# HOW THE ELECTRODEPOSITION CONDITIONS OF PALLADIUM AFFECT HYDROGEN ABSORPTION: AN X-RAY DIFFRACTION EVALUATION


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## Introduction

Palladium is widely used both as final coating and as an intermediate layer to improve corrosion resistance and act as a diffusion barrier layer.

A recurring limitation of **Pd** and **PdFe** alloys electroplating baths is the formation of deposits marked by microcracks, as a consequence of the substantial hydrogen evolution during metal reduction and subsequent co-deposition. Indeed, Pd can absorb and dissolve hydrogen to form two bulk hydride phases [1]:

**α-PdHx** (x ~ 0.02) and **β-PdHx** (x ~ 0.67)

The latter phase is predominant under the deposition conditions typically used. The transition to the thermodynamically stable α-phase causes hydrogen desorption-induced lattice contraction, leading to microfractures [2]. When depositing α-phase, instead, the lattice structure remains unchanged Moreover, Pd deposits take different colors depending on the content of hydrogen co-deposited.

A proprietary innovative pure Pd electroplating bath (*PalmetECO*), kindly supplied by Valmet Plating s.r.l. was used and the deposits made therefrom were analyzed using XRD technique.

## Materials and methods

Different operative conditions were used to electroplate pure Pd on brass samples (5 x 3.5 cm). The electrodepositions were performed in becher using a mixed oxide anode. Some samples were made in pulsed current because of the advantages it can offer in terms of deposit quality, decreased organic content and lower metal consumption.

***PalmetECO* formulation:**

- Pd: 3 g/L
- ECOX: 5.5 g/L
- ECO BR1: 5 mL/L
- ECO BR2: 2.5 mL/L
- ECO BR3: 4 mL/L

**General operative Conditions:**

- T: 40 - 60 °C
- pH: 7 - 7.5
- J: 0.8 - 1 A/dmq
- η (bath efficiency): 0.1 µm/min

**XRD Analysis:**

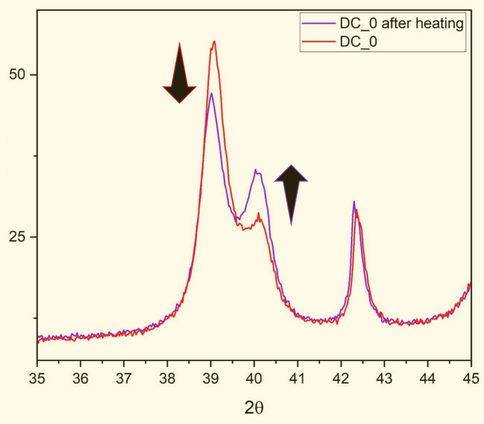
Diffrattograms were recorded with the diffractometer Bruker New D8 Da Vinci equipped with Euler cradle for massive samples and Bruker Lynxeyexe detector. The scan were performed in the range of 2Θ = 35 – 45°, with 2Θ = 0.05° increment and 0.03 seconds of integration per step.

## Experimental and Results

This study aims to assess how electroplating conditions and bath composition can affect the physical properties of the innovative *PalmetECO* pure palladium electroplating bath. The evaluation of the samples was performed using X-ray diffraction technique that offers a clear differentiation between the two hydride phases based on the diagnostic peaks at **39°** and **40°** corresponding to the β and α phases, respectively. Experiments were performed with both direct and pulsed current.

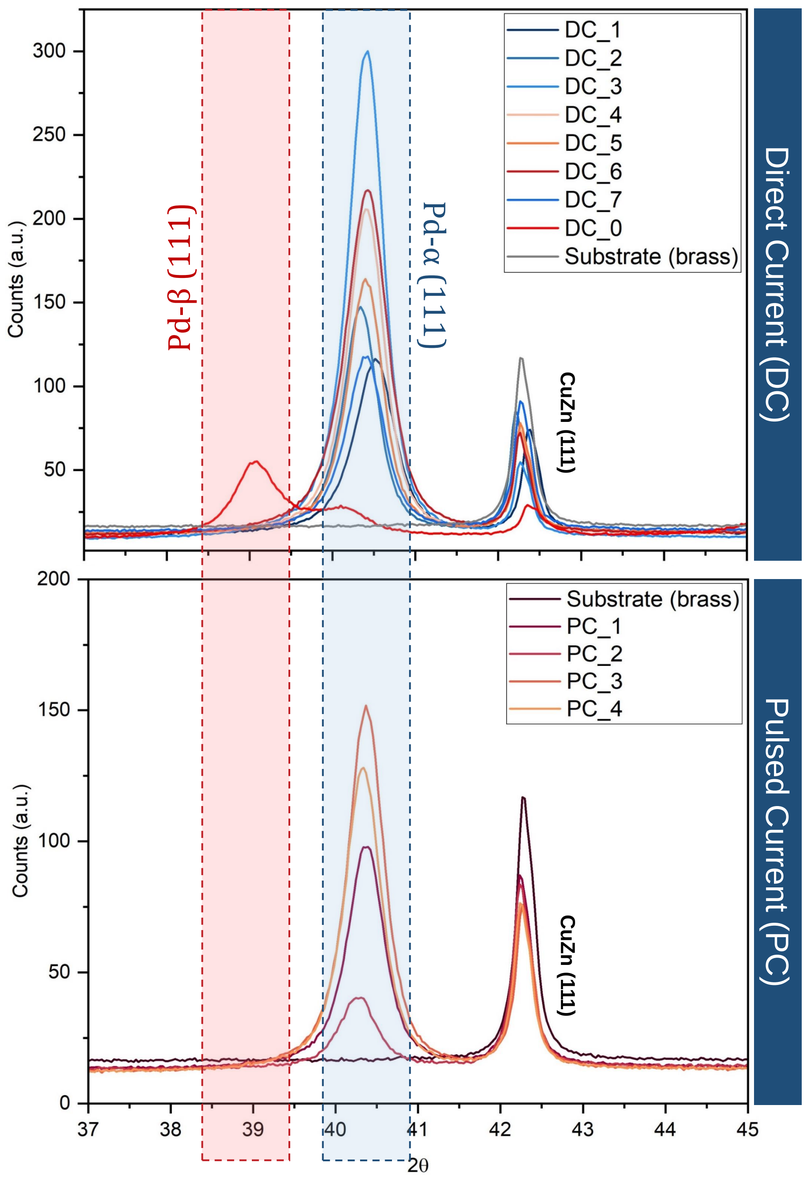
To confirm the peaks attribution, the DC_0 sample was heated in an oven at 90 °C to promote hydrogen desorption.

As expected, a decrease in the peak at 39° (β) and an increase in the peak at 40° (α) were observed after the treatment.




**Direct current samples:** four parameters were selected to be varied: T (°C), t (min), BR1 and BR2 (ppm) representing the organic content of the bath. Only for a sample an additional treatment in hot water was tested.

**Pulsed current sample:** three different waveforms were selected while keeping the average current density ($J_{AV}$) constant.




| Sample | BR1 (ppm) | BR2 (ppm) | T (°C) | t (min) | Hot water (70°C) treatment |
|---|---|---|---|---|---|
| DC_1 | 250 | 125 | 50 | 3 | ✗ |
| DC_2 | 250 | 125 | 60 | 3 | ✗ |
| DC_3 | 250 | 125 | 60 | 5 | ✓ |
| DC_4 | 300 | 200 | 60 | 3 | ✗ |
| DC_5 | 300 | 200 | 60 | 5 | ✗ |
| DC_6 | 300 | 200 | 50 | 5 | ✗ |
| DC_7 | 300 | 200 | 50 | 3 | ✗ |

| Sample | tON (ms) | tOFF (ms) | $J_{ON}$ (A/dmq) | $J_{AV}$ (A/dmq) | T (min) |
|---|---|---|---|---|---|
| PC_1 | 100 | 100 | 2 | 1 | 5 |
| PC_2 | 50 | 250 | 6 | 1 | 5 |
| PC_3 | 100 | 100 | 2 | 1 | 5 |
| PC_4 | 100 | 100 | 2 | ≈1* | 5 |

* In the very first 100 ms the current was set to 10 A/dmq to promote nucleation

## Conclusion

From this preliminary study, it appears that the innovative pure palladium galvanic bath: ***PalmetEco* is able to deposit mainly the α-phase of Pd hydride** which, being thermodynamically stable, does not cause the formation of microfractures over time. Indeed, regardless of the height and width of the diffractometric peaks (which may depend on various factors including the degree of crystallinity of the deposit and the amount of metal deposited), the β-phase peak was never observed except for one sample realized in industrial environment. Further analysis should be conducted to identify the conditions that led to this result.


[1] Wang, S. et al. Electrochem commun, 102 (2019) 67–71.
[2] Manchester, F. D. et al. Journal of Phase Equilibria 15, 1 (1994).
[3] Bhat, V. V. et al. Nanotechnology 20, 20, (2009).