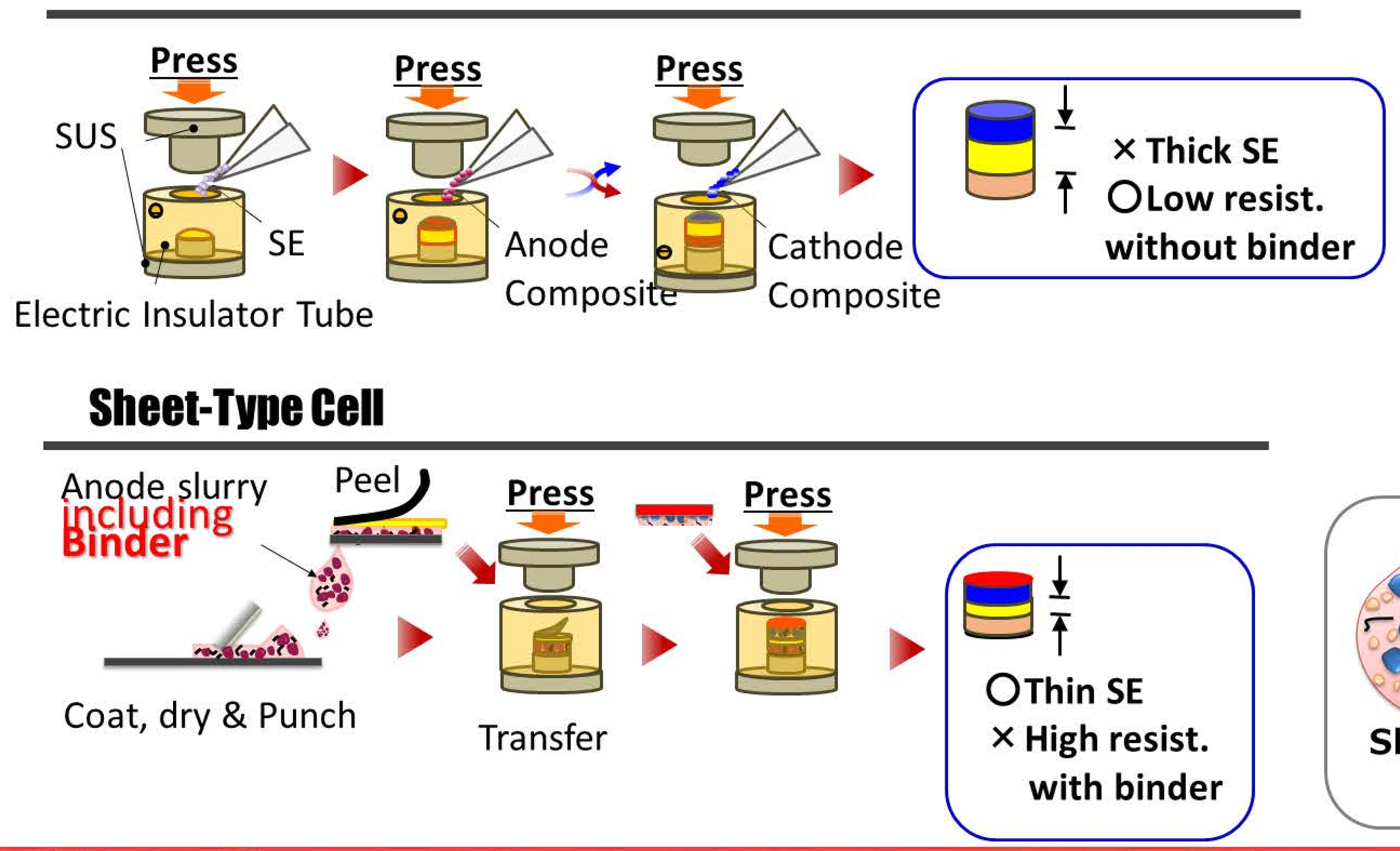
Realization of high rate performance of sheet-type all-solid-state batteries by slurry coating

Masanari Takahashi,[1,2] Atsutaka Kato,[1] and Mari Yamamoto,[1,2]
([1]Osaka Research Institute of Industrial Science and Technology, [2]Nara Institute of Science and Technology)
masataka@omtri.or.jp

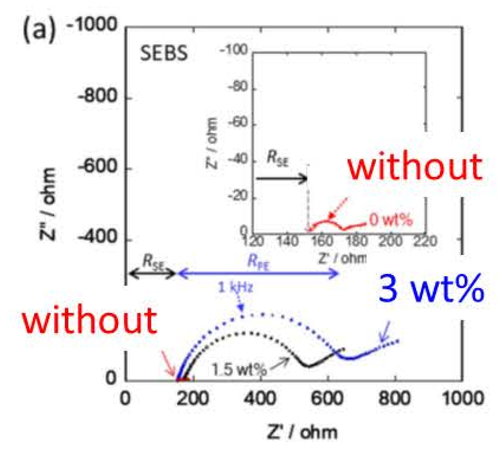
Introduction

Lithium Ion Batteries (LIB)

All Solid-State LIB

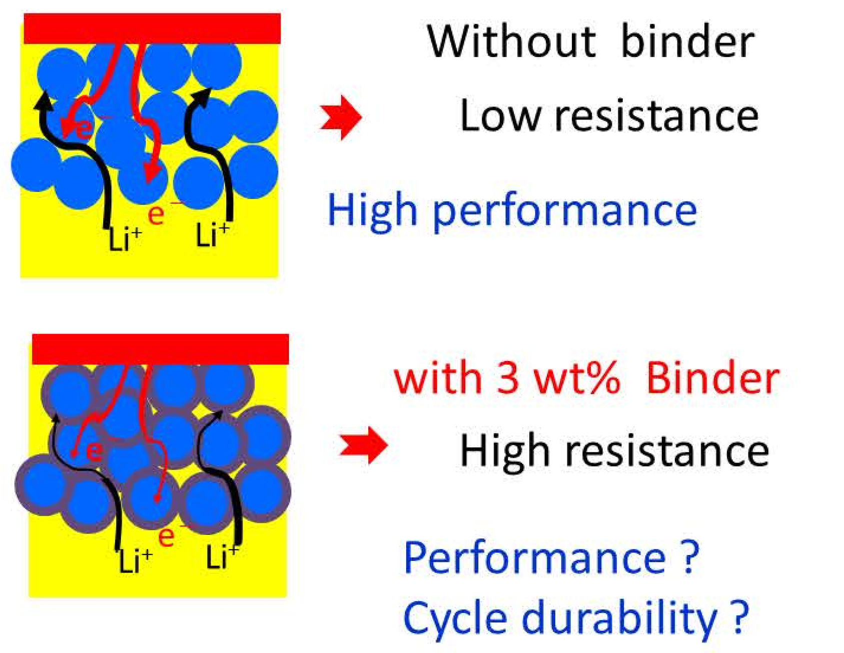


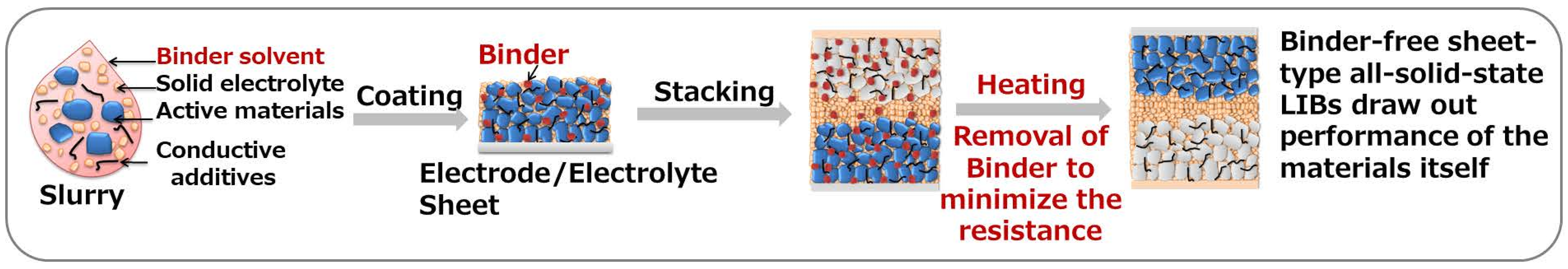
2.High Energy Density: Effect of binder addition



Impedance profiles of all-solid-state half cells prepared using binders, SEBS.

A. Sakuda et. al., *J. Electrochem. Soc.*, 164 (12) A1–A5 (2017)

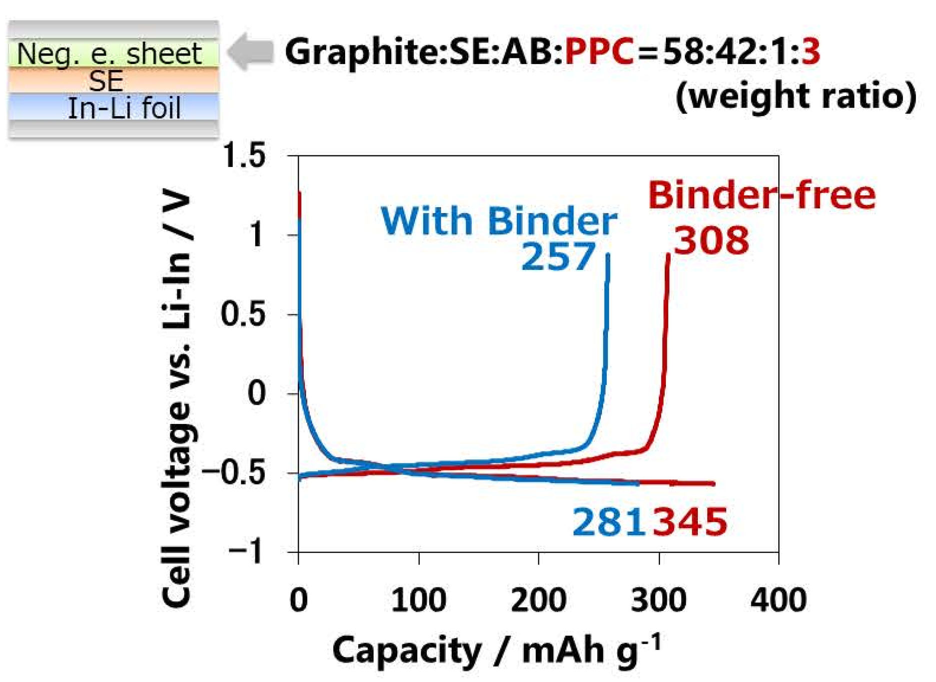




Results

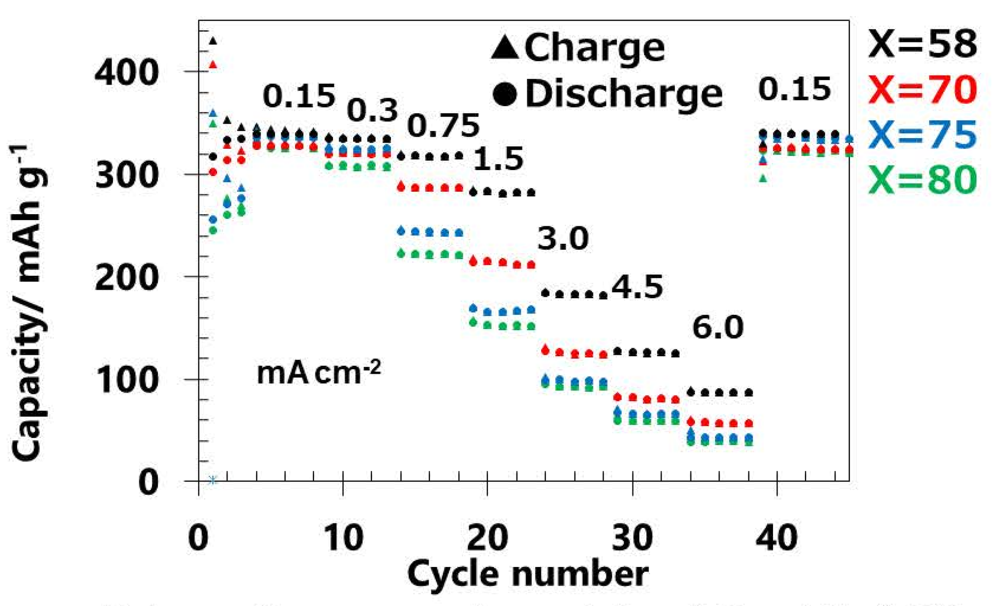
Negative Half Cell

Effect of binder removal



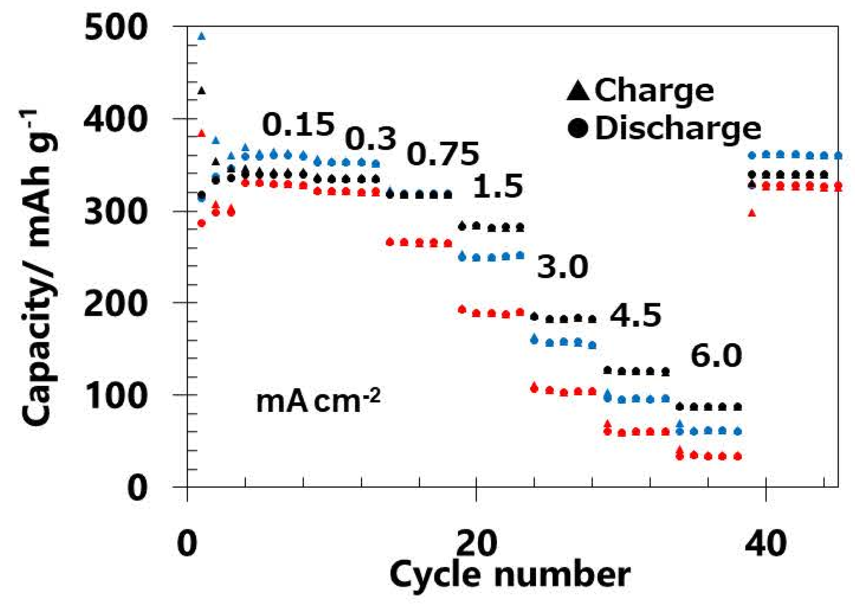
Charge-discharge curves

Effect of Graphite/SE ratio



Rate performance of a variety of Graphite/LPS content in anode composites.

Effect of kneading of slurry

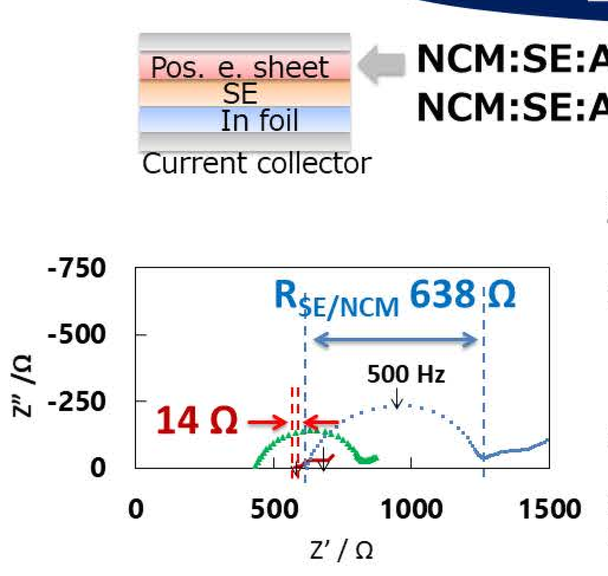


Rate performance of a variety of Graphite/LPS content in anode composites.

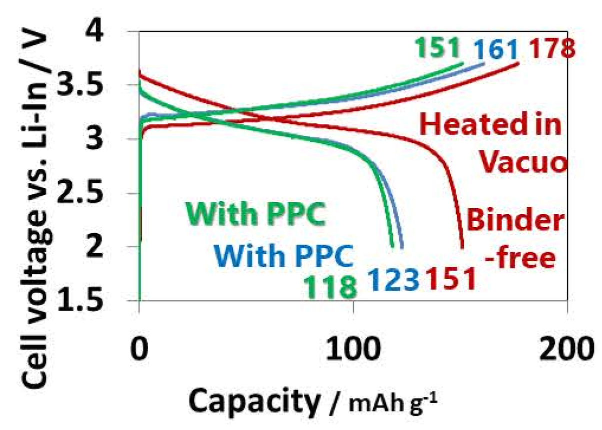
Positive Half Cell

Effect of binder removal

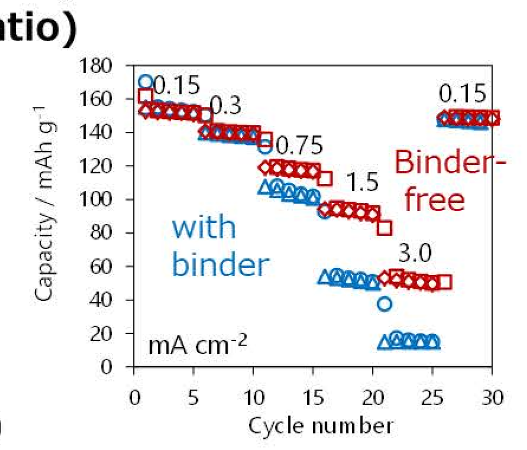
NCM:SE:AB:PPC=80:20:2:3 (weight ratio)
NCM:SE:AB:PPC=80:20:2:1 (weight ratio)



Impedance plots

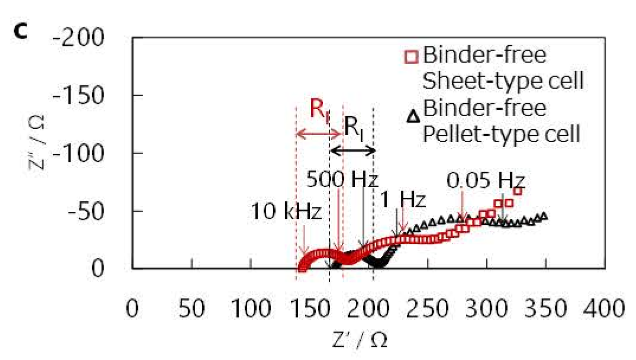


Charge-discharge curves



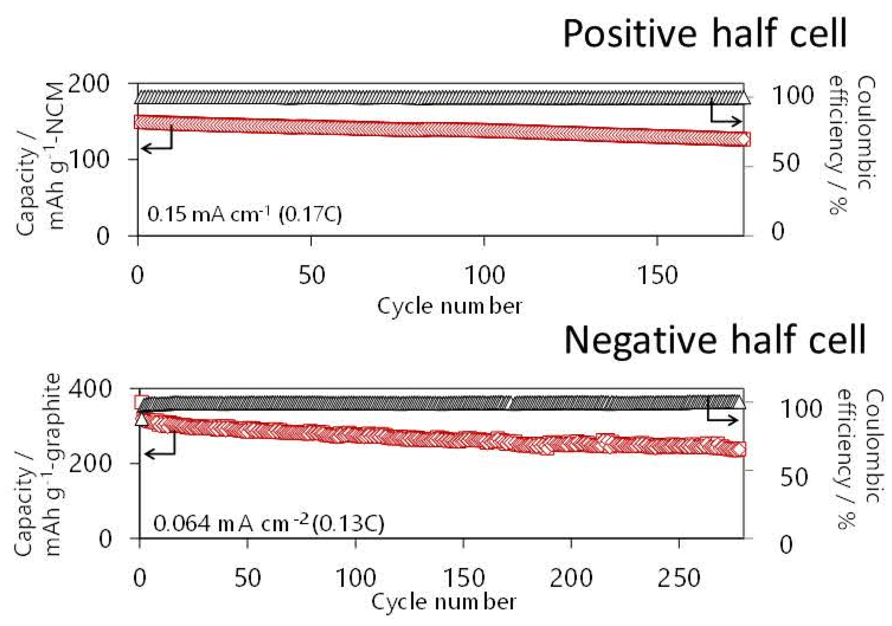
Rate performance of Positive half cells

Pellet or sheet type



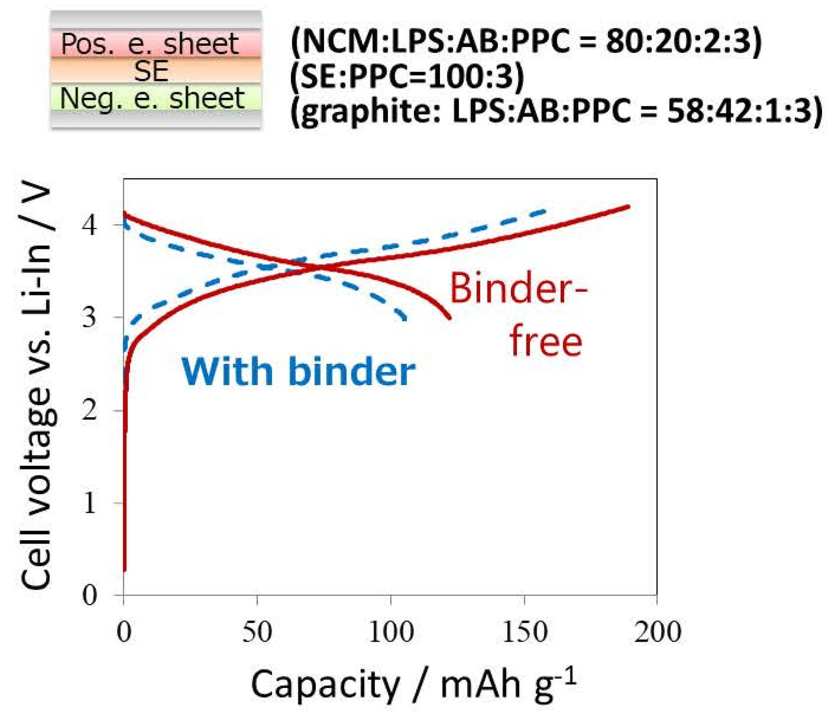
Comparison of Impedance plots for binder-free sheet-type and pellet-type cells

Cycling durability



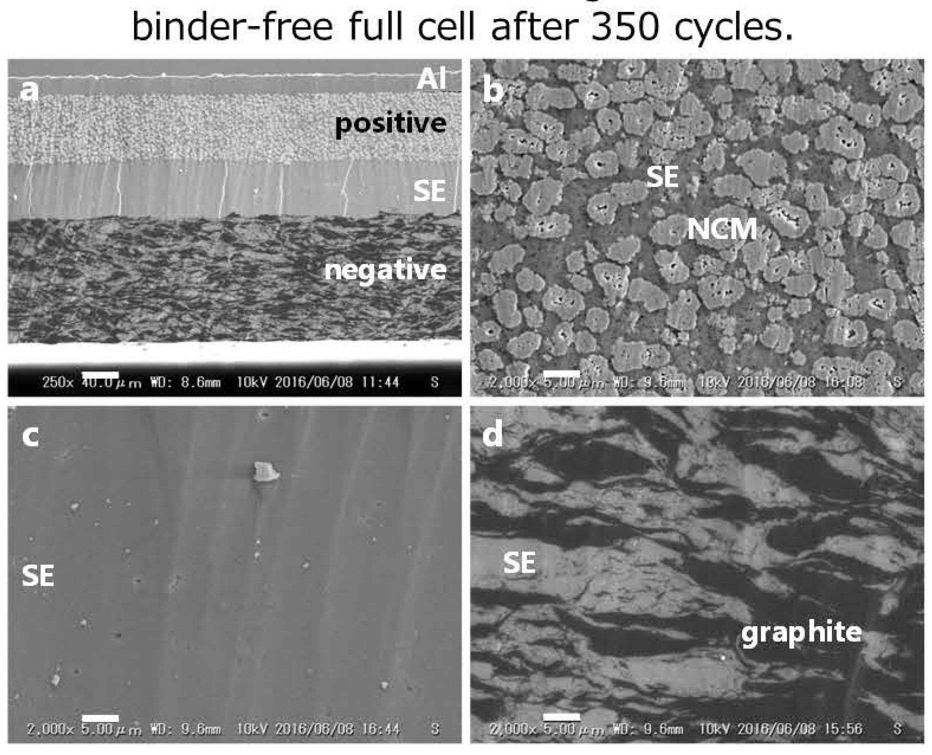
Full Cell

(NCM:LPS:AB:PPC = 80:20:2:3)
(SE:PPC=100:3)
(graphite: LPS:AB:PPC = 58:42:1:3)



Charge discharge curves

Cross-sectional SEM images of the binder-free full cell after 350 cycles.



Experimental

Cathode sheet
LiNbO$_3$ coated-LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC)
Li$_3$PS$_4$ glass(SE), S=4x10^{-4} scm^{-1}
Acetylene black (AB)
Polypropylene carbonate(PPC)
(NMC:SE:AB:PPC = 80:20:2:3 weight ratio)
Anisole

Anode sheet
graphite:SE:AB:PPC = 58:42:1:3 weight ratio
Anisole

Planetary Mixer
Ultrasonic Homogenizer

Slurry of Composite

Coating
Drying at RT for 24 h.
Punch(φ9.5 or 9.9 mm)
Press(37 MPa)


Composite Electrode Sheets

Summary

Binder-free sheet type all solid state battery based on sulfide electrolyte can be fabricated by the slurry coating method with use of decomposable binder PPC, anisole and Li$_3$PS$_4$ glass.

1. A removal of the PPC binder worked well to reduce interface resistance of active materials and SE.
2. Binder-free cells exhibited
   ○significantly higher capacities.
   ○high rate performance and stable cycling durability.
3. Active materials and SE make intimate contact without binder after 350 charge-discharge cycles in an all-solid-sate battery.

Acknowledgement

This work was supported by a Grant-in-Aid for Japan Society for the Promotion of Science (JSPS) KAKENHI(16K06787) and Japan Science and Technology(JST), Advanced Low Carbon Technology Research and Development Program, and Specially Promoted Research for Innovative Next Generation Batteries (ALCA-SPRING) Project.

29-P-S20-02

PACRIM13 2019/10/29

Fabrication of silicon-composite electrodes by slurry coating for all-solid-state batteries

Mari Yamamoto,[1,2,*] Yoshihiro Terauchi,[1] Atsushi Sakuda,[3] Atsutaka Kato[1] and Masanari Takahashi[1,2]

([1]Osaka Research Institute of Industrial Science and Technology, [2]Nara Institute of Science and Technology, [3]Osaka Prefecture Univ.)

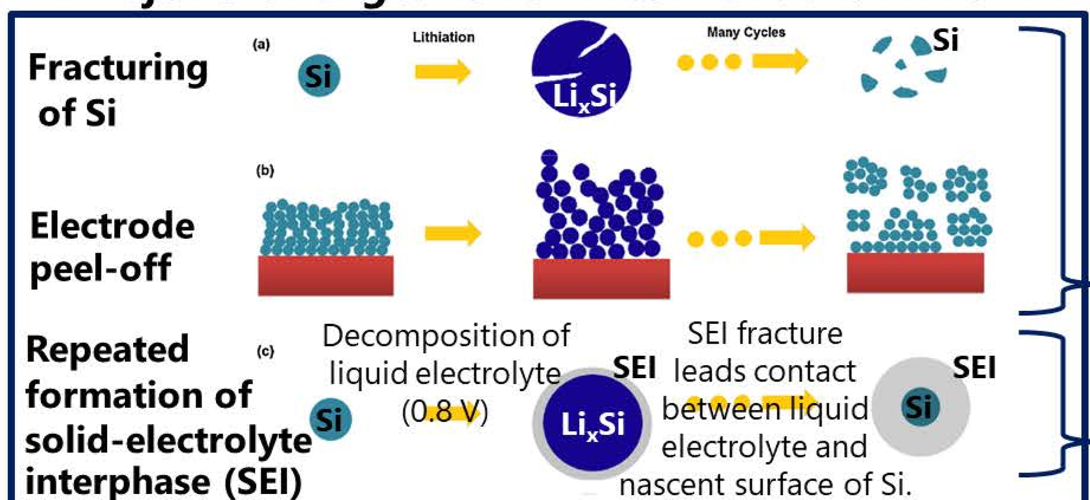
mari@omtri.or.jp

Introduction

Negative electrode with high capacity

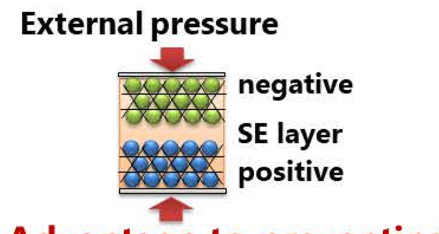
Negative electrode	Theoretical capacity (mAh g^{-1})	Volume change (%)
Graphite	372	110
Silicon	4200	420

Major challenges for Si in conventional LIBs[1)]



1) H. Wu, Y. Cui, *Nano Today* 7 (2012) 414–429.

All-solid-state LIBs



Advantage to preventing fracturing of Si and electrode peel-off.

Solid electrolyte is hard to contact with nascent surface of Si through the crack of SEI.

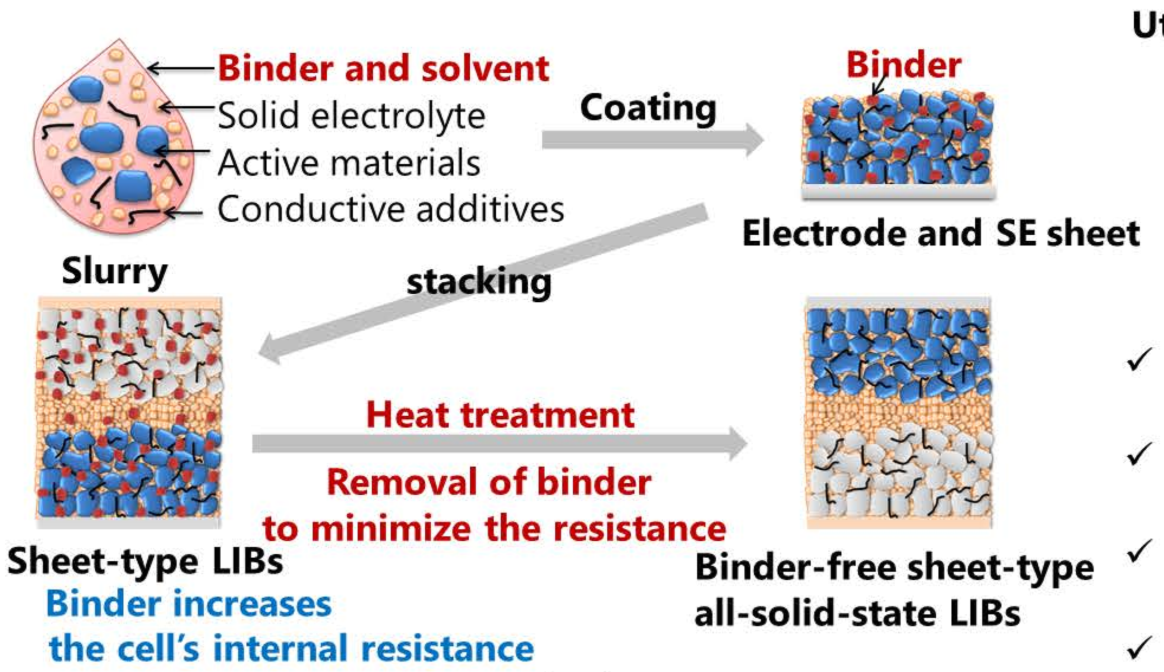
Application of Si electrode for all-solid-state LIBs

Si electrode	Cycling stability	Areal loading (mg cm^{-2})
thin film(t 50 nm)[2)]	2500 mAh g^{-1} (100[th])	0.009
nanoparticles(50 nm)[3,4)]	1200 mAh g^{-1} (20[th])	0.22

2) R. Miyazaki, *et. al.* J. Power Sources 272 (2014) 541–545.
3) J. E. Trevey, *et. al.*, Electrochem. Solid-State Lett., 13 (11) (2010) A154–A157.
4) D. M. Piper, *et. al.* J. Electrochem. Soc. 160 (2013) A77–A81.

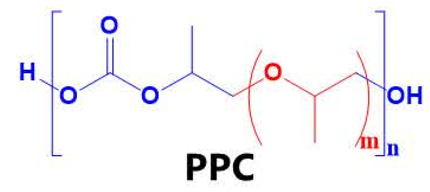
Satisfying the requirement of both cycling stability and practical areal loading remains a critical challenge.

Binder-free sheet-type all-solid-state LIBs [2,3)]



2) M. Yamamoto, *et. al.*, *Sci. Rep.*, 8, Art. No. 1212 (2018)
3) WO/2017/030127

Utilizing poly(propylene carbonate) as a volatile binder.



- ✓ Lower decomposition temperature (225 °C)
- ✓ No residual carbon under inert atmosphere
- ✓ High ratio of active materials by improving dispersibility
- ✓ High power density by minimizing the cell resistance

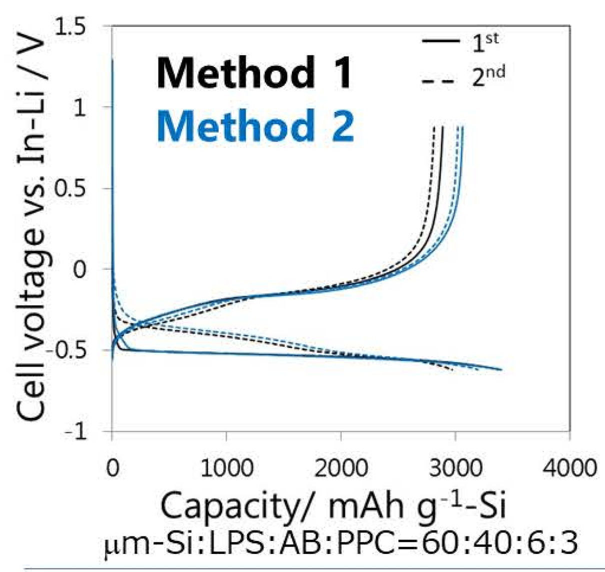
This work: Development of Si-composite sheet with stable cycling and practical areal loading

- ➢ Comparison of slurry mixing methods and Si particle sizes
- ➢ Optimization of the ratio of conductive additives and particle size of SE
- ➢ Mechanism of stable cycling estimated by cross-sectional observation
- ➢ Fabrication of sheet-type full-cells with high energy density

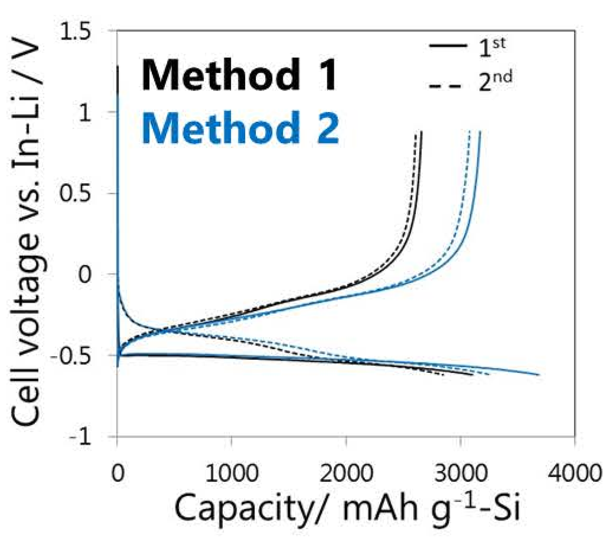
Results and discussion

Comparison of the slurry-mixing methods

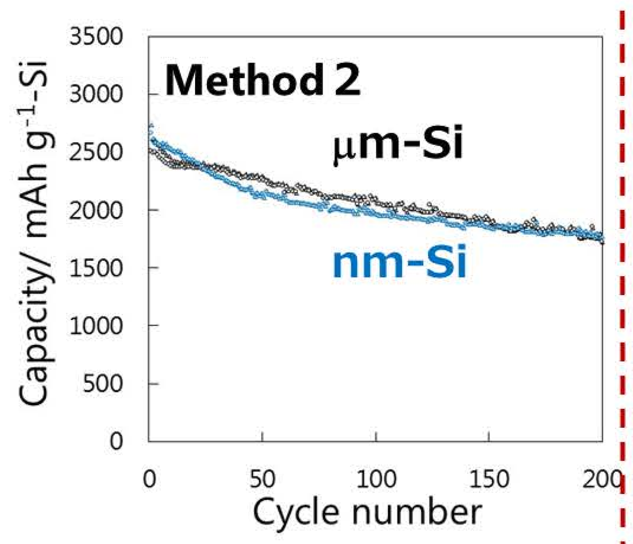
μm-Si



nm-Si



Cycle stability



μm-Si:LPS:AB:PPC=60:40:6:3

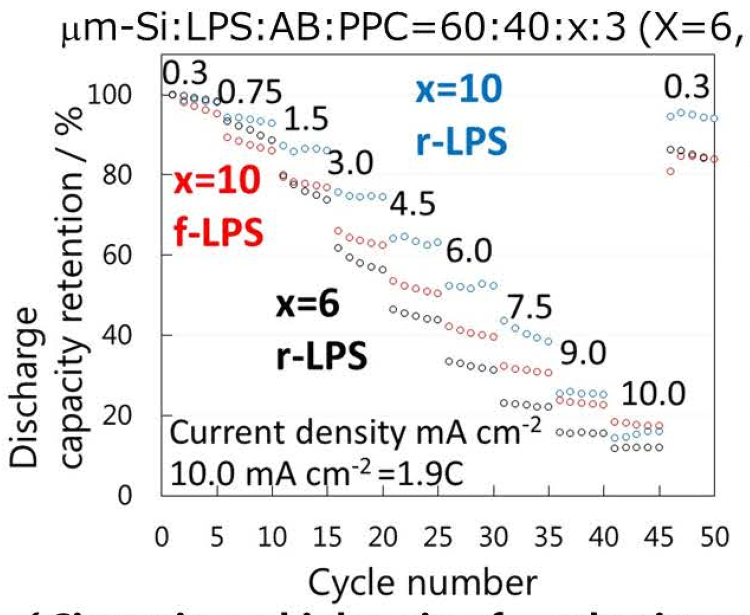
Initial CE	μm-Si	nm-Si
Method 1	85%	84%
Method 2	90%	86%

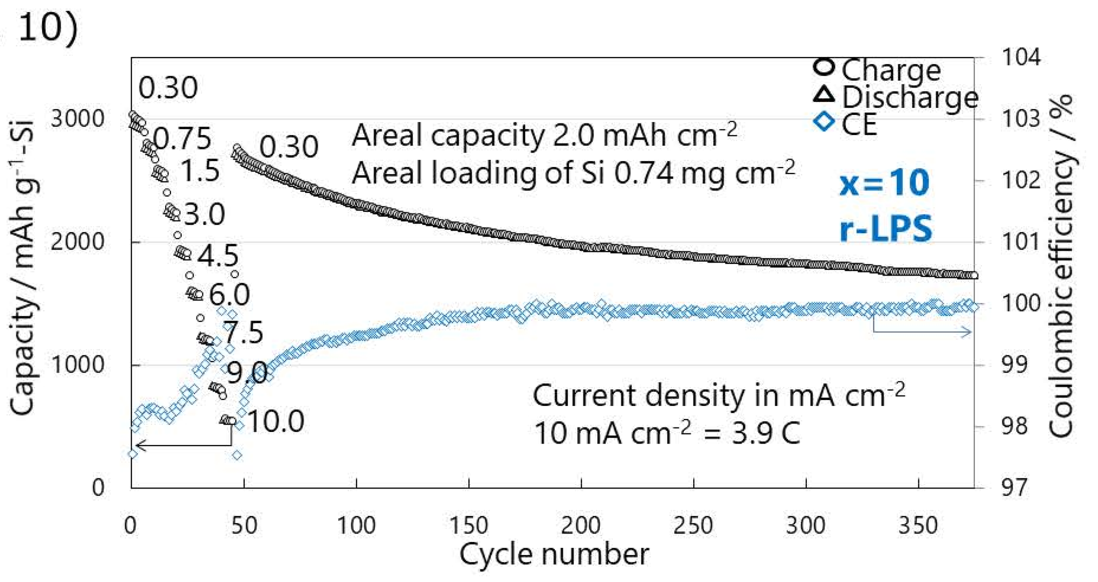
In Method 2, partially pulverized r-LPS increases the contact area between Si and LPS.

Pulverization of Si and electrode peel-off should be suppressed by compressing pressure.

Optimization of the AB ratio and LPS size

μm-Si:LPS:AB:PPC=60:40:x:3 (X=6, 10)





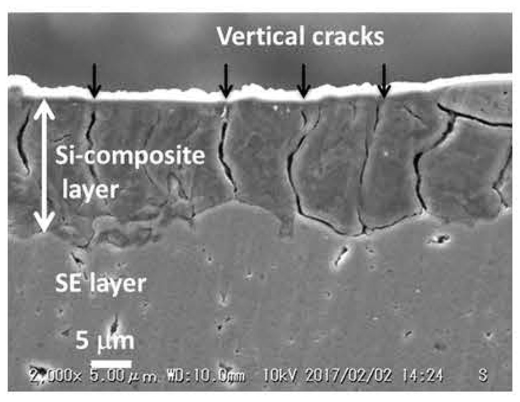
✓ Si requires a high ratio of conductive additive to form sufficient electronic conduction path.

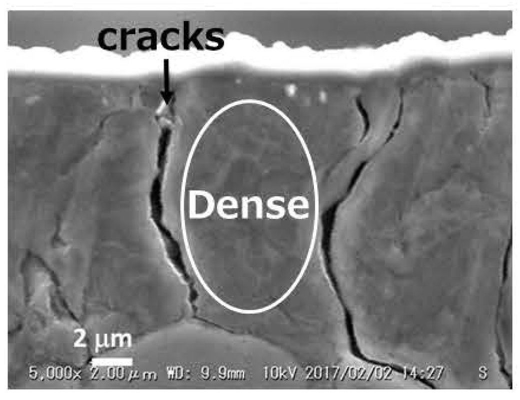
✓ Partial pulverization of r-LPS should be efficient enough to enable contact with μm-Si and to minimize the decrease in ionic conductivity.

Good cyclability 100[th] 2300 mAh g^{-1}
375[th] >1700 mAh g^{-1}
under high areal loading

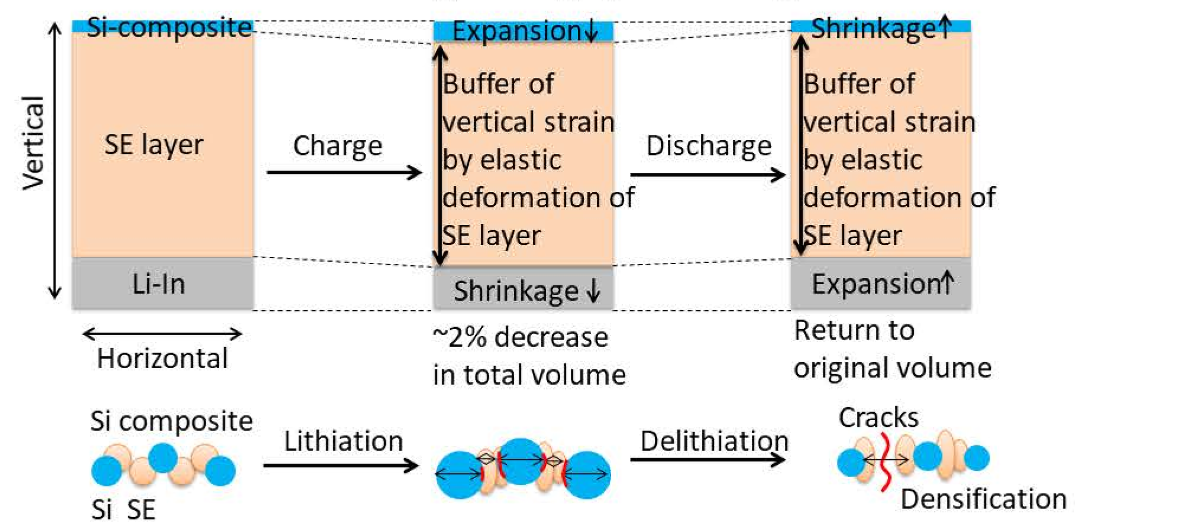
Mechanism of stable cycling

Cross-sectional SEM images after 350 cycles





Schematic diagram of half-cell during charge/discharge



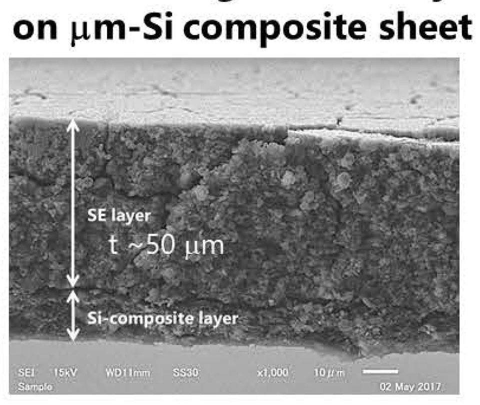
Because amount of SE is too small to buffer horizontal strain through the elastic deformation, subsequent plastic deformation occurs.

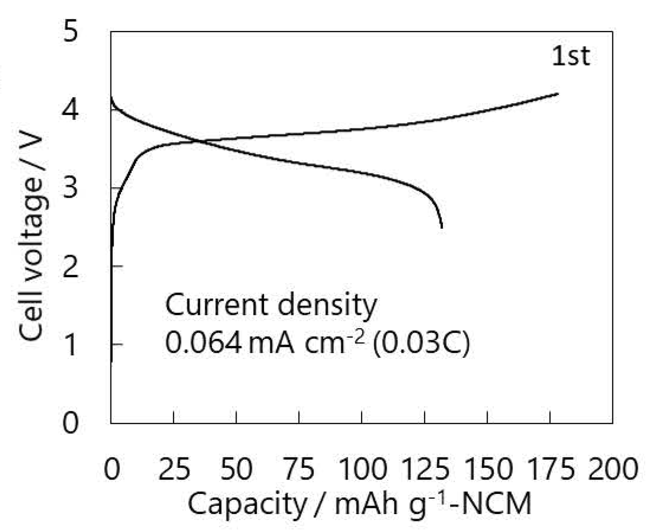
Vertical cracks are formed by the horizontal tension. During the charge/discharge, the cracks repeatedly open and close at the same position, leading to densification.

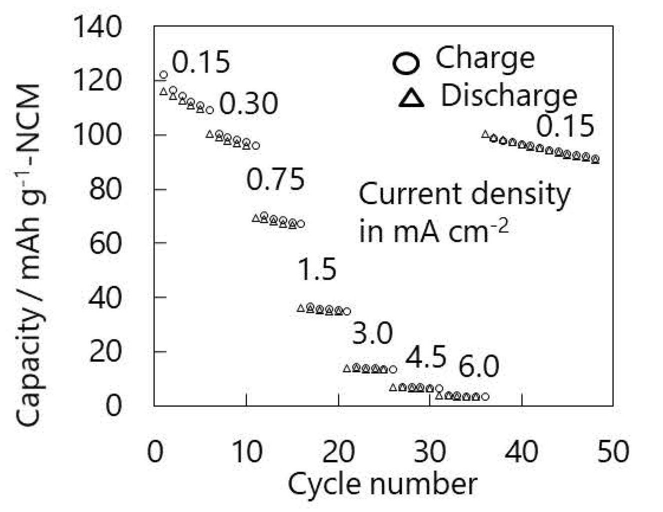
Ionic and electronic conductive paths are vertically connected, contributing to the stable cycling.

Sheet-type full-cells with high energy density

Over coating of SE slurry on μm-Si composite sheet







Cell-based energy density 212 Wh kg^{-1}

Initial discharge capacity 132 mAh g^{-1}, avg. discharge voltage 3.40 V,
Positive sheet 17.8 mg, SE coated-negative sheet 9.7 mg

Experiments

Materials
- nm-Si (ϕ50 nm, Alfa Aesar)
- mm-Si (ϕ1~5 mm, Alfa Aesar)
- r-LPS ($75Li_2S{\cdot}25P_2S_5$, ϕ10 μm, 4×10^{-4} S cm^{-1})
- f-LPS ($75Li_2S{\cdot}25P_2S_5$, ϕ2~3 μm, 2×10^{-4} S cm^{-1})
- Poly(propylene carbonate) (PPC) (Mw = 357,000)

Slurry mixing method
1. Planetary centrifugal mixer
2. Shaker (1500 rpm, 60 min.; ZrO_2 ball ϕ4, ϕ1 mm)

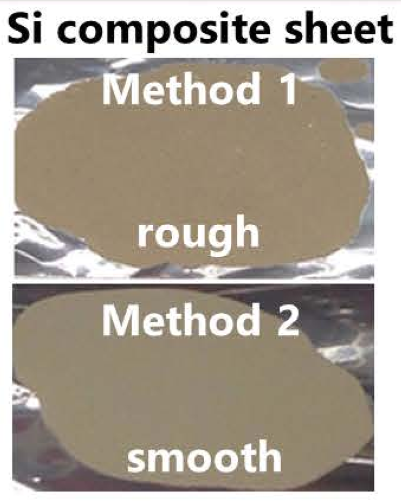
Negative Si:LPS:AB:PPC=60:40:x:3 (x=6, 10) (weight ratio)
Areal loading of Si 0.74~1.36 mg cm^{-2}

Positive $LiNbO_3$-coated-NMC:f-LPS:AB:PPC=80:20:4:5

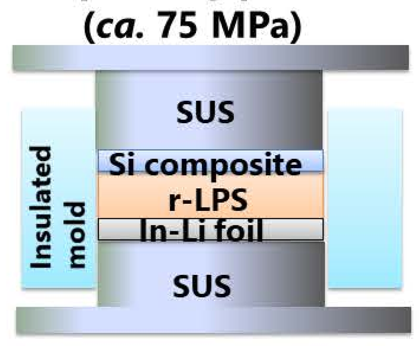
SE layer f-LPS:PPC=100:6

Charge-discharge measurements
- 1[st]~3[rd] CC-ch CC-dis, 4[th]~ CC-CV-ch CC-dis, 30℃
- half-cell -0.62~0.88 V (vs. Li-In)
- full-cell 4.2~2.5 V
- C-rate is defined based on 1C=4200 mAh g^{-1}

Si composite sheet



Compressing pressure (*ca.* 75 MPa)



PPC is removed by heating at 225℃ under vacuum, followed by attaching In-Li foil.

Conclusions

1. Slurry mixing assisted by ZrO_2 balls forms good ionic/electronic conduction paths.
2. Compression of cells suppress the pulverization of μm-Si and electrode peel-off, resulting in same cycling stability with nm-Si.
3. The μm-Si-composite sheet with practical areal capacity (2.0 mAh cm^{-2}) has excellent performance with a discharge capacity of 2300 mAh g^{-1} after 100[th] cycles.
4. Vertical cracks buffer the strain from Si volume change, contributing to the stable cycling of Si and facilitating its reversible expansion and contraction.
5. The slurry overcoating of solid electrolyte affords thin SE layer at 50 μm before pressing, resulting in high cell-based energy density.

Acknowledgements : This work was supported by JST ALCA-SPRING and JSPS KAKENHI JP16K05949 and JP19K05685.