

Scanning Ion Conductance Microscopy – Scanning Electrochemical Microscopy

Hybrid SICM-SECM Techniques for Measuring Electrochemical Information

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Since the inception of scanning tunneling microscopy (STM) [1], electrochemists applied the scanning probe microscopy (SPM) technique to develop scanning electrochemical microscopy (SECM), also known as the chemical microscopy. The SECM is now widely used to examine localized electrochemical properties and reactivity of various materials/interfaces, such as electrode surfaces and interfaces membranes, and biological systems. Despite SECM's many powerful uses, its performance has been limited by its lack of reliable probe-sample distance control. As a result, any variation in surface topography results in changes in probe-sample distance, which creates convolution to the measured faradaic current, which in turn complicates the subsequent data interpretation [2].

Meanwhile, scanning ion conductance microscopy (SICM) [3], has emerged as a versatile non-contact imaging tool. SICM is used to investigate the surface topography of both synthetic and biological membranes [4, 5], ion transport through porous materials, dynamic properties of living cells [6, 7, 8], and suspended artificial black lipid membranes [9]. In addition, integration of complementary techniques with SICM has led to many exciting new applications, including scanning near-field optical microscopy (SNOM) [10] and patch-clamping [11, 12]. Powerful as it is, however, SICM is inherently chemically-blind with no chemical specificity.

To overcome the limitations in constant-height SECM imaging, a hybrid technique of SICM-SECM has been developed that complements SECM with SICM technique. In Hybrid SICM-SECM, the SICM compartment provides the accurate probe-sample distance control, while the SECM compartment measures the faradaic current for electrochemical information collection. In this paper, we demonstrate simultaneous acquisition of SICM-SECM topography imaging and electrochemical mapping data.

Hybrid SICM-SECM

For Hybrid SICM-SECM, there is a number of pipette-based probes that have been de-

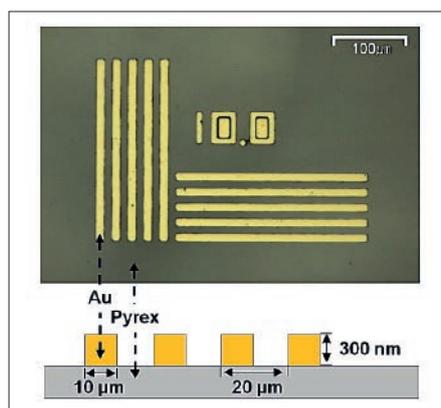


Fig. 1: SICM-SECM standard sample. The sample consisted of Au bars with a width of 10 μm and a height of 300 nm on Pyrex substrate. The pitch width is 20 μm .

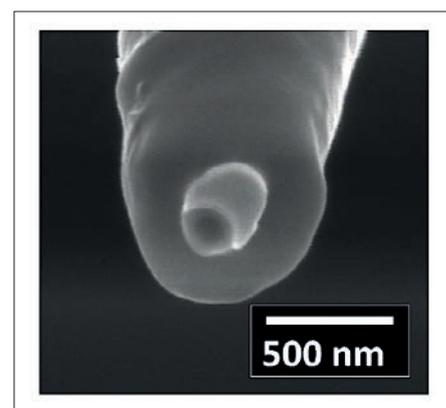


Fig. 2: Representative scanning electron micrograph of the SICM-SECM probe. Pore opening ≈ 250 nm. Au crescent coating ≈ 200 nm.

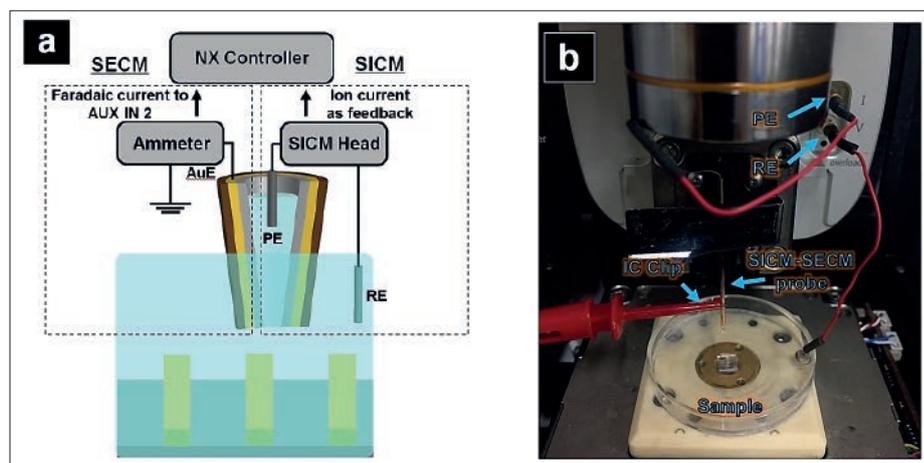


Fig. 3: a) Cartoon illustration of SICM-SECM imaging; b) Setup of the SICM-SECM measurement performed with the probe mounted on the SICM head of a Park NX12 system.

signed for this imaging technique. Bard and his colleagues have developed a gold-coated micropipette insulated with electrophoretic paint. A similar approach has been reported by Hersam and his colleagues, in which the Au-coated pipette was first completed insulated by atomic layer deposition of Al_2O_3 , followed by focus ion beam (FIB) milling to expose both the nanopore and gold electrode. In an alternate approach, a theta pipette is used, one barrel filled with electrolyte for SICM and the other barrel filled with pyrolyzed carbon for SECM. In SICM-SECM

operation, the probe-sample distance can be controlled via the SICM compartment and the electrochemical activity can be measured via the SECM compartment, enabling truly independent concurrent topographical and electrochemical imaging.

Experimental

Sample

As shown in figure 1, the standard sample used for SICM-SECM experiment described

herein consists of Au bars that are 10 μm in width and 300 nm in height on Pyrex substrate. The pitch width is 20 μm .

Probe

The probe used herein is adopted from a method described in Shi *et al.* [13]. In brief, nanopipettes obtained via laser pulling were first coated with 10 nm Cr adhesion layer, followed by 200 nm Au layer by thermal evaporation. Next, chemical vapor deposition of parylene C was performed such that the Au-coated nanopipettes were completely covered by parylene C. Finally, a focused ion beam (FIB) technique was used to expose the nanopore and the Au crescent. A representative scanning electron micrograph of the SICM-SECM probe is shown in figure 2. The diameter of the central pore ranges from 200 – 250 nm. The Au crescent thickness is \approx 200 nm.

Cyclic Voltammetry

Prior to SICM-SECM imaging, cyclic voltammetry (CV) in a bulk solution consisted of 100 mM KCl and 10 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ was performed. The purpose of the CV measurement is to 1) characterize the Au crescent electrode performance and 2) to choose the potential at which the Au crescent electrode will be biased at during SICM-SECM imaging experiments.

To carry out the CV measurement, a potentiostat (Model 760E, CH instrument, Austin, TX) with a three-electrode electrochemical cell is used. The Au crescent electrode served as the working electrode (WE) with respect to a Ag/AgCl reference electrode (RE) and a Pt counter electrode (CE) in the bulk solution.

SICM-SECM Imaging

To realize SICM-SECM imaging, a Park NX12 system in combination with an ammeter (Chem Clamp, Dagan Corp., Minneapolis, MN) is used. A schematic diagram of the SICM-SECM setup is depicted in figure 3a. Ion current between the Ag/AgCl electrodes inside the pipette (PE: pipette electrode) and another Ag/AgCl pallet electrode in the bath solution (RE: reference electrode) is employed as feedback to control probe-substrate distance. The Au crescent electrode (AuE) is used to acquire electrochemical signal. The potential applied between the PE and RE was 0.1 V, and the potential at the AuE was held at -0.5 V. The ammeter is used for both applying potential to the AuE and measuring the faradaic current at the AuE. The measured faradaic current is then fed to one of the auxiliary recording channels (AUX IN 2) of the NX12 controller and recorded in real-time via the Park SmartScan RTM10e software. As a result, simultaneous topographical imag-

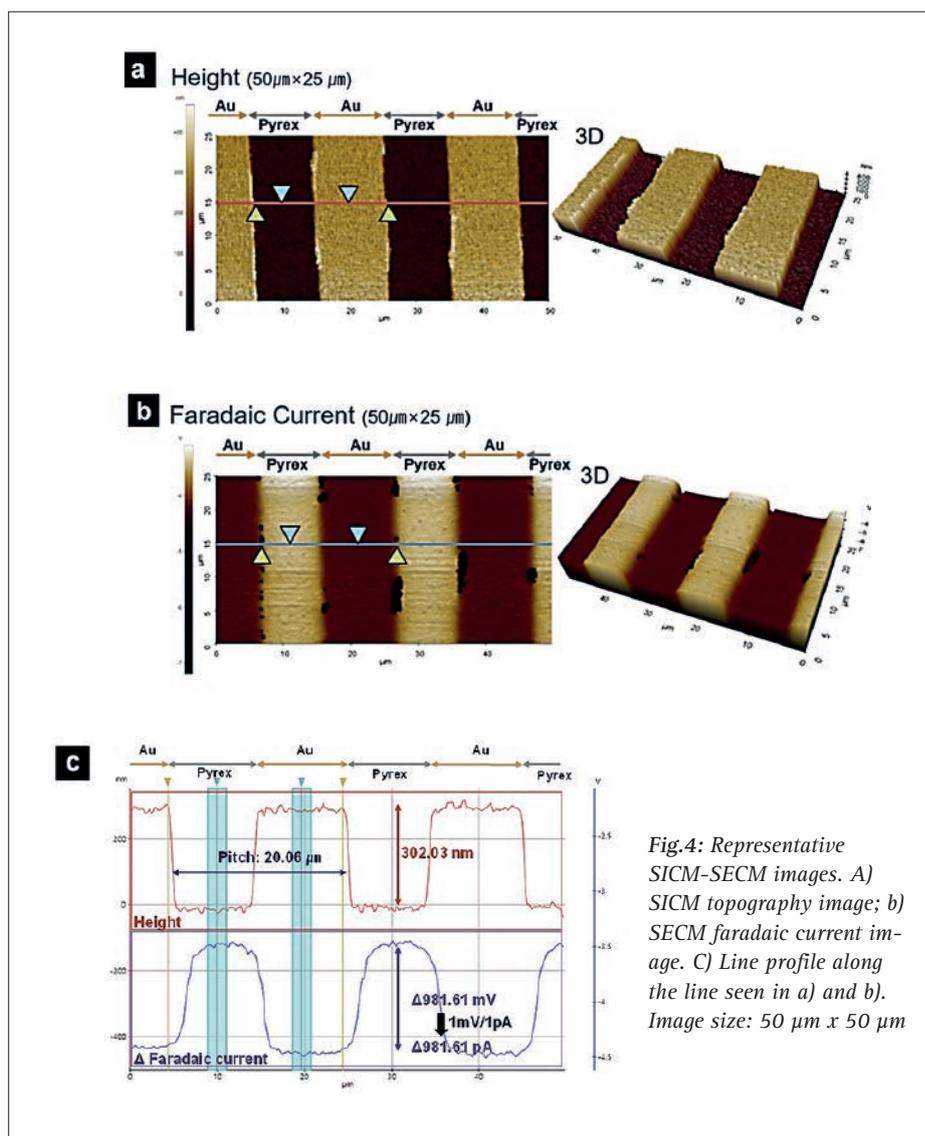


Fig.4: Representative SICM-SECM images. A) SICM topography image; b) SECM faradaic current image. C) Line profile along the line seen in a) and b). Image size: 50 μm x 50 μm

ing (from SICM) and electrochemical activity mapping (from SECM) is accomplished.

Conclusions

We demonstrated the application use of the used system in combination with an ammeter for concurrent topography imaging and electrochemical mapping. The SICM-SECM probe utilized here consisted of a Au crescent electrode (AuE) on the peripheral of a nanopipette. High resolution probe-substrate distance control was obtained by the ion current feedback from SICM, while simultaneous electrochemical signal collection was achieved via the AuE from SECM. As a proof-of-concept experiment, a Au/Pyrex pattern standard sample was imaged with the SICM-SECM technique. The Au bar and the Pyrex substrate were clearly resolved from the SICM topography image, with the bar height and pitch

width closely matching the actual values. In terms of the electrochemical property mapping, higher faradaic current was seen when the probe was scanned over Au bar as a result of redox cycling, while lower faradaic current was observed when the probe was over Pyrex substrate due to hindered diffusion. The capability of the SICM-SECM technique described here holds promise of many exciting applications in the field of electrochemistry, material science and battery research.

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