Scanning Electrochemical Microscopy (SECM)

**PRINCIPLE OF SECM**

When a micro- or nano-electrode is scanned above a surface at a distance comparable to its dimensions / diffusion layer then, in the presence of an electroactive probe, its current depends on substrate reactivity and tip-substrate distance.

\[ I_\infty = 4nFDCr \]

- **Current enhancement due to regeneration** ⇒ \( I > I_\infty \)
- **Current attenuation due to screening** ⇒ \( I < I_\infty \)

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SECM setup

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APPLICATIONS OF SECM

- Topographic information over samples of uniform electrochemical activity (conductors of uniform electrocatalytic activity or insulators).

- Mapping of electrocatalytic activity over relatively flat samples.

- Mapping of enzymatic activity over relatively flat samples.

- Mapping of membrane porosity for relatively flat membranes.

- Substrate surface modification by tip-induced electrochemical reactions.

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EXAMPLES OF SECM APPLICATIONS

Topography of a human breast cell (insulator)

Constant current SECM image of a 10 µm × 10 µm portion of a human breast cell using a 120 nm radius tip and optical micrograph of the same cell.

Constant height SECM operation and image of a 1 µm × 1 µm portion of a human breast cell using a 47 nm radius tip.

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EXAMPLES OF SECM APPLICATIONS
Mapping of electrocatalytic activity of substrates

(A) 80 µm × 80 µm AFM image of a disk-like region of boron-doped diamond. (B) SECM image over such a region with a Pt 2.5 µm microdisc.

Array of metal mixture catalytic spots on a glassy carbon substrate.

(1) SEM of the array (2) - (3) SECM images with substrate biased at 0.2 V and 0.75 V tested for oxygen reduction.

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EXAMPLES OF SECM APPLICATIONS

Mapping of enzyme catalytic centers

SECM image over an immobilized glucoze oxidase enzyme probing catalytic activity for glucose oxidation producing $\text{H}_2\text{O}_2$ which is detected by its oxidation at a **Pt 25 $\mu$m microdisc**.

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EXAMPLES OF SECM APPLICATIONS

Surface modification

(A) Scheme of SECM metal deposition: metal ions are reduced at the tip and oxidation occurs at the substrate/polymer interface.

(B) SEM of a pattern of silver lines deposited in a Nafion® film.

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DIFFERENCES BETWEEN SECM AND EC-STM

(SCANNING ELECTROCHEMICAL MICROSCOPE AND ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE)

• **Different principle:** faradaic (SECM) vs. tunneling (STM) current.

• **Different resolution:** no less than tens of nm for SECM; less than nm possible for STM.

• **Substrate versatility:** SECM can picture insulators too; STM cannot.

• **Information provided:** SECM can map surface reactivity too; STM can only provide topography.

• **Specifications and cost:** Despite setup similarities (piezo-positioner, bipotentiostat, feedback electronics) lower fidelity is required for SECM components and its tips are easier to fabricate and more robust, rendering it much cheaper.

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