Scanning Nanoelectrochemistry and Nanoelectrical Liquid Imaging with Nanoelectrode Probe

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Atomic Force Microscopy
3D Optical Microscopy
Fluorescence Microscopy
Tribology
Stylus Profilometry
Nanoindentation
Outline

• Overview
• Nanoelectrode Probe
• AFM-SECM
  • PeakForce SECM
  • Force Volume SECM
  • Contact Mode SECM
  • Tapping Mode SECM
• Nanoelectrical Measurements in Liquid
  • Conductive AFM
  • PFM: Nano-Electromechanics
  • Kelvin Probe Force Microscopy
• Conclusion
Success from Collaboration

- Nanoelectrode Probe
- Scanning Nano-Electrochemistry
- Nanoelectrical Measurements in Liquid

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<td>JCAP/Caltech</td>
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<td>PF-TUNA in Liquid</td>
<td>Universität Bayreuth (Germany)</td>
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<td>Solar Fuels</td>
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<td>Surface Chemistry</td>
<td>University of Oregon</td>
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<td>University of Leeds (UK)</td>
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<td>Battery</td>
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<td>Fujian Normal University (China)</td>
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<td>Force Volume SECM</td>
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<td>PFM in Liquid</td>
<td>East China Normal University</td>
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Some Publications

- Nellist et al. *Nature Energy* 2017, accepted
- Nellist et al. *Nanotechnology* 2017, 28, 095711
- Huang et al. *Bruker Application Note* 2017
- Huang et al. *Microscopy Today* 2016, 24, 18
Nanoelectrode Probe
Active Tip for SECM (local EC studies) & Electrical Characterization in Liquid

- **Probe**
  - Batch (wafer) manufactured
  - Exposed tip height: ~ 250 nm
  - End tip radius: ~ 25 nm
  - $k = 1.5 \text{ N/m}$, $f = 65 \text{ kHz}$

- **Package**
  - Fully isolated, encapsulated in two parts glass
  - Easy to handle, robust ESD protection
  - Chemical resistant (pH 1-13 & battery solution)

$Pt \quad SiO_2$

$r \sim 25 \text{ nm} \quad h \sim 250 \text{ nm}$

Nellist et al. *Nanotechnology* 2017, 28, 095711
High Electrochemical Performance

- Robust for handling and electrochemistry:
  \([\text{Ru(NH}_3\text{)}_6]^{2+/3+}\): 4 rinse-and-dry cycles, 5 min amperometry, and 29 CVs
  
  \([\text{Fe(CN)}_6]^{3+/4+}\): 50 CVs and 2 hr amperometry sub-pA noise level

Nellist et al. *Nanotechnology* 2017, 28, 095711
High Spatial Sensitivity

- Approach Curves
  - Current vs tip-sample distance
  - Inactive/active area: negative/positive feedbacks
  - Kinetic quantification: shape vs. surface activity

- Consistent with simulation
  - No leakage current

- Changes mostly occur within 150 nm
  - High spatial sensitivity
  - Consistent with diffusion layer structure

Nellist et al. Nanotechnology 2017, 28, 095711
Scanning Electrochemical Microscopy (SECM)

- A tiny electrode brings electrochemistry to micro- or nano-scale
- Local EC characterizes active site, diffusion, ionic transport, permeability, etc.
- Resolutions are primarily defined by the probe electrode dimension
SECM Applications

Mauzeroll et. al., Chem. Rev. 2016, 116, 13234
PeakForce Tapping

The probe is sinusoidally modulated at 1~2 kHz:

- No cantilever tuning required.
- Low and stable force, < 50 pN.
- Automatic image optimization.
- Quantitative NanoMechanics (QNM).
- Simultaneous nanoelectric capture.

Contact
High imaging force
Tapping
Rely on resonance

PeakForce Tapping
Precise force control

PF-QNM
PF-TUNA
PeakForce Tapping: Application Examples

**Embedded CNT on P3HT lamellar**

Leclere et al. Nanoscale, 2012, 4, 2705

**SAM on Au**

Microscopy Today 2016, 24, 18

**ULDPE PS/LDPE**

**DNA**

Small 2014, 10, 3257

**Live E. Coli cells**

**Calcite**

**Si NW**

**Electrochemistry**

Microscopy Today 2016, 24, 18

**PeekForce Tapping: Application Examples**

11/15/2017

Bruker Confidential
PeakForce SECM

- Simultaneously multimodal imaging:
  Topography, mechanics, conductivity, electrochemistry, etc.

Nellist et al. Nanotechnology 2017, 28, 095711
PeakForce SECM Hardware

- Low noise electronics, limited only by potentiostat
- Robust ESD protection
- Compatible with glovebox operation
- Wide range of chemical compatibility

Operation inside a glovebox

Huang et al. Microscopy Today 2016, 24, 18
PeakForce SECM

- Multimodal imaging at 15 nm lift height

- Lift height-dependent current.
- Changes mostly occur within 100 nm lift height.
- Confirm the compact structure of the diffusion layer.
Defects on HOPG Electrode

Topography
900 nm x 600 nm
0.4 nm step
800 nm

Adhesion
4 nN difference
800 nm

SECM
(left) 2~5 pA higher
55 pA difference
800 nm

Nellist et al. Nanotechnology 2017, 28, 095711
PeakForce SECM
Pt/p⁺-Si for Catalysis

- Settings:
  - 10 mM [Ru(NH₃)₆]³⁺, 0.1M KCl
  - Tip potential: -0.4 V vs AgQRE
  - Sample potential: -0.1 V vs AgQRE
  - Peak force: 700 pN; Scan rate: 0.2 Hz; Lift height: 100 nm;

- PeakForce Tapping is required to measure these loosely attached particles
- Contact current measures interfacial conductivity
- SECM current measures electrochemical activity
Force Volume Scanning Electrochemical Microscopy
Kinetic Quantification of Surface Reaction

Inhomogeneous conductivity

Inhomogeneous electrochemical activity

Approach curves of distinct characteristics
Force Volume
Quantitative mechanical mapping modes

- Linear ramping to collect the complete force curve from every tap
- Multiple property maps calculated
  - Multiple ramp data channels acquired
- Ramp and hold functionality
Force Volume SECM

- Array of approach curves for improved EC quantification.
- EC activity in function of distance to sample surface, in every pixel (mapping).
- Correlated topography, nanomechanics and nanoelectrics
Force Volume SECM
Insulating Flake on Au Substrate

- Sample Courtesy: Liming Zhang, J. Tyler Meffordd, Andrew Akbashev, and William Chueh, Stanford University
Force Volume SECM Density Plot

- Density plot shows which EC activities are most commonly present
- Two distinct areas are differentiated by the two density plots
- Sample Courtesy: Liming Zhang, J. Tyler Meffordd, Andrew Akbashev, and William Chueh, Stanford University
Ramp and Hold with FV-SECM

1. On Pt, positive feedback and electrically connected with the Pt electrode.

2. On nitride, negative feedback and electrically disconnected with the Pt electrode.
Nanoelectrode AFM probes enable the in-operando measurement of surface electrochemical potentials during oxygen evolution catalysis.

- Catalyst voltage ($V_{\text{tip}}$) identical whether on ITO or illuminated hematite
- Holes transfer from hematite to CoPi, where water oxidation occurs

Nanoelectrical Measurements in Liquid
AFM Nanoelectrical Measurements

- Bruker provides a versatile array of electrical techniques for a multitude of applications.

<table>
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<tr>
<th>Conductivity/Resistivity</th>
<th>C-AFM, TUNA, PeakForce-TUNA, SSRM</th>
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<tr>
<td>Electric Field</td>
<td>EFM</td>
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<tr>
<td>Charge</td>
<td>EFM, SCM</td>
</tr>
<tr>
<td>Surface Potential / Work Function</td>
<td>KPFM, PeakForce KPFM</td>
</tr>
<tr>
<td>Carrier Density</td>
<td>SCM, SSRM, sMIM, PeakForce-sMIM</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>PFM</td>
</tr>
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</table>
PeakForce Nanoelectrical Measurements

- For previously AFM-inaccessible, delicate samples and adds correlated nanomechanical data
  - Improve tip lifetime with hard samples
  - Decrease sample wear with soft samples
  - Improve resolution due to sharper tips & less sample damage

PeakForce TUNA (A) topography, (B) current, and (C) adhesion maps reveal the influence of an embedded nanotube on P3HT lamellar ordering and current pathways. Image size 500 nm.

Leclere et al. Nanoscale, 2012, 4, 2705
Nanoelectrical Liquid Imaging

- **Applications**
  - Energy research
  - Bio-electricity
  - Catalysis
  - Sensing

- **Challenges**
  - Compatibility:
    - Environment & chemicals
  - Localized signals
  - High S/N

Lee et al. *Adv. Mater.*, 2014, 26, 4880

Nanoelectrical Liquid Imaging

- Probe and sample are fully immersed in solution
- High quality, localized signal
  - Fully-insulated but the tip apex
  - Conductive path to minimize stray capacitance
  - High bandwidth, next-to-tip amplifier
TUNA & PeakForce TUNA in Liquid
PeakForce TUNA in Liquid (DMC) in Glove Box

- Sample was in DMC, a solvent for battery research
- Measurement was done inside a glove box
- Clearly differentiates exposed Pt on the current map
- I-V spectra confirms the difference in conductivity
- Negligible background current at nitride surface

Nellist et al. Nanotechnology 2017, 28, 095711
PeakForce TUNA in Liquid in 1M KCl Aqueous Solution at High Bias

- Low parasitic currents on Si$_3$N$_4$:
  - At -0.5V: 1.06 pA
  - At +0.5V: 0.07 pA
- Low current noise level: ~1 pA
PeakForce TUNA in Liquid Interfacial Energetics on a Photoelectrode

- Semiconductor/Metal Junction in Liquid
- Sample shows diode behavior in air
- I-V characteristics in H$_2$O totally changes

Huang et al. *Microscopy Today* 2016, 24, 18
Pt/p⁺-Si: PeakForce SECM

- Resistive interface: contact current (interfacial conductivity) is correlated with SECM current
- Conductive interface: EC activity is compared (e.g. #2 vs. #3, higher contact current but lower SECM current)

PeakForce KPFM in Liquid
PeakForce KPFM in Liquid (H\textsubscript{2}O, 1 mM KCl, or DMC)

- In Air: \(~125\) mV difference

- In H\textsubscript{2}O: \(~150\) mV difference
Piezoresponse Force Microscopy (PFM) in Liquid
High-Resolution Electromechanical Imaging of Bio-compatible Ferroelectric Materials in Air, Water and NaCl Electrolyte.

- Slides contributed from Anyang Cui, East China Normal University.
- Measurements were in collaboration with Bruker.
- Cui & Hu et al., manuscript in preparation.

Unpublished Results, Manuscript in Preparation
Phase Contrast at Contact Resonance

Measurements were in collaboration with Cui&Hu et. al. at ECNU in China

- Sample: PPLN; Electrolyte: NaCl; Image Force: 100 nN
Conclusion

- Bruker’s new AFM-SECM probe technology improves SECM lateral resolution by orders of magnitude and opens the door to new measurements on individual nanoparticles, -phases, and -pores.

- PeakForce SECM enables the highest spatial resolution and multi-modal imaging on soft and fragile samples.

- Force Volume SECM allows for improved kinetic quantification and provides 3D electrochemical mapping, through capturing a complete data cube.

- PeakForce nanoelectrical measurements in liquid provide new capabilities for visualization of electrical processes in solution.

Huang et al. Microscopy Today 2016, 24, 18
KPFM Sensitivity Scales with Q/k

- In Air
  - $f_0 \sim 62 \text{ kHz}$
  - $Q \sim 215$

- In di-H$_2$O
  - $f_0 \sim 29 \text{ kHz}$
  - $Q = 10$

- In liquid, the sensitivity is about 20x lower (vs. air) with these cantilevers
Cells were overgrown and covered the whole petri dish.
SECM probe successfully imaged the topography of live cells without sample damages.
Defects on HOPG Electrode

- Topography
- Electrochemistry