

電子顕微鏡による 酸化物型全固体電池のオペランド評価

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山本和生, 野村優貴



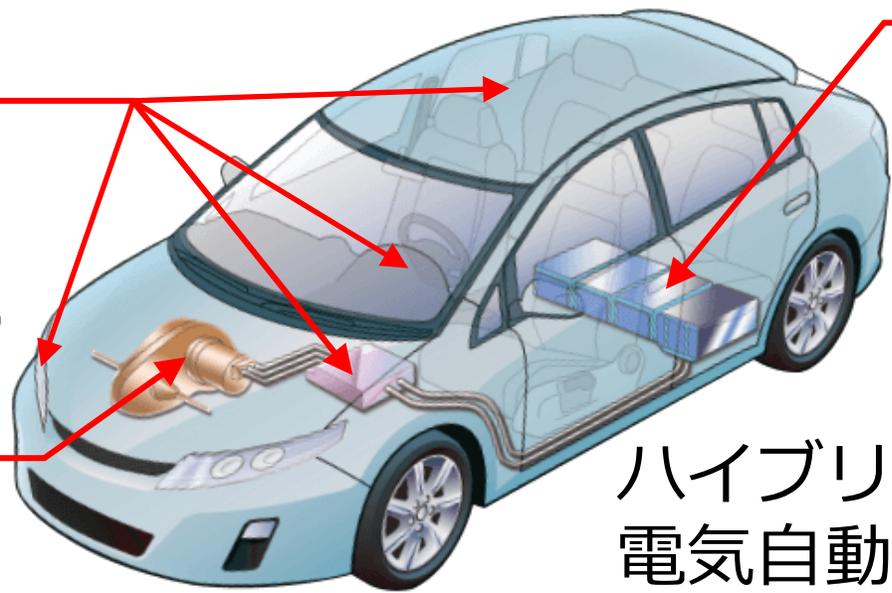
背景・課題

半導体

- LED、パワーデバイス、ディスプレイ、太陽電池 (GaN、SiC、有機半導体等)

磁性体

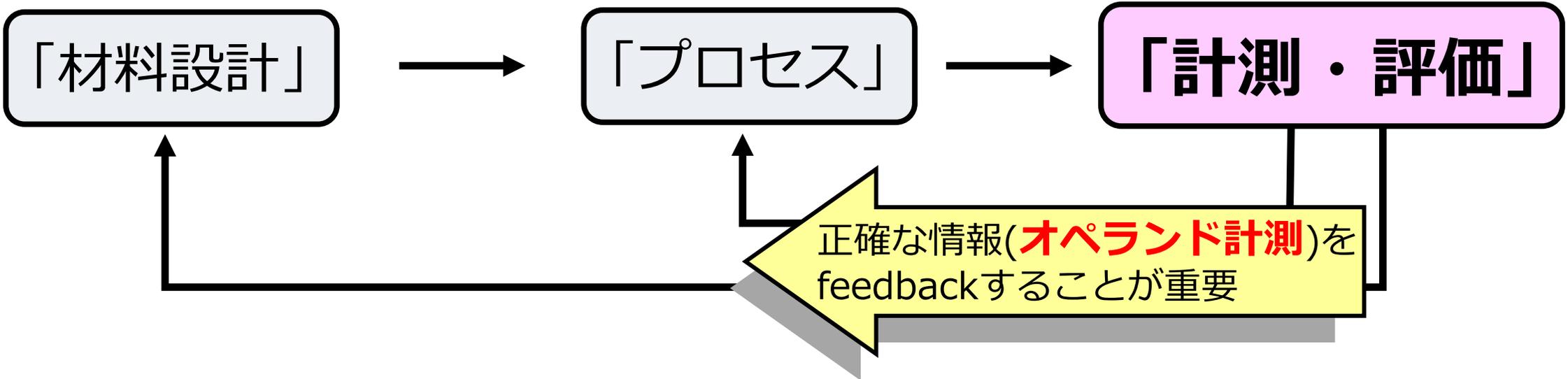
- 高性能モーター (NbFeB、SmCo等)



蓄電池

- Liイオン電池, 燃料電池 (LiCoO₂、LATP、PtCo等)

ハイブリッド自動車
電気自動車



走査／透過電子顕微鏡（加速電圧：300 kV）



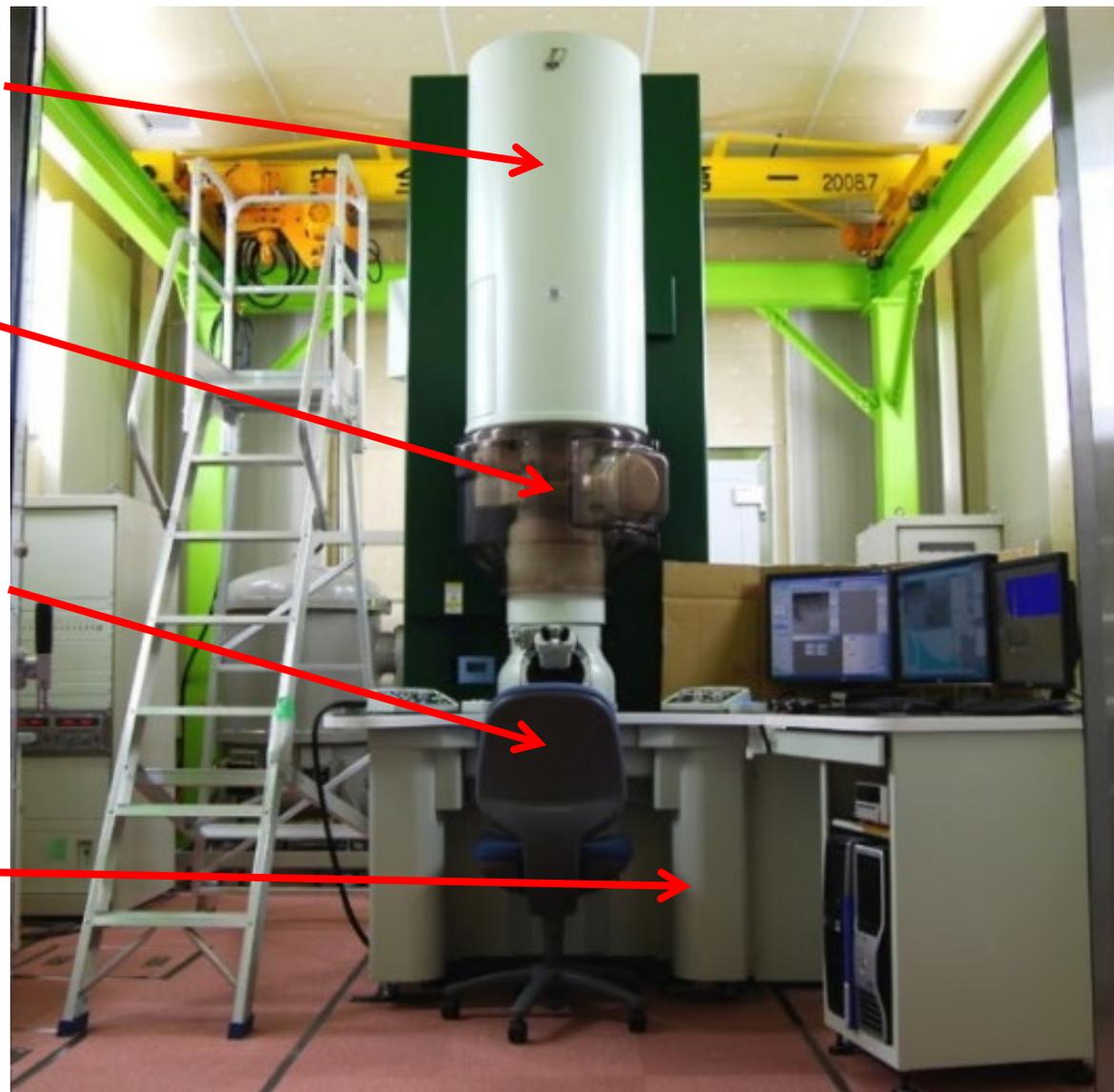
日立ハイテク製 HF3300 EH

電子銃

試料

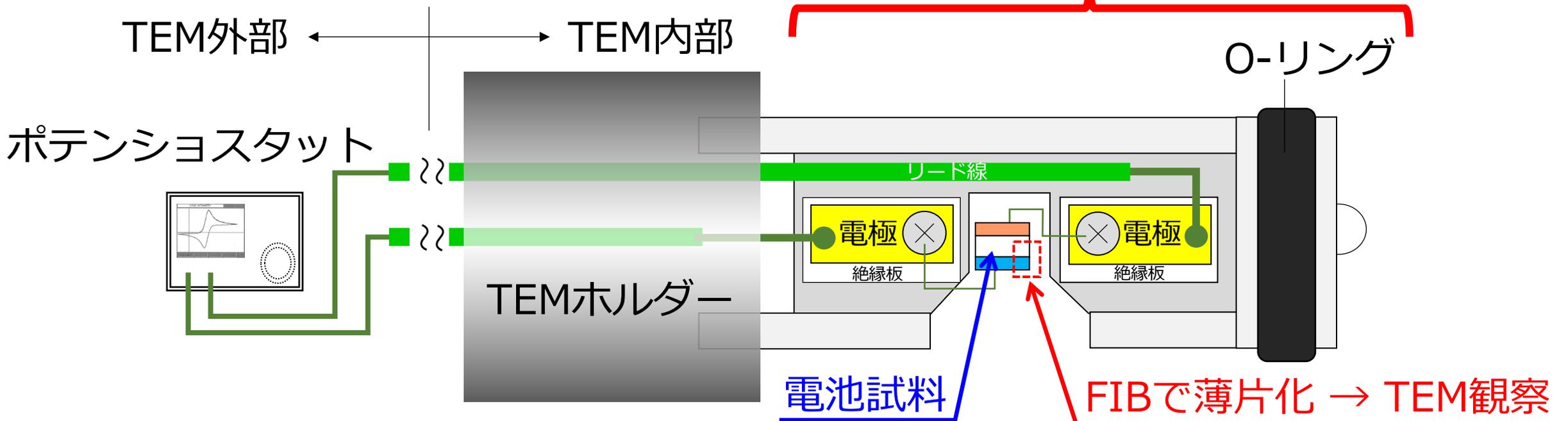
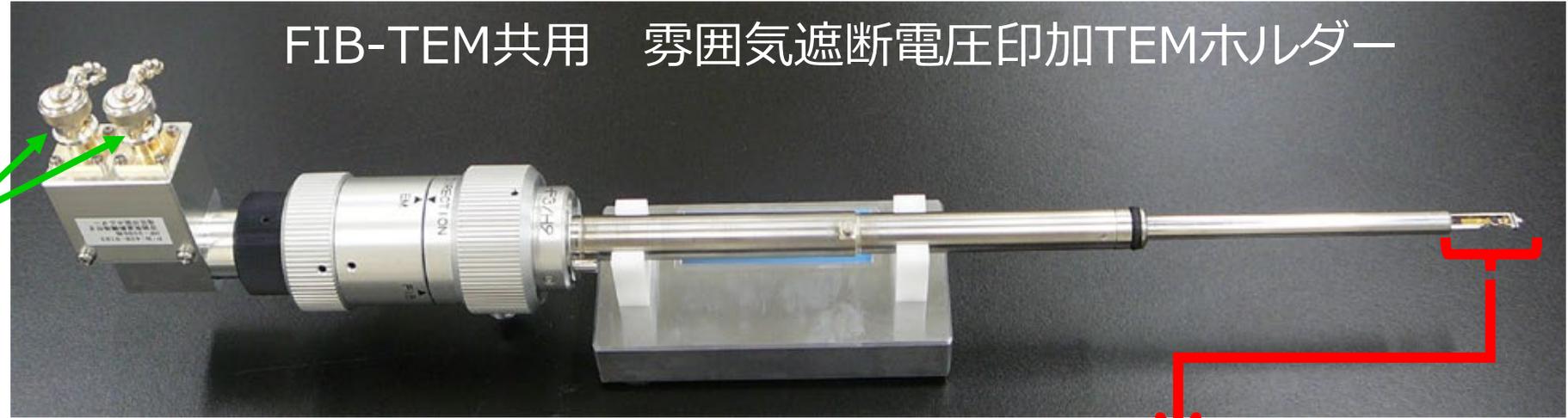
TEM用
カメラ

EELS
検出器

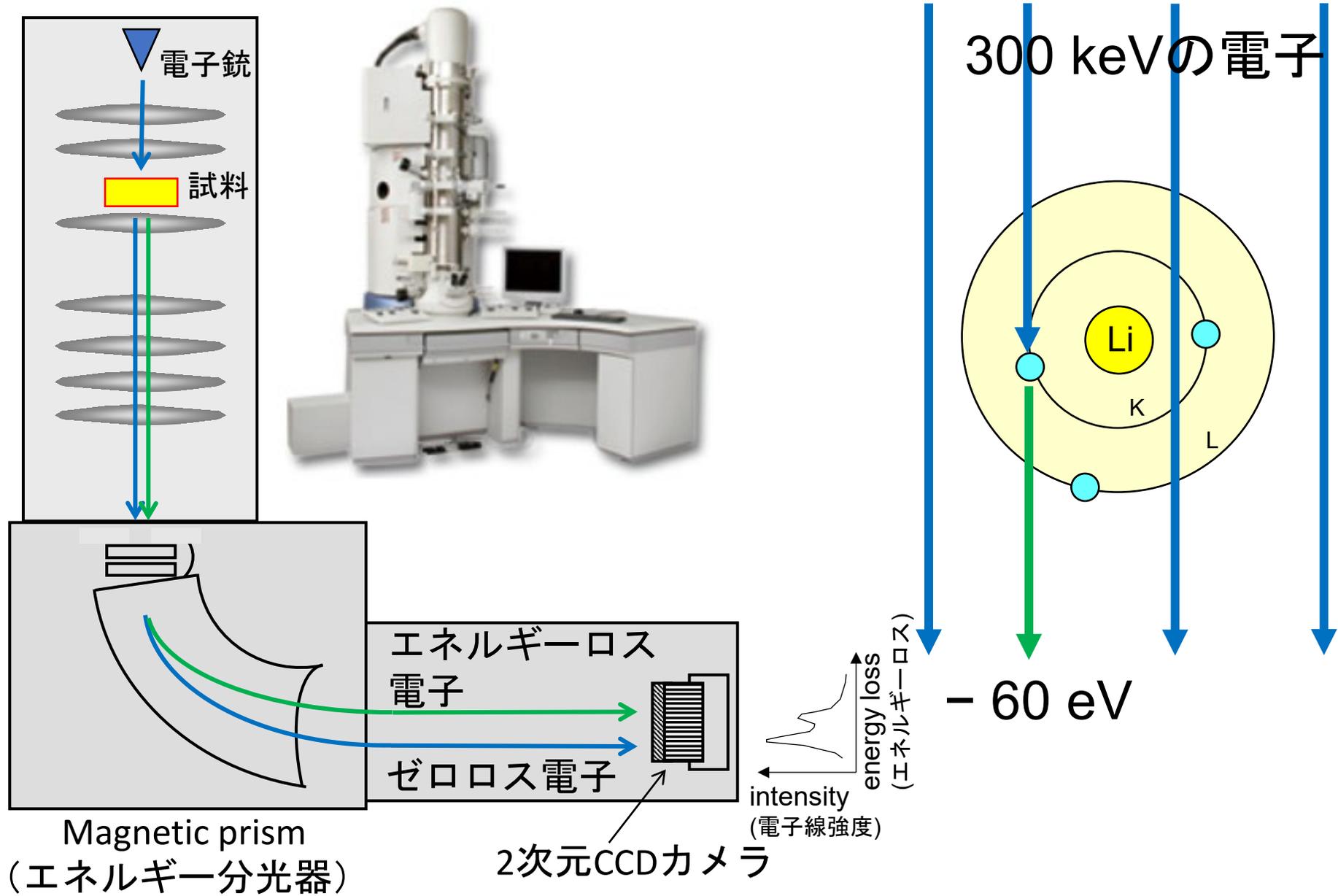


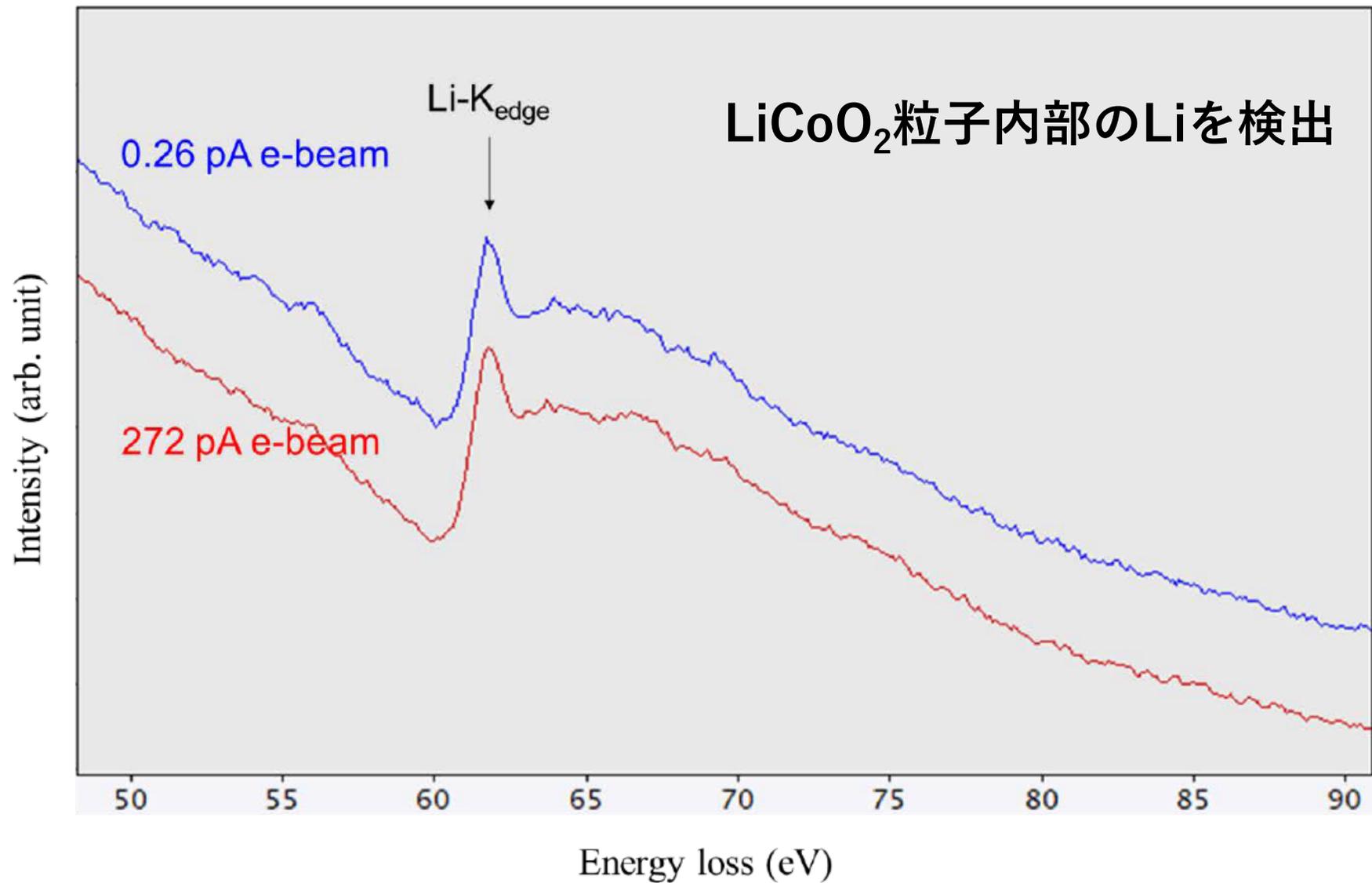
日本電子製 JEM-2400FCS

背景・課題



電子エネルギー損失分光法 (Electron Energy-Loss Spectroscopy: EELS)



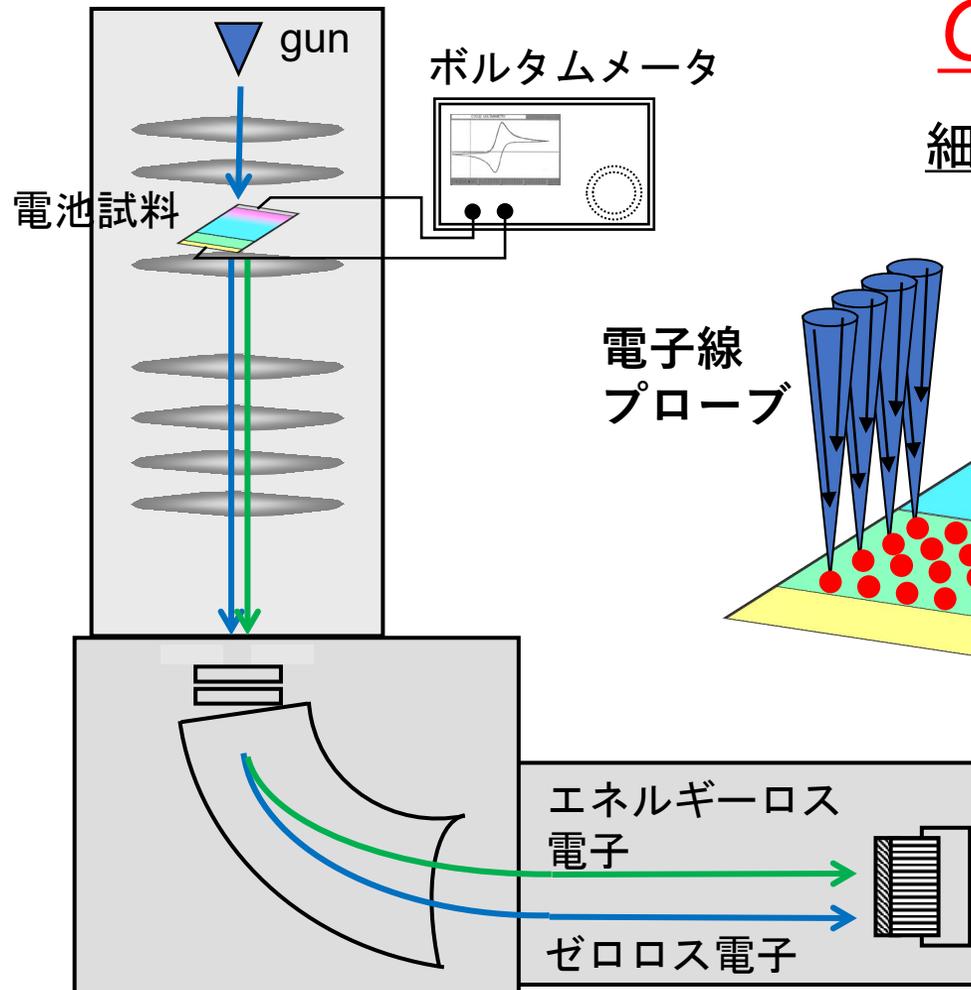


Supplementary Figure 3. Comparison of two Li-K EEL spectra acquired using 0.26 and 272 pA e-beams. The STEM probes were positioned at the same LiCoO_2 region with the same probe size (about 5 nm).

LiCoO₂正極内の2次元Li分布を観察する.

Operando-STEM-EELS

細く絞った電子線を2次元でScanする



各点で, Li-Kピーク
(約60 eV) を取得



2次元のLi分布が見える.

operando STEM-EELSによる2次元Li分布の可視化

2018年 走査透過電子顕微鏡 (STEM) と
電子エネルギー損失分光法(EELS)で、
2次元Li分布の観察に成功。

パナソニック，名古屋大学との共同研究

NANO LETTERS

Cite This: Nano Lett. 2018, 18 (9), 5892–5898

Letter

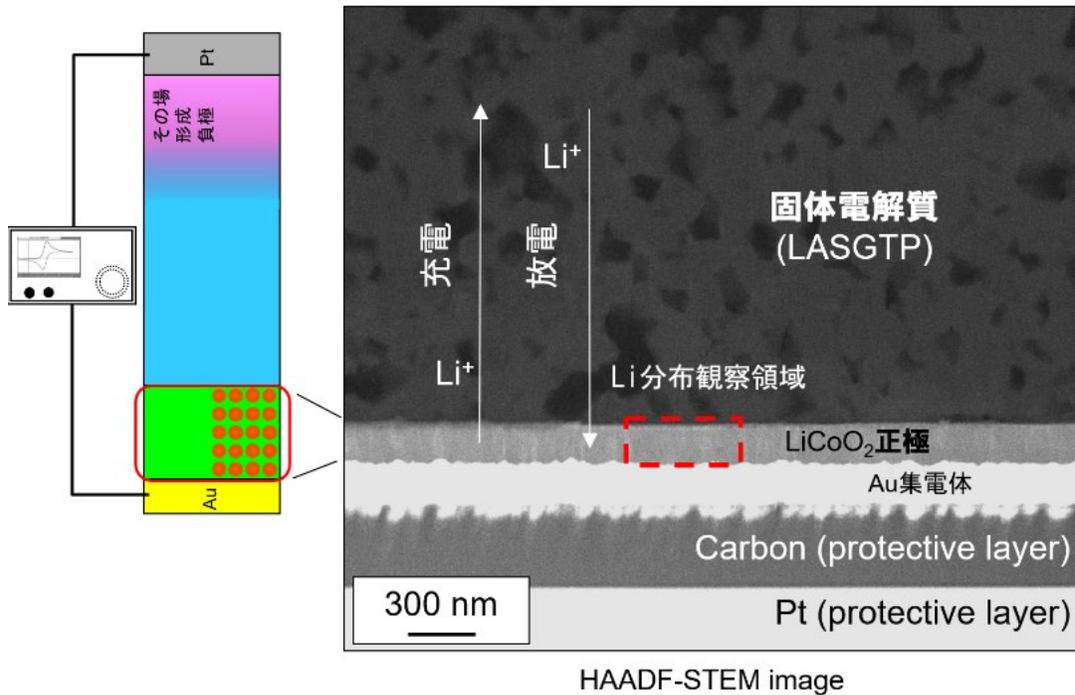
pubs.acs.org/NanoLett

Quantitative *Operando* Visualization of Electrochemical Reactions and Li Ions in All-Solid-State Batteries by STEM-EELS with Hyperspectral Image Analyses

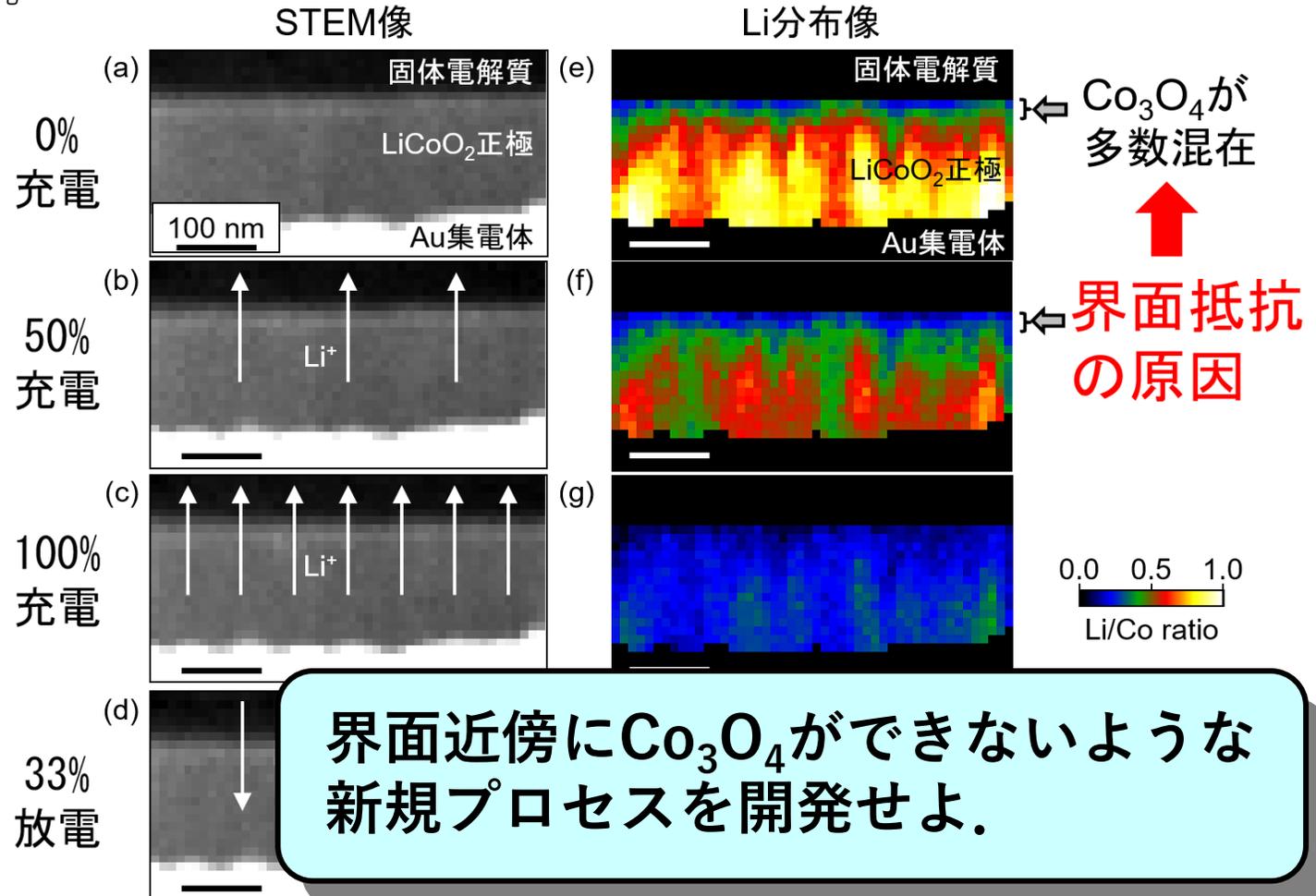
Yuki Nomura,^{*,†,‡} Kazuo Yamamoto,[§] Tsukasa Hirayama,^{§,¶} Mayumi Ohkawa,[†] Emiko Igaki,[†] Nobuhiko Hojo,[†] and Koh Saitoh[¶]



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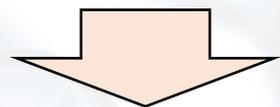


Nano Lett. **18** (2018) 5892-5898.



界面近傍にCo₃O₄ができないような新規プロセスを開発せよ。

Li分布をもっと高速に見たい！

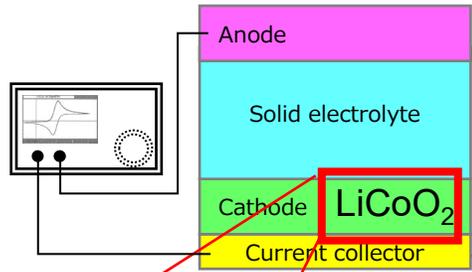


電子顕微鏡計測インフォーマティクス
(機械学習 + *operando* 電顕計測)

高速 *operando* STEM-EELS + スパースコーディング & 超解像

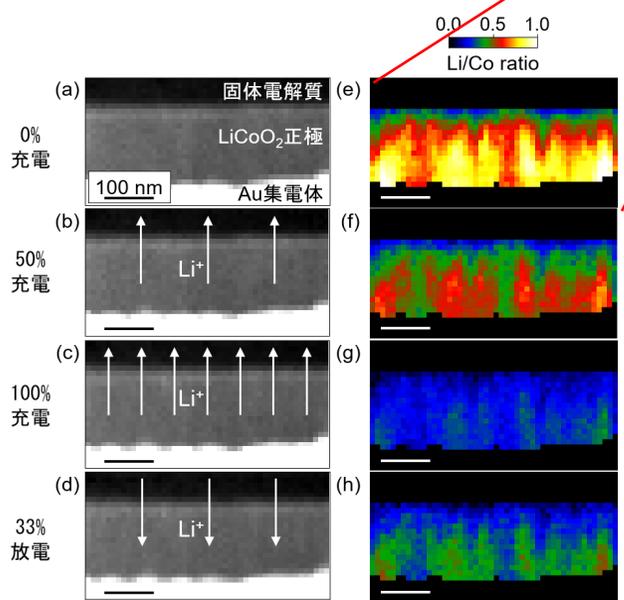


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薄膜型全固体電池

スパースコーディングによるノイズ除去と超解像



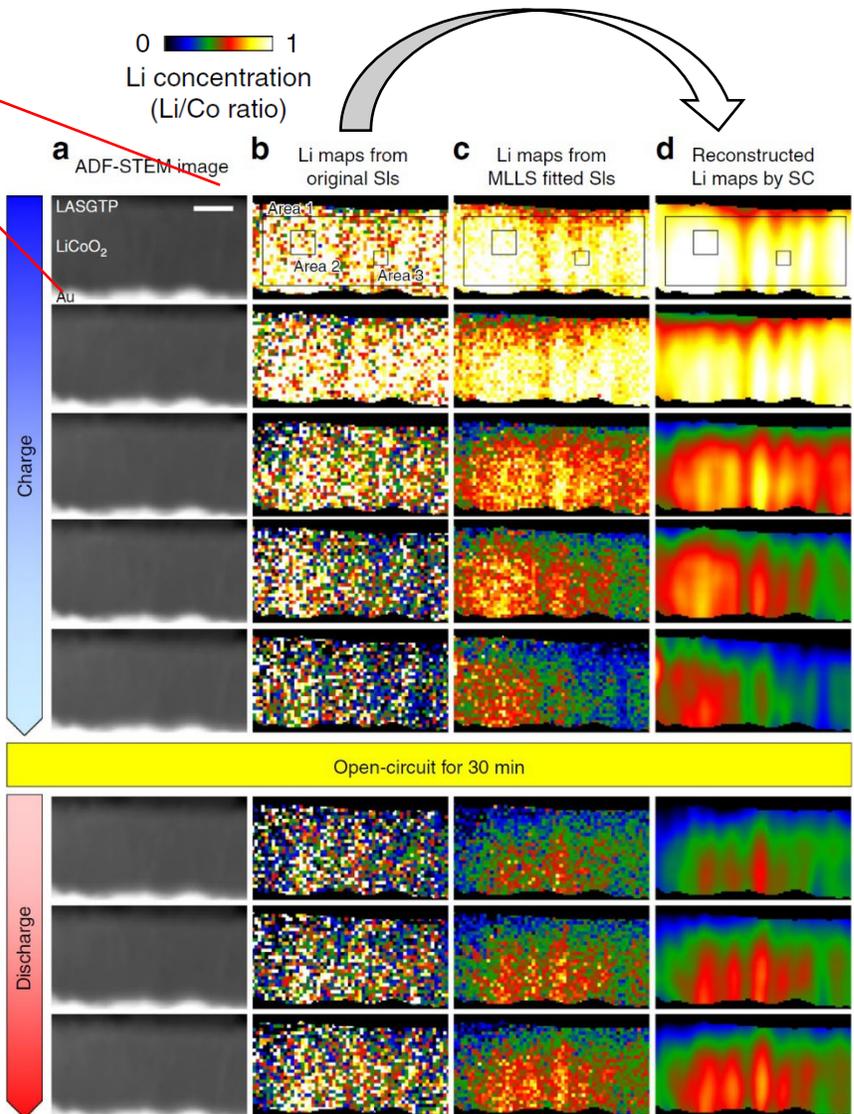
Y. Nomura, K. Yamamoto et al. Nano Lett. 18 (2018) 5892-5898.

2018年 (900秒/1画像)

15分

パナソニック, 名古屋大学との共同研究

x 30 高速化
2020年
30秒/1画像



Y. Nomura, K. Yamamoto et al. Nat. Commun. 11 (2020) 2824.

高速 *operando* STEM-EELS + スパースコーディング & 超解像

STEM Image



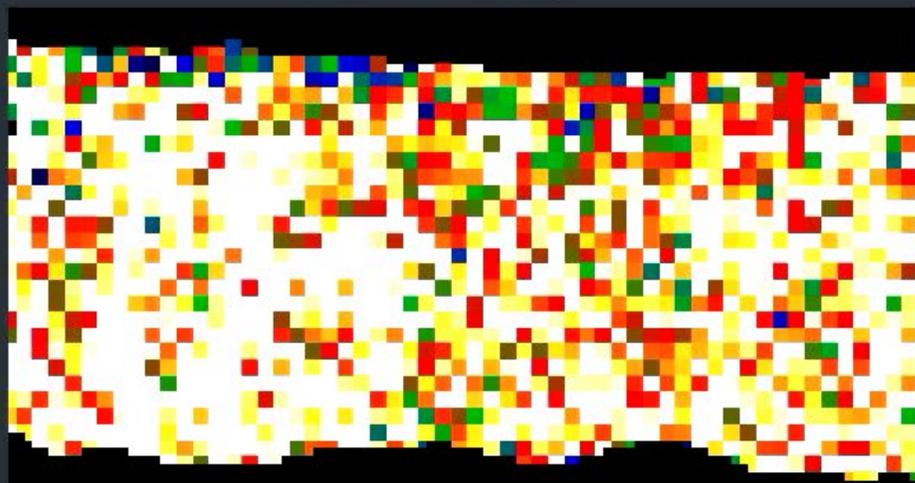
Charge 0%

Discharge 0%

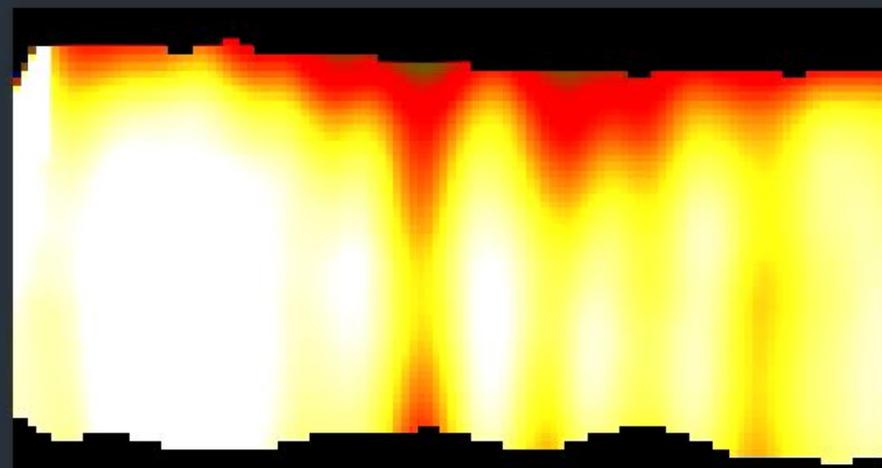
Low  High

Li concentration

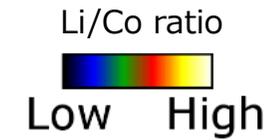
Raw Li map



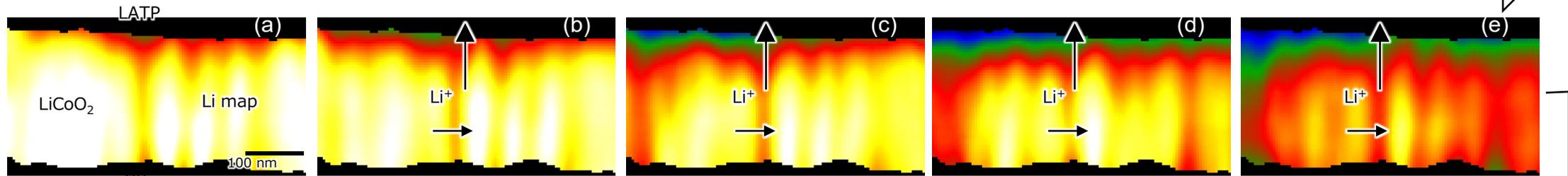
Reconstructed Li map with Sparse Modeling



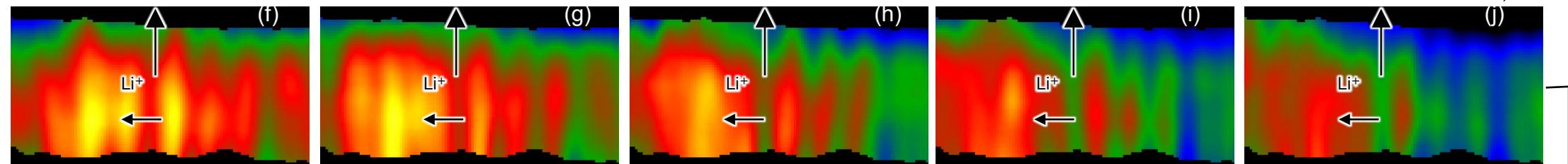
Snapshots of the Li map movie



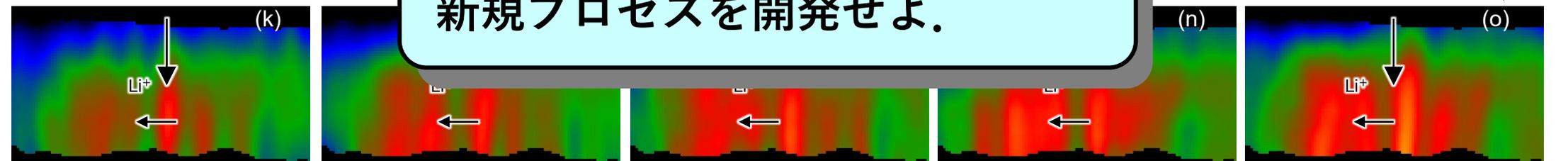
Charge (Extraction of Li-ions)



Charge (Extraction of Li-ions)



LiCoO₂薄膜の結晶方位を揃える
新規プロセスを開発せよ。

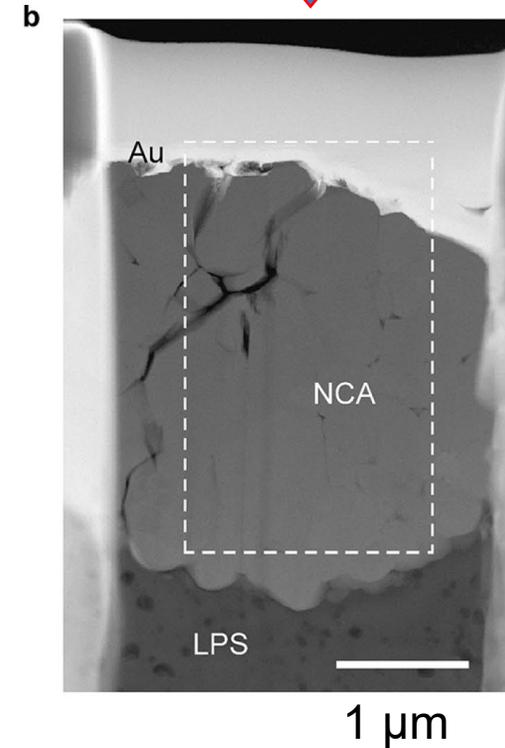
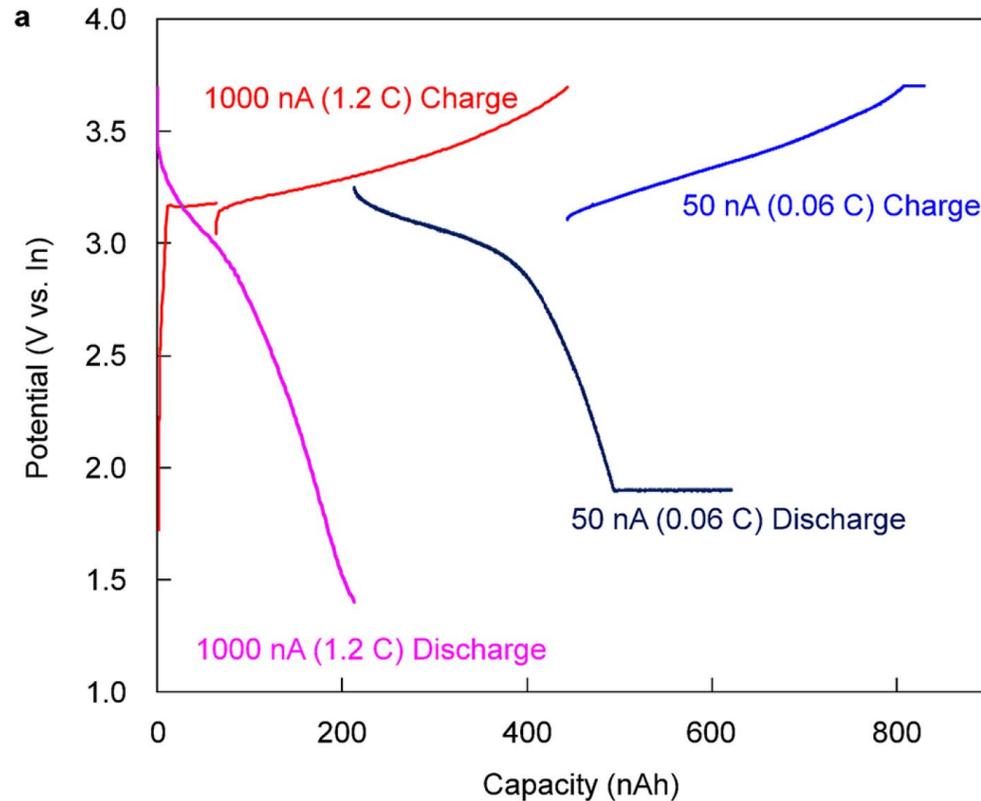
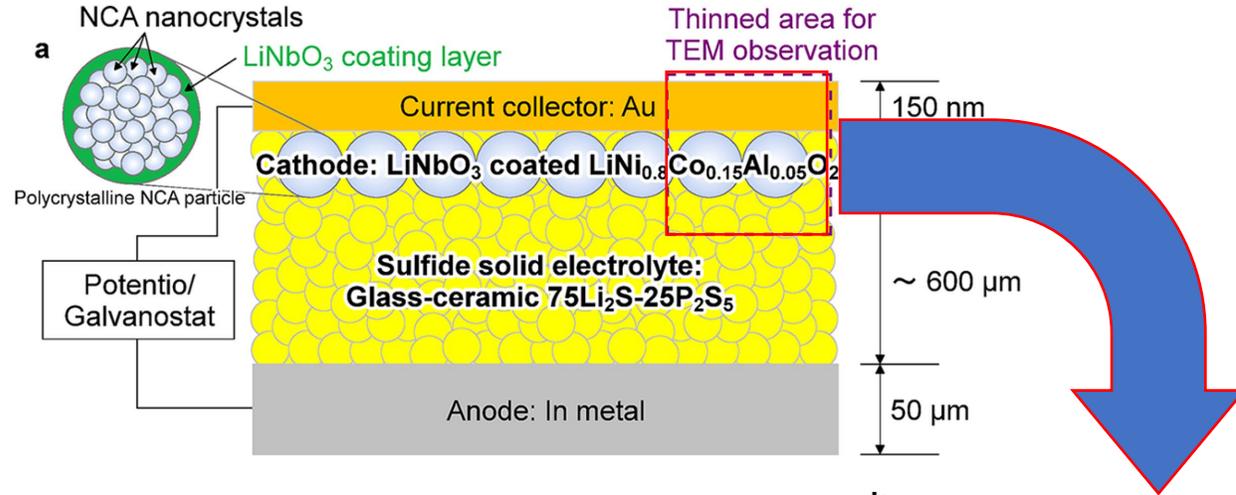


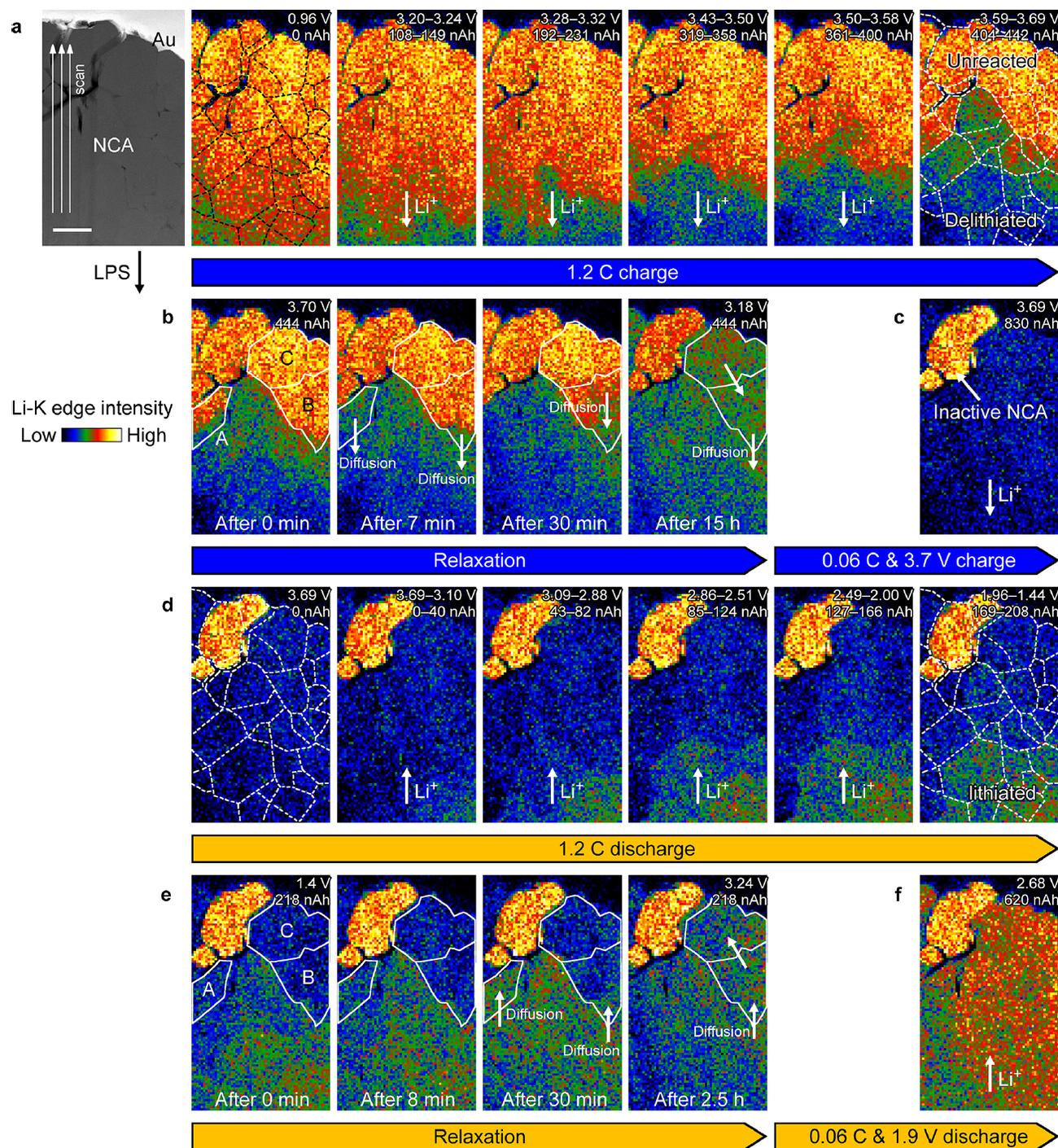
Li-ions moved in not only perpendicular direction but also parallel direction to the interface

バルク型全固体電池の正極粒子内部のLi分布の可視化



野村優貴

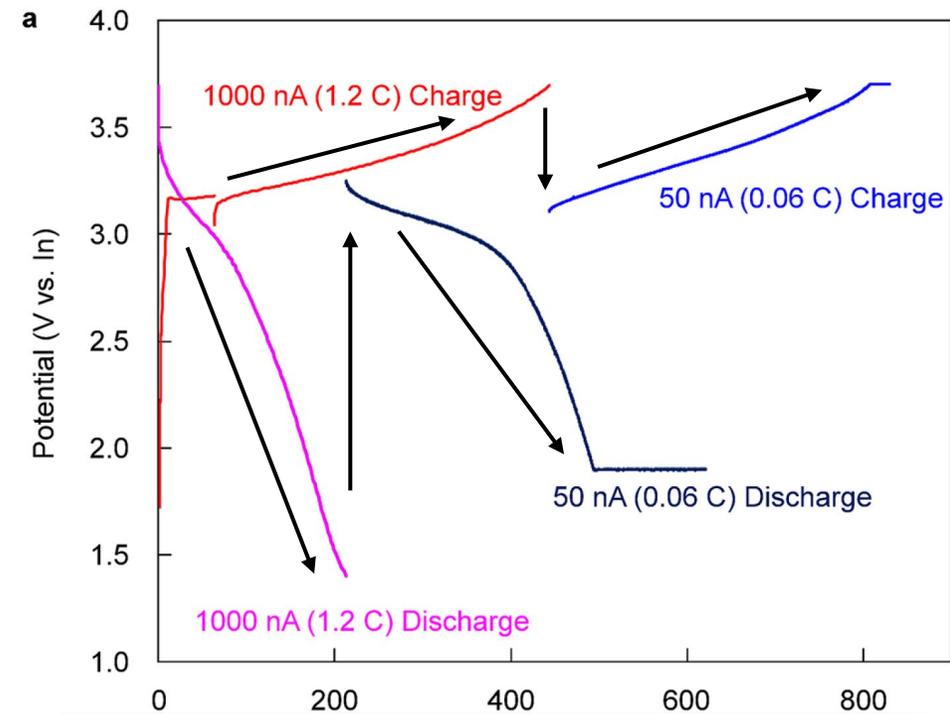




Y. Nomura, K. Yamamoto et al.
ACS Energy Lett. 5 (2020) 2098-2105.



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一次粒子の結晶方位を揃える
新規プロセスを開発せよ。



Li伝導度 : $1.2 \times 10^{-11} \text{ cm}^2/\text{s} > 1.0 \times 10^{-13} \text{ cm}^2/\text{s}$

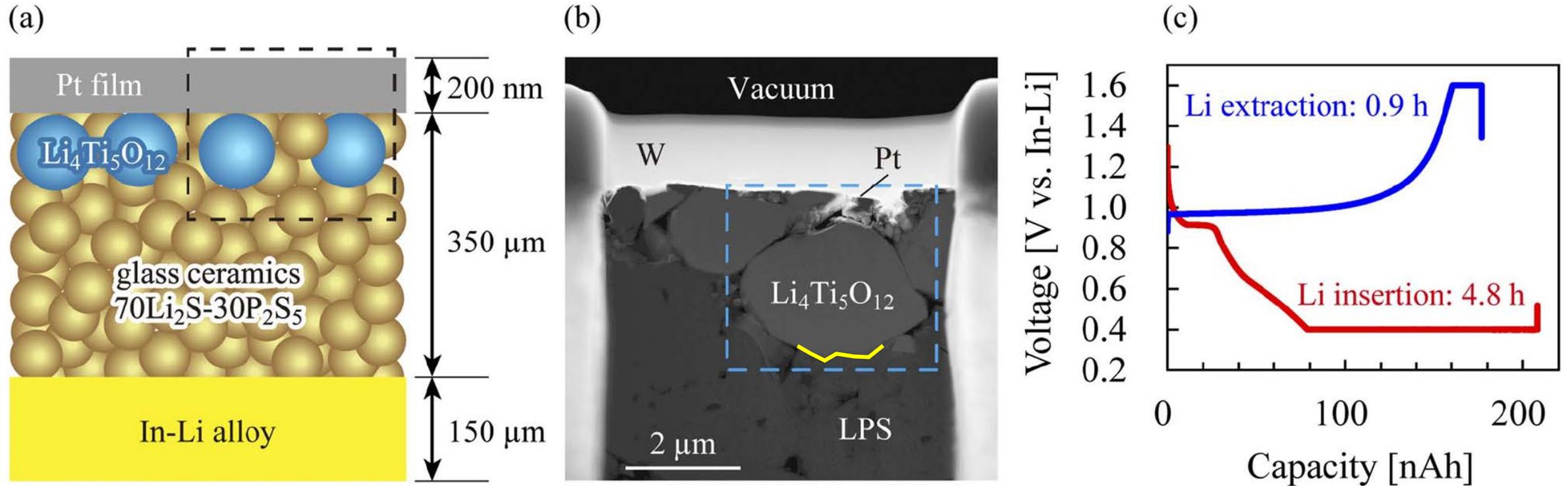
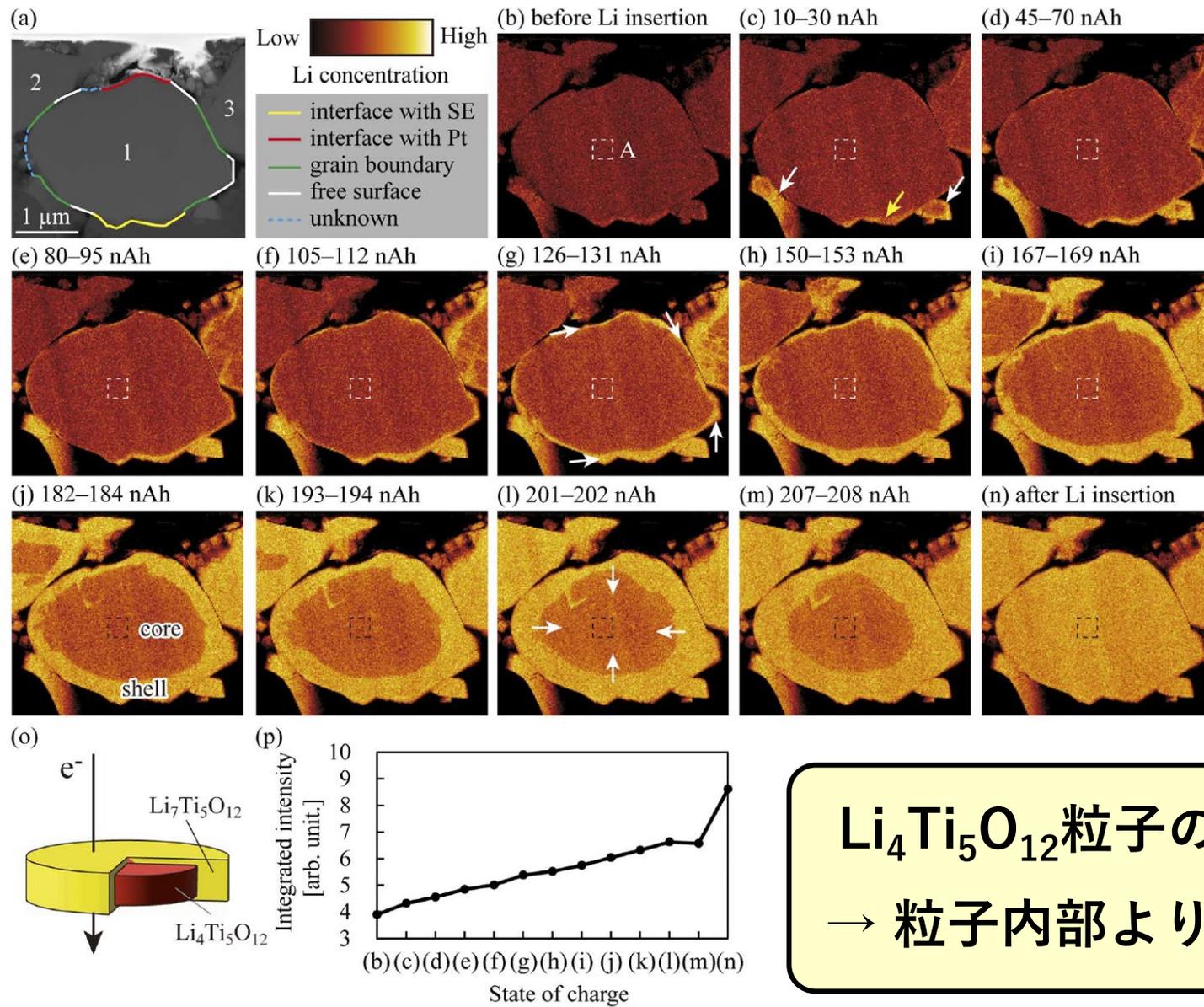
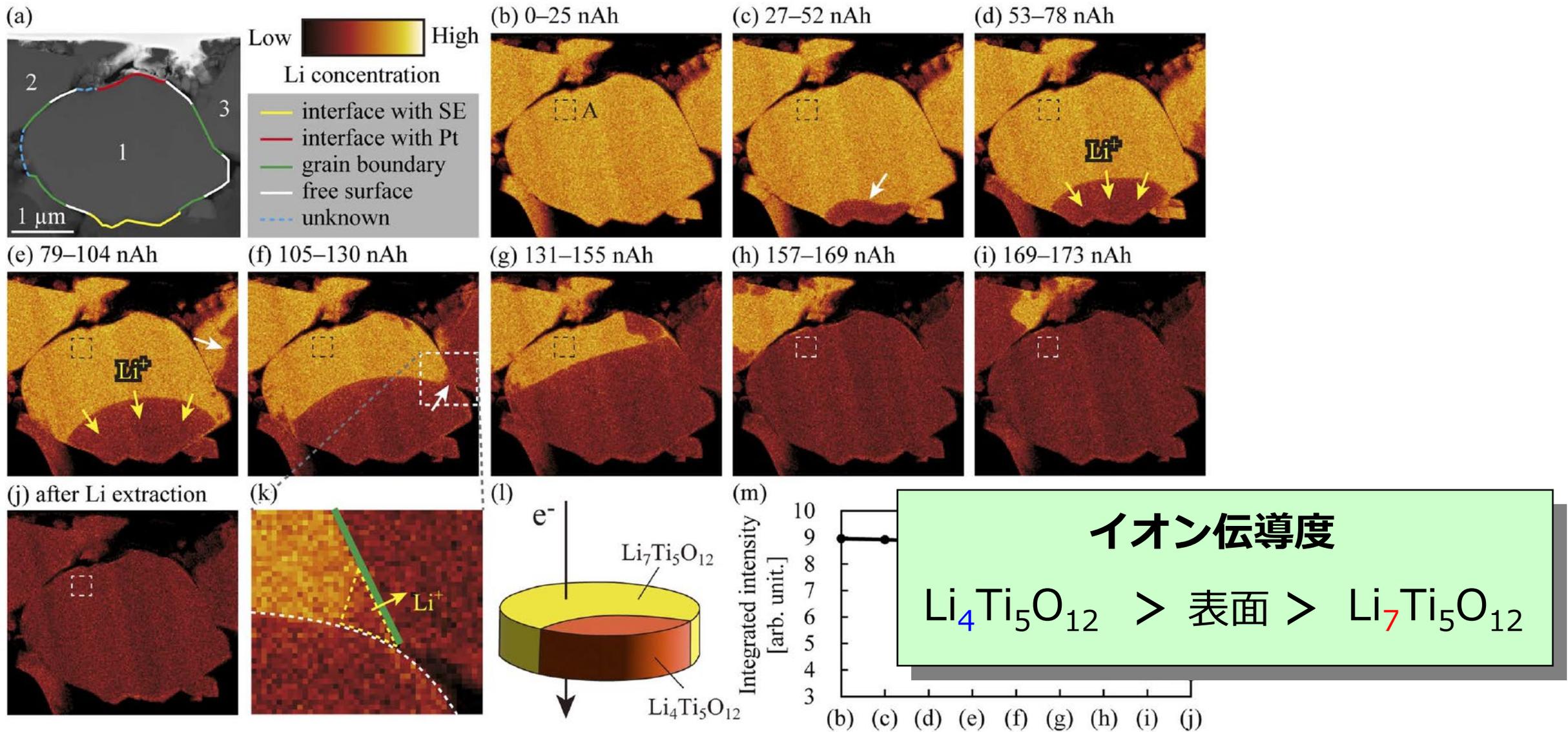


Fig. 1 Solid-state Li-ion battery used for *operando* STEM-EELS observations. (a) Schematic of a bulk-type sulfide-based solid-state battery used in this study. (b) ADF-STEM image of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. (c) Charge-discharge curves of the thinned battery cell operated in a transmission electron microscope.



$\text{Li}_4\text{Ti}_5\text{O}_{12}$ 粒子の表面に回り込んでLiが挿入する！
→ 粒子内部よりも、表面の方がLi伝導度が高い。

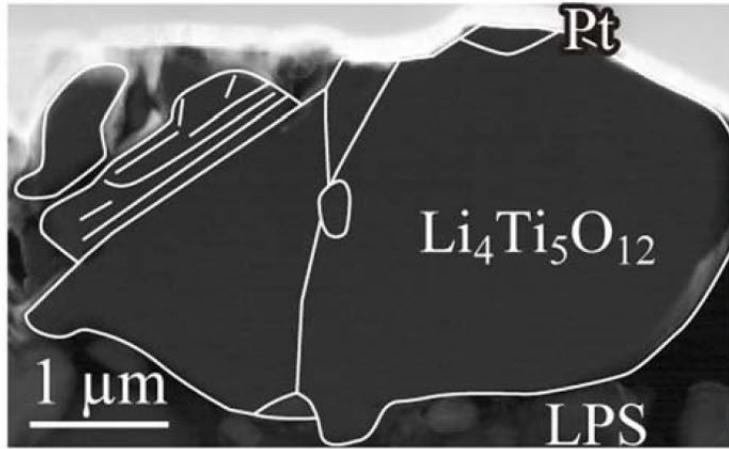
Fig. 2 Phase transition with surface Li diffusion and core–shell structure during Li insertion. (a) ADF-STEM image with color lines highlighting different surface categories. The yellow lines represent the interfaces between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -1 particle and SE. The red lines represent the interfaces between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -1 particle and current collector. The green lines show the grain boundaries between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The white lines represent the surfaces that are not in contact with anything. The dashed cyan lines represent the surface with unknown categories. (b–n) Change in the Li distribution visualized by *operando* STEM-EELS. The amount of inserted Li ions is shown in each panel. (o) 3D schematic of the lithiated lamella during Li insertion. SE and current collector have been omitted for ease of viewing. (p) Change in the Li concentration in region "A" in (b)–(n). The x-axis shows the label of each Li distribution.



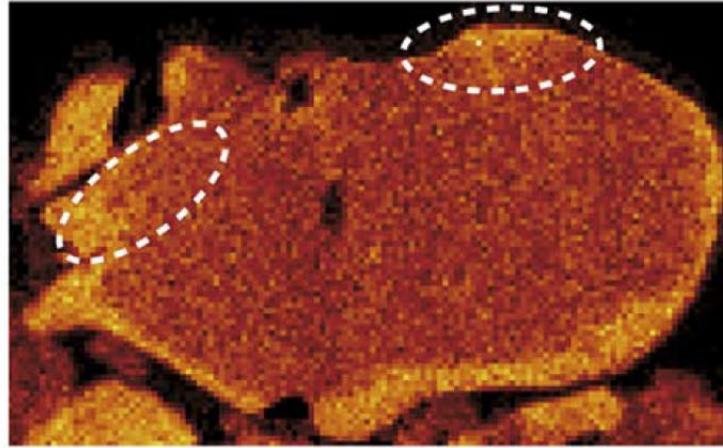
Li₇Ti₅O₁₂ 粒子と固体電解質の接する面からLiが脱離する！
→ 表面よりも、粒子内部の方がLi伝導度が高い。

Fig. 3 Phase transition without surface Li diffusion lighting surface categories. (b–j) Change in the Li dis each panel. (k) Magnified image of the dashed white region expanded radially in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -1 particle. ease of viewing. (m) Change in the Li concentration

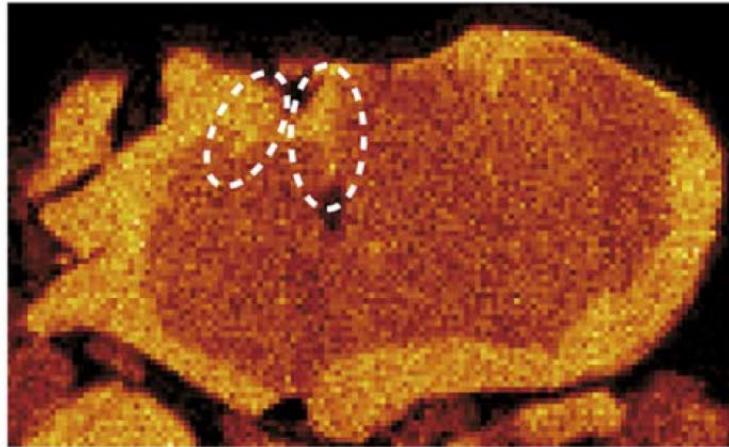
(a) グ레인境界, 欠陥位置



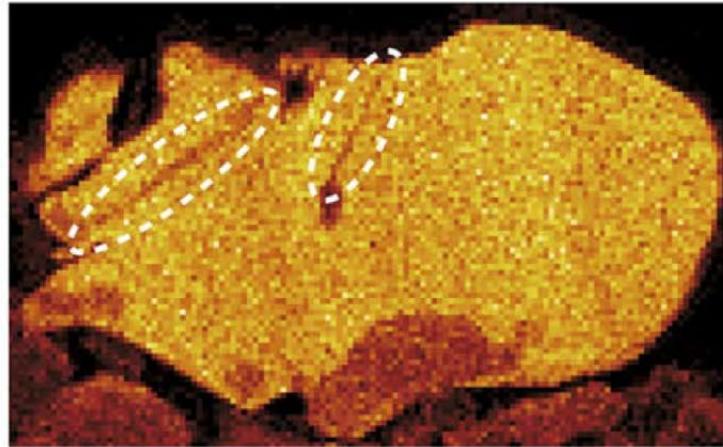
(b) Li挿入時



(c) Li挿入時



(d) Li脱離時



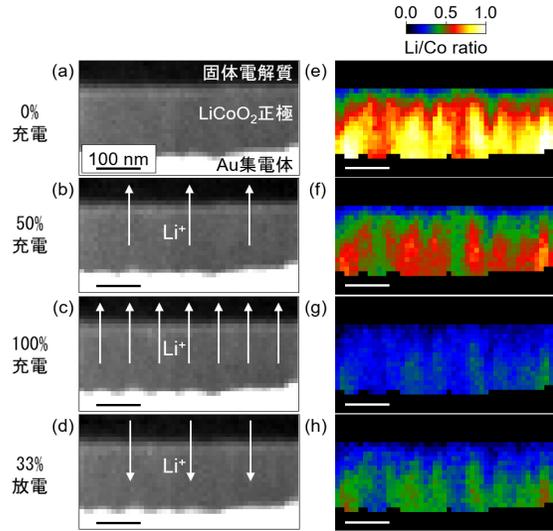
グ레인境界や欠陥では,
Li挿入脱離が速い!

小さめの粒子で, 欠陥が多い
LTO粒子の方が良い.

Fig. 4 Correlation between the grain architecture and Li distribution. (a) ADF-STEM image with lines to highlight $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grains. (b and c) Li distributions acquired during Li insertion. (d) Li distribution acquired during Li extraction.

まとめ オペランドSTEM-EELSにより，全固体電池内部のLi分布を捉えることが可能
 → プロセスへフィードバックして，高性能な電池開発に貢献できる。

薄膜型全固体電池



バルク型全固体電池

