Combined Atomic Force-Scanning Electrochemical Microscopy (AFM-SECM)

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Outline

◆ Advantages of micro- and nanoelectrodes
◆ Introduction to scanning electrochemical microscopy
◆ Integrating microelectrodes into AFM tips
  - fabrication
  - characterization
◆ Selected applications
  - mapping material properties
  - mapping enzyme activity
  - inducing/imaging pitting corrosion
◆ Outlook
Combined analytical techniques involving AFM

AFM combined with

**Fluorescence microscopy**
- Live cell imaging
  - Optical image
  - Deflection
  - Alveolar type II (ATII) cells

**Microelectrochemistry**
- Simultaneously recorded topography and electrochemistry
  - Topography
  - Current

**Spectroscopy (IR-ATR)**
- Simultaneously recorded molecular information
  - Topography
  - IR
  - Dissolution of urea

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E. Hecht et al., Anal. Chem. 84, 5716, 2012
A. Eifert et al., Micron, in press 2014
M. Brucherseifer et al., Anal. Chem. 79, 8803 2007
Unique properties microelectrodes

- **Enhanced mass transfer**

  ![Macroscopic disc electrode](image)

  Cottrell equation: \[ I(t) = nFAC_R \sqrt{\frac{D}{\pi t}} \]

  ![Microscopic disc electrode](image)

  Modified Cottrell equation: \[ I(t) = nFADc^0_{\pi r} + nFAC_R \sqrt{\frac{D}{\pi t}} \]

- **Reduced ohmic potential (iR_s) drop**

  \[ E_{\text{eff}}(t) = E_{\text{app}}(t) - iR_s \]

- **Reduced capacitive currents**

  \[ i_c = \frac{\Delta E}{R_s} e^{-t/(R_s C)} \]

  ![Electrical circuit diagram](image)
Scanning electrochemical microscopy

Derived from EC-STM


Electrochemical signal at the UME is influenced by properties of the sample (processes at the sample surface), size of the tip, and distance tip-sample.

- Miniaturized potentiometric sensors
- Micro-amalgam electrodes
- Microbiosensors

Ultramicroelectrode (UME)

r: Radius (several tens of nanometer to 25 μm)

d: UME-to-sample distance
SECM operation modes

Feedback mode (artificial redox mediator) for positioning and imaging

For redox reactions with fast electron transfer rates

**Negative feedback mode**

For UMEs with RG of 10

![Graph showing negative feedback mode](image)

Dimensionless parameters: $i_T = i_T / i_{T,\infty}$; $L = d / a_{tip}$

$F^{\text{ins}}_T(L) = \frac{i_T}{i_{T,\infty}} = \frac{1}{0.40472 + \frac{1.60185}{L} + 0.58819 \exp(-2.37294 L)}$

$F^{\text{cond}}_T(L) = \frac{i_T}{i_{T,\infty}} = 0.72627 + \frac{0.76651}{L} + 0.26015 \exp\left(-\frac{1.41332}{L}\right)$

SECM image of a structured polymer surface with conductive stripes.

Feedback mode image recorded in 10 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl vs SCE, 10 µm s$^{-1}$

Operation modes of SECM

Generation collection mode

Substrate generation- tip collection mode (SG/TC)

Tip generation- substrate collection mode (TG/SC)

Substrate: **Pt-microelectrode** biased at - 0.5 V vs. Ag/AgCl → **generation of** \( \text{H}_2\text{O}_2 \); SECM imaging UME:

**PB-modified IBID-UME** biased at -0.05 V vs. Ag/AgCl → **reduction of** \( \text{H}_2\text{O}_2 \)

SECM images of an gold electrode (25 μm diam.) biased at -0.5 V vs. Ag/AgCl.; A and B: images recorded with Pt UME (diam. of 25 μm) modified with three layers of PB–Ni–HCF and with only Ni–HCF, respectively.

Several drawbacks of individual SPM techniques

**AFM:** High resolution topographical information; physical properties (adhesion, etc.)
- limited chemical resolution

**SECM:** Information on (electro)chemical surface processes; but UME to sample distance dependent on size of the miniaturized electrode
- limited lateral resolution
Constant height imaging convolution of electrochemistry and topography

Combined AFM-SECM
Combined AFM-SECM

AFM-SECM probe design

- Nanometer-sized electrodes
- High lateral “resolution” in topographical and electrochemical imaging
- Direct contact between electrode and sample surface
- Sequential imaging required

+ No contact between electrode and sample surface
+ Integration of sensing layers
+ Simultaneous constant distance for imaging of topology and current
- Larger electrodes
- Higher fabrication costs

Gullo et al., Anal. Chem. 2006
Abbou et al., Anal. Chem. 2002
Gullo et al., Anal. Chem. 2006
MacPherson et al., Anal. Chem. 2005
Pust et al., Nanotechnology 2010
FIB-based fabrication

Non-coated $\text{Si}_x\text{N}_y$ cantilever

1) Sputtering of electrode layer ($\text{Au}$, $\text{Pt}$, $\text{Ir}$, etc.)
2) Deposition of insulation layer

Parylene C (force constant after modification: $\sim 0.5$ N/m)
$\text{Si}_x\text{N}_y$ (force constant after modification: $\sim 1-2$ N/m)
3) FIB-milling

Ion-column and E-column

Cross section face

Stage

52°
Electrochemical characterization

Cyclic voltammetry (CV)

CVs recorded in 10 mM Ru(NH$_3$)$_6^{3+}$/0.1 M KCl solution (E vs. Ag/AgCl); scan rate 100 mV/s; a) insulated AFM-SECM probe; b) after exposing frame-shaped electrode.
Combined AFM-SECM set-up
Simulation of electrochemical response

Boundary element method

\[ \frac{\partial c(r,t)}{\partial t} = 0 = \nabla^2 c(r) \]

\[ i_T \approx nFD \sum_i \int_{\Gamma_{el,i}} \frac{\partial c_i}{\partial n_i} d\Gamma_{el,i} = nFD \sum_i \left( \frac{\partial c_i}{\partial n_i} \Gamma_{el,i} \right) \]

O. Sklyar et al., Anal. Chem. 77, 764, 2005
AFM-SECM imaging

FIB-assisted patterning

Images recorded in AFM contact and SECM feedback mode in 10mM [Ru(NH$_3$)$_6$]$^{3+}$/0.1 M KCl; Pt-coated glass slide with FIB-structured patterns. AFM images are 1$^{st}$ order flattened, SECM images are line-corrected.
AFM-SECM imaging of composite material

Boron-doped diamond (BDD) / silicon carbide (SiC)

All experiments performed in 10 mM \([\text{Ru(NH}_3\text{)}_6\text{Cl}_3]/0.1 \text{ M KCl}\) \(E_{\text{tip}}: -400 \text{ mV vs. Ag/AgCl}\).

Collaboration: Nianjun Yang, University Siegen
Corrosion

Pitting corrosion

Ohio: collapsed Silver-Bridge

Image source: Wikipedia.org

AFM investigation of pitting corrosion:

304L steel sample: AFM contact mode images a) before, and b) after pitting. (a) and (b) have not been taken at the same spot but on the same sample.

SECM investigation of pitting corrosion:

SECM images of 304 stainless steel biased at +0.45 V vs. Ag/AgCl/KCl (3 M) during immersion in 0.1 M NaCl. $E_{\text{tip}}$: (A) +0.50, and (B) +0.10 V vs. Ag/AgCl/KCl (3 M); tip-substrate distance: 10 μm; scan rate: 25 μm s$^{-1}$.

F. A. Martin et al., Corrosion Sci. 50, 84, 2008

J. Izquierdo et al., J. Electroanal. Chem. 728, 148, 2014
Localized AFM-SECM corrosion studies

Locally induced corrosion on Fe alloys

Induced pit corrosion:
$E_{\text{tip}} = +0.95 \text{ V vs. Ag/AgCl}$
scan area: 3x3 µm
scan speed: 0.74 lines/s

Electrolyte: 0.5 M NaCl/0.1 M NaNO$_2$

Formation of passivation layer in nitrite solution: $\text{Fe}^{2+} + 2 \text{OH}^- + 2 \text{NO}_2^- \rightarrow 2 \text{NO} + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$

Oxidation of nitrite to nitrate $\rightarrow$ by product protons $\rightarrow$ localized acidification of the medium, attack of chloride ions
Corrosion studies

Local induced corrosion on Fe alloys

Top: 3D AFM contact image of polished iron sample immersed in 0.5 M NaCl/0.1 M NaNO₂ recorded with an unbiased AFM-SECM tip; bottom: line scan.

Top: Zoomed out 3D AFM contact image of iron sample immersed in 0.5 M NaCl/0.1 M NaNO₂ recorded after scanning a 3x3 µm² area with the AFM-SECM tip biased at 0.95V vs. Ag/AgCl; bottom: line scan.
Advantage of AC-SECM imaging

- Localized measurement of changes in solution resistance
- Mediator free imaging with ultramicroelectrodes (UME)
- Mapping of corrosion processes
- Resolving pit corrosion at micro-/nanoscale
- Combined AFM-AC-SECM: Simultaneous imaging of topography and impedance changes with bifunctional probes

Collaboration: W. Schuhmann
Ruhr University, Germany
AFM-SECM-AC mode imaging

AFM topography and AC–SECM recorded with AFM tip-integrated ring Pt microelectrode at a structured glass/gold substrate: (left) topography (contact mode); scan speed: 0.15 lines/s, (right) simultaneously recorded AC–SECM image at 5.01 kHz and 110 mVpp superimposed onto a -100 mV DC bias applied to the AFM-SECM tip in 1 mM KCl.

Images of periodically micro-structured silicon nitride/gold structure with recessed 1 μm gold spots: (left) topography (contact mode); scan speed: 0.1 lines/s, (right) AC–SECM image at 14.92 kHz and 110 mVpp superimposed onto a -100 mV DC bias applied to AFM-SECM probe in 1 mM KCl.

Imaging enzyme activity

Enzyme-catalyzed reaction

\[ \text{Glucose} + \text{O}_2 \rightarrow \text{Gluconolacton} + \text{H}_2\text{O}_2 \]

Electrode reaction (+0.65V vs. Ag/AgCl)

\[ \text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- + \text{O}_2 \]

- GOx immobilized in electro-deposited soft polymer\(^1\)
- AFM operated in dynamic mode
- SECM operated in generator/collector mode:
  \[ E_{\text{tip}} = 0.65 \text{V vs. Ag/AgCl} \]

\(^1\) C. Kurzawa et al., Anal. Chem. 74, 355, 2002

Electrode materials

Surface modification of AFM tip-integrated electrode and/or new electrode materials

- Increased electroactive area (Pt/C)
- AFM tip-integrated PPy electrode
- Boron-doped diamond electrodes
  - Si cantilever with diamond overgrowth

Collaboration: M.J. Higgins IPRI, Univ. Wollongong
Collaboration: C. Nebel (IAF, Freiburg)

Boron-doped diamond (BDD)

Characteristics

- Conduction band (CB)
  - N: 1.6 eV below CB (donor)
  - B: 0.37 eV above VB (acceptor)
- Band gap: 5.45 eV

Advantages:

- Significantly extended potential window
- Wide optical window (near UV 0.25 – far IR 100 μm)
- Less electrode fouling
- Enhanced chemical and mechanical stability
- Reduced background currents

Wear-resistant diamond SPM probes

CVs recorded at a BDD-AFM-SECM probe in 10 mM $\text{K}_4\text{[Fe(CN)]}_6$; 0.1 M KCl; vs. Ag/AgCl; scan rate: 0.1 V/s
AFM-SECM imaging with integrated BDD-electrode

Topography
Electrochemistry

Electrode size: 2.8 µm, tip length: 1.2 µm, scan speed: 0.5 lines/s
10 mM [Ru(NH$_3$)$_6$]Cl$_3$/0.1 M KCl $E_{tip}$: -400 mV vs. Ag/AgCl

Polypyrrol-modified AFM-SECM probes

Novel AFM-SECM probes for cell stimulation

Stimulation: highly localized electrical charge

Incorporation of bioactive molecules through doping

Release of anionic bioactive molecules

P. Knittel, M. Higgins, C. Kranz, Nanoscale 6, 2255, 2014
Outlook: Multifunctional platforms

Electropolymerization of 3,4 ethylenedioxythiophene

ELECTROCHEMISTRY

+ 

ATOMIC FORCE MICROSCOPY

+ 

INFRARED SPECTROSCOPY

SPECTROELECTROCHEMISTRY

= 

MULTIFUNCTIONAL ANALYTICAL PLATFORMS

→ EC: PEDOT formation
→ AFM: topography/phys. properties
→ IR: molecular information

BDD-coated diamond ATR crystal

D. Neubauer et al., Analyst, 138, 6746, 2013
Outlook: Towards advanced cell measurements

AFM-implemented stretching device

Ongoing research combining cell stretching device + AFM tip-integrated sensing

Dynamic mode images recorded in PBS (pH 7.4) with A’ tip-integrated glucose biosensor, (E_T at 0.65 V / AgQRE) imaging glucose diffusion through etched membrane: lower compartment: 3mM glucose

Ca^{2+} channels (L-VSCC) inhibited (Nifedipin) → lower level of ATP
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