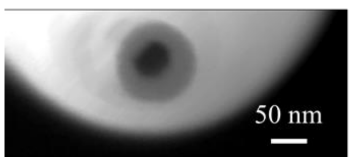
Spatially Resolved Electrochemical Imaging on Energy Materials

A. Kumatani[1,2]

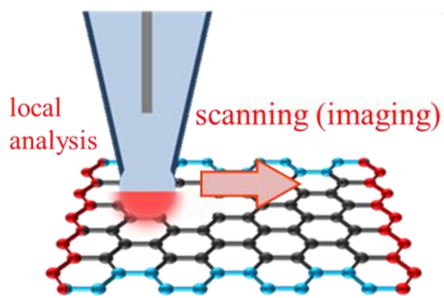
1 Advanced Institute for Materials Research (AIMR), Tohoku University.
2 Graduate School of Environmental Studies, Tohoku University.

8th Oct. 2018, Birck Nanotechnology Center, Purdue University

Self-developed Scanning Electrochemical Microscopy



nanopipette

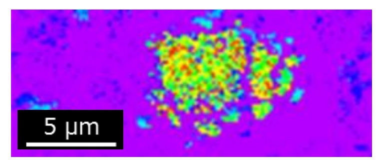


SECCM: scanning electrochemical cell microscopy

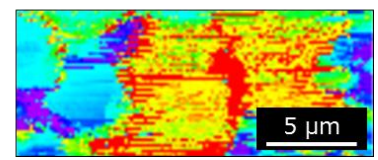
Nanoscale Electrochemical Imaging

Li^+ transport

- Composite electrode



- Thin film



Mediator redox

8×6.35 μm

Hydrogen Evolution Reaction

3 × 3 μm

Advanced Institute for Materials Research

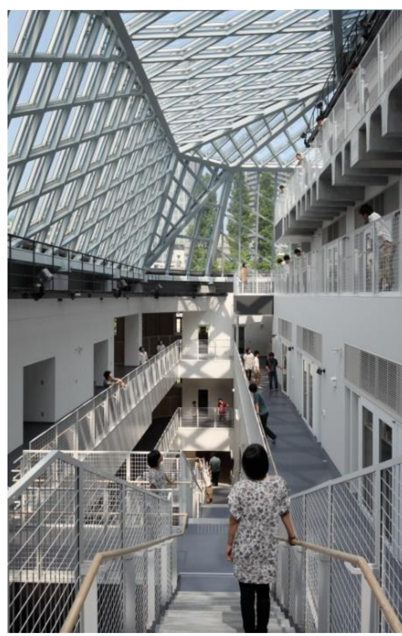
Established in 2007 till 2016

World Premier International Research Center Initiative

by MEXT

Tohoku University

Advance Institute for Materials Research **(AIMR)**



Advanced Institute for Materials Research

Tohoku University (since 2017)

Selected as <u>Designated National University</u>: Material Science and Spintronics

AIMR Director:

Prof. Motoko Kotani

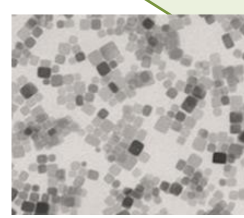
Total Researcher101(45)
Principal Investigators(PI): 26(11)
Other Researchers : 75(34)

Materials Physics Group

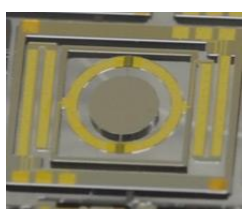
Mathematical Science Group

Non-equilibrium Materials Group

Soft Materials Group



Device/System Group

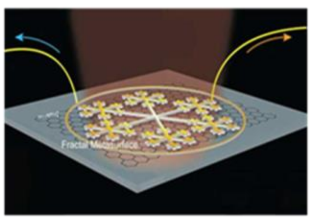


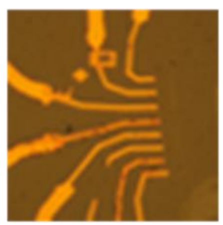
Establish new and noble material science with mathematics

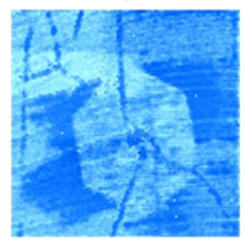
“Quantum Materials and Spintronics” (QMS) Lab.
in AIMR, Tohoku Univ.

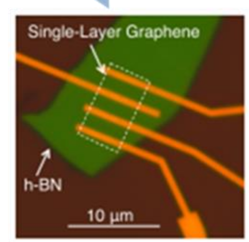
to work on a wide range of quantum materials
(2D materials and their heterostructures and topological materials)
including device fabrications, transport measurements, characterizations

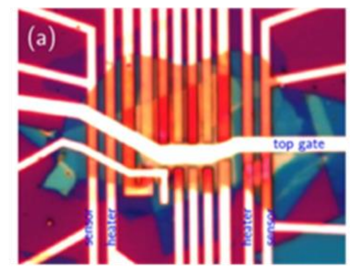
2D materials and van der Waals heterostructures


Photodetectors


Phototransistors


Nanoelectrochemical Imaging





Graphene-BN Heterostructures

Photoelectronics

Prof. Y. P. Chen

Electrochemistry

Assoc. Prof. A. Kumatani

Thermoelectronics

Spintronics

Assi. Prof. H. Idzuchi

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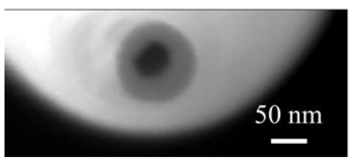

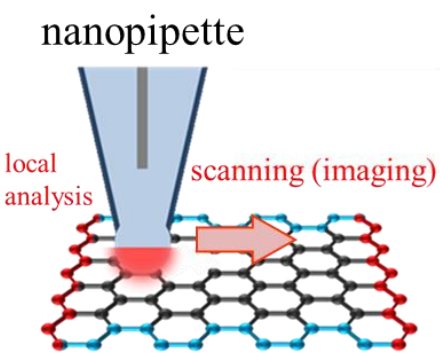

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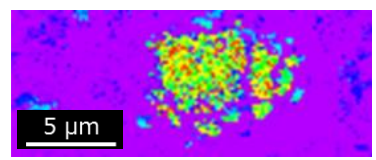
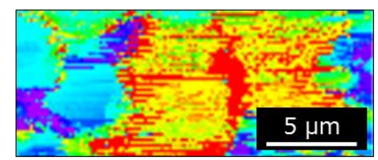


- Thin film



Mediator redox

8 × 6.35 µm

Hydrogen Evolution Reaction

3 × 3 µm

Outline:

1. Key technique for Electrochemical Imaging:

    Scanning Electrochemical Cell Microscopy (SECCM)

2. Visualization of Electrochemical Activities

    2-1. Lithium-ion Transport

    - Practical/model electrodes

    2-2. Mediator redox ($Ru^{3+/2+}$)

    - Graphene, $NbSe_2$

    2-3. Hydrogen evolution / Oxygen reduction reaction

    - SnS_2 , BN

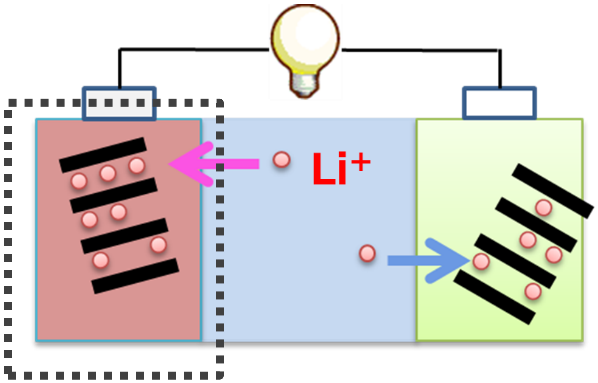
    2-4. Other application:

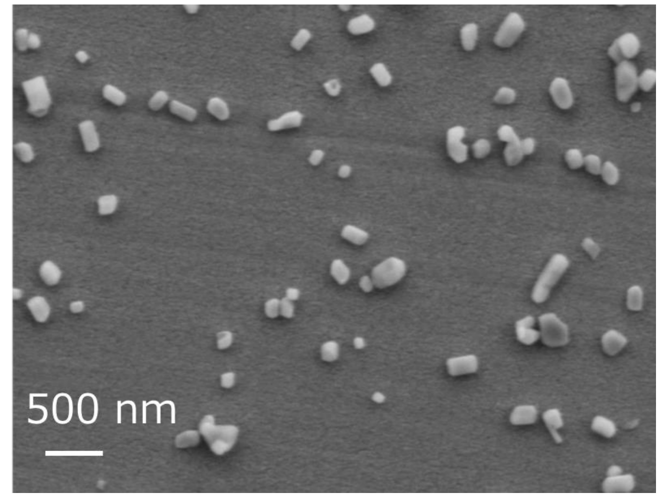
3. Conclusion

Why we set up a new microscope?

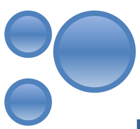
For lithium-ion batteries (LIBs) :

From Nikkei HP

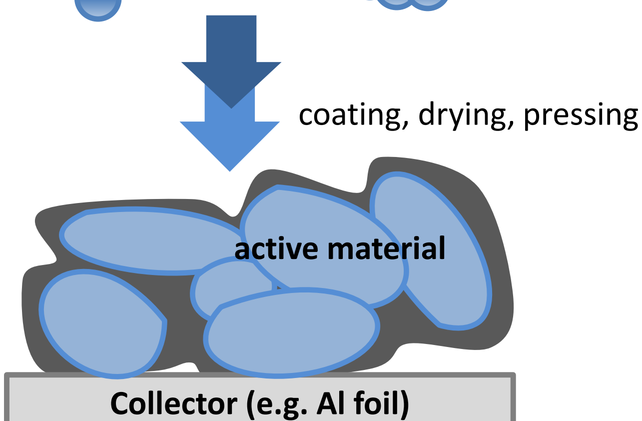




Primary particle :
~ 100 nm



Secondary particle :
~ 20 μm



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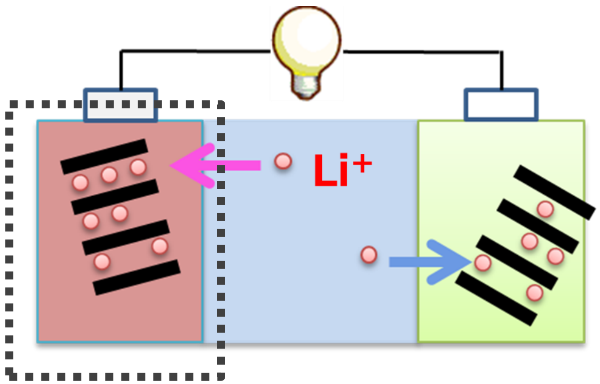
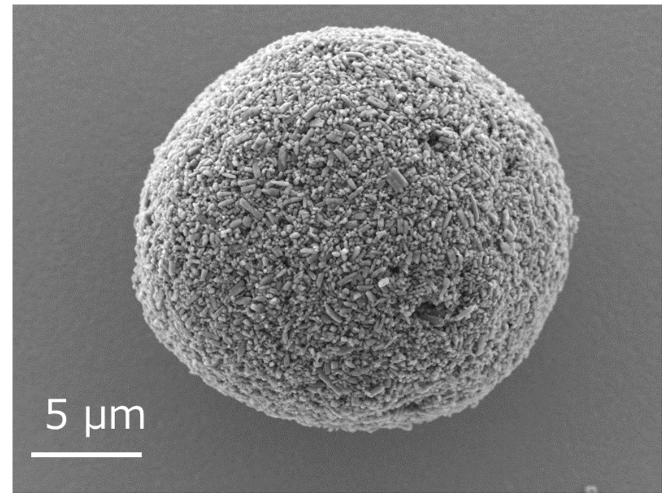
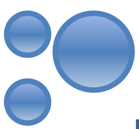


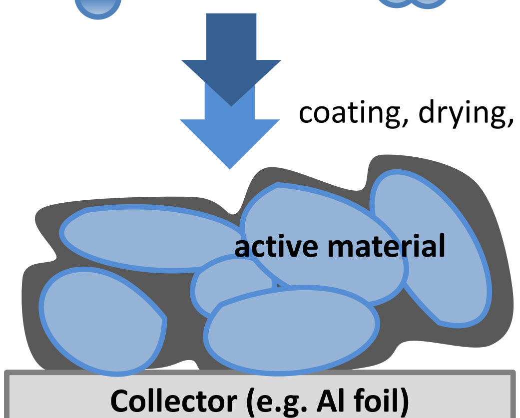


Primary particle : ~ 100 nm



Secondary particle : ~ 20 µm

coating, drying, pressing



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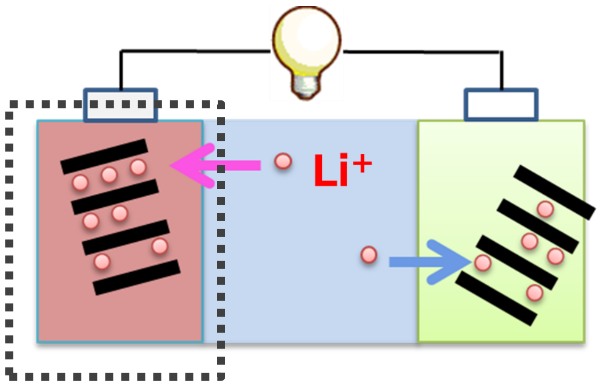
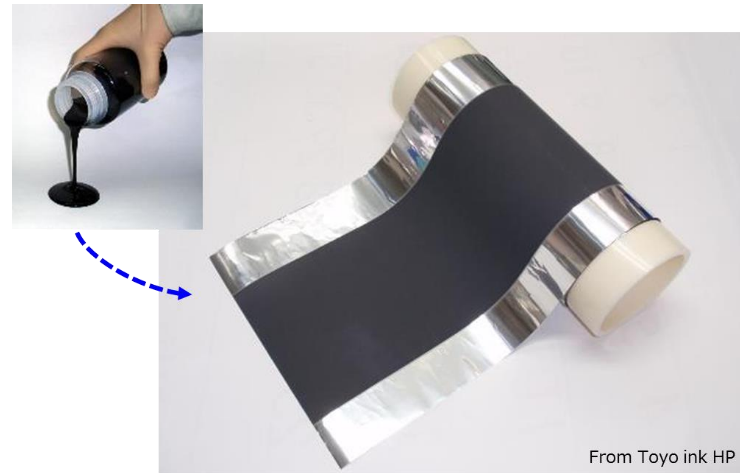
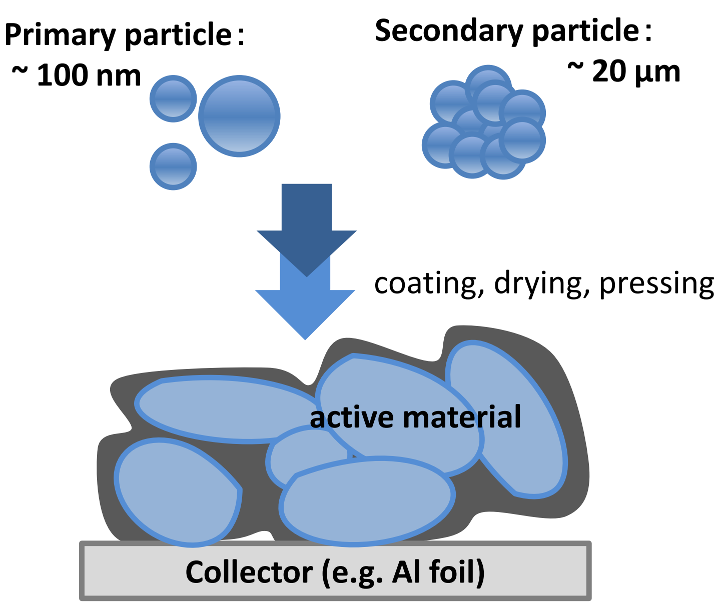
<u>For lithium-ion batteries (LIBs) :</u>

From Nikkei HP




From Toyo ink HP



Why we set up a new microscope?

For lithium-ion batteries (LIBs) :

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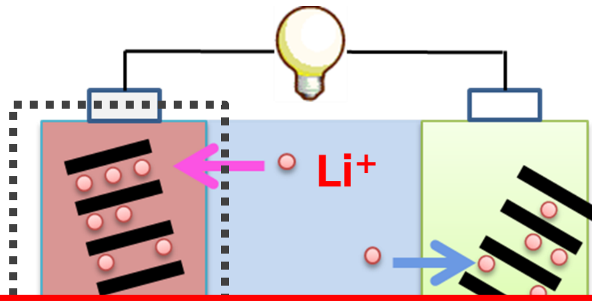
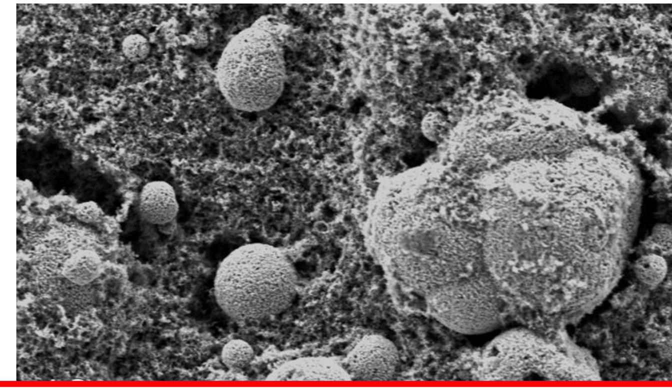
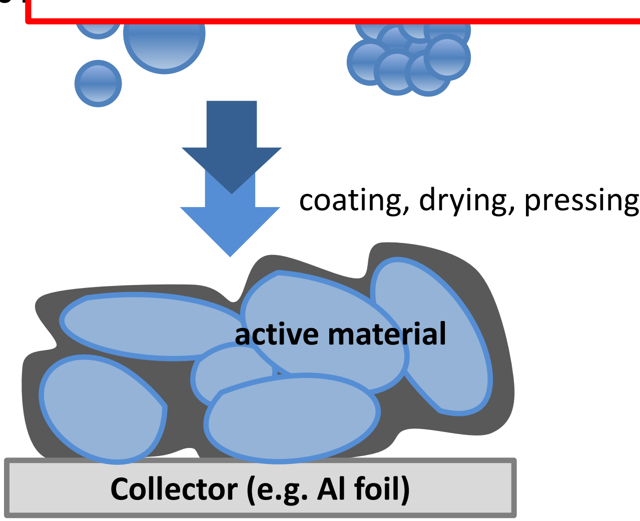
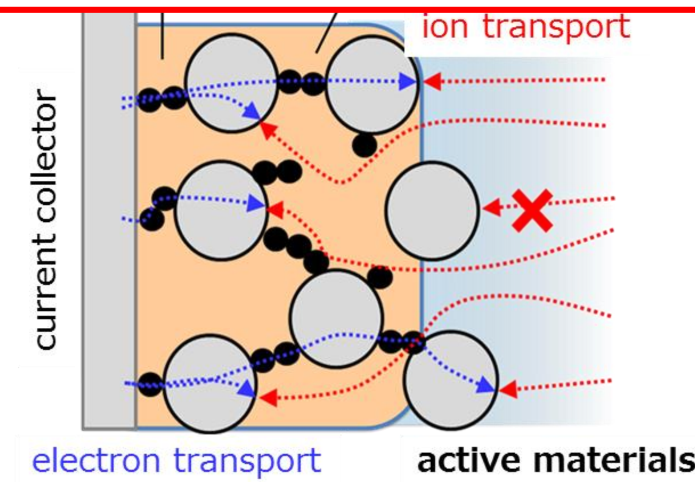




Primar
~ 100 r

No characterization technique can detect local ion transport directly:





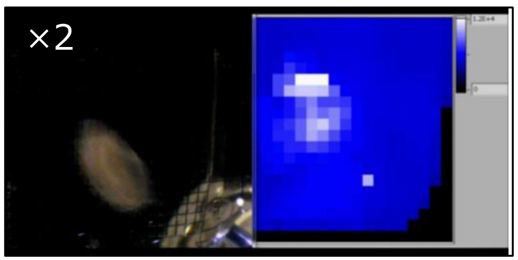
Matsue Lab. in AIMR

Prof. T. Matsue
Grad. Sch. of Env. Studies
Tohoku Univ. and
Vice president of ISE

Assoc. Prof.
Y. Takahashi
Current add.:
WPI-NanoLSI
Kanazawa Univ.

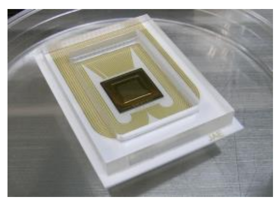
Electrochemistry

Electrochemical Integrated Devices

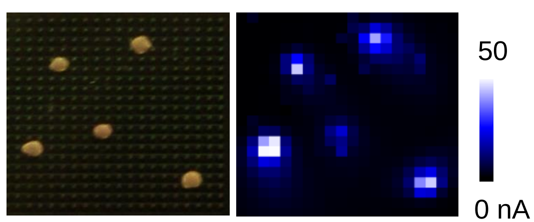


Electrochemically monitoring movement of water flea

Bio-LSI devices

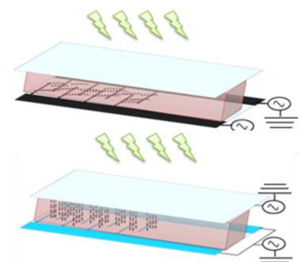


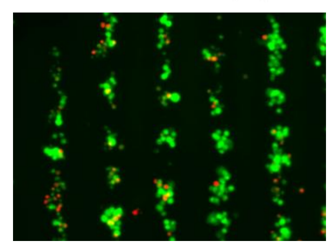
Optical **Electrochemical**



Electrochemical images of embryoid bodies (ES cells)

Tissue Engineering

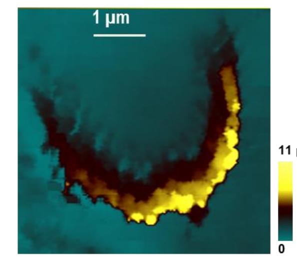




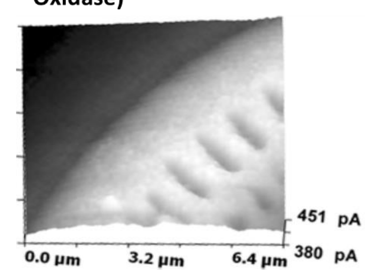
Control of cell growth and direction

Scanning probe imaging

Hair cell

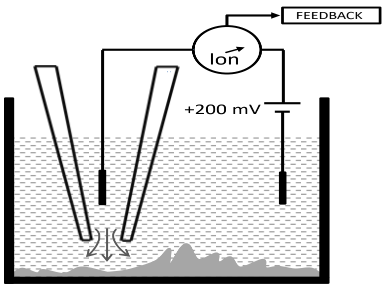


Enzyme activity (Glucose Oxidase)

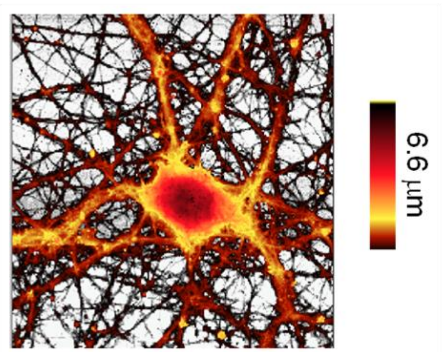


SECM Families in Matsue Lab.:

Scanning Ion Conductance Microscopy（SICM）

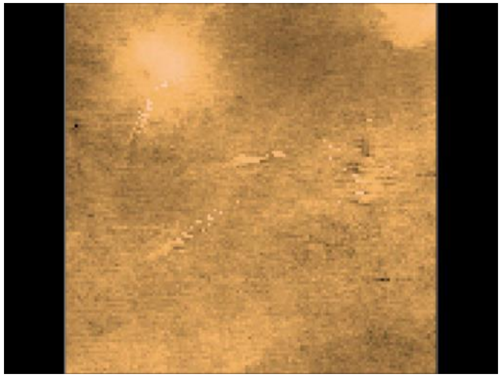


neural network in hippocampus



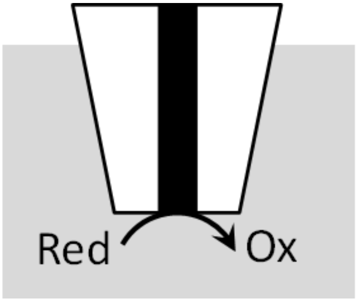
100×100 μm

Visualization of dynamics on microvillus

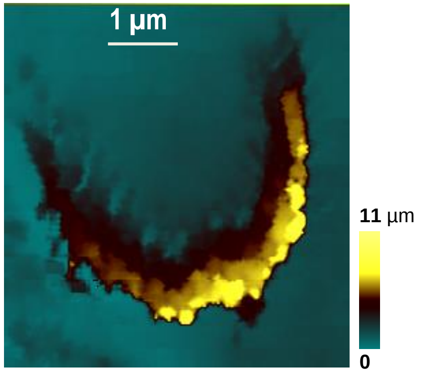


90 s/frame : 64 x64

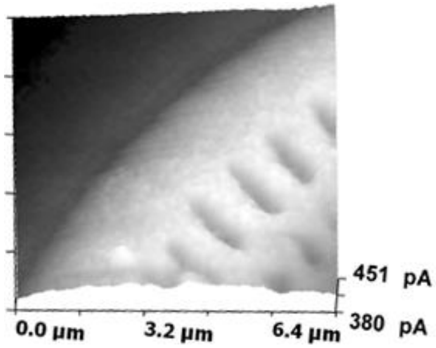
Scanning Electrochemical Microscopy（SECM）



Hair cell



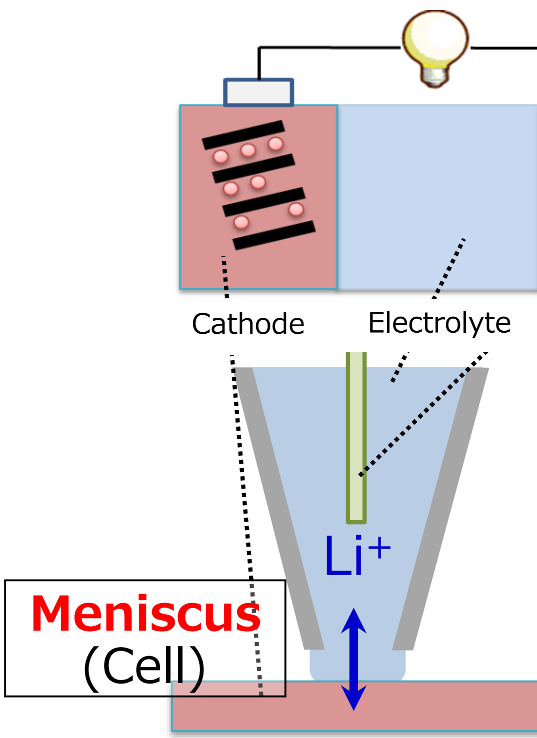
Enzyme activity (Gox)

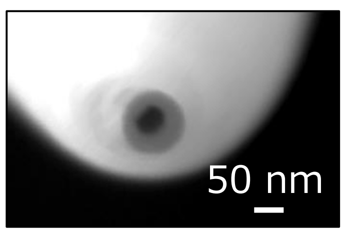


SECCM: Scanning Electrochemical Cell Microscopy with a Single Barrel Nano-pipette

Y. Takahashi, **A. Kumatani** *et al.*, ***Nature Communications*** 2014.

Mechanism



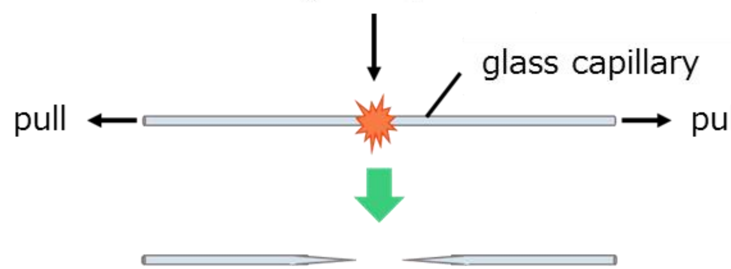


glass nano-pipette

nano-scale cell simulator

Nanopipette

Sutter inc
CO_2 laser puller



size controllable

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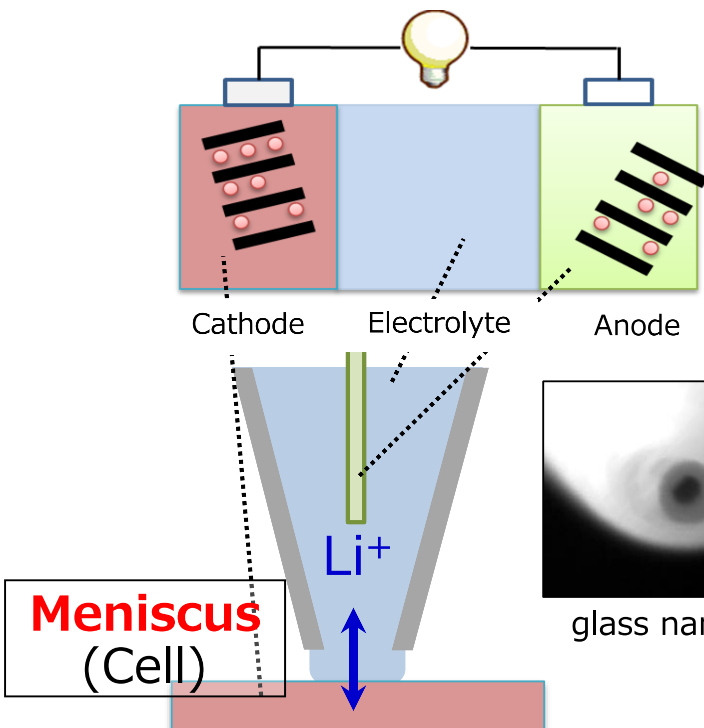
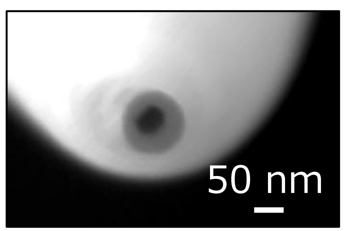


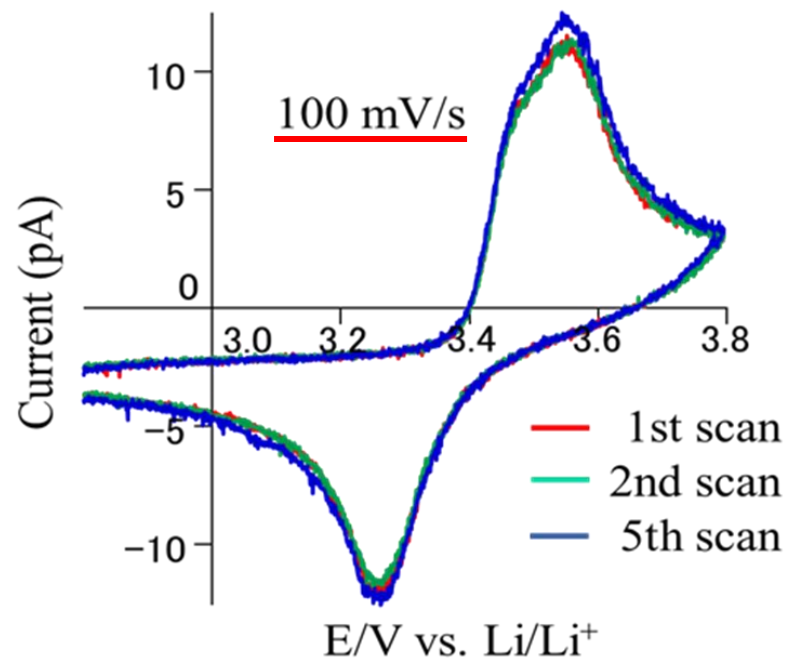


glass nano-pipette

nano-scale cell simulator

CV (cyclic voltammetry)

$LiFePO_4$ thin film from Hitosugi Lab. in Tokyo Inst. of Tech.



scan rate: up to 100 V/s

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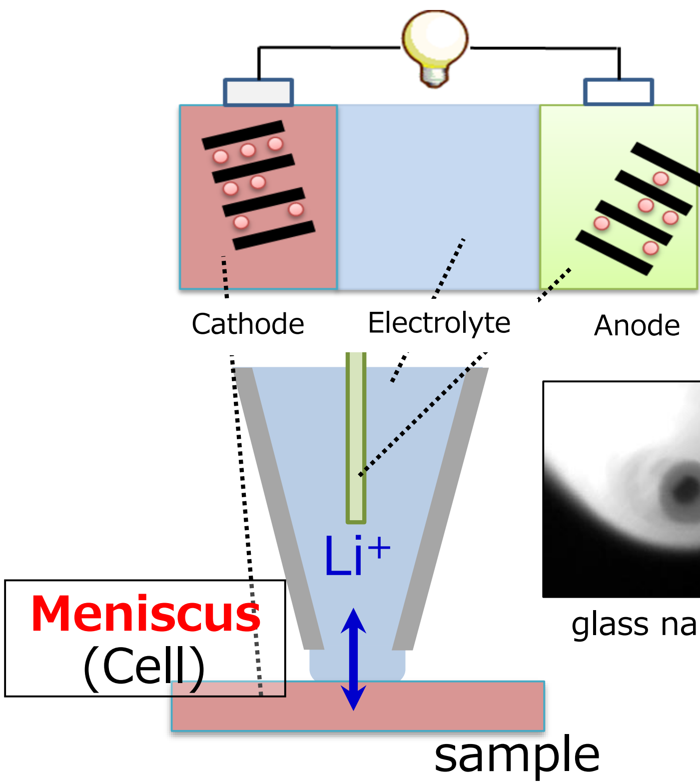
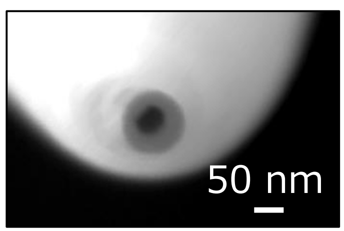




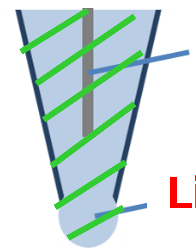
glass nano-pipette

nano-scale cell simulator

EC: ethylene carbonate

DEC: diethyl carbonate

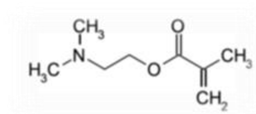
DMC: dimethyl carbonate



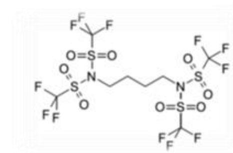
Li reference electrode

$LiPF_6$ in **EC** : **DEC** : **DMC** for organic electrolyte

Organic electrolyte gel



PDMAEMA: Poly(dimethyl aminoethyl Methacrylate)



C6TFSA: *N,N',N'N'*-Tetra (trifluoromethanesulfonyl) -hexane-1,6-diamine

purchased from Kanto Chemical

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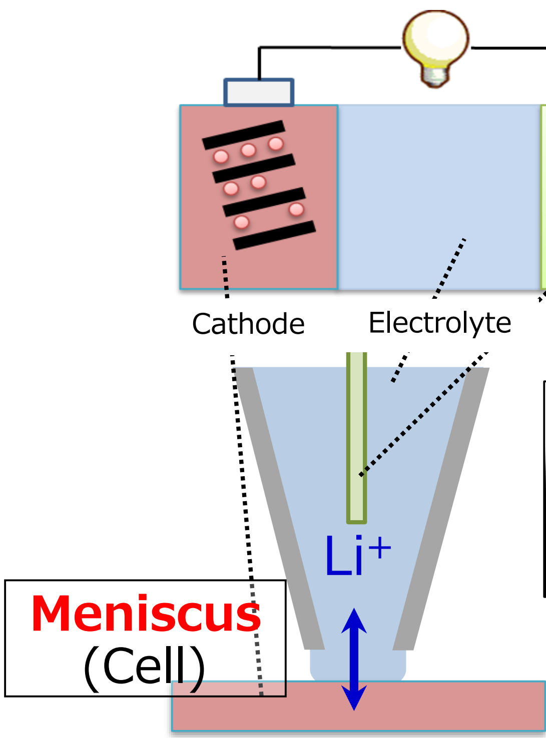
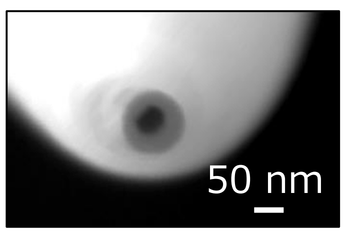
Mechanism

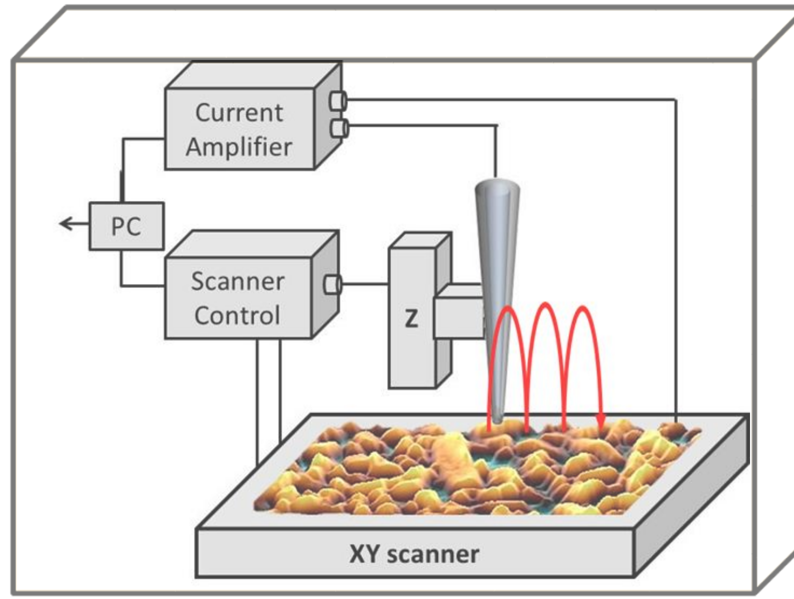




glass nano-pipette

nano-scale cell simulator

SECCM System setup



Inside glove-box (H_2O: < 0.1 ppm O_2: < 0.1 ppm)

resolution:	x,y-axis	50 nm
	z-axis	few nm
scan-size:	up to	50 × 50 μm

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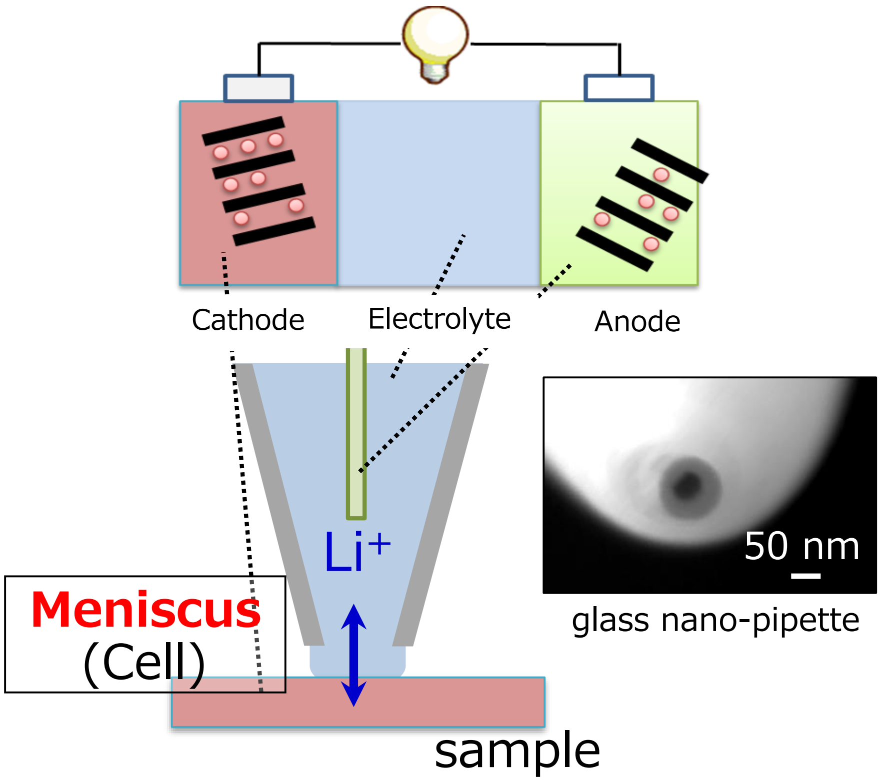
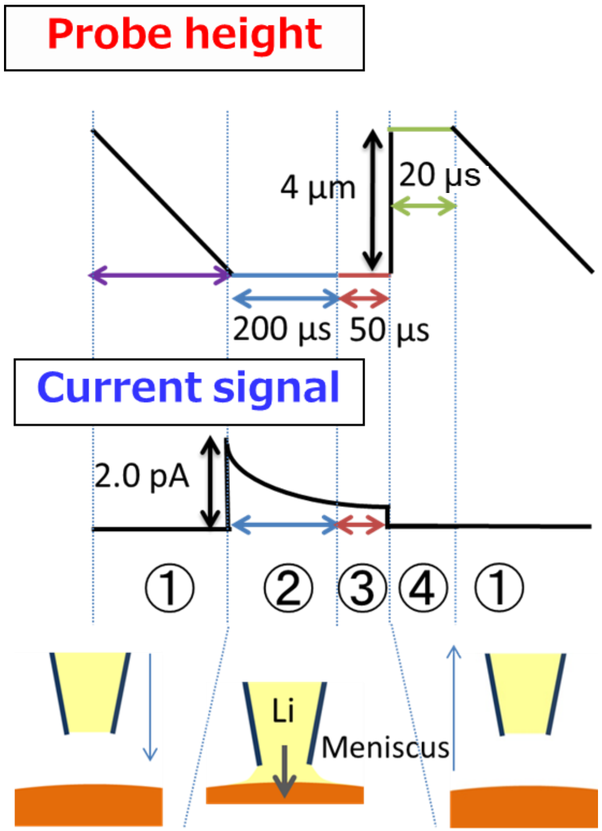


nano-scale cell simulator

Scanning Protocol



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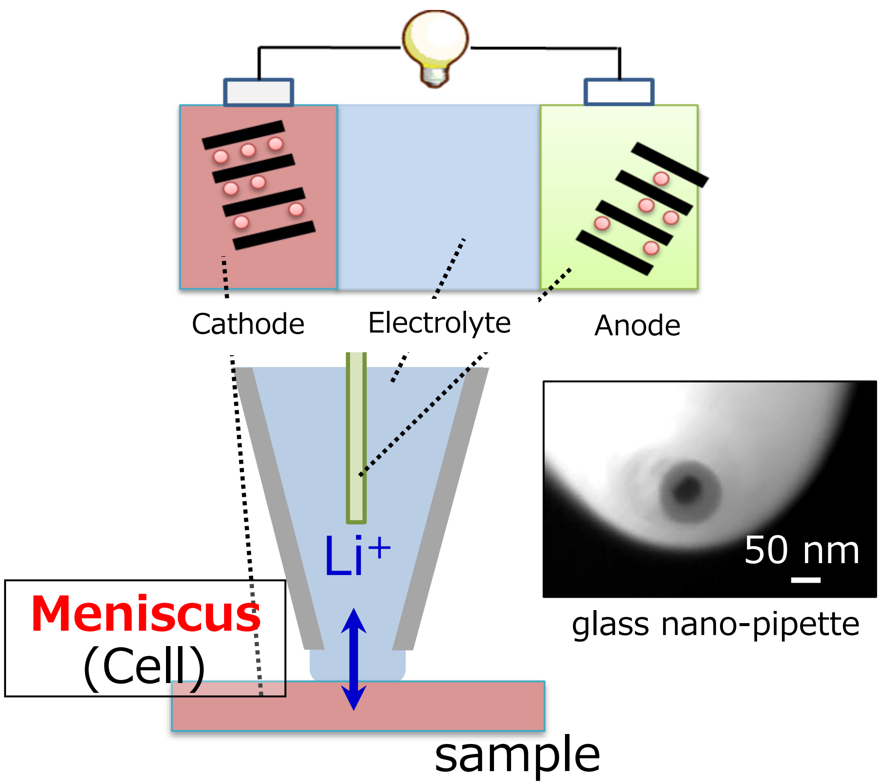
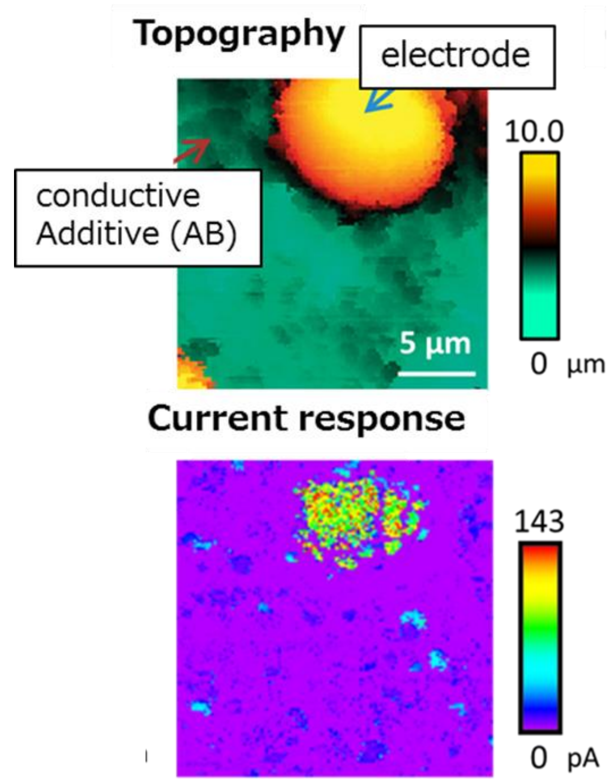
Y. Takahashi, **A. Kumatani** *et al.*, ***Nature Communications*** 2014.

Mechanism



nano-scale cell simulator

Scanning(Visualization)

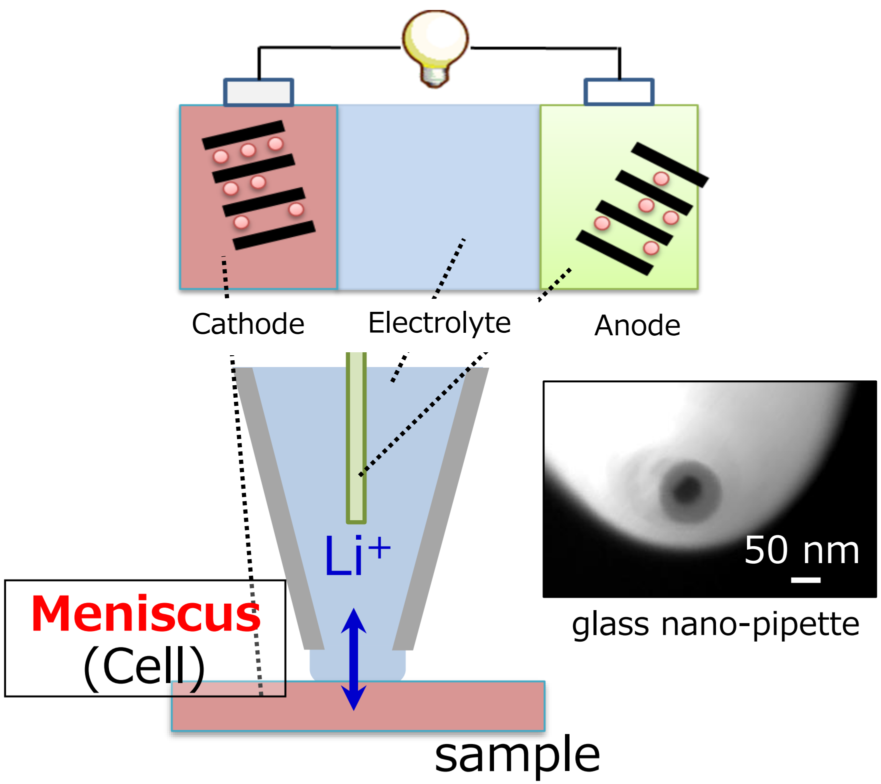


LiFePO$_4$ composite electrode from
Kanamura Lab. in Tokyo Metropolitan Univ.

SECCM: Scanning Electrochemical Cell Microscopy with a Single Barrel Nano-pipette

Y. Takahashi, **A. Kumatani** *et al.*, ***Nature Communications*** 2014.

Mechanism



nano-scale cell simulator

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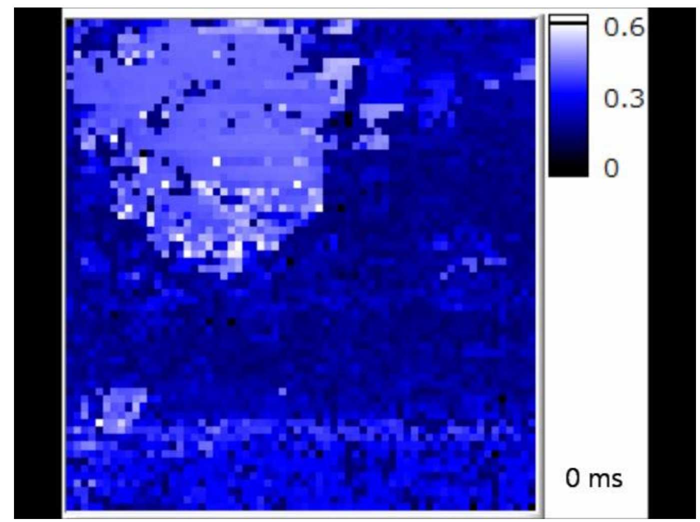
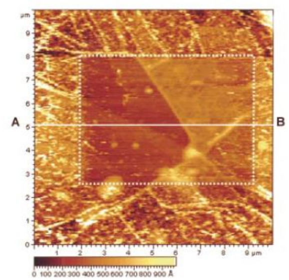


$LiFePO_4$ composite electrode from
Kanamura Lab. in Tokyo Metropolitan Univ.

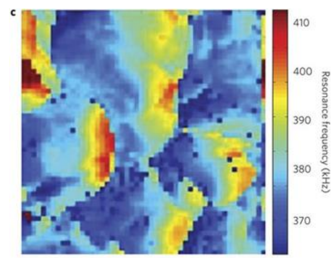
Other SPM Families

AFM



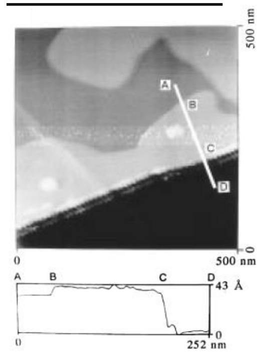
S. K. Jeong et al.,
J. Electrochem. Soc. 2001.

ESM



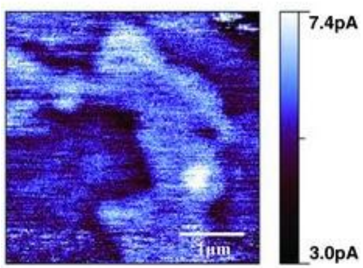
N. Balke et al.,
Nat. Nanotech. 2010.

EC-STM



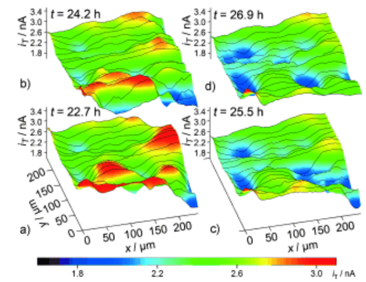
M. Inaba et al.,
Chem. Lett. 1995.

SICM



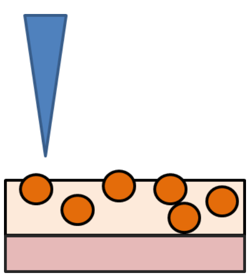
A. L. Lipson et al.,
Adv. Mater. 2011.

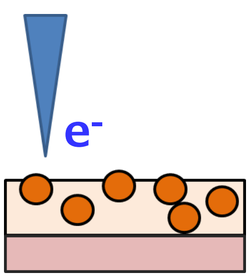
SECM

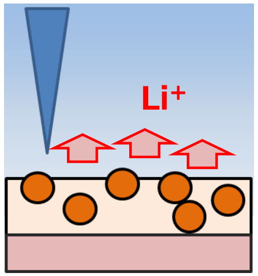


M.S.H. Bülter et al.,
Angew. Chem. 2014.

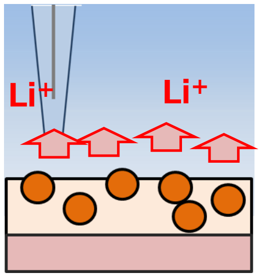
tip



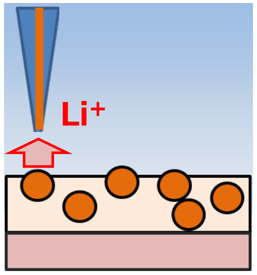




pipette



microelectrode



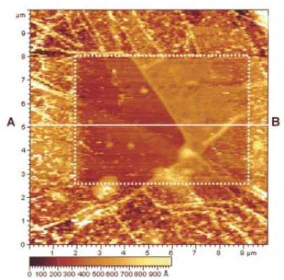
● Active material

* lower resolution

ESM: Electrochemical strain microscopy, EC-STM: Electrochemical-STM
SICM: Scanning ion conductance microscopy, SECM: Scanning electrochemical microscopy

Other SPM Families

AFM



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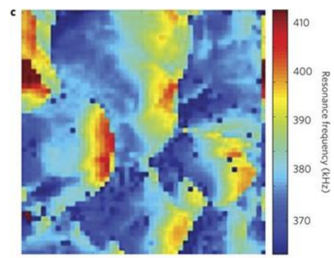
ESM



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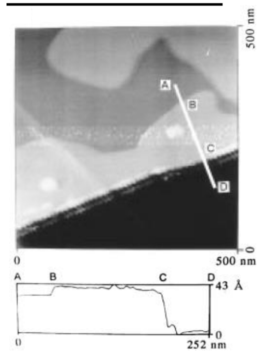

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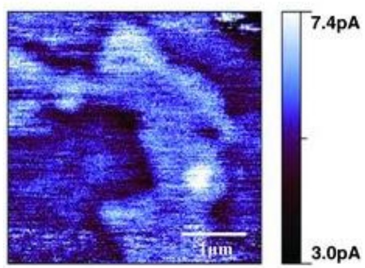

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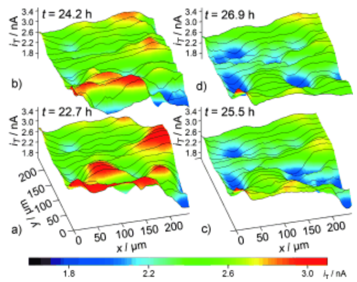
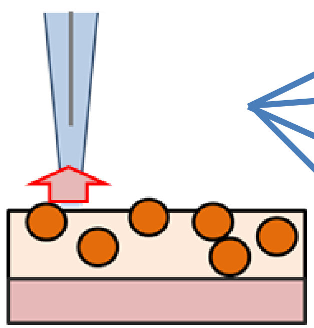


M.S.H. Bülter et al.,
Angew. Chem. 2014.

SECCM



Other secondary batteries:
- Li^{+}, Na^{+}, K^{+}, Mg^{2+} etc

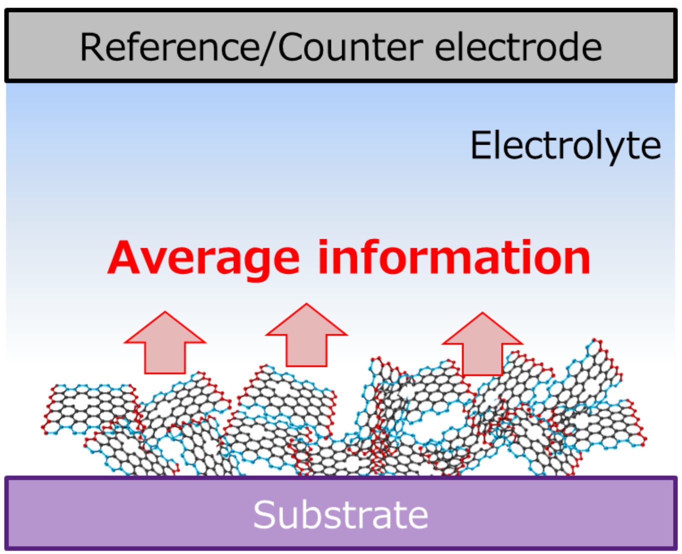
Redox (mediator):
- $Ru^{2+/3+}$, ferrocenemethanol etc

Electrocatalytic reaction:
- oxygen reduction reaction (ORR)
- hydrogen evolution reaction (HER)

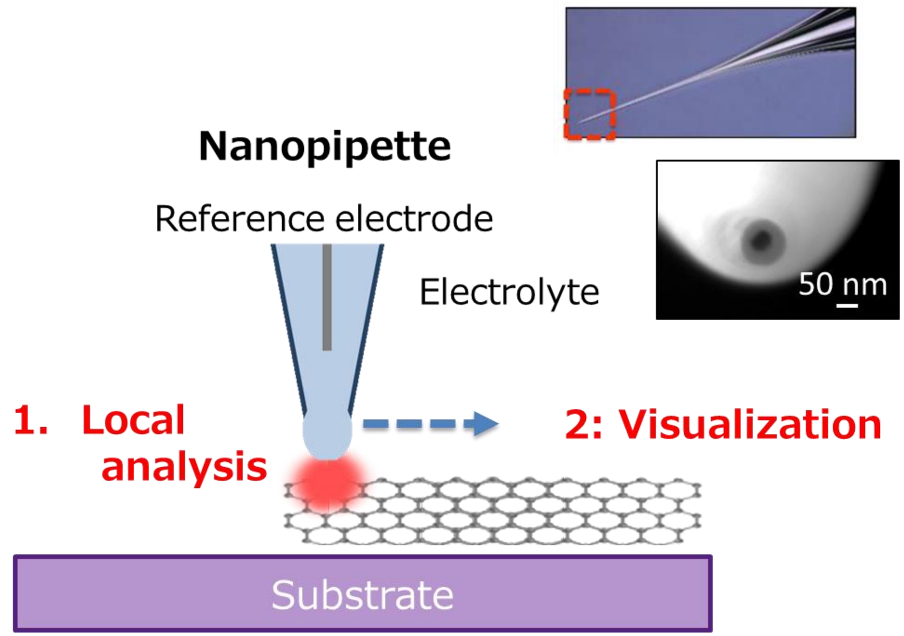
Other electrochemical activities:
- nanotube detection / - corrosion etc

Bulk vs Local measurement

conventional



SECCM



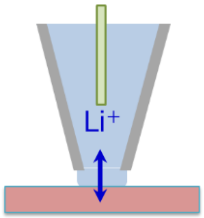
Outline:

1. Key technique for Electrochemical Imaging:
   Scanning Electrochemical Cell Microscopy (SECCM)

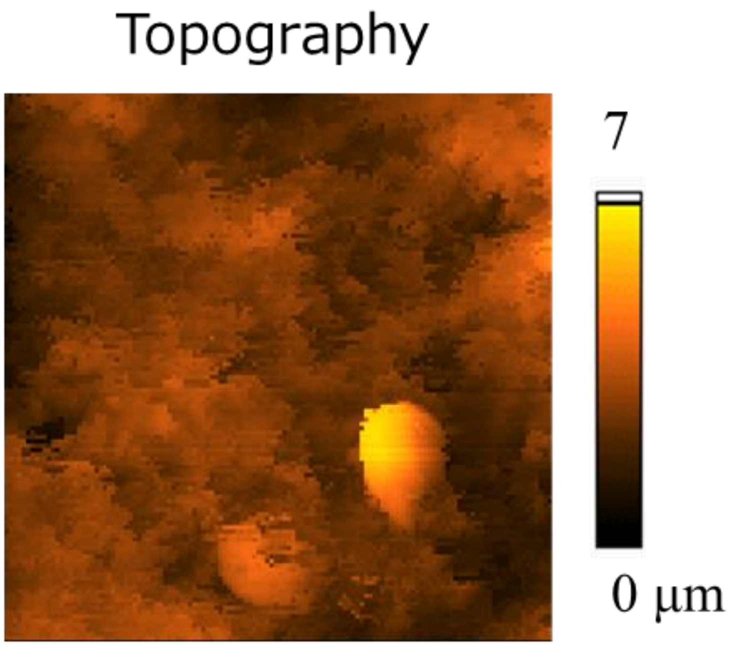
2. **Visualization of Electrochemical Activities**
   - **2-1. Lithium-ion Transport**
     - Practical/model electrodes
   - **2-2. Mediator redox ($Ru^{3+/2+}$)**
     - Graphene, $NbSe_2$
   - **2-3. Hydrogen evolution / Oxygen reduction reaction**
     - SnS_2 , BN
   - **2-4. Other application:**

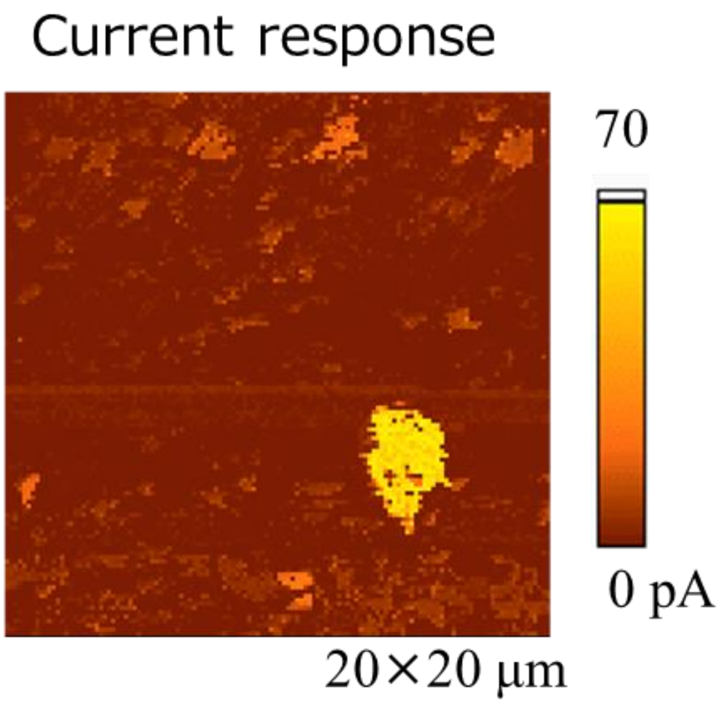
3. Conclusion

Electrochemical Imaging: Li^+ Transport



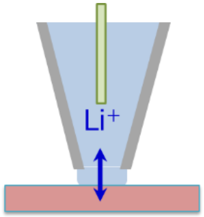
$LiFePO_4$ composite electrode
($LiFePO_4$ microparticle + Acetylene Black + PVdF)





$V_{applied}$ = 0.65 V vs. Ag/AgCl
(3.65 V vs Li/Li^+)

Electrochemical Imaging: Li^+ Transport



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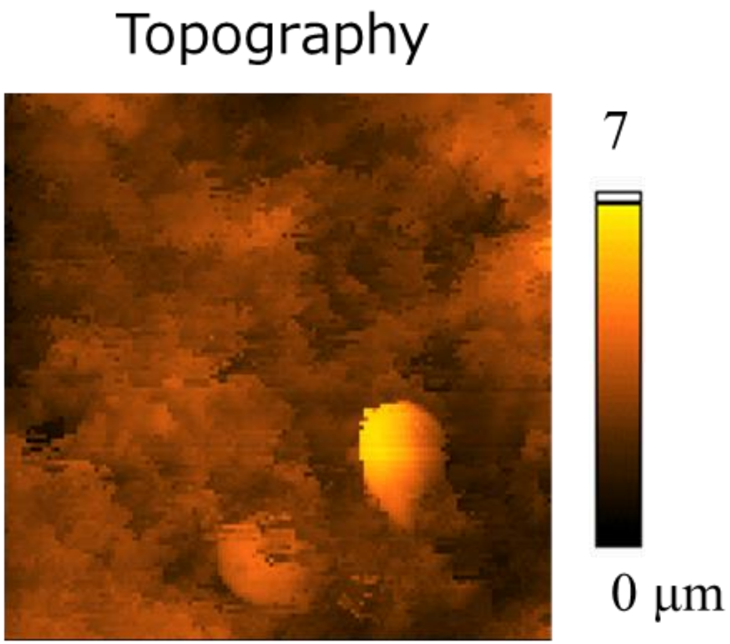
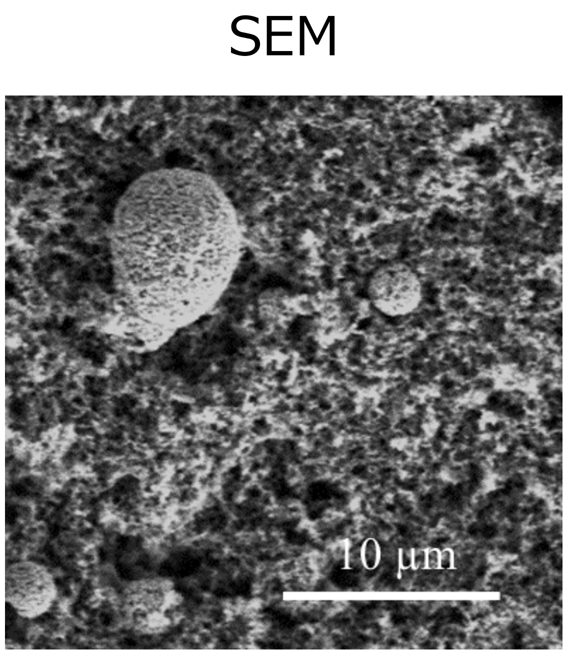
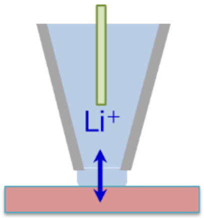




Electrochemical Imaging: Li^+ Transport



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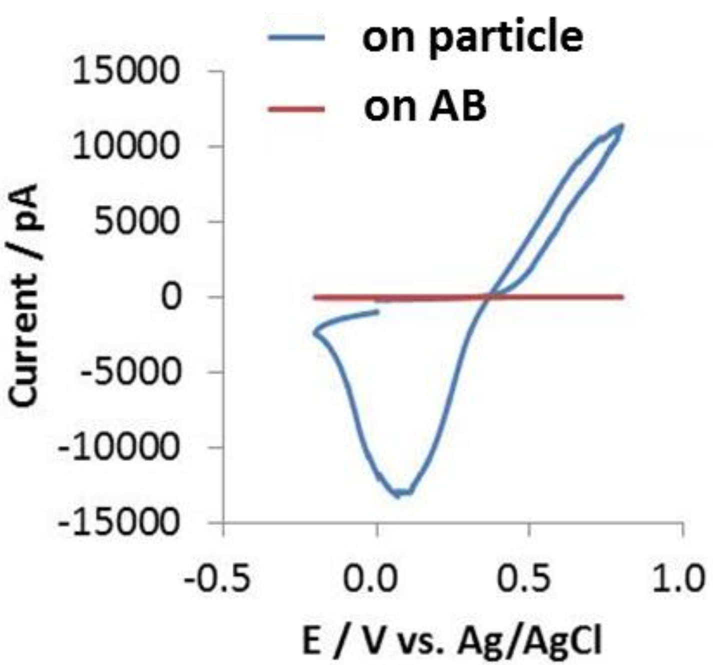
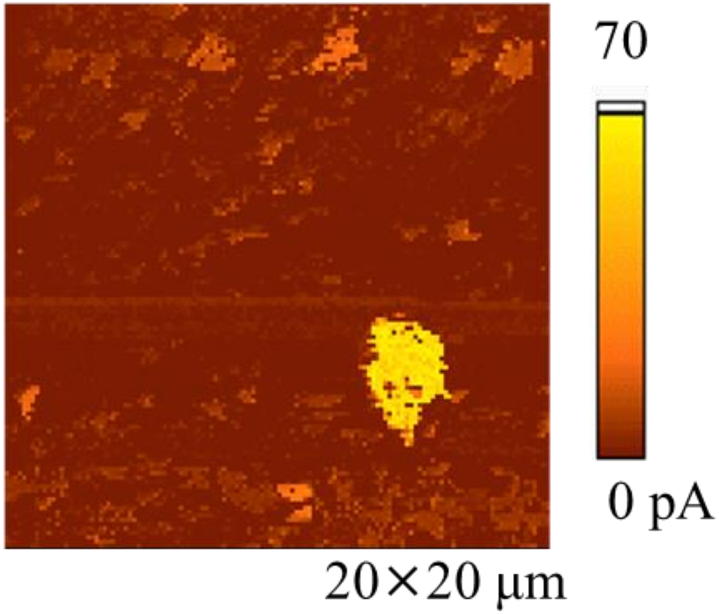


Current response



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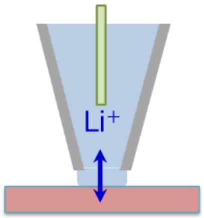

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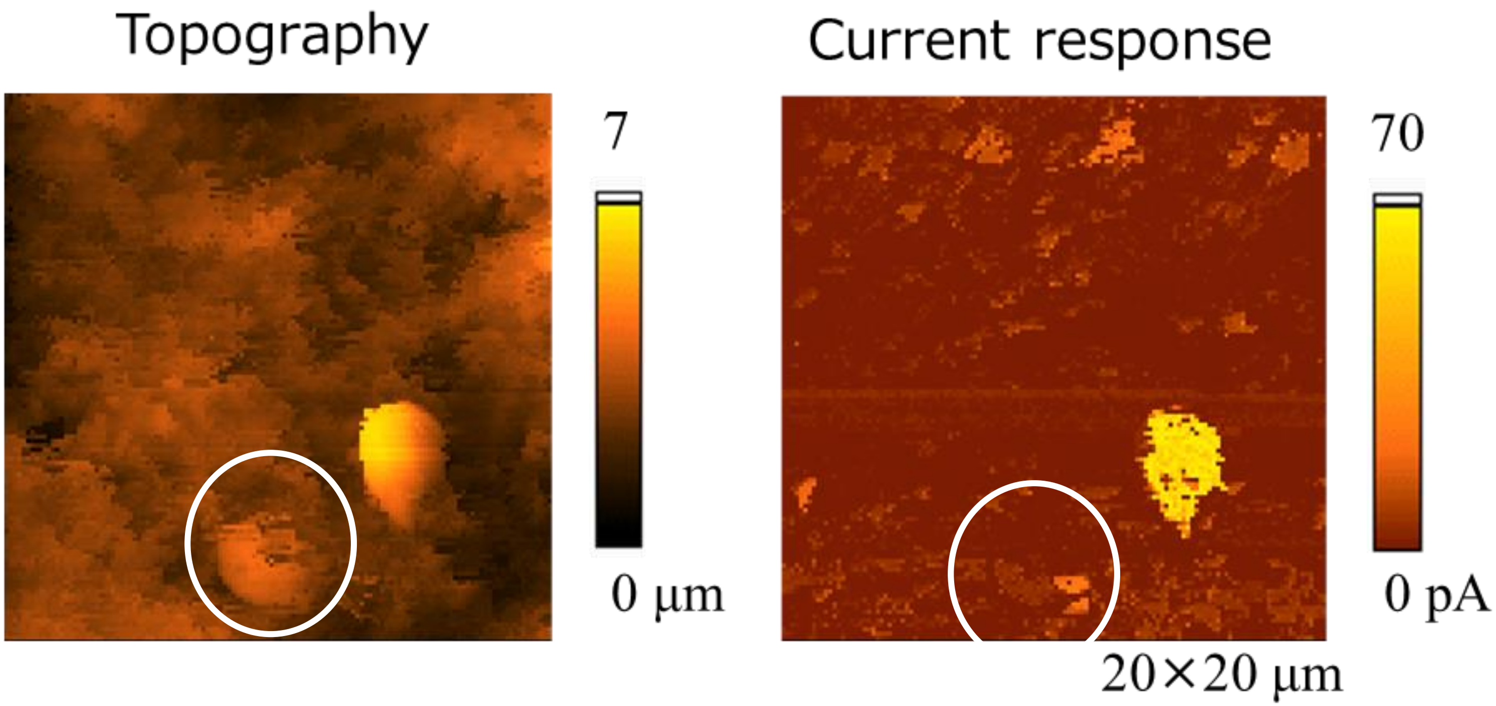
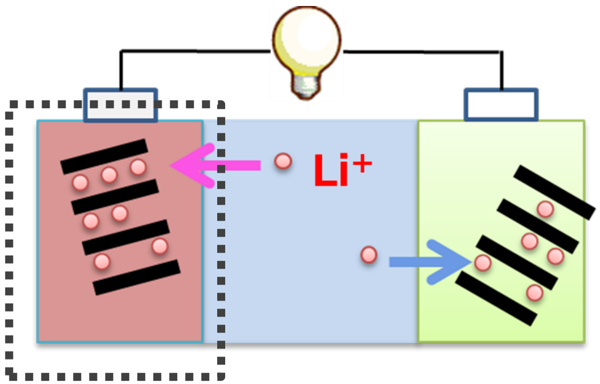


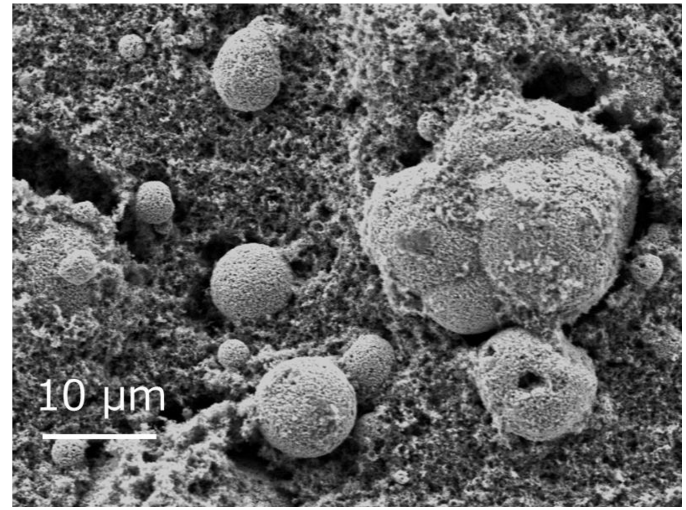
$V_{applied}$ = 0.65 V vs. Ag/AgCl
(3.65 V vs Li/Li^+)

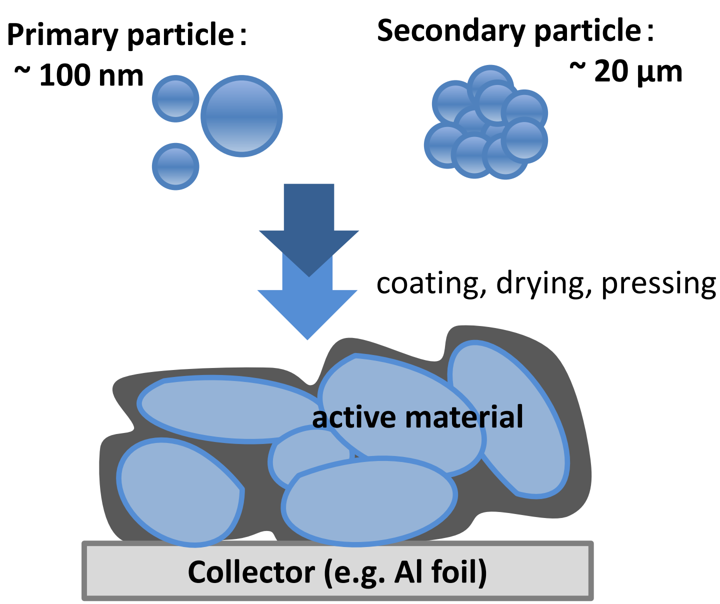
Why we set up a new microscope?

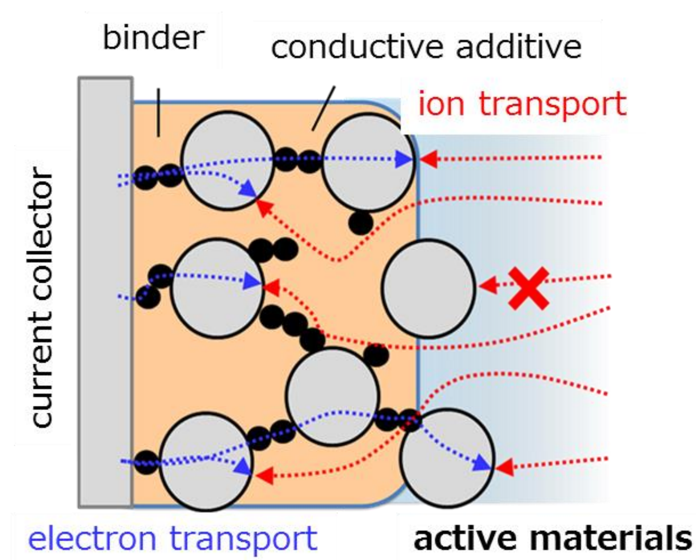
For lithium-ion batteries (LIBs) :

From Nikkei HP

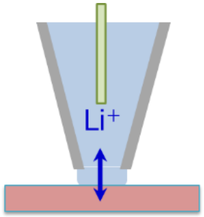








Electrochemical Imaging: Li^+ Transport



$LiFePO_4$ composite electrode
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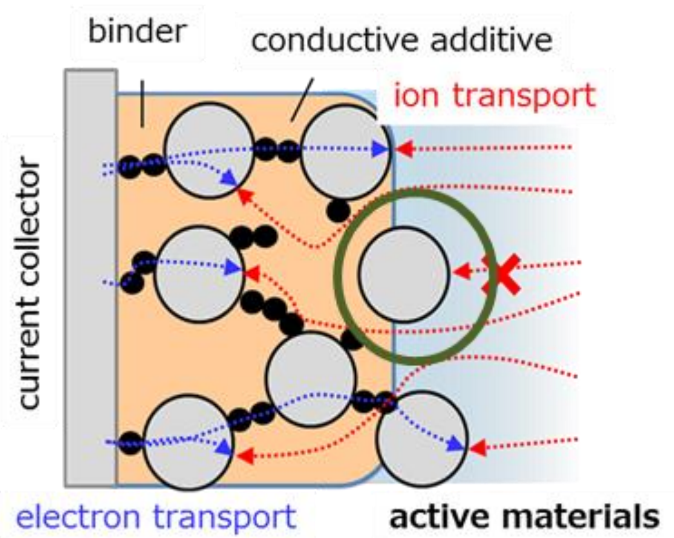

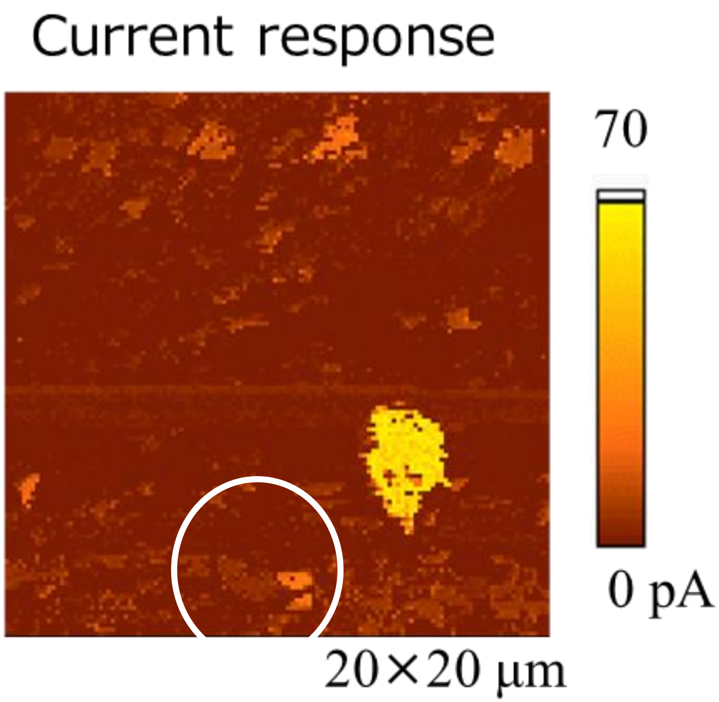

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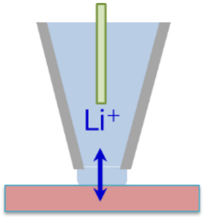
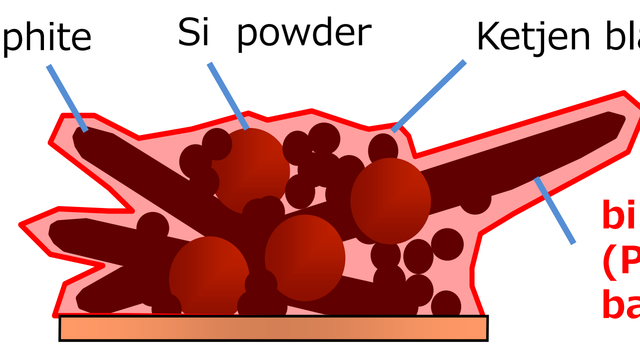
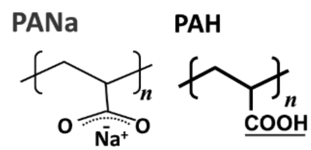
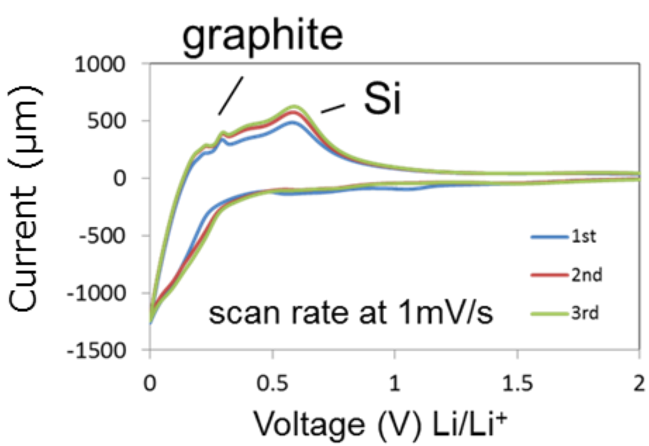


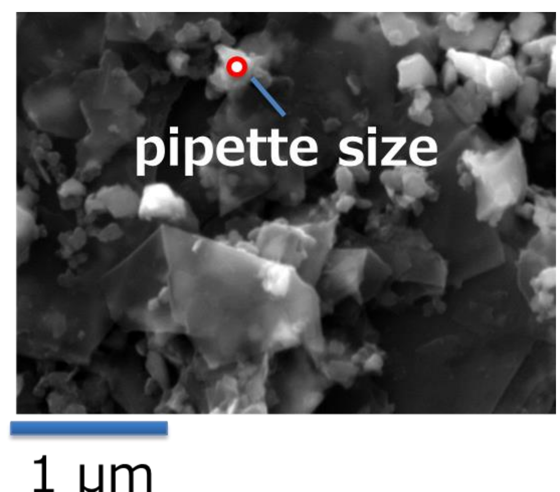
Silicon/carbon negative composite electrode



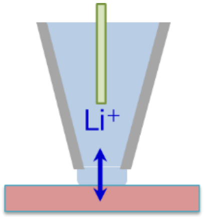


CV results in bulk

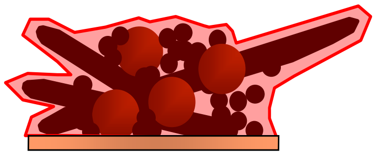


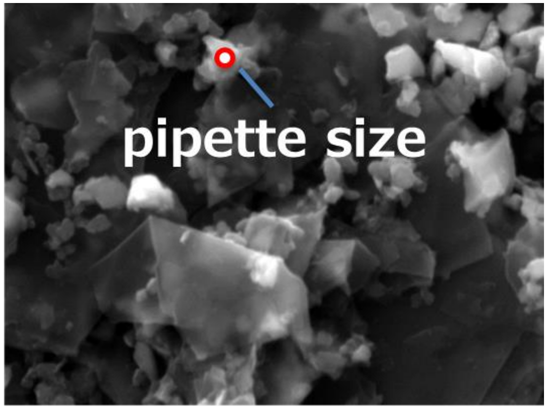


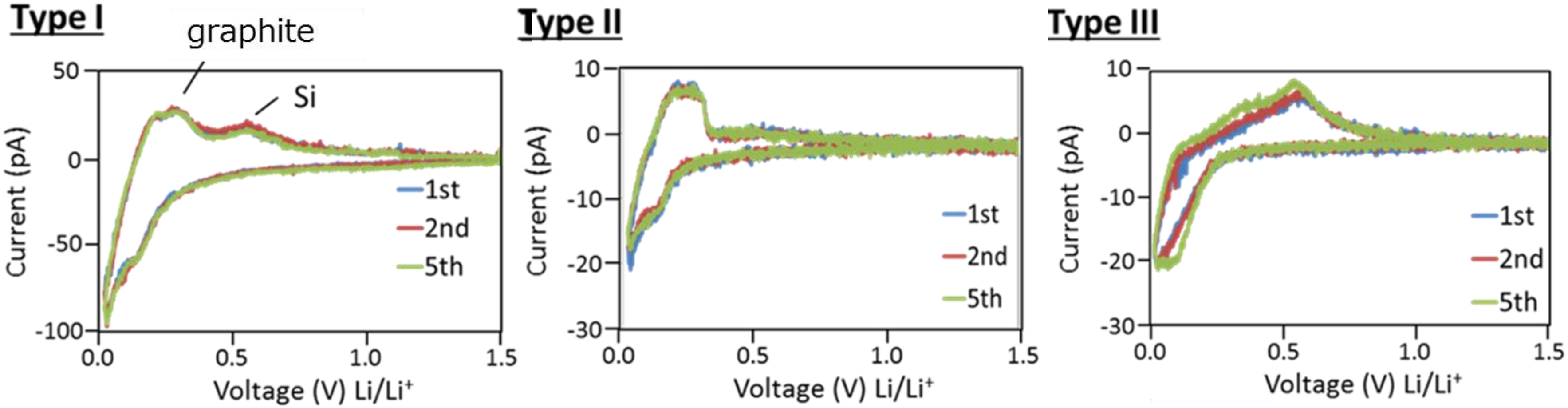
Electrochemical Imaging: Li^+ Transport



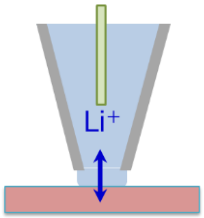
Silicon/carbon negative composite electrode







Electrochemical Imaging: Li^+ Transport



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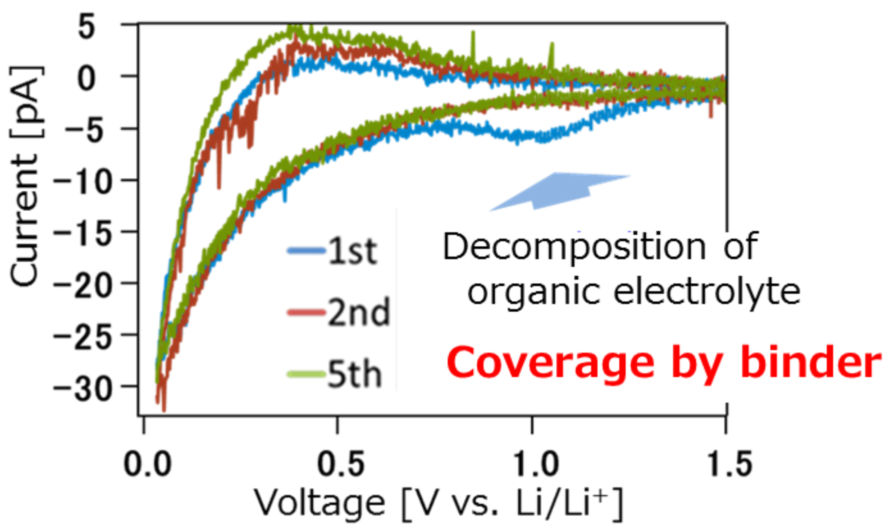

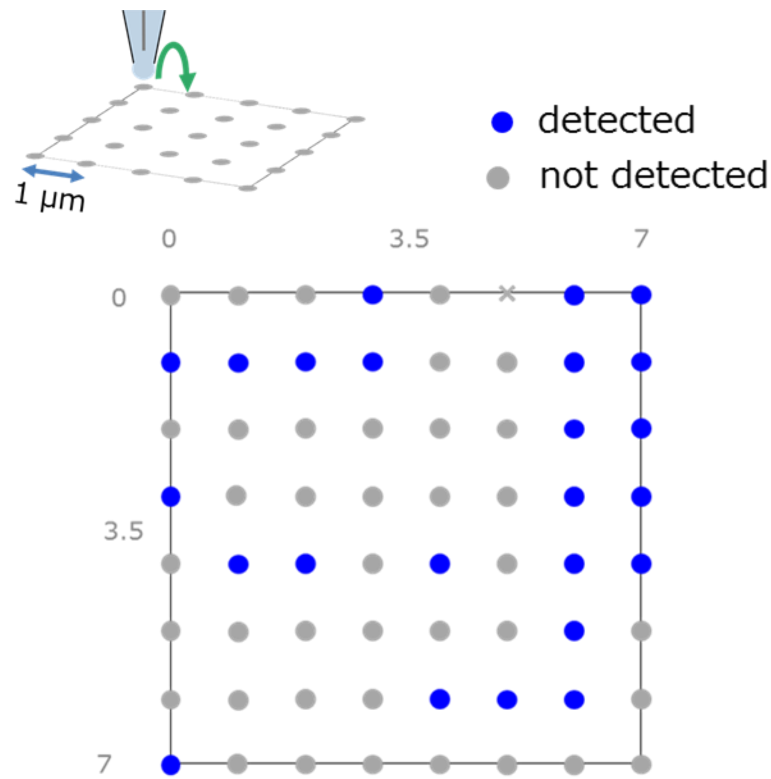

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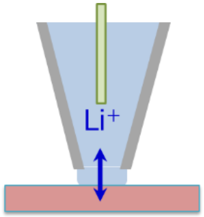
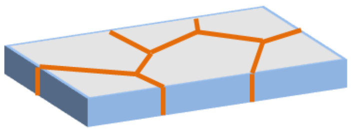
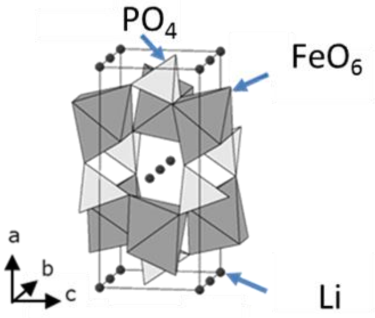


$LiFePO_4$ multi-crystalline thin film

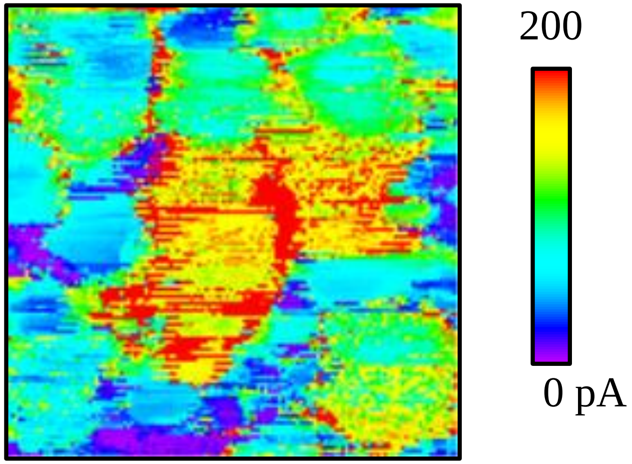
$LiFePO_4$ thin film



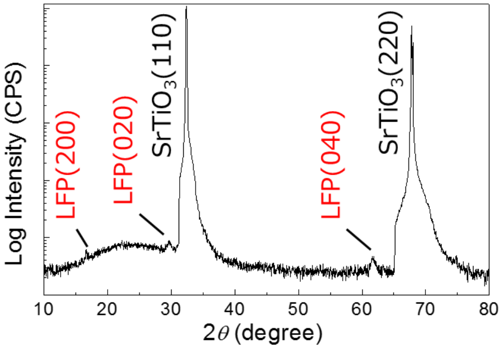


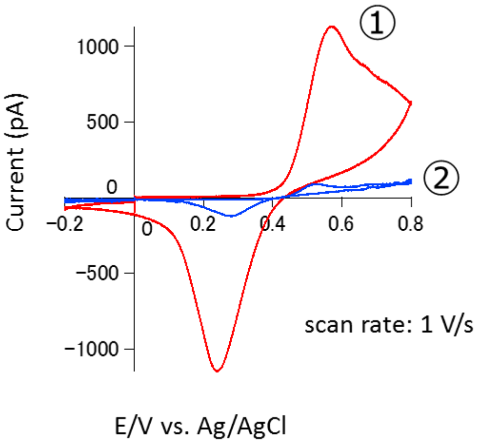
$LiFePO_4$ unit cell

Lithium-ion transport



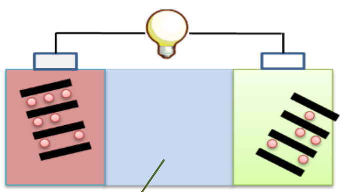
X-ray diffraction (out-of-plane)



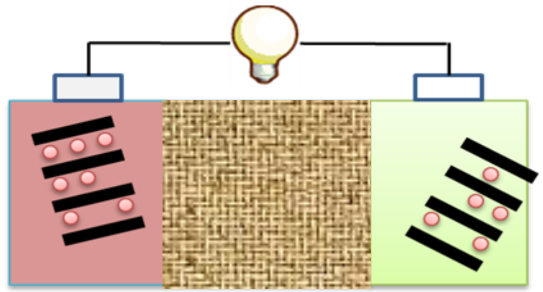


$LiFePO_4$ thin film from Hitosugi Lab.
in Tokyo Inst. of Tech.

Future collaboration: All-solid state batteries



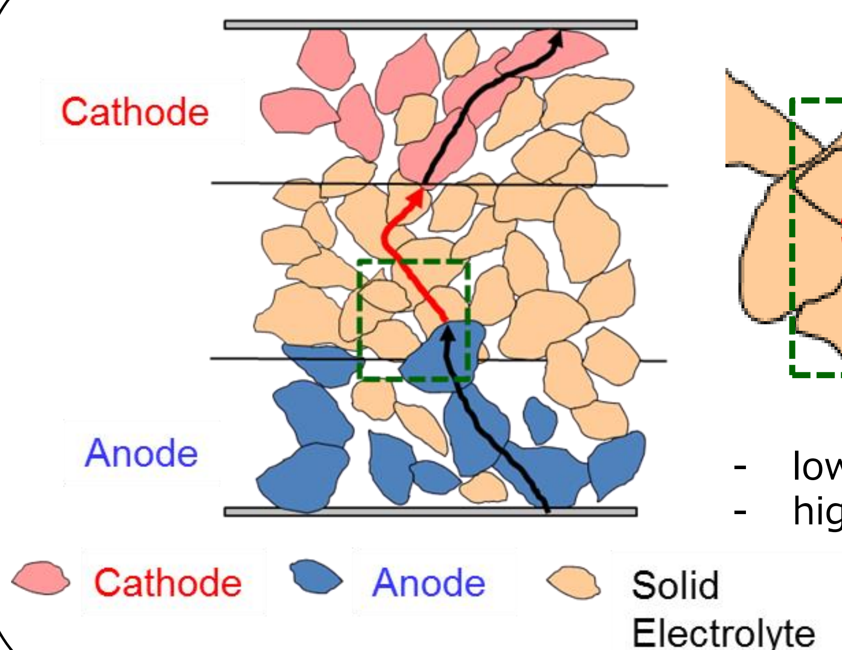
Liquid:
organic electrolyte,
ionic liquid etc

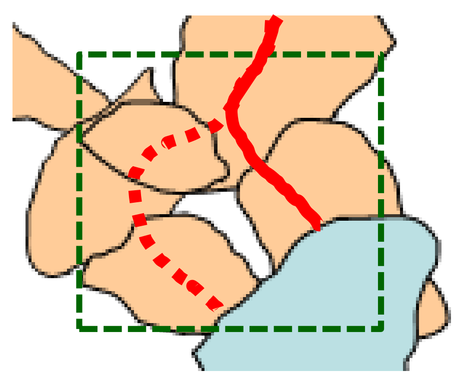


Solid electrolyte

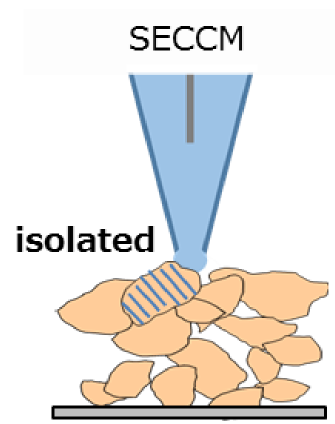
e.g. $Li_7La_3Zr_2O_{12}$ (LLZO)

Prof. E. Marinero





- low performance
- high ionic resistance



Try to visualize how the inactivated solid electrolyte is inside practical electrodes

Outline:

1. Key technique for Electrochemical Imaging:
   Scanning Electrochemical Cell Microscopy (SECCM)

2. **Visualization of Electrochemical Activities**

   2-1. Lithium-ion Transport

   - Practical/model electrodes

   2-2. Mediator redox ($Ru^{3+/2+}$)

   - Graphene, $NbSe_2$

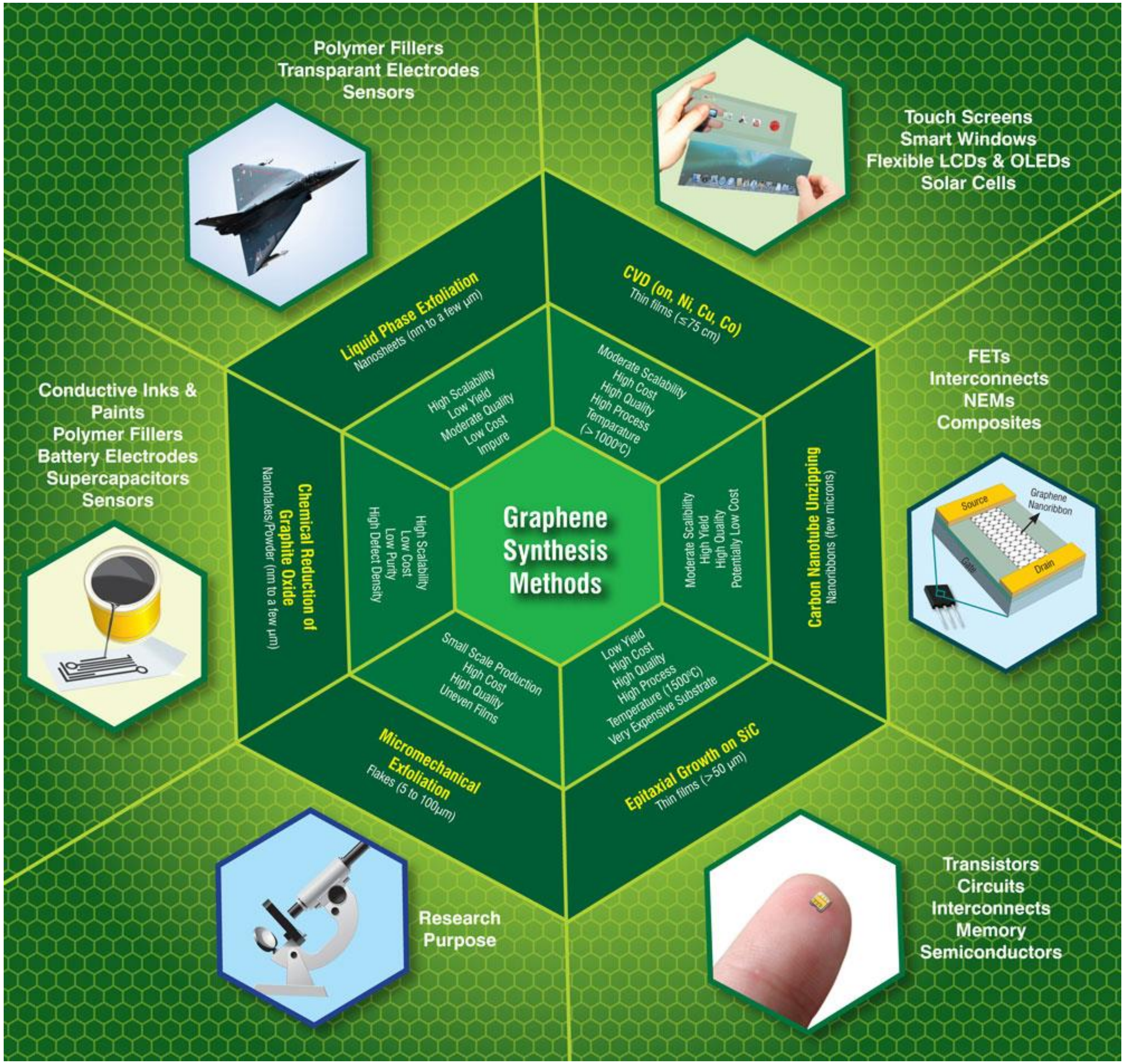
   2-3. Hydrogen evolution / Oxygen reduction reaction

   - SnS_2 , BN

   2-4. Other application:

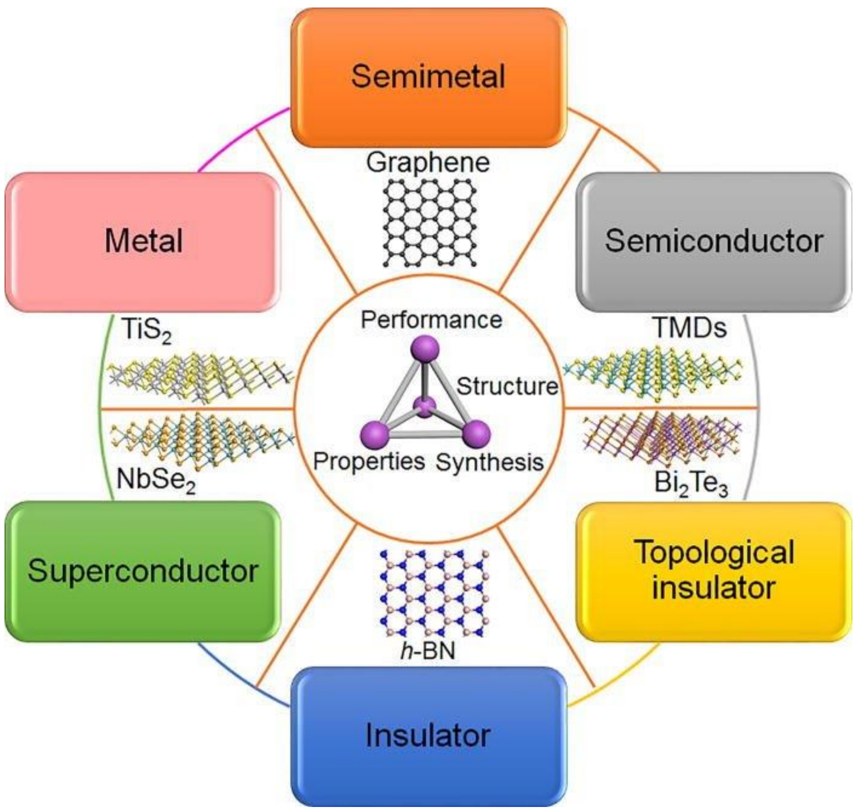
3. Conclusion

Research Background

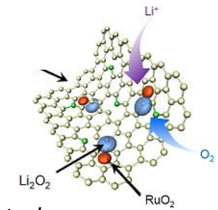


From Nanowerk HP

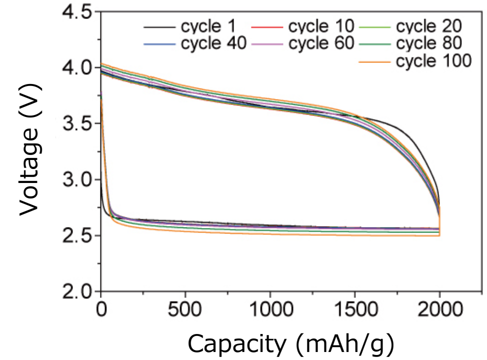
2D Materials



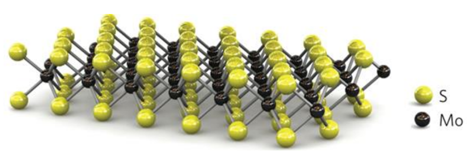
Li-air battery



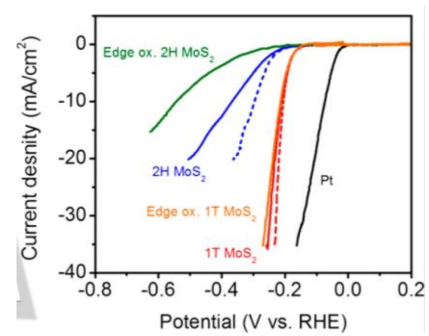
Y. Ito *et al.*,
Adv. Mater. **27** 6137 (2015).



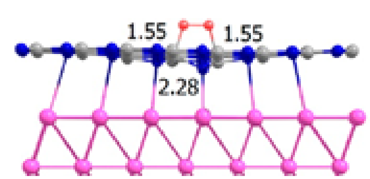
Electrocatalytic reaction (HER)



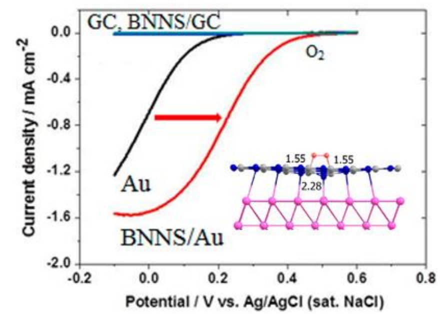
D. Voiry *et al.*,
Nano Lett. **13** 6222 (2013).



Electrocatalytic reaction (ORR)



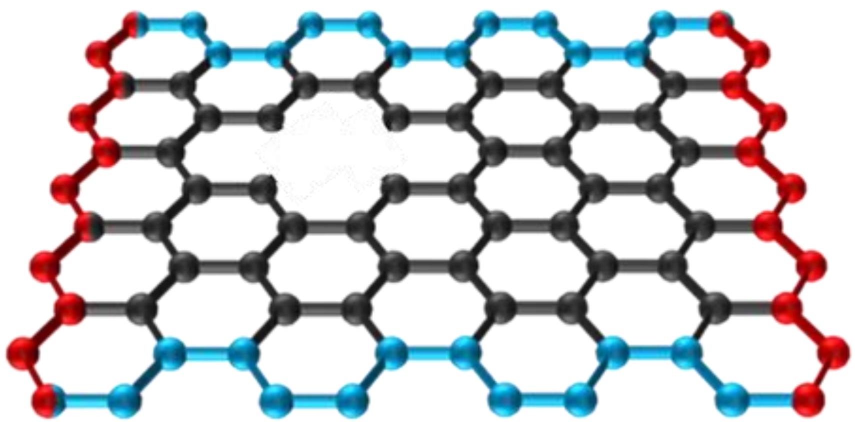
K. Uosaki *et al.*,
JACS **5** 5450 (2014).



BN: Boron nitride
TMD: Transition metal dichalcogenides
HER: hydrogen evolution reaction
ORR: oxygen reduction reaction

Research Objectives

2D materials are great electrochemical performance!
But why?



Possible factors :

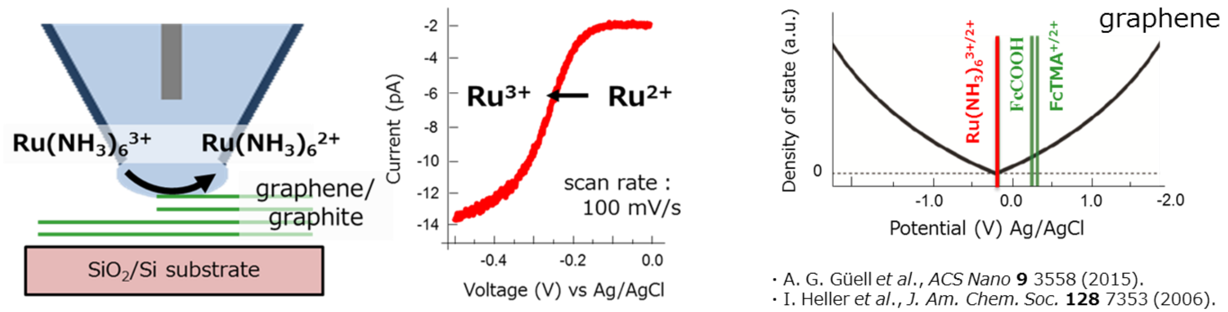
1. Defects
2. Edge structures
3. Number of layers
4. Chemical doping

etc

We challenge to solve the questions:
[what], [how] and [why] high performance on 2D materials

Electrochemical Imaging: Mediator Redox

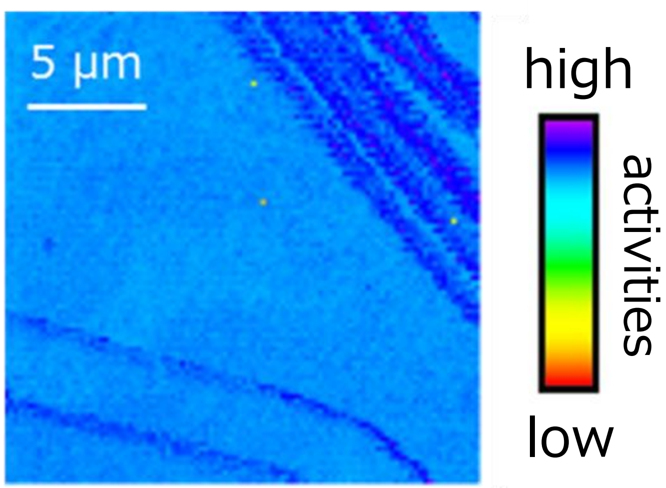
Graphene/graphite edges



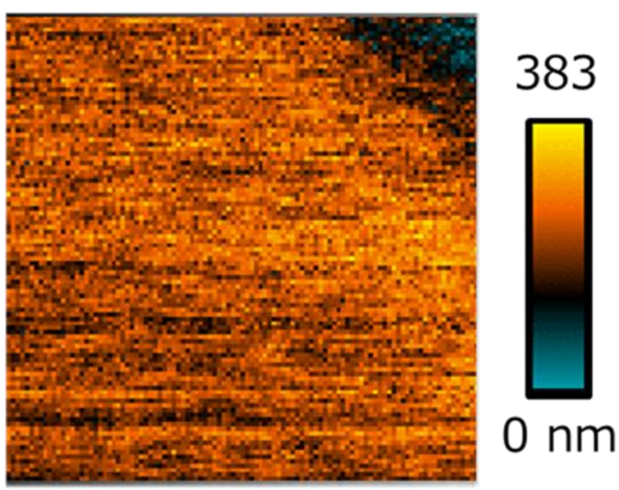
- A. G. Güell *et al.*, *ACS Nano* **9** 3558 (2015).
- I. Heller *et al.*, *J. Am. Chem. Soc.* **128** 7353 (2006).
- C. M.A. Brett and A. M. O. Brett, *Electrochemistry, Oxford Univ. Press* (1993).

Cleaved kish graphite

Electrochemical



Topography



Surface structure : edge (number of layers)

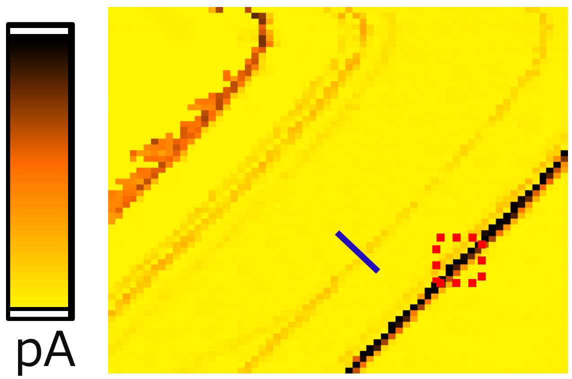
Electrochemical

-200

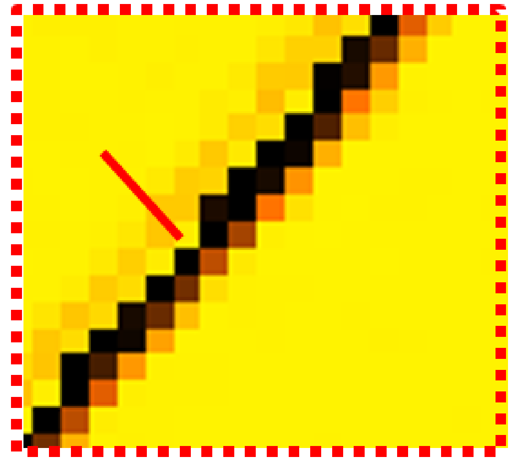
high

Activity

low -1 pA

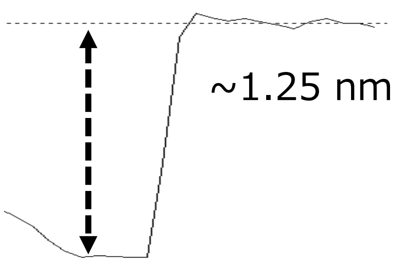


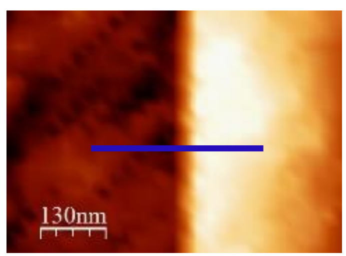
8×6.35 μm

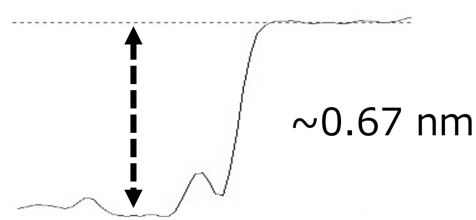


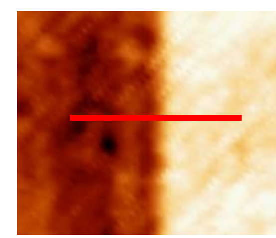
4 layers : -2.3 pA

bilayer : -1.5 pA







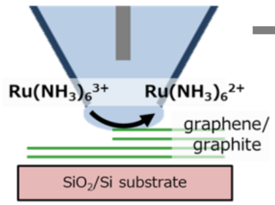


c.f. monolayer : 0.33 nm

multi-layer : -166 pA
(Thin film graphite)

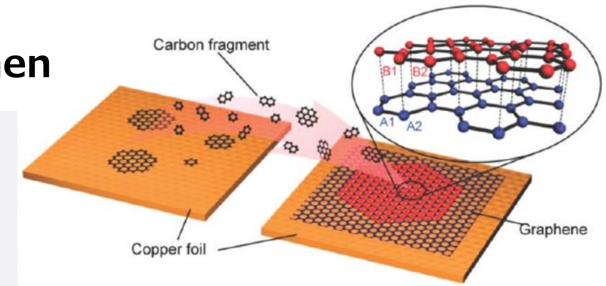
Edge activity has correlated to a number of graphene layers

Detection of Bilayer Graphene Structure from Electrochemical Imaging

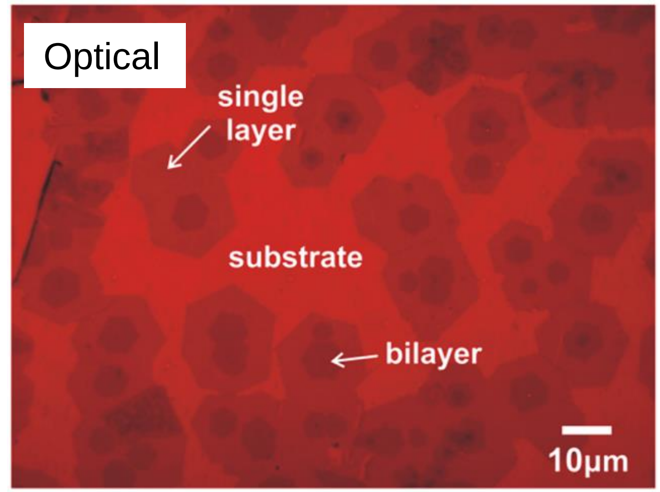


Prof. Y. P. Chen

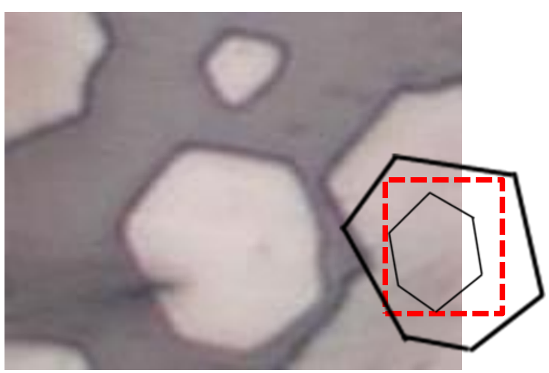
CVD growth Graphene:



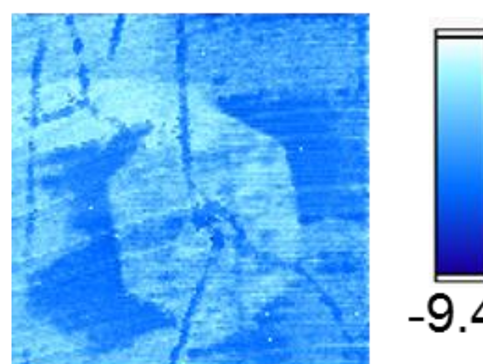
Y. P. Chen Nano Lett. 2011, Nat. Mater. 2013,



Measured area



Electrochemical



-0.53

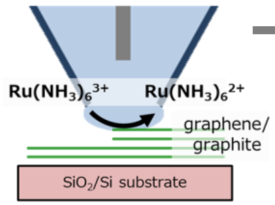
-9.49

(pA)

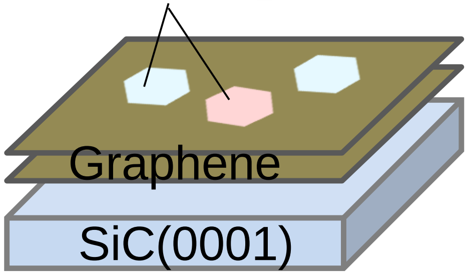
6×6 μm

Activity bilayer
< monolayer

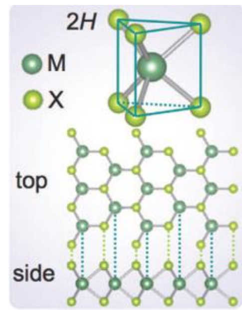
Other 2D Materials:



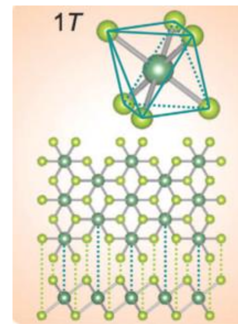
Collaboration with Prof. T. Takahashi in Tohoku Univ.



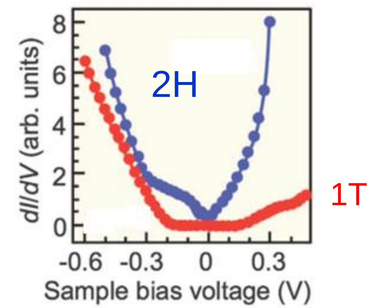
2H



1T



DoS: $NbSe_2$

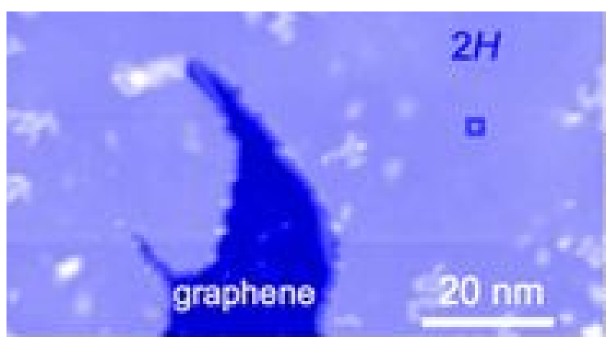


Yuki Nakata *et al.*, *NPG Asia Materials* (2016) **8** , 321

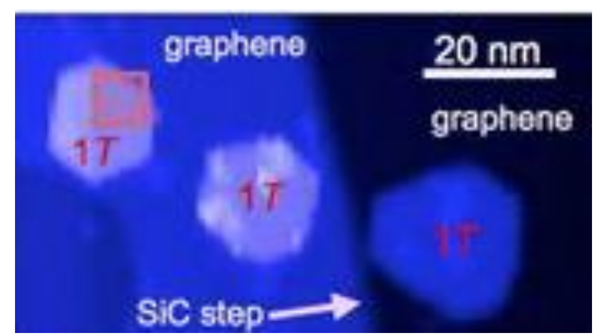
Typical characterization (STM)

- UH vacuum
  <2 x 10^{-10} Torr
- Low temp.
  T= 4-6 K

2H-$NbSe_2$

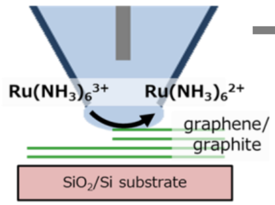


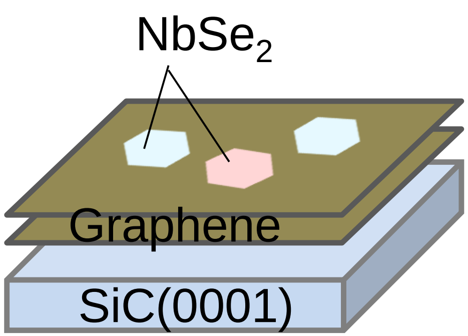
1*T*-$NbSe_2$



STM: Scanning tunneling microscopy

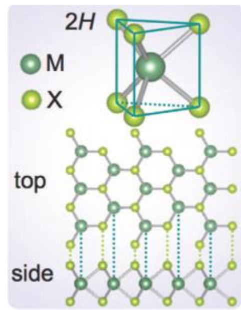
Other 2D Materials:



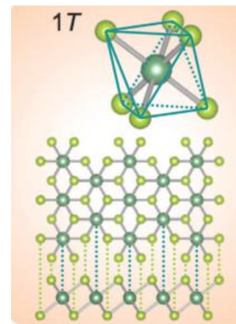


Collaboration with Prof. T. Takahashi in Tohoku Univ.

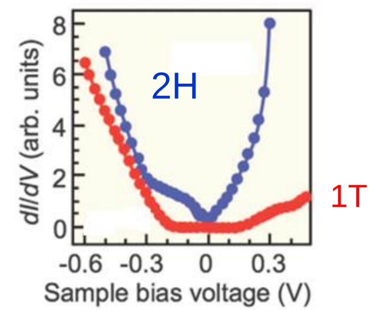
2H



1T



DoS: NbSe$_2$



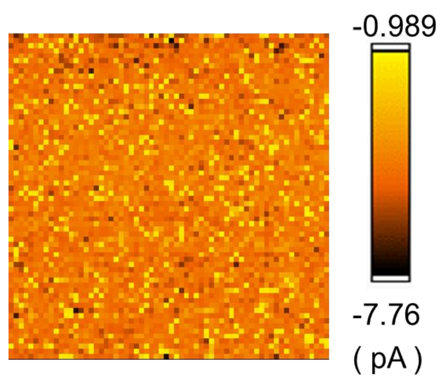
Yuki Nakata *et al.*, *NPG Asia Materials* (2016) **8** , 321

Our method (SECCM)

- atmosphere
- T= RT

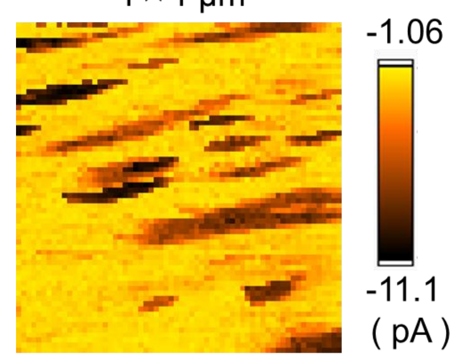
Easy to investigate

2H-NbSe$_2$



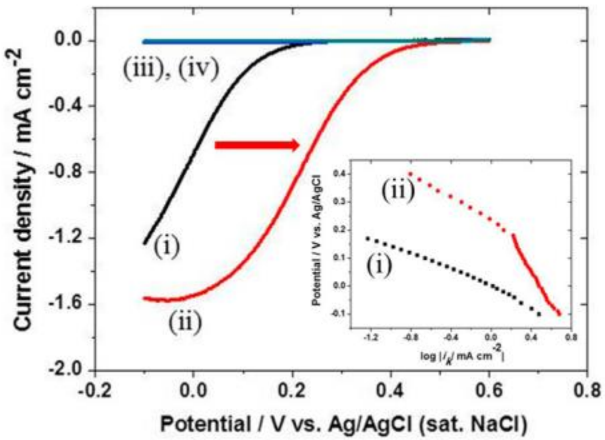
1T-NbSe$_2$

1×1 μm



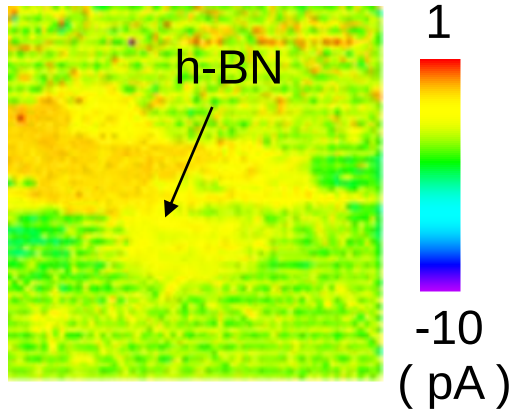
Hydrogen Evolution / Oxygen Reduction Reaction

h-BN



K. Uosaki *et al.*, *JACS* 2014

Electrochemical (ORR)

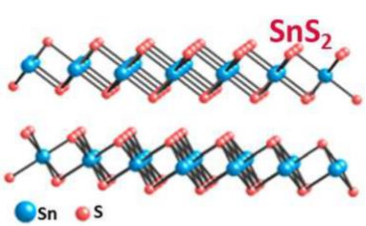


(i)bare Au (ii)BN on Au
(iii)bare glassy carbon (GC) (iv)BN on GC

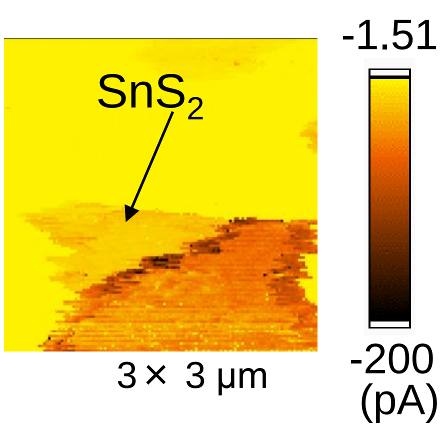
Collaboration with Prof. K. Uosaki in NIMS

SnS_2

low cost, rare metal free,
good for HER electrode



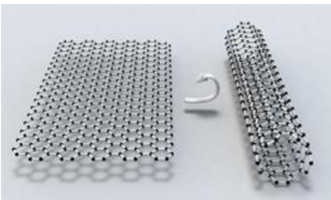
Electrochemical (HER)



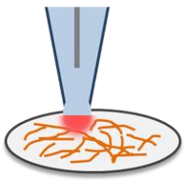
HER: hydrogen evolution reaction
ORR: oxygen reduction reaction

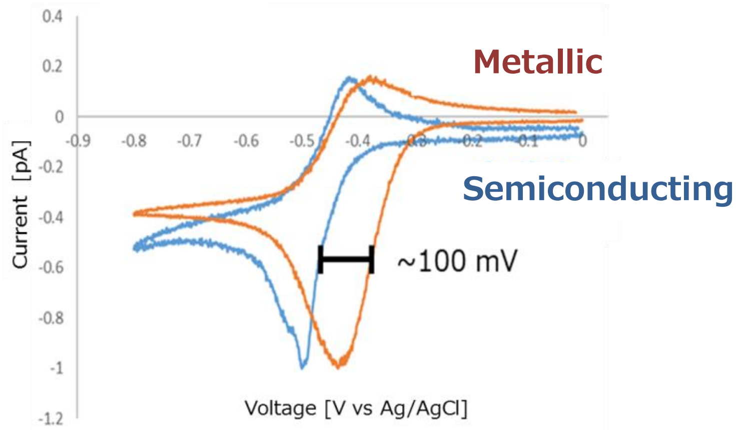
Other reactions:

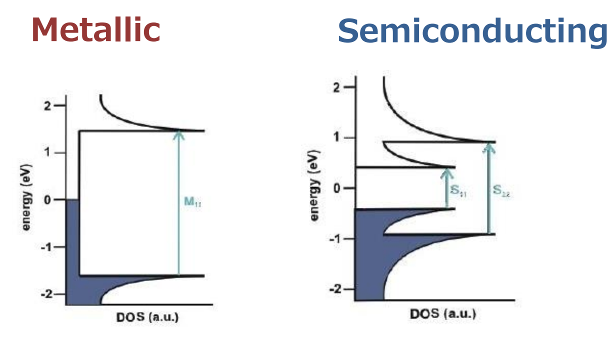
Carbon nanotubes detection: semiconducting or metallic



From Meijo Nano Carbon Co. Ltd. HP

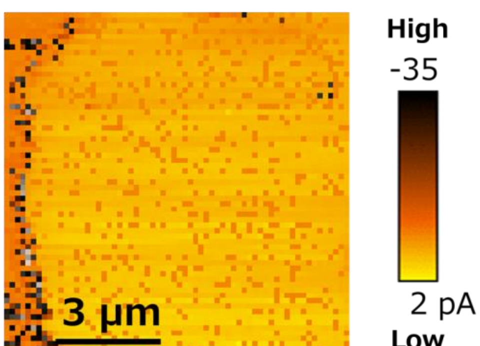




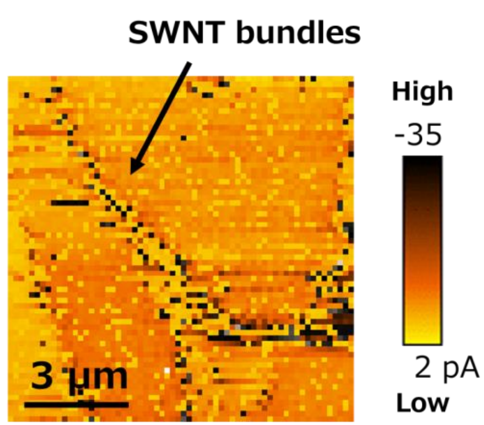


Metallic SWNTs

Electrochemical Activity

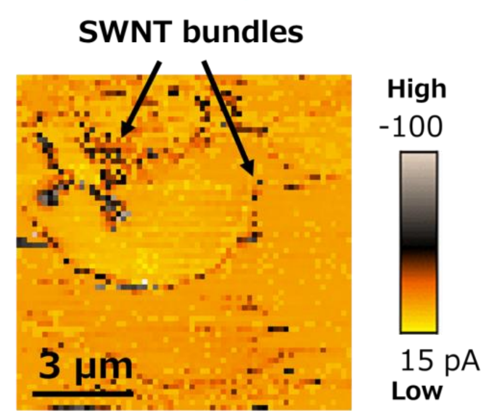


$V_{appl.}$ = -400 mV (vs Ag/AgCl)



$V_{appl.}$ = -500 mV (vs Ag/AgCl)

Semiconducting SWNTs



$V_{appl.}$ = -600 mV (vs Ag/AgCl)

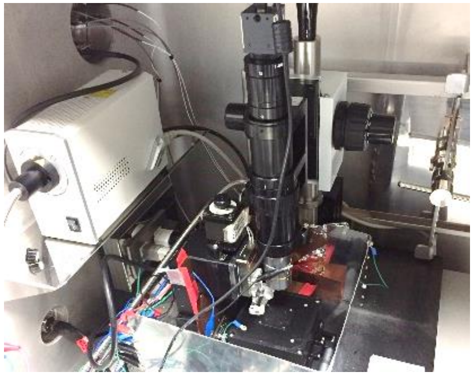
Conclusion

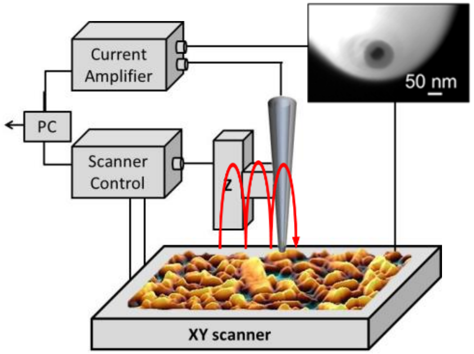
Visualization of Electrochemical Activities

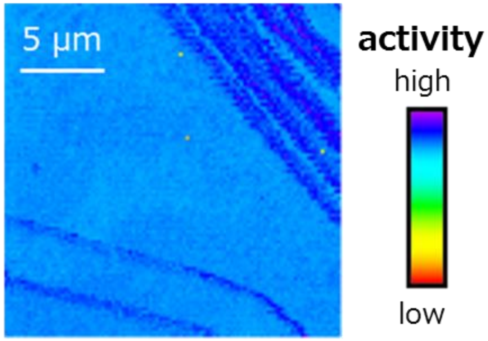
Our self-developed SECCM system can visualize

a variety of **electrochemical reaction**
(ion transport, mediator redox, electrocatalytic, *corrosion* etc.)

on different electrode materials
Battery electrodes
2D materials: graphene, $NbSe_2$, SnS_2, BN, etc







SECCM is a strong technique for investigation of electrochemical electrode performance

Acknowledgements:

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Asso. Prof. Y. Takahashi (Kanazawa Univ.) Prof. H. Shiku (Tohoku Univ.)
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C. Miura, H. Inomata, M. Tanaka, T. Watanabe, K. Ogasawara

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Prof. K. Kanamura, Assi. Assi. Prof. H. Munakata (Tokyo Metropolitan Univ.)

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