

Submission Date: 08/12/2024

2023 Academic Year Bio-SPMs Collaborative Research Research Report Summary

Title of the research project		Resolving the hydration layer structure of copper(100)/halides systems with 3D-AFM	
PI (Person in charge of the research project)	Name	Dr Christopher Kley	
	Affiliated Institution and Department/Division/etc.	Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Fritz Haber Institut der Max Planck Gesellschaft	
	Position	CE-NCE	
Bio-SPMs that you used (Check the boxes)		<input checked="" type="checkbox"/>	Atomic resolution/3D-AFM
		<input type="checkbox"/>	High-speed AFM
		<input type="checkbox"/>	SICM
		<input type="checkbox"/>	AFM for Cell Measurement
Collaborative NanoLSI Faculty Members		Dr. Ayhan Yurtsever	
<p>While halides significantly impact the selectivity of copper-based catalysts for the CO₂ electroreduction reaction (CO₂RR), their specific role remains debated. Recently, electrolyte modification with large cations such as Cs⁺ alongside halide anions such as iodine has been shown to promote CO₂RR selectivity towards multi-carbon products. In this context, investigating the interaction between adsorbed iodide and cations as well as unravelling how these ions modify the interfacial hydration structure is key to achieve fundamental mechanistic understanding. In this project, the interfacial hydration layer of a single crystal Cu(100), immersed at open circuit potential (OCP) to different iodine containing electrolytes, was imaged using FM-AFM 3D-AFM. Through varying the size of cations and pH, both the location of cations within the first water layers and the role of co-adsorbed OH radicals on the hydration layer structure via hydrogen bonds were studied. The adsorbate surface phase observed on Cu(100) in 30 mM KI, LiI and CsI is revealed as mixed c(2x6) structure, composed of both iodide and OH at pH 7 to pH 4. A first water layer was imaged, displaying an in-plane periodicity matching with the underlying OH periodicity, i.e., likely originating from OH - H₂O hydrogen bonds, ~ 3 Å from the surface. This lateral periodicity was not observed at pH 3, at which OH is not adsorbed on the surface anymore, with solely a c(2x5) iodine phase is present. At neutral pH, a second water layer was resolved, located at distances between 3 to 5 Å from the first water layer and displaying almost no lateral periodicity. The size of the water depletion region located in between was found to increase with the size of cation present in the electrolyte, following the trend: Li⁺, Cs⁺, K⁺. 2D FFT analysis of the water depletion plane revealed the appearance of a new p(2x2) structure in the case of Cs⁺, indicating the presence of cations within the water depletion layer. In the next step of this project, we will complement these experimental findings with theoretical modeling to evaluate and rationalize such cation co-adsorption through a potential halide induced local charge inversion (as here OCP > PZC) and to extend the study to lower potentials in order to reveal the mechanisms of cation-mediated halide desorption. These efforts and findings are of direct relevance for reaching fundamental understanding of processes at electrochemical interfaces and building reliable structure-property relationships for rational optimization of catalysts.</p>			

*This form (Form 3) will be open on the NanoLSI website in the following academic year.

*Note that this form should be prepared in one A4-size paper.

*Submission Deadline: May 10, 2024 (Friday). **Submit it as a PDF file.**