Atomic-scale model of the platinum (111)-water interface revealed by angstrom resolution off-axis phase shifting holography

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Background
The colossal challenge against climate change highlights the necessity of scaling up renewable energy storage capacity and enhancing green hydrogen production by electrocatalysis. However, developing stable and high-performance electrocatalysts for hydrogen production using abundant materials requires a further fundamental atomic-scale understanding of the charge transfer process at the catalytic interfaces.

Although the metal-water interface is the preeminent part of interest for a basic understanding of electrocatalysis and has become an extensively discussed topic in current catalysis research, the atomic structure of the electrolyte, the active sites of the reactions, and the role of single atoms and step edges on the catalyst surfaces remain elusive. Environmental TEM research enables atomic-scale assessments of metal-water interfaces. We present an open-cell in-situ study of the interface between catalytically active platinum (111) and water vapor under experimentally feasible pressures. Under a water ambient condition, we measure the projected potential across the interface using the angstrom-resolution electron holography method. The results obtained at various external bias conditions are compared to the atomic structures from ab initio molecular dynamics (AIMD) simulations. We will discuss the metal-water interface structures and their natures from experiment and theory.

Methods
A two-electrode MEMS setup is exposed to 50 microbar water vapor, which forms an ultrathin condensed water layer at the Pt electrode surfaces. An in situ analysis is carried out by employing an image-aberration-corrected Titan environmental TEM. Off-axis phase-shifting electron holography is used in conjunction with an improved drift-correction scheme to reconstruct the exit-wave with a spatial resolution up to the information limit of the microscope (<1.0 Å).

Results
The in-situ HRTEM image series and phase reconstructions identify dynamic platinum adatoms at the metal-water interface. The adatoms are residues of the metal-water interface formation and appear only after the electrode is exposed to the water. The existence of the adatoms may depend on the preparation procedures of the metal electrode. By comparing the quantitative frozen-lattice multi-slice simulations, we retrieve the specimen thickness at the edge and, subsequently, the coverage of the dynamic platinum adatoms. At the metal-water interface, the oscillations of the projected potential up to 5 Å above the platinum adatoms are monitored. We interpret the oscillations as preferential orientations of the water molecules in the first water layer with the help of predicted holography data from multi-slice simulations using the AIMD trajectories of the model interface configurations. Furthermore, we provide an outlook on the influence of external bias on the potential profiles and expectations based on AIMD-simulation for different surface conditions.

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Conclusions

In conclusion, we identify the dynamic platinum adatoms at the platinum- (111) interface to water in an open cell ETEM experiment under in-situ conditions. Applying the angstrom resolution phase shifting off-axis electron holography captures the signatures in the projected potential of the first water layers. Based on the multi-slice simulations derived from AIMD trajectories, we attribute these signatures as the preferential ordering of the interfacial water. First experimental indications of the influence of external an bias on the water layer are discussed with respect to AIMD predictions.

Keywords:

metal-water interface, atomic-scale, holography, environmental-TEM

Reference:

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