## High-resolution imaging and correlative scanning electrochemical microscopy

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The last three decades have established scanning electrochemical microscopy (SECM) as the tool of choice for studying spatially resolved electrochemical reactivity and kinetics at interfaces. One of the fundamental challenges stems from the universal use of micron-sized electrodes that hinder the spatial resolution and introduce crosstalk between the electrochemical signal and sample topography. Extending the areas of applications to soft matter, such as living cells, viruses, proteins, etc. requires the application and development of high-quality nanoprobes with sub-50 nm radius of curvature, as well as an AFM-based SECM design which entangles the electrochemical signal from the acquisition of sample topography and its mechanical properties. Furthermore, this enables simultaneous optical acquisition and a functional correlative microscopy.

We have developed an AFM-based SECM add-on that uses a high-quality nanoprobe (PeakForce SECM, Bruker) that has a platinum tip apex of 50 nm, whereby the conductive path to the apex is isolated. The cantilever comes ready to use and is held in a dedicated probe holder. To enable correlative optical measurements, the SECM probe and holder are placed in a transparent electrochemical cell, where a Pt-wire counter electrode and a Ag/AgCl reference electrode are used in a four-electrode configuration, with the tip and sample as first and second working electrode respectively. The recorded low tip-current is fed to a bi-potentiostat unit through a current preamplifier (noise floor lower than 1 nA).

We will demonstrate the SECM performance on two different samples. Platinum microelectrodes on glass were measured in tapping mode, while the Faradaic current of the  reduction to  at a tip potential of -0.3V was recorded in an interleaved mode at a constant distance of 50 nm between the tip and sample. To study the local interfacial charge transfer dynamics in the volume above the sample, individual high-speed force curves were recorded at each pixel. We will demonstrate how this can be used to reconstruct a 3D SECM data cube, which enables the computation of electrochemical activity at arbitrary cross-sections across the entire volume. We will further show how SECM can be applied to capture mass transport across two polycarbonate membranes, while operating the AFM in PeakForce Tapping mode, without the need for interleaved scanning. Here, the polycarbonate membranes with well-defined 100 vs. 400 nm pores are used to separate different volumes, one containing and one free of . The tip was biased to -0.3 V to trigger the reduction of the ruthenium complex if present, hence the detected Faradaic current is an expression of the local concentration of the mediator.

The technique can potentially be applied to various soft matter applications such as the study of enzyme-catalysed reactions, adsorption/desorption phenomena at interfaces, diffusion processes across membranes, as well as metabolitic and physiological activity of living cells and bacteria.