Operando Nanoscale Imaging of Electrochemically Induced Strain in a Locally Polarized Pt Grain

Dina Sheyfer,*,# Ruperto G. Mariano,*,# Tomoya Kawaguchi, Wonsuk Cha, Ross J. Harder, Matthew W. Kanan, Stephan O. Hruszkewycz, Hoydoo You,* and Matthew J. Highland

ABSTRACT: Developing new methods that reveal the structure of electrode materials under polarization is key to constructing robust structure–property relationships. However, many existing methods lack the spatial resolution in structural changes and fidelity to electrochemical operating conditions that are needed to probe catalytically relevant structures. Here, we combine a nanopipette electrochemical cell with three-dimensional X-ray Bragg coherent diffractive imaging to study how strain in a single Pt grain evolves in response to applied potential. During polarization, marked changes in surface strain arise from the Coulombic attraction between the surface charge on the electrode and the electrolyte ions in the electrochemical double layers, while the strain in the bulk of the crystal remains unchanged. The concurrent surface redox reactions have a strong influence on the magnitude and nature of the strain changes under polarization. Our studies provide a powerful blueprint to understand how structural evolution influences electrochemical performance at the nanoscale.

KEYWORDS: coherent X-ray imaging, electrochemical double layer, operando electrochemistry, platinum catalysts, thin films, nanopipette electrochemical cell

Under operating conditions, electrocatalysts are known to undergo structural rearrangements that yield surfaces distinct from their as-prepared forms.1−2 These structural changes impede the development of accurate structure–activity relationships because it is difficult to image surface structures and their evolution at high resolution at an active electrochemical interface.3 A variety of methods have been developed to try to address this fundamental challenge.4−10 Electron microscopy methods have been used to image catalytic materials during operation,11,12 but these methods can be used only under limited electrochemical conditions because of the strong interaction of electrons with the sample and environment, and the low pressures necessary for imaging.13−15 In situ X-ray diffraction experiments can access a broader range of electrochemical environments and pressures closer to realistic operating conditions. However, they typically provide ensemble-averaged structural information rather than locally resolved information on strain evolution in materials.16−21

X-ray Bragg coherent diffractive imaging (BCDI) can correlate structural changes at the nanoscale with externally applied stimuli.22−28 Previous studies have used a thin-layer electrochemical cell or a pipet cell with a relatively large droplet (1 mm) to perform BCDI under electrochemical conditions.29 These in situ electrochemical BCDI studies have revealed connections between crystallographic defects and dissolution rates of Ag nanocrystals,30 as well as strain evolution in Pt–Ni alloy nanoparticles31 under electrochemical control. However, the electrochemical cells commonly used for in situ X-ray diffraction experiments can result in mass transport limitations, Ohmic losses, and unevenly polarized surfaces, depending on the positioning of counter and reference electrodes.32 These effects motivate the development of improved methods to polarize electrodes during in situ BCDI experiments.

Nanopipette electrochemical cells (NEC) with sub-micrometer droplet sizes have been developed to polarize and understand electrochemical interfaces at the nanoscale.32−34 Here, we integrated a NEC with BCDI to probe structural changes of a Pt surface under localized polarization. Pt-based materials are well-studied electrocatalytic systems and serve as convenient models for studying structure–property relationships. Several studies have shown that engineering Pt

Received: March 13, 2022
Revised: December 8, 2022
Published: December 21, 2022
nanomaterials with enhanced strain improves electrocatalytic performance,\textsuperscript{35,36} but how strain is spatially redistributed in Pt under electrochemical conditions, particularly at the surface where catalysis occurs, has not previously been investigated. A micrometer-scale contact area is essential because it enforces small absolute currents on the order of hundreds of pA, minimizing Ohmic losses\textsuperscript{37} (see comment on iR drop in the Supporting Information). Moreover, current density distributions in an area aligned with both the X-ray beam and nanopipette are homogenized compared to the thin-layer electrochemical cells used for in situ X-ray diffraction studies.\textsuperscript{38,39} Using a small electrolyte droplet results in an X-ray transmission factor exceeding 99%. This allows collection of BCDI data with improved spatial resolution compared to sacrificing temporal resolution compared to a cell with greater attenuation of the beam. Co-location of the region of X-ray illumination and NEC polarization allows for direct correlations to be drawn between applied electrode potential and structural changes observed using BCDI.

We prepared a polycrystalline Pt surface by sputtering Pt onto a flat SiO\textsubscript{2}/Si substrate. This was followed by a high-temperature annealing step to yield grain sizes suitable for BCDI measurements. Imaging the Pt film with electron backscatter diffraction indicated that the Pt film is (111) textured, with the vast majority of the grains in the film possessing an orientation close to Pt(111) (see Figures S1 and S2). A single Pt grain satisfying the non-specular (111) Bragg condition was selected for study. The NEC (filled with 0.1 M H\textsubscript{2}SO\textsubscript{4}) was co-located with a Pt grain and contacted to establish electrochemical control. The nanopipette is in contact with multiple grains. A schematic view of the setup is shown in Figure 1. Details of the sample preparation, nanopipette fabrication, experimental setup, and procedures can be found in the Supporting Information. We collected BCDI measurements of the Pt grain under polarization first at increasingly anodic potentials (0.27, 0.77, 1.27, 1.77, 1.97 V, all potentials quoted versus the reversible hydrogen electrode [RHE]); then, we stepped the electrode potential more cathodically (0.77, 0.27 V). At each applied potential, the 3D intensity distribution of the non-specular (111) Bragg peak was obtained by collecting diffraction frames as the sample was rotated by 0.4° in Δθ steps of 0.01° (θ being the rotational degree of freedom about the y-axis in Figure 1). By stacking the diffraction slices together, a complete 3D diffraction pattern was obtained, as in Figure 2a.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** A schematic view of the NEC/BCDI setup: a sub-micrometer sized droplet was formed at the end of an electrolyte-filled nanopipette in contact with a Pt grain illuminated by the X-ray beam. Diffraction patterns from the Pt grain were collected at the non-specular (111) Bragg angle while potential was applied between the electrode and Pt film. See the experimental scattering geometry in Figure S10a.

The volume-averaged lattice spacing (across the entirety of the grain and not just the surface) \(d_{111} = 2\pi/q_{111}\) was obtained by determining the length of the reciprocal lattice vector \(q_{111}\) from the intensity-weighted center of mass of the 3D data. We calculated the absolute change \(\Delta d_{111} = d_{111} - d_{111}^{0}\), where \(d_{111}^{0}\) corresponds to the first applied potential of 0.27 V. The potential dependence of \(\Delta d_{111}\) (Figure 2d) mirrors the trends observed in the integrated Bragg intensity \(I_{\text{sum}}\) profiles (Figure 2b) as a function of potential. This behavior suggests that surface electrochemical processes impact both \(d_{111}(<10^{-4} \text{Å})\) and \(I_{\text{sum}}\) and that the two effects have a common cause. The evolution of the internal strain field distribution of the grain impacts the measured lattice spacing, while changes in the degree of disorder in the bulk and surfaces of the grain influence the total integrated scattering intensity.

The measured BCDI data were inverted to images using well-established BCDI phase-retrieval algorithms.\textsuperscript{24,35,40} Typical to BCDI experiments, the phase of the 3D image was converted to units of local strain \((\partial u_{111}/\partial r_{111})\) representing the fractional compression/dilation of the Pt(111) planes. An example 3D image of the grain is shown in Figure 2c, in which the coloration corresponds to the lattice strain at the grain surface.

The surface nature of the potential-induced structural changes could be examined by segmenting the strain distribution of the volume voxels at all of the applied potentials into histograms that correspond to the top, bottom, and sides...
of the grain. As one example, representative histograms of the voxel strains at 0.77 V are shown in Figure 3. The probability histogram that includes all voxels in the grain volume is asymmetric (Figure 3a). This asymmetry becomes more pronounced when considering the strain distribution for voxels in the top 20 nm-thick layer (Figure 3b), with a significant tensile component becoming apparent. The heterogeneous nature of the strain distribution is most marked in the histogram corresponding to voxels from the top 10 nm-thick layer (Figure 3c), with the peak of the distribution shifting to a positive value. The solid lines in parts a–c are a guide for the eye.

Figure 3. (a) The probability distribution of the strain magnitude $\partial u_{111}/\partial x_{111}$ per voxel at 0.77 V for the whole crystal, (b) for the top 20 nm, and (c) for the top 10 nm. All three distributions are asymmetric, and for the 10 nm case, the peak position shifts to a strain positive value. The solid lines in parts a–c are a guide for the eye.

Thus, we focus the remainder of our analysis on the response of the top Pt grain interface.

The lattice expansion for the 10 nm top surface (see Figure 4) is consistent with an expansion induced by an electrochemical process such as surface oxidation (leaving the bulk largely unperturbed).\textsuperscript{18,42} The 10 nm top surface is expanded by 3 × 10$^{-4}$ at 0.27 V, a relatively small expansion of the lattice. However, application of a more anodic potential of 0.77 V significantly dilates the lattice of the topmost 10 nm-thick layer by 6 × 10$^{-4}$. As the potential is increased further to 1.27 V, the expansion first decreases and then increases again at the higher potentials of 1.77 and 1.97 V. Surprisingly, a potential jump from 1.97 V back to 0.77 V, where the largest expansion was observed in the positive scan, introduced a slightly compressive strain. The distinct responses observed at 0.77 V between the anodic and cathodic sweeps suggested that the structural rearrangements depended on the history of the surface. A return to dilation in the top layer was observed upon further reduction at 0.27 V. At these potentials, the whole-grain average strain exhibited small changes, while the top 20 nm surface of the grain exhibited similar but less pronounced behavior compared to the top 10 nm of the grain.

We propose that this strain evolution arose from the interaction of the Pt grain with the electrochemical double layer at the Pt/electrolyte interface that formed in response to polarization and concomitant place-exchange oxidation (PEO) and oxygen-evolution reactions (OERs).\textsuperscript{18} The surface-specific nature of this response was consistent with the diminished strain response observed when sampling a 20 nm-thick surface layer as compared to a 10 nm-thick layer. We expect an exponentially diminishing strain response from the surface, and the expansion in the topmost 1 nm surface layer was likely

Figure 4. Mean strain distribution in the top surface layers (see legend) as a function of applied potential in the positive (solid line) and negative (dashed line) branches of the potential sweep. The successively reduced responses as the thickness increases indicate that the strain is mainly confined to the top few (111) layers. The two insets show the 3D strain distribution in the top surface of the grain at 0.77 V on the positive- and negative-going sweeps. The triangle markers correspond to the potential dependence of the mean of the strain distribution in the whole grain. Error bars are approximately the symbol size unless shown explicitly.
larger than the strain over the 10 nm surface layer, though 1 nm length scales fall below the resolution of the current measurement.

We constructed a step-by-step model to account for the strain evolution at the top surface of the grain, shown schematically in Figure 5. Polarization at 0.27 V induced a $3 \times 10^{-4}$ tensile strain on the top surface of the grain. At this potential, the under-potential deposition of hydrogen is expected to occur on Pt(111), which screens double layer formation and attenuates the near-surface charge density (Figure 5a). Nonetheless, charge buildup near the Pt surface is accompanied by the Coulombic attraction of oppositely charged electrolyte ions, collectively inducing tensile strain in the Pt lattice (see the estimation of electrostatic force and strain in the Supporting Information). We observe cathodic current (see Figure S8 in the Supporting Information) at this potential, due to the oxygen reduction reaction (ORR) since the cell is open to air.

As the Pt grain was polarized more anodically from 0.27 to 0.77 V, we observed a large increase ($6 \times 10^{-4}$) in tensile strain (Figure 4). The increases we observed in both the surface strain and lattice spacing were consistent with a model (Figure 5b) involving a large increase in surface excess charge (+) density in the Pt grain. This high surface charge density, i.e., the large decrease in the Coulombic screening by electrons, induced an electrostatic repulsion between the platinum atoms in the grain, effectively expanding the average lattice parameter (Figure 2d) and inducing tensile strain. While an applied potential of 0.77 V induced a large interfacial field, it was insufficient to induce complete PEO, leading to charge buildup and concomitant tensile strain. The formation of such a strained top surface layer is consistent with the decrease in total scattering intensity (Figure 2b) as the degree of crystallinity of the Pt grain also decreases.

Applying a more oxidizing potential of 1.27 V led to a decrease in tensile strain to $5 \times 10^{-4}$ from $9 \times 10^{-4}$ (Figure 4), consistent with a decrease in surface charge. We propose that the decrease in the electrostatic attraction, and subsequent decreasing surface charge density at the Pt/electrolyte interface, is associated with the formation of a sub-monolayer (~0.3 monolayer) inverted O–Pt species due to the PEO reaction (Figure 5c). The formation of surface Pt–O bonds and the electrostatic attraction between adjacent Pt–O and O–Pt dipoles at the Pt surface could induce a relative compression in the near-surface lattice. However, the overall charge in the whole grain still increased, consistent with the rise in lattice spacing (Figure 2d) and the decrease in the integrated intensity (Figure 2b) as the grain was polarized from 0.27 to 1.27 V.

As the potential was further increased from 1.27 to 1.77 and 1.97 V, the tensile strain increased further, but only marginally from $5 \times 10^{-4}$ to $6 \times 10^{-4}$. We associate these mild increases in strain with the formation of a full surface PtOx layer. The mild increase in tensile strain from 1.77 to 1.97 V likely arises from the self-limiting nature of PtOx surface formation, as Pt oxidation is dependent on the interaction with the electrolyte, and consequently does not continue into the bulk (Figure 5d). With the surface oxide in the steady state, the accumulation of positive surface charge again induced a mild surface lattice expansion.

This surface lattice expansion did not, however, manifest as a decrease in Bragg peak intensity and an increase in average grain lattice parameter, at least for 1.77 V (Figure 2b and d). We interpret this to correspond to a decrease in the charge density of the whole Pt grain, perhaps due to charge screening by the surface PtOx species or due to electrons from ongoing OER flowing into the Pt grain. However, the further accumulation of positive charge in the grain at 1.97 V likely led to a higher degree of electrostatic repulsion between Pt atoms, and would be consistent with the decrease in integrated intensity (Figure 2b) and an increase in the lattice parameter (Figure 2d), which we observe.

Our BCDI measurements also support previous electrochemical measurements indicating that the Pt oxidation–reduction reactions are electrochemically irreversible, i.e., the reduction of PtOx species occurs at a more cathodic potential than its formation. From 1.97 V, we applied a more cathodic potential of 0.77 V, which led to complete removal of the tensile strain, from $5 \times 10^{-4}$ to $-1 \times 10^{-4}$, a slight compression. The surface PtOx is only partially reduced at 0.77 V, leading to a heterogeneous strain distribution at the Pt surface. We hypothesize that, because PtOx reduction is incomplete in this reductive step, we did not observe the large tensile strain that originally arose upon first polarizing the grain at 0.77 V. We propose that residual surface PtOx species destabilize the Coulombic attraction and surface charge responsible for the tensile strain, lowering the surface charge density of the Pt grain and leading to the complete removal of the tensile strain that otherwise would have existed at 0.77 V at equilibrium. These residual PtOx species screened the surface charge.

**Figure 5.** Simplified model of the step-by-step proposed electrochemical processes occurring under different potentials. Atoms and ions are not drawn to scale. A detailed explanation of the phenomena at the Pt/electrolyte interface can be found in the text.
charge at the Pt/electrolyte interface, reducing the extent to which the Pt grain expanded upon polarization at 0.77 V. Indeed, application of a more reducing potential of 0.27 V returned the strain state of the grain back to values close to the beginning of the electrochemical cycle, which would be consistent with full reduction of the surface Pt oxides. Our observation of both a local tensile maximum and a local compressive minimum at 0.77 V in the anodic and cathodic scans, respectively, suggests that the strain changes are modulated not only by the applied potential but also by the electrochemical history of the polarized grain.

The combination of BCDI with NEC revealed previously unknown details of how the strain in a single Pt grain changes in response to electrochemical polarization under conditions relevant to PEO and OER. We found that only the top 10 nm of Pt at the electrode/electrolyte interface responded sensitively to applied potential, while a much more muted response was observed for the near-surface region and the bulk of the Pt grain. The potential-dependent strain responses were not present at grain boundaries and at the bottom interface, neither of which were exposed to electrolyte. Taken together, these support our hypothesis that the strain evolution we observed has an electrochemical origin. Strikingly, our measurements suggested that even highly stable electrodes such as Pt are subject to irreversible structural changes during polarization, highlighting the importance of operando techniques to draw faithful structure—activity relationships in electrochemistry. These observations were afforded by the high strain sensitivity of BCDI combined with the near-zero X-ray scattering background of the sub-micrometer scale NEC setup. These results motivate the broader inclusion of both operando and post-mortem analysis of strain-engineered electrocatalytic materials in order to develop robust structure—activity relationships.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c01015. Additional information about nanopipette fabrication and sample preparation, details on scattering experiments, and data analysis (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Dina Sheyfer — X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; orcid.org/0000-0003-4189-3899; Email: dsheyfer@anl.gov

Ruperto G. Mariano — Department of Chemistry, Stanford University, Stanford, California 94305, United States; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02141, United States; Email: rmariano@stanford.edu

Hoydoo You — Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; orcid.org/0000-0003-2996-9483; Email: you@anl.gov

**Authors**

Tomoya Kawaguchi — Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; Institute for Materials Research, Tohoku University, Sendai 9808577, Japan

Wonsuk Cha — X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Ross J. Harder — X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Matthew W. Kanan — Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-3932-6289

Stephan O. Hruszkewycz — Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; orcid.org/0000-0002-9394-9252

Matthew J. Highland — X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

**Author Contributions**

*D.S., R.G.M.: Contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The NEC/BCDI X-ray and electrochemistry measurements and data analysis were supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Science (BES), Materials Sciences and Engineering Division. The use of the Advanced Photon Source (APS) was made available by the DOE BES Scientific User Facilities Division under Contract No. DE-AC02-06CH11357. The work at Tohoku University (T.K.) was supported by JSPS KAKENHI Grant No. 21H01646. Work at Stanford University was supported by the NSF under CHE-1855950 (R.G.M. and M.W.K.) and by a Stanford DARE fellowship (R.G.M.). Parts of this work were performed at the Stanford Nano Shared Facilities, which is supported by the National Science Foundation under award ECCS-1542152.

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