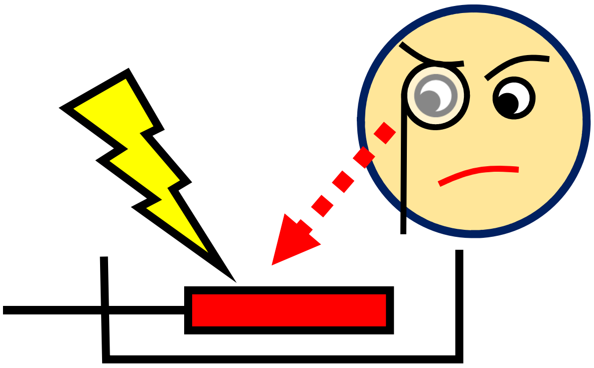
電気化学会関西支部　第 51 回電気化学講習会

電気化学の基礎と新しいアプローチ

５．電気化学その場測定
～回折法，分光法，顕微鏡観察～（その１）

（北海道大学）松井雅樹
（立命館大学）折笠有基
（京都大学）内山智貴
西　直哉
宮原雄人
（千葉大学）津田哲哉
（産業技術総合研究所）乙山美紗恵



This supplementary material is the presentation file provided at the 51st Electrochemistry Workshop held by Kansai in response to the comprehensive paper in *Electrochemistry*, **90(10)**, 102009 (2022) https://doi.org/10.5796/electrochemistry.22-66093 entitled,

Electrochemical In Situ/*operando* Spectroscopy and Microscopy Part 1: Fundamentals

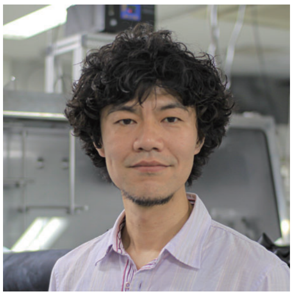
Masaki MATSUI,[a,*] Yuki ORIKASA,[b] Tomoki UCHIYAMA,[c] Naoya NISHI,[d] Yuto MIYAHARA,[d] Misae OTOYAMA,[e] and Tetsuya TSUDA,[f]

[a] *Department of Chemistry, Hokkaido University, Kita10 Nishi 8, Kita-ku, Sapporo, 060-0810, Japan*
[b] *Department of Applied Chemistry, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, 525-8577, Japan*
[c] *Department of Interdisciplinary Environment, Kyoto University, Yoshida-Honmachi, Sakyoku, Kyoto, 606-8501, Japan*
[d] *Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto daigaku-katsura, Nishikyo-ku, Kyoto, 615-8510, Japan*
[e] *Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, 563-8577, Japan*
[f] *Department of Materials Science, Chiba University, 1-33 Yayoicho, Inage-ku, Chiba 263-8522, Japan*

* *Corresponding author: matsui@sci.hokudai.ac.jp*

© The Author(s) 2022. Published by ECSJ. This is an open access material distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.50892/data.electrochemistry.21357900].

電気化学その場測定
～回折法，分光法，顕微鏡観察～
1 基礎編



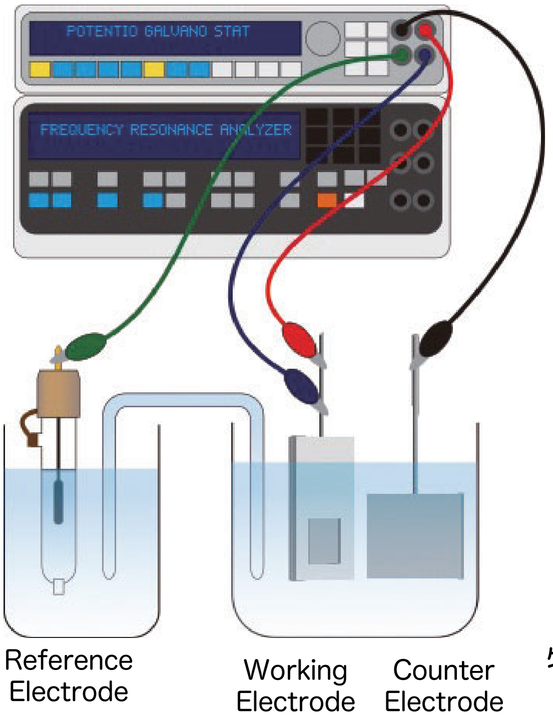
北海道大学大学院理学研究院化学部門

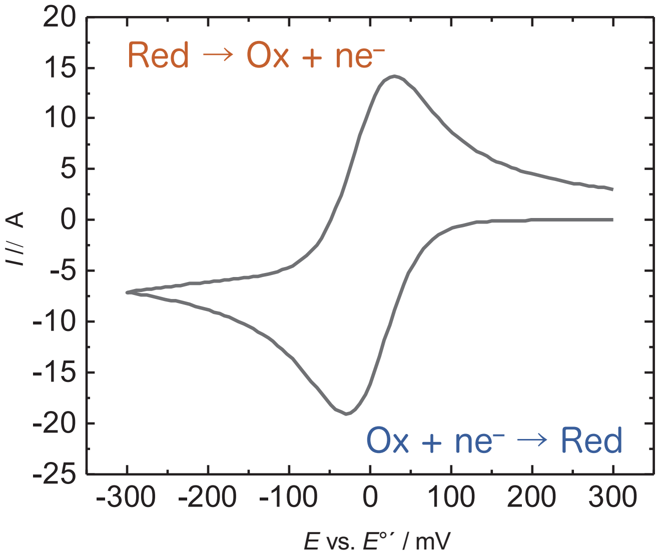
松井 雅樹

matsui@sci.hokudai.ac.jp

電気化学測定データを構成するパラメータ

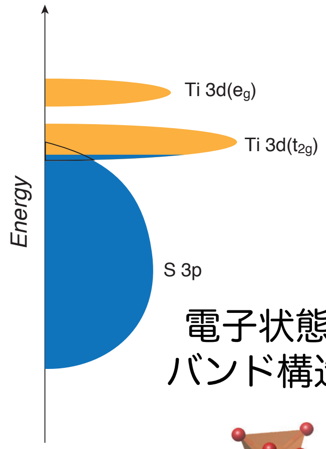
電流、電圧、時間


POTENTIO GALVANO STAT
FREQUENCY RESONANCE ANALYZER
Reference Electrode
Working Electrode
Counter Electrode

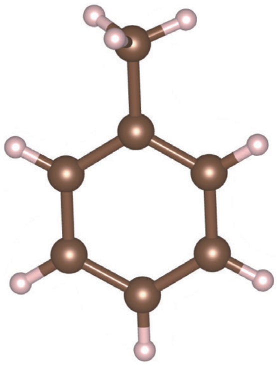


物質や材料に関する直接的な情報がない

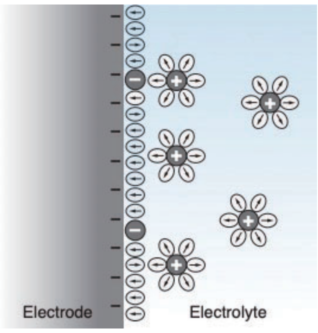
知りたい情報の例


Ti 3d(e_g)
Ti 3d(t_2g)
Energy
S 3p

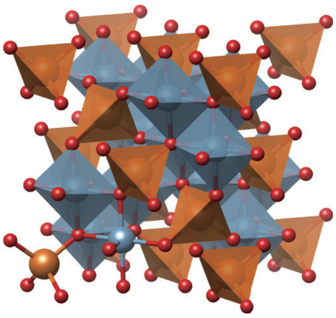
電子状態
バンド構造



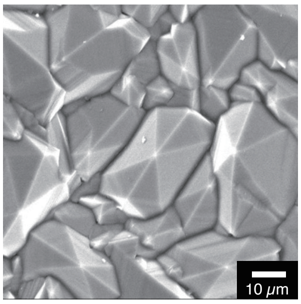
分子構造


Electrode
Electrolyte

電極／電解液界面の構造



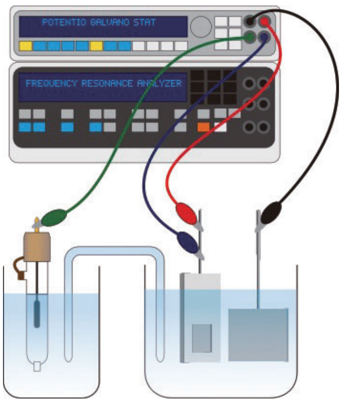
結晶構造



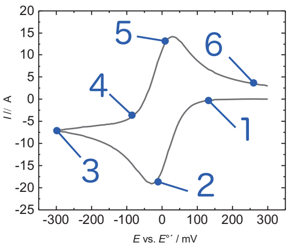
材料組織

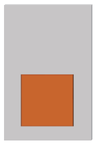
分子や結晶の構造や物性（とその変化）に関する情報

通常の実験スキーム(ex situ測定)


POTENTIO GALVANO STAT
FREQUENCY RESONANCE ANALYZER

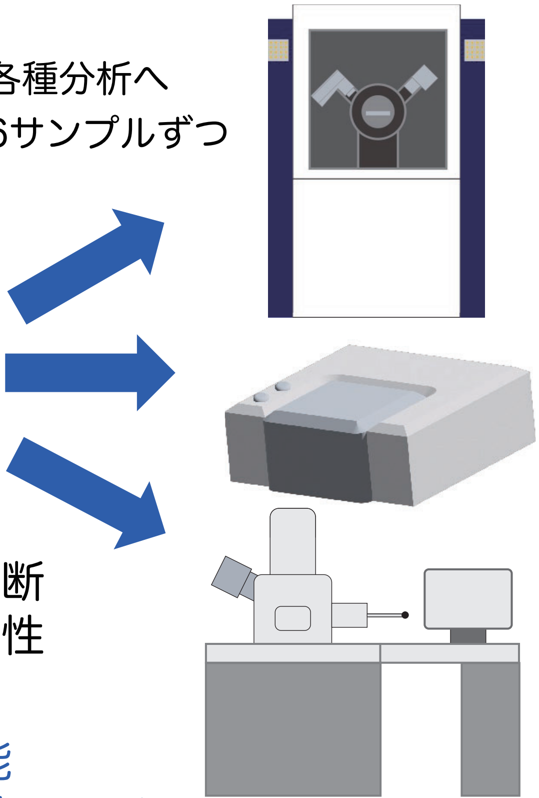
電気化学測定





サンプル

各種分析へ
6サンプルずつ



ex situ測定

- ✓ 動的な挙動は電気化学測定で判断
- ✓ サンプリングで状態変化の可能性

in situ測定

- ✓ 1回で連続したデータ取得が可能
- ✓ 反応過程を理解するための強力なツール！

本講習会で紹介する電気化学その場測定法

5-2. X線回折・X線吸収分光

講師　折笠 有基（立命館大学）
　　　内山智貴（京都大学）

5-3. 赤外・可視光レーザーを用いた分光法

赤外分光法・表面プラズモン共鳴・ラマン分光法

講師　松井 雅樹　（北海道大学）
　　　西 直哉　　（京都大学）
　　　宮原 雄人　（京都大学）

5-4. 顕微鏡観察

共焦点顕微鏡・走査型/透過型電子顕微鏡

講師　乙山 美紗江（産総研）
　　　津田 哲哉　（千葉大学）

各測定の入射電磁波・検出電磁波

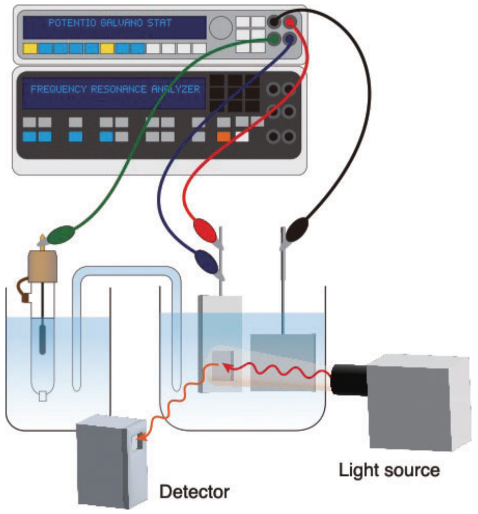
	入射電磁波	検出電磁波*	得られる情報
X線回折法	X線	X線（一次）	結晶構造
X線吸収分光法	X線	X線（一次）	酸化状態・配位構造
赤外分光法	赤外光	赤外光（一次）	分子振動・格子振動
表面プラズモン共鳴	可視光 etc.	可視光 etc.（一次）	界面の屈折率変化
ラマン分光法	可視光 etc.	可視光 etc.（二次）	分子振動・格子振動
共焦点顕微鏡	可視光	可視光（一次）	表面形態
走査型電子顕微鏡	電子線	電子線（二次）	表面形態・元素の分布
透過型電子顕微鏡	電子線	電子線（一次）	表面形態・元素の分布

電気化学セルにどう取り込んで、どう検出するのか？

*厳密には二次光でも一次光と同等の場合、ここでは一次と示す

電気化学測定系への電磁波の取り込み・取り出し

通常の電気化学セルに電磁波を取り込むには？


POTENTIO GALVANO STAT
FREQUENCY RESONANCE ANALYZER
Detector
Light source

光路の問題

- ✓ セルや電解液による光の吸収
- ✓ 光量不足により測定不可
- ✓ 電子線の場合大気中での照射不可
- ✓ 屈折による光路の変化

電気化学系の問題

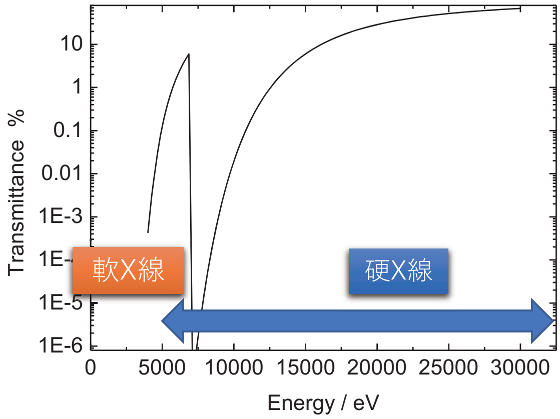
- ✓ 適切な電極配置が取れない
- ✓ 電解液のもれや揮発

用いる電磁波にあわせて

セル設計：窓の選択と電極配置

光学系：光源・検出器の選択・セルの配置

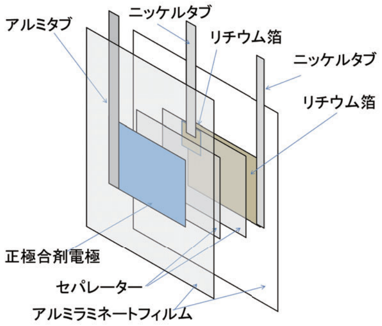
X線を用いた測定

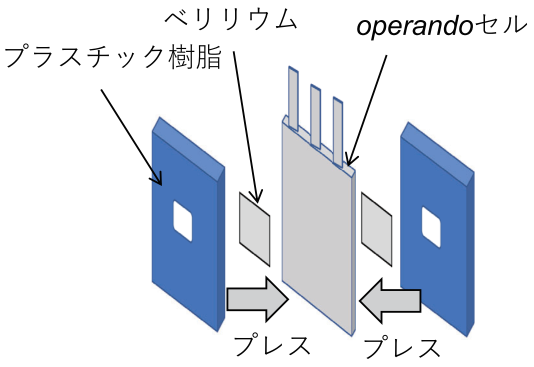


セル・光学系の特徴

- ✓ 紫外光・可視光と比較してエネルギーが高く透過能を示すため、実用に近い形態のセルが使用できる
- ✓ 放射光を用いた場合は輝度が高く、高時間分解能測定などが可能

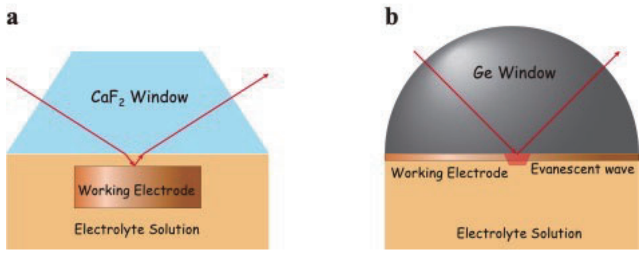
リチウムイオン電池系の測定セル


アルミタブ
ニッケルタブ
リチウム箔
ニッケルタブ
リチウム箔
正極合剤電極
セパレーター
アルミラミネートフィルム

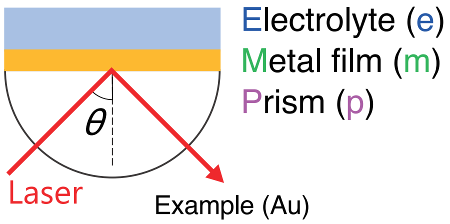

ベリリウム
プラスチック樹脂
*operando*セル
プレス
プレス

赤外光・可視光を用いた測定

赤外分光の光学系

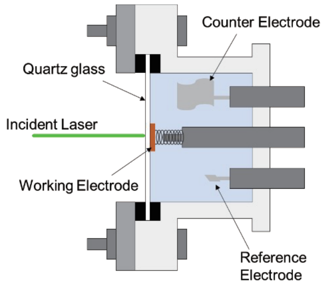

a
CaF$_2$ Window
Working Electrode
Electrolyte Solution
b
Ge Window
Working Electrode
Evanescent wave
Electrolyte Solution

SPRの光学系


Electrolyte (e)
Metal film (m)
Prism (p)
θ
Laser

Example (Au)
Prism: BK7 glass
Laser: He-Ne laser (632.8 nm)

ラマン分光の光学系


Counter Electrode
Quartz glass
Incident Laser
Working Electrode
Reference Electrode

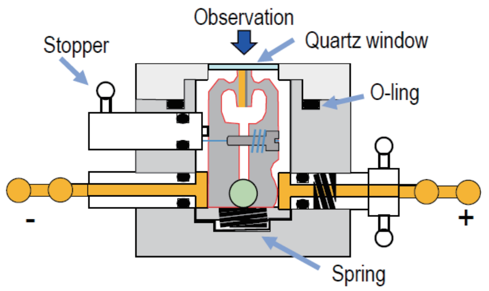
セル・光学系の特徴

- ✓ 外部反射：入射光が電極表面で反射
  →電極を窓に押し付ける
- ✓ 内部反射：入射光がプリズムの底面で全反射
  →電極の裏から分光測定

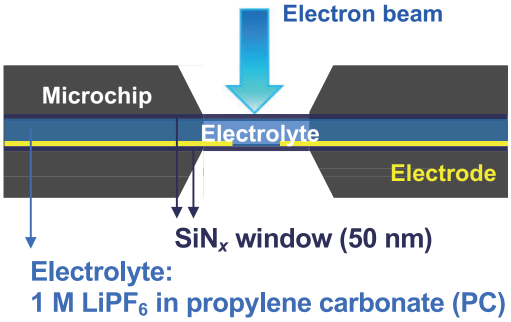
顕微鏡観察

共焦点顕微鏡

Outside part (cross section)

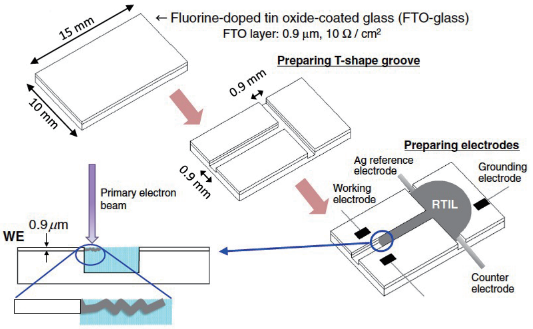

Observation
Stopper
Quartz window
O-ling
-
+
Spring

走査型電子顕微鏡


Electron beam
Microchip
Electrolyte
Electrode
SiN$_x$ window (50 nm)
Electrolyte:
1 M LiPF$_6$ in propylene carbonate (PC)

セル・光学系の特徴

- ✓ セル断面もしくは観察用の穴を開けた箇所の近傍のみが視野となる。
- ✓ 電子顕微鏡の場合、電子線を透過できる密閉型セルが一般的。
- ✓ イオン液体の利用により開放系セルの可能性が拓けた。


15 mm
10 mm
← Fluorine-doped tin oxide-coated glass (FTO-glass)
FTO layer: 0.9 µm, 10 Ω / cm²
Preparing T-shape groove
0.9 mm
0.9 mm
Preparing electrodes
Ag reference electrode
Grounding electrode
Working electrode
RTIL
Counter electrode
Primary electron beam
0.9 µm
WE

基礎編まとめ

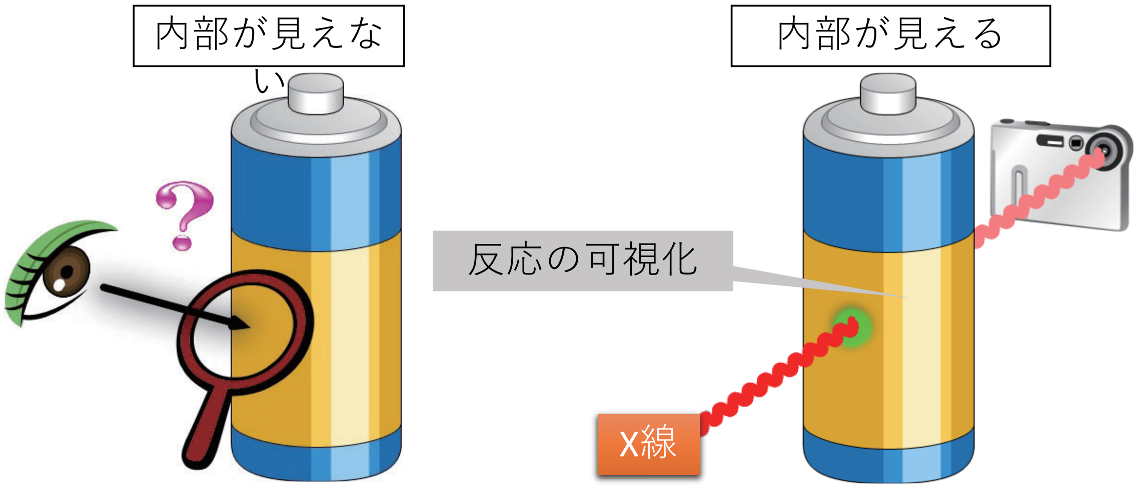
- ✓ その場測定は電気化学反応を連続して観測する手法であり、反応過程を理解する上で極めて強力なツールとなり得る。
- ✓ 赤外光・可視光を用いた測定は、多くの場合にセル構成上の制約が加わる。
- ✓ 各分析手法も電気化学測定との組み合わせによって、感度や分解能などに制約が加わる。
- ✓ SFG, ESR, SPMなど、今回取り上げることのできなかった、その場測定も有用なツールとなる。

---

2. X線回折・X線吸収分光

折笠有基（立命館大学）
内山智貴（京都大学）

電気化学測定中のスペクトル観察



内部が見えない

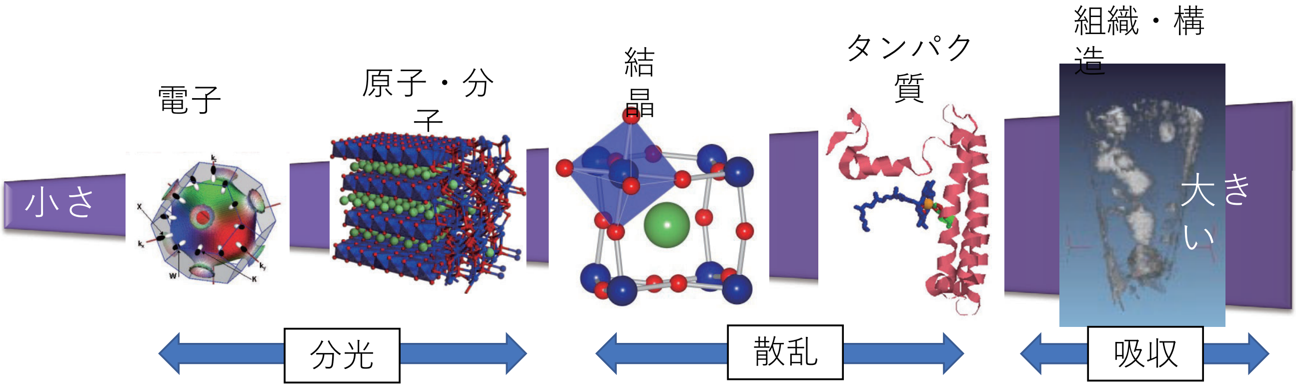
内部が見える

反応の可視化

X線

高い透過能を有するX線は測定対象の制限が小さく、多くの反応解析に適用可能

X線を用いた解析がカバーする領域



電子

原子・分子

結晶

タンパク質

組織・構造

小さい

大きい

分光

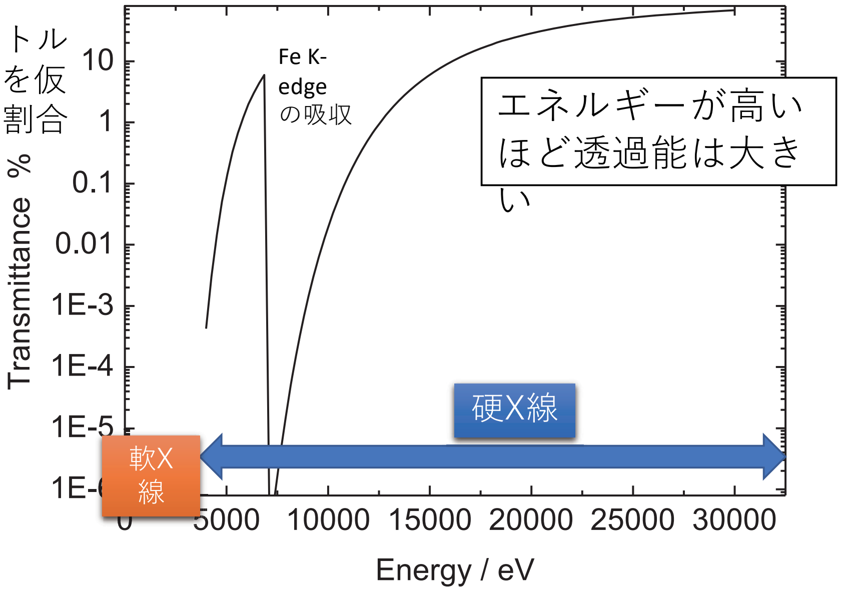
散乱

吸収

測定対象に応じて、使用する波長・プローブを使い分ける

X線のエネルギーと透過率

厚み100マイクロメートルのFe（密度5.0 g/cm³を仮定）を透過するX線の割合



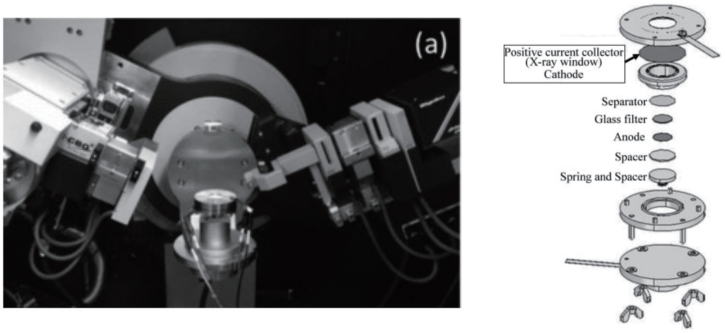
エネルギーが高いほど透過能は大きい

硬X線

軟X線

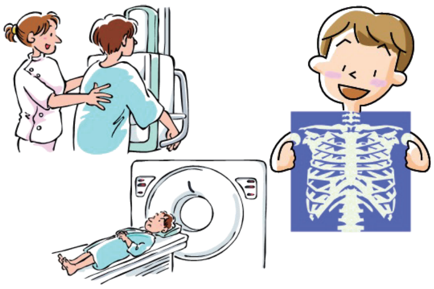
実験室で使用するX線

X線回折


(a)
Positive current collector
(X-ray window)
Cathode
Separator
Glass filter
Anode
Spacer
Spring and Spacer

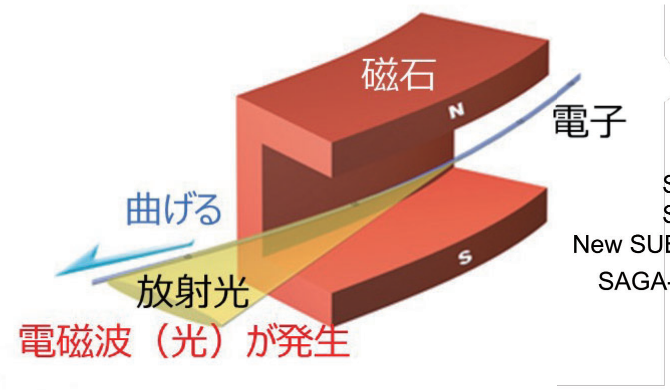
T. Konya, Y. Shiramata, T. Nakamura, *BUNSEKI KAGAKU*, **68** 793-800 (2019).

レントゲン・X線CT

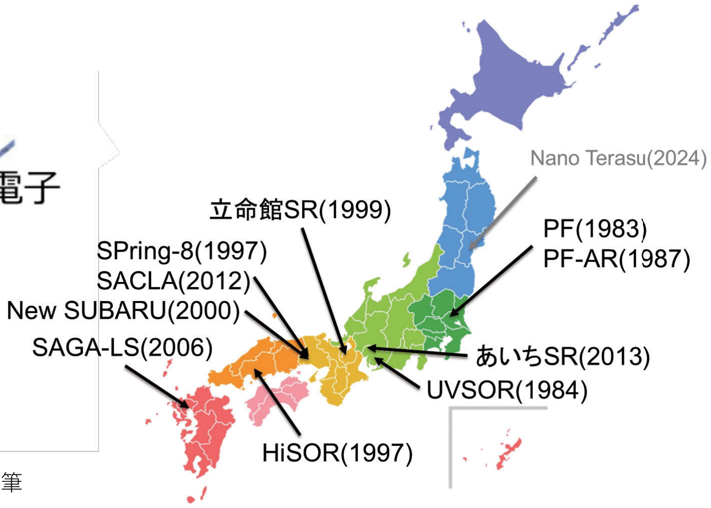


波長（エネルギー）を固定した測定法は実験室でもオペランド計測が可能

放射光の利用

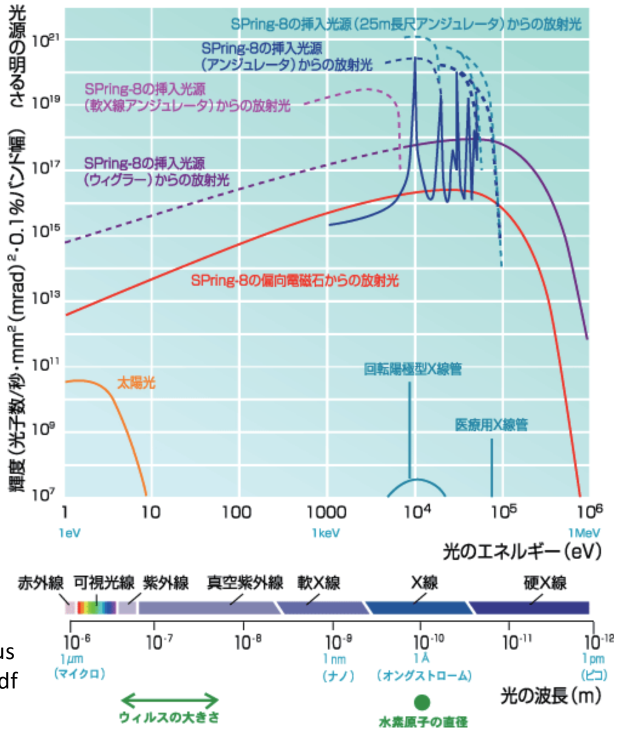

磁石
N
S
電子
曲げる
放射光
電磁波（光）が発生

https://www.ritsumei.ac.jp/acd/re/src/aurora.htmlに加筆


Nano Terasu(2024)
立命館SR(1999)
PF(1983)
PF-AR(1987)
SPring-8(1997)
SACLA(2012)
New SUBARU(2000)
SAGA-LS(2006)
あいちSR(2013)
UVSOR(1984)
HiSOR(1997)

エネルギーを変えることが容易で、光が明るい

放射光はどのくらい明るいのか？



http://www.spring8.or.jp/ja/about_us/whats_sp8/whats_sr/pdf/spectra.pdf

放射光実験の利点

単色光

連続Ｘ線源であるため、モノクロメーターにより単一の波長のＸ線を取り出す事が可能

➡ **$K\beta$線や$K\alpha_1$と $K\alpha_2$線による反射の重なり等がなくなり、高分解能の回折パターンが得られる。**

高輝度

実験室系で用いられるＸ線の10^3〜10^6倍もの高輝度なＸ線源である

平行光

発散の少ない光源であるため、回折計を用いる場合、平行ビーム光学系を採用でき、 Ｘ線の位置に対して試料や検出器等の光学系の配置の自由度が大きい。

➡ **極微小（〜数µm）の試料を扱え、あるいは非常に短時間で回折データの収集が行える。**

任意の波長のＸ線を使える

試料を構成している元素の吸収端前後の波長を用いて回折データを収集することにより、 原子散乱因子の近い隣り合った原子番号の元素を区別することが出来る。

➡ **波長の単色性が優れていることに加えて、ガウス分布関数に近い、 対称性のよい、半値幅の小さな回折プロファイルが得られる。**

実験できる主な手法と適用の目安

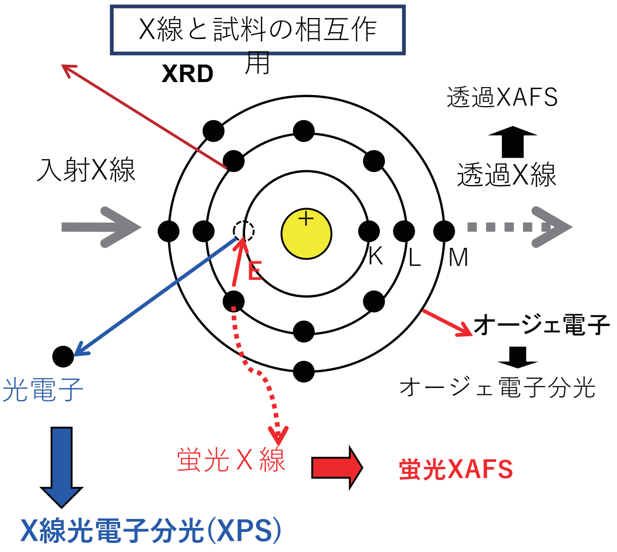
主な手法

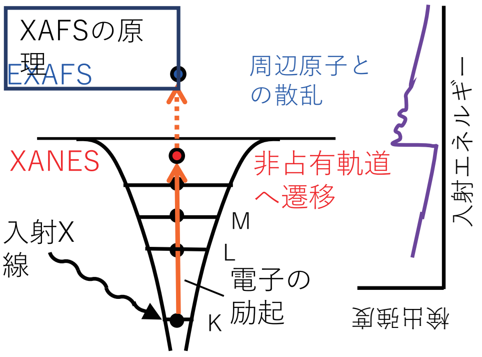
- X線回折－結晶構造
- X線吸収－電子・局所構造
- X線蛍光分析－元素分析
- X線光電子分光－化学状態
- X線反射率－表面構造
- 小角散乱－微細構造
- X線散乱－短中距離の構造情報
- X線CT（イメージング）－3次元形態
- 赤外分光－分子の化学構造

申請から実験まで半年位かかるケースもあり、初めての人は良く使っている方と一緒にやることが望ましい

- ラボの実験装置ではできない測定手法
  - X線吸収分光（エネルギー掃引）
  - X線散乱（広角散乱）
- 位置分解測定
  - マイクロメートルオーダーの分解能
- 時間分解測定
  - ミリ秒オーダーの回折・過渡状態の解析
- 微少量サンプルの測定
  - ナノ粒子、非晶質
- 大量個数サンプル測定、ハイスループット
- ラボでできることはラボで行う

放射光X線を用いた分光測定手法


X線と試料の相互作用
XRD
入射X線
透過XAFS
透過X線
K
L
M
E
光電子
オージェ電子
オージェ電子分光
蛍光Ｘ線
蛍光XAFS
X線光電子分光(XPS)

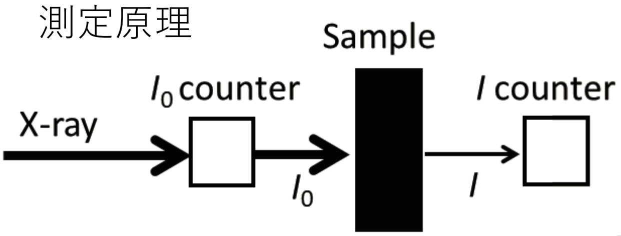

XAFSの原理
EXAFS
周辺原子との散乱
XANES
非占有軌道へ遷移
入射X線
M
L
K
電子の励起
入射エネルギー
検出強度

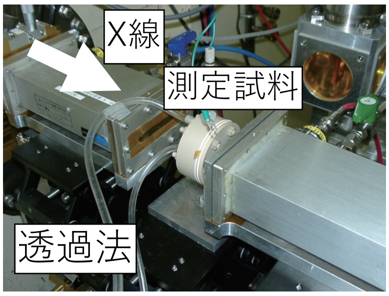
XANES: 非占有軌道への励起過程
⇒電子状態(価数)、対称性など

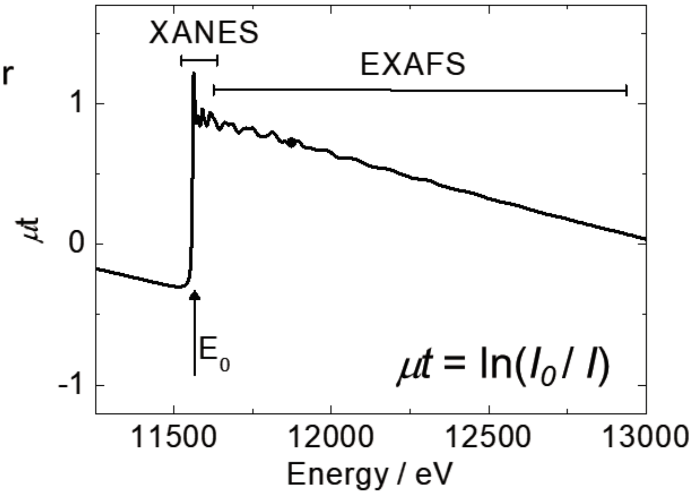
EXAFS: 散乱効果による振動
⇒ 局所構造(配位数、結合距離など)

X線吸収分光法

測定原理

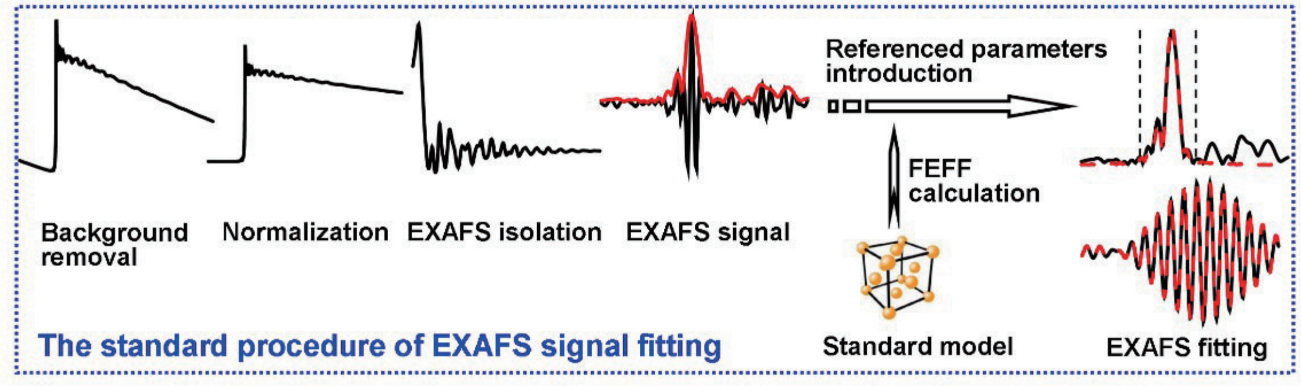

Sample
X-ray
I_0 counter
I counter
I_0
I





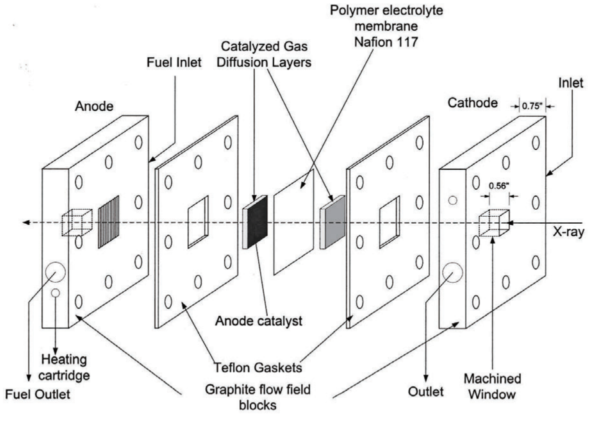
$\mu t = \ln(I_0/I)$

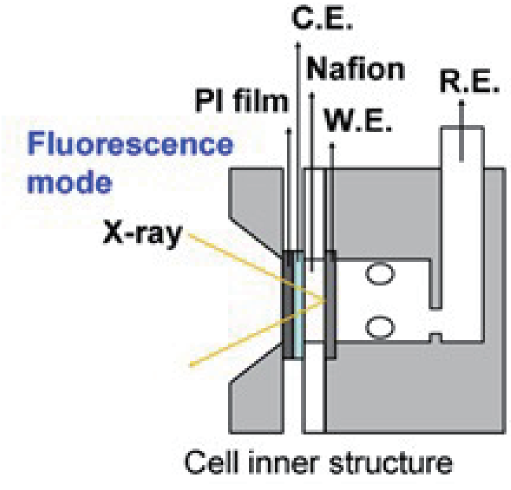
解析方法


Background removal
Normalization
EXAFS isolation
EXAFS signal
Referenced parameters introduction
FEFF calculation
Standard model
EXAFS fitting
The standard procedure of EXAFS signal fitting

X. Wang, Y. Orikasa, Y. Takesue, H. Inoue, M. Nakamura, T. Minato, N. Hoshi, Y. Uchimoto, *J. Am. Chem. Soc.*, **135**, 5938 (2013).

燃料電池オペランドセルの例


Polymer electrolyte membrane Nafion 117
Catalyzed Gas Diffusion Layers
Fuel Inlet
Anode
Cathode
0.75"
Inlet
0.56"
X-ray
Anode catalyst
Heating cartridge
Fuel Outlet
Teflon Gaskets
Graphite flow field blocks
Outlet
Machined Window

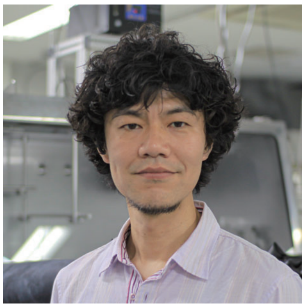

C.E.
Nafion
R.E.
PI film
W.E.
Fluorescence mode
X-ray
Cell inner structure

R. Viswanathan, R. Liu, E.S. Smotkin, *Rev. Sci. Instrum.*, **73**, 2124 (2002).

X. Wang, Y. Orikasa, Y. Takesue, H. Inoue, M. Nakamura, T. Minato, N. Hoshi, Y. Uchimoto, *J. Am. Chem. Soc.*, **135**, 5938 (2013).

Electrochemical in situ/operando measurement
~diffraction, spectroscopy, microscopy~

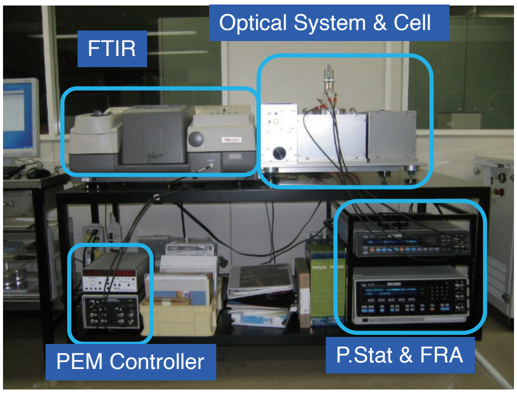
3. Infrared Spectroscopy



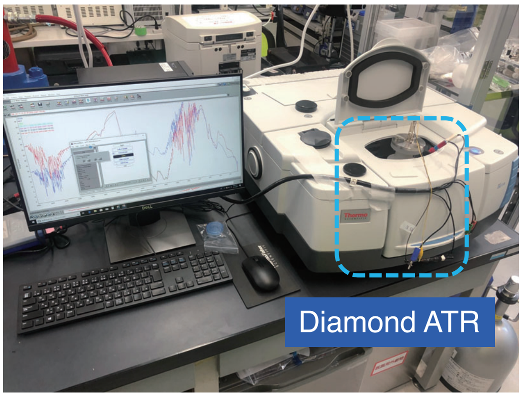
Masaki MATSUI
Department of Chemistry, Hokkaido University
matsui@sci.hokudai.ac.jp

---

in situ/operando FTIR setup


FTIR
Optical System & Cell
PEM Controller
P.Stat & FRA

IRRAS setup


Diamond ATR

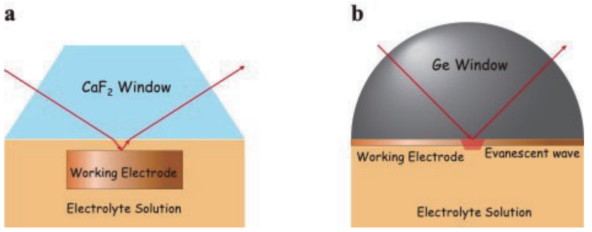
ATR setup

PIKE
VeeMAX III

https://www.piketech.com/product/sr-veemax/

https://www.czitek.com/pages/micromatr-1

Optical setup


a
CaF$_2$ Window
Working Electrode
Electrolyte Solution
b
Ge Window
Working Electrode
Evanescent wave
Electrolyte Solution

External reflection Internal reflection

a. External reflection geometry

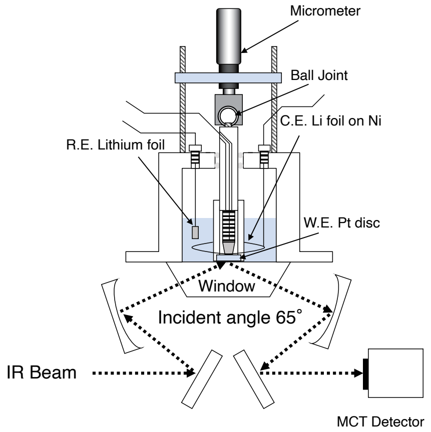
- ✓ Incident beam reflects at the electrode surface.
- ✓ The electrode needs to have high infrared reflectivity. Carbon is not applicable.
- ✓ The window has a close refractive index to electrolyte solution.

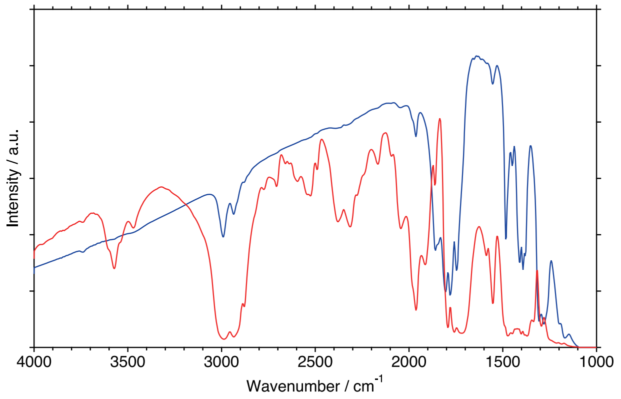
b. Internal reflection geometry

- ✓ Incident beam reflects at the window/electrolyte interface.
- ✓ Composite electrode containing carbon-based material is applicable.
- ✓ The window needs to have a high refractive index for the total reflection.

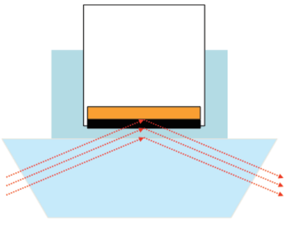
Material	Range (cm^{-1})	Refractive Index (at 2μm)
BaF_2	67000–740	1.46
CaF_2	77000–1,100	1.42
CdTe	10000–400	2.4
CsI	40000–200	1.74
GaAs	7000–650	3.33
Ge	5500-600	4.00
KRS-5	20000–250	2.37
LiF	50000–1,700	1.4
NaCl	40000–200	1.52
Si	83300–660	3.40
ZnSe	20000-454	2.40

external reflection cell measurement tips

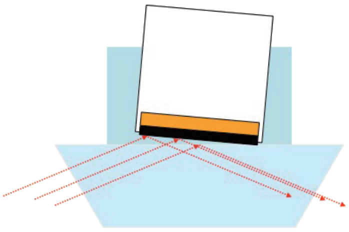

Micrometer
Ball Joint
C.E. Li foil on Ni
R.E. Lithium foil
W.E. Pt disc
Window
Incident angle 65°
IR Beam
MCT Detector



- ✓ The working electrode is pressed on the CaF_2 (or BaF_2) window.
- ✓ Since the very tiny amount of the electrolyte solution remains at the electrode surface, a fast reaction is difficult.
- ✓ Mercury Cadmium Telluride (MCT) detector is better to obtain high intensity.

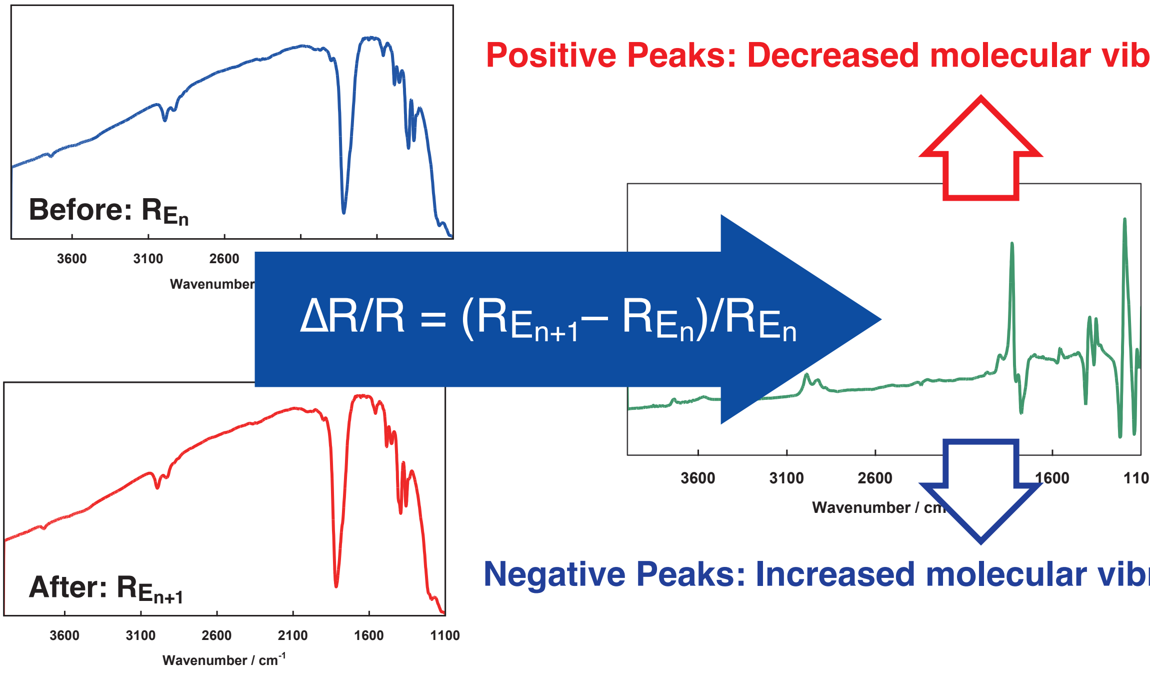


Ideal external reflection (blue)



Non-uniform gap between electrode and window (red)

SNIFTIR spectrum calculation

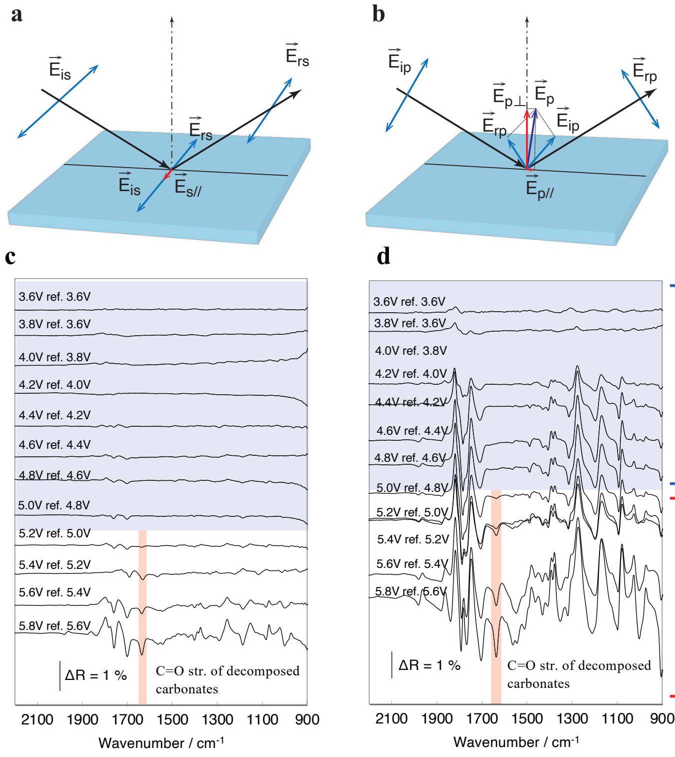


$$\Delta R/R = (R_{E_{n+1}} - R_{E_n})/R_{E_n}$$

Positive Peaks: Decreased molecular vibration

Negative Peaks: Increased molecular vibration

Surface enhancement by p-polarized beam



p-polarized beam enhances the molecular vibration perpendicular to the substrate at the surface of the electrode

≤ 5.0 V

All the negative peaks ≤ 5.0 V are assigned to the solvent molecules adsorbed on the Pt substrate
Negligible changes for the spectra using *s*-polarized beam

> 5.0 V

Decomposed products dissolved in the bulk electrolyte solution can be detected using *s*-polarized beam.

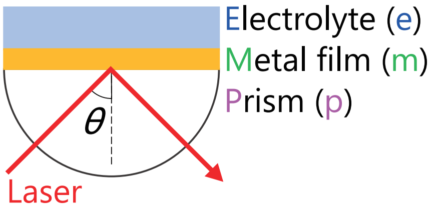
in situ FTIR spectra for the oxidation process of 1 mol L^{-1} LiPF$_6$ in EC:DEC (1:1) solution on Pt electrode taken with *s*-polarized beam (c) and *p*-polarized beam (d)

4. Surface plasmon resonance

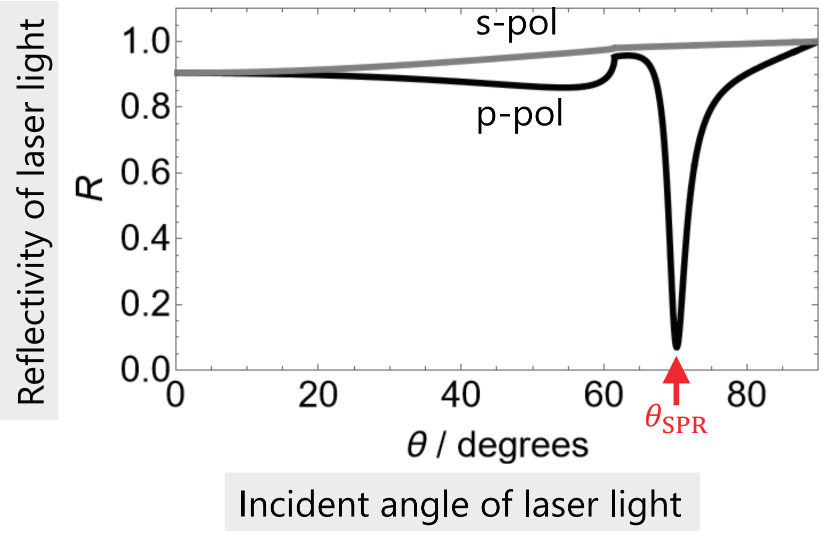
Naoya Nishi
Graduate School of Engineering, Kyoto University, Japan
nishi.naoya.7e@kyoto-u.ac.jp

Surface Plasmon resonance (SPR)

SPR as a phenomenon:	resonance between free-electron oscillation at the metal film surface and light wave
SPR as a interfacial probe:	sensitive probe of the interfacial refractive index near the metal film surface via θ_{SPR}

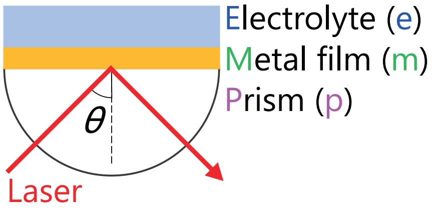


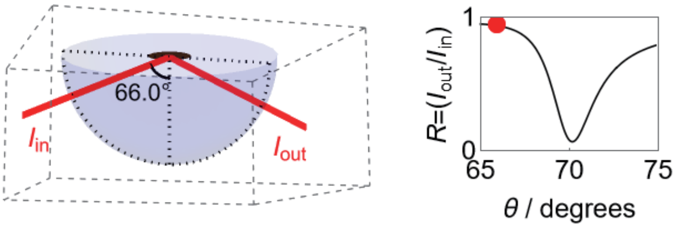
Material
Electrolyte: any liquid (or gas)
Metal: Au, Ag, Cu, Al
Prism: high-*n* glass



SPR condition

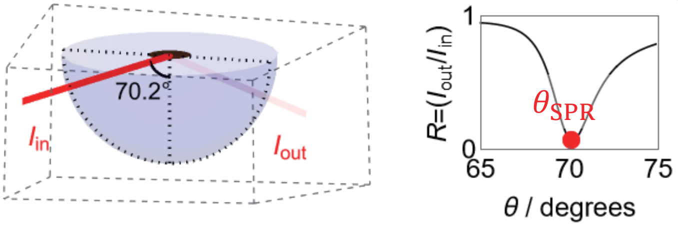
Scan θ and find θ_{SPR} where $R = R_{\min}$

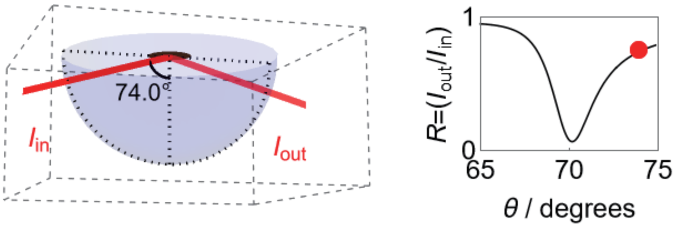

Electrolyte (e)
Metal film (m)
Prism (p)
θ
Laser



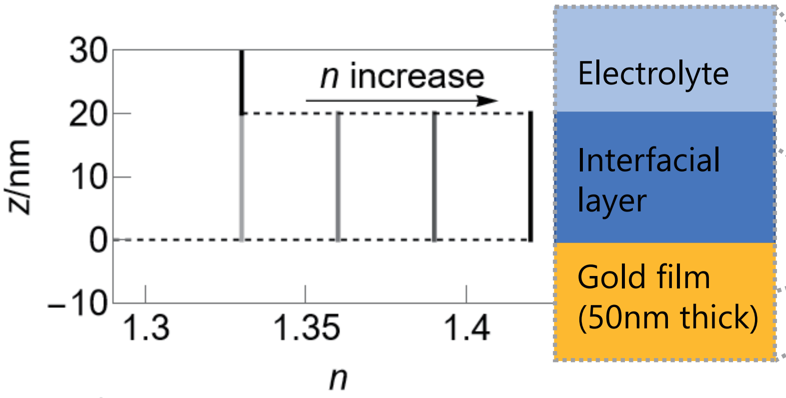
SPR condition:

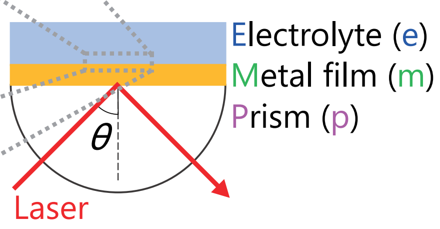
$$\theta_{\mathrm{SPR}} = \arcsin\left(\frac{1}{n_{\mathrm{p}}}\sqrt{\frac{1}{1/\mathrm{Re}[n_{\mathrm{m}}^2] + 1/n_{\mathrm{e}}^2}}\right)$$





Interfacial n change leads to θ_{SPR} shift


30
20
10
0
−10
z/nm
n increase
1.3
1.35
1.4
n
Electrolyte
Interfacial layer
Gold film (50nm thick)


Electrolyte (e)
Metal film (m)
Prism (p)
θ
Laser

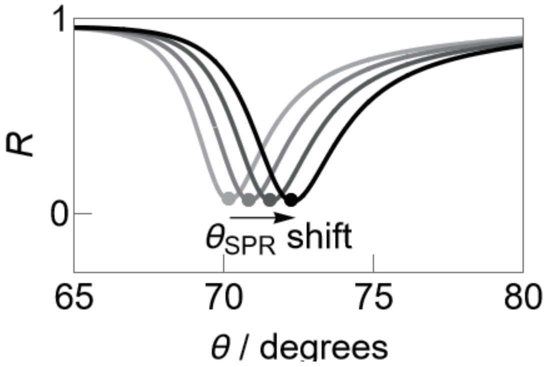
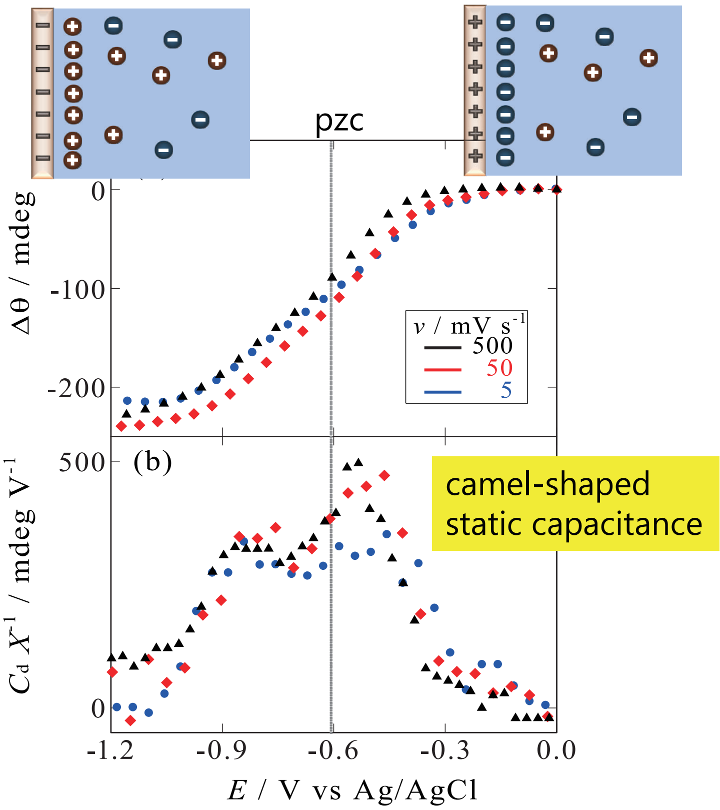


Table. Interfacial structures that change *local* n_{e} and n_{m} during electrochemical processes.

	Faradaic	Non-Faradaic
n_{e}	Diffusion layer Adsorbed layer	Electric double layer
n_{m}	Deposited metal	Charged skin layer

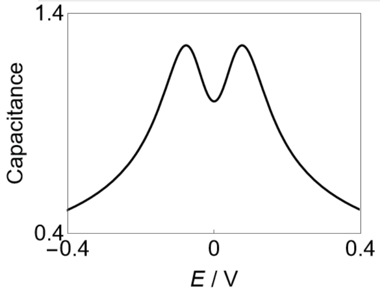
Example 1: electric double layer in an ionic liquid



camel-shaped static capacitance

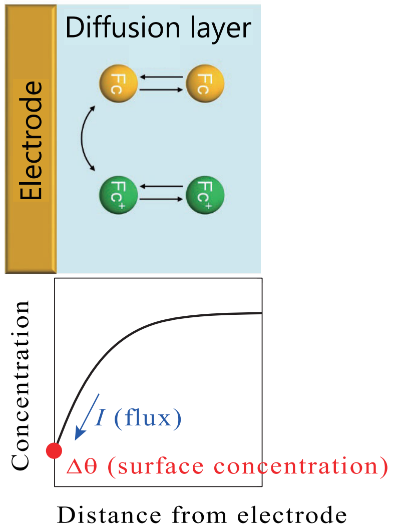
A. A. Kornyshev, *J. Phys. Chem. B*, 111 (2007) 5545.

Theoretical prediction

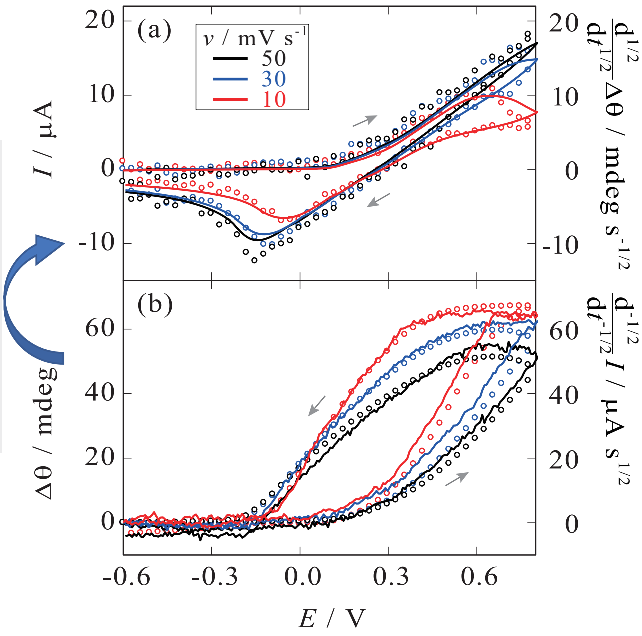


Reprinted with permission from S. Zhang et al., *J. Chem. Phys.*, 153 (2020) 044707, Copyrights (2020) AIP Publishing.

Example 2: diffusion layer sensing


Electrode
Diffusion layer
Fc
Fc
Fc+
Fc+
Concentration
I (flux)
Δθ (surface concentration)
Distance from electrode

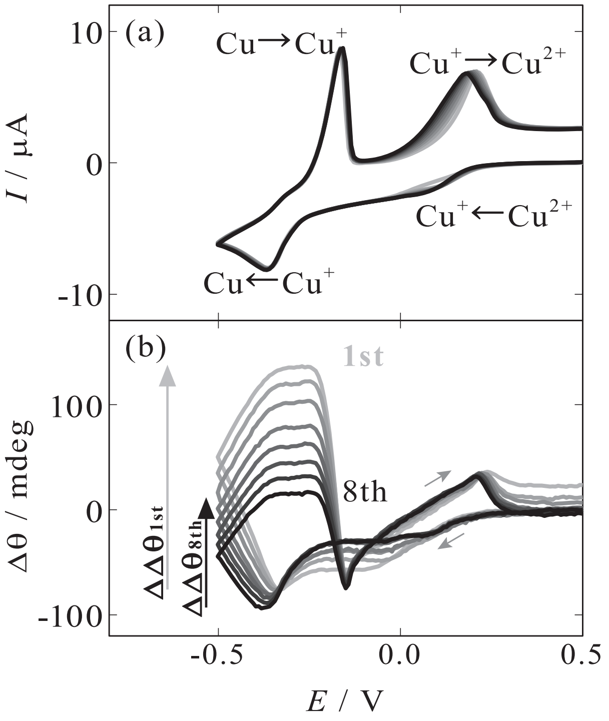
Δθ to *I* semi differentiation



I to Δθ semi integration

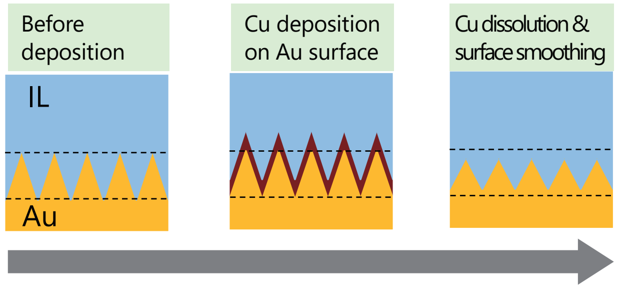
Reprinted with permission from N. Nishi et al., *J. Electroanal. Chem.*, 817 (2018) 210, Copyrights (2018) Elsevier.

Example 3: surface roughness sensing in electrodeposition



Reprinted with permission from K. Ezawa et al., *J. Electroanal. Chem.*, 877 (2020) 114611, Copyrights (2020) Elsevier.

- ✓ Surface smoothing due to repeated Cu deposition/dissolution on Au
- ✓ No CV shape change during cycles
  no change in deposited Cu amount and effective surface area
- ✓ BIG Δθ change –
  ΔΔθ due to Cu deposition decrease with increasing CV cycles


Before deposition
Cu deposition on Au surface
Cu dissolution & surface smoothing
IL
Au

第51回電気化学講習会
電気化学の基礎と新しいアプローチ
2022/11/18

電気化学その場測定～回折法、分光法、顕微鏡観察～

ラマン分光法

京都大学大学院　工学研究科

宮原　雄人

*miyahara(at)elech.kuic.kyoto-u.ac.jp

Fundamentals of Raman spectroscopy

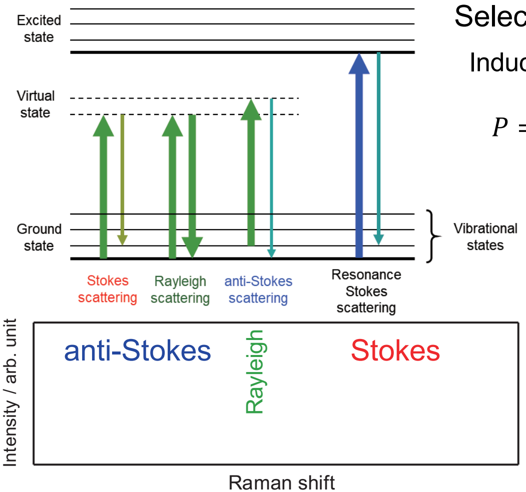

Excited state
Virtual state
Ground state
Vibrational states
Stokes scattering
Rayleigh scattering
anti-Stokes scattering
Resonance Stokes scattering
Intensity / arb. unit
anti-Stokes
Rayleigh
Stokes
Raman shift

Fig. Schematic illustrations of scattering processes and an example of Raman spectrum.

Selection rule: rate of **polarizability change** with atomic vibration

Induced dipole moment *P*

(Classical theory)

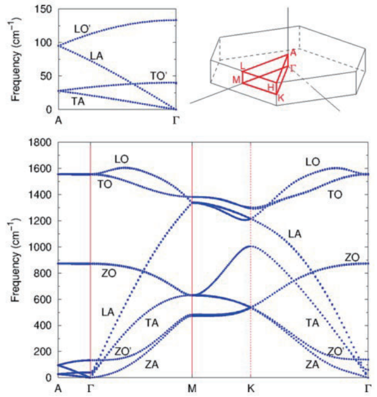
$$P = \underbrace{\alpha_0 E_0 \cos \omega_i t}_{\text{Rayleigh}} + \frac{1}{2}\boxed{\Sigma_k \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0} Q_k E_0 \{\underbrace{\cos(\omega_i - \omega_k)t}_{\text{Stokes}} + \underbrace{\cos(\omega_i + \omega_k)t}_{\text{anti-Stokes}}\}$$

α: polarizability E: electrical field induced by incident photon

ω_i, ω_k: angular frequencies of incident laser, and atomic vibration

Q_k: normal coordinate at equilibrium

Relationship between Raman shift and phonon dispersion



conservation of momentum

$$\vec{k_\mathrm{i}} = \vec{k_\mathrm{s}} \pm \vec{q}$$

wave vector

$\vec{k_\mathrm{i}}$: incident photon $\vec{q}$: phonon

$\vec{k_\mathrm{s}}$: scattered photon

Since $|\vec{q}| \ll \pi/a$,

Raman: Γ point

*Fig. Graphite phonon dispersion calculated with the optB88-vdW functional starting from the optimized equilibrium structure.

Definition of Raman shift

$$\Omega\ [\mathrm{cm}^{-1}] = \frac{10^7}{\lambda_i\ [\mathrm{nm}]} - \frac{10^7}{\lambda_{Raman}\ [\mathrm{nm}]}$$

Intensity ratio

$$\frac{I_\mathrm{AS}}{I_\mathrm{S}} = \frac{\sigma_\mathrm{AS}}{\sigma_\mathrm{S}} \frac{[(\nu_\mathrm{laser} + \Omega)^4]}{[(\nu_\mathrm{laser} - \Omega)^4]} \exp(-\frac{h\Omega}{k_\mathrm{B}T})$$

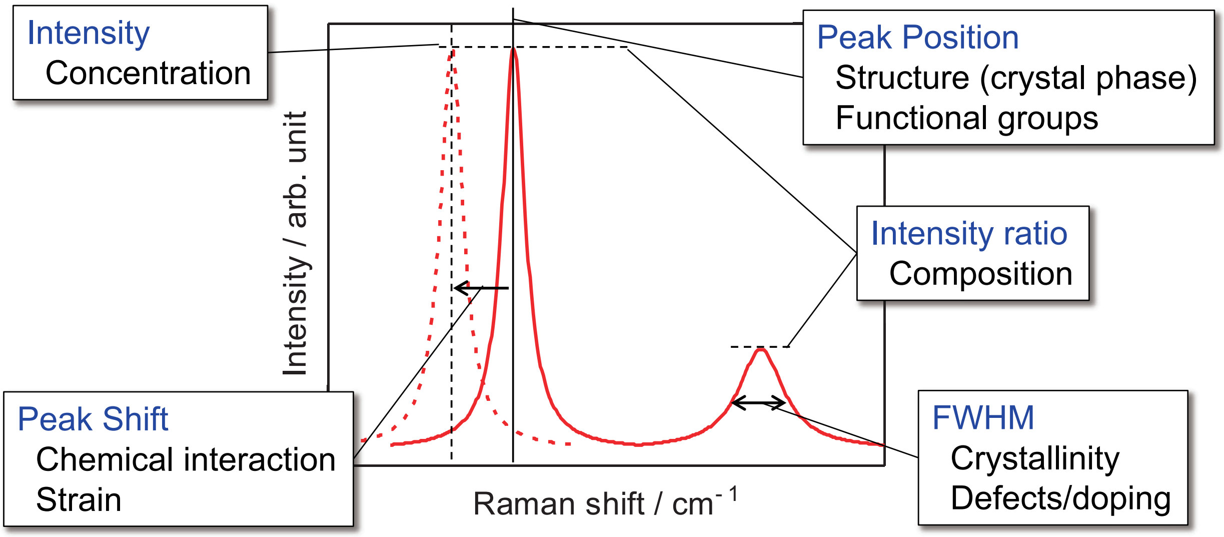
Ω: Raman shift

λ_laser: laser wavelength, λ_Raman: signal wavelength

ν_laser: laser wavenumber,, σ: cross section

*Reprinted with permission from [E. Hazrati *et al.*, *Phys. Rev. B*, **90,** 155448 (2014)]. Copyright 2014 by the American Physical Society.

Characteristics and comparison with other techniques


Intensity / arb. unit
Raman shift / cm-1

Intensity
Concentration

Peak Position
Structure (crystal phase)
Functional groups

Intensity ratio
Composition

Peak Shift
Chemical interaction
Strain

FWHM
Crystallinity
Defects/doping

Compared with IR…

- ☺ Complementary relation
- 😆 (μ-Raman) Better spatial resolution
- 😆 Suitable for Inorganics and Carbons
- ☹ Less informative for Organics

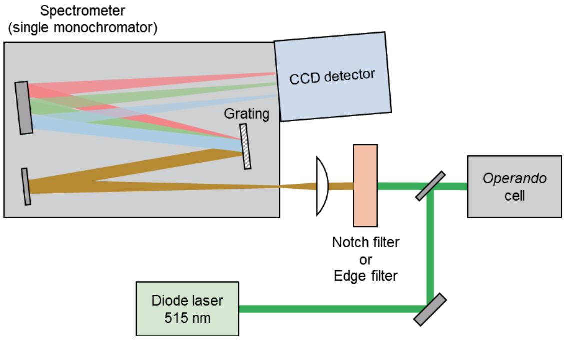
Compared with XRD…

- ☺ Surface characterization
  cf. optical skin depth (δ_p)
- 😆 Easier to fabricate the cell
- ☹ Unmeasurable for Metals

$$\delta_p = \sqrt{\frac{2\lambda}{\mu\sigma}}$$

λ: laser wavelength
μ: magnetic permeability
σ: electronic conductivity

Experimental setup of Raman spectrometer

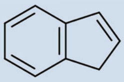

Spectrometer
(single monochromator)
CCD detector
Grating
Operando cell
Notch filter
or
Edge filter
Diode laser
515 nm

Detector

UV, VIS: CCD NIR: InGaAs

Recommendation:

calibration by Si wafer, indene etc…
(every time before use)



Spectrometer

longer focal length

→ { higher resolution
weaker stray light

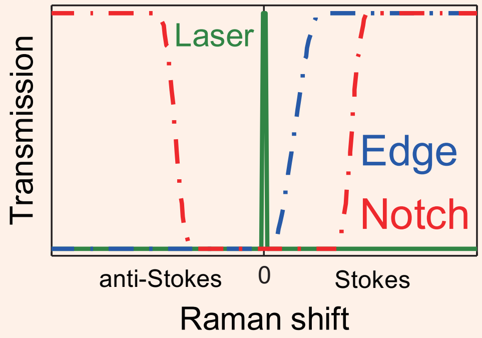
Grating

higher groove density

→ { higher resolution
lower spectral range

Filter

Edge filter	Notch filter
😆 small Stokes shifts	😆 anti-Stokes
☹ anti-Stokes	☹ small Raman shifts



Laser

Power (proportional to Raman signal) should be <1 mW μm^{-2}
Spectral stability should be confirmed in in situ/*operando* cell

Tips for the choice of wavelength (λ)

Raman intensity (I): $I \sim \lambda^{-4}$

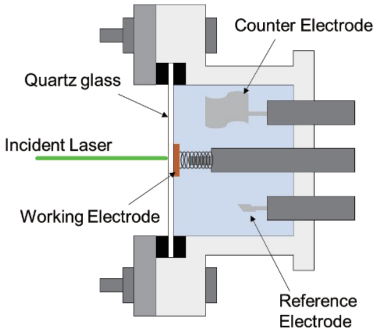
Enhanced intensity under resonant Raman condition
cf. UV–VIS spectrum, band gap

Electrolyte fluorescence: longer λ preferred to reduce

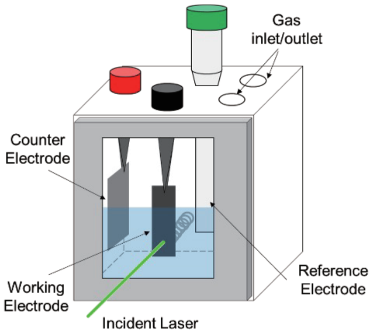
Examples of in situ/*operando* Raman cell

In-plane EC-Raman in our lab

For non-aqueous electrolytes


Counter Electrode
Quartz glass
Incident Laser
Working Electrode
Reference
Electrode

For aqueous electrolytes


Gas
inlet/outlet
Counter
Electrode
Working
Electrode
Incident Laser
Reference
Electrode

*Cross-sectional EC-Raman

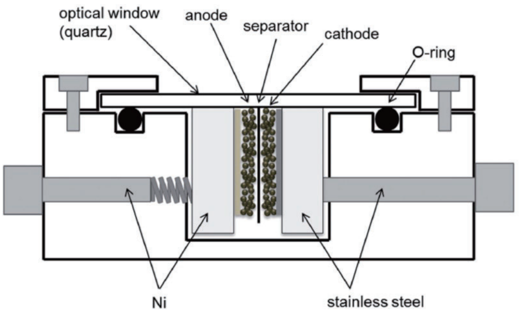
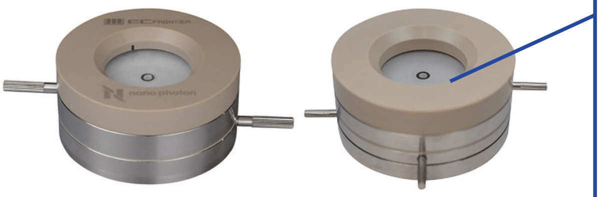

optical window
(quartz)
anode
separator
cathode
O-ring
Ni
stainless steel

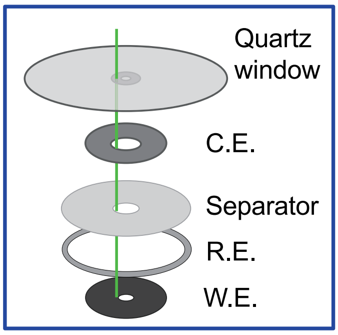
Fig. A schematic illustration (cross sectional view) of the in situ Raman cell. Reproduced from article written by H. Fukumitsu *et al.*, *Electrochemistry,* **83**, 993 (2015), with permission of The Electrochemical Society of Japan.

Commercially available cell

EC Frontier (Japan)*

SB6 (2 electrode) SB1300 (3 electrode)




Quartz
window
C.E.
Separator
R.E.
W.E.

Reprinted from https://ec-frontier.co.jp/product/index_cell.php.
Copyright EC FRONTIER CO., LTD.

Other companies

MTI (USA)

EL-CELL (Germany)

Redox.me (Sweden)

etc…

Signal enhancement by near-field effect

Near-field effect

→ resolution up to “*single molecule*” level

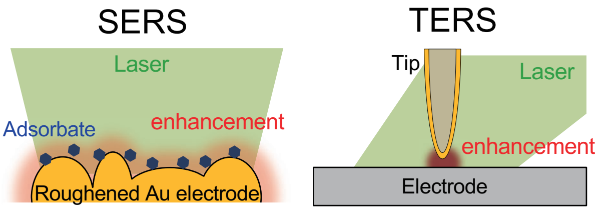

SERS
TERS
Laser
Adsorbate
enhancement
Roughened Au electrode
Tip
Laser
enhancement
Electrode

Fig. Schematic illustrations of SERS and TERS.

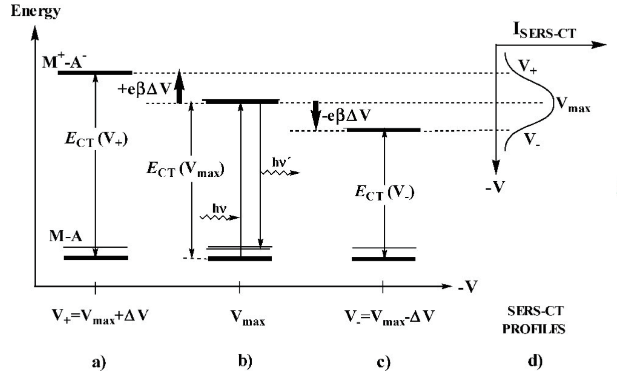

Energy
$I_{SERS\text{-}CT}$
$M^+\text{-}A^-$
$+e\beta\Delta V$
$-e\beta\Delta V$
$E_{CT}(V_+)$
$E_{CT}(V_{max})$
$E_{CT}(V_-)$
hν
hν′
M-A
V_+
V_{max}
V_-
-V
-V
$V_+=V_{max}+\Delta V$
V_{max}
$V_-=V_{max}-\Delta V$
SERS-CT PROFILES
a)
b)
c)
d)

Fig. Dependence of the energy of the CT level (ECT(V)) on the electrode potential (V) in the RR-CT mechanism of SERS.[2]

First EC-Raman: SERS by Fleischmann

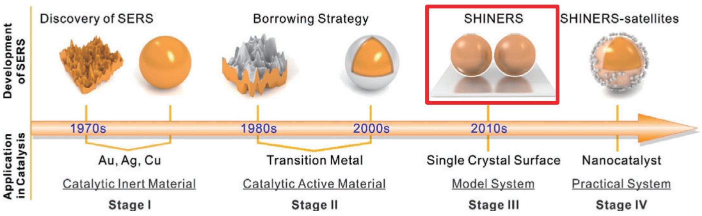

Development of SERS
Application in Catalysis
Discovery of SERS
Borrowing Strategy
SHINERS
SHINERS-satellites
1970s
1980s
2000s
2010s
Au, Ag, Cu
Catalytic Inert Material
Stage I
Transition Metal
Catalytic Active Material
Stage II
Single Crystal Surface
Model System
Stage III
Nanocatalyst
Practical System
Stage IV

Fig. Development of SERS and its applications in catalysis.[1]

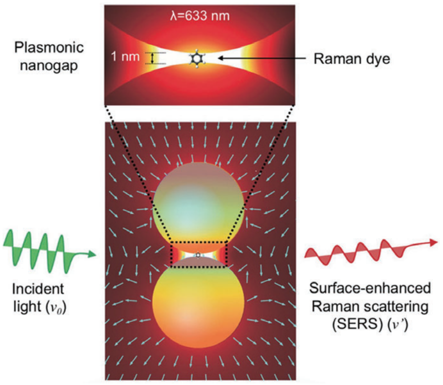
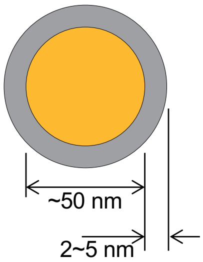

Plasmonic nanogap
λ=633 nm
1 nm
Raman dye
Incident light (ν_0)
Surface-enhanced Raman scattering (SERS) (ν')

Fig. Highly enhanced electromagnetic fields in the 1 nm gap of a dimer, and SERS from a dimeric nanostructure.[3]

SHINERS



Au@SiO$_2$

Electrochemically- and chemically-inert enhancer!

Reprinted with permission from [1]*Acc. Chem. Res.*, **53**, 729 (2020), [2]*J. Phys. Chem. B*, **107**, 13143 (2003), [3]*Acc. Chem. Res.*, **49**, 2746 (2016), Copyrights (2020) American Chemical Society, (2003) American Chemical Society, (2016) American Chemical Society,

---

Peak fitting of Raman spectra

(In principle) **Lorentzian** profile

$$f_L = A\frac{2}{\pi}\frac{\sigma}{4(x-x_0)^2+\sigma^2}$$

Environmental factors adds **Gaussian** profile

defects, inhomogeneities etc…

$$f_G = A\frac{2\sqrt{\ln 2}}{\sigma\sqrt{\pi}}\exp\left\{-4\ln(2)\frac{(x-x_0)^2}{\sigma^2}\right\}$$

[Note] suitable for amorphous materials

Useful functions in most cases

Voigtian profile

$$f_V(x) = A\int_{-\infty}^{+\infty} f_G(s) f_L(x-s)\,ds$$

or

Gaussian–Lorentzian (G–L) profile (**Pseudo-Voigt**)

$$f_{G-L}(x) = A(\alpha f_G + (1-\alpha) f_L)$$

Flowchart of peak fitting

Smoothing (if necessary)

Background subtraction by spline curve

Peak search, fitting by suitable function

[Note] “Fano effect” causes asymmetric profile

Interaction between discrete phonon and continuum electronic states

ex. Si, stage-1 GIC etc…

Solutions

- Introduction of asymmetric factor to G–L profile
- Use of Pearson type IV function*

Appl. Spectrosc.*, **71, 2325 (2017).

顕微鏡観察
～コンフォーカル顕微鏡観察とラマンイメージング測定～

国立研究開発法人 産業技術総合研究所
エネルギー・環境領域 電池技術研究部門
蓄電デバイス研究グループ 研究員
乙山 美紗恵

コンフォーカル顕微鏡の特長・歴史

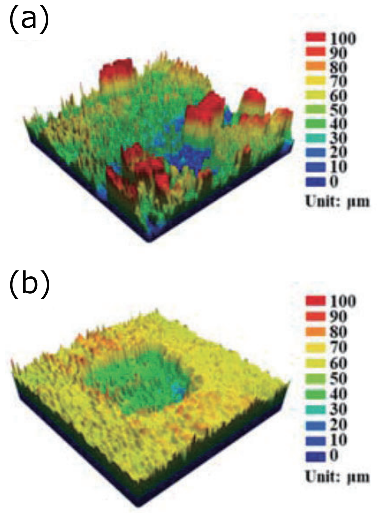
【特長】

- ●サンプルをz方向(深さ方向)に動かしながら、様々な深さでのピントの合った2次元画像を取得し、それを再構築することで、凹凸のあるサンプルでも観察領域全体でピントの合った、高分解能・高コントラストで鮮明な観察像を得ることが可能
- ●非破壊・非接触で三次元情報の取得が可能
- ●反応が進行する様子を観察したり、表面形状の変化を3次元的に観察したりする際に、in situ/*operando*顕微鏡観察が用いられる（分野は多岐にわたる）

【歴史】

- ●ミンスキー氏が1957年にコンフォーカル顕微鏡のコンセプトを発表
- ●1987年に市販のコンフォーカル顕微鏡が登場

(a)改質前と(b)改質後のN-doped carbon hostに対するZn析出の3D図 [1]

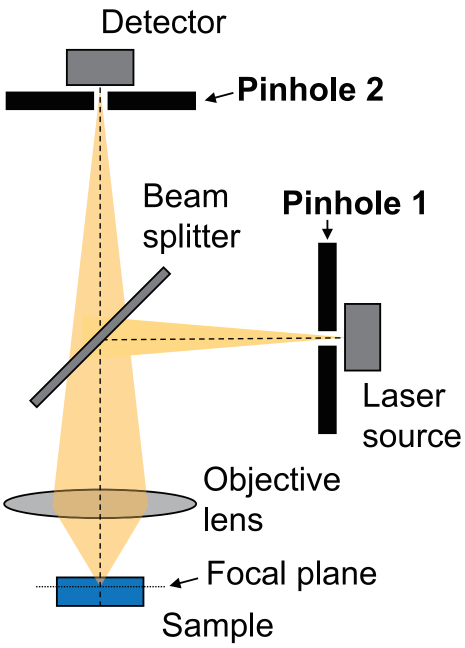


---

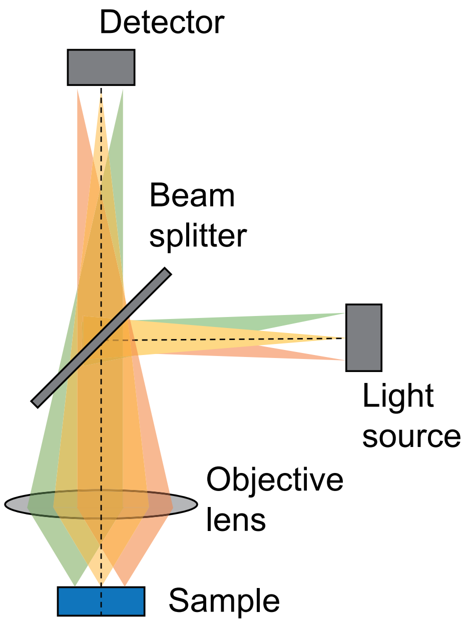
[1] Reprinted with permission from L. Zeng *et al.*, *Adv. Energy Mater.*, **12**, 2103708 (2022). Copyright 2022, Wiley-VCH GmbH.

コンフォーカル光学系

(a) コンフォーカル顕微鏡


Detector
Pinhole 2
Beam splitter
Pinhole 1
Laser source
Objective lens
Focal plane
Sample

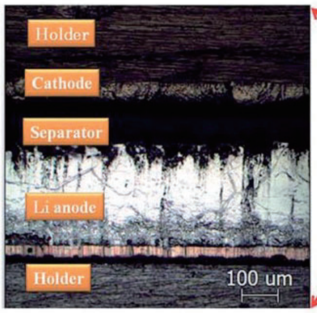
(b) 従来の光学顕微鏡


Detector
Beam splitter
Light source
Objective lens
Sample

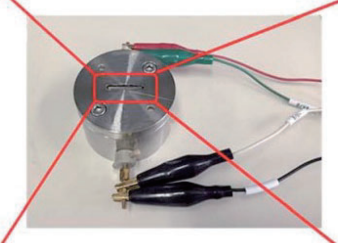
- コンフォーカル顕微鏡は、ピンホールが二つある。
- 焦点が合っていない場合は反射光がピンホール 2 で遮られ、焦点のあった反射光のみ検出する。そのため、凹凸のあるサンプルでも鮮明な像が得られる。

Liデンドライト発生の*operando*観察

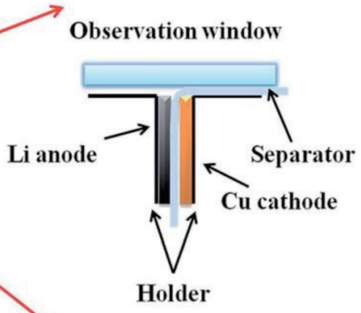
顕微鏡像


Holder
Cathode
Separator
Li anode
Holder
100 um

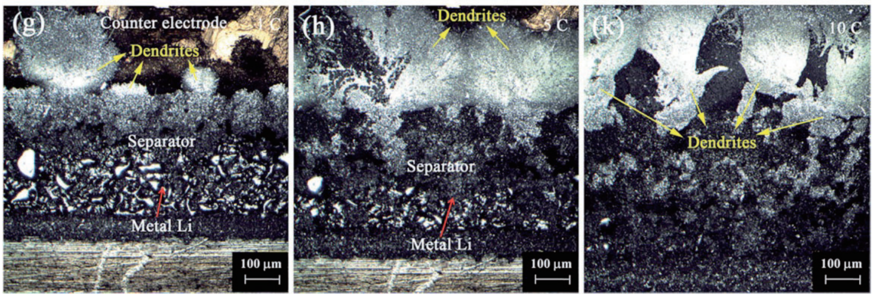
観察用セル



セル内の様子


Observation window
Li anode
Separator
Cu cathode
Holder

Liデンドライト発生の様子


1C (0.5 mA cm⁻²) 5C (2.5 mA cm⁻²) 10C (5.0 mA cm⁻²)
(g)
Counter electrode
1C
Dendrites
Separator
Metal Li
100 µm
(h)
Dendrites
5C
Separator
Metal Li
100 µm
(k)
10C
Dendrites
100 µm

各Cレートで3時間ずつ溶解析出試験を行い、計18時間観察し、最終的に30秒の動画を作成

[2] Reprinted with permission from Y. J. Zhang *et al.*, *J. Mater. Chem. A*, **4**, 15597 (2016). Copyright 2016 Royal Society of Chemistry.

第51回電気化学講習会
電気化学の基礎と新しいアプローチ

電気化学その場測定
～ 顕微鏡観察 ～
基礎編

津田　哲哉
千葉大学　大学院工学研究院　物質科学コース
ttsuda@chiba-u.jp

Chiba University

光学顕微鏡と電子顕微鏡

光学顕微鏡

長所

- 大気中で観察可能
  → 液体中にある試料をそのまま観察できる
- 試料の前処理が不要
- 観察によるアーティファクトがない
- 色情報を得ることができる

短所

- 高倍率になればなるほど、焦点深度が浅くなる
- 観察対象が10 μmを下回ると観察が難しい

電子顕微鏡

長所

- 原子レベルの観察が可能（TEM）
- ナノスケールまで観察できる（SEM）
- 元素の種類によって、輝度が異なる
  → 元素分布に関する情報が得られる
- 電子線回折像が得られる（TEM）
- 多元素マッピングが容易（EDX）

短所

- 電子線照射により、アーティファクトが生じる
- 観察対象は真空条件下で安定なものに限られる
- 試料に電子伝導性がないとチャージアップする

電気化学反応の光学顕微鏡･電子顕微鏡観察

光学顕微鏡像

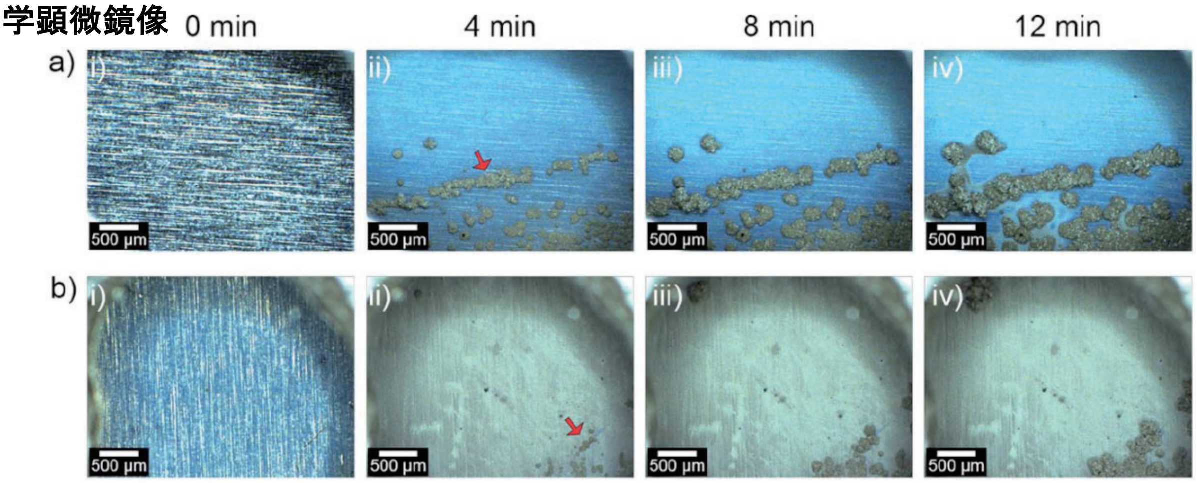
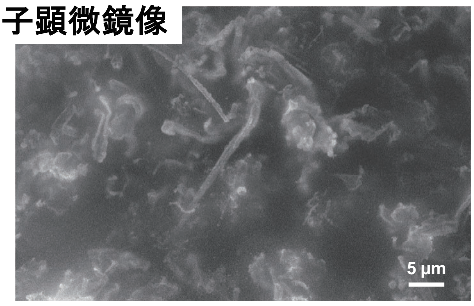

0 min
4 min
8 min
12 min
a)
i)
ii)
iii)
iv)
b)
500 μm

Figure 7. Deposition of Li metal as captured in optical cells using an electrolyte consisting of 1.0 M $LiPF_6$ in EC/DEC with a current density of 4 mA cm^{-2}. (a) A bare stainless-steel electrode shown at various times during deposition; (b) an Ag-coated electrode at various times during deposition. Red arrows denote dendritic growth in (ii).

McDowell, *et al.*, *J. Electrochem. Soc.*, **168**, 100517 (2021).

電子顕微鏡像



← Typical example of in situ SEM observation of Li deposition.

広範囲の情報が必要

→ **光学顕微鏡（デジタル顕微鏡）**

微小領域/元素分布の情報が必要

→ **電子顕微鏡** **最近はこちらが主！**

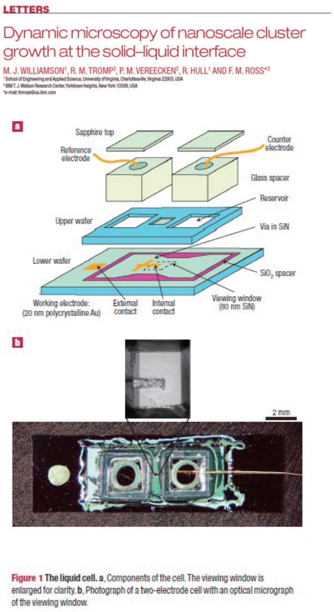
欲しい情報によって、顕微鏡の種類を選択する。

電気化学反応の電子顕微鏡観察

最近では、低真空や大気圧で測定できるSEMが市販されている

種々の理由から（電解液の揮発、分解能の低下など）、その場観察には適さない！

フィードスルーを備えた通常型電子顕微鏡と電子線が透過できる窓を持つ密閉型電気化学セルを組み合わせることが一般的



LETTERS

Dynamic microscopy of nanoscale cluster growth at the solid–liquid interface

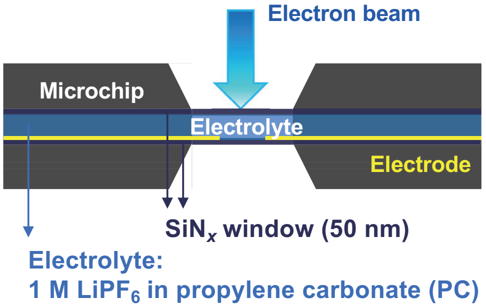
M. J. WILLIAMSON[1], R. M. TROMP[2], P. M. VEREECKEN[2], R. HULL[1] AND F. M. ROSS*[2]

[1] School of Engineering and Applied Science, University of Virginia, Charlottesville, Virginia 22903, USA
[2] IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, USA
*e-mail: fmross@us.ibm.com

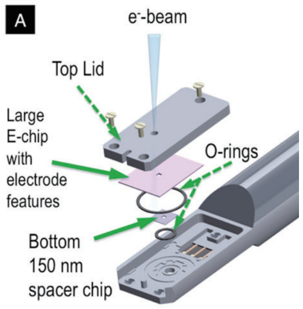
a
Sapphire top
Reference electrode
Counter electrode
Glass spacer
Reservoir
Upper wafer
Via in SiN
Lower wafer
SiO_2 spacer
Working electrode: (20 nm polycrystalline Au)
External contact
Internal contact
Viewing window (80 nm SiN)
b
2 mm

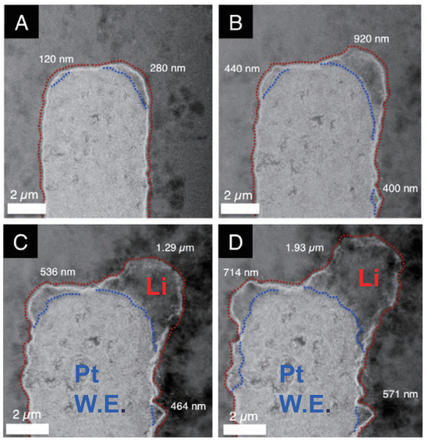
Figure 1 The liquid cell. a, Components of the cell. The viewing window is enlarged for clarity. **b**, Photograph of a two-electrode cell with an optical micrograph of the viewing window.

Ross, *et al.*, *Nat. Mater.*, **2**, 532 (2003).


Electron beam
Microchip
Electrolyte
Electrode
SiN_x window (50 nm)

Electrolyte:
1 M $LiPF_6$ in propylene carbonate (PC)


A
e⁻-beam
Top Lid
Large E-chip with electrode features
O-rings
Bottom 150 nm spacer chip


A
120 nm
280 nm
2 μm
B
920 nm
440 nm
400 nm
C
1.29 μm
536 nm
Li
Pt W.E.
464 nm
D
1.93 μm
714 nm
571 nm

Browning, *et al.*, *Chem. Commun.* **50**, 2104 (2014).
Browning, *et al.*, *Nano Lett.* **15,** 2168 (2015).

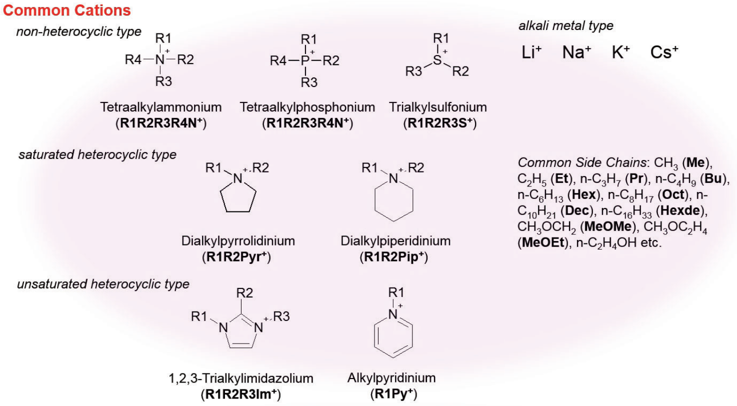
電極の交換がすぐにはできない！
セットアップが難しい！
十分な解像度が得られない！

密閉型電気化学セルを使用しない方法は？

イオン液体や固体電解質のような難揮発性電解質であれば、
密閉セルを使用する必要はない！

イオン液体の特徴

- 電気化学窓が広い (~ 5.5 V)、イオン伝導度が比較的高い (~ 110 mS cm^{-1})、使用温度域が広い (173 ~ 623 K)
- 難燃性、難揮発性、難帯電性 → 環境調和性が高い（＝ グリーンソルベント）

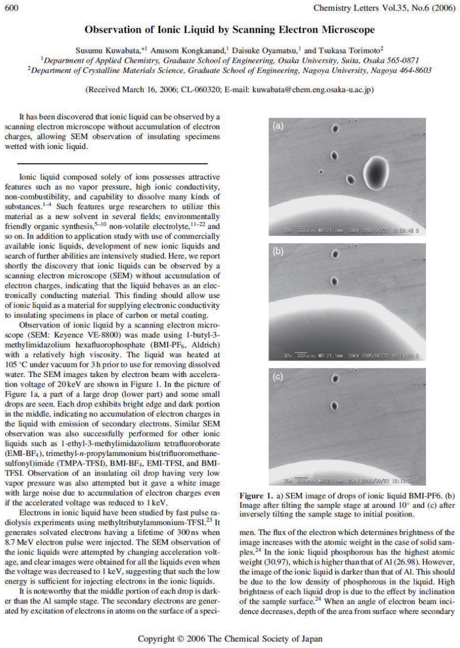

Common Cations
non-heterocyclic type
Tetraalkylammonium
(R1R2R3R4N+)
Tetraalkylphosphonium
(R1R2R3R4N+)
Trialkylsulfonium
(R1R2R3S+)
alkali metal type
Li+ Na+ K+ Cs+
saturated heterocyclic type
Dialkylpyrrolidinium
(R1R2Pyr+)
Dialkylpiperidinium
(R1R2Pip+)
unsaturated heterocyclic type
1,2,3-Trialkylimidazolium
(R1R2R3Im+)
Alkylpyridinium
(R1Py+)
R1
R2
R3
R4

Common Side Chains: CH$_3$ (**Me**), C$_2$H$_5$ (**Et**), n-C$_3$H$_7$ (**Pr**), n-C$_4$H$_9$ (**Bu**), n-C$_6$H$_{13}$ (**Hex**), n-C$_8$H$_{17}$ (**Oct**), n-C$_{10}$H$_{21}$ (**Dec**), n-C$_{16}$H$_{33}$ (**Hexde**), CH$_3$OCH$_2$ (**MeOMe**), CH$_3$OC$_2$H$_4$ (**MeOEt**), n-C$_2$H$_4$OH etc.

Common Anions

BF$_4^-$, B(CN)$_4^-$, CF$_3$BF$_3^-$, C$_2$F$_5$BF$_3^-$, *n*-C$_3$F$_7$BF$_3^-$, *n*-C$_4$F$_9$BF$_3^-$, PF$_6^-$, (C$_2$F$_5$)$_3$PF$_3^-$ (**FAP$^-$**), CF$_3$CO$_2^-$, CF$_3$SO$_3^-$ (**TfO$^-$**), N(SO$_2$CF$_3$)$_2^-$ (**Tf$_2$N$^-$**), N(COCF$_3$)(SO$_2$CF$_3$)$^-$, N(SO$_2$F)$_2^-$ (**FSA$^-$**), EtOSO$_3^-$, N(CN)$_2^-$, C(CN)$_3^-$, SCN$^-$, SeCN$^-$, CuCl$_2^-$, AlCl$_4^-$, Al$_2$Cl$_7^-$, ZnCl$_4^{2-}$, F(HF)$_{2.3}^-$ etc.

イオン液体そのものを観察することはもちろん、チャージアップや乾燥を防ぐコーティング剤としての利用も可能


600 Chemistry Letters Vol.35, No.6 (2006)

Observation of Ionic Liquid by Scanning Electron Microscope

Susumu Kuwabata,*[1] Anusorn Kongkanand,[1] Daisuke Oyamatsu,[1] and Tsukasa Torimoto[2]
[1]*Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871*
[2]*Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Nagoya 464-8603*

(Received March 16, 2006; CL-060320; E-mail: kuwabata@chem.eng.osaka-u.ac.jp)

It has been discovered that ionic liquid can be observed by a scanning electron microscope without accumulation of electron charges, allowing SEM observation of insulating specimens wetted with ionic liquid.

Ionic liquid composed solely of ions possesses attractive features such as no vapor pressure, high ionic conductivity, non-combustibility, and capability to dissolve many kinds of substances.[1–4] Such features urge researchers to utilize this material as a new solvent in several fields; environmentally friendly organic synthesis,[5–10] non-volatile electrolyte,[11–22] and so on. In addition to application study with use of commercially available ionic liquids, development of new ionic liquids and search of further abilities are intensively studied. Here, we report shortly the discovery that ionic liquids can be observed by a scanning electron microscope (SEM) without accumulation of electron charges, indicating that the liquid behaves as an electronically conducting material. This finding should allow use of ionic liquid as a material for supplying electronic conductivity to insulating specimens in place of carbon or metal coating.

Observation of ionic liquid by a scanning electron microscope (SEM: Keyence VE-8800) was made using 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF$_6$, Aldrich) with a relatively high viscosity. The liquid was heated at 105 °C under vacuum for 3 h prior to use for removing dissolved water. The SEM images taken by electron beam with acceleration voltage of 20 keV are shown in Figure 1. In the picture of Figure 1a, a part of a large drop (lower part) and some small drops are seen. Each drop exhibits bright edge and dark portion in the middle, indicating no accumulation of electron charges in the liquid with emission of secondary electrons. Similar SEM observation was also successfully performed for other ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF$_4$), trimethyl-*n*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI), BMI-BF$_4$, EMI-TFSI, and BMI-TFSI. Observation of an insulating oil drop having very low vapor pressure was also attempted but it gave a white image with large noise due to accumulation of electron charges even if the accelerated voltage was reduced to 1 keV.

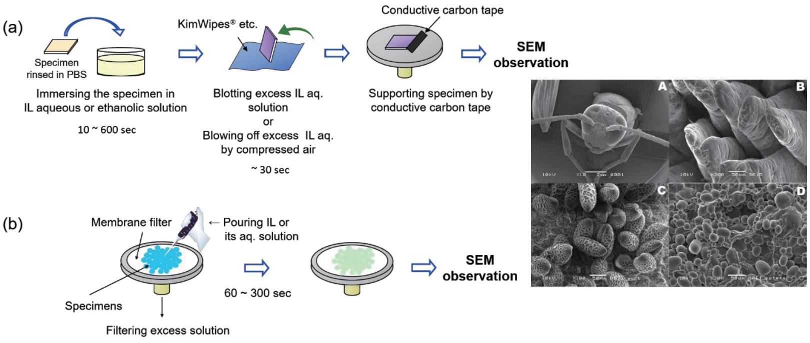
Electrons in ionic liquid have been studied by fast pulse radiolysis experiments using methyltributylammonium-TFSI.[23] It generates solvated electrons having a lifetime of 300 ns when 8.7 MeV electron pulse were injected. The SEM observation of the ionic liquids were attempted by changing acceleration voltage, and clear images were obtained for all the liquids even when the voltage was decreased to 1 keV, suggesting that such the low energy is sufficient for injecting electrons in the ionic liquids.

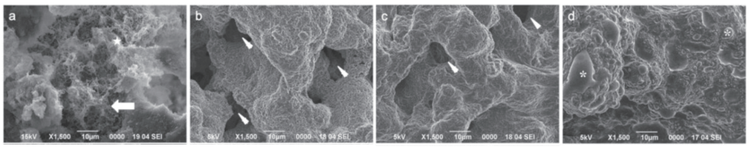
It is noteworthy that the middle portion of each drop is darker than the Al sample stage. The secondary electrons are generated by excitation of electrons in atoms on the surface of a specimen. The flux of the electron which determines brightness of the image increases with the atomic weight in the case of solid samples.[24] In the ionic liquid phosphorous has the highest atomic weight (30.97), which is higher than that of Al (26.98). However, the image of the ionic liquid is darker than that of Al. This should be due to the low density of phosphorous in the liquid. High brightness of each liquid drop is due to the effect by inclination of the sample surface.[24] When an angle of electron beam incidence decreases, depth of the area from surface where secondary

Figure 1. a) SEM image of drops of ionic liquid BMI-PF6. (b) Image after tilting the sample stage at around 10° and (c) after inversely tilting the sample stage to initial position.

(a)
(b)
(c)
30x 333μm WD:21.1mm 20kV 2005/08/23 16:08:48 S
30x 333μm WD:21.1mm 20kV 2005/08/23 16:11:28 S
30x 333μm WD:21.1mm 20kV 2005/08/23 16:13:53 S

Copyright © 2006 The Chemical Society of Japan


(a)
Specimen rinsed in PBS
KimWipes® etc.
Conductive carbon tape
SEM observation
Immersing the specimen in IL aqueous or ethanolic solution
10 ~ 600 sec
Blotting excess IL aq. solution
or
Blowing off excess IL aq. by compressed air
~ 30 sec
Supporting specimen by conductive carbon tape
(b)
Membrane filter
← Pouring IL or its aq. solution
Specimens
60 ~ 300 sec
SEM observation
Filtering excess solution
A
B
C
D



↑ SEM images of S. mutans biofilms pretreated with (a) conventional way and (b-d) Scheme a. The used ILs are (b) [Ch][Lac], (c) [C$_2$mim][CH$_3$CO$_2$], and (d) [C$_4$mim][Tf$_2$N].

Microscopy, **69**, 183 (2020).

電気化学反応のその場電子顕微鏡観察にも利用できる！