

Elucidation of Capacity Degradation for Graphite in Sulfide-based All-Solid-State Lithium Batteries: A Void Formation Mechanism

National Institute of Advanced Industrial Science and Technology (AIST)

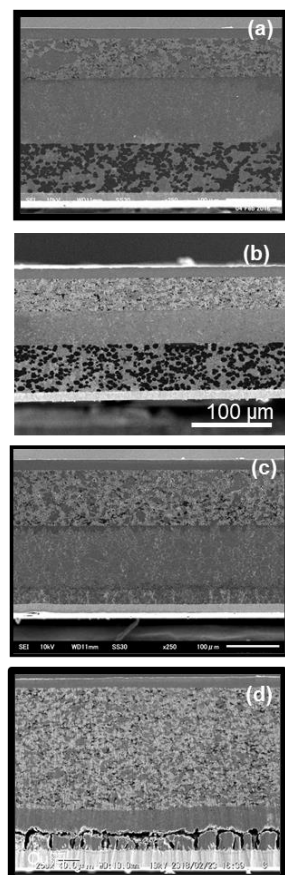
Kentaro KURATANI

Introduction

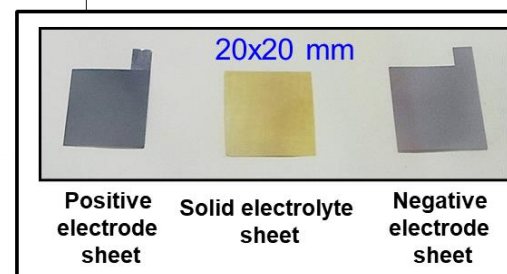
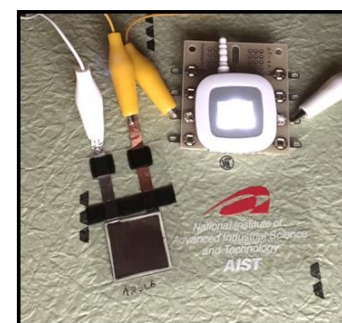
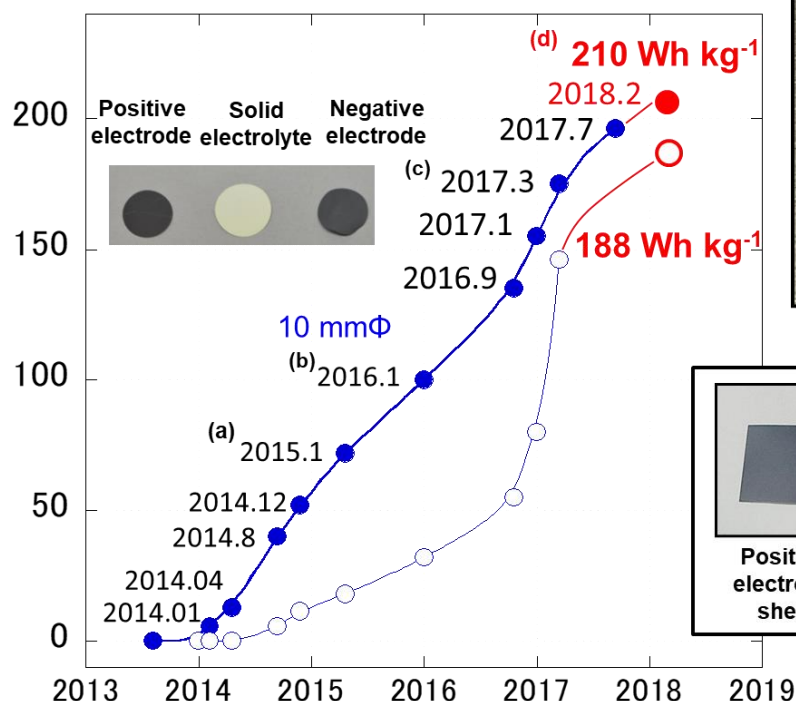
All-Solid-State Lithium Secondary Batteries (ASSBs)

Batteries which can support high energy density and high safety at the same time

Energy density transition



Energy density, E / Wh kg⁻¹ (Total sheet weight)



A. Sakuda, K Kuratani et al., *J. Electrochemical Soc.*, **164** (12) A2474-A2478 (2017)

Introduction

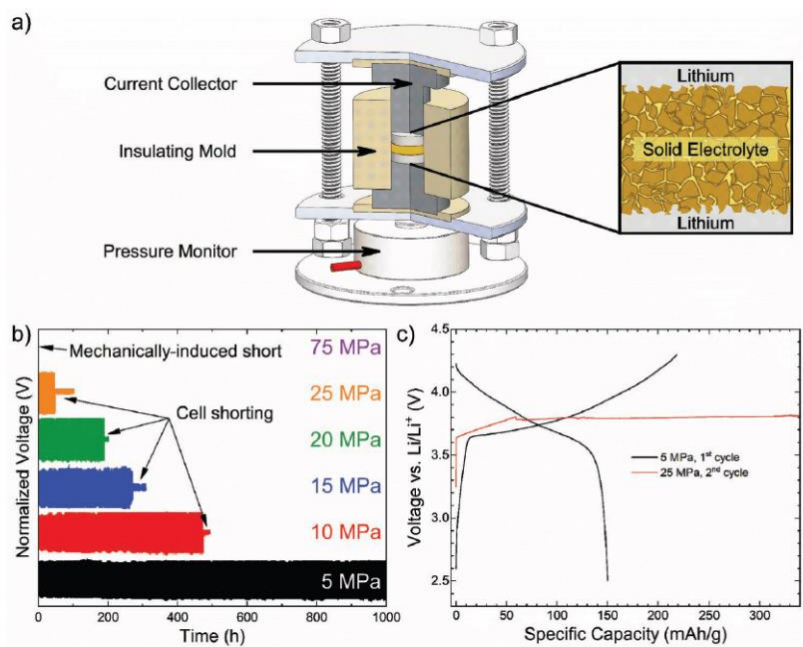
Toward the practical use of ASSBs...

- **Development of new solid electrolyte
(Ionic conductivity, Humidity resistance)**
- **Construction of good solid/solid interface**
- **Optimization of cell assembling process
(Press, Mold conditions)**

Introduction

Stack Pressure Considerations for Room-Temperature All-Solid-State Lithium Metal Batteries

Jean-Marie Doux, Han Nguyen, Darren H. S. Tan, Abhik Banerjee, Xuefeng Wang, Erik A. Wu, Chiho Jo, Hedi Yang, and Ying Shirley Meng* *Adv. Energy Mater.* **2020**, 10, 1903253



The press condition strongly affects on the electrochemical performance in ASSBs.

Herein, we demonstrate the impact of press condition during cell assembling on the cycle properties and suggest a unique capacity degradation mechanism.

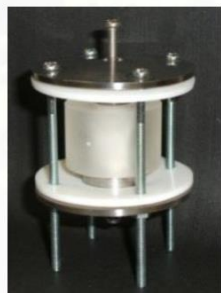
Experimental

Materials

Active material ; Graphite

Solid electrolyte ; $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (LPS)(in mol%)

Cell assembling



Composition of electrode ;

Graphite : LPS = 58 : 42 (in wt.%)

SE layer ; $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (in mol%)

Counter electrode ; Li-In

Press conditions ; 275, 330, 550 MPa

Electrode area ; 0.785 cm^2 ($\phi 10 \text{ mm}$)

Electrode weight ; 10 mg

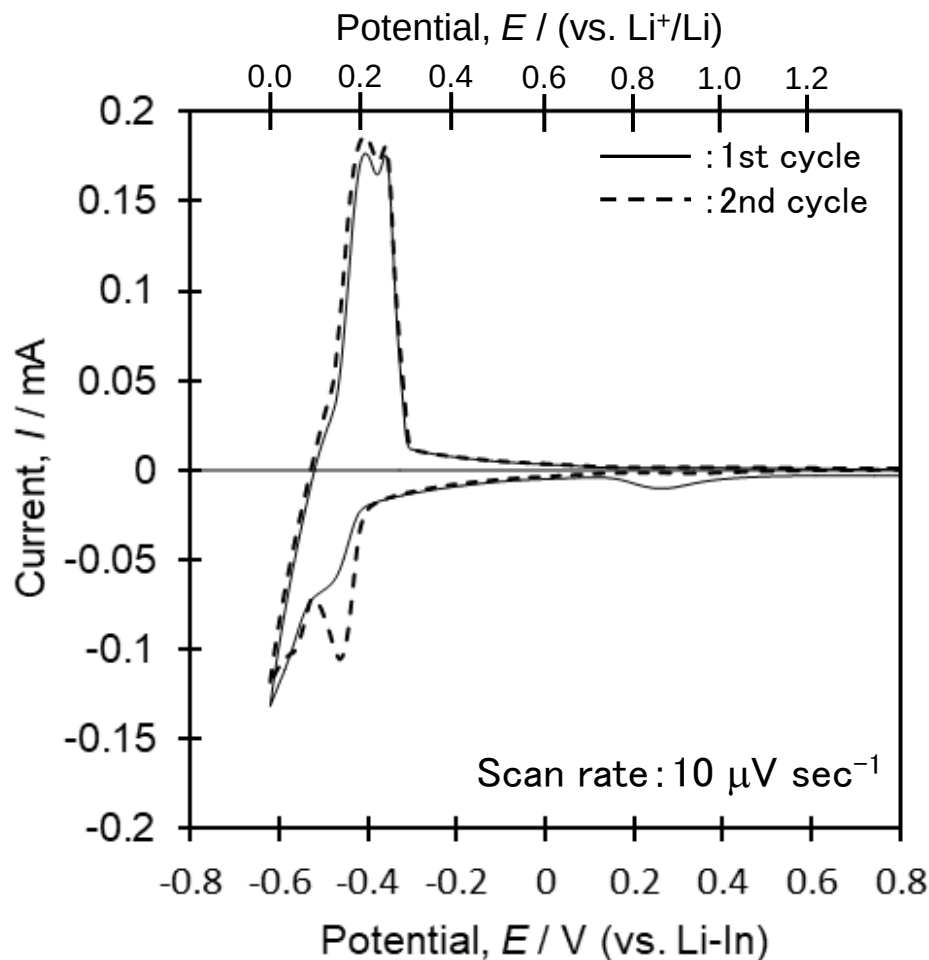
Measurements

Cyclic voltammetry, X-ray diffraction (XRD),

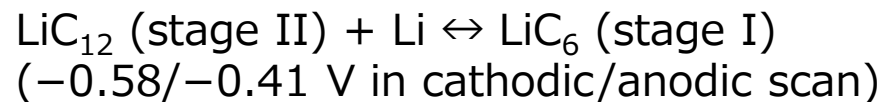
Charge/discharge test, Electrochemical impedance

Scanning electron microscopy (SEM)

Redox reaction of graphite



➤ Reversible redox reaction



Ref.) M.D. Levi and D. Aurbach, *J Electroanal. Chem.* 421 (1997) 79

➤ Irreversible reduction peak around 0.25V (vs. Li-In) only in 1st cycle

Fig. Cyclic voltammograms of the graphite electrode pressed at 550 MPa.

Stage transition of graphite

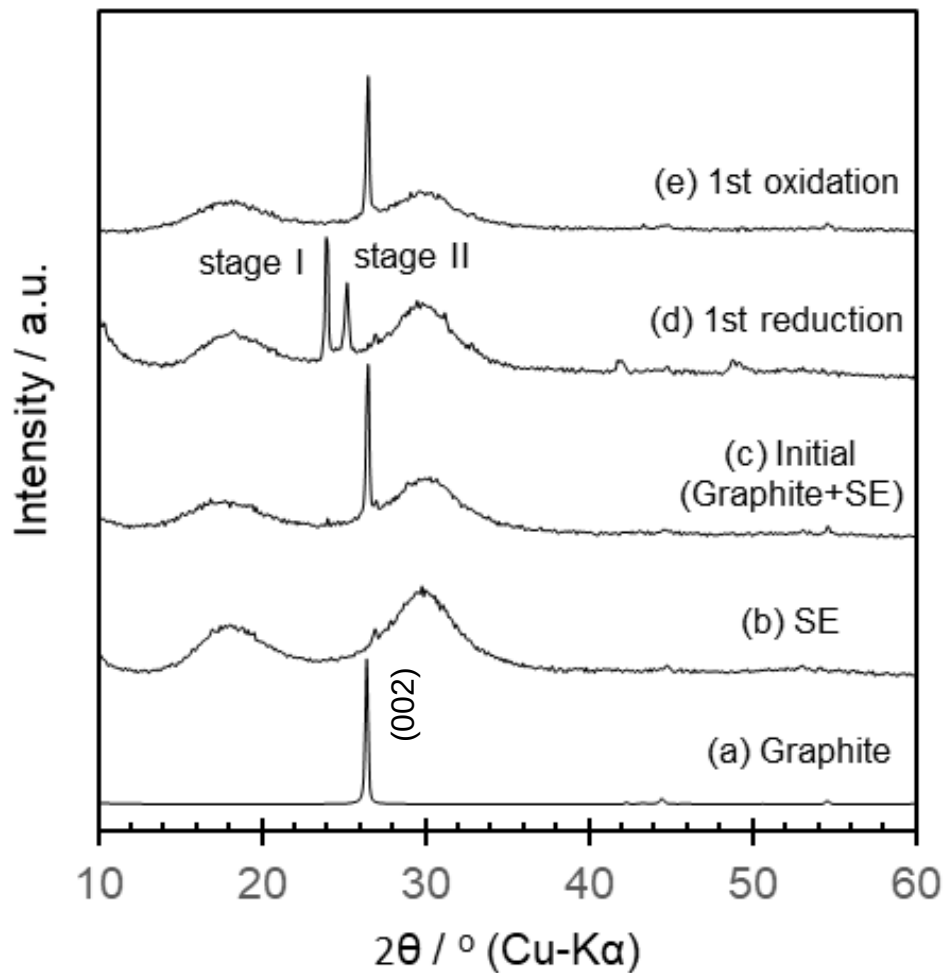
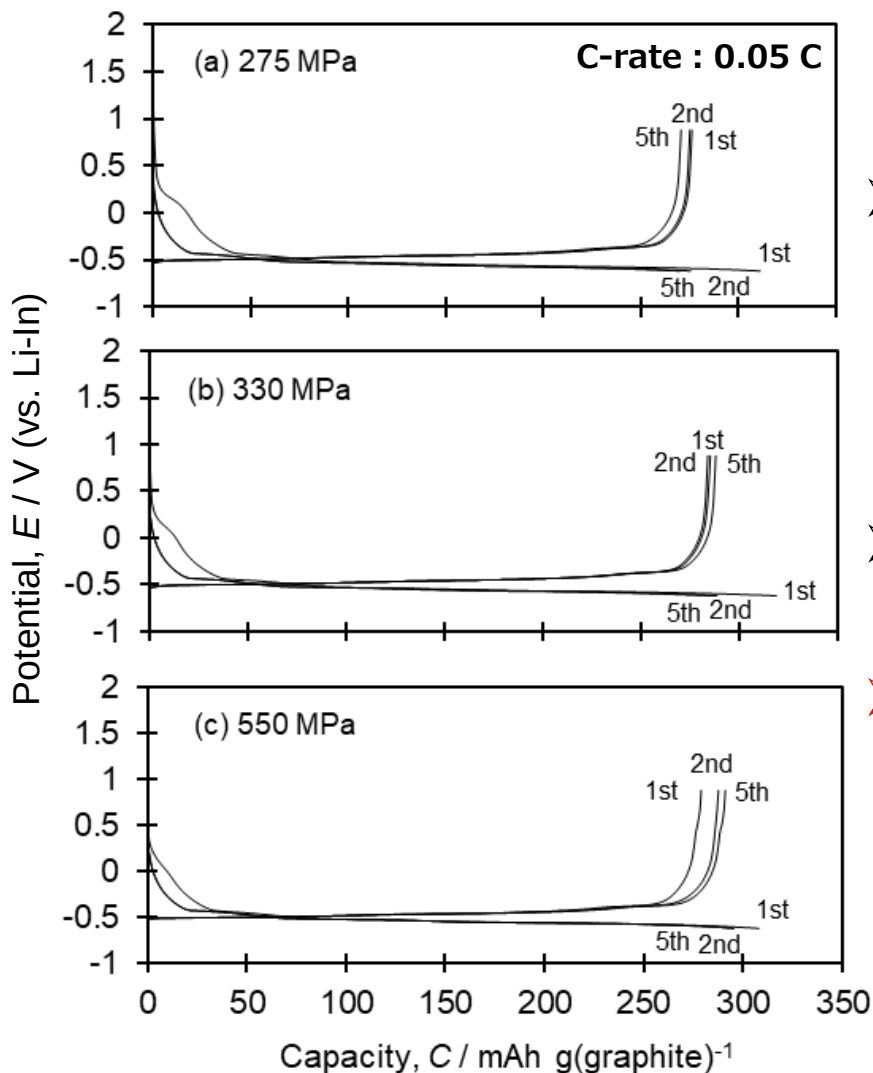


Fig. X-ray diffraction patterns.

- We confirm the peaks assigned to stage I and II after reduction.
- Reversible structural change of graphite during charge/discharge

Charge/discharge test



- Initial charge/discharge capacity
Charge : ca. 310 mAh g⁻¹
Discharge : ca. 270 mAh g⁻¹
⇒ low availability of graphite compared with liquid-type cell
- Fluctuation of capacity increases with increasing press pressure.
- These capacity do not depend on the press condition.

Fig. Charge-discharge curves of graphite electrodes with various press conditions.

Cycle properties of graphite

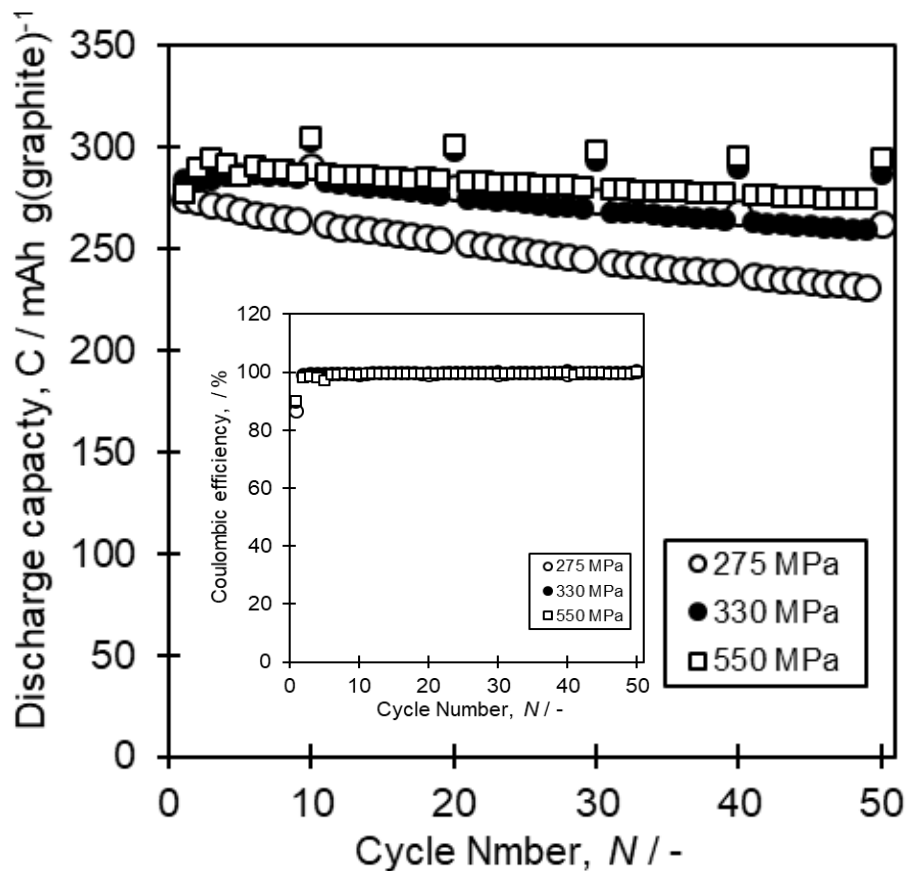
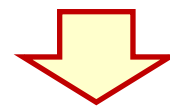


Fig. Cycle properties of graphite electrodes with various press conditions. Coulombic efficiency is indicated as inset.

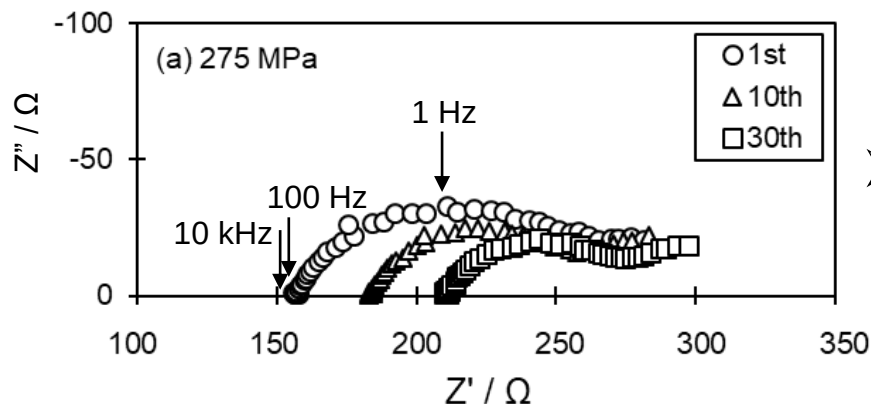
- Cycle properties improve with increasing press condition.
- Coulombic efficiency is almost 100 % in all conditions.



- Side reactions such as the decomposition of SE do not occur through cycling.
- Li inserted into graphite is mostly extracted in every cycles

It becomes difficult for Li to be inserted into graphite with increasing cycle number

Electrochemical impedance spectra

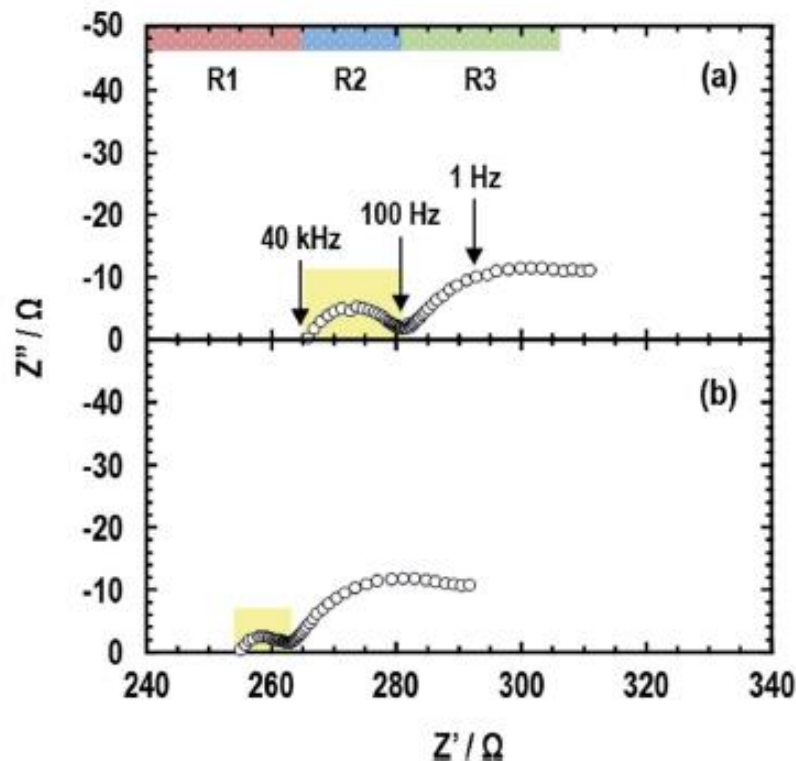


- **R1** : Resistance of bulk solid electrolyte(R_{SE})
- R2** : Resistance of active material/SE interface (R_{inter})
- R3** : Resistance of Li-In/SE interface(R_{Li-In})

➤ **We can find R_{SE} and R_{Li-In}**

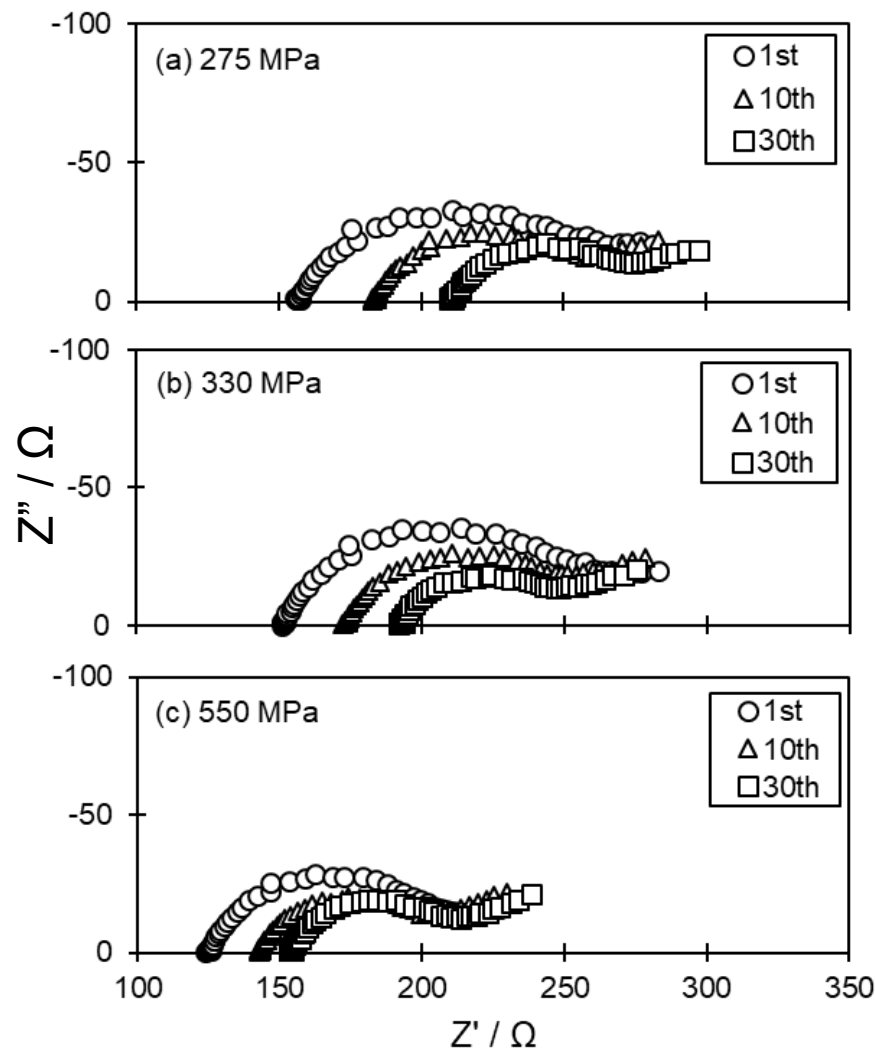


Resistance between graphite/SE interface(R_{inter}) is too small to observe.



Ref.) Y. Ito et al., *J Mater. Chem. A*, 2017, **5**, 10658

Electrochemical impedance spectra

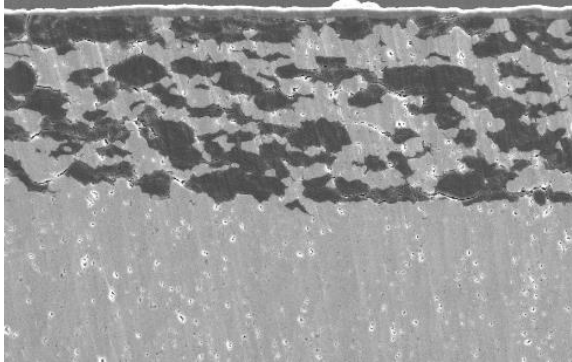


- Resistance of R_{SE} decreases with increasing press condition.
- R_{SE} of 275-cell increased constantly with increasing cycle number. In the case of the 330-cell, the increment of R_{SE} became small compared with that of 275-cell, though the increase of R_{SE} during cycling was observed.
- The 550-cell exhibited the smallest increase of R_{SE} and kept almost the same value of R_{SE} after 10 cycles.

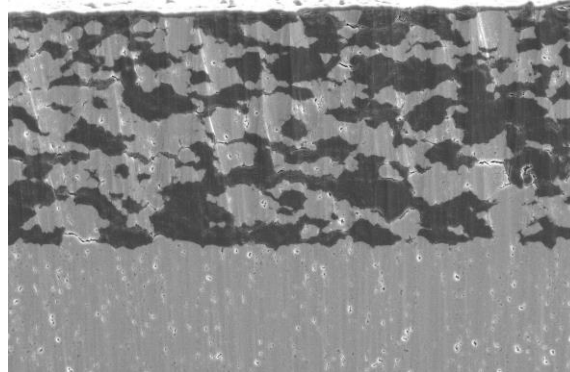
Cross-sectional SEM images

Before cycling

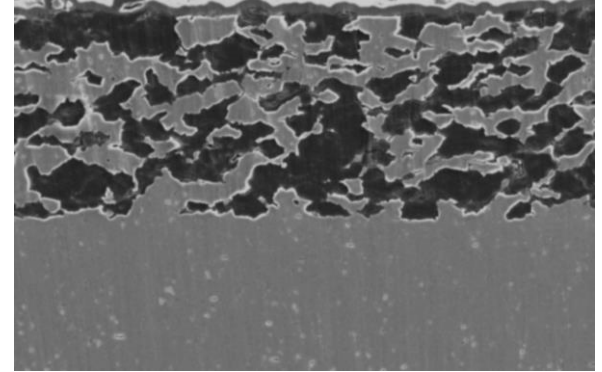
275 MPa



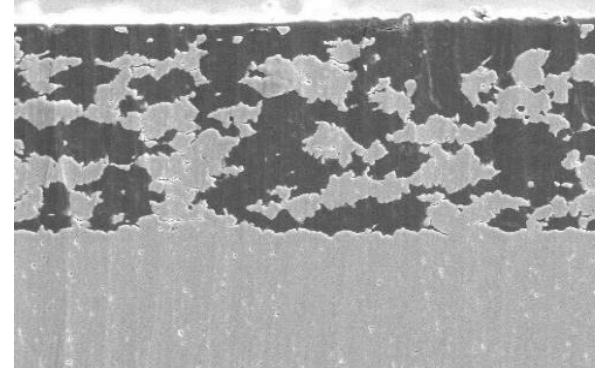
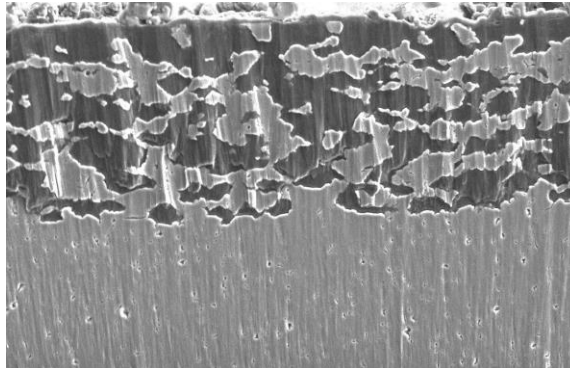
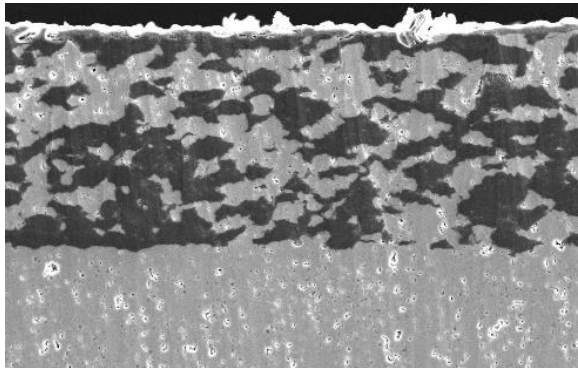
330 MPa



550 MPa



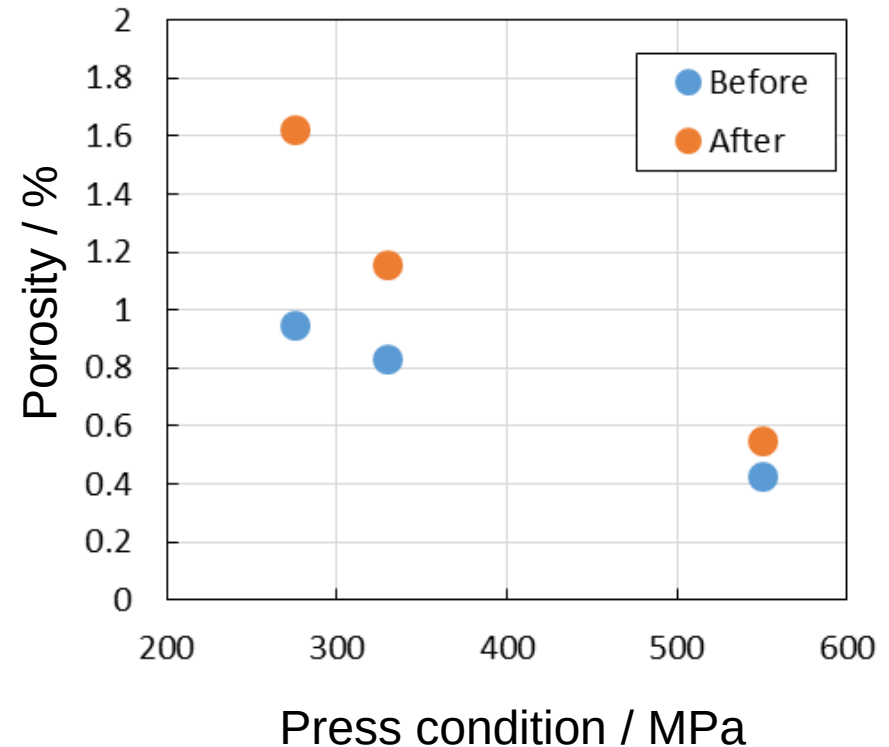
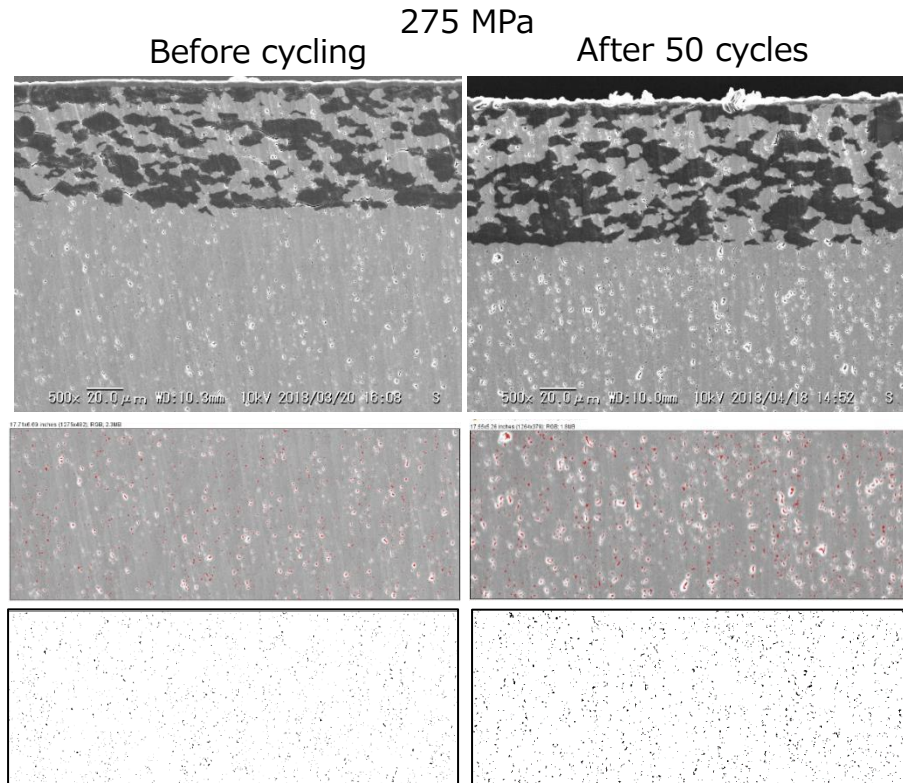
After 50 cycles



- The bulk SE of the 550-cell maintained almost the same number of voids after 50 cycles; by contrast, we could find many voids in the bulk SE of the 275-cell.

Porosity change in SE during cycling

Binarization treatment



- After cycling, the area ratio of the 550-cell rose slightly, whereas 275- and 330-cell exhibited a larger area ratio. The 275-cell, especially, possessed about twice the area ratio compared with the one before cycling.
- Void formation in SE occurs during cycling in all cells and the number of voids in the cells after cycling depends on the molding pressure.

Conclusions

- We have investigated the effect of press conditions on electrochemical properties for graphite electrodes in sulfide-based ASSBs.
- Cycle properties of graphite electrodes improved with increasing the press condition.
- Cross-sectional SEM observation revealed the void formation in the electrodes pressed with the lower press condition after cycling.
- This void formation contributes to the increment of the tortuosity in the bulk SE and is probably responsible for the degradation of discharge capacity during cycling.