

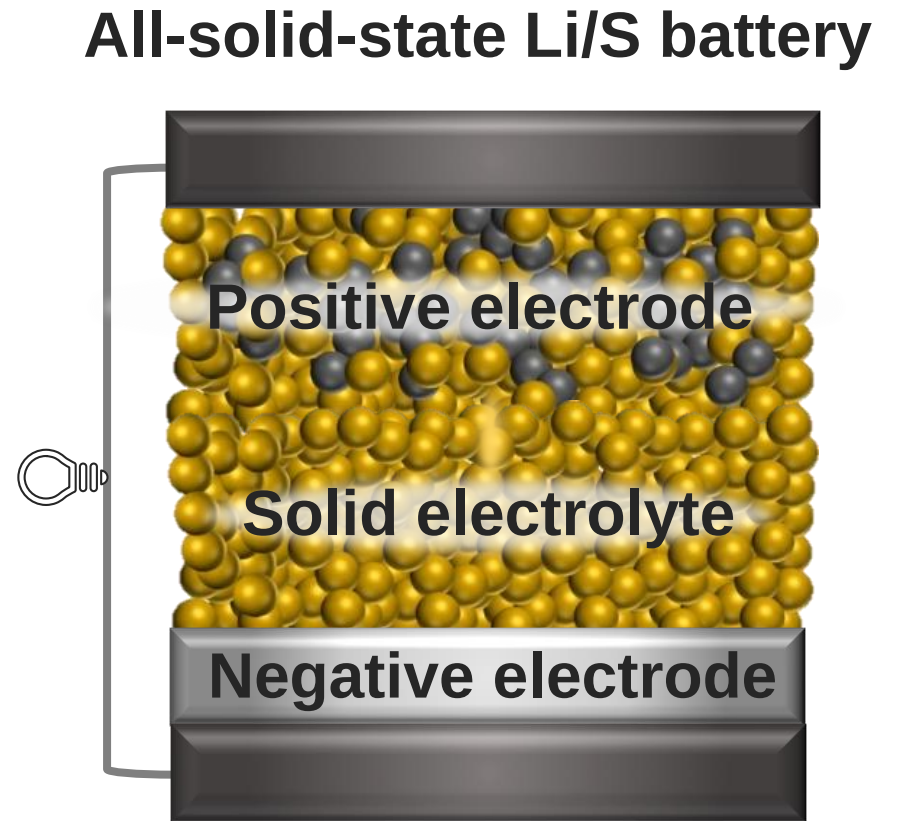
# Investigation in charge-discharge mechanism of $\text{Li}_2\text{S}$ – $\text{LiI}$ solid solution



Osaka Metropolitan University

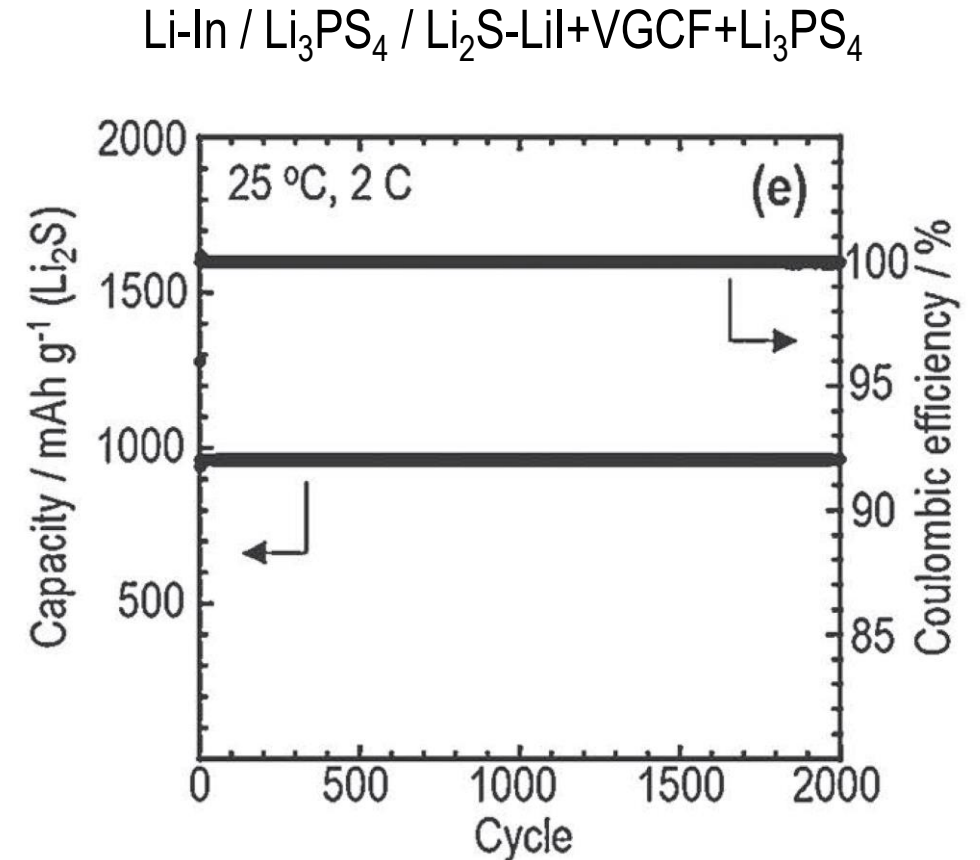
Yushi Fujita, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

- ✓ All-solid-state lithium sulfur (Li/S) batteries
  - High safety
  - High energy density
  - High cycle performance
- ✓ Lithium sulfide ( $\text{Li}_2\text{S}$ )
  - High theoretical capacity ( $1167 \text{ mAh g}^{-1}$ )
  - Allows for Li-free negative electrodes
  - But: low ionic and electronic conductivity



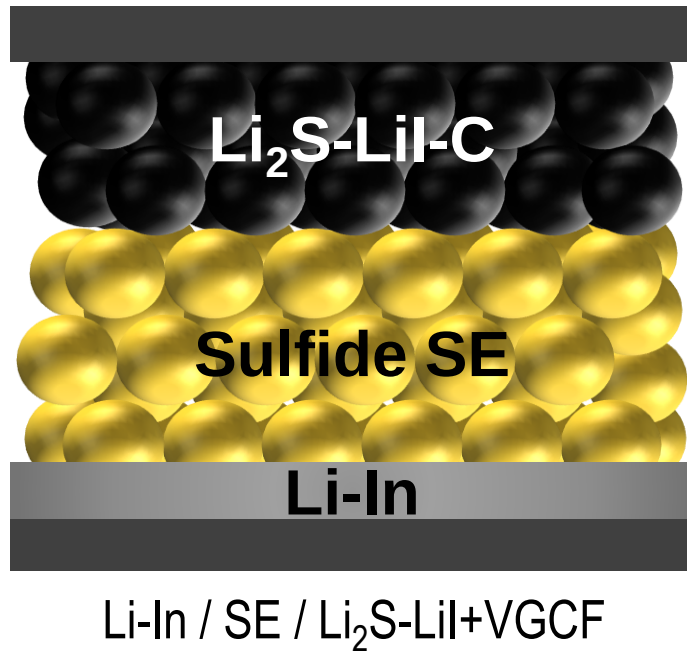
# Introduction

- ✓  $\text{Li}_2\text{S}$ -LiI solid solution
  - Prepared by ball-milling
  - Higher ionic conductivity than  $\text{Li}_2\text{S}$  ( $\sim 10^{-6} \text{ S cm}^{-1}$  vs.  $\sim 10^{-9} \text{ S cm}^{-1}$  in  $\text{Li}_2\text{S}$ )
- ✓ All-solid-state cells with solid solution as active material
  - Excellent cycle performance at 2C rate for 2000 cycles at 25 °C
- Charge-discharge mechanism of  $\text{Li}_2\text{S}$ -LiI?

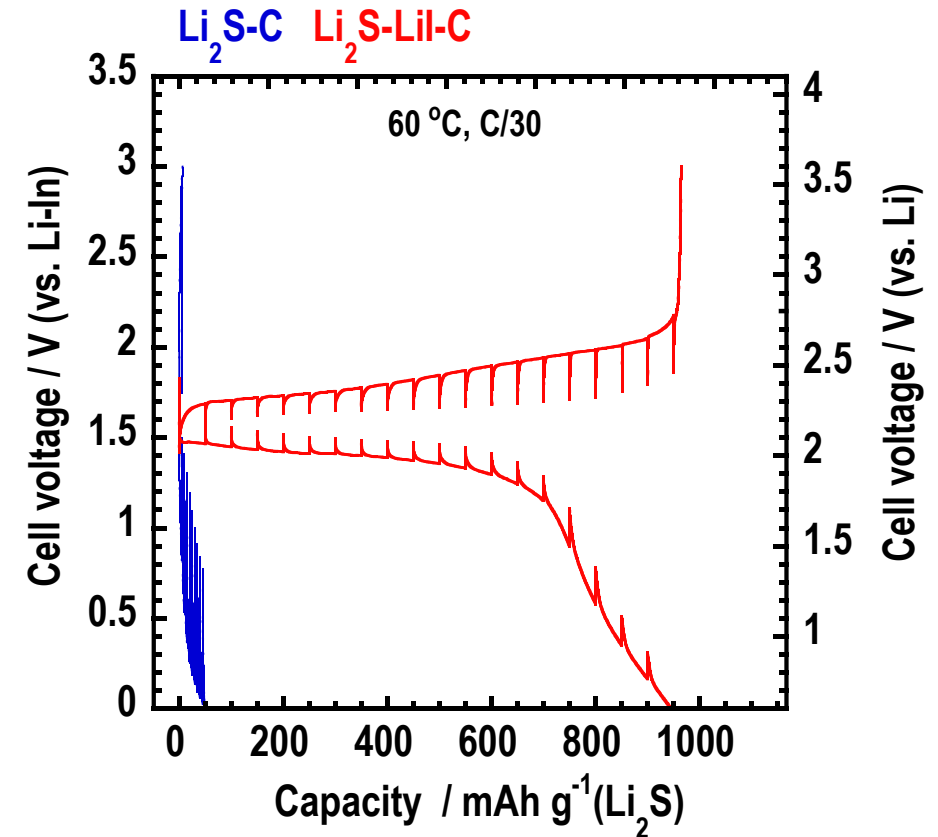


[1] T. Hakari *et al.*, *Adv. Sustain. Syst.*, **1** (2017) 6.

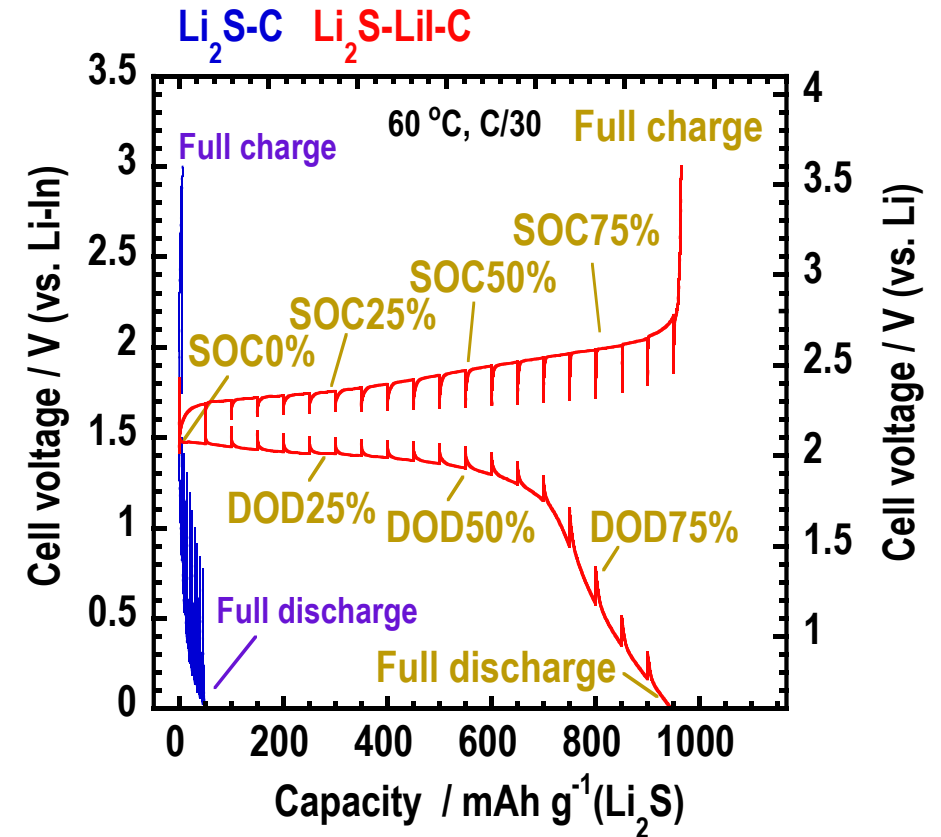
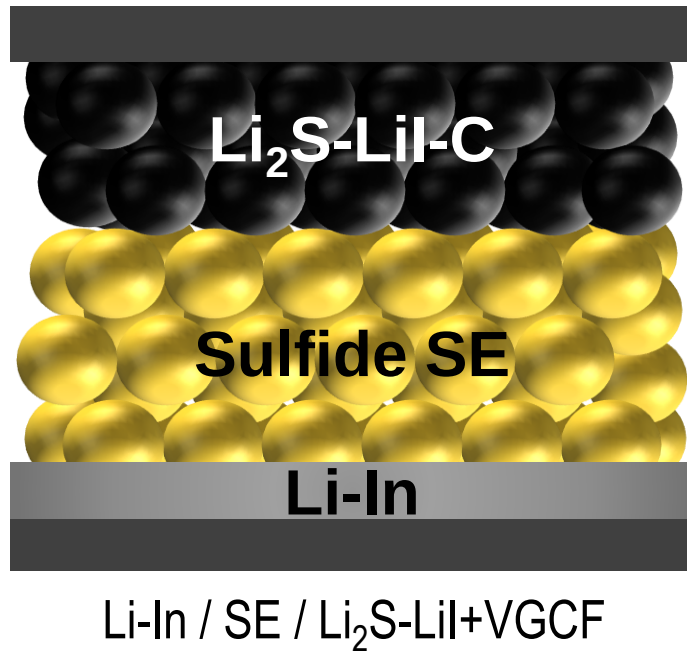
- ✓ In this study  
Investigation of charge-discharge mechanism of the cells with  $\text{Li}_2\text{S}$ -LiI solid solution
  
- ✓ Method  
*ex-situ* measurements
  - DC polarization
  - XPS analysis
  - XRD measurement
  - SEM and TEM observation



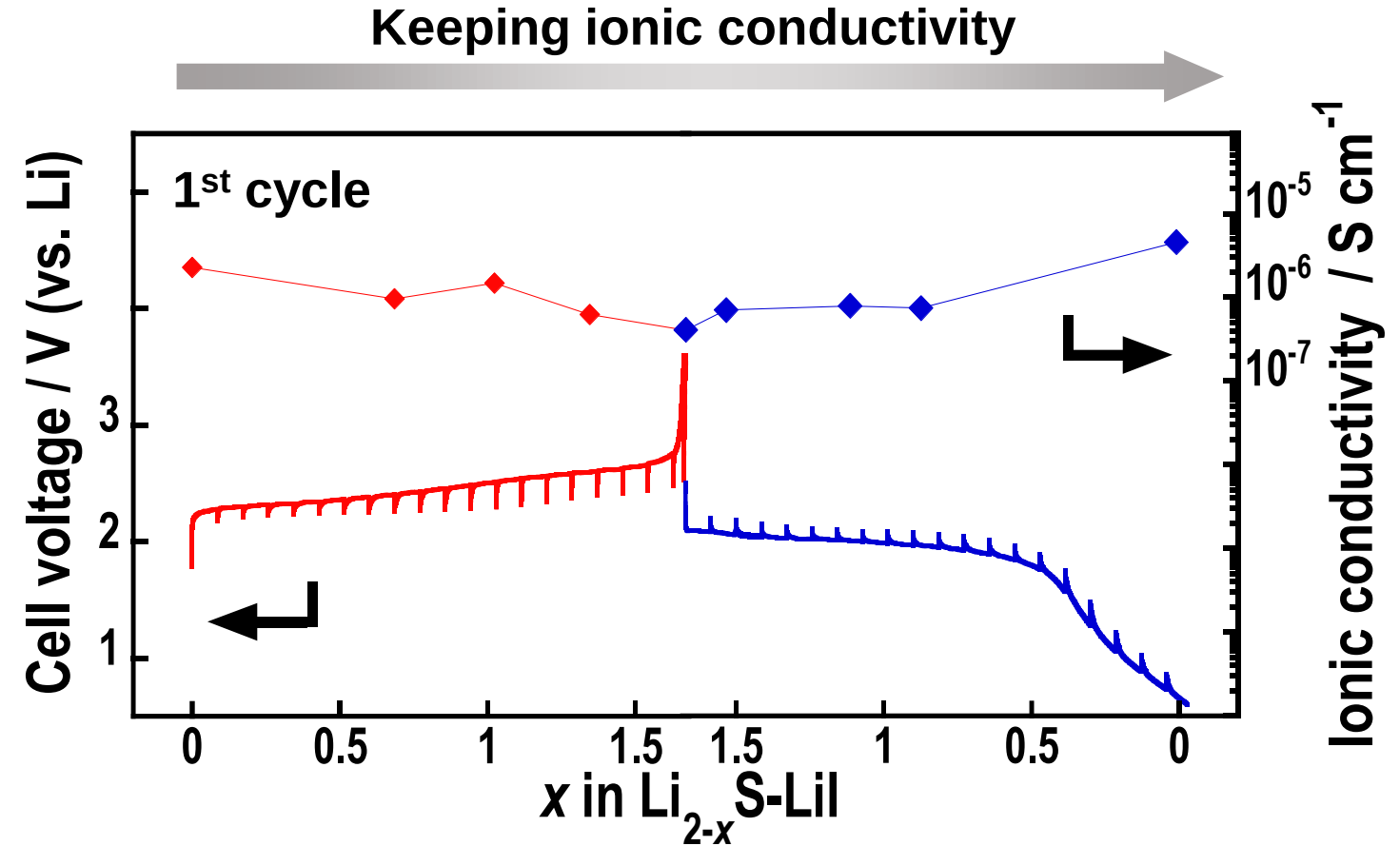
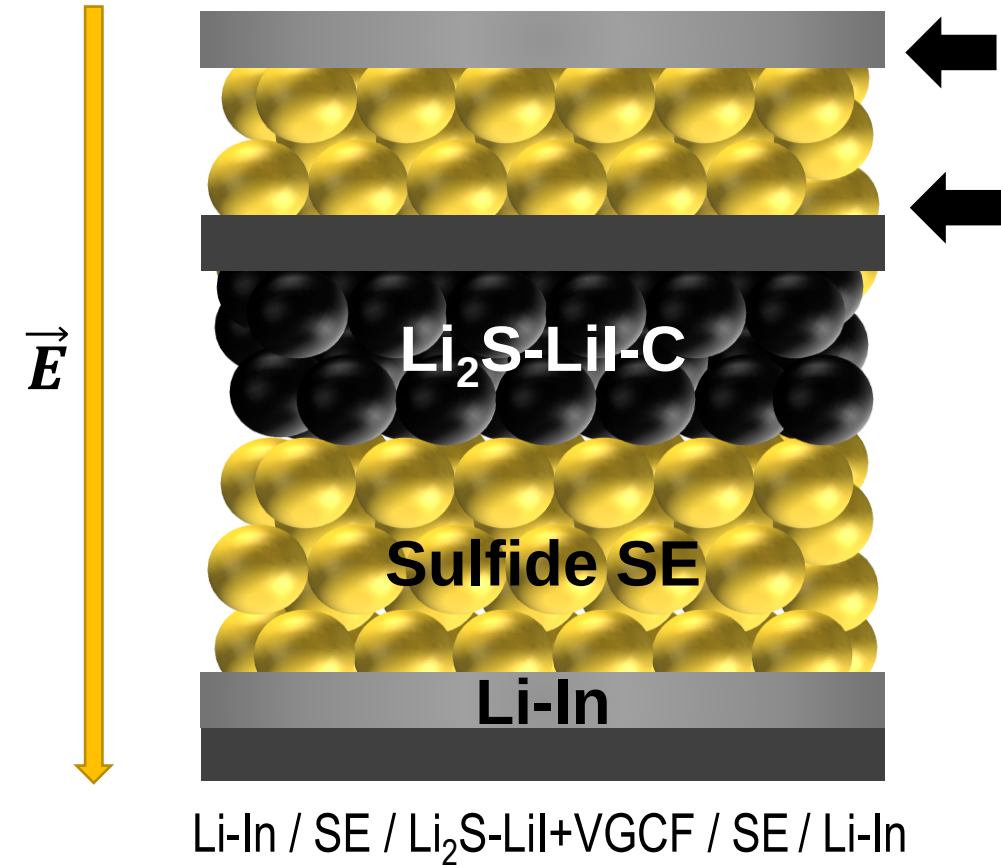
- ✓ Only solid solution as positive electrode layer (no sulfide SE)



- ✓ The cell with solid solution shows large capacity



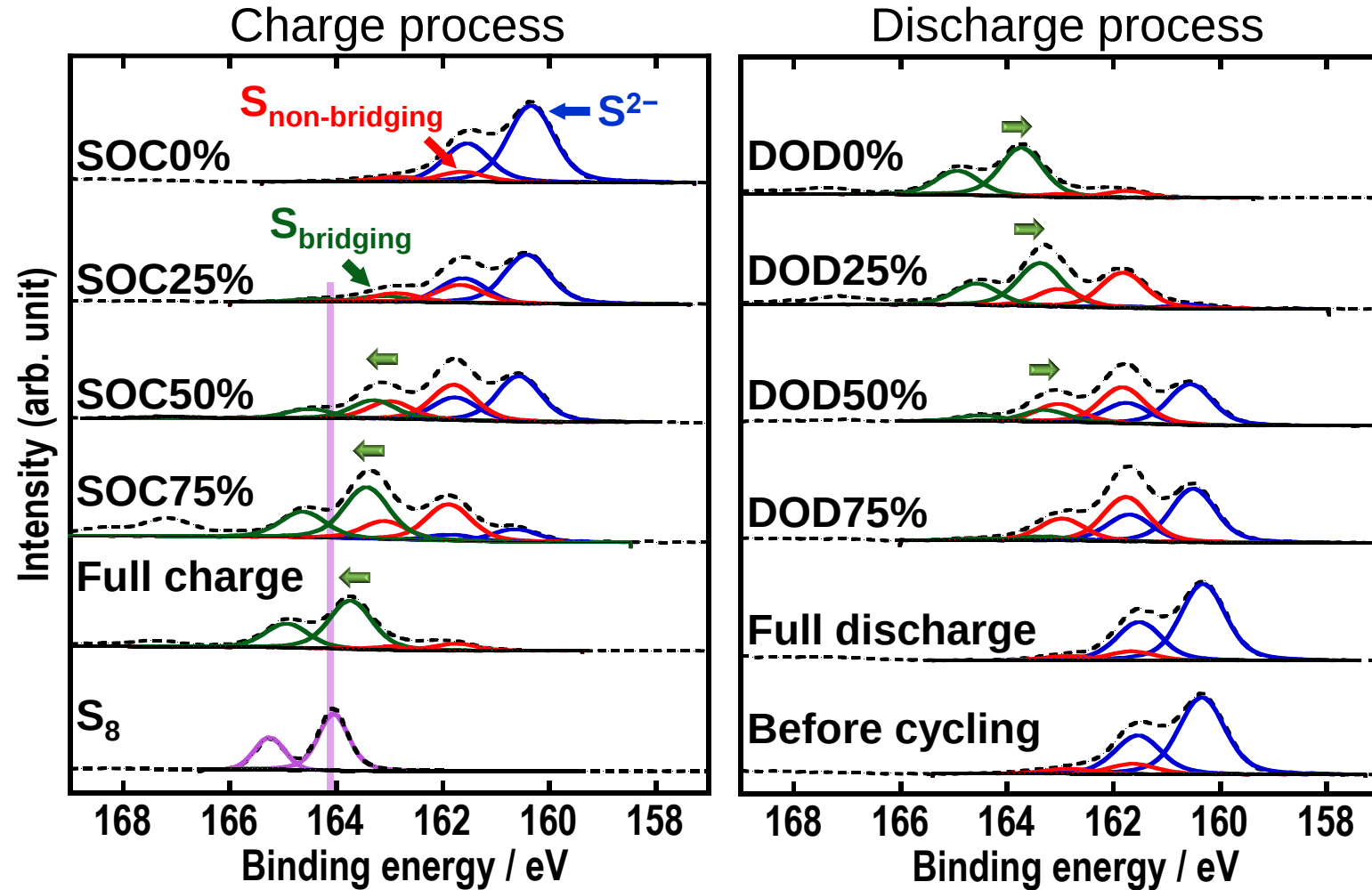
- *Ex-situ* measurements are performed at different SOC and DOD during the initial cycle



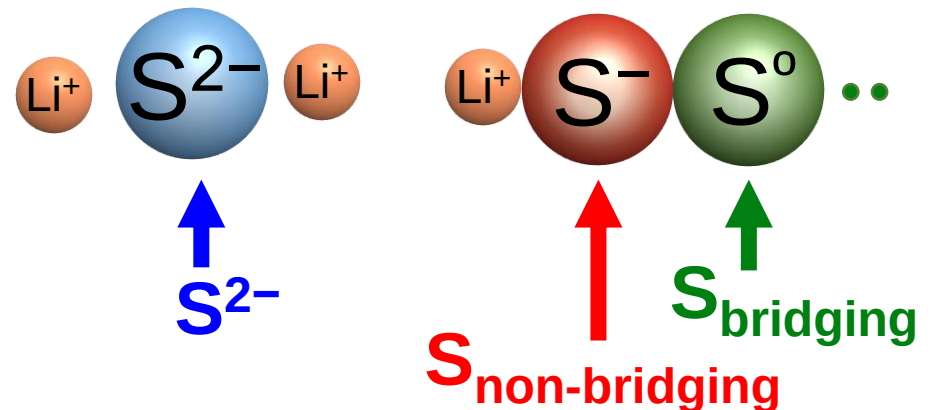
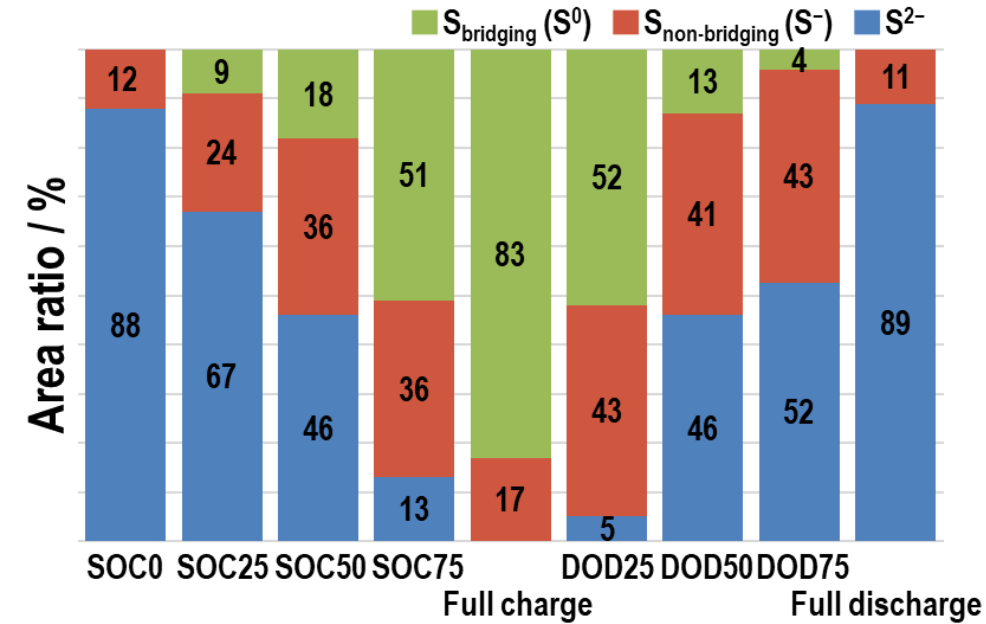
✓ Five-layered pellets are prepared for different SOC and DODs

✓ No significant decrease in ionic conductivity during cycling

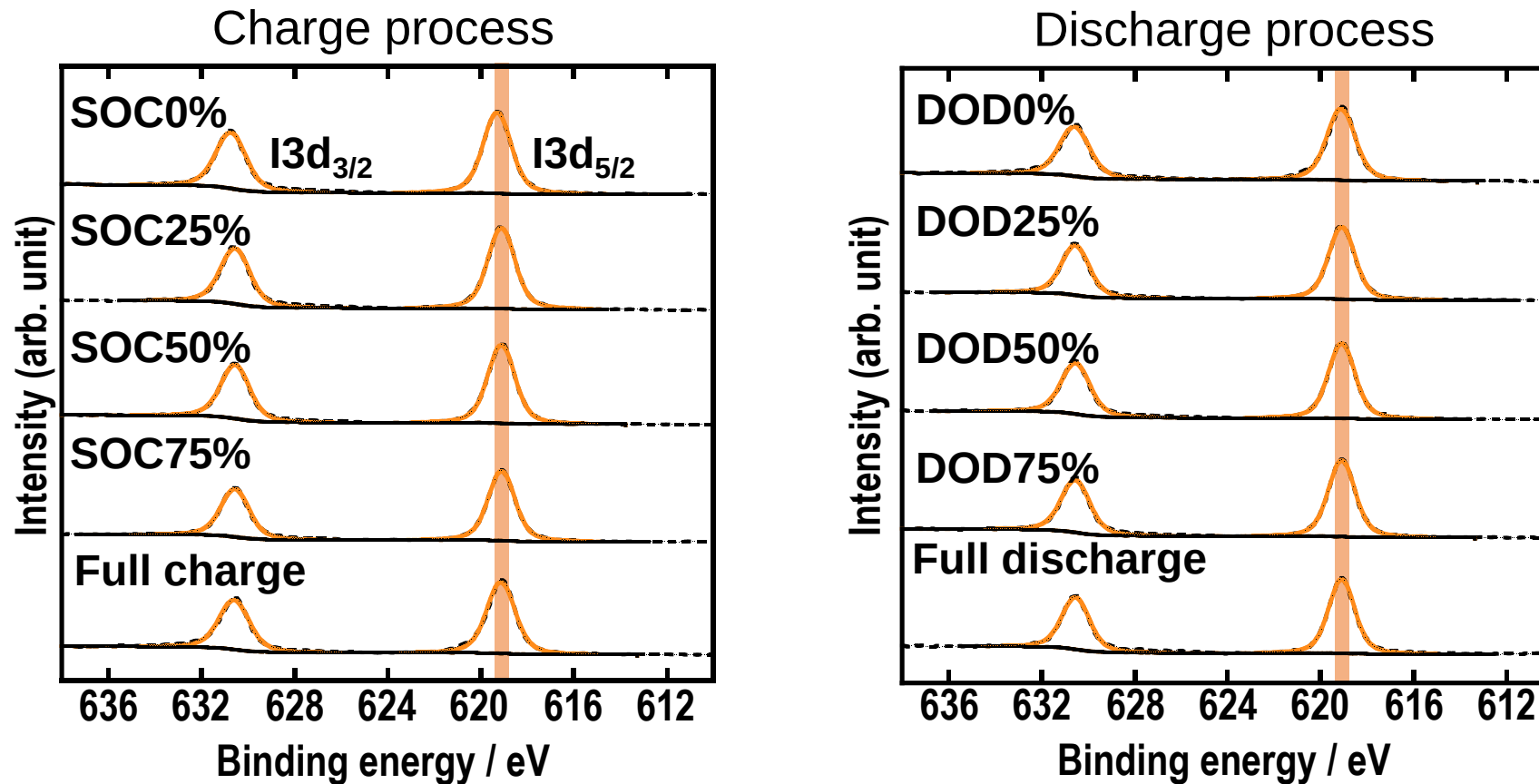
# S2p XPS analysis



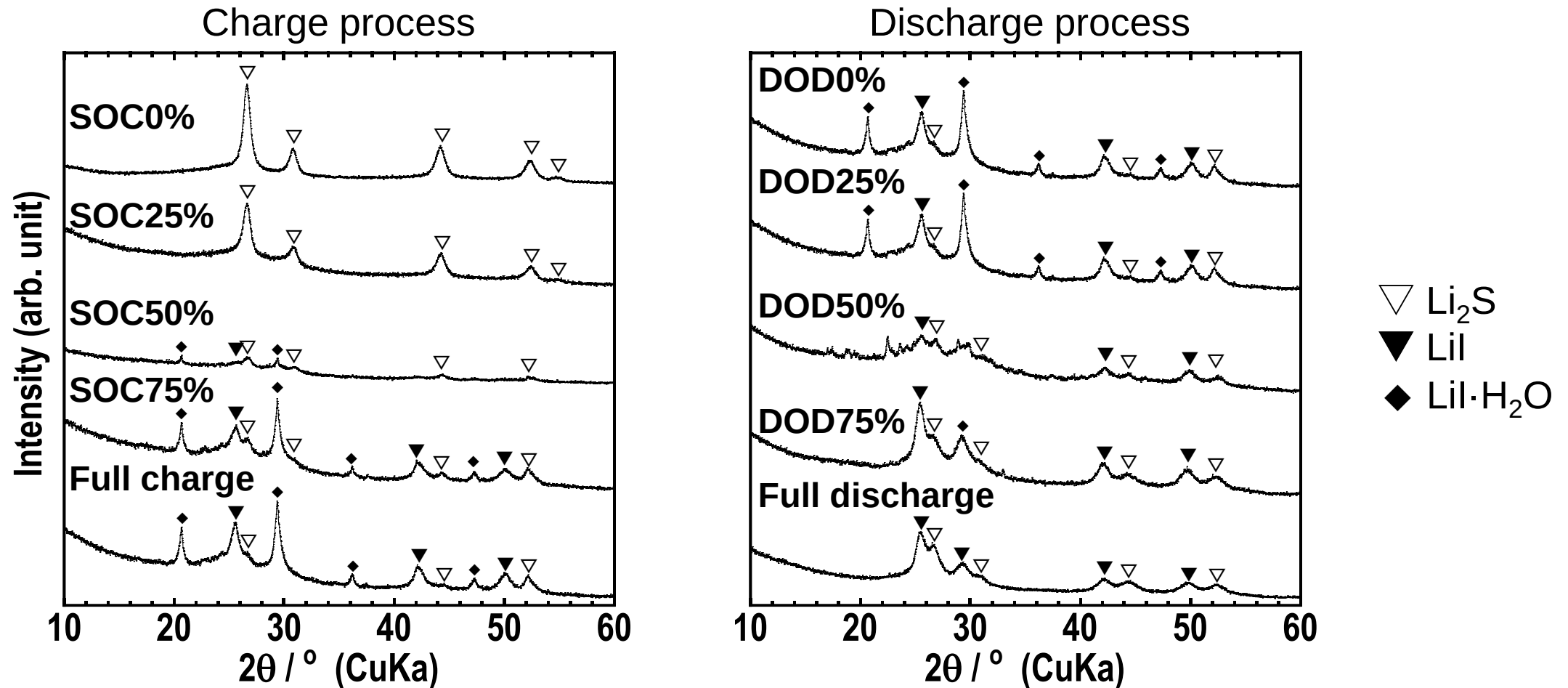
- ✓ Sulfur species are detected and quantified by XPS
- ✓ Composition changes reversibly during cycling



# I3d XPS analysis



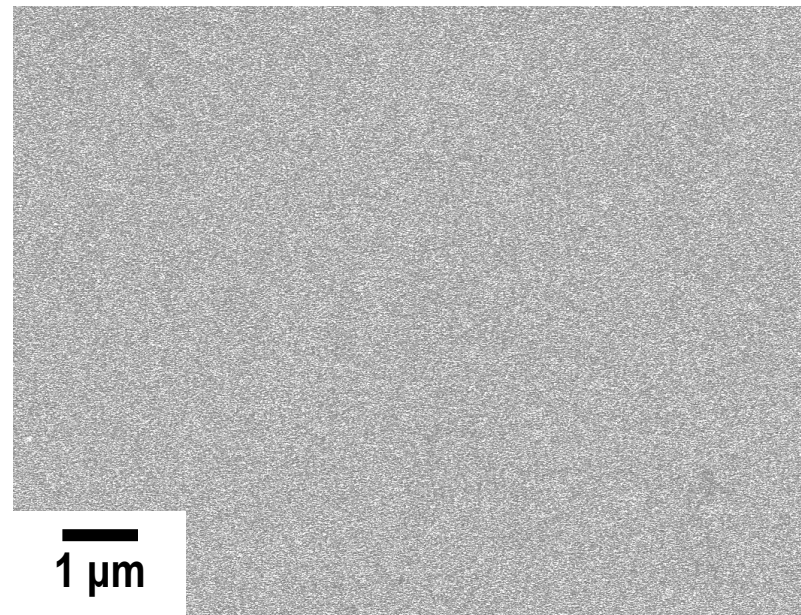
- ✓ I3d signals do not shift during the initial cycle
- LiI is not redox-active and does not contribute to the cell capacity
- LiI increases ionic conductivity in the active material



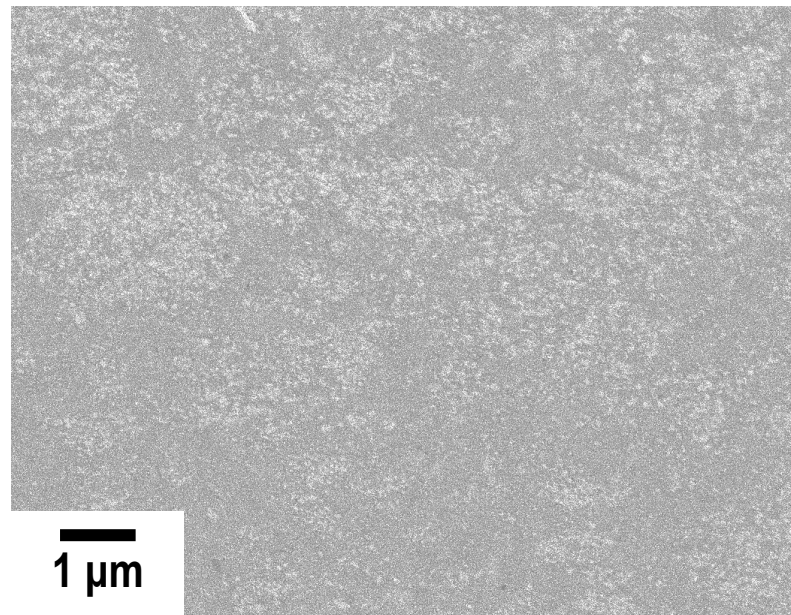
- ✓  $\text{Li}_2\text{S}$ - $\text{Lil}$  solid solution is decomposing and forming again during cycling
- ✓  $\text{Lil}$  phase is detected after 1<sup>st</sup> charge and remains after discharging

Backscattered electron image

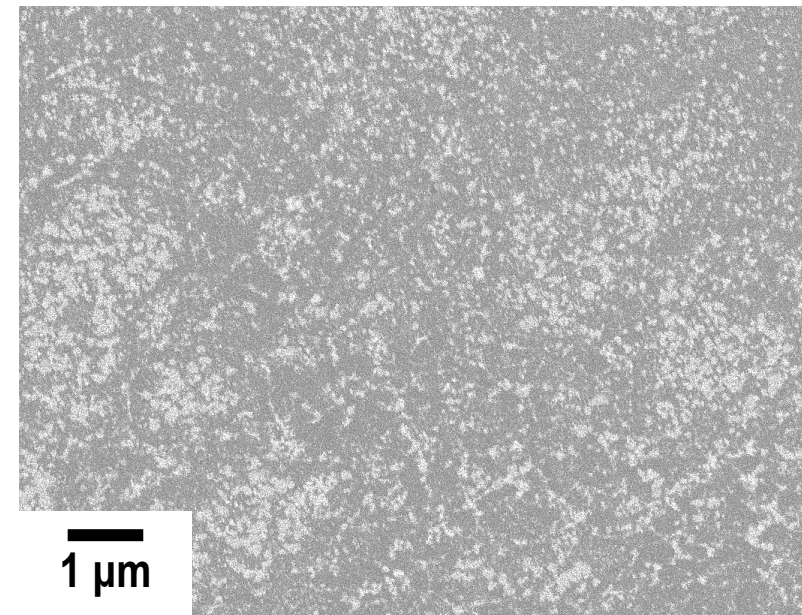
**Before cycling**



**Full charge**

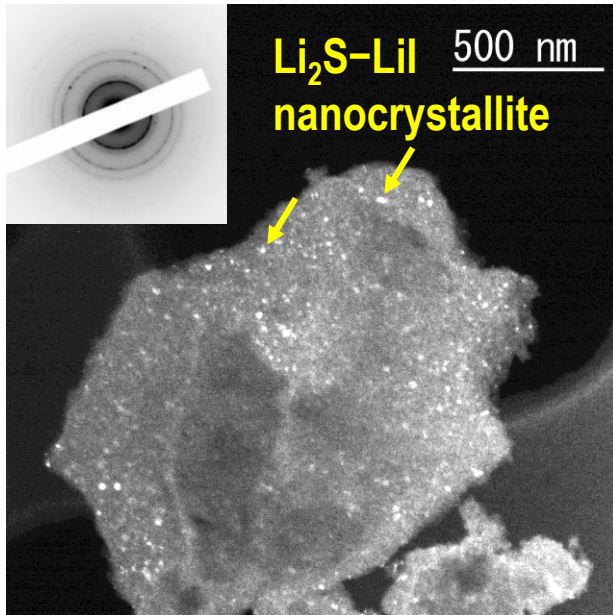


**Full discharge**

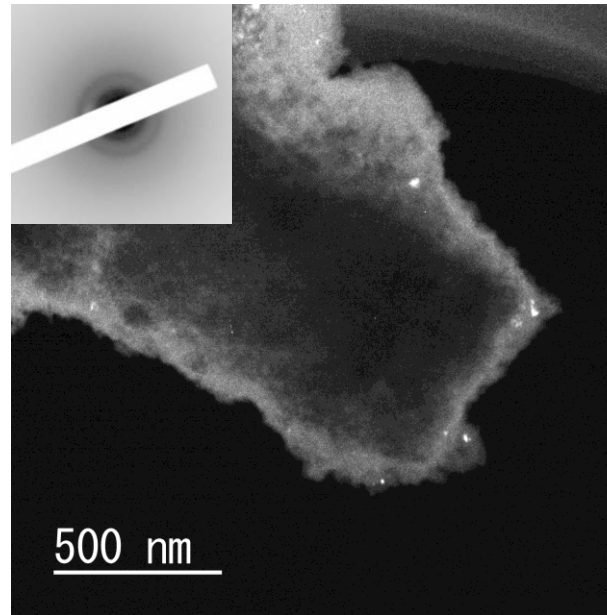


- ✓ Phase separation occurs during the initial cycling
- Lil-rich domains are formed

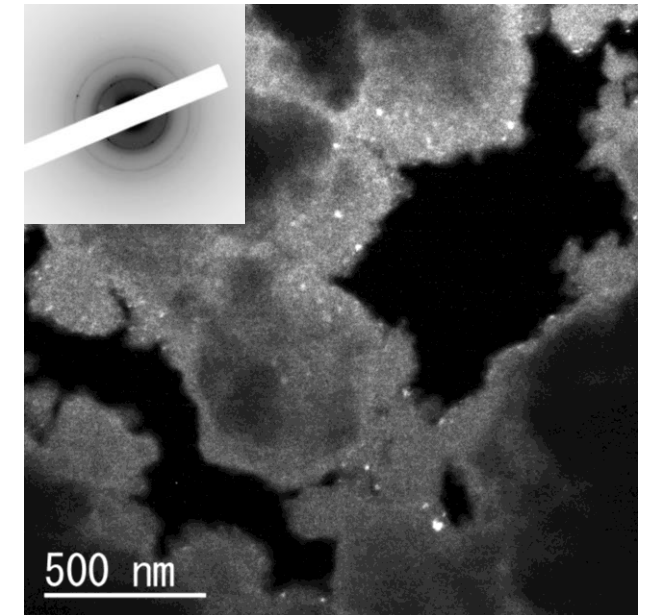
Before cycling



Full charge



Full discharge



- ✓ Electron diffraction confirms Li<sub>2</sub>S-LiI nanocrystallite before charging and after discharging
- Li<sub>2</sub>S-LiI solid solution is forming again during discharging

# Charge-discharge mechanism of $\text{Li}_2\text{S}$ - $\text{LiI}$ solid solution

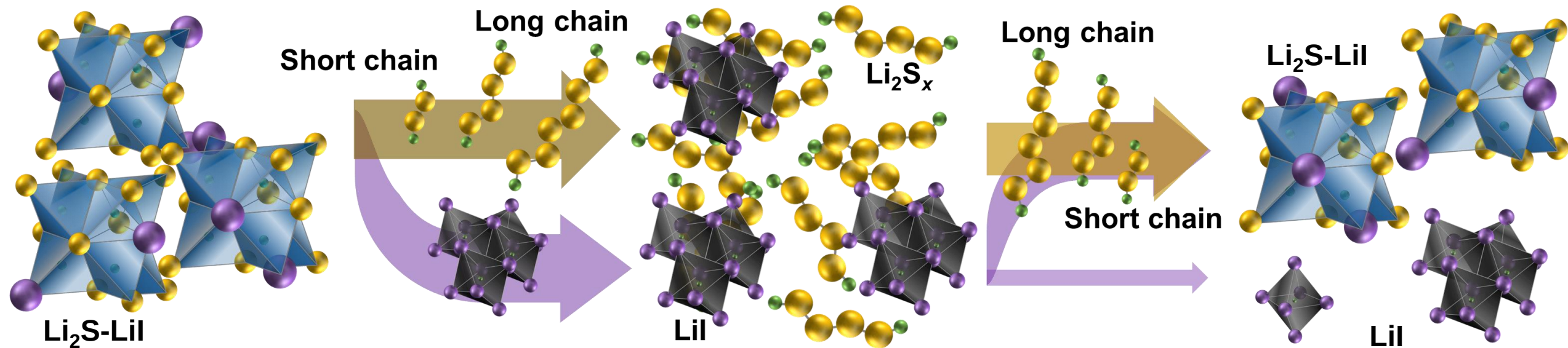
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Before cycling

Full charge

Full discharge



- ✓ Charge-discharge mechanism of  $\text{Li}_2\text{S}$ - $\text{LiI}$  solid solutions as positive electrodes was investigated by electrochemical measurements and structural analyses.
- ✓ The ionic conductivity of the positive electrode was largely maintained during the charge-discharge process.
- ✓ XPS analysis confirmed that the conversion reaction in  $\text{Li}_2\text{S}$ - $\text{LiI}$  is reversible, which results in excellent electrochemical performance.
- ✓ XRD, SEM and TEM show a phase separation into  $\text{LiI}$ -rich and -poor domains during initial charging, and the phase separation is maintained during further cycling.

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