

Application of Metal-sulfur Composite for Li-S Battery Systems

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Nov. 17, 2025 at 12th Workshop
“Lithium-Sulfur Batteries”

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KYUSHU UNIVERSITY

Outline of this talk;

1. Li-S battery in my career
2. Liquid electrolyte system
3. All-solid-state battery system
4. Future prospect of metal use in Li-S system
5. Summary

Liquid system: RISING and RISING2(JPNP16001) by NEDO

Solid system: SOLiD-EV (JPNP18003) by NEDO

Newly started liquid system: Li-S battery project (JPMJGX23S0)
in GteX by JST

RISING:

Research and Development Initiative for Scientific Innovation of New Generation Batteries

SOLiD-EV:

Development of Fundamental technologies for All Solid State Battery applied to Electric Vehicles

NEDO:

New Energy and Industrial Technology Development Organization

GteX:

The Green Technologies of Excellence

JST:

Japan Science and Technology Agency

Co-author of main part:

[National Institute of Advanced Industrial Science and Technology (AIST)]

Misae Otoyama, Tomonari Takeuchi, Mitsunori Kitta, Naoya Ishida, Noboru Taguchi, Kentaro Kuratani



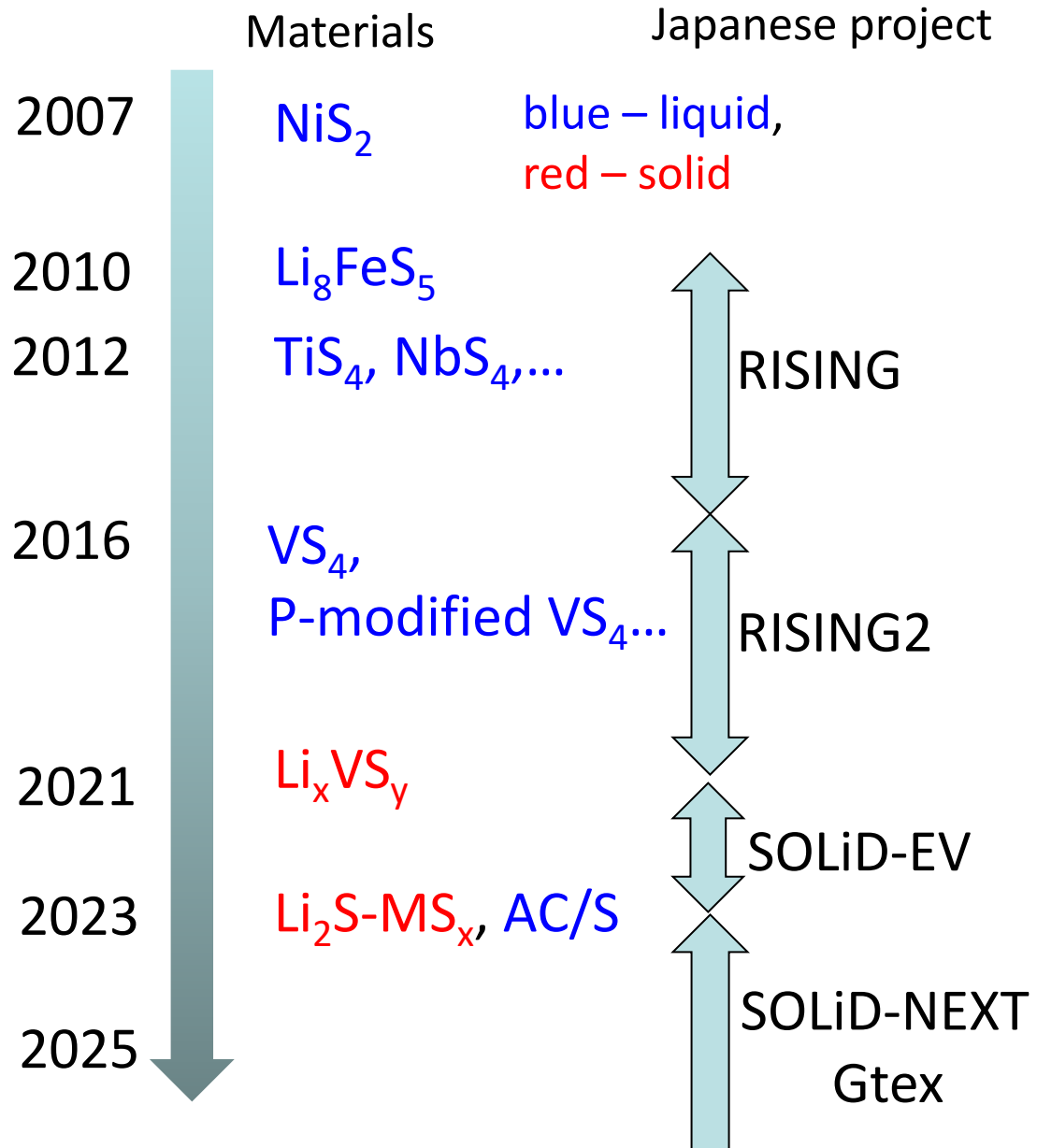
[Consortium for Lithium Ion Battery Technology and Evaluation Center (LIBTEC)]

Mizue Wanibuchi, Hikaru Sano, Koji Kawamoto

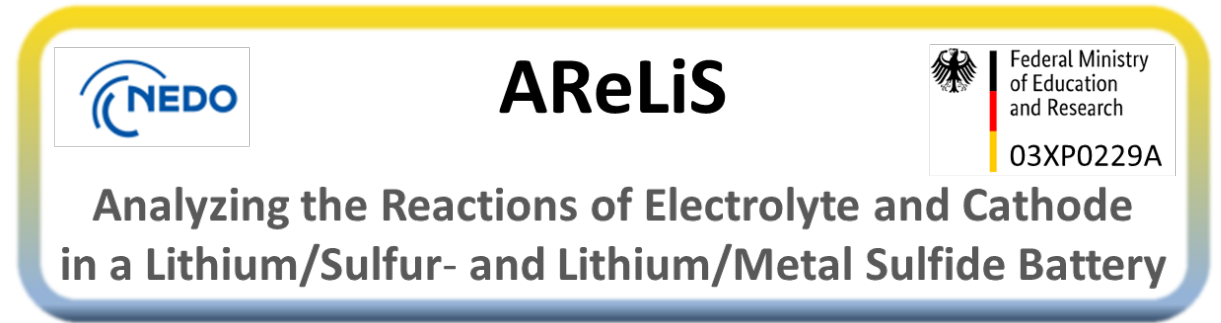


Li-S battery in my career

4

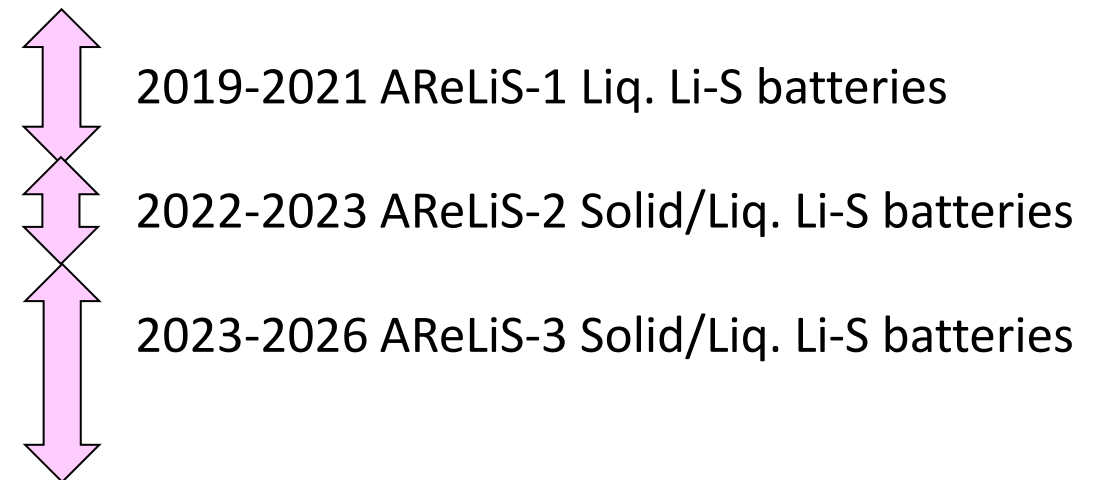


Collaboration with Germany

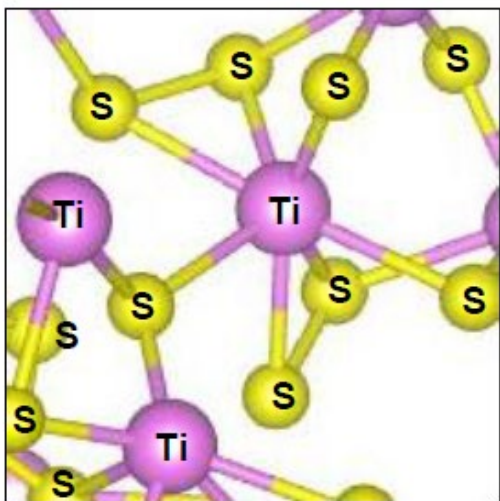


In 2015 4th Workshop »Lithium-sulfur batteries«

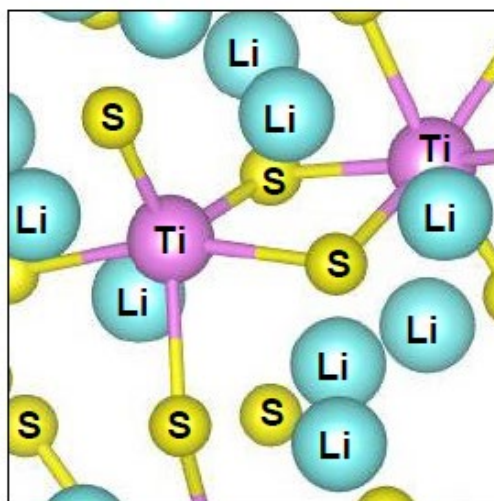
In 2018 visit lab. In Fraunhofer IWS



Metal polysulfides



Initial state



Li inserted state

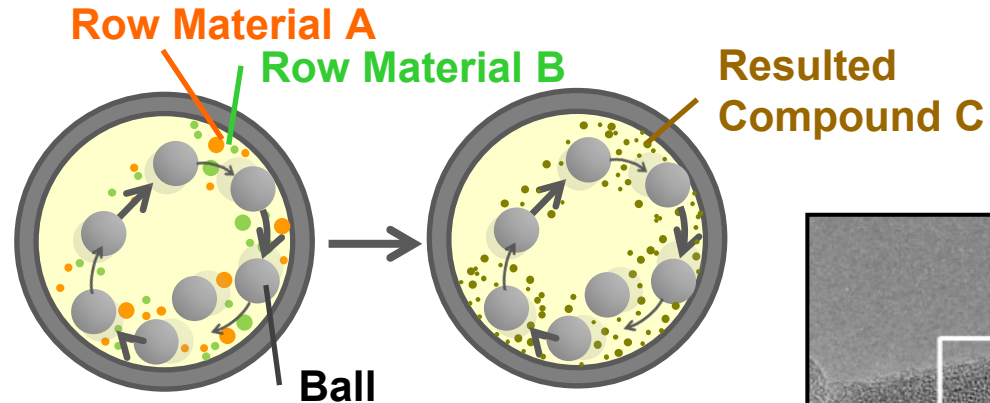
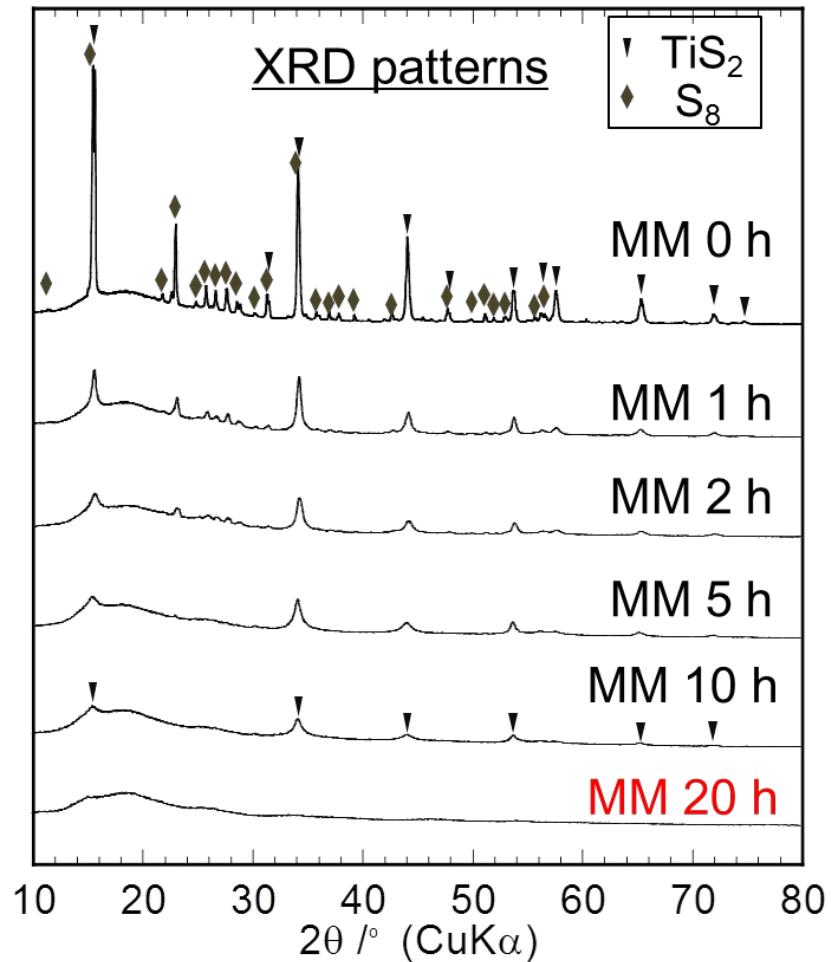
For e⁻ conduction improvement;
Composite of metal and sulfur with chemical bonding
→ Suppress the redox in the liquid state
Avoid full conversion reaction of sulfur
Reduce the amount of conducting material, porosity of the electrode, and electrolyte.

A. Sakuda, H. Sakaebe, *et al.*, *J. Am.Chem.Soc.*, 2017, 139 (26), pp8796–8799

	Subject	Sulfur-Carbon composite	Metal polysulfides
1	Electronic conductivity	× (Sulfur itself)	$10^{-5} \sim 10^{-1} \text{ S cm}^{-1}$
2	Capacity based on S or MS_x	theore. 1600 mAh g^{-1}	$\sim 800 \text{ mAh g}^{-1}$
3	Polysulfide dissolution	Possible	No
4	Density of active material	2.07 g cm^{-3} ($\alpha\text{-S}$)	2.67 g cm^{-3} (VS_4)
5	Carbon required	More than 30 %	$\sim 5 \%$

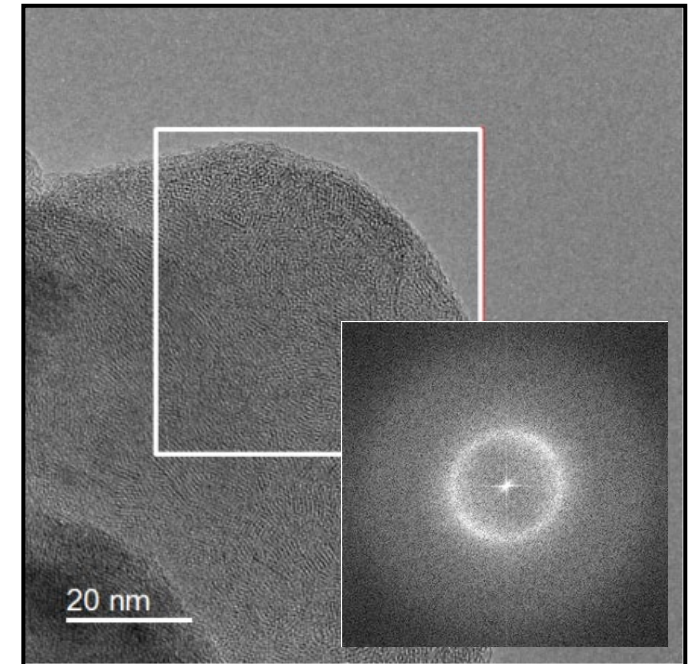
Preparation of new materials: α -TiS₄

TiS₂ + S₈ (Ti:S=1:4 atom%)



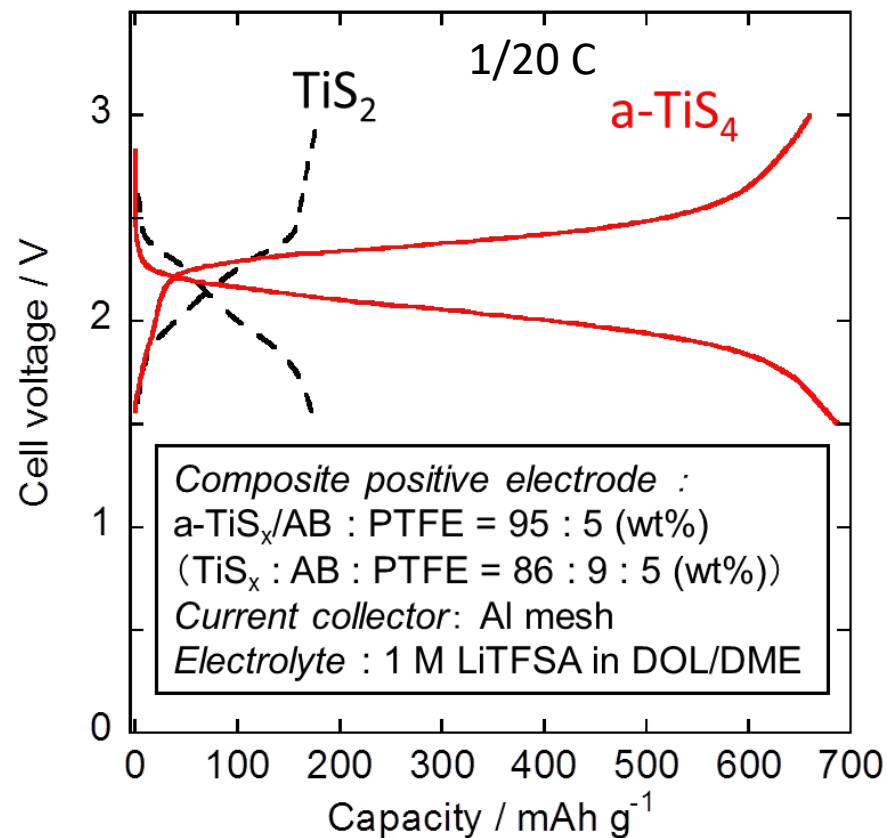
Bragg peaks disappeared after 20 h milling.

Almost amorphous phase in TEM image.



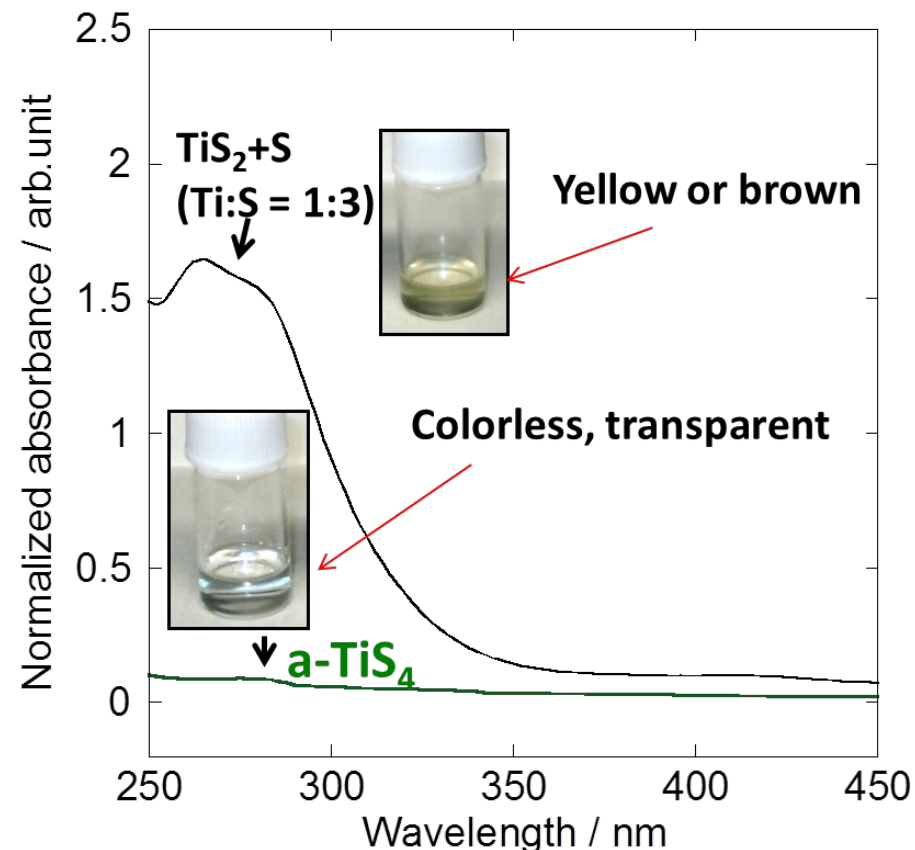
A. Sakuda, H. Sakaebe, Z. Ogumi *et al.*,
Electrochem. Commun. 31 (2013) 71.

Initial discharge-charge curves of α -TiS₄



9 wt % of carbon is enough. 4.6 Li⁺ can be inserted into TiS₄ down to 1.5 V. It can be cycled in carbonate also.

UV-VIS spectra of electrolyte after cycling.



Dissolution of Li-polysulfides into the ether electrolyte was reasonably suppressed. Carbonate can be used.

Electrolyte analysis after cycling of α -TiS₄



AReLiS

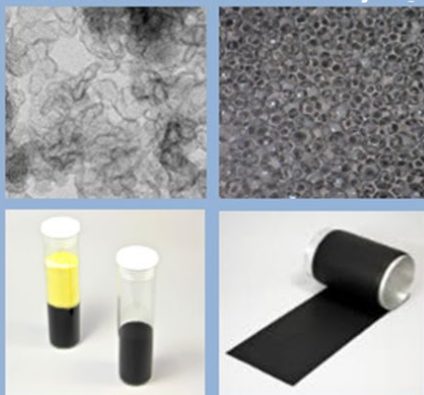


Federal Ministry
of Education
and Research

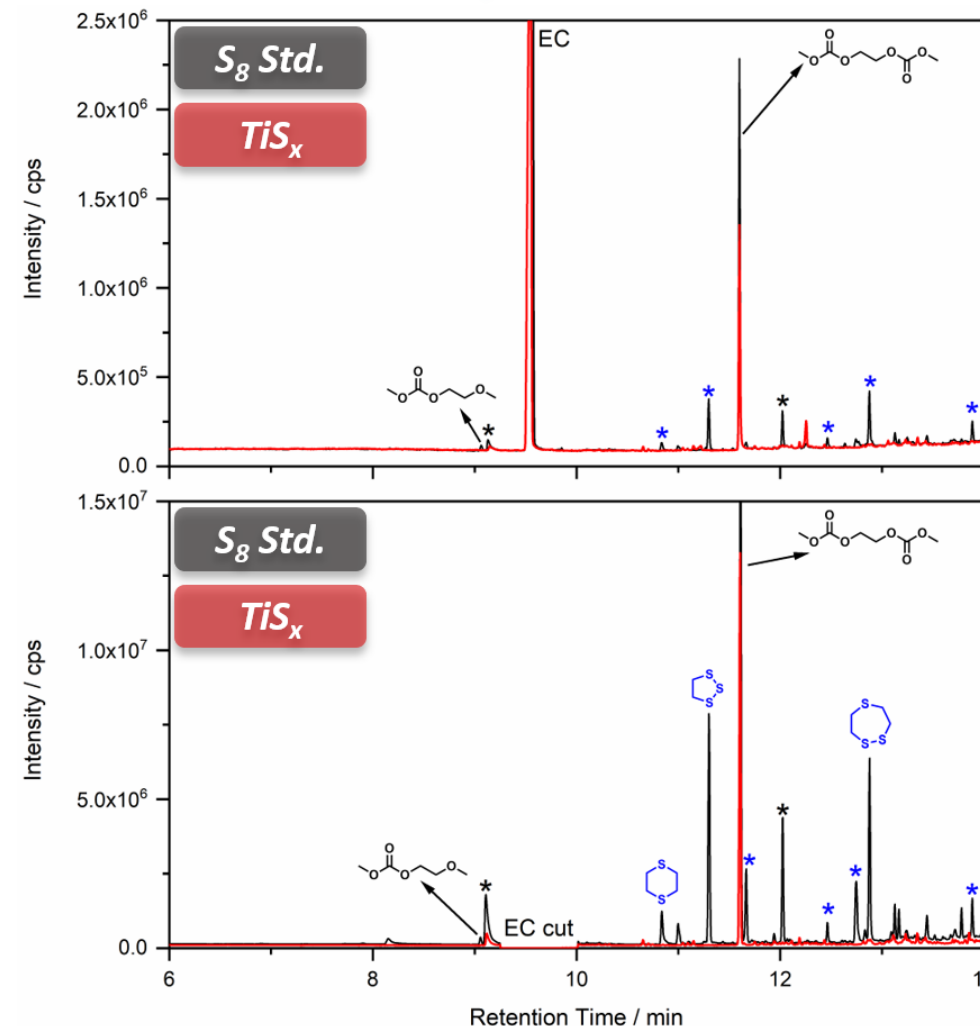
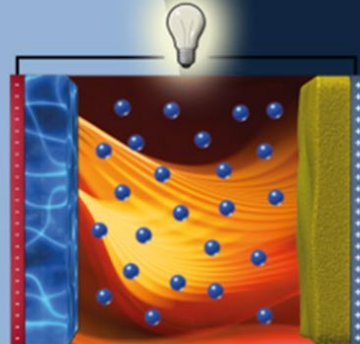
03XP0229A

Analyzing the Reactions of Electrolyte and Cathode
in a Lithium/Sulfur- and Lithium/Metal Sulfide Battery

Adaption of Active Material-
Current Collector Systems



Analysis of Cathode-
Electrolyte interactions



No sulfur related species was found in electrolyte.



AIST
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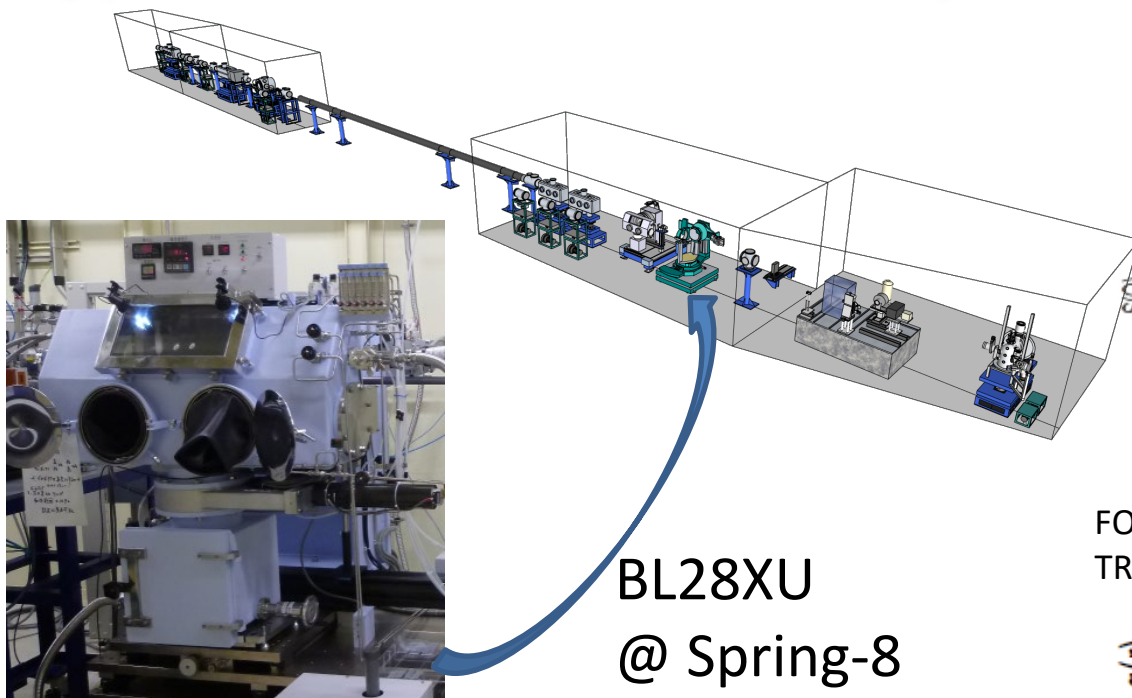
WWU
MÜNSTER

JÜLICH
Forschungszentrum



**TECHNISCHE
UNIVERSITÄT
DRESDEN**

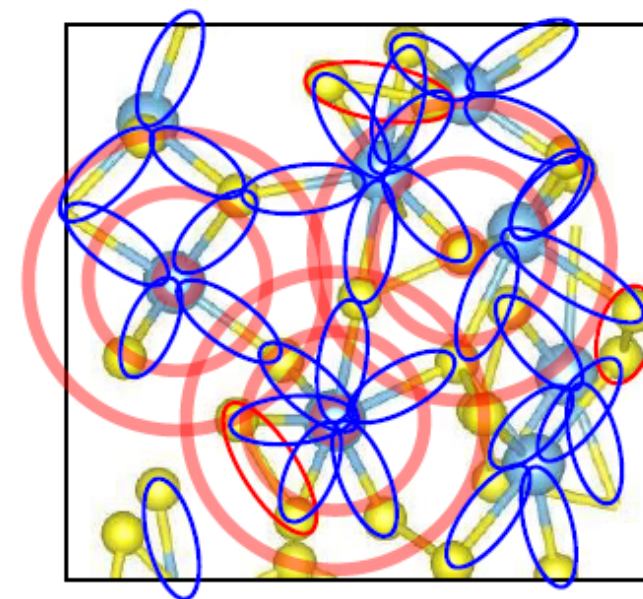
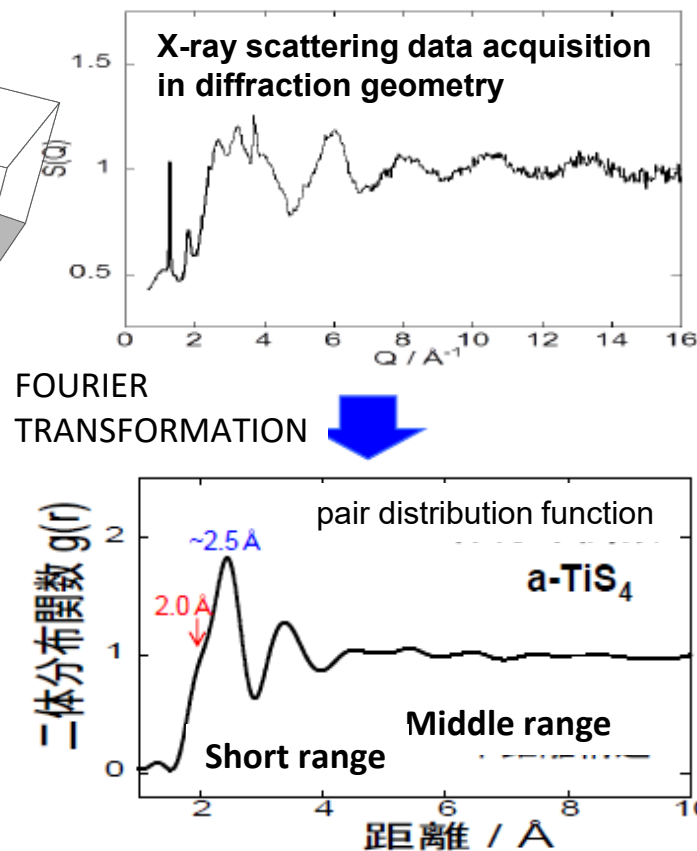
Application of Advanced Analysis Platform



BL28XU
@ Spring-8

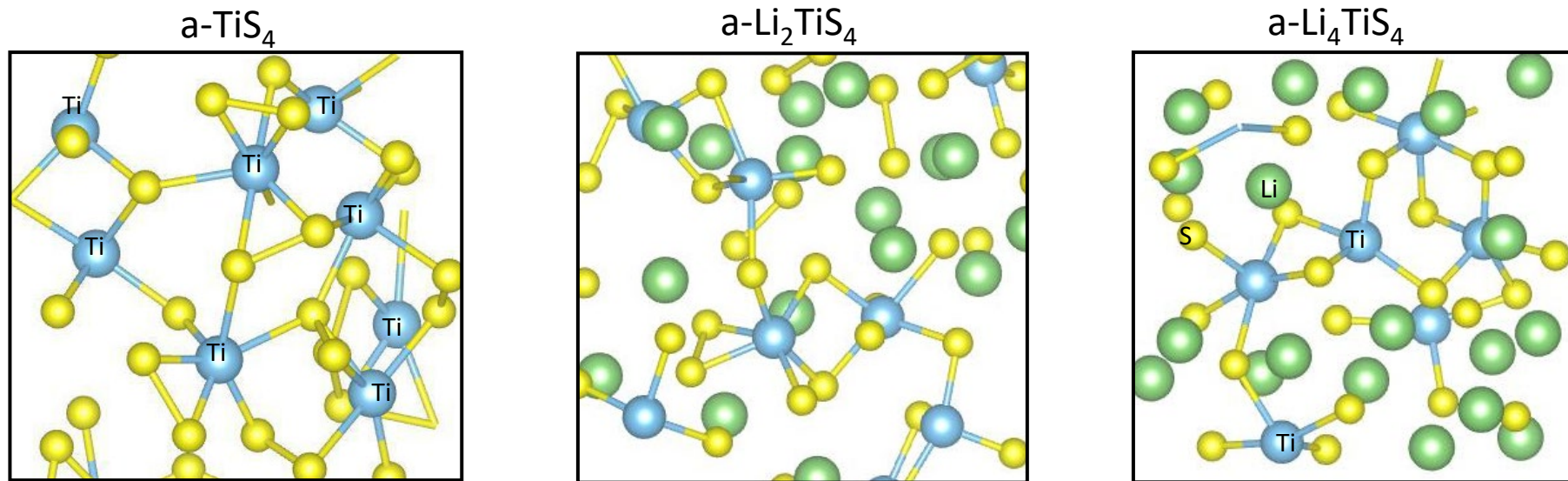
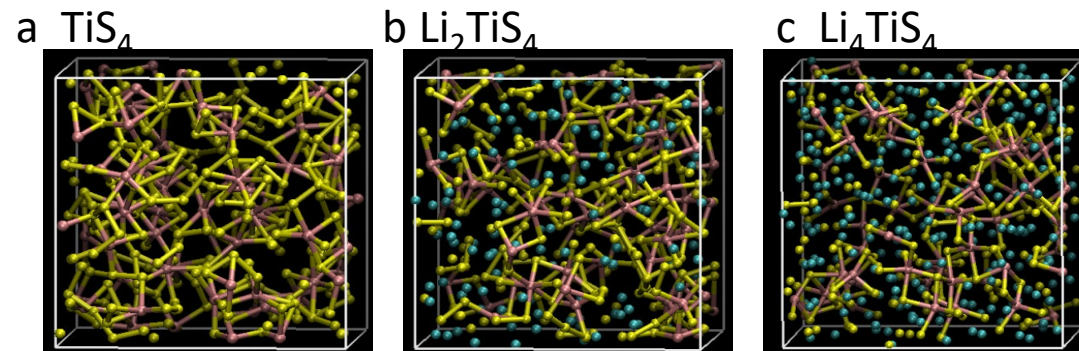
X-ray analysis by coherent and high energy beam (~ 38 keV). Beamline was build in RISING-RISING2 framework. High spatial and time resolution, Operando measurement can be carried out. Measurement in this study was carried out *ex-situ* but in the glove box. XAFS, PDF(Pair Distribution Function) analysis and DFT-MD calculation was combined.

Structure analysis of amorphous phase
by PDF analysis using X-ray scattering measurement

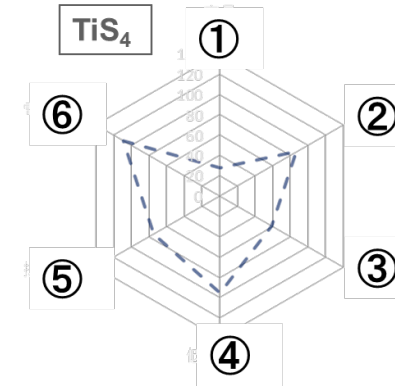
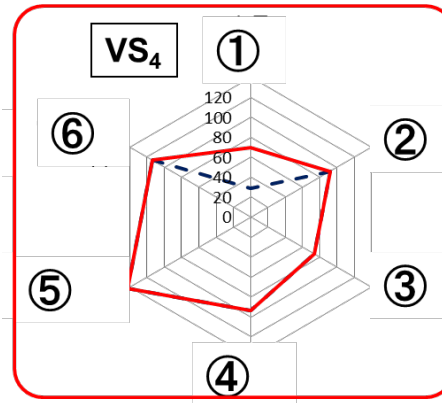
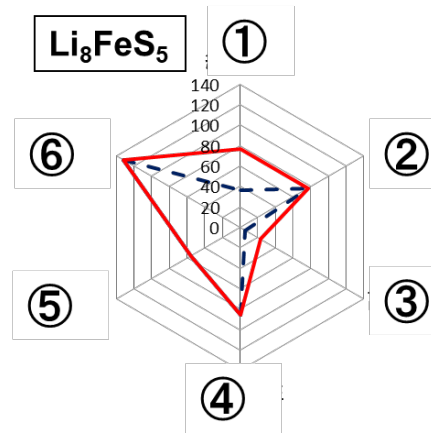


PDF analysis will provide the structural information like atomic distance and atomic distribution even in amorphous materials.

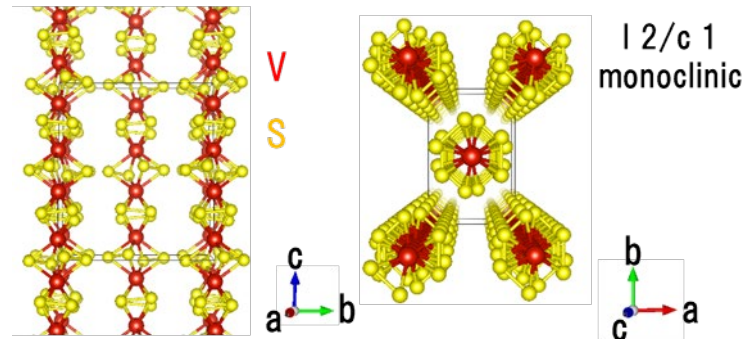
An amorphous structure model was developed for titanium polysulfides (TiS_4 , Li_2TiS_4 , and Li_4TiS_4) by melt quenching using DFT-MD simulations (2000 K to R.T.)



As Li increase in TiS_4 , Li first correlates with S that is located far from Ti, and short S-S cleavage occur. Ti-S network becomes chain-like structure during further Li insertion. This is due to the “soft” nature of sulfur atom.



- ① Capacity retention
- ② Rate properties
- ③ High temp. tolerance
- ④ Low temp. tolerance
- ⑤ AC resistant change
- ⑥ Gravimetric energy density of the electrode



VS_4 ;

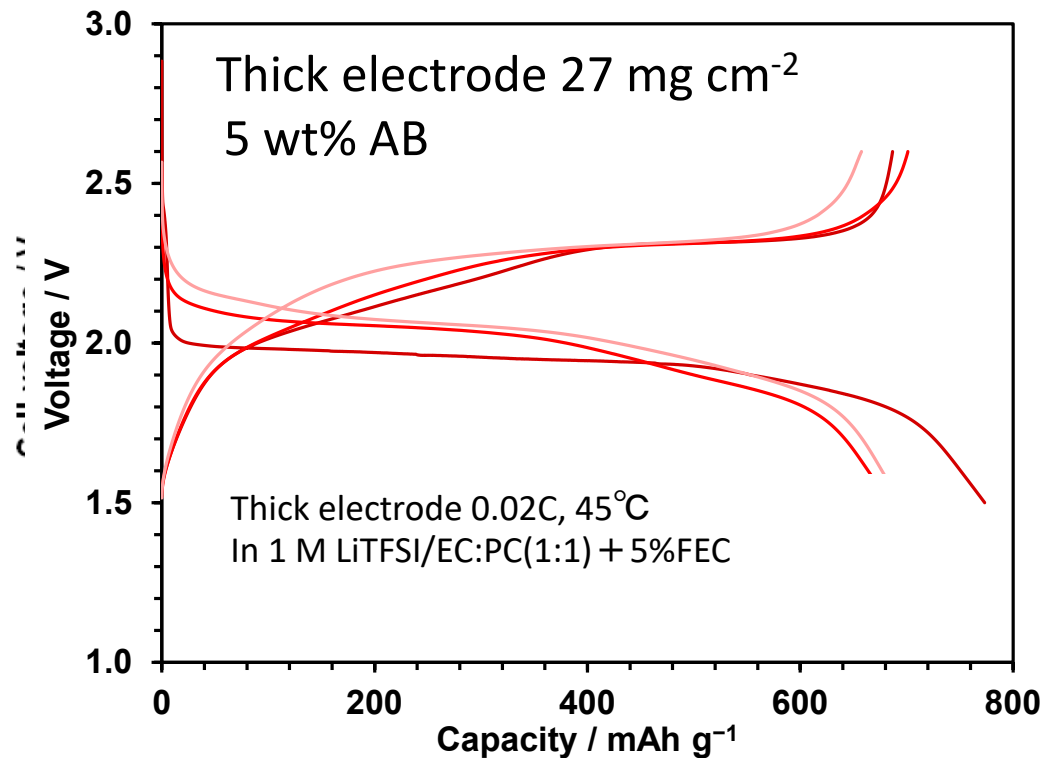
already published as anode material by full conversion reaction.

How to use effectively as cathode ? → Voltage region & crystallinity

VS_4 : K. Koganei, H. Sakaebe, *et al.*, *Electrochemistry*, **89** (2021) pp. 239-243.

Fe system: T. Takeuchi, *et al.*, *J. Electrochem. Soc.*, **162**, A1745 (2015).

Li/*a*-VS₄ full cell (coin cell size)



511 Wh/kg, 718 Wh/L

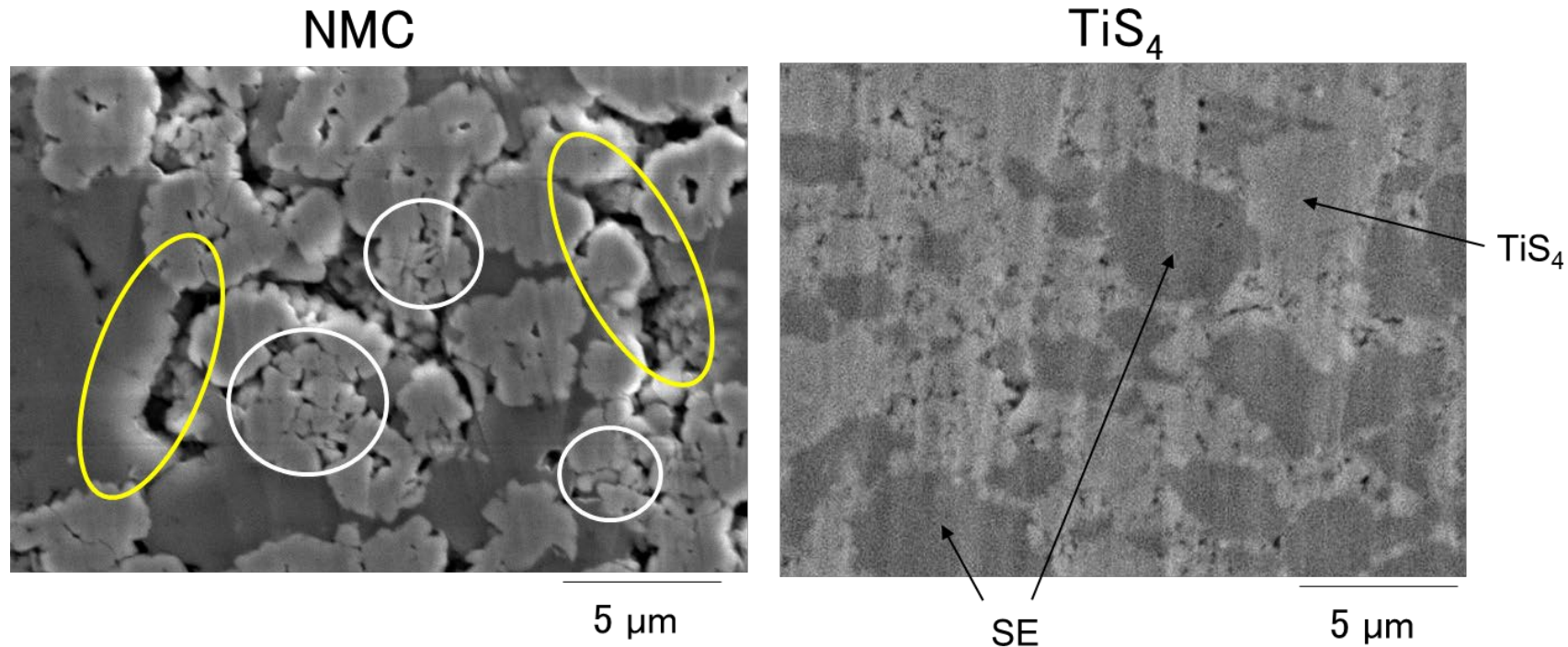
	RISING2 <i>MSx</i>	Conventional <i>S/C</i>
Carbon content in electrode	3-10 wt%	>30wt%
Porosity of electrode	34%	>55%*
E/S (μL / mg)	~1.0	>3
Volumetric Energy density / Gravimetric energy density	~1.5	<1

*:N. Kang, et al., *Nat Commun* **10**, 4597 (2019).

Metal polysulfides show potential for high energy battery electrode in vehicle use.

Balancing energy density and other properties ...future subject

- *Better contact with electrolyte in solid state electrode.
- *Less carbon is necessary in the electrode when compared with S_8 .



Pressed by 550 MPa after mixing the active material and solid electrolyte. AM:SE=75:25 (in wt.%)

Development of new positive electrode material;
for solid-state Li-ion system **with Si negative electrode**

→ Li containing phase

Demonstration of energy density over 800 Wh/L
and advantage of the material compared with NMC

M. Otoyama, H. Sakaebe, *et al.*, *ECS Advances*, **2** (2023) 010501.

M. Otoyama, H. Sakaebe, *et al.*, *Energy Mater.* 2025, 5, 500126.

High capacity

--- more Li and S in the material

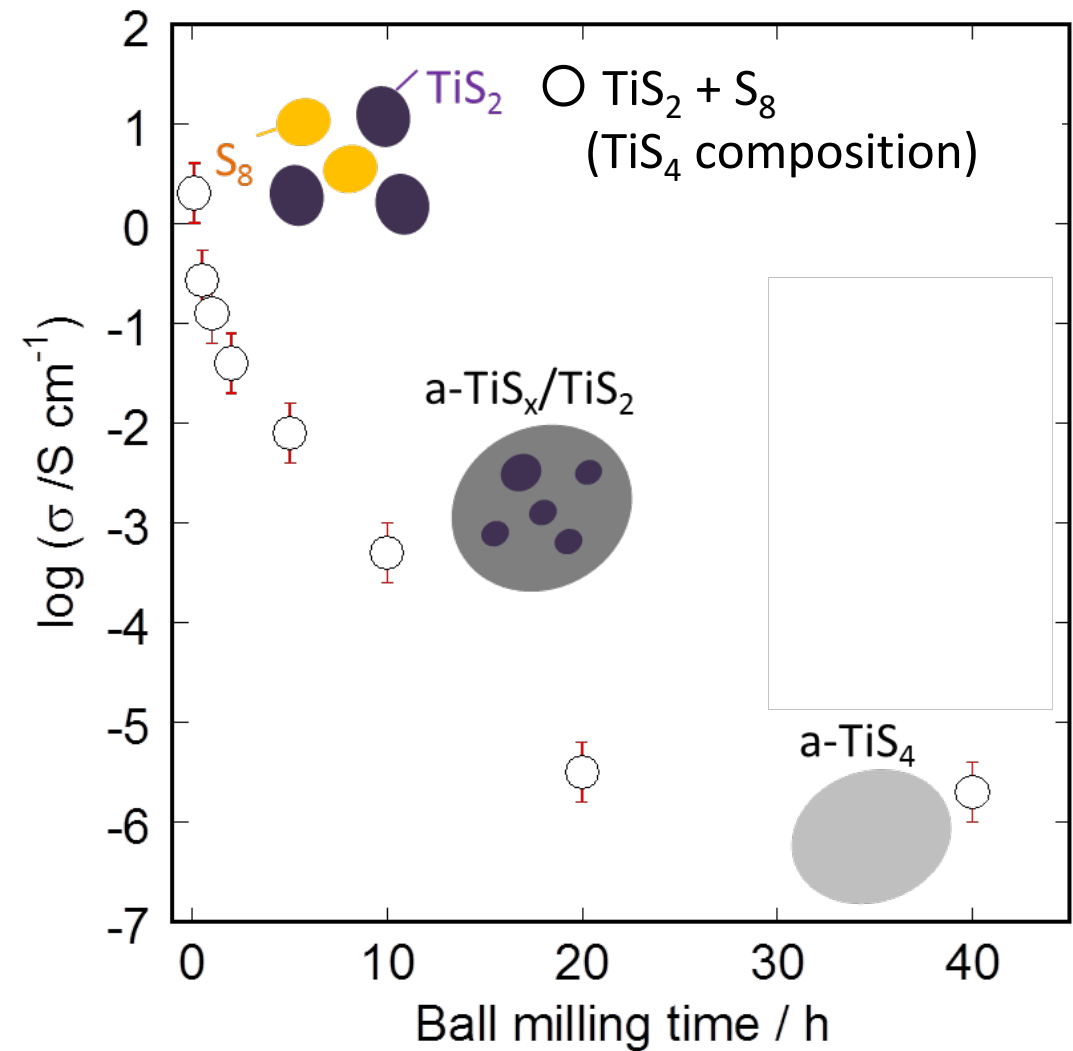
Less amount of conducting carbon in the electrode

--- high electric conductivity

Less amount of solid electrolyte in the electrode

--- high ionic conductivity

Nano-composite material of Li_2S and LiMS_x with high e^- and Li^+ conductivity



LiVS₂ was chosen as conductive part

Electric conductivity (10^3 S cm^{-1} as VS₂)

Ionic conductivity

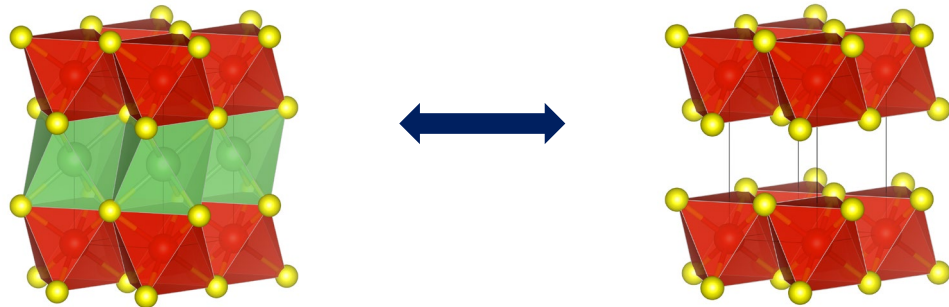
(Li⁺ transfer barrier 0.22 eV as VS₂)

Ji, Q et al., Nano Lett. 2017, 17, 4908 - 4916

Reversible capacity (1.5 – 3.0 V):170 mAh/g

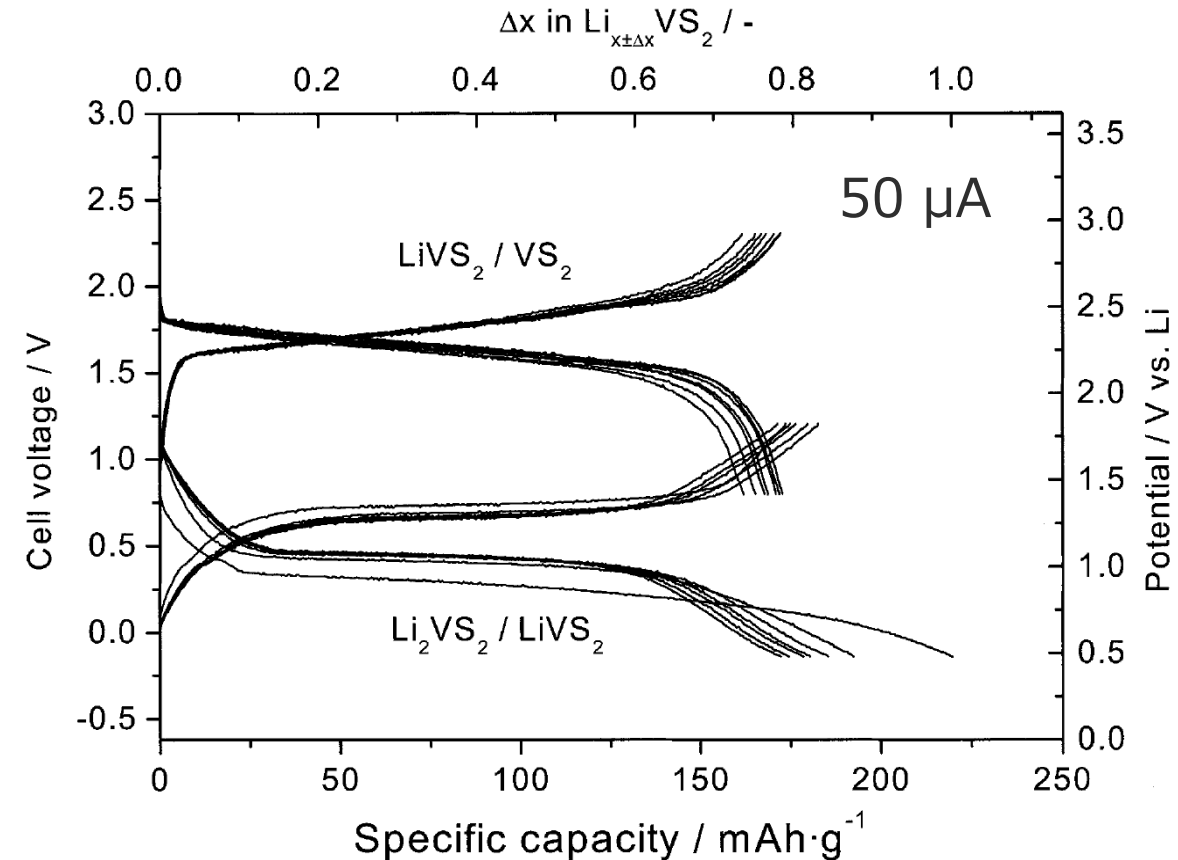
LiVS₂
(P-3m1 #164)
ICSD #16303

VS₂
(P-3m1 #164)
ICSD #651361



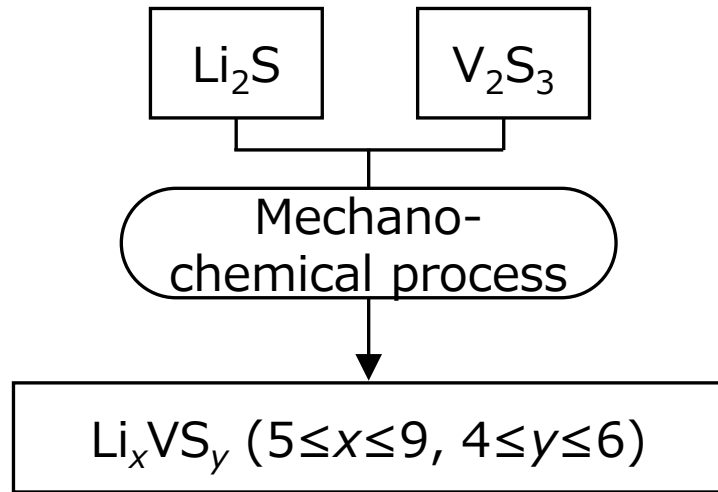
D. W. Murphy et al., *Inorg. Chem.*, **16** (1977) 3027.

S. Xu et al., *Adv. Funct. Mater.*, **31** (2021) 2004239.



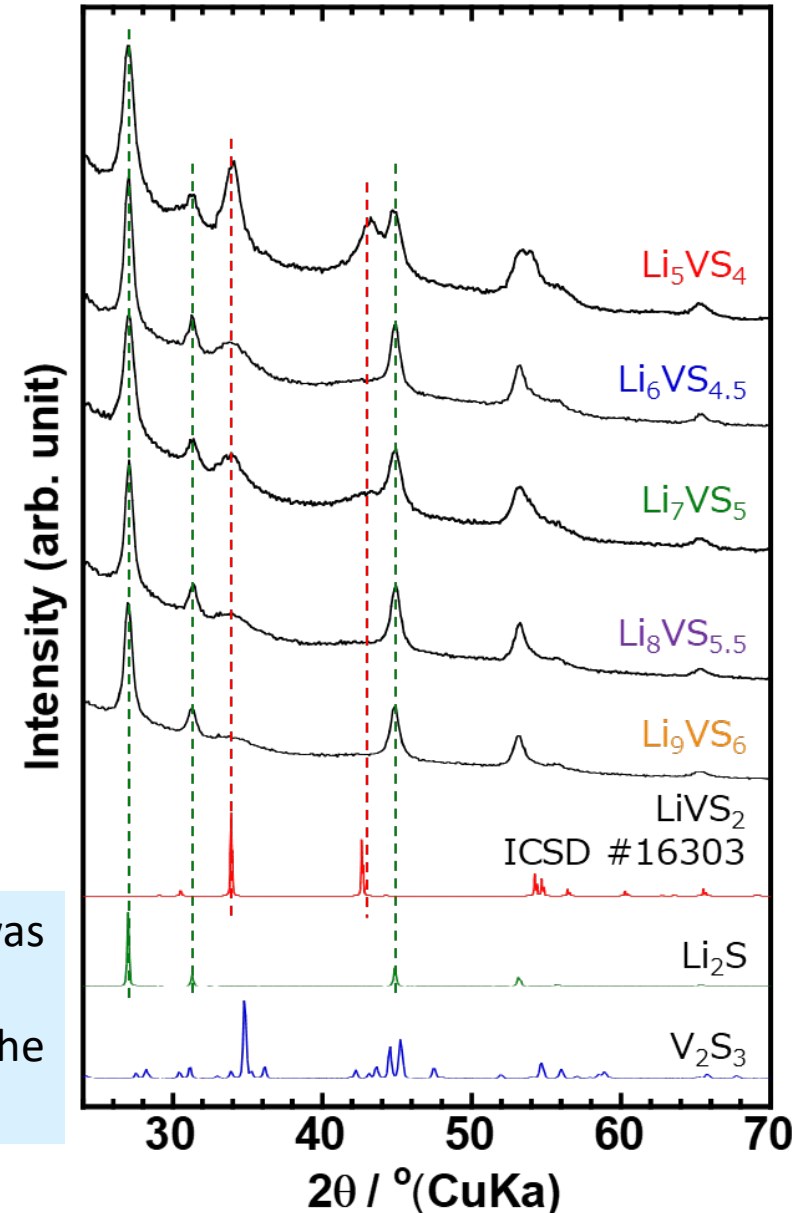
LiVS₂/SE/Li-In Electrode: LiVS₂:SE = 1:1 (w) 20 mg
SE: 0.01Li₃PO₄-0.63Li₂S-0.36SiS₂

K. Takada et al., *J. Power Sources*, **97–98** (2001) 762.



Conditions of mechano-chemical process;
300 or 400 rpm, 160 h

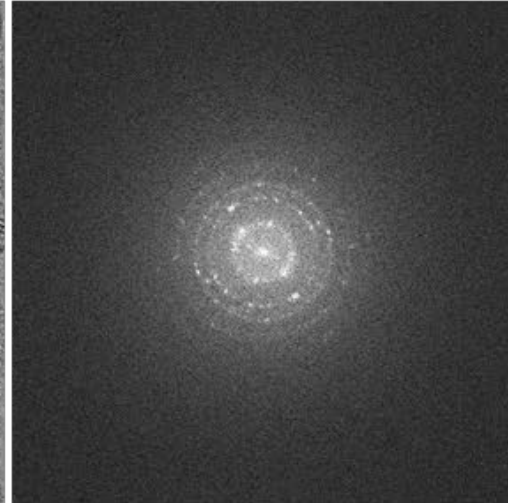
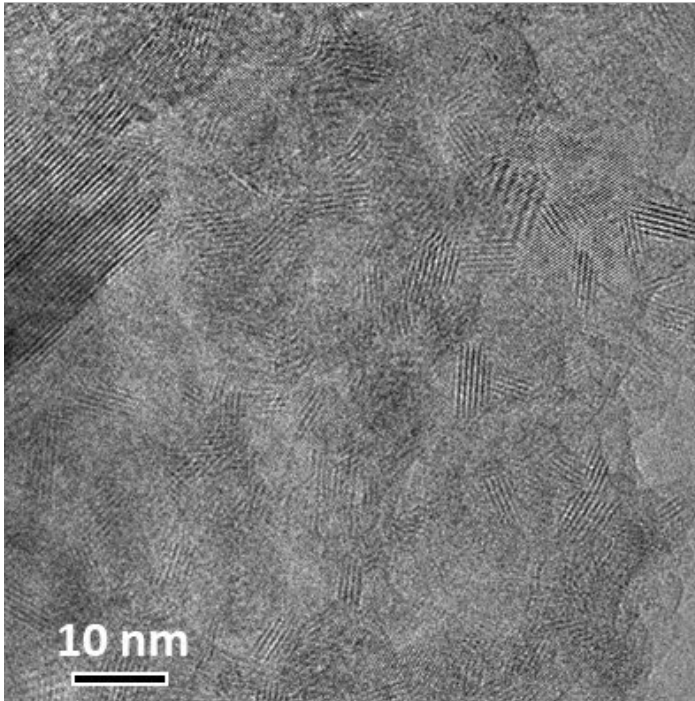
Composite of Li₂S and LiVS₂ was obtained judging from XRD. LiVS₂ intensity correlates the composition and e⁻ conductivity.



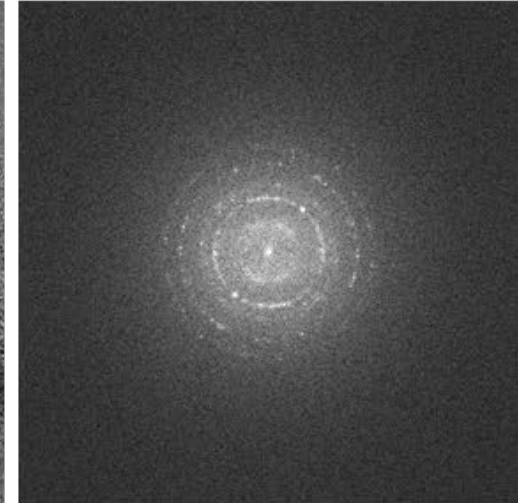
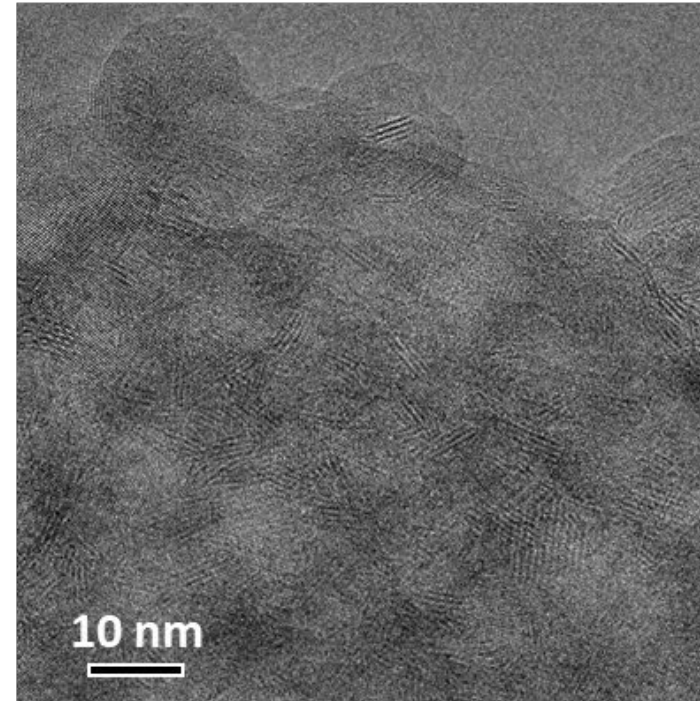
Li ₂ S : V ₂ S ₃	e ⁻ conductivity (S cm ⁻¹)	Li ⁺ conductivity (S cm ⁻¹)
Li ₅ VS ₄ (5 : 1)	0.13	2.0 × 10 ⁻⁶
Li ₆ VS _{4.5} (6 : 1)	0.18	7.6 × 10 ⁻⁶
Li ₇ VS ₅ (7 : 1)	0.11	4.5 × 10 ⁻⁶
Li ₈ VS _{5.5} (8 : 1)	0.059	5.6 × 10 ⁻⁶
Li ₉ VS ₆ (9 : 1)	0.035	8.3 × 10 ⁻⁶

TEM images

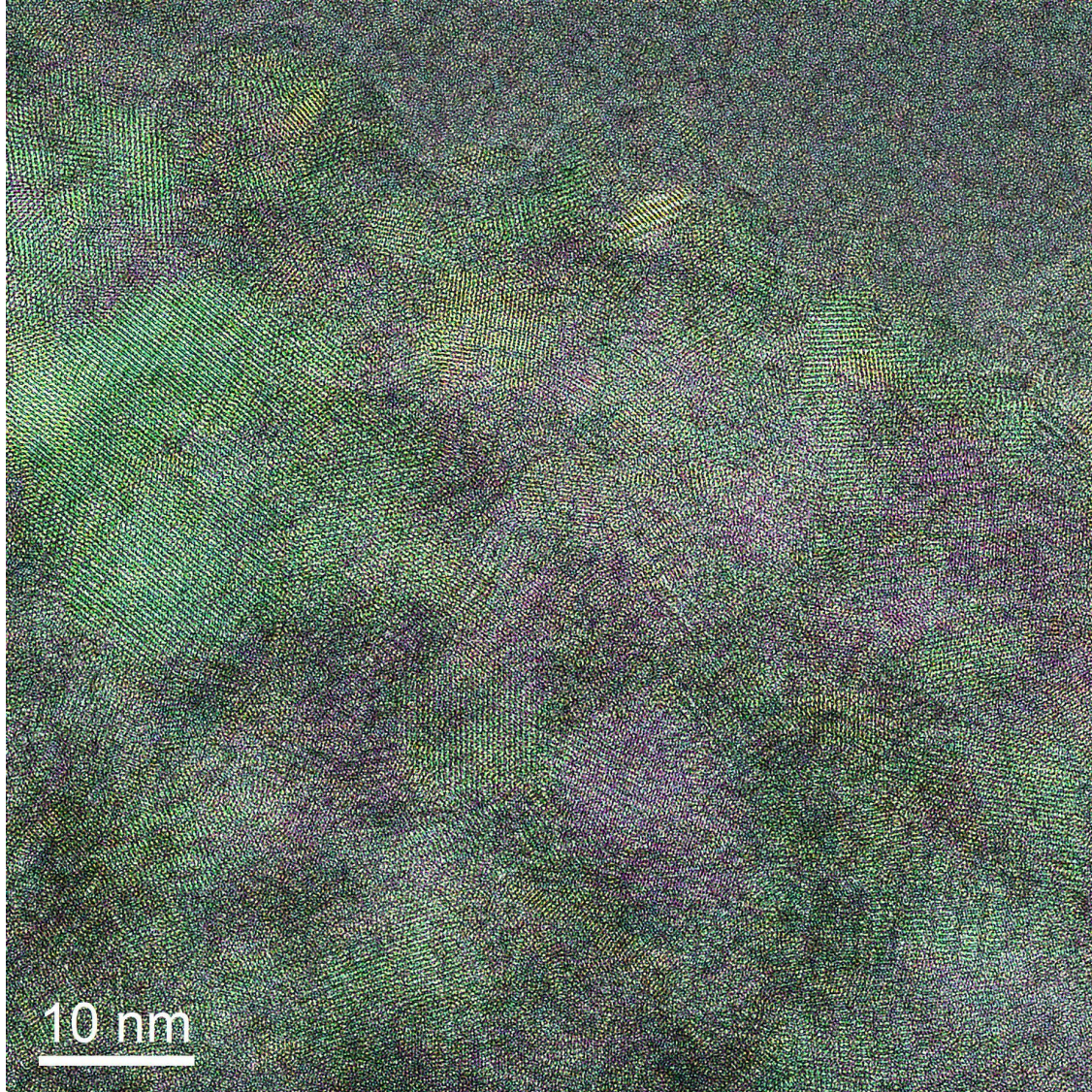
Li_5VS_4



$\text{Li}_8\text{VS}_{5.5}$



Mosaic structure of nano-crystalline and amorphous part



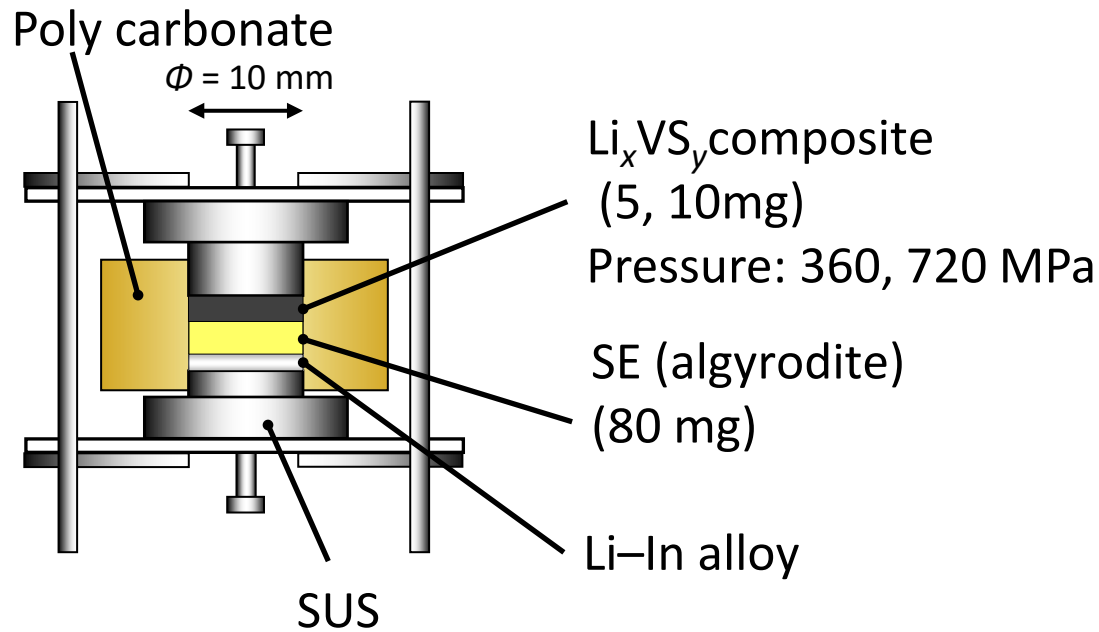
Nano-meter sized LiVS_2 and Li_2S are highly distributed in the composite. Amorphous part is a major component.

Li_2S (0.31 nm)

LiVS_2 (0.60 nm)

V_2O_3 (0.26 nm) (impurity)

All-solid-state battery system: Charge-discharge test results @ AIST²⁰

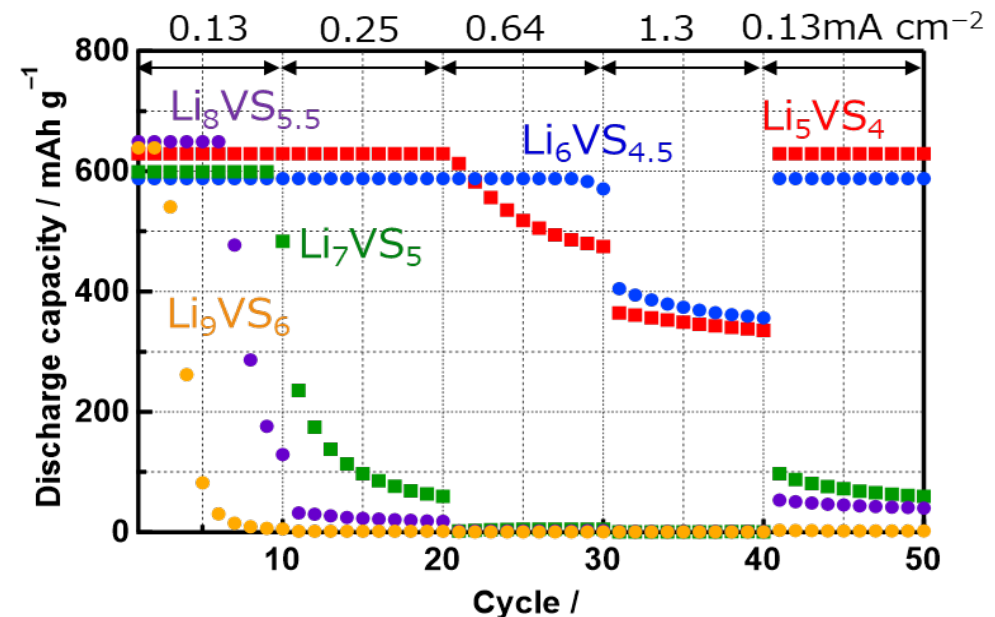
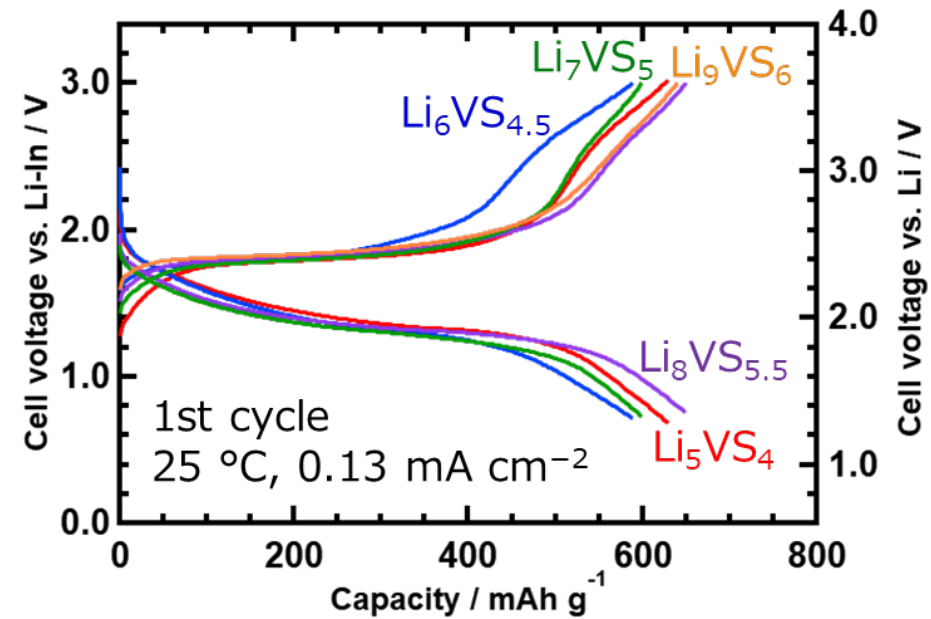


LVS : SE : AB = 40 : 50 : 10 (wt.%)

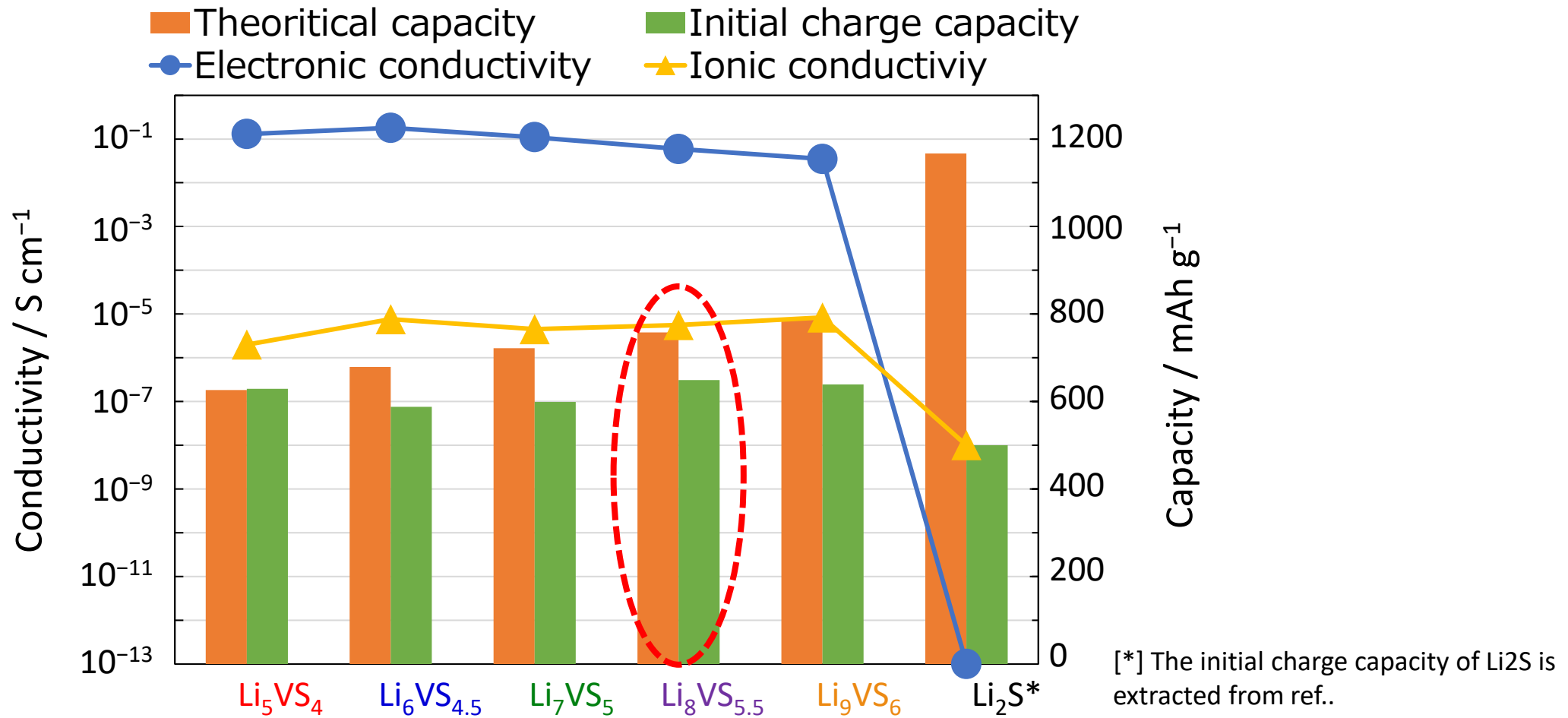
Loadings: 10 mg

Capacity: $600 \sim 700 \text{ mAh g}^{-1}$

Li_5VS_4 and $\text{Li}_6\text{VS}_{4.5}$ showed better cycleability and rate properties



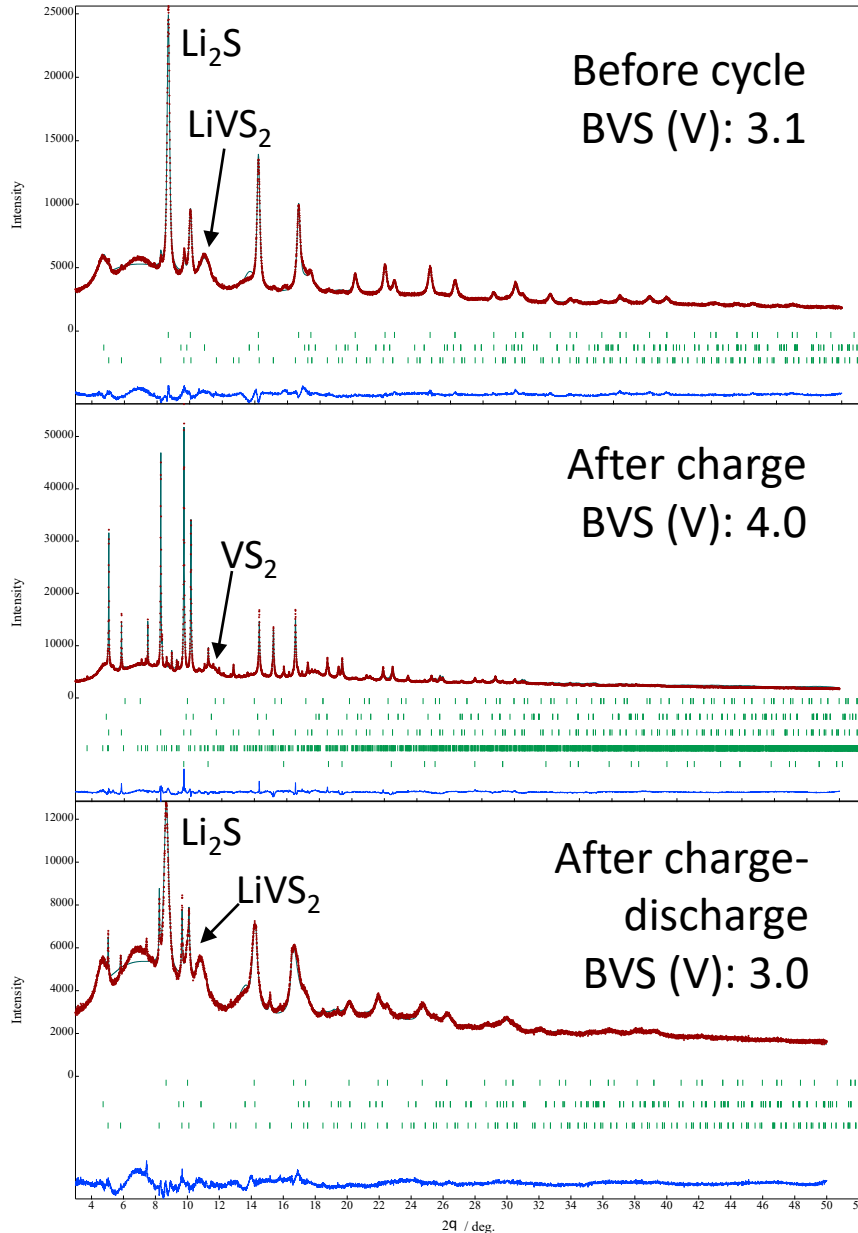
All-solid-state battery system: Charge-discharge test results @ AIST²¹



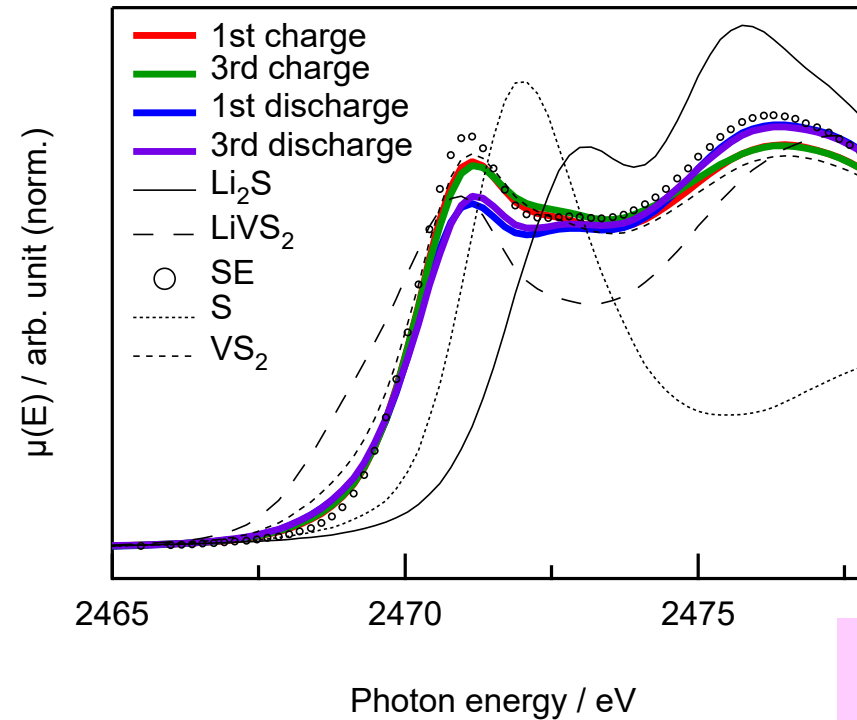
All-solid-state cells with Li_xVS_y samples show high capacities due to their high electronic and ionic conductivities compared with Li_2S .

All-solid-state battery system: Charge-discharge test results @ AIST 22

XRD@SPring-8 BL19B2

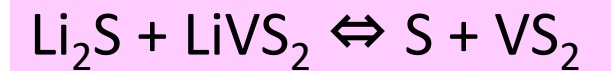


XAFS@Ritz SR center



Charged state and discharged state at 1st and 3rd cycle completely the same. Good reversibility

Charge discharge reaction

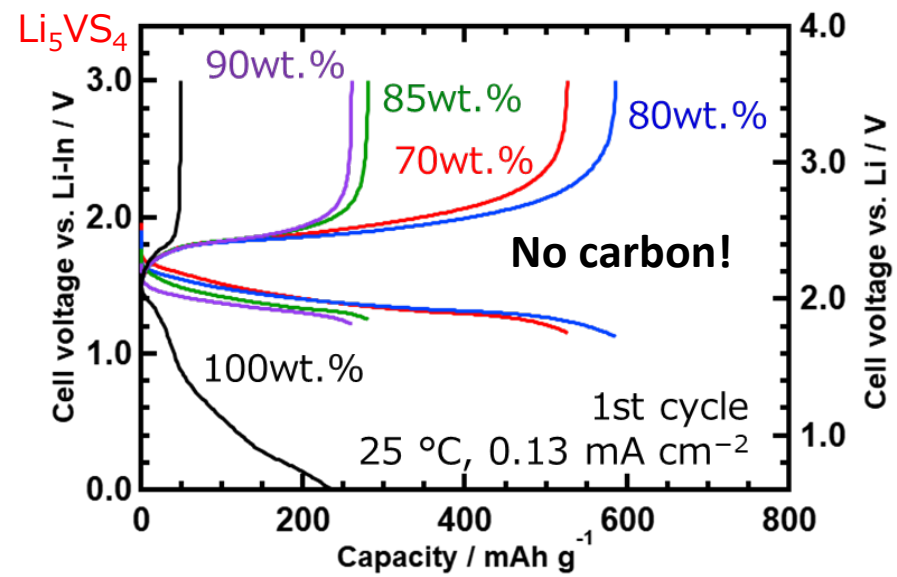


LiVS_2 Lattice parameter	a (Å)	c (Å)
Before cycle	3.374(2)	6.064(3)
After charge	3.233(5)	5.847(9)
After charge-discharge	3.393(4)	6.055(7)

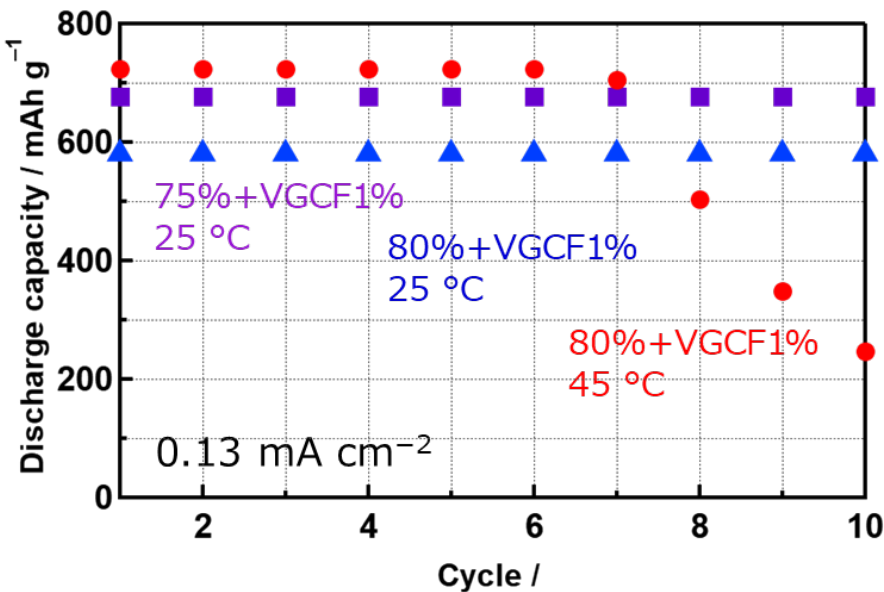
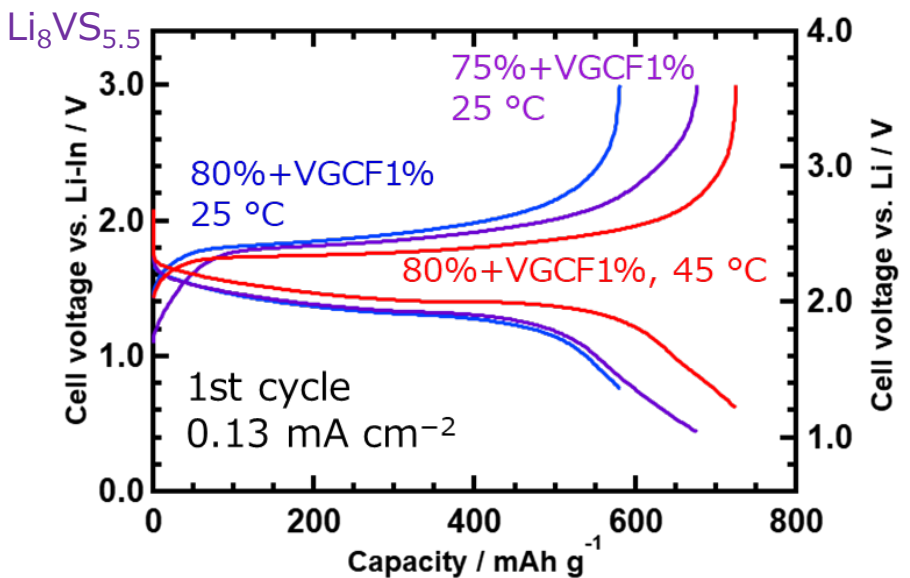
LiVS_2 [4]	VS_2 [4]
a : 3.381 Å	a : 3.218 Å
c : 6.139 Å	c : 5.755 Å

[4] D. W. Murphy *et al.*, *Inorg. Chem.*, **16** (1977) 12.

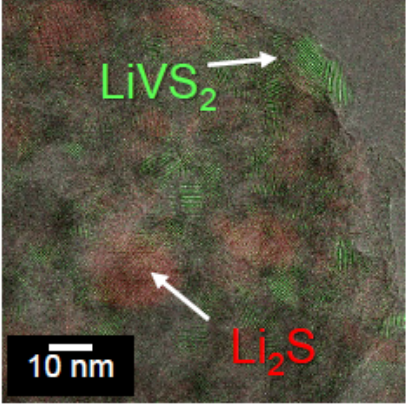
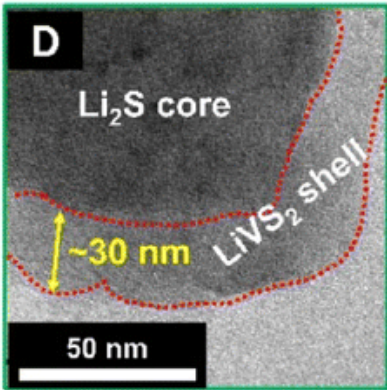
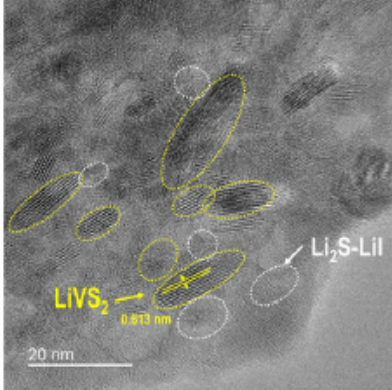
All-solid-state battery system: Charge-discharge test results @ AIST ²³



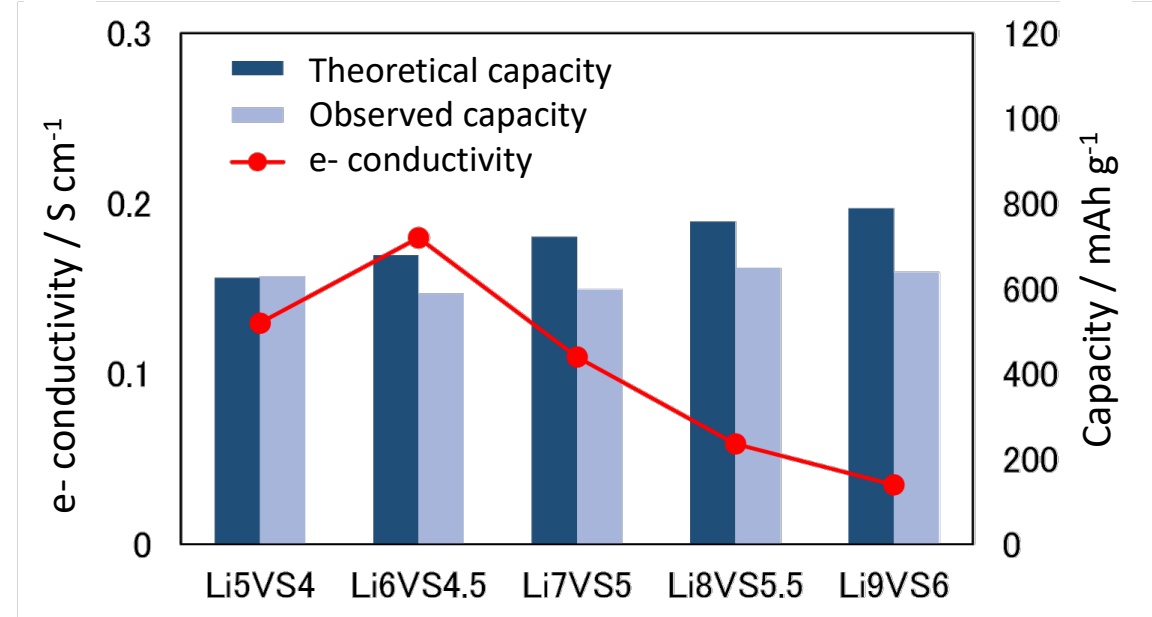
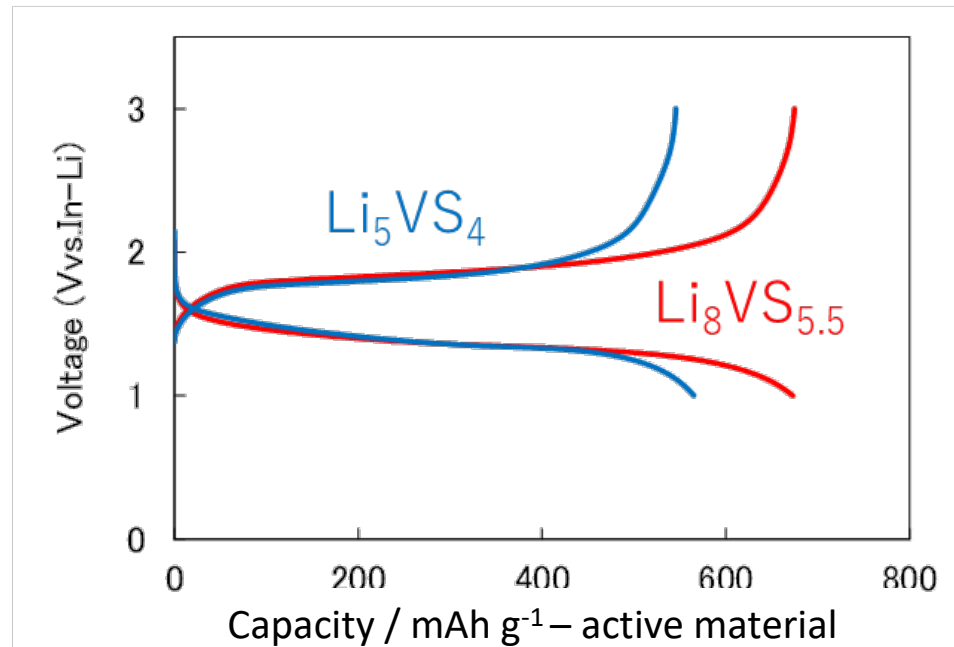
Li ₅ VS ₄ : SE (wt.%)	Loadin g (mg)	1 st Charge capacity (mAh g ⁻¹)	Percentage against theoretical capacity	e ⁻ conductivity @RT (S cm ⁻¹)	Li ⁺ conductivity @RT (S cm ⁻¹)
100 : 0	3.1	48	8%	1.3 × 10 ⁻¹	2.0 × 10 ⁻⁶
90 : 10	5.2	260	42%	3.1 × 10 ⁻³	1.8 × 10 ⁻⁵
85 : 15	5.4	280	45%	4.3 × 10 ⁻³	9.4 × 10 ⁻⁶
80 : 20	5.3	586	94%	1.8 × 10 ⁻³	1.3 × 10 ⁻⁵
70 : 30	5.3	574	92%	1.6 × 10 ⁻⁴	1.2 × 10 ⁻⁵



Li₅VS₄ can be operated without carbon.
94% of Li was extracted and inserted.
Li₈VS_{5.5} cycles with less carbon.
70-90% of Li was utilized @RT.

	$\text{Li}_8\text{VS}_{5.5}$ (this work)	Core shell of $\text{Li}_2\text{S}/\text{LiVS}_2$ [*1]	$90(0.75\text{Li}_2\text{S}\cdot0.25\text{V}_2\text{S}_3)\cdot10\text{LiI}$ [*2]
Structure	 Nanocomposites of Li_2S and LiVS_2 in amorphous matrix	 Li_2S core and LiVS_2 shell	 LiVS_2 and $\text{Li}_2\text{S-LiI}$ nanoparticles dispersed in the $\text{Li}_2\text{S-V}_2\text{S}_3\text{-LiI}$ amorphous matrix
Feature	Nano LiVS_2 forms sufficient electronic conduction paths to Li_2S.	Li_xVS_2 acts as interfacial redox mediator.	electrode-electrolyte bifunctional material
Synthesis	Ball milling	Reacting Li_2S with VCl_4 in tetrahydrofuran	Ball milling
$\text{Li}_2\text{S}:\text{LiVS}_2$	77.8:22.2 (wt.%)	$\sim 60:\sim 40$ (wt.%)	50:50 (wt.%)
Conductivity	$\sigma^{\text{e-}}: 0.059 \text{ S cm}^{-1}$ $\sigma^{\text{Li+}}: 5.6 \times 10^{-6} \text{ S cm}^{-1}$	$\sigma^{\text{e-}}: 5.5 \text{ S cm}^{-1}$ $\sigma^{\text{Li+}}: 1.3 \times 10^{-5} \text{ S cm}^{-1}$	$\sigma^{\text{e-}}: >0.1 \text{ S cm}^{-1}$ $\sigma^{\text{Li+}}: 2.5 \times 10^{-4} \text{ S cm}^{-1}$
High-loading performance	$26.4 \text{ mg cm}^{-2}, 15 \text{ mAh cm}^{-2}$ (full cell, 60°C , 0.2 mA cm^{-2})	$10 \text{ mg cm}^{-2}, 5.3 \text{ mAh cm}^{-2}$ (half cell, 60°C , 0.25 mA cm^{-2})	ca. $4.5 \text{ mg cm}^{-2}, 1.7 \text{ mAh cm}^{-2}$ (half cell, 25°C , 0.13 mA cm^{-2})

Li_xVS_y shows high capacity because nano-sized LiVS_2 forms sufficient electron conduction paths to high amount of Li_2S .



Cell and test conditions (pressed pellet)

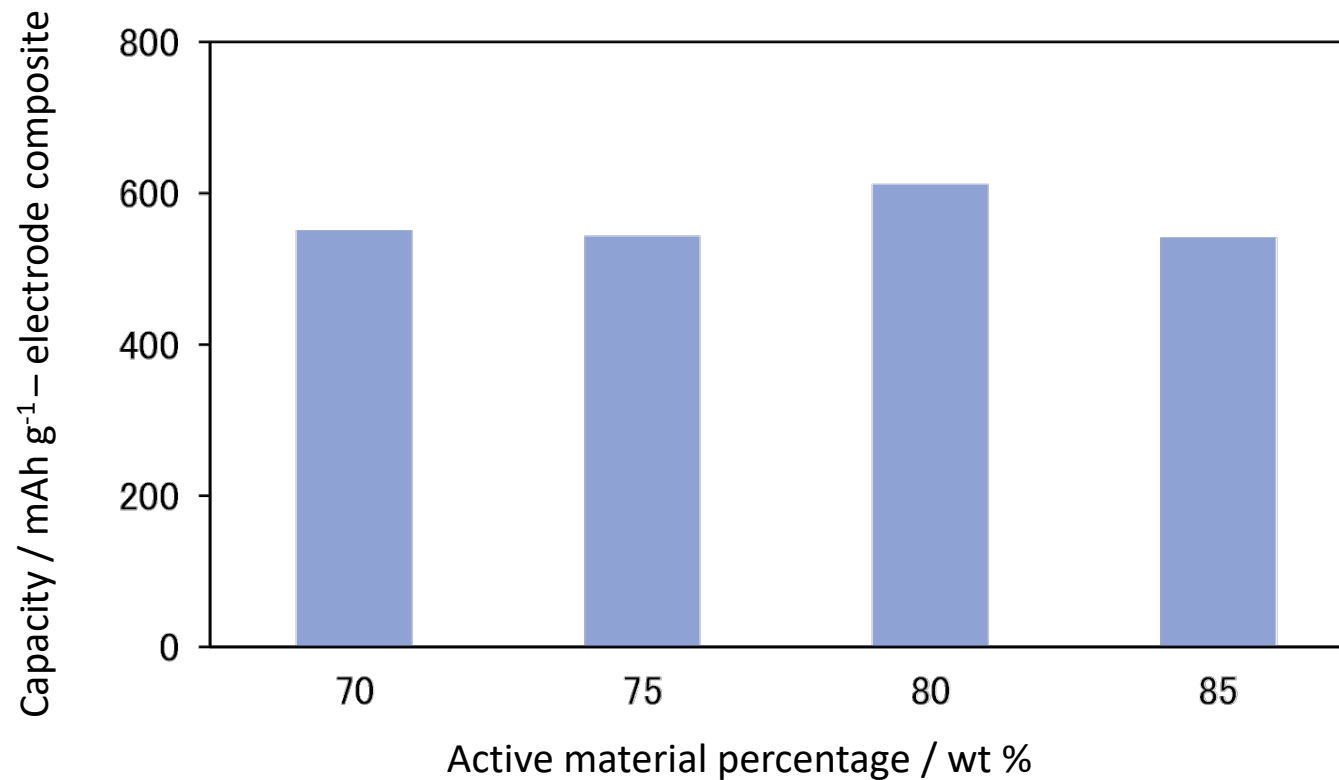
Cathode composite	Li_xVS_y	8.5 mg
	$\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$	1.5 mg
SE layer	$\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$	80 mg
Test conditions	0.02 C 1.0-3.0 V vs. In-Li 25°C	

$\text{Li}_8\text{VS}_{5.5}$ was chosen as an active material for energy density demonstration as the observed capacity was largest among samples.

Electronic conductivity low
Ionic conductivity high

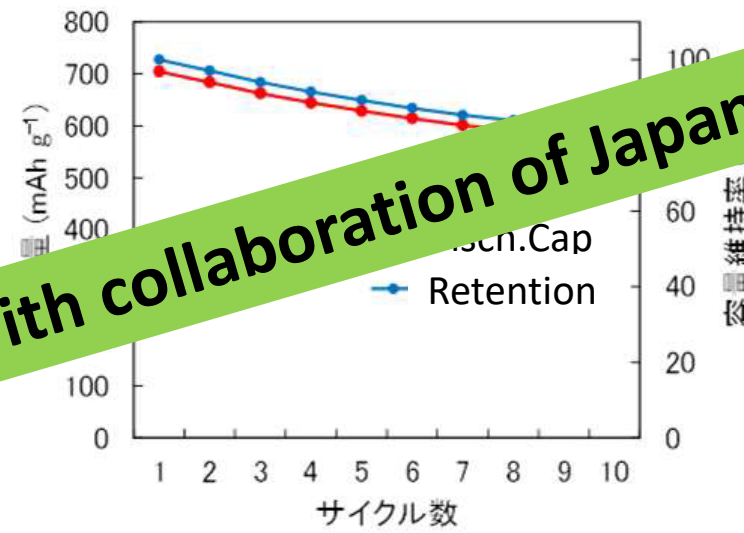
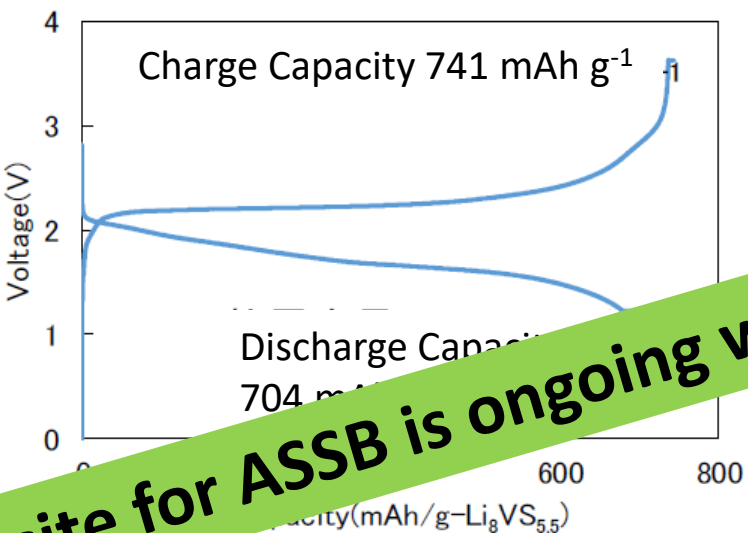


Electronic conductivity high
Ionic conductivity low



Active material percentage was decided to 80%

Energy density of 853Wh L⁻¹、515Wh kg⁻¹ was estimated using the LIBTEC cell specification of A4 size



Cross section



Nano composite for ASSB is ongoing with collaboration of Japanese industry

Cell and test conditions	
Cathode	Li ₈ VS _{5.5} :SE = 80:20 : loading 33 mg cm ⁻² (c.a. 20 mAh cm ⁻²)
SE layer	Li _{7-x} PS _{6-x} Cl _x
Anode	Si composite electrode ; loading 10.4 mg cm ⁻²
Test conditions	CCCV 0.01 C (0.001 C cut) 1.22-3.62 V 60 °C Av, voltage 1.646 V



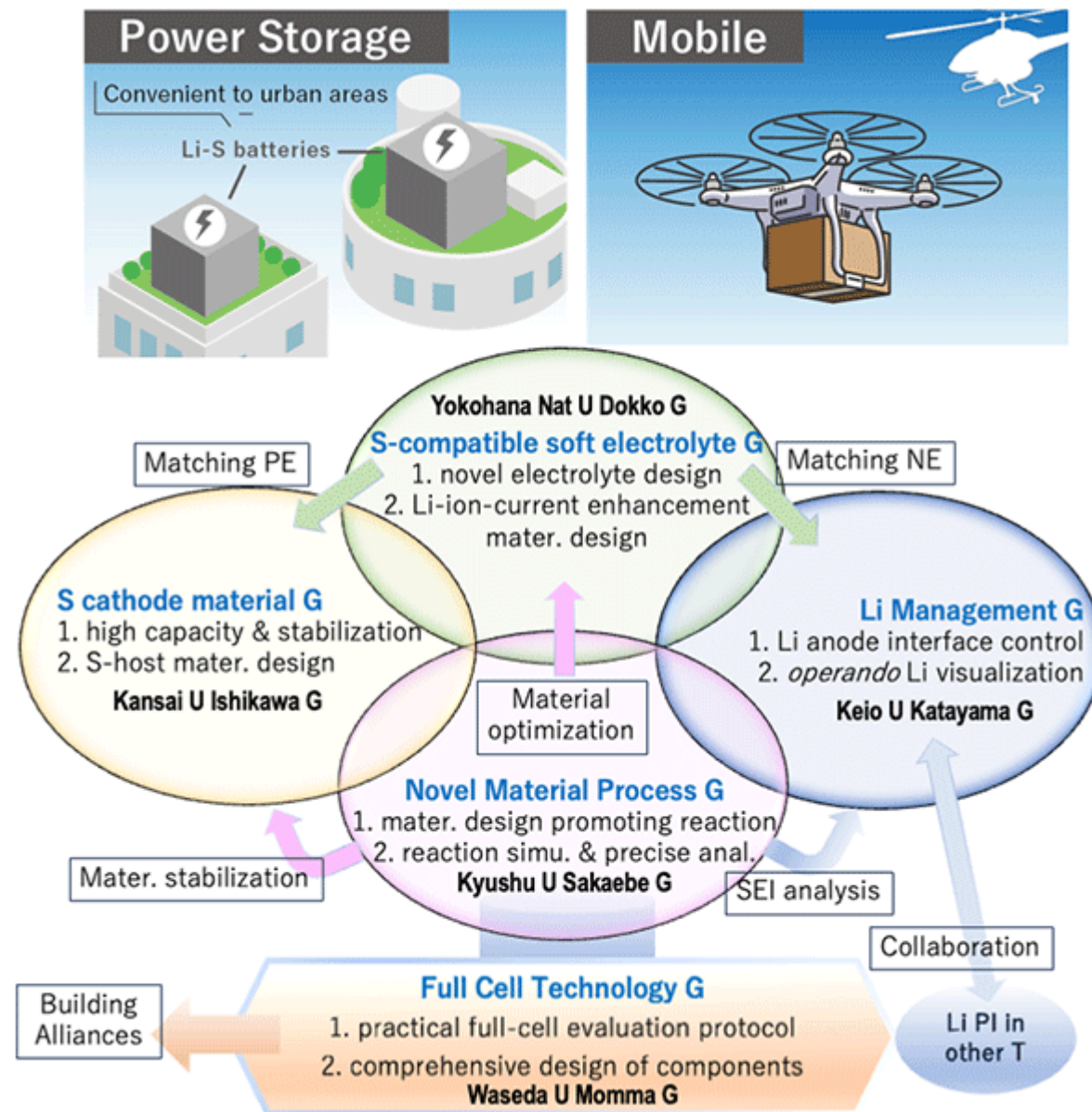
Back to liquid system, and my first challenge for S-carbon composite



Team leader

Prof. ISHIKAWA Masashi

Kansai University



- Metal sulfides have been applied to Li-S battery.
- New material, metal polysulfides was developed for liquid and solid system. These materials worked with less amount of carbon.
- New nano-composite materials for all solid state batteries, contains a highly distributed LiVS_2 and Li_2S nanocrystalline with amorphous part.
- Charge-discharge reaction ; $\text{Li}_2\text{S} + \text{LiVS}_2 \rightleftharpoons \text{S} + \text{VS}_2$
At least initial few cycle, structural change is reversible.
- High energy full cell $\text{Li}_8\text{VS}_{5.5}/\text{Si}$ was developed.
- Recently I'm back to the liquid system with metal sulfides additives.

Thank you for your kind attention !