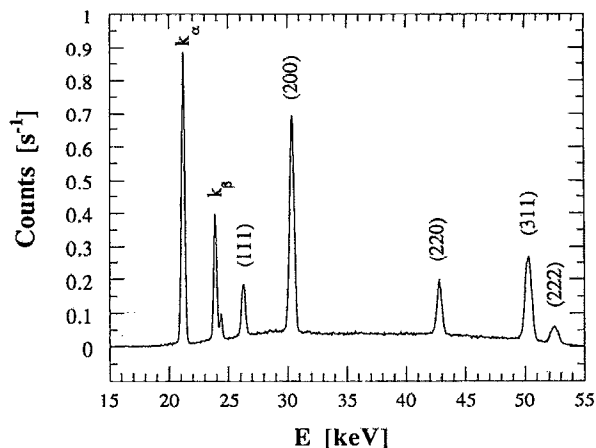


FIG. 5. X-ray-diffraction measurement of a palladium cathode inside the cell before starting the electrolysis. The counting time was 2 h. The k_α and k_β fluorescence lines of palladium at 21.10 and $23.87\ \text{keV}$ are clearly visible and they are used to monitor the stability of the acquisition electronic.

The sample was annealed at 970°C for some hours in an argon atmosphere to remove the oxygen from the surface. We started the electrolysis with a low constant current ($20\ \text{mA}$). X-ray-diffraction patterns were collected daily and, after 4 days, they showed the simultaneous presence of the α and β phases. As expected, the intensity of the β -phase Bragg peaks were increasing with electrolysis time while those of the α phase were decreasing. After 7 days we observed that only the peaks corresponding to the β phase were present, i.e., the sample volume, illuminated by the x-ray beam (first $10\ \mu\text{m}$), was all in the β phase.

In Fig. 6 we report the diffraction patterns before starting the electrolysis (bottom line); after 5 days of electrolysis (middle line), in this case the pattern shows the presence of both the α and β phases, and after 10 days (top line) when

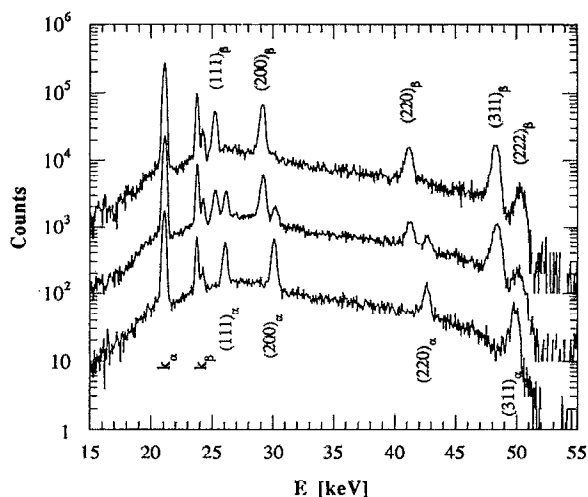


FIG. 6. Diffraction patterns from a palladium cathode. The bottom line is measured before starting the electrolysis. The middle one is measured after 5 days of charging. This data shows the coexistence of well defined α - and β -phase domains. Top line, after 10 days of charging; only the β phases are present.

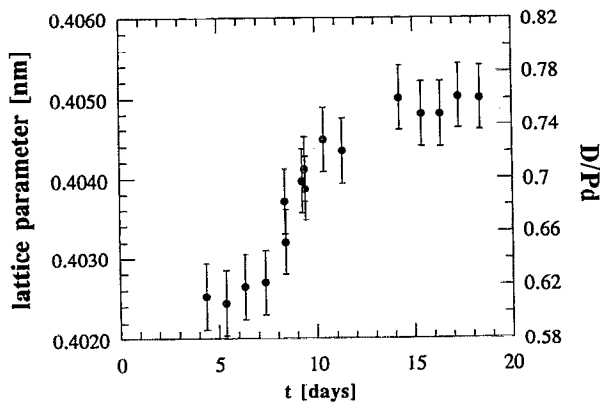


FIG. 7. β -phase lattice parameter and D/Pd ratio as a function of the electrolysis time.

only the β phase is present. We have then applied a pulsed current to determine its effect on a possible increase of charging. The pulsed square current had the following characteristics: minimum current 20 mA, maximum current 200 mA, and periods varying between 4400 and 6000 s. In Fig. 7 we report the dependence of the lattice parameter of the β phase as a function of the electrolysis time for the first 18 days of charging for the volume illuminated by the x-ray beam. The plot shows that the sample keeps increasing D concentration for about 2 weeks up to a maximum ratio of about 0.76 ± 0.02 .

We then raised the temperature of the cell up to 50 °C. After about a week we cooled the sample at room temperature and measured the lattice parameter again. We did not observe any change in the D/Pd ratio. The measurements performed at high temperature were not comparable with respect to the room-temperature ones because of the thermal expansion of the cell holder which caused the sample to move in height. This displacement induced a variation of the angle of scattering, producing shifts in the observed Bragg-peak positions. During the entire experiment we did not observe any dependence of the charging with respect to the distance from the electrolysis surface, meaning the charging was uniform in the explored volume. After about 3 weeks of electrolysis, the sample was removed from the cell and degassed in a known volume. The final D/Pd ratio so measured was 0.77 ± 0.05 (in the error we included the loss due to the sample degassing while it was removed from the cell and put in the known volume¹⁶). This value is in good agreement with the x-ray determination, confirming that the charging was uniform in the whole sample.

We also performed measurements under different electrolysis conditions. In all cases the final D/Pd ratio measured by degassing the cathode in a known volume was in very good agreement with the value determined by x-ray-diffraction measurements.

We have shown that the energy dispersive x-ray-diffraction technique can be employed to determine the concentration of deuterium inside a palladium lattice during electrolysis and, then, it can be very useful to study the dynamics of the loading. This is due to the strong penetration of hard x rays, which can easily cross the cell walls and a few centimeters of electrolyte solution, and to the fixed angle geometry, making the design of the cell very simple. We performed some experiments and we verified that the final concentration determined with this method was in a very good agreement with the data measured by degassing the sample in a known volume.

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