

***In situ* Conductive Atomic Force Microscopy for Localized Analysis of CO₂ Electrocatalysts**

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A key challenge in catalysis and energy conversion research remains probing, at the nanoscale and under liquid phase reaction conditions, a material's local electric conductivity, catalytic activity, product selectivity or the chemical nature of its reaction environment. Particularly, *in situ* derived structure-property relationships are required to rationally innovate (photo-) electrochemical interfaces that dictate major catalytic reactions including CO₂ electroreduction (CO₂RR) and water splitting.

In this work, we introduce *in situ* correlative atomic force microscopy (AFM) to simultaneously image an electrode's conductivity, chemical-frictional and morphological properties. By combining functional imaging with the high spatial resolution afforded by AFM, we address the challenge of resolving nanoscale heterogeneities of electrode surfaces and associated spatial variations in the interfacial electron transfer. Here, we demonstrate the feasibility of using conductive AFM (c-AFM) for electric current imaging¹ in relevant aqueous electrolytes, beyond the common operation in air² or nonpolar liquids³.

For the case of CO₂RR, we show that *in situ* c-AFM allows laterally resolved analysis of variations in the electric current occurring across the electrode/electrolyte/probe interface, where the electrode is exemplified by bimetallic copper-gold CO₂RR electrocatalysts in air, water and bicarbonate electrolyte⁴. In line with contrasts of current images, current-voltage curves reveal resistive CuO_x islands, while frictional imaging indicates qualitative variations in the hydration layer molecular ordering upon change from water to electrolyte. *In situ* c-AFM imaging of nanocrystalline Au, at the granular length scale, suggests that concave intergranular regions are more resistive than convex intragranular regions. Furthermore, we report a correlation indicating that higher friction forces are accompanied by reduced interfacial currents, thus highlighting variations in the interfacial molecular ordering with the electrolyte composition and ionic species present, characterized by their chaotropic or kosmotropic effects.

Our approach facilitates disentangling the effects of electrochemical micro-environments onto interfacial charge transfer or adsorption processes and sets the basis for addressing fundamental challenges in photo-electrocatalysis, battery technology, corrosion science and tribology.

References

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