Nanoelectrical SPM in Liquid

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

- AFM Nanoelectrical Measurements
- Nanoelectrical Measurements in Liquids
  - Nonpolar Liquids
  - Polar Liquids
- Conclusion
Bruker provides a versatile array of nanoelectrical techniques for a multitude of applications.

- **Surface Potential / Workfunction:** KPFM
- **Carrier density:** SCM, SSRM, sMIM
- **Piezoelectric properties:** PFM
- **Conductivity & Resistivity:** C-AFM, TUNA, SSRM
- **Electric Fields, Charge:** EFM, KPFM
- **Impedance:** sMIM
- **Other:** Scanning Gate, Pyro-Electric AFM, Photoconductive AFM,...
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
DataCubes:
Nanoelectrics with Fast Force Volume

- Fast Force Volume imaging: a force-distance spectrum in every pixel
- Insert a ‘hold segment’ (= ‘dwell time’) and perform an electrical measurement during the hold segment: electrical spectrum in every pixel
- Retain advantages of Peak Force nanoelectrics
- Big data & deep data characterization

Previous webinar by Dr. Peter De Wolf:
Nanoelectrical SPM in Nonpolar Liquids

- Clean surface: Mimicking vacuum for fundamental studies
- Free from capillary force: Low force imaging
- High-resolution mapping
- Generally, no need for special probes

Non-polar liquid
Alkanethiols on SAMs tune the work function of the underlying metal, which is attractive for optoelectronics.

Obtaining reliable CPD requires clean surface. Different from UHV, KPFM in nonpolar liquids is much less technically demanding.

Results are in excellent agreement with UPS.

Decane: non-polar liquid
PFM in Nonpolar Liquids: High Resolution Electromechanical Imaging

- SCM-PIT probe
- Free from capillary force
- Resolution is only limited by the tip radius
- Domain wall, ~ 10 nm

• Drive near or coincide with the contact resonance (CR) for signal enhancement.
• Single frequency measurement is insufficient.
• DCUBE-CR-PFM: frequency sweep on every image pixel for resonance tracking

• Phase at contact resonance is robust to differentiate domains of different polarizations

DCUBE-CR-PFM: PPLN in Decane

- High Volume, High Throughput: 260 image / channel x 4 channels = 1040 images
- High Spectra Resolution: 0.67 kHz / image
- Correlated Images and Channels
- All QNM images

DCUBE-CR-PFM: PPLN in Decane
Dynamic Electromechanical Properties

• PFM amplitude channel
• Dynamic electromechanical properties along drive frequency
• Spatial dynamic changes along X and Y directions

DCUBE-CR-PFM: PPLN in Decane

Statistical Analysis

- Correlation of amplitude channel with phase channel
- Density plots show which PFM responses are most commonly present
- Two distinct PFM domains are differentiated by the two density plots
DCUBE-CR-PFM: PPLN in Decane
Quantitative Analysis

DCUBE-CR-PFM: PPLN in Decane Phase at Contact Resonance

- DCUBE enables the generation of a map of PFM phase at contact resonance.
Nanoelectrical SPM in Polar Liquids

• **Applications**
  - Energy research
  - Bio-electricity
  - Electromechanics
  - Catalysis
  - Sensor

**Battery**


**Energy/Catalysis**

Jiang et al. *ChemSusChem*, 2017, 10, 4657

**Bio-electricity**

Lee et al. *Adv. Mater.* 2014, 26, 4880
Nanoelectrical SPM in Polar Liquids

- **Challenges**
  - Compatibility:
    - Environment & chemicals
  - Parasitic EC reactions:
    - Background signal
  - Stray capacitance
    - Background signal & slow response
  - Conductive liquid:
    - De-localized electric field
Nanoelectrical Liquid Imaging

**Bruker Solution**

- Isolated, leakage-free nanoelectrode
- Optimized, special tip holders, container (EC cells)
- Good implementation of electrical modes (existing from air)
PFM in Biomimetic Environment

- Physiological environment: ~ 150 mM, pH ~ 7.0.
- Bio-compatible ferroelectric crystal in NaCl electrolytes.
- Insulated probe for enhanced resolution.
- < 0.5 M, OP domain wall can be recognized clearly.

In collaboration with Dr. Anyang Cui from East China Normal University. Paper under review.
PFM in Biomimetic Environment

- High-resolution PFM in liquid: domain wall ~ 30 nm, superior to non-insulated probe

In collaboration with Dr. Anyang Cui from East China Normal University. Paper under review.
KPFM in Polar Liquids

- KPFM for research in battery, corrosion etc.

- Corrosion behaviors of Cu and stainless steel.
- Areas of higher potential correspond to corrosion sites.

- Challenges: only work for low concentration electrolyte

- Alternatives: SECPM or tech by Boettcher’s group

- PF-KPFM: DMC, H₂O, dilute NaCl solution
PeakForce TUNA in Liquid Interfacial Energetics on a Photoelectrode

- Semiconductor/metal catalyst photoelectrodes.
- Electrolyte solution impacts interfacial energetics.
- Sample shows diode behavior in air.
- I-V characteristics in H$_2$O totally changes.

Huang et al. Microscopy Today 2016, 24, 18

Surface Layer or SEI for Li Batteries

Surface layer or solid electrolyte interface (SEI)

- Ionically conductive, electrically insulating, and mechanically elastic and robust.
- Essential for good power cyclability, cycle life and cell safety
- Dynamic phase during voltage cycling

LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Cathode: Facet Effect, in situ study

- Facet-dependent SEI formation during the first charge–discharge process.
- The surface film with a thickness of 4–5 nm was formed on the (111) surface.
- Not detectable change for (100)

Liu et. al. Chem. Commun. 2014, 50, 15756
LiCoO$_2$ Cathode in Glovebox
1 M LiPF$_6$ : EC: DMC (1:1 in volume)
300 mV sample bias

- In Situ imaging of topography, mechanics, conductivity change of the surface layer
- Edges of particles smoothen out
- Some boundaries show conductivity

Before any charging
After stabilizing at 4.2 V (de-lithiation)

Voltage pattern

Featureless low current
$I_{ave}$: 180 pA

Saturated

Courtesy: Prof. Zhigao Huang, Prof. Yingbin Lin, and Dr. Yue Chen, Fujian Normal University, China
Conclusion

• Bruker offers a set of unique solutions that enables nanoelectrical studies in liquids

• Using isolated nanoelectrode tips, one can carry out high-performance electrical measurements in polar liquids in multiple modes for a variety of applications
  • TUNA & PeakForce TUNA
  • KPFM & PeakForce KPFM
  • PFM
  • DCUBE

• Nanoelectrical SPM enables new research areas