



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2)

(北海道大学) 松井雅樹

(立命館大学) 折笠有基

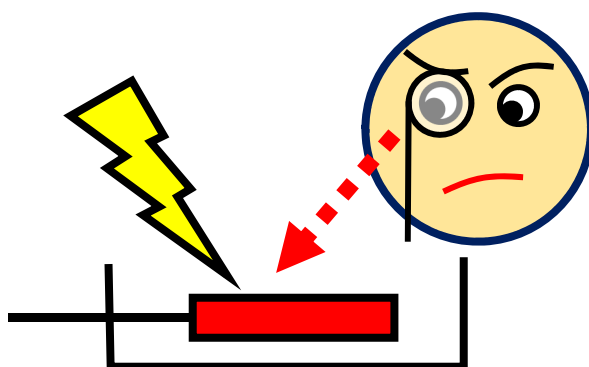
(京都大学) 内山智貴

西 直哉

宮原雄人

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(産業技術総合研究所) 乙山美紗恵



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Electrochemical In Situ/*operando* Spectroscopy and Microscopy Part 2: Battery Applications

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X線回折・X線吸収分光

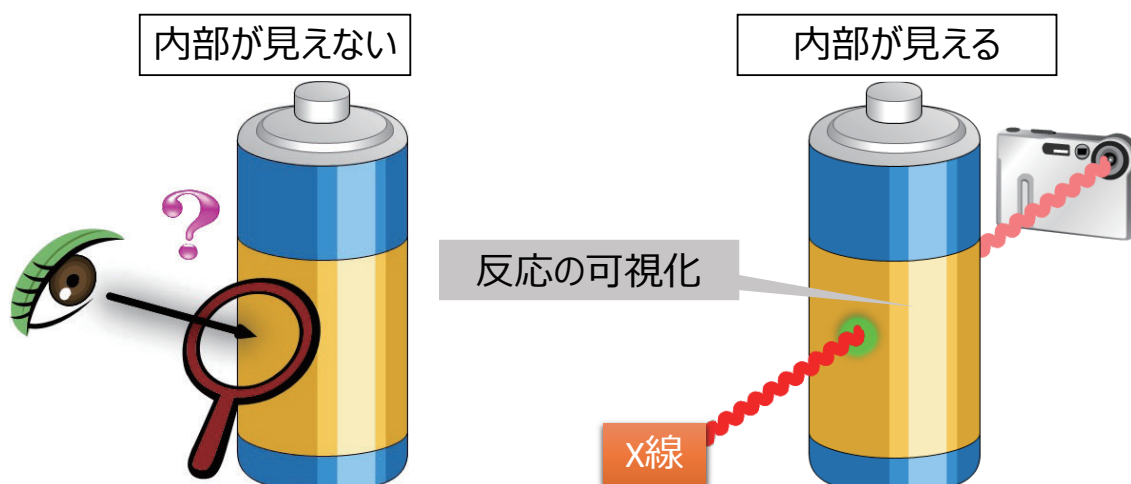


折笠有基（立命館大学）
内山智貴（京都大学）



1

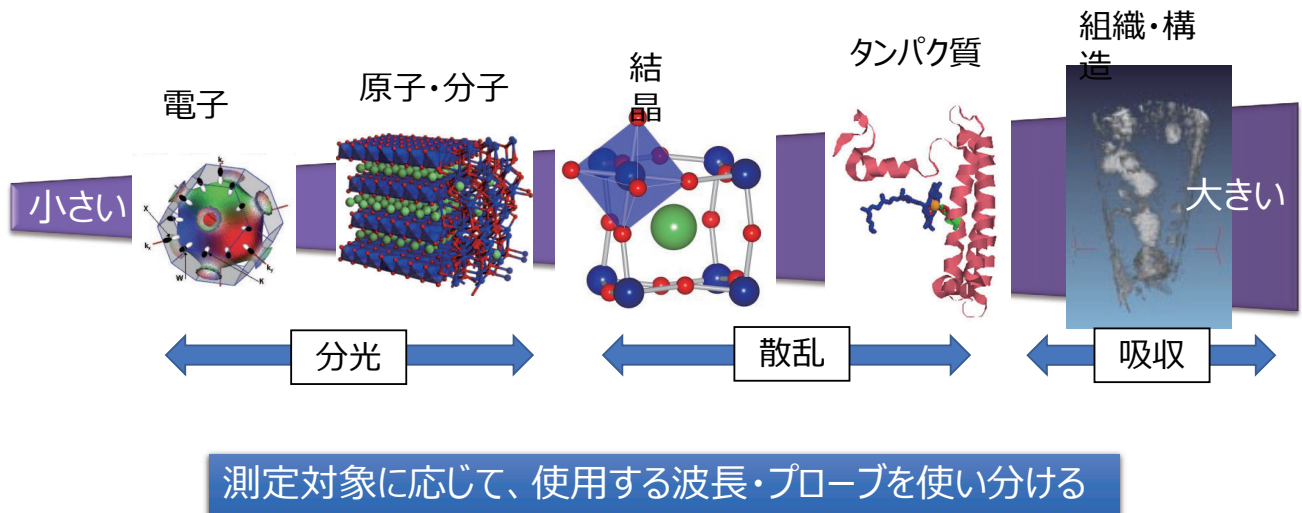
電気化学測定中のスペクトル観察



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

2

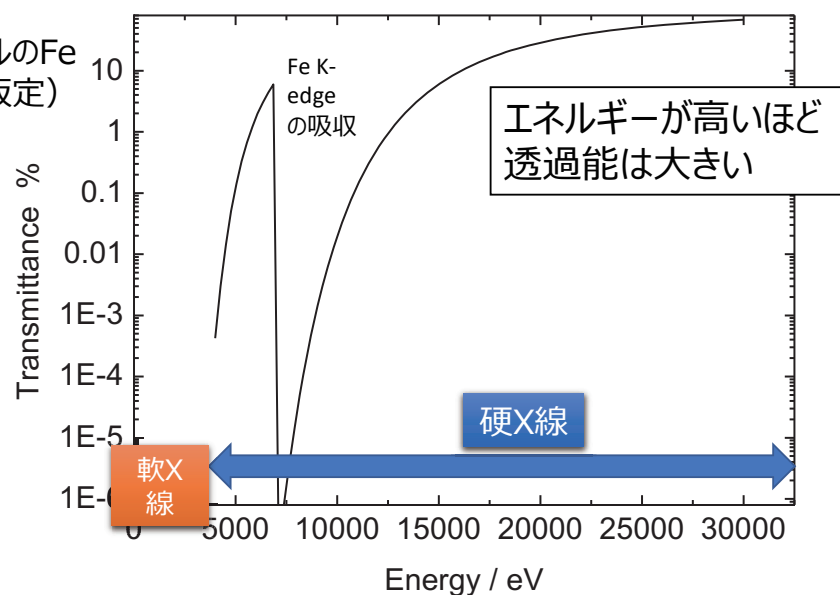
X線を用いた解析がカバーする領域



3

X線のエネルギーと透過率

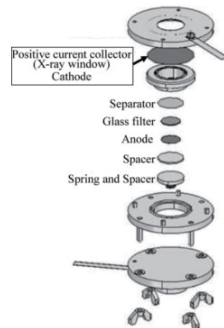
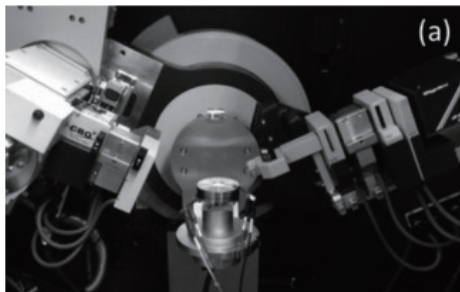
厚み100マイクロメートルのFe
(密度5.0 g/cm³を仮定)
を透過するX線の割合



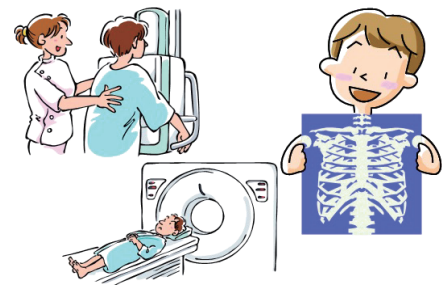
4

実験室で使用するX線

X線回折



レントゲン・X線CT

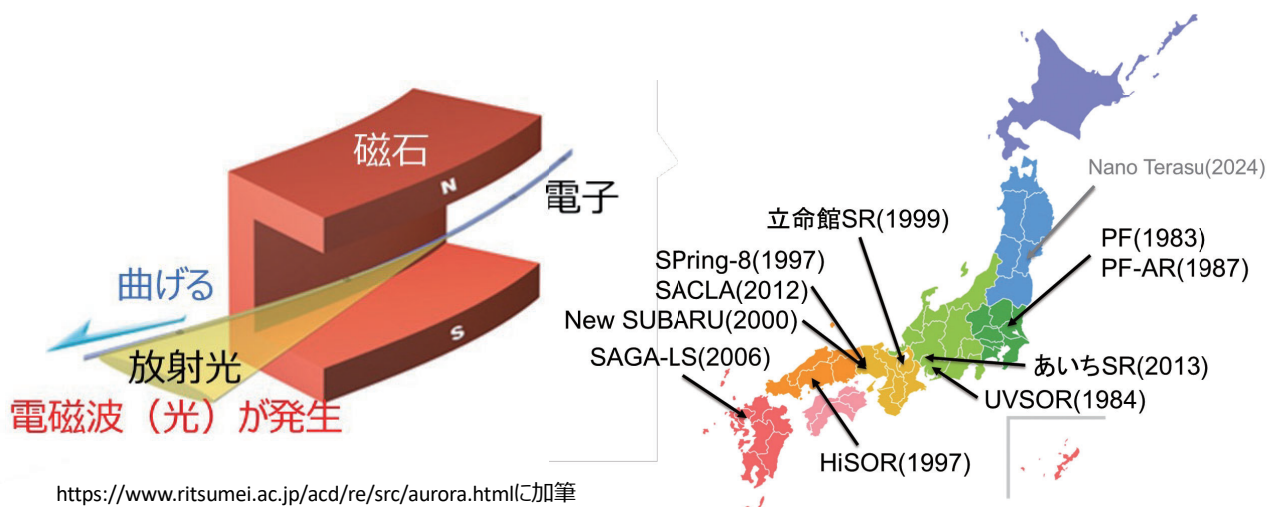


T. Konya, Y. Shiramata, T. Nakamura, *BUNSEKI KAGAKU*, **68** 793-800 (2019).

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

5

放射光の利用

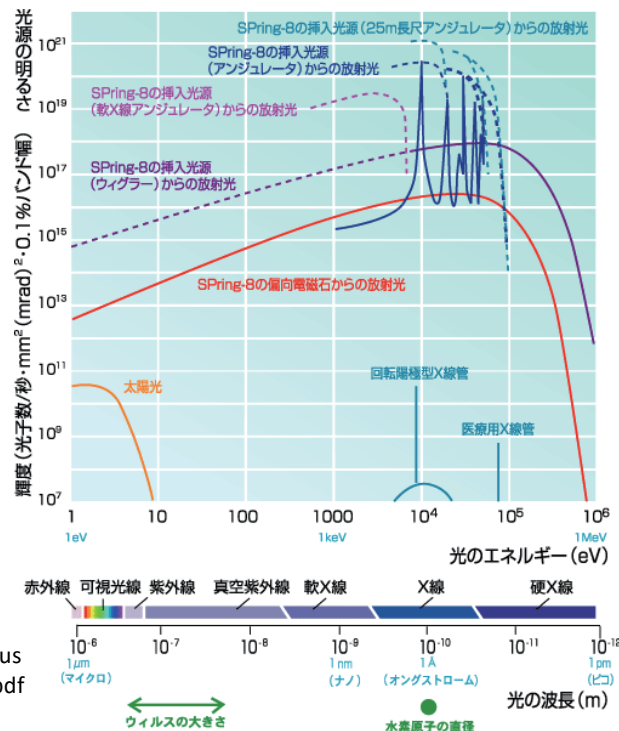


<https://www.ritsumeai.ac.jp/acd/re/src/aurora.html>に加筆

エネルギーを変えることが容易で、光が明るい

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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

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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 $10^3 \sim 10^6$ 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。

8

実験できる主な手法と適用の目安

主な手法

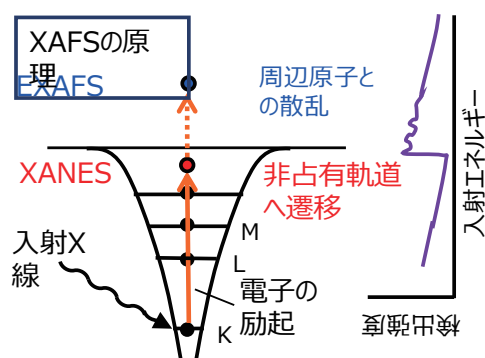
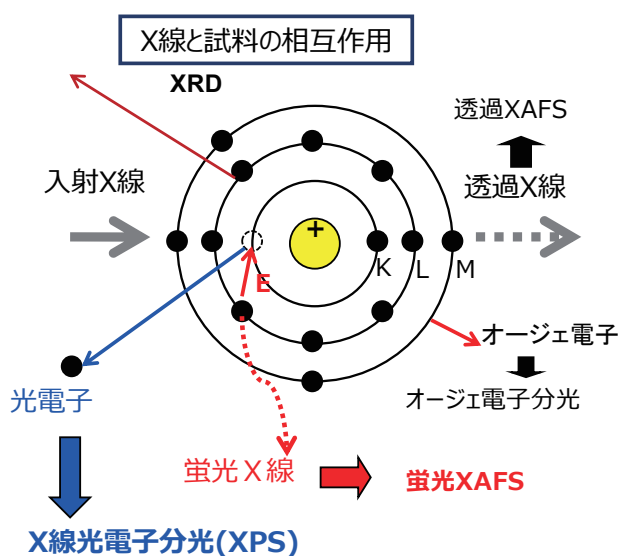
- X線回折 – 結晶構造
 - X線吸収 – 電子・局所構造
 - X線蛍光分析 – 元素分析
 - X線光電子分光 – 化学状態
 - X線反射率 – 表面構造
 - 小角散乱 – 微細構造
 - X線散乱 – 短中距離の構造情報
 - X線CT（イメージング） – 3次元形態
 - 赤外分光 – 分子の化学構造
- 等

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のが望ましい

- 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

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放射光X線を用いた分光測定手法

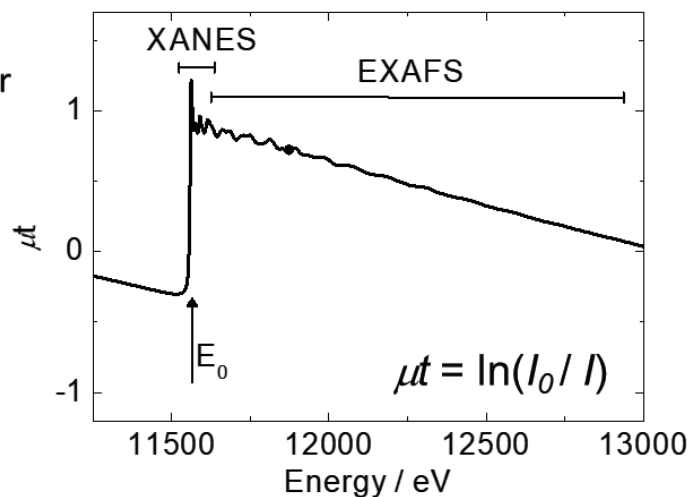
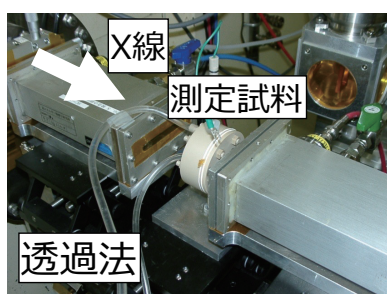
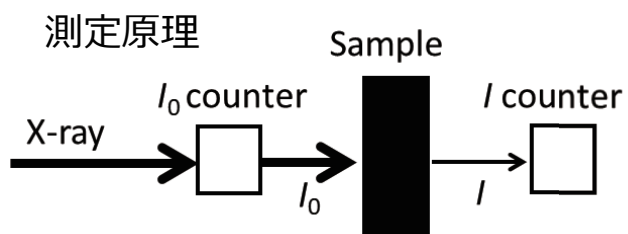


XANES: 非占有軌道への励起過程
⇒ 電子状態(価数)、対称性など

EXAFS: 散乱効果による振動
⇒ 局所構造(配位数、結合距離など)

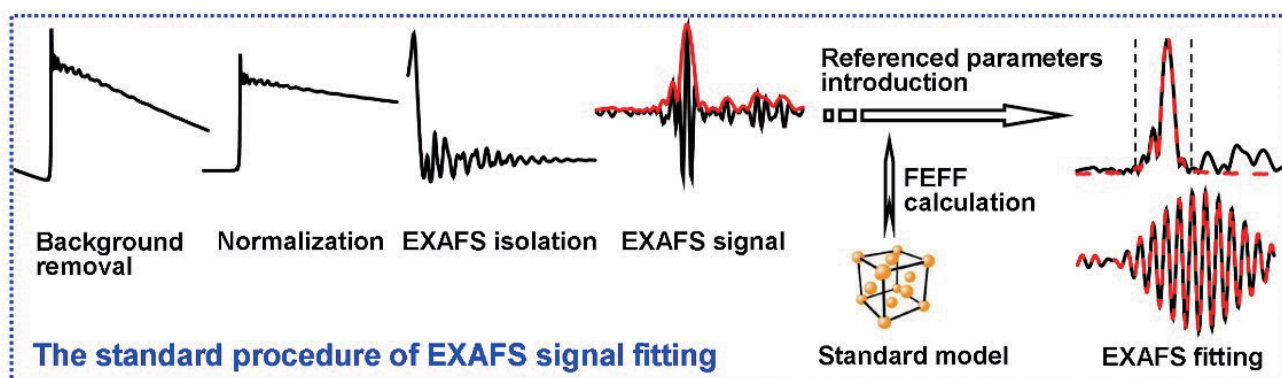
10

X線吸収分光法



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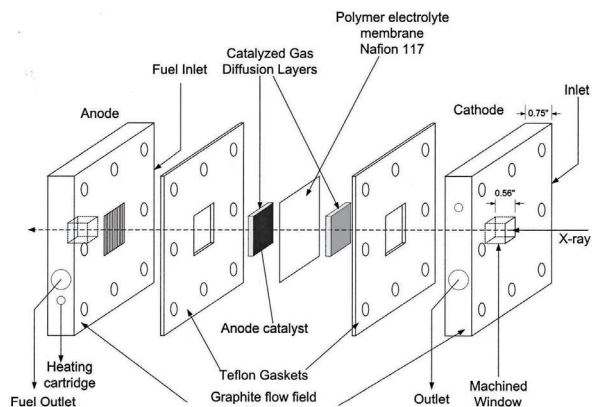
解析方法



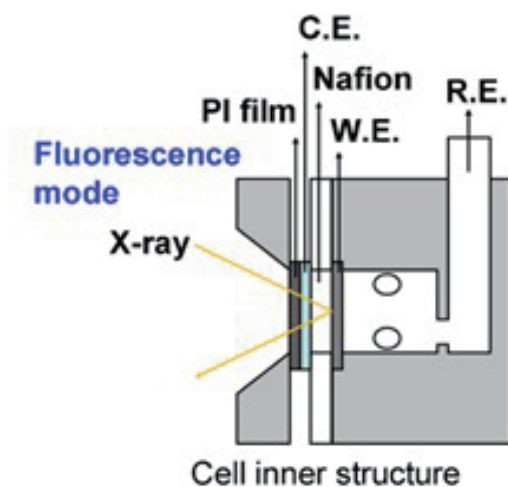
X. Wang, Y. Orikasa, Y. Takesue, H. Inoue, M. Nakamura, T. Minato, N. Hoshi, Y. Uchimoto, *J. Am. Chem. Soc.*, **135**, 5938 (2013).

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燃料電池オペランドセルの例



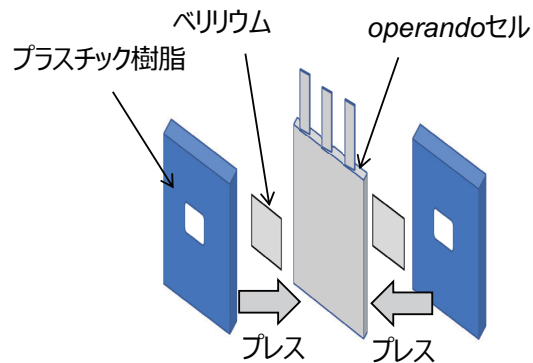
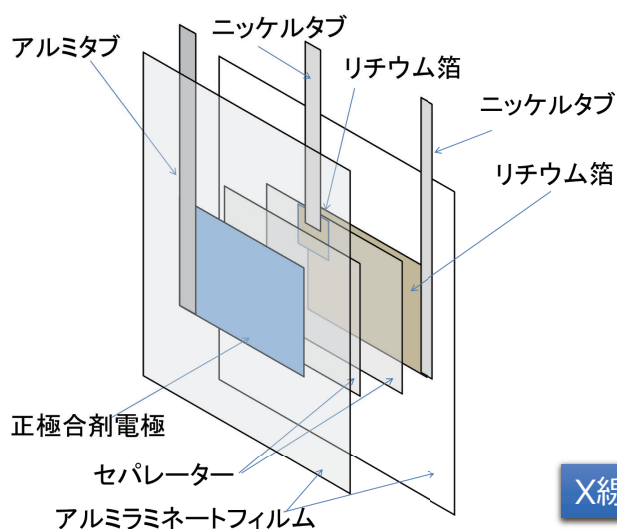
R. Viswanathan, R. Liu, E.S. Smotkin, *Rev. Sci. Instrum.*, **73**, 2124 (2002).



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

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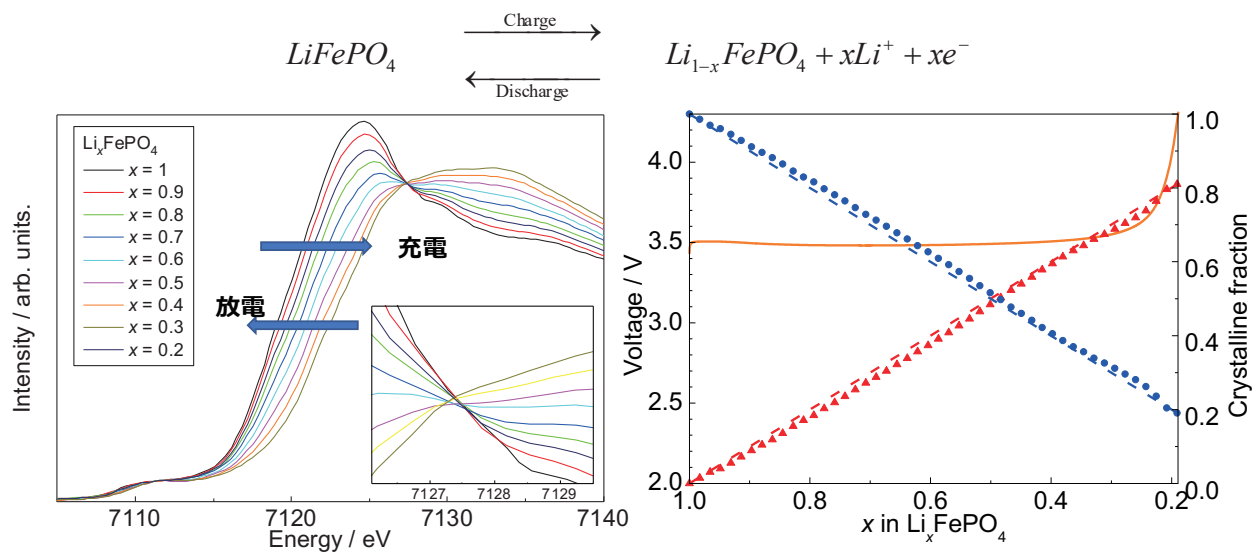
リチウムイオン電池における適用例



X線の通り道にある元素をすべて把握することが重要

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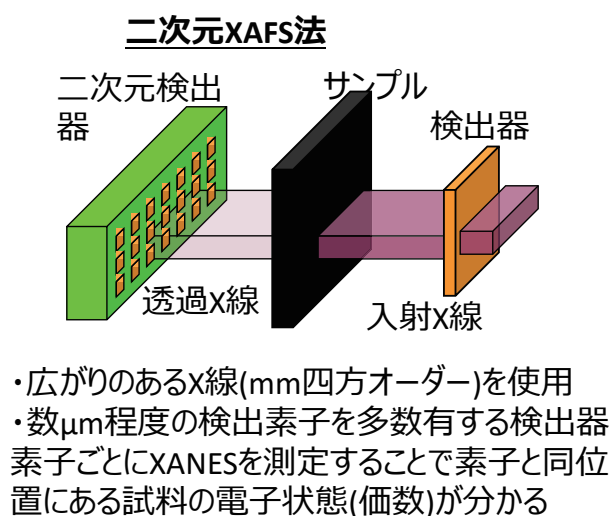
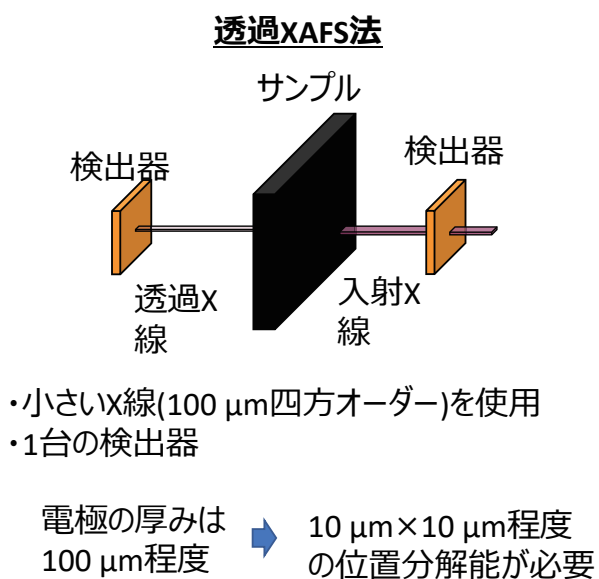
正極反応とXANESスペクトル



電池を充電すると遷移金属が酸化され、吸収端エネルギーが高エネルギー側にシフトする

15

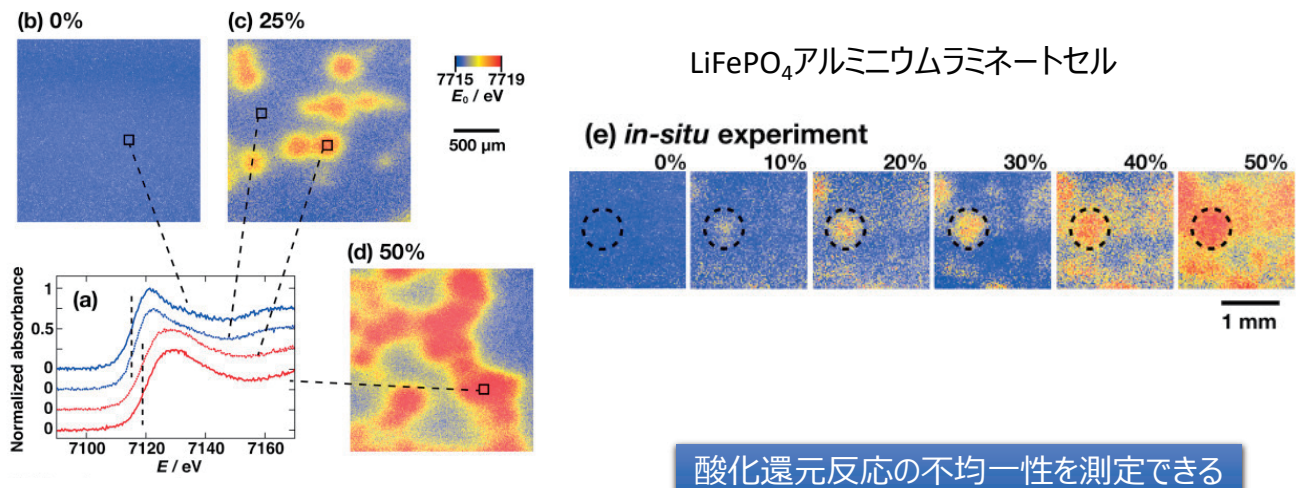
二次元XAFS測定方法



位置分解能を有するXAFS測定が可能

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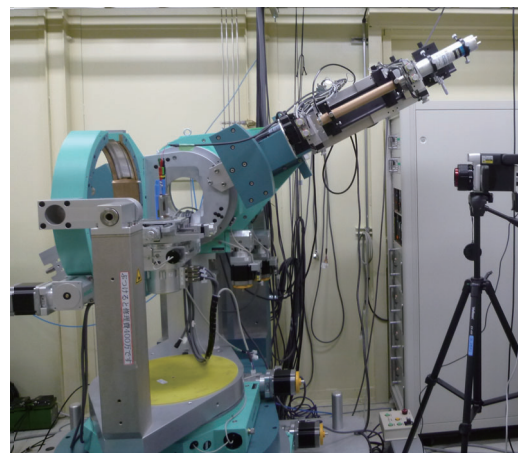
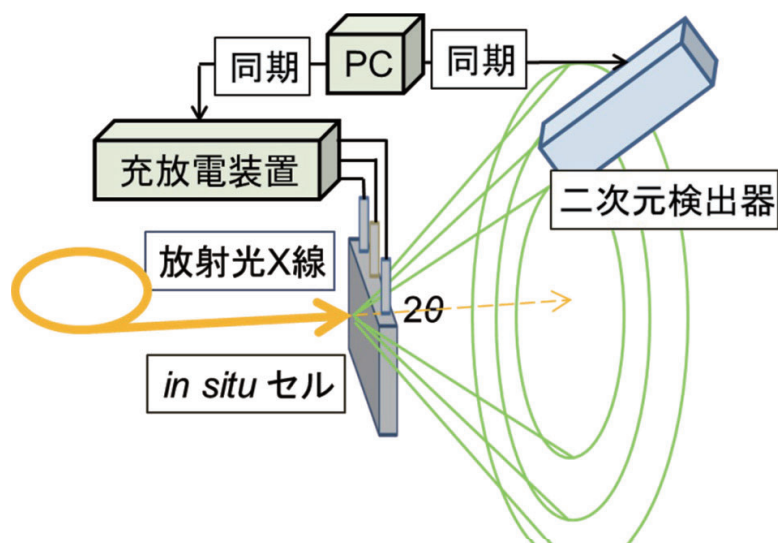
二次元XAFSによる電極不均一性



M. Katayama et al, *J. Power Sources*, **269**, 994 (2014).

17

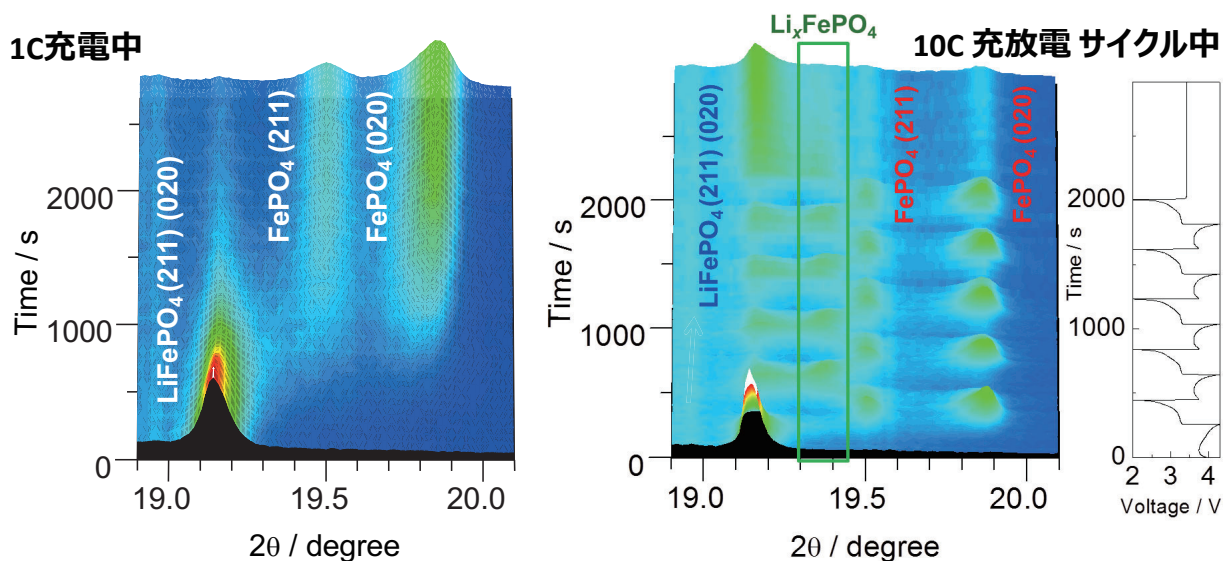
X線回折



デバイリングの一部を連続的に計測すると時間分解測定ができる

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オペランドXRDの例

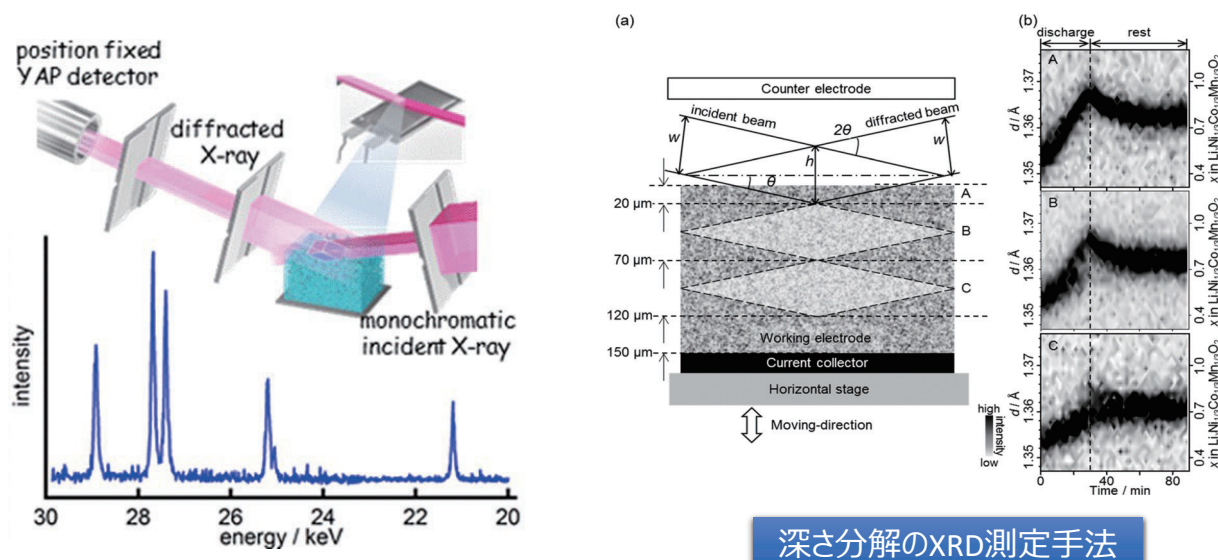


Y. Oriokasa, T. Maeda, Y. Koyama, *et al*, *Chem. Mater.*, **25**, 1032-1039 (2013).

Y. Oriokasa, T. Maeda, Y. Koyama, *et al*, *J. Am. Chem. Soc.*, **135**, 5497-5500 (2013).

19

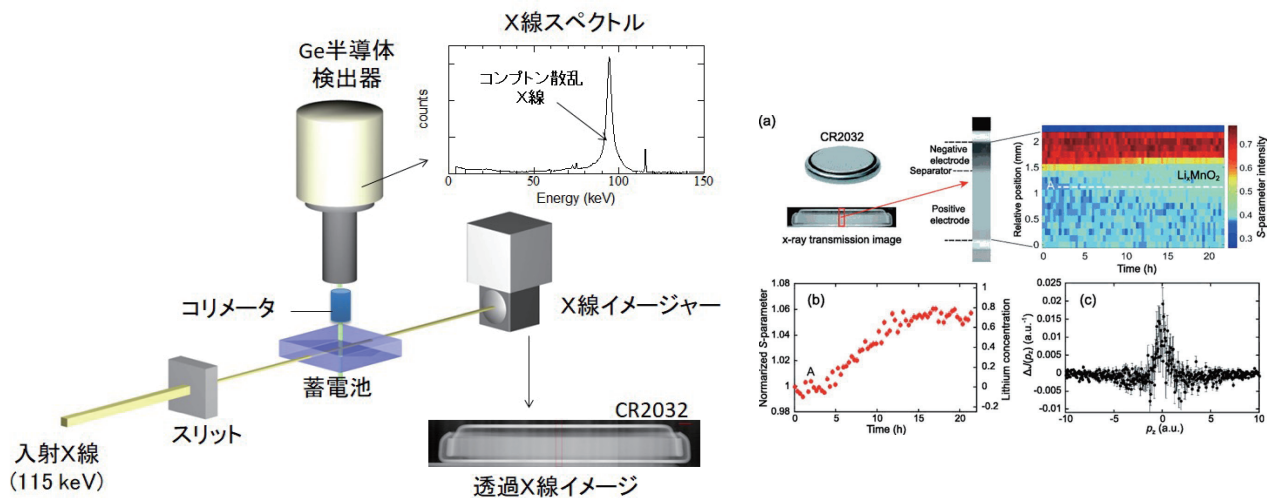
共焦点X線回折法



H. Murayama, K. Kitada, K. Fukuda, A. Mitsui, K. Ohara, H. Arai, Y. Uchimoto, Z. Ogumi, E. Matsubara, *J. Phys. Chem. C*, **118** 20750-20755 (2014).

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X線コンプトン散乱



K. Suzuki, *et al*, *J. Appl. Phys.*, **119**, 25103-25103 (2016).

高いエネルギーのX線を使うと、大きなセルもそのまま測定できる

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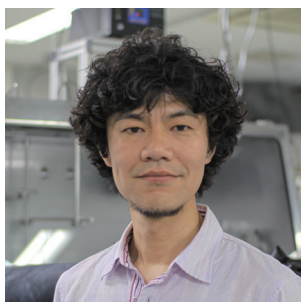
まとめ

- 高い透過能を有するX線は、特殊な電気化学セルを用いなくてもオペランド解析が可能。
- 波長を変えない測定法では、実験室で実施可能なセットアップが市販されている。
- 放射光X線を用いると、ほとんどのX線を使用した測定法でオペランド測定が可能。
- 高いエネルギーのX線を用いる場合は、構成部材すべての情報を反映することに注意する。
- それぞれの測定原理を理解した上で、測定セルの設計は高い質のデータ取得にとって重要。

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

Infrared Spectroscopy

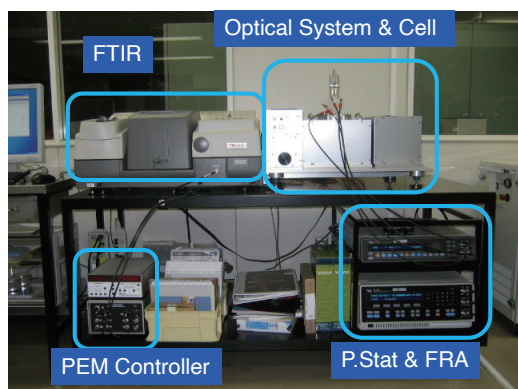


Masaki MATSUI

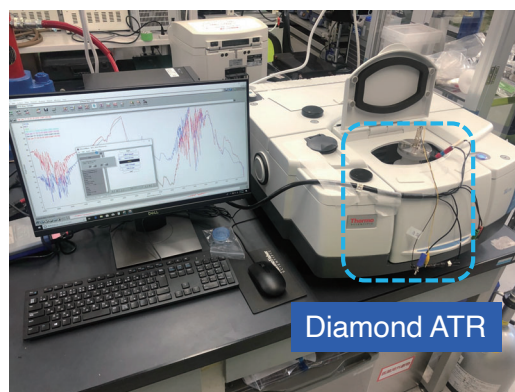
Department of Chemistry, Hokkaido University
matsui@sci.hokudai.ac.jp

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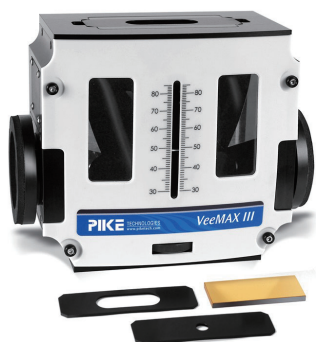
in situ/operando FTIR setup



IRRAS setup



ATR setup



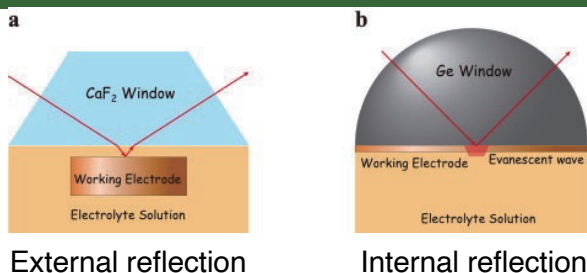
<https://www.piketech.com/product/sr-veemax/>



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

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Optical setup



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.

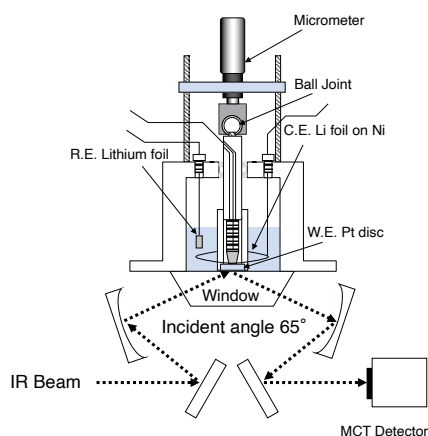
b. Internal reflection geometry

- ✓ 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.

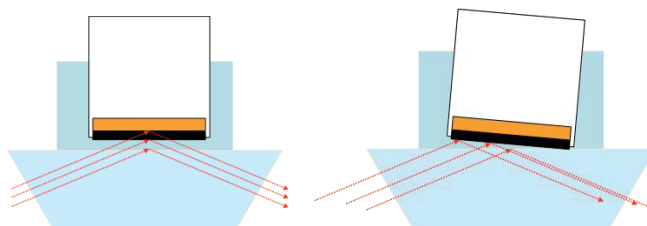
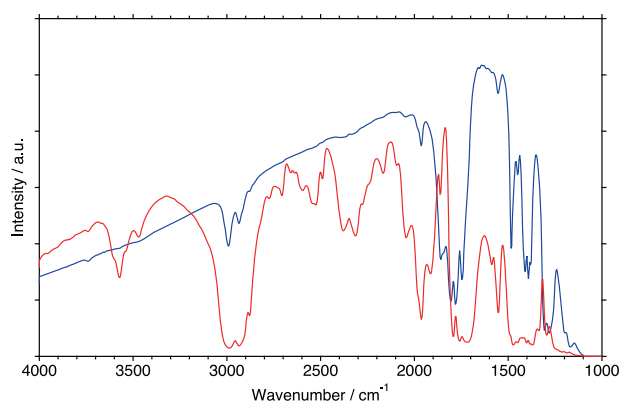
Material	Range (cm ⁻¹)	Refractive Index (at 2μm)
BaF ₂	67000–740	1.46
CaF ₂	77000–1,100	1.42
CdTe	10000–400	2.4
CsI	40000–200	1.74
GaAs	7000–650	3.33
Ge	5500–600	4.00
KRS-5	20000–250	2.37
LiF	50000–1,700	1.4
NaCl	40000–200	1.52
Si	83300–660	3.40
ZnSe	20000–454	2.40

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external reflection cell measurement tips



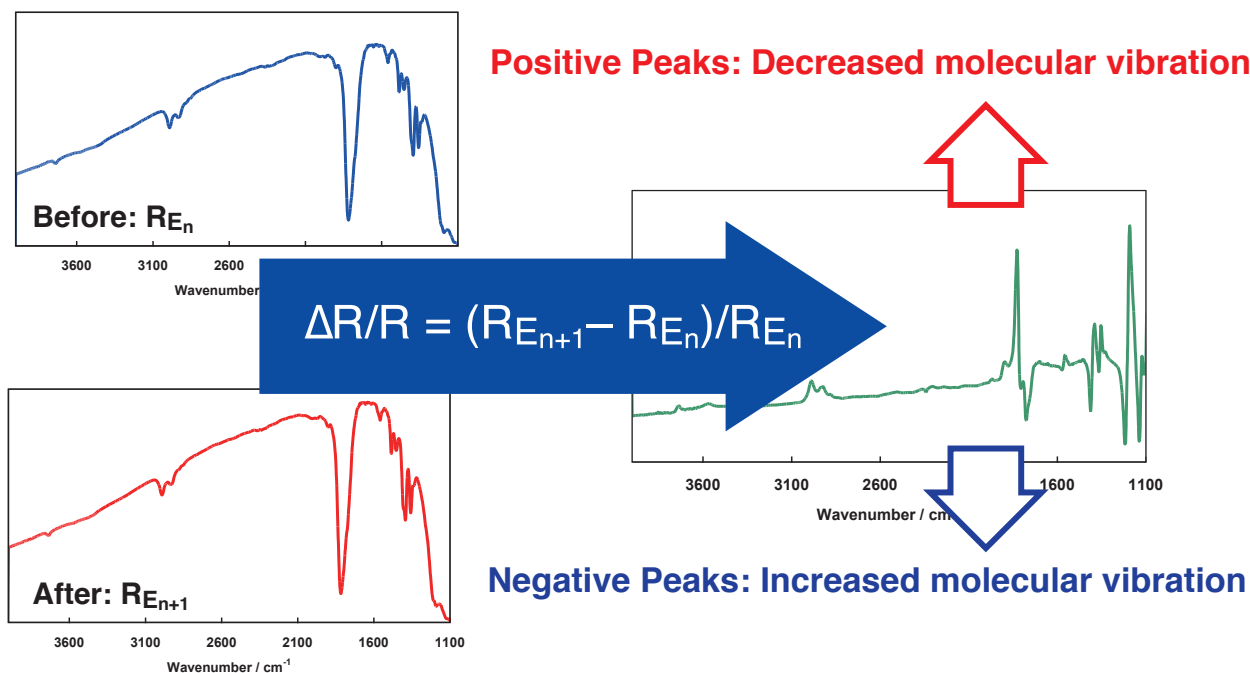
- ✓ The working electrode is pressed on the CaF₂ (or BaF₂) window.
- ✓ Since the very tiny amount of the electrolyte solution remains at the electrode surface, a fast reaction is difficult.
- ✓ Mercury Cadmium Telluride (MCT) detector is better to obtain high intensity.



Ideal external reflection (blue)

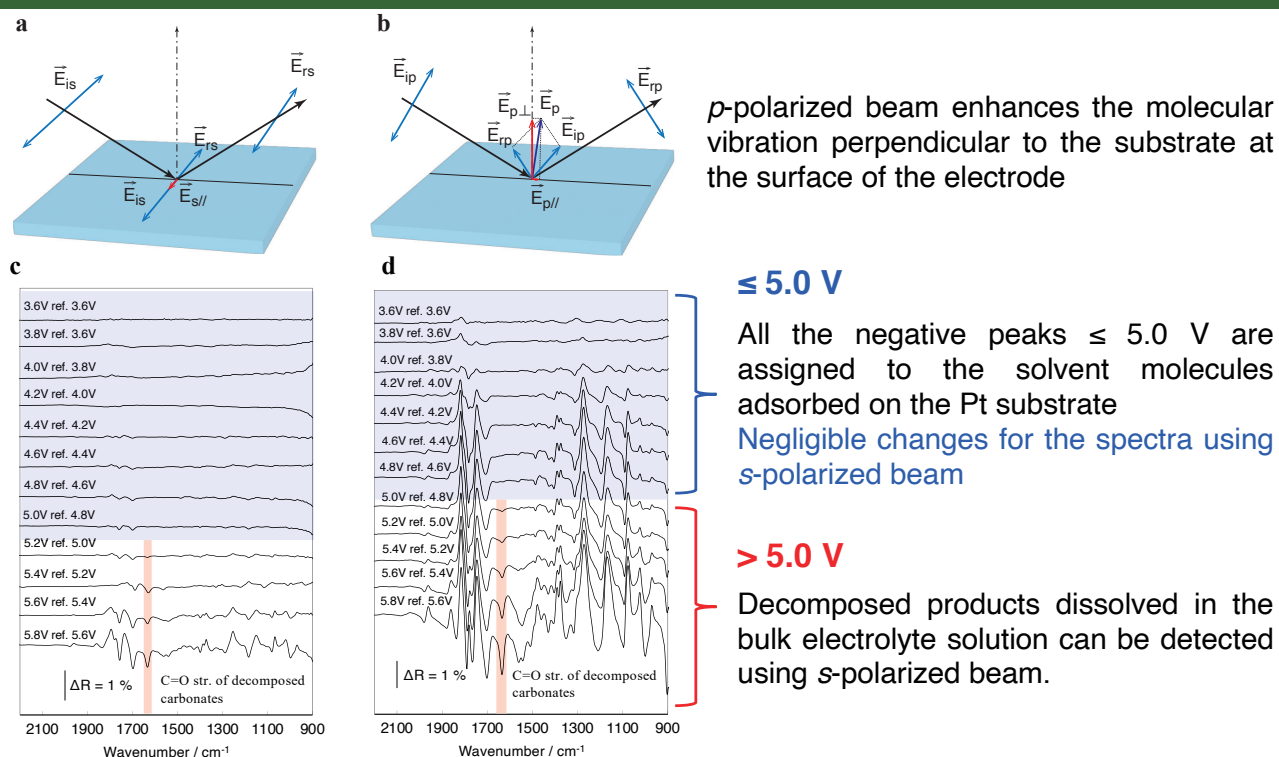
Non-uniform gap between electrode and window (red)

26



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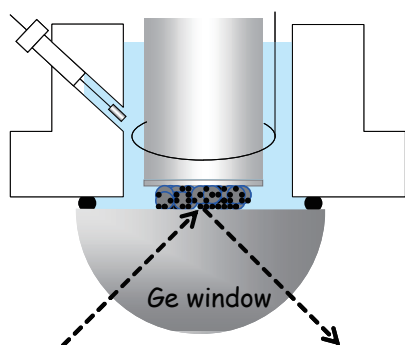
Surface enhancement by p-polarized beam



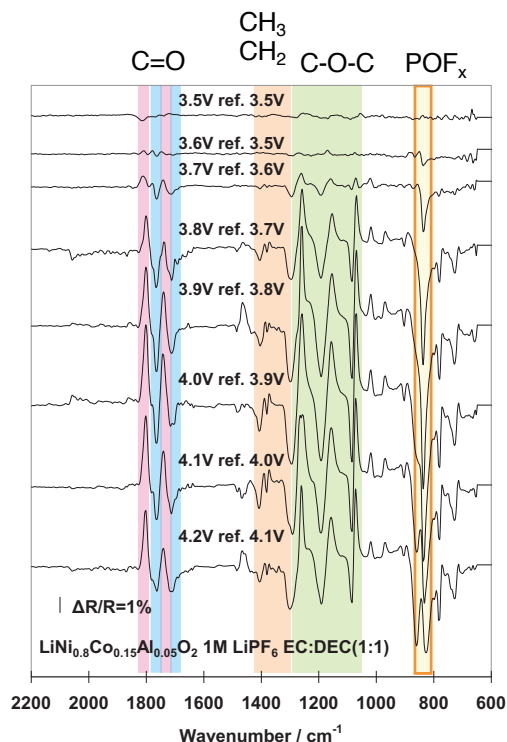
in situ FTIR spectra for the oxidation process of 1 mol L⁻¹ LiPF₆ in EC:DEC (1:1) solution on Pt electrode taken with *s*-polarized beam (c) and *p*-polarized beam (d)

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Internal reflection geometry

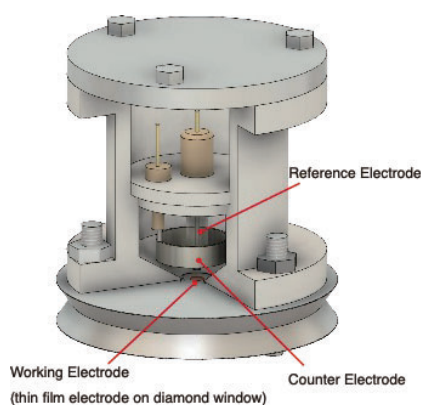


- ✓ An internal reflection cell with Ge window, which has refractive index of 4.0 is applicable for the composite electrode. However, the Ge window is easily oxidized during the 1st charging process.
- ✓ Since composite electrode has rough surface, measurement with polarized beam shows no surface selection rule.



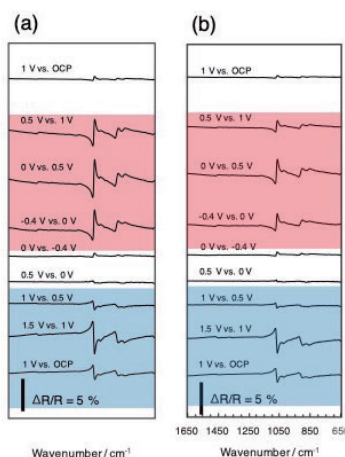
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Application: Surface analysis of Mg metal anode

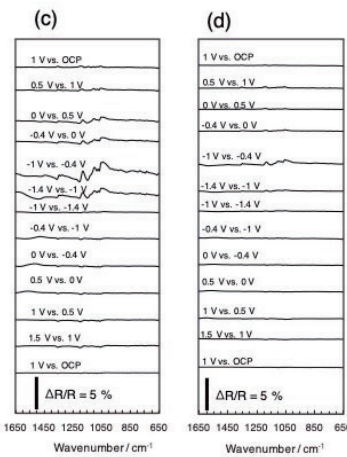


- ✓ Fabricate thin film electrode on the diamond window.
- ✓ Need to maintain electrical connection between the electrode and ATR disc.
- ✓ Avoid electrical connection between the ATR disc and ATR accessory

AEC electrolyte



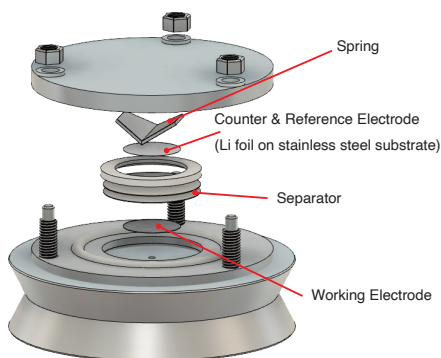
Mg(TFSA)₂-based electrolyte



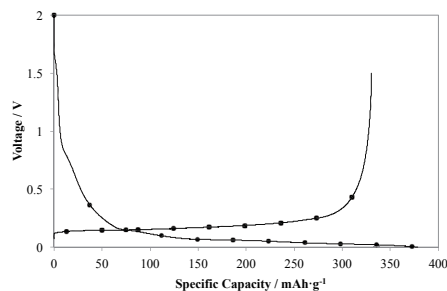
- ✓ AEC electrolyte shows reversible spectrum change suggesting no passivation layer formation, while the Mg(TFSA)₂-based electrolyte shows passivation during the 1st cathodic scan

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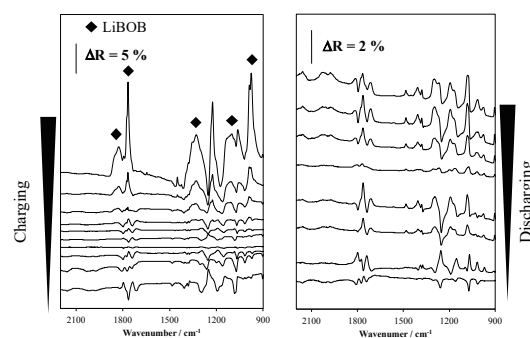
Application: Graphite composite electrode



- ✓ Applicable for composite electrode containing carbon.
- ✓ Since, the cell configuration is like a coin cell, the spectroscopic measurement can be performed under a standard charge-discharge protocol such as 1C constant current.



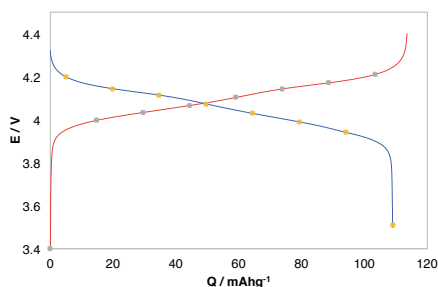
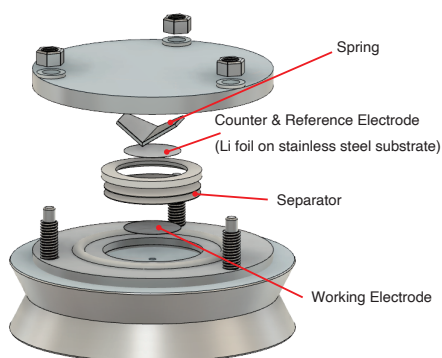
- ✓ Charge-discharge profile of the operando FTIR cell at C/10



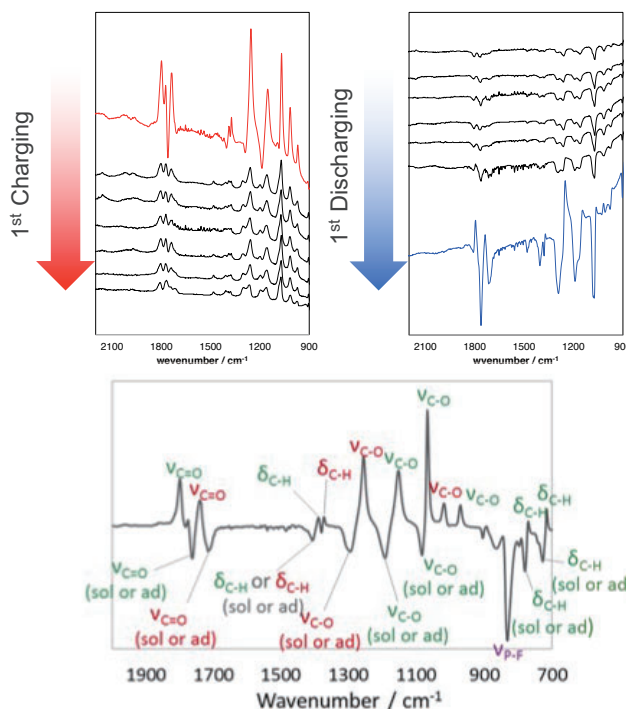
- ✓ Operando FTIR spectra for graphite anode during the 1st cycle

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Application: LiMn₂O₄ composite electrode



- ✓ Charge-discharge profile of LiMn₂O₄ composite electrode cycled at C/5



- ✓ All the peaks observed in the operando FTIR spectra correspond to concentration change of the electrolyte solution

32



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

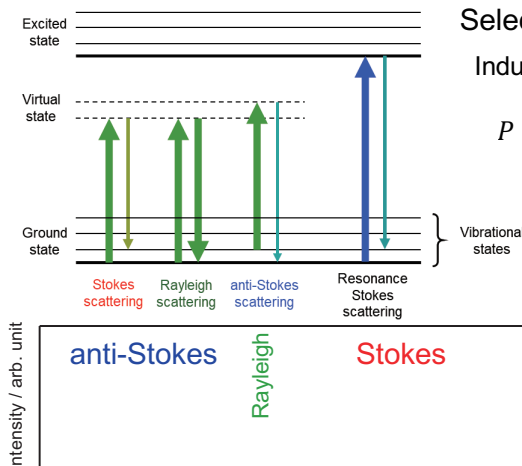
宮原 雄人

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



Fundamentals of Raman spectroscopy

Kyoto University



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

Induced dipole moment P

(Classical theory)

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

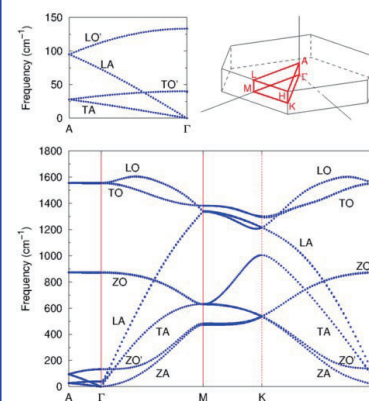
α : polarizability

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

$$\vec{k}_i = \vec{k}_s \pm \vec{q}$$

wave vector

$\vec{k}_i$: incident photon $\vec{q}$: phonon

$\vec{k}_s$: 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.

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

Definition of Raman shift

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

Intensity ratio

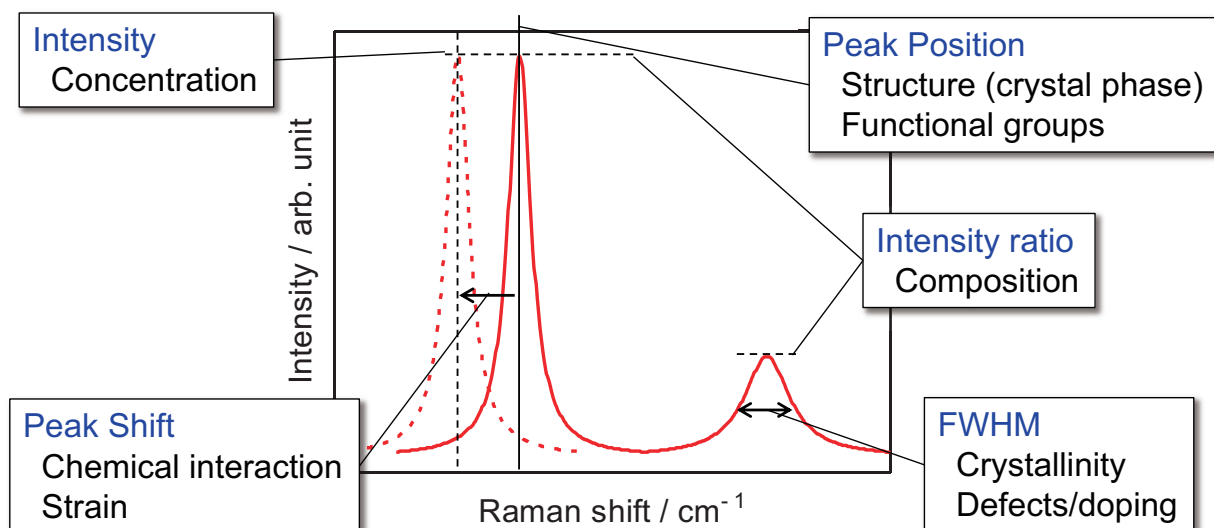
$$\frac{I_{\text{AS}}}{I_{\text{S}}} = \frac{\sigma_{\text{AS}}}{\sigma_{\text{S}}} \frac{[(\nu_{\text{laser}} + \Omega)^4]}{[(\nu_{\text{laser}} - \Omega)^4]} \exp\left(-\frac{h\Omega}{k_{\text{B}}T}\right)$$

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.



Compared with IR...

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

Compared with XRD...

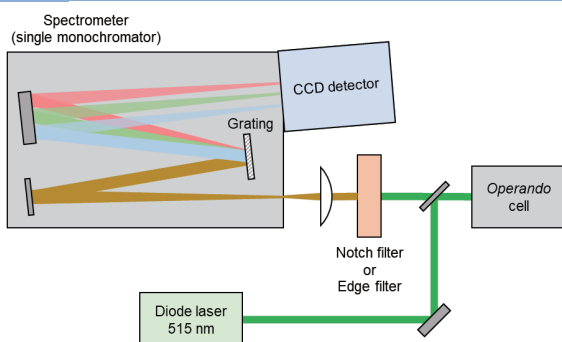
- ☺ Surface characterization
cf. optical skin depth (δ_p)
- ☹ Easier to fabricate the cell
- ☹ Unmeasurable for Metals

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

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

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Experimental setup of Raman spectrometer

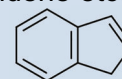


Detector

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

Laser

Power (proportional to Raman signal) should be $< 1 \text{ mW } \mu\text{m}^{-2}$
 Spectral stability should be confirmed 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

Filter

Edge filter

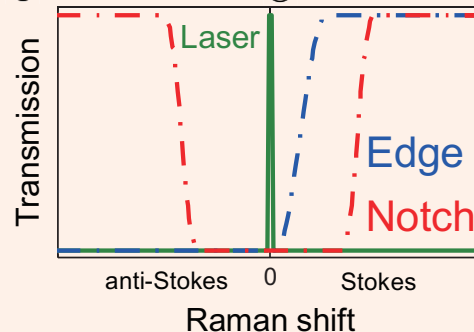
☹ small Stokes shifts

☹ anti-Stokes

Notch filter

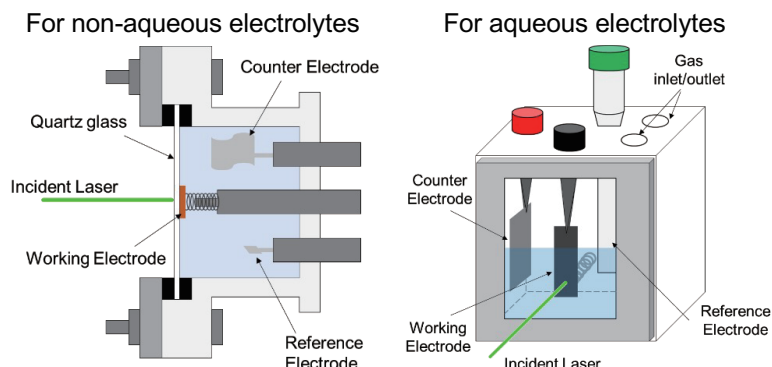
☹ anti-Stokes

☹ small Raman shifts



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In-plane EC-Raman in our lab



*Cross-sectional EC-Raman

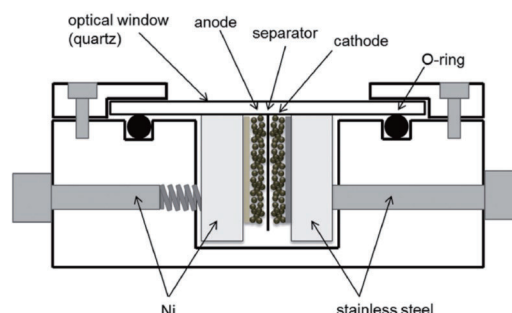
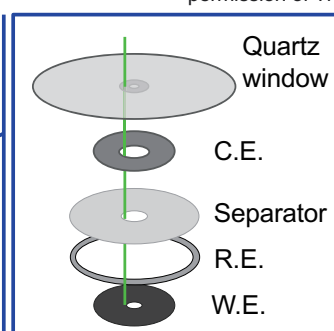


Fig. A schematic illustration (cross sectional view) of the in situ Raman cell. Reproduced from article written by H. Fukumitsu *et al.*, *Electrochemistry*, **83**, 993 (2015), with permission of The Electrochemical Society of Japan.

Commercially available cell EC Frontier (Japan)*



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Other companies

MTI (USA)

EL-CELL (Germany)

Redox.me (Sweden)

etc...

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Signal enhancement by near-field effect

Near-field effect

→ resolution up to "single molecule" level

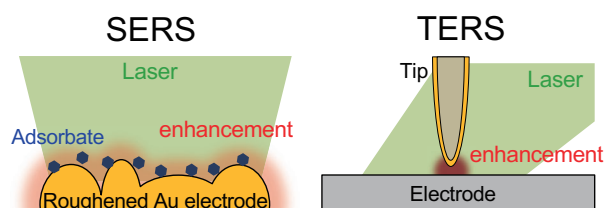


Fig. Schematic illustrations of SERS and TERS.

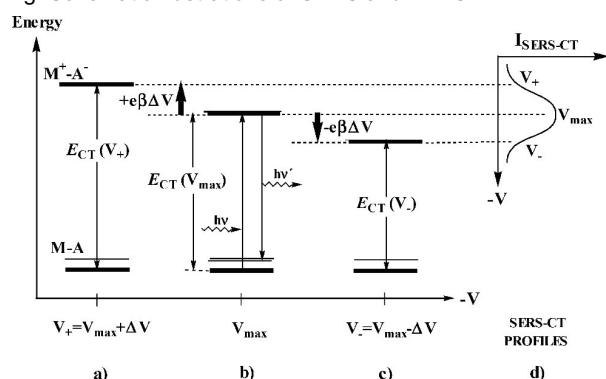


Fig. Dependence of the energy of the CT level (ECT(V)) on the electrode potential (V) in the RR-CT mechanism of SERS.²

First EC-Raman: SERS by Fleischmann

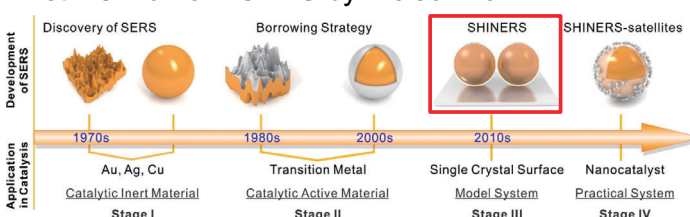


Fig. Development of SERS and its applications in catalysis.¹

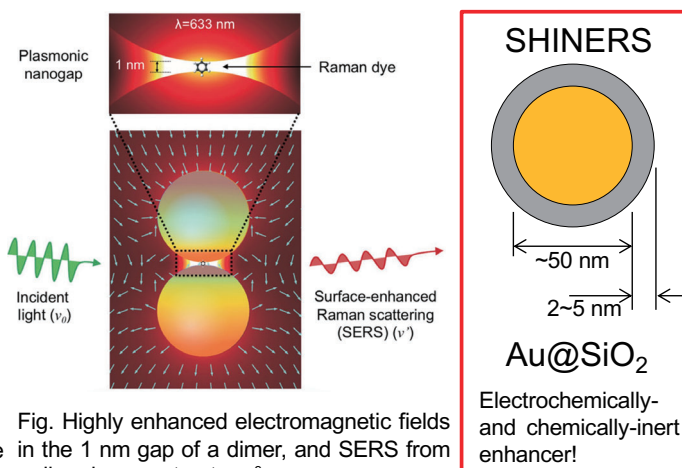


Fig. Highly enhanced electromagnetic fields in the 1 nm gap of a dimer, and SERS from a dimeric nanostructure.³

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(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**)

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

[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).

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Flowchart of peak fitting

Smoothing (if necessary)

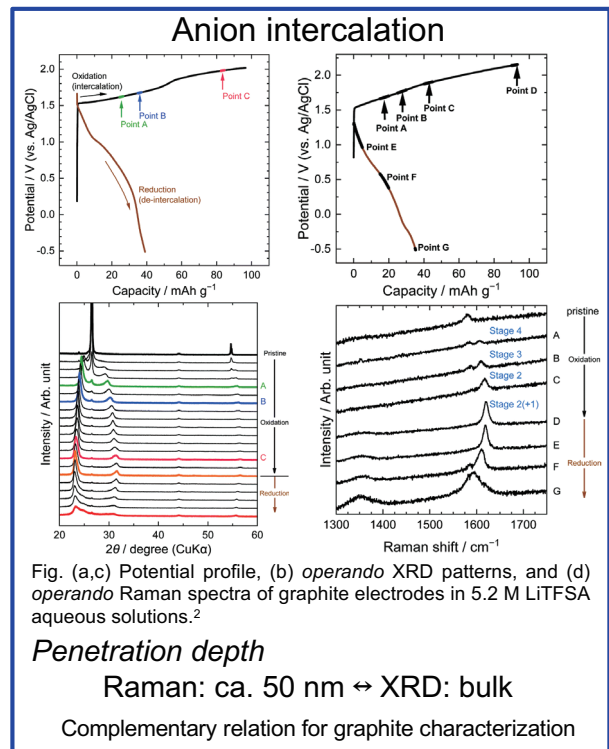
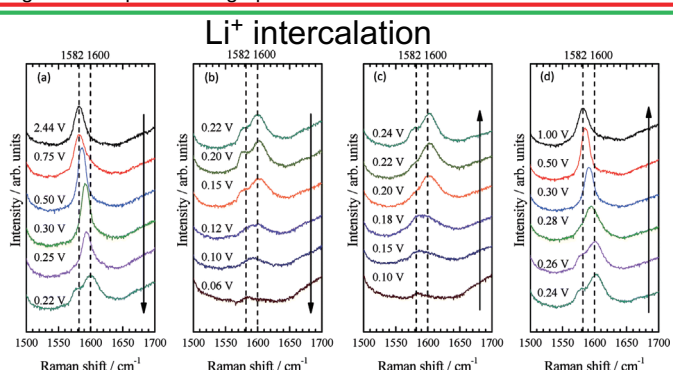
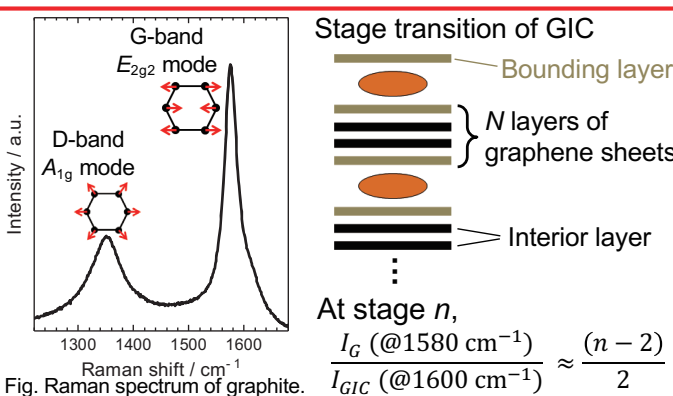


Background subtraction
by spline curve



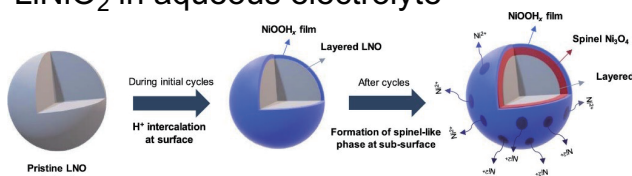
Peak search, fitting
by suitable function

Examples of *operando* analyses: graphite



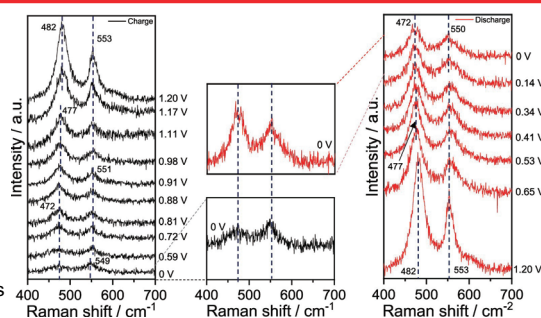
Reproduced with permission from ¹J. Mater. Chem. A, 6, 1128 (2018), ²Mater. Adv., 2, 2310 (2021). Copyrights (2018) the Royal Society of Chemistry, (2021) the Royal Society of Chemistry.

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LiNiO₂ in aqueous electrolyte

Scheme. Schematic diagram of the mechanism of capacity degradation of LiNiO_2 electrodes in an aqueous electrolyte¹

Fig. *In situ* Raman spectra of LiNiO_2 electrodes at 2nd cycle in 1.0 mol dm^{-3} aqueous LiNO_3 electrolytes.¹



SEI components of Sn electrode

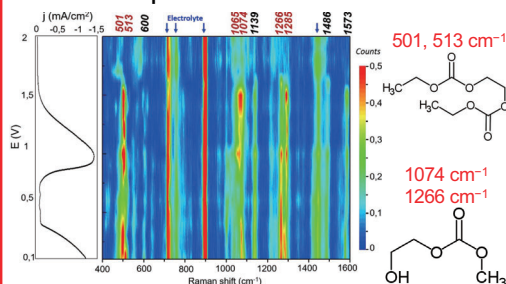


Fig. 4 A linear sweep voltammogram between 2.0 and 0.1 V (versus lithium) at 1 mV/s. The 2D color map representing the Raman band intensity as a function of the applied potential allows an appreciation of the dynamics of composition of the tin electrode/electrolyte interface.²

Electrolyte (solvation structure)

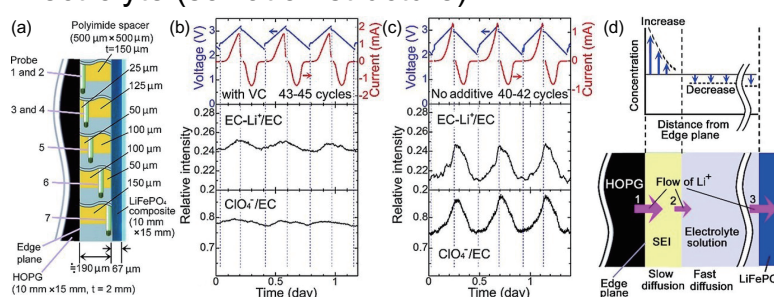


Fig. (a) Structure of the cell. EC-Li⁺/EC and ClO₄⁻/EC averaged over different positions measured with seven probes. (b) Results obtained with the electrolyte solution (b) containing 2% VC and (c) without additives. (d) Schematic illustration of a possible mechanism of the decrease in the total amount of ions in the electrolyte solution during deintercalation of Li⁺ from HOPG.³

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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
2022/11/14-18

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

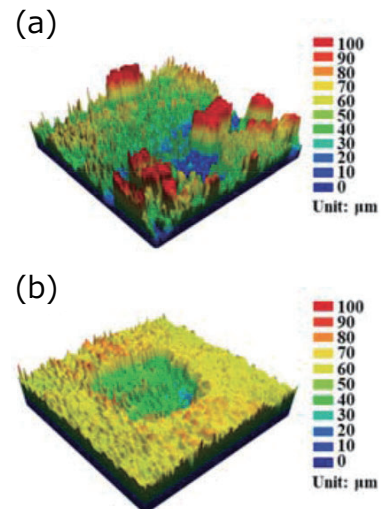
【特長】

- 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]

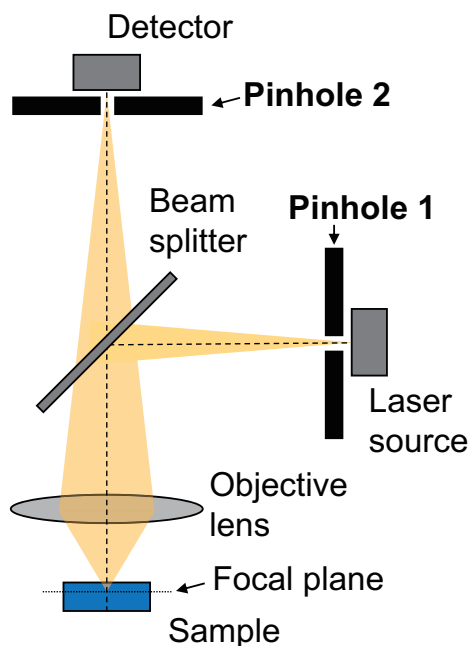


[1] Reprinted with permission from L. Zeng et al., *Adv. Energy Mater.*, **12**, 2103708 (2022). Copyright 2022, Wiley-VCH GmbH.

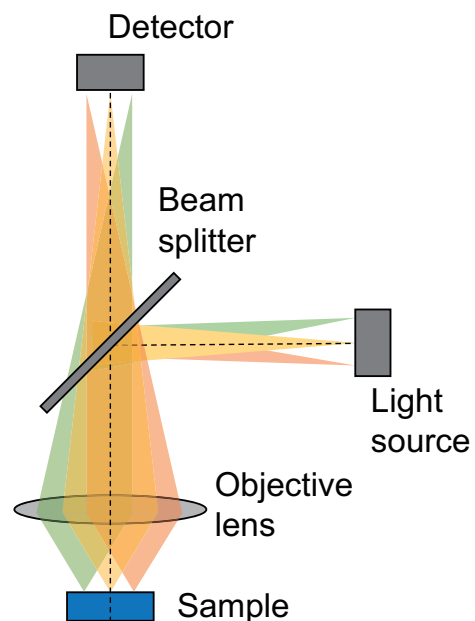
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コンフォーカル光学系

(a) コンフォーカル顕微鏡



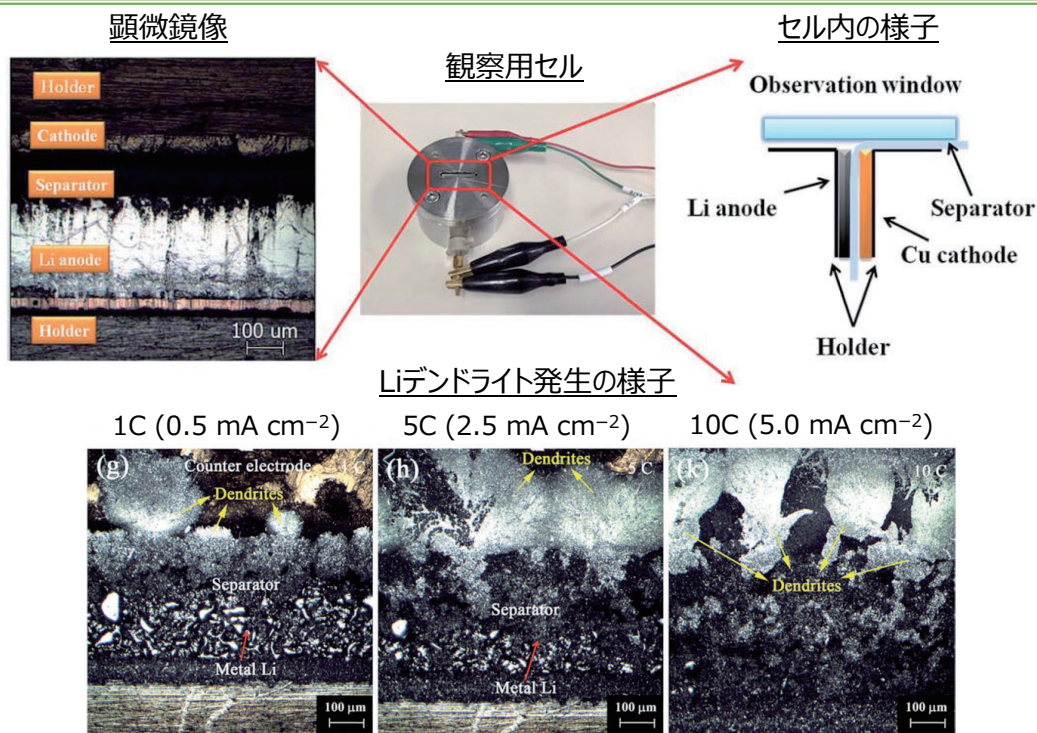
(b) 従来の光学顕微鏡



- 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。

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Liデンドライト発生のoperando観察

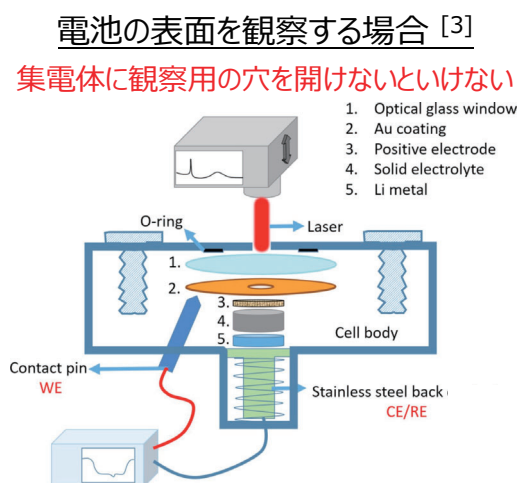


各Cレートで3時間ずつ溶解析出試験を行い、計18時間観察し、最終的に30秒の動画を作成

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

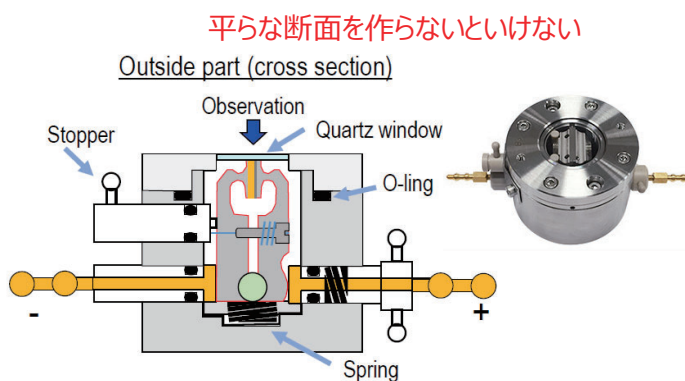
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全固体電池のoperando観察に向けたセットアップの例

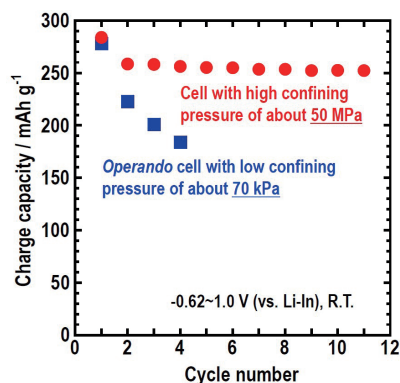


- ・ 観察したい場所によって、セルの設計を変更する
- ・ 高い拘束圧もかけられるような設計にする
- ・ 高い気密性が得られる設計にする
- ・ ラマン測定時にも応用可能

電池の断面を観察する場合 [4]



拘束圧の違いによる容量の比較 [4]

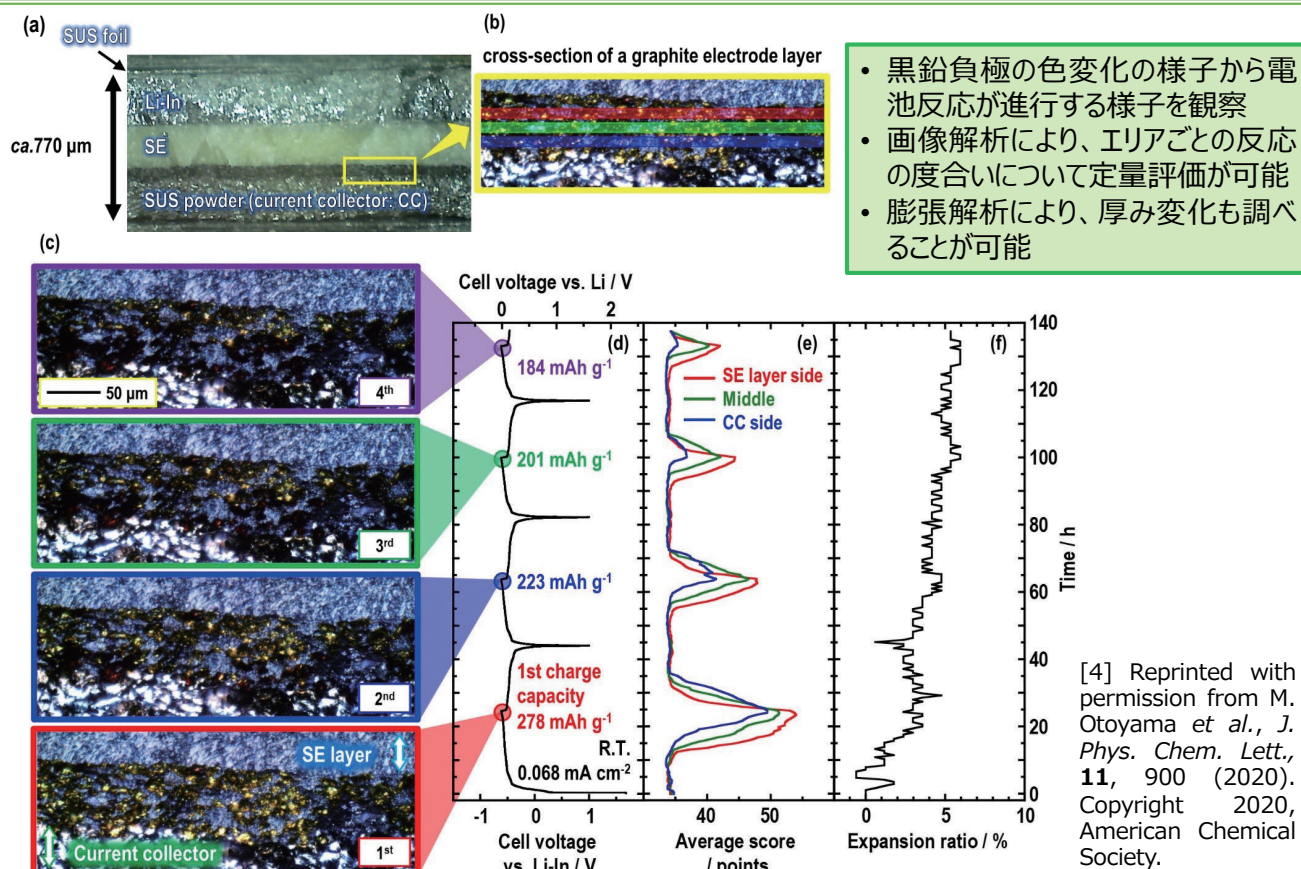


[3] Reprinted with permission from Y. Zhou *et al.*, *Batter. Supercaps.*, **3**, 647 (2020). Copyright 2020, WILEY-VCH Verlag GmbH & Co.

[4] Reprinted with permission from M. Otoyama *et al.*, *J. Phys. Chem. Lett.*, **11**, 900 (2020). Copyright 2020, American Chemical Society.

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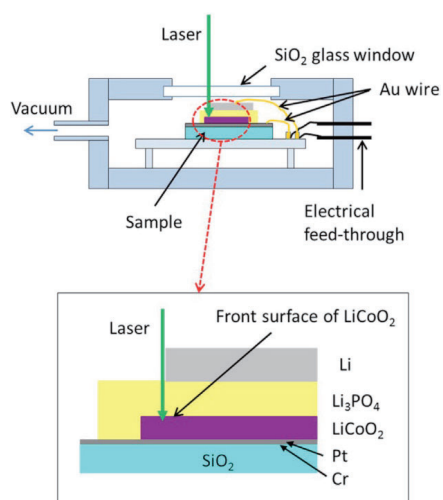
黒鉛負極を用いた全固体電池断面のoperando顕微鏡観察



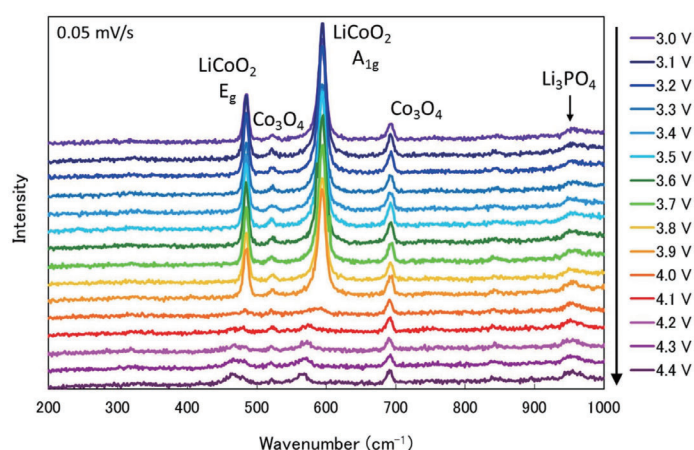
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全固体薄膜電池のin situラマン分光分析

薄膜電池測定のためのセットアップ [5]



充電時のラマンスペクトル [5]



- 電解質薄膜やITO電極を通して、測定をすることも可能
- 充電時にLiCoO₂からLiが脱離するにつれて、LiCoO₂のE_g, A_{1g}モード由来のラマンバンドの強度が低下し、低波数シフトすることを観測

[5] Reprinted with permission from Y. Matsuda et al., *Solid State Ionics*, **335**, 7 (2019). Copyright 2019, Elsevier.

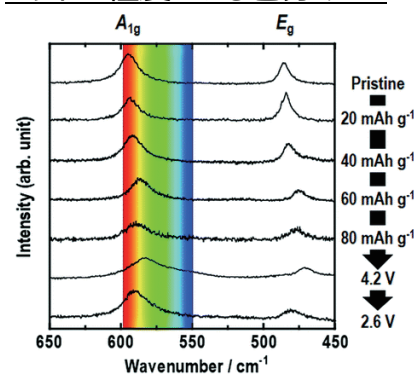
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ラマンイメージングの特長・電池を測定する際のポイント

【特長】

- 測定範囲内の複数個所のラマンスペクトルについて、波数や強度の違いから色分けを行うことで、顕微鏡像に対応するイメージング像を得ることができる
- 各成分の分布を見たり、電池内の反応分布を調べたりすることが可能

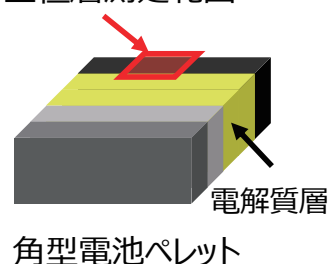
シフトの程度による色分け [6]



【電池を測定する際のポイント】

- 平滑な観察面が必要で、イオンミリングなどの断面加工を行い、電極内の各成分の粒子の区別がつかようにする
- 広範囲を測定しようとする、数時間要するため、充放電しながら測定する場合は、測定範囲を限定する必要がある

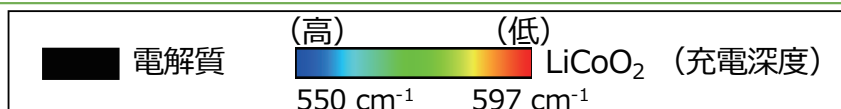
正極層測定範囲



[6] Reprinted with permission from M. Otoyama et al., *Phys. Chem. Chem. Phys.*, 22, 13271 (2020). Copyright 2020, Royal Society of Chemistry.

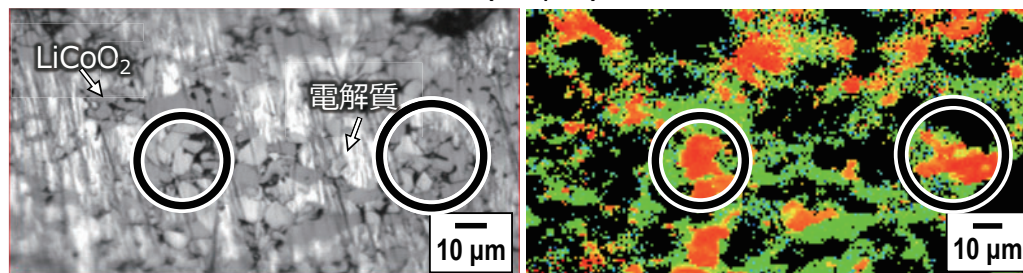
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充電後の全固体電池のラマンイメージング結果



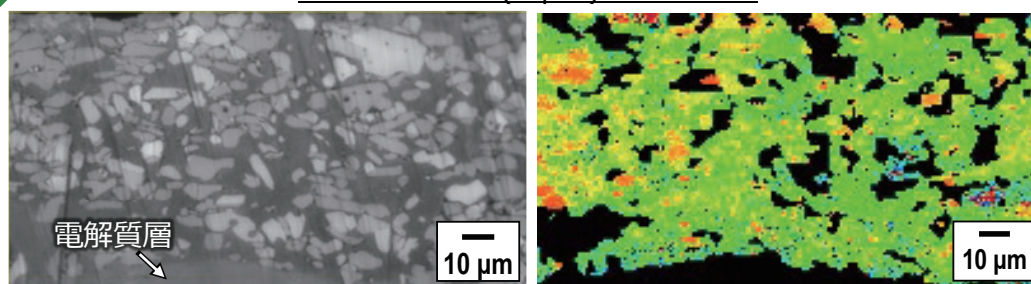
大粒径の電解質(15 μm)を用いた場合

大粒径の電解質を用いるとLiCoO₂が凝集して存在し、充電反応が進行しない箇所ができる



小粒径の電解質(3 μm)を用いた場合

電解質の微粒子化による
活物質－電解質間の
接触点の増加を検討



電解質の粒径の違いにより、反応分布が異なることをラマンイメージングにより明らかにした

[6] Reprinted with permission from M. Otoyama et al., *Phys. Chem. Chem. Phys.*, 22, 13271 (2020). Copyright 2020, Royal Society of Chemistry.

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電気化学その場測定 ～ 顕微鏡観察 ～



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ttsuda@chiba-u.jp



光学顕微鏡と電子顕微鏡

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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

光学顕微鏡像 0 min

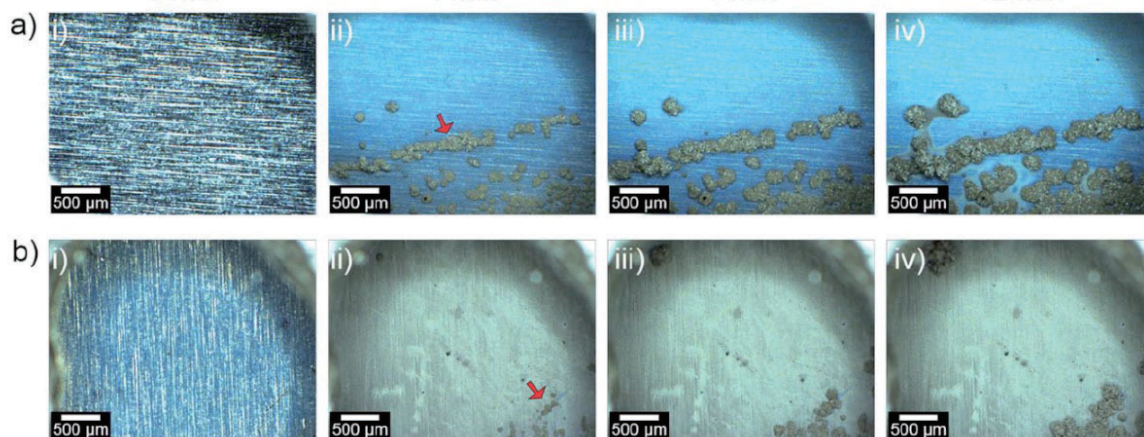
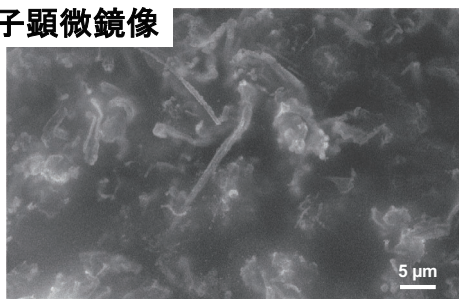


Figure 7. Deposition of Li metal as captured in optical cells using an electrolyte consisting of 1.0 M LiPF_6 in EC/DEC with a current density of 4 mA cm^{-2} . (a) A bare stainless-steel electrode shown at various times during deposition; (b) an Ag-coated electrode at various times during deposition.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

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

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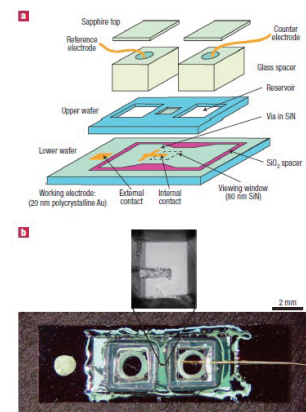
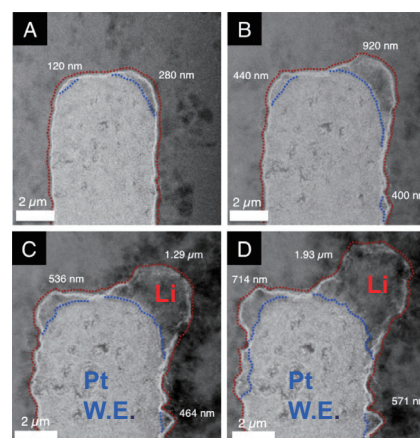
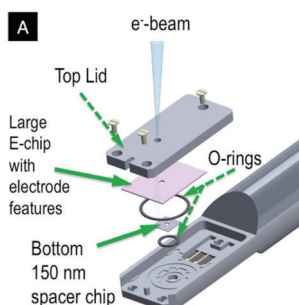
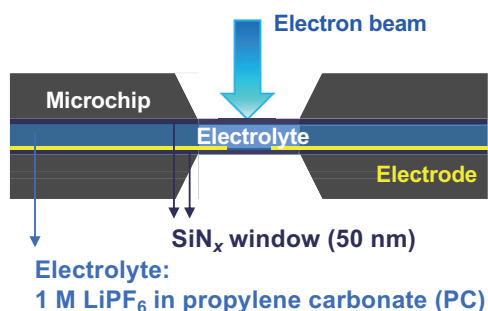


Figure 1 The liquid cell. a, Components of the cell. The viewing window is enlarged for clarity. b, Photograph of a two-electrode cell with an optical micrograph of the viewing window.

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



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 $\sim$ 623 K)
- 難燃性、難揮発性、難帯電性 → 環境調和性が高い (= グリーン溶媒)

Common Cations

non-heterocyclic type

Tetraalkylammonium
(R1R2R3R4N $^{+}$)Tetraalkylphosphonium
(R1R2R3R4P $^{+}$)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 $^{+}$)

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 $_{33}$ (Hexdec),
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 $_2^-$, N(CN) $_2^-$,
C(CN) $_3^-$, SCN $^-$, SeCN $^-$, CuCl $_2^-$, AlCl $_4^-$, Al $_2$ Cl $_7^-$, ZnCl $_4^{2-}$, F(HF) $_2$ $^-$ 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

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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.¹⁻³ Such features urge researchers to utilize this material as a new solvent in several fields, environmentally friendly organic synthesis,⁴⁻¹⁰ non-volatile electrolyte,^{11,12} 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 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-800) was made using 1-ethyl-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 kV 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 $_4$), trimethylpropylammonium bis(trifluoromethyl)sulfoniomide (TMAP-TfSI), EMI-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 kV.

Electrons in ionic liquid have been studied by fast pulse radiolysis experiments using methyltriethylammonium TfSI.¹³ 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 kV, suggesting that such 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 speci-

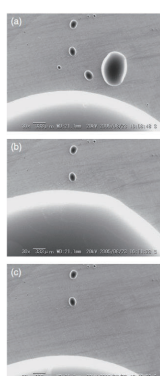
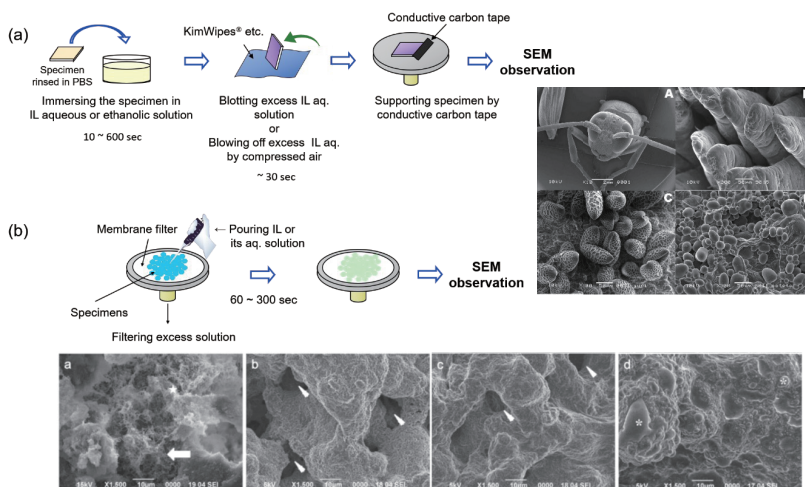


Figure 1. a) SEM image of drops of ionic liquid BMI-PF $_6$. (b) Image after tilting the sample stage at around 10° and (c) after inversely tilting the sample stage to initial position. The flux of the electron which determines brightness of the image increases with the atomic weight in the case of solid samples.¹⁴ In the ionic liquid phosphonium has the highest atomic weight (3097), 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 phosphonium in the liquid. High brightness of each liquid drop is due to the effect by inclination of the sample surface.¹⁵ When an angle of electron beam incidence decreases, depth of the area from surface where secondary

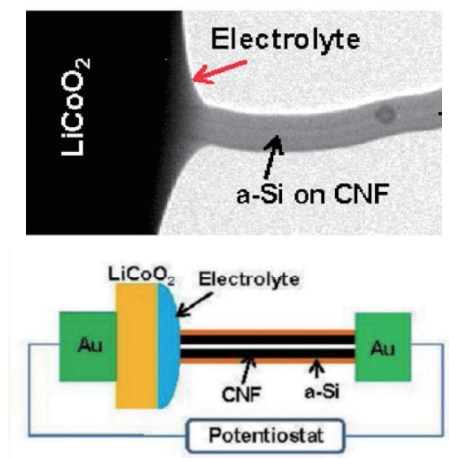


↑ SEM images of *S. mutans* biofilms pretreated with (a) conventional way and (b-d) Scheme a. The used ILs are (b) [Ch][Lac], (c) [C $_2$ mim][CH $_3$ CO $_2$], and (d) [C $_4$ mim][Tf $_2$ N].

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

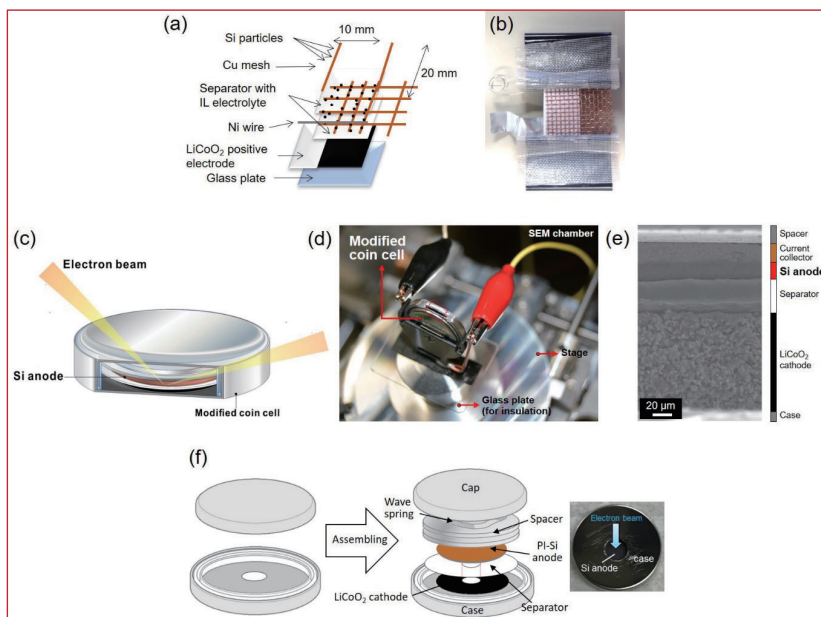
電気化学反応のその場電子顕微鏡観察にも利用できる！

電子顕微鏡の専門家がデザインしたイオン液体用セルは... イオン液体などの難揮発性電解質に特化すると...



Wang, et al., *Nano Lett.*, **12**, 1624 (2012).

- 実電池の構造とかけ離れている
- 電池研究者にとって、使い勝手が悪い...

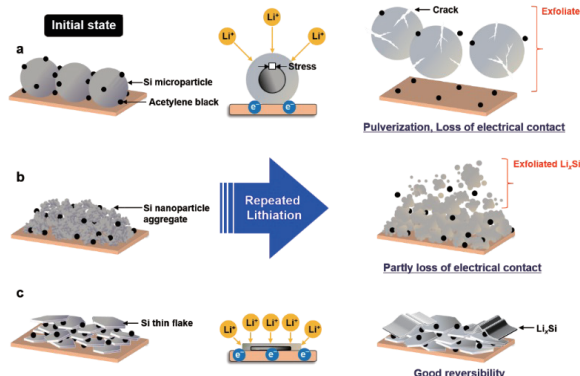
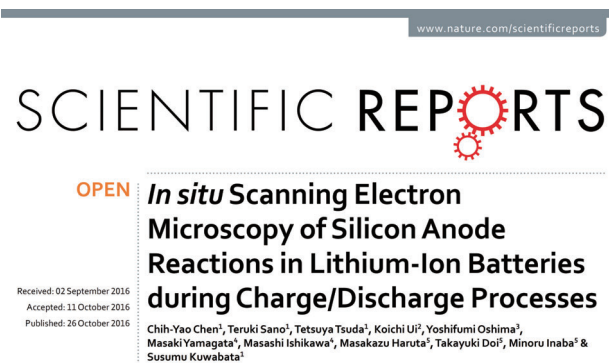


Microscopy, **69**, 183 (2020).

- 実電池に近い形状であり、電池研究者にとって取り扱いやすいセルが使える！

イオン液体電解液を用いると...

Sci. Rep., **6**, 36153 (2016).

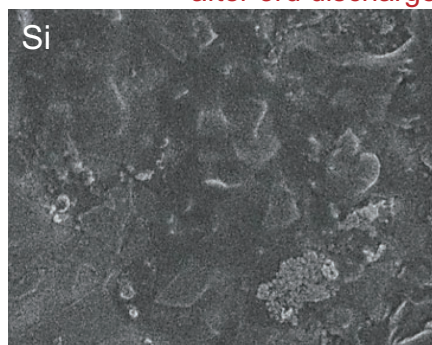
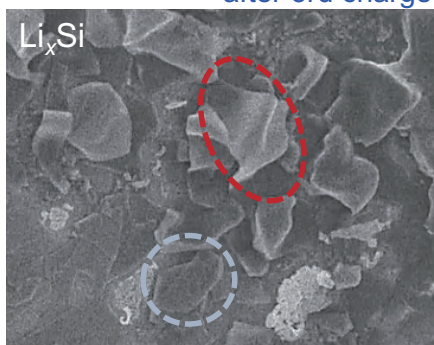
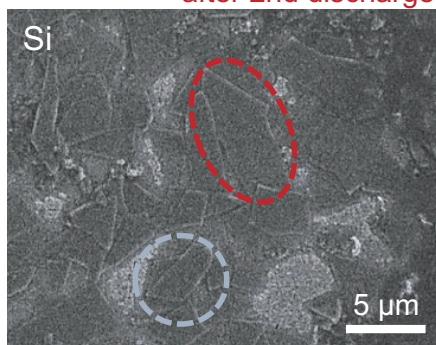


電極: バインダーフリー鱗片状Siアノード

after 2nd discharge

after 3rd charge

after 3rd discharge

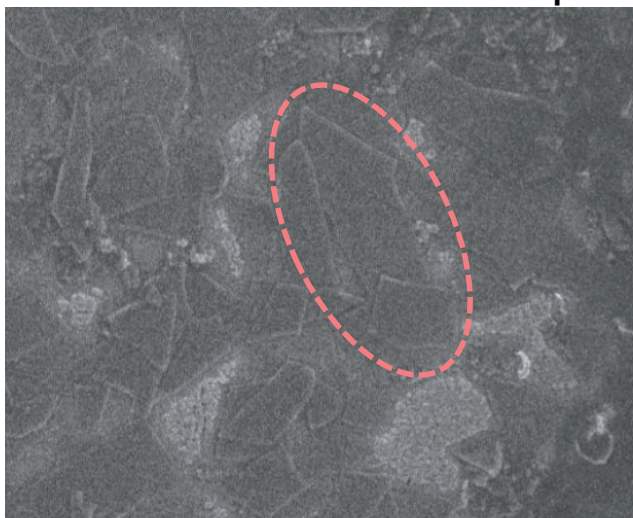


イオン液体電解液を用いると...

Sci. Rep., 6, 36153 (2016).

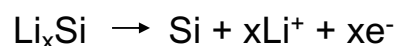
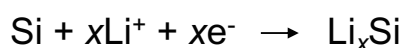
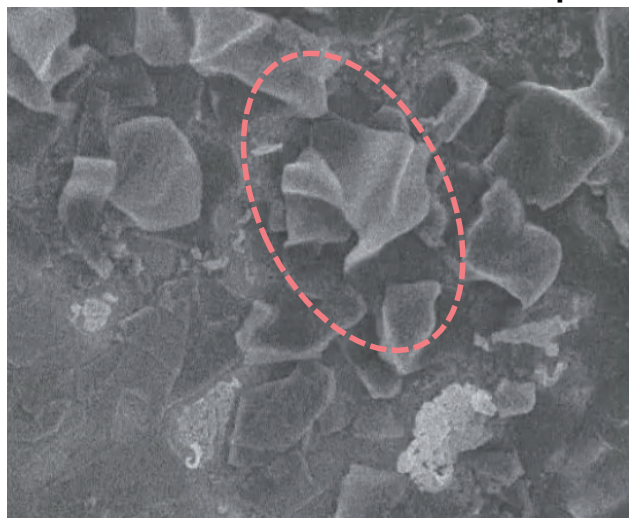
after 3rd charge

800x speed



after 3rd discharge

800x speed

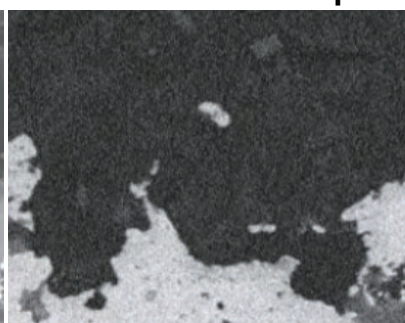
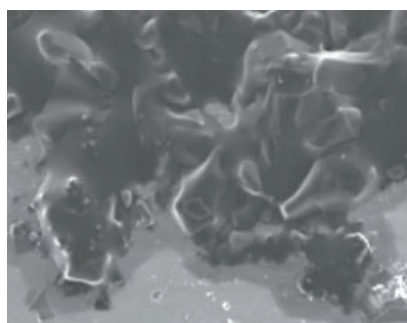


この材料は、リチウム化・脱リチウム化のプロセスにおいて生じる
応力変化を自発的に緩和できることを視覚的に確認！

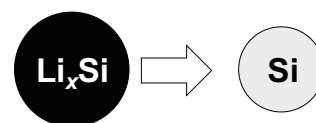
after 2nd discharge

BSE

270x speed



BSE像観察時

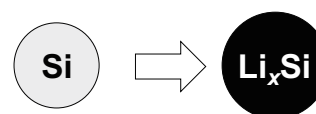
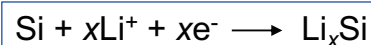
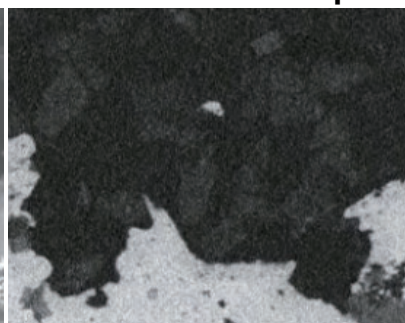
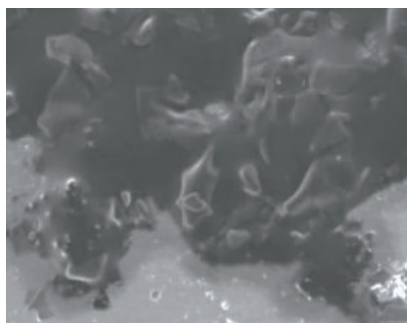


コントラストの変化(暗→明)は
収縮しながら進行

after 3rd charge

BSE

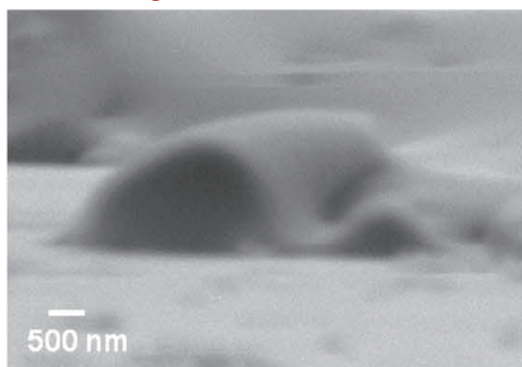
270x speed



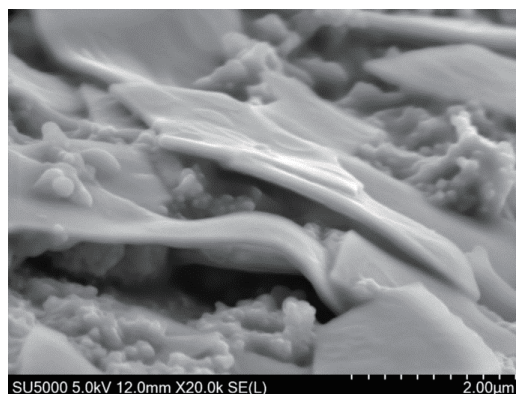
コントラストの変化(明→暗)は
膨張しながら進行

鱗片状Siのリチウム化・脱リチウム化反応は、
局所的ではなく、均一に進行しているように見える。

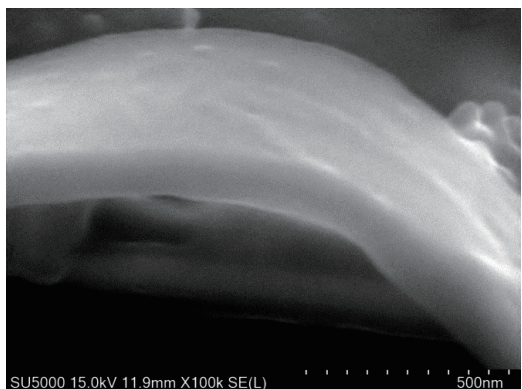
SEM image



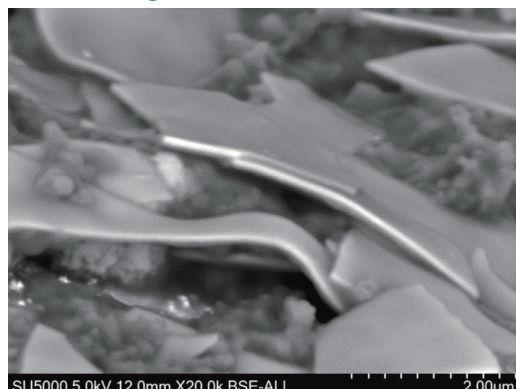
FE-SEM image



FE-SEM image



BSE image



in situ/ex situ XPS 測定の結果と併せることで、形態変化の差異が Siと電解液の界面で形成されるSEIの成分に依存することを見出した。

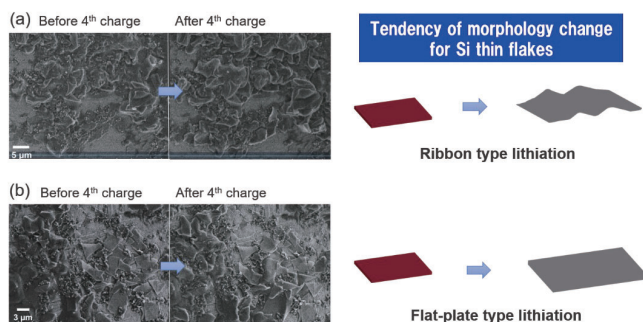


Fig. バインダーフリー鱗片状Si負極の充電前後のオペランドSEM像. 電解液: (a) 83.3-16.7 mol% [C₂mim][FSA]-Li[TFSA] and (b) 83.3-16.7 mol% [C₂mim][FSA]-Li[FSA].

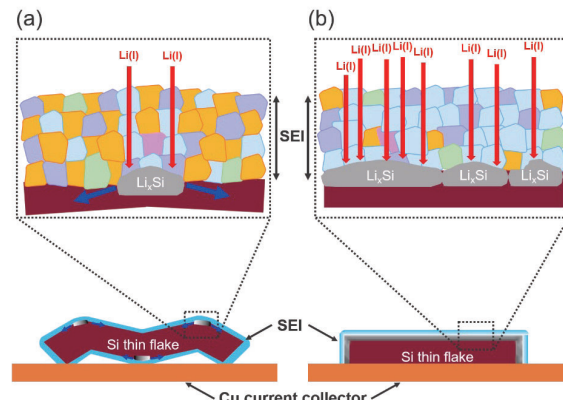
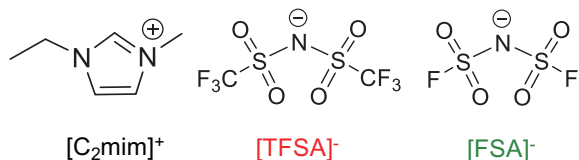
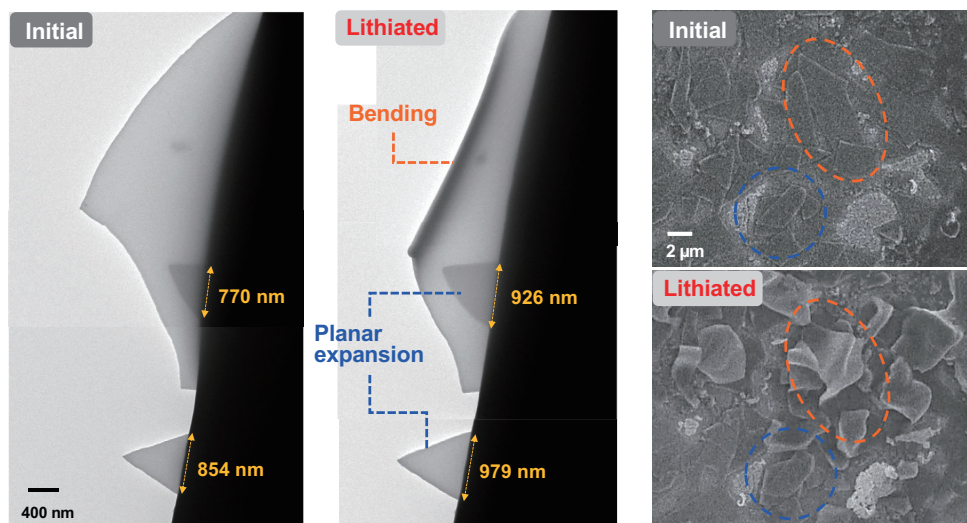


Fig. in situ/ex situ XPS測定とoperando SEM観察の結果から想定される鱗片状SiのLi化プロセスのモデル図. 電解液: (a) 83.3-16.7 mol% [C₂mim][FSA]-Li[TFSA] and (b) 83.3-16.7 mol% [C₂mim][FSA]-Li[FSA]. SEIの構成成分: (青) LiF; (ピンク) Li₃N; (紫) Li₂SO₄; (緑) Li₂S; (オレンジ) sulfone.

Mater. Adv., **1**, 625 (2020).

ウィンドーレスTEMホルダー(Fig. 14e)の使用例
～ 鱗片状Si負極(充電)のin situ 観察 ～



2種類のリチウム化反応挙動を確認することができた。

→ オペランドSEM観察の結果と同様

