ESRF	**Experiment title:** ***In situ* 3D Coherent X-ray Diffraction Imaging of Pd Nanocrystals during electrochemical cycling**	**Experiment number**: HC4753
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Report:

1. ***Brief description of the experiment***

Bragg Coherent Diffraction Imaging (BCDI) method was employed to measure Pd nanocrystals (NCs) under electrode potential control. We aimed to obtain a comprehensive understanding of Pd catalysts from bulk electrode to single nanoparticle level during the hydriding transformation of a Pd NC. The experiments were performed in a home-design *in situ* electrochemical cell. The obtained results would help to identify the kinetics of Pd nanoparticles during the hydriding phase transition reaction in terms of structural properties such as strain and displacement fields. The hydriding of Pd nanoparticles has already been studied using BCDI technique in multiple gas experiments, however it is the first time that the problem is considered in an electrochemical environment.

2. Results and discussion

We succeeded in measuring *in situ* a Pd nanocrystal using BCDI under electrochemical conditions. We scanned the same Pd NC at 7 relevant electrode potentials. As shown in **Figure 1 a**, diffracted intensity evolution of a Pd nanoparticle is presented under different potentials. When decreasing the potential we observed significant change in the diffraction pattern which split as a result of the hydrogen-rich phase formation (β phase, lower diffraction spot on **Figure 1 a**, -0.10 V) whose lattice parameter is larger than that of the hydrogen-poor phase (α phase). The diffraction pattern itself shows usual features of significant strain also confirmed by the reconstructed objects (**Figure 1 b**). Such strain changes are due to hydrogen adsorption onto the surface and hydrogen absorption into the bulk that results in a global increase of the lattice parameter

of the NC. The missing region corresponds to the β phase. We successfully bring back the NC to the initial potential and observed that the transformation was not reversible as a part of the NC is still missing. We suggest that the missing part is no more β phase but has rearranged itself and thus is no longer in Bragg geometry. In addition, the Bragg peak of the α migrates during reaction, highlighting a significant change in the average d-spacing. By tracking the Bragg peak of the α phase, we observed that the associated d-spacing expanded during the hydriding transition. When going back to initial potentials, the d-spacing went back to normal, but a hysteresis behavior is clearly observable (**Figure 1 c** top graph). Finally, from the diffraction pattern again we estimated a lattice expansion of 3.5% in the beta phase region (**Figure 1 c** bottom graph) which is in good agreement with the literature.

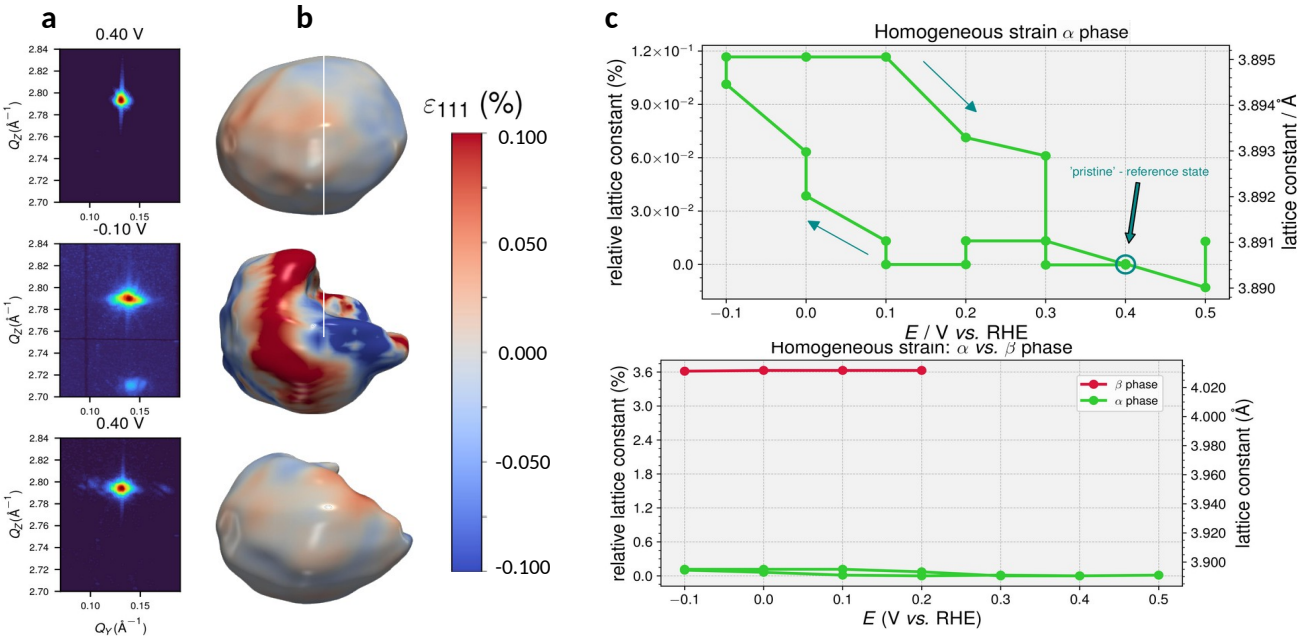

Figure *1*: *a*, diffraction patterns. ***b***, reconstructions of the same Pd NC at 3 different potentials, from top to bottom: 0.4 V, -0.1 V, back to 0.4 V *vs.* RHE. ***c***, Homogeneous strain and lattice parameter variations given by the positions of the maximum of the Bragg peak as a function of electrode potential.

3. Outlook

We managed to measure a Pd nanocrystal under relevant electrode potential. To our knowledge it is the first time the hydriding transformation of a Pd nanocrystal in electrochemical reaction is captured using BCDI. Note that in electrochemical conditions, probed nanocrystals often move away due to the simultaneous effects of the interaction with the beam and the occurring reaction. Therefore, experiments combining BCDI and electrochemistry together are challenging. The results here also show the robustness of reconstruction algorithms that allowed us to reconstruct a highly strained crystal. We are confident that such results are suitable for publication. However, for now the kinetics of the reaction and the role of size effects of the NCs are unclear and remain of great interest.