PhD Defense

Composite Solid Electrolytes for High-Performance Room-Temperature Solid-State Batteries

16h30 - 17h30, Room 204 - Building 6

June 12, 2023

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Supervisor: Professor Chan-Jin Park

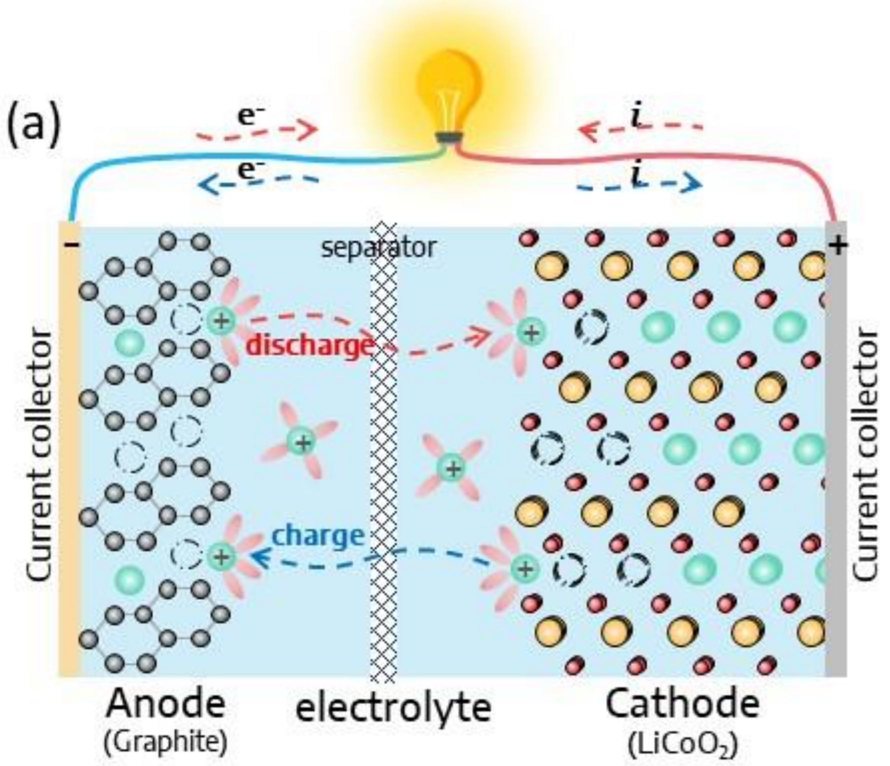
M/E lab

Content

Energy density of LIBs

Working principle of LIBs

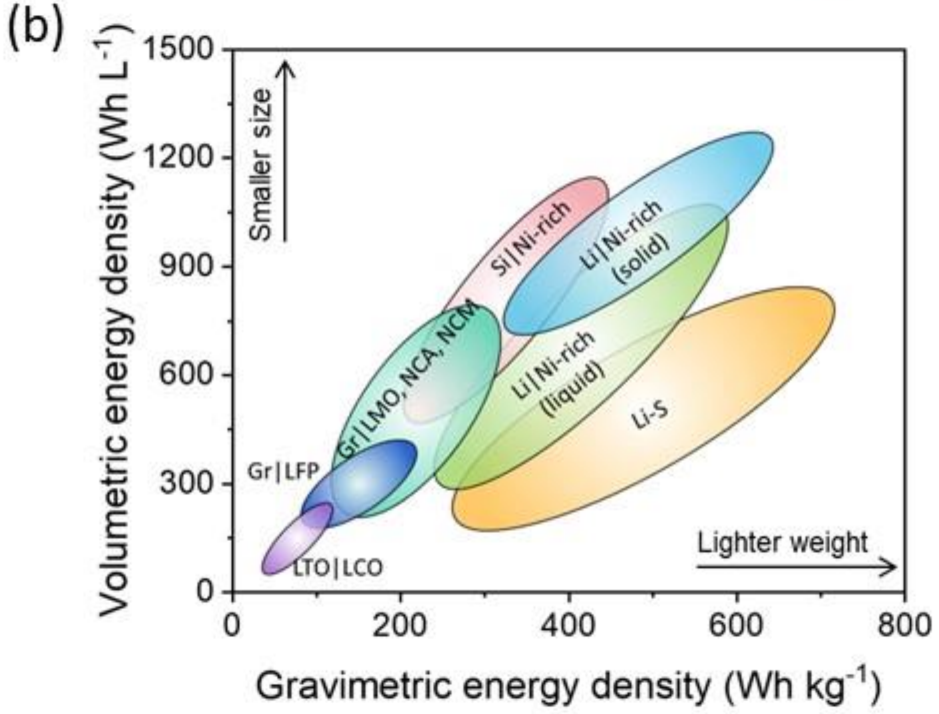
$$LiCoO_2 + C \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC + Li_{1-x}CoO_2$$



Portable to stationary (mW to MW)
Instant

How to increase Energy Density of LIBs?

$$Wh\ kg^{-1} = V \times Ah\ kg^{-1}$$
$$Wh\ L^{-1} = V \times Ah\ L^{-1}$$

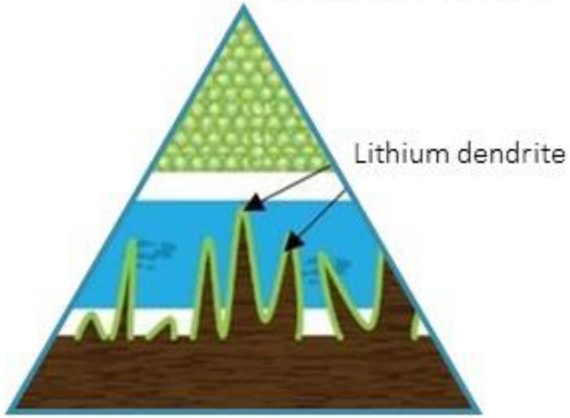


We need higher energy density batteries!

Safety issue

Graphite | LFP (HighTechLab)

Fuel
- Flammable electrolyte



Oxygen
- Cathode decompose

Trigger Factor
- Internal: Overcharge
- External: Accident

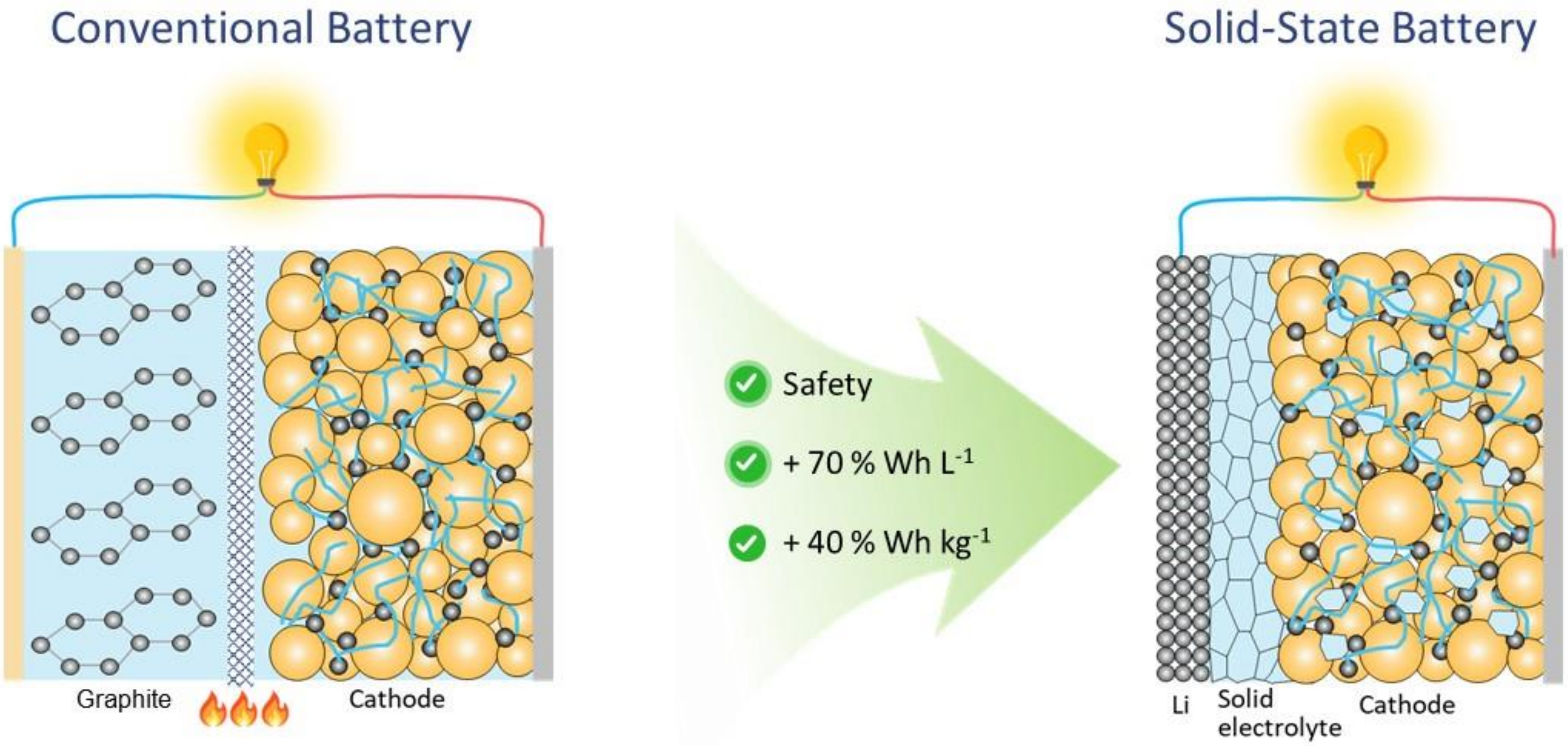
Initiation
- Battery temperature ~120 °C
- Exothermic decomposition of SEI
- Melt of the separator

Propagation
- Battery temperature >180 °C
- Exothermic reaction of cathode with electrolyte

Thermal runway

We also need safer batteries!

Why Solid-State Batteries?

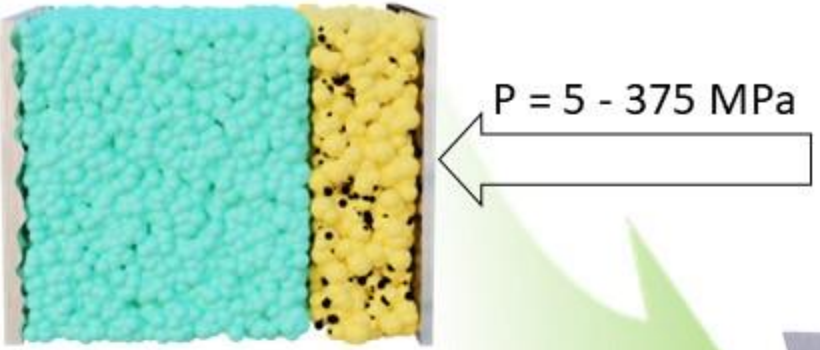


Solid-State Batteries (SSBs): safer and higher energy density

Why Composite Solid Electrolyte?

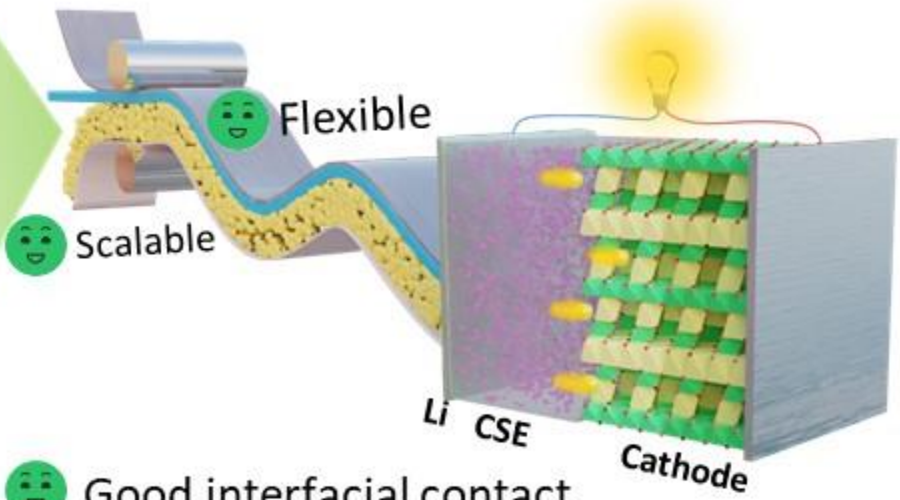
Toward solid-state lithium metal batteries by using composite solid electrolyte

- High ionic conductivity ($>10^{-3}$ S cm^{-1})
- High mechnical strength
- Good dedrite suppression
- Poor interfacial contact



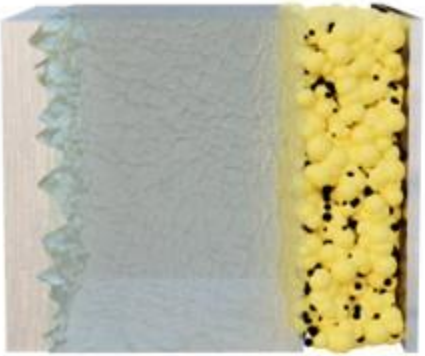
Inorganic Solid Electrolyte

Composite Solid Electrolyte (CSE)



- Good interfacial contact
- Good ionic conductivity (10^{-4} S cm^{-1})

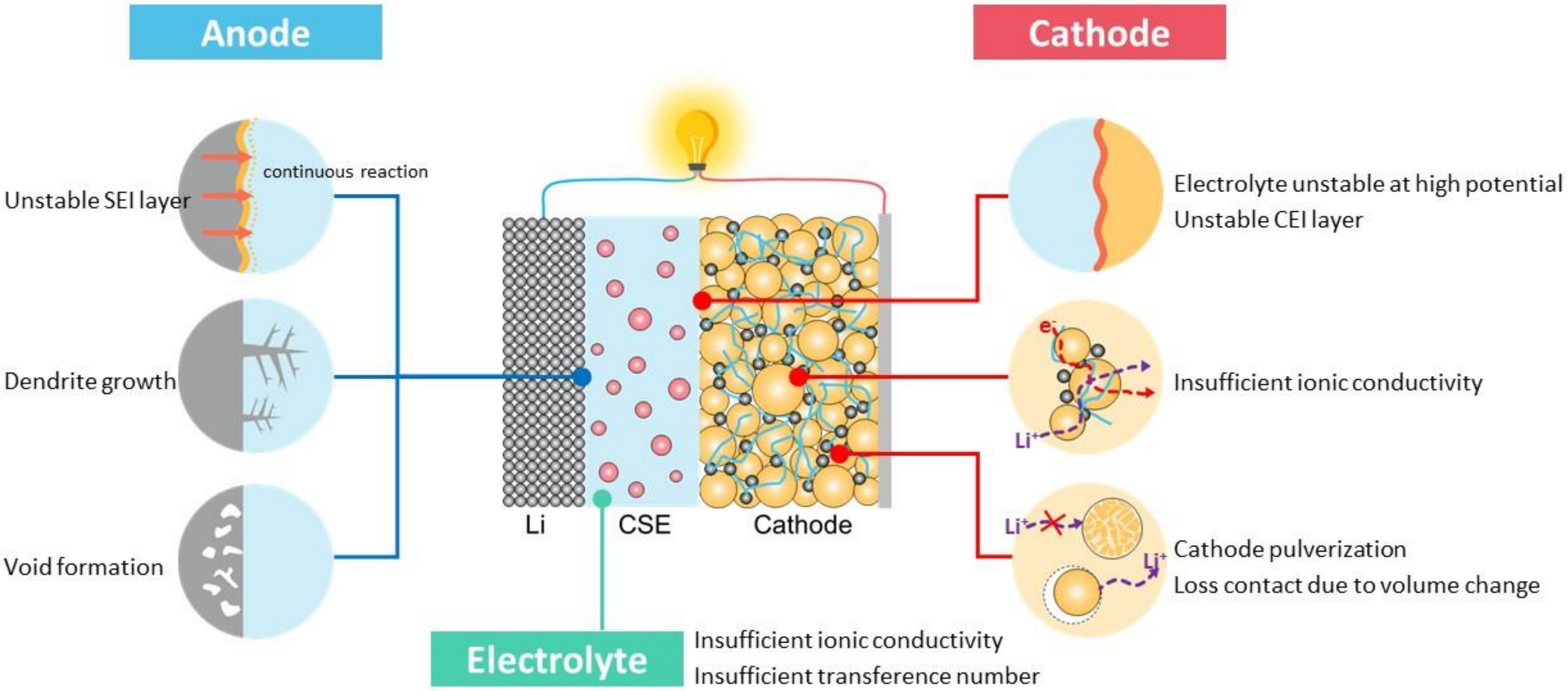
- Good interfacial contact
- Scalable
- Poor dedrite suppression
- Low ionic conductivity ($<10^{-5}$ S cm^{-1})



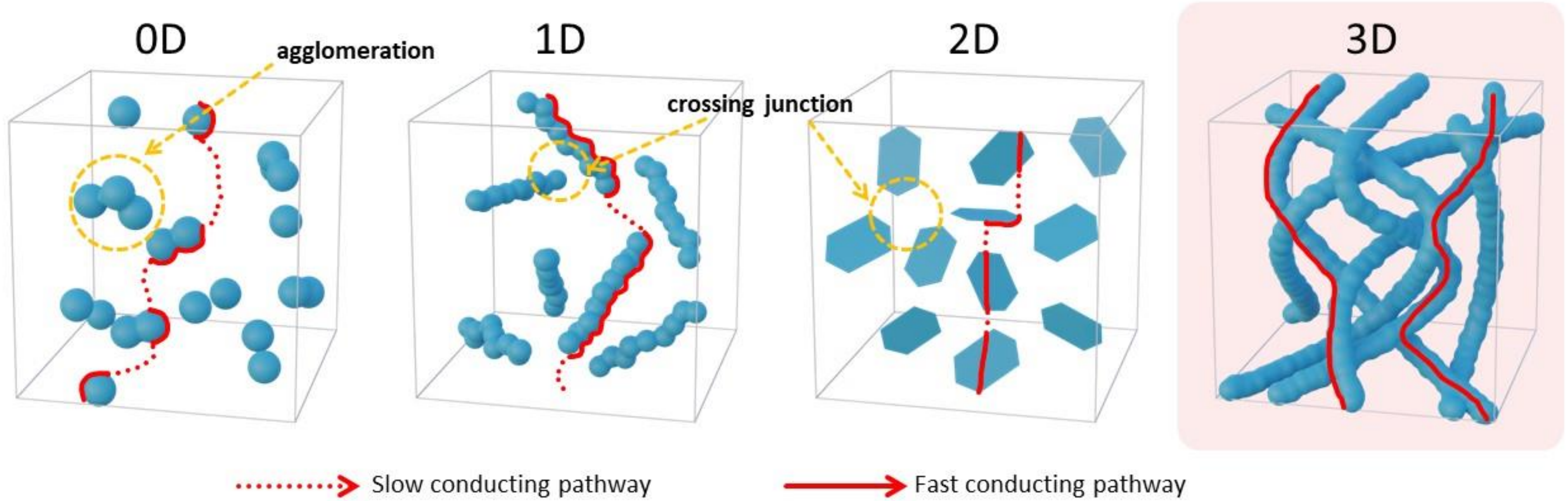
Solid Polymer Electrolyte

A.G. Nguyen *et. al.*, Journal of Membrane Science, 2023, 675, 121552

Issues in CSE-based SSBs



Effect of filler dimension in CSEs



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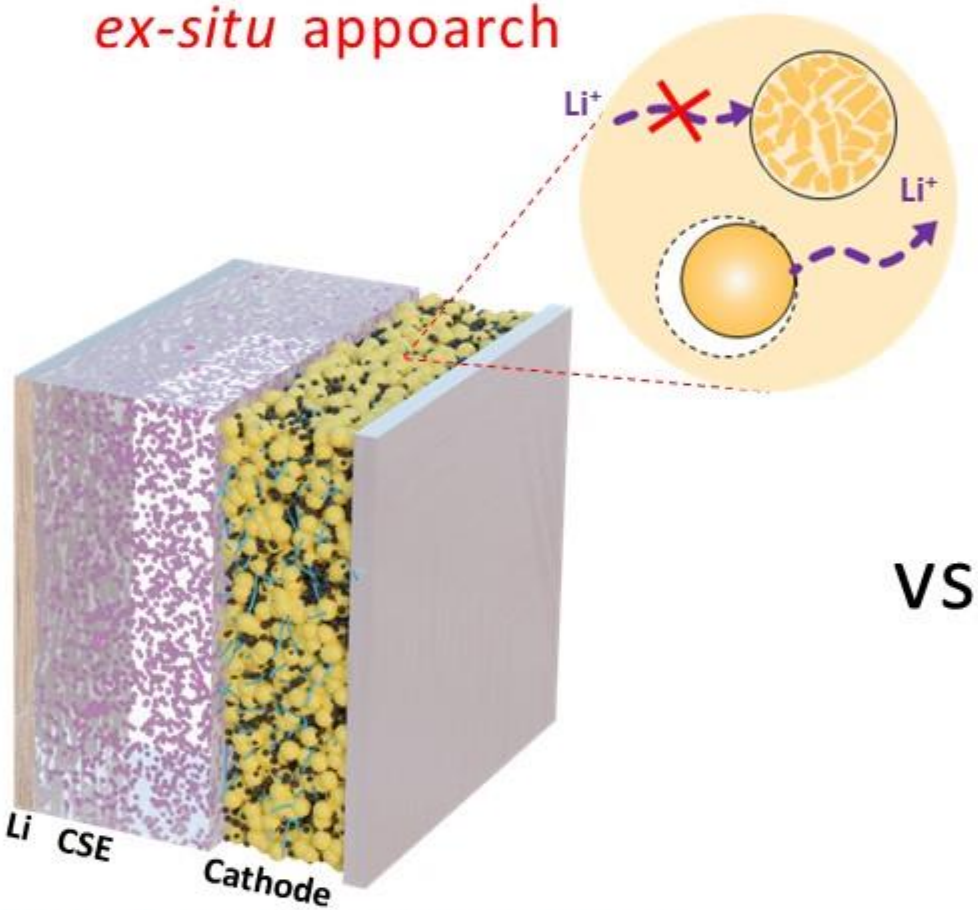
Control the filler dimension in composite solid electrolyte

Improve the ionic conductivity on the cathode side

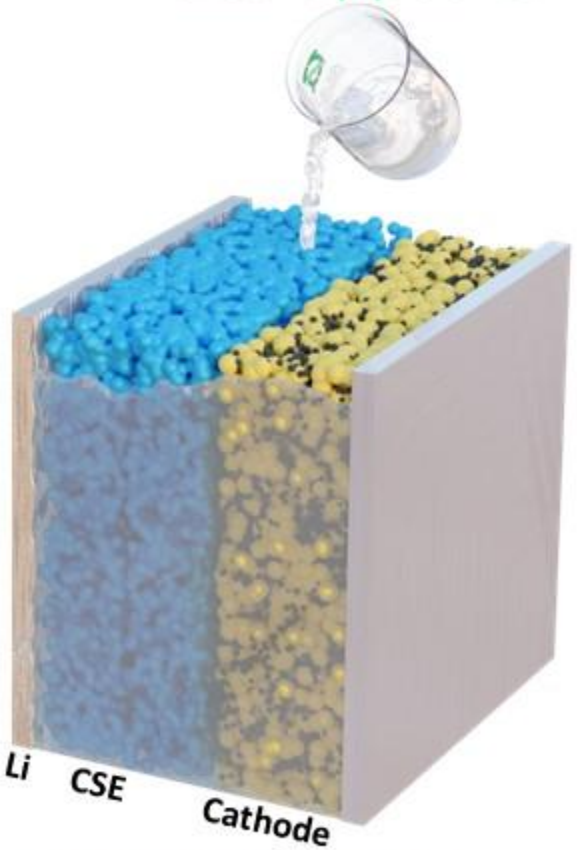
ex-situ appoarch



× Electrode-electrolyte interphase issue
× Insufficient ionic conduction on the cathode

vs.

in-situ appoarch



✓ Integrated structure
✓ Good interphase contact
✓ Ionic conduction network on the cathode

➡ In-situ polymerization on a 3D ceramic frameworks as composite solid electrolytes

Part 1

In-situ Polymerization on a 3D Ceramic Framework of Composite Solid Electrolytes for Room-Temperature Solid-State Lithium Batteries

A.G. Nguyen *et. al.*, Advanced Science, 2023, 2207744

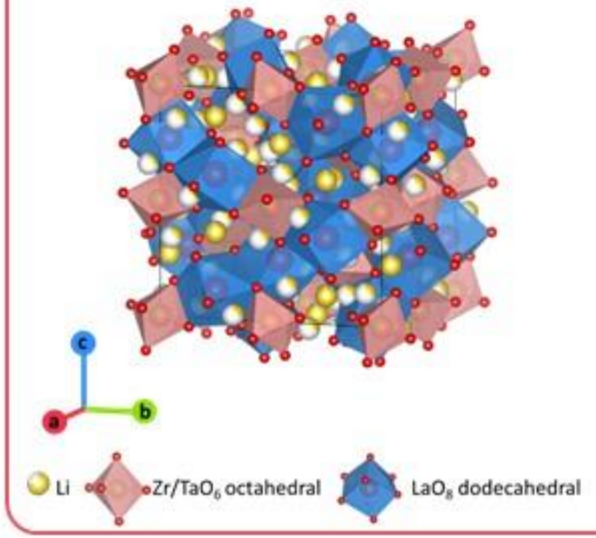
Objective

- Develop a simple and effective method to fabricate 3D ceramic framework
- Improve the ionic conductivity and electrode-electrolyte interfacial compatibility of CSE

Ceramic

Garnet $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$

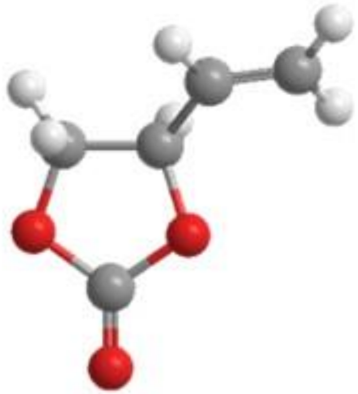
- ✓ Stability against electrodes
- ✓ High conductivity



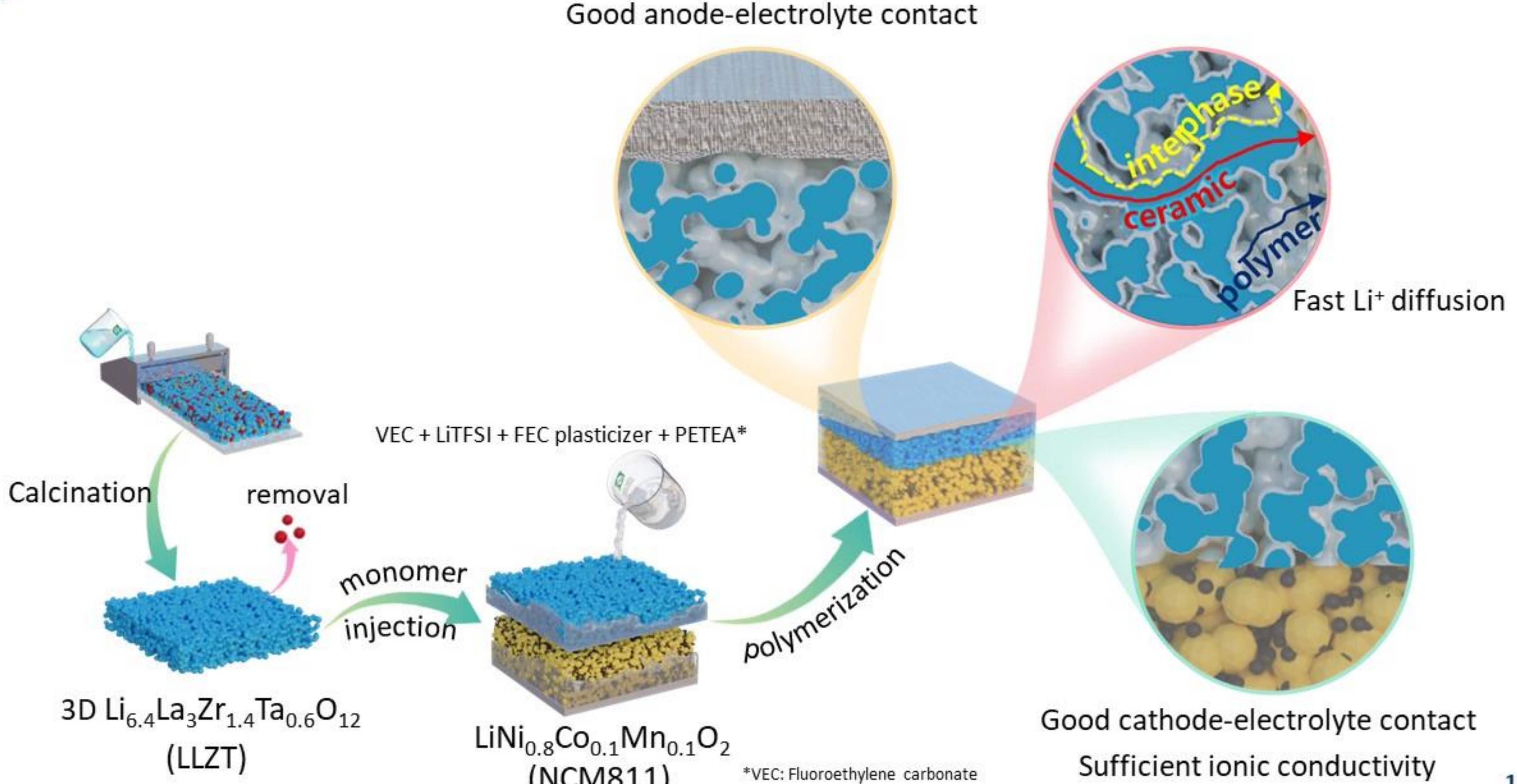
Polymer

Vinylene Ethylene Carbonate

- ✓ Can be polymerized
- ✓ Facilitate ions transportation



Preparation of CSE for Solid-State Lithium Batteries

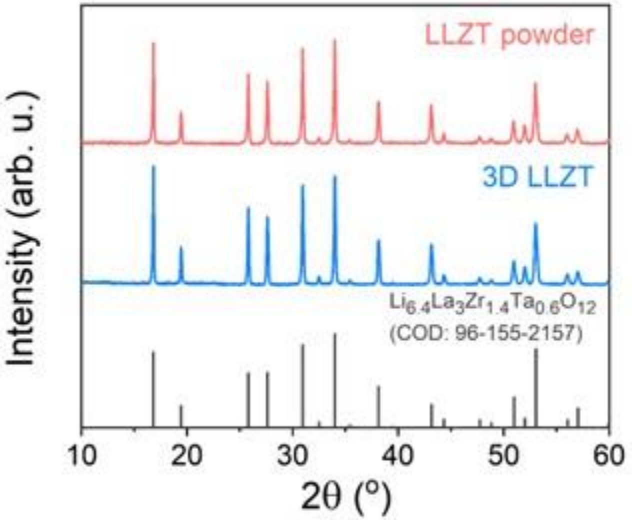


*VEC: Fluoroethylene carbonate
PETEA: Pentaerythritol tetraacrylate

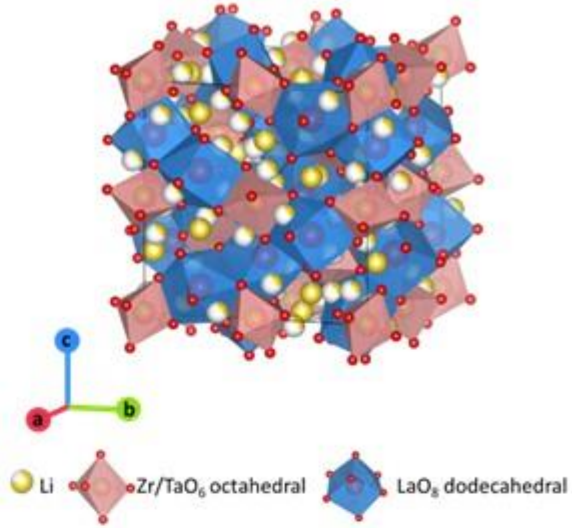
Crystal structure of 3D-LLZT

(a)

LLZT powder and 3D LLZT

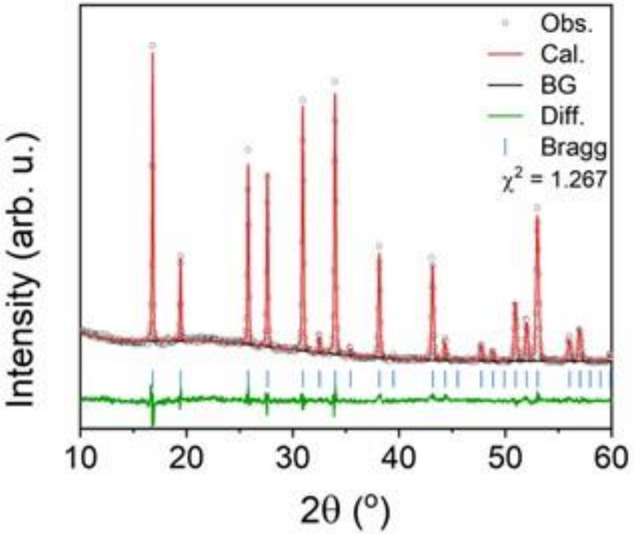


(b)



(c)

3D LLZT



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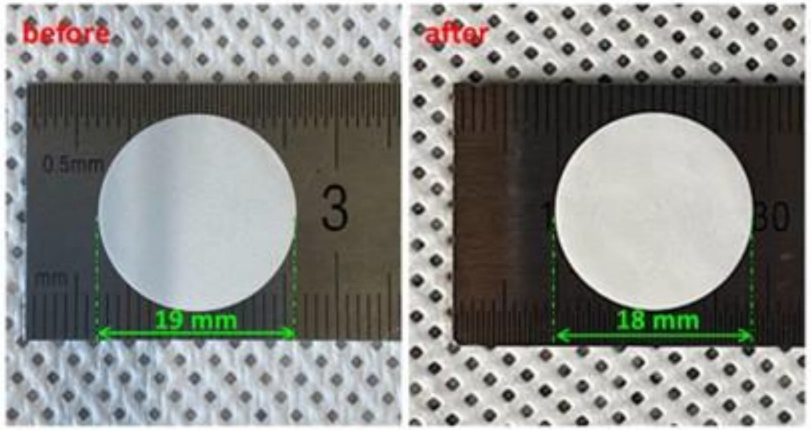
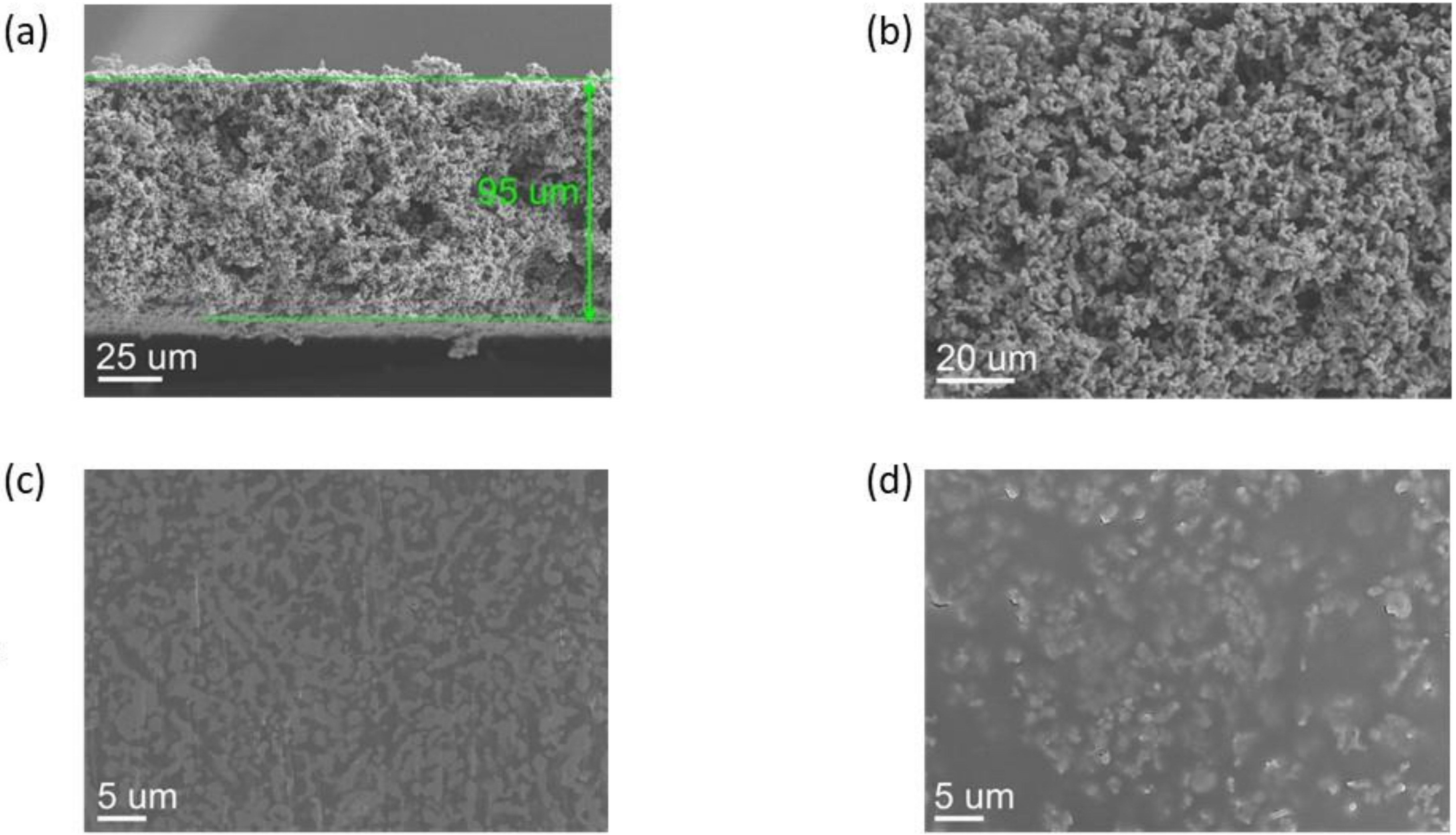


3D LLZT maintaine the cubic structure, which favor for good ionic conductivity at room temperature

SEM images of 3D-LLZT and CSE

3D LLZT

In-situ polymerization (3D-LLZT-CSE)

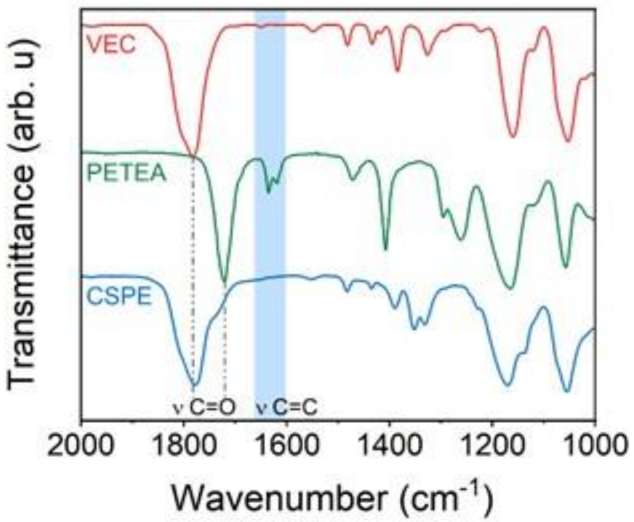


Polymer evenly occupy the pores of the 3D-LLZT framework

Generate continuous Li^+ transport channels

Polymerization mechanism

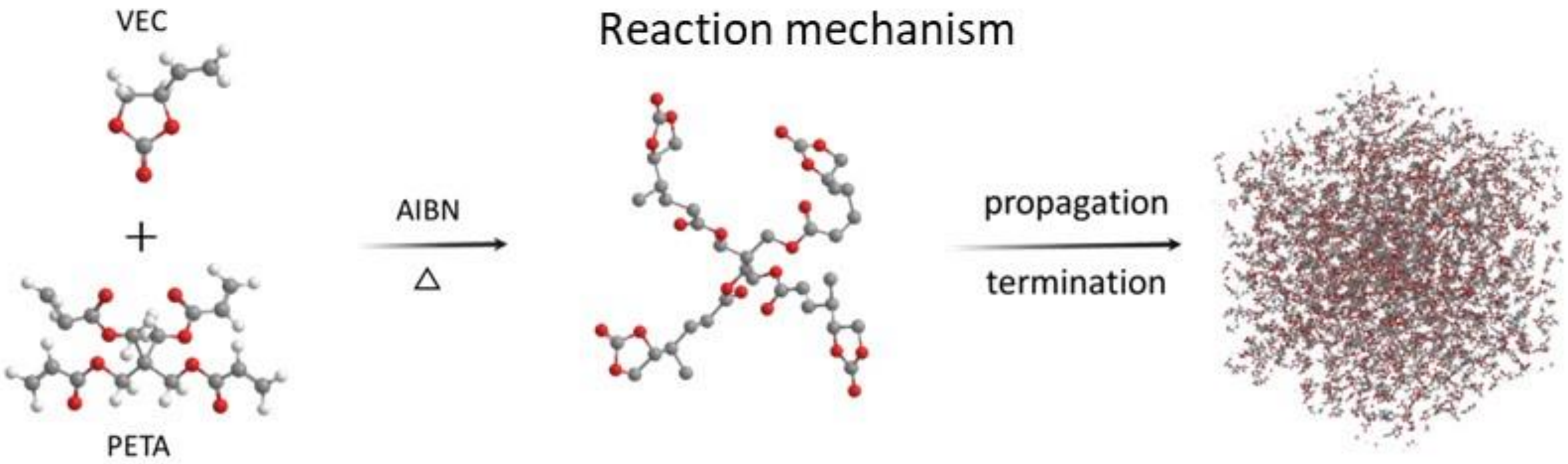
(a)



(b)

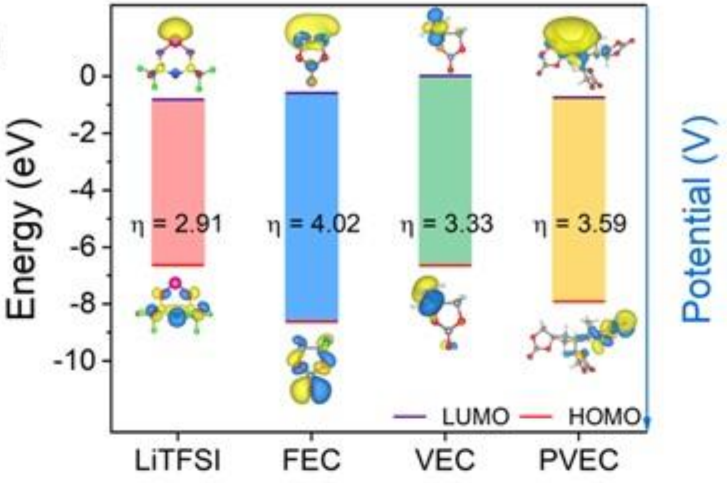
C=C peak located at 1650 cm^{-1} disappeared after polymerization, implying the complete polymerization

(c)



Calculation

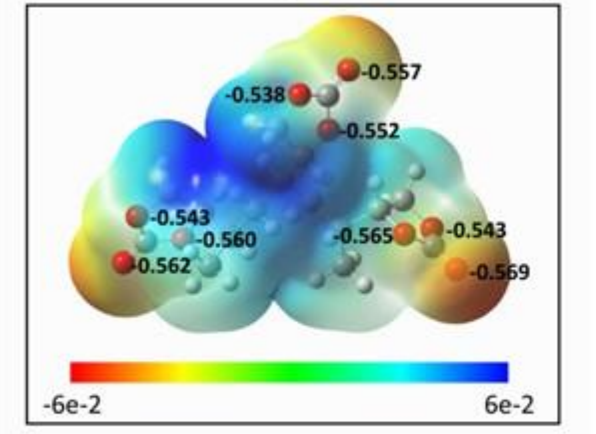
(a)



LiTFSI tends to decompose to form interphases

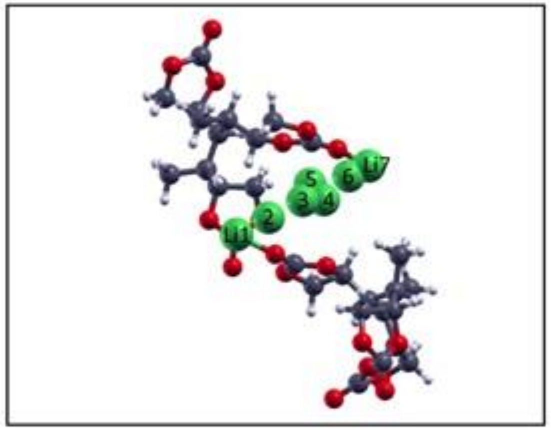
Electrostatic potential maps

(b)



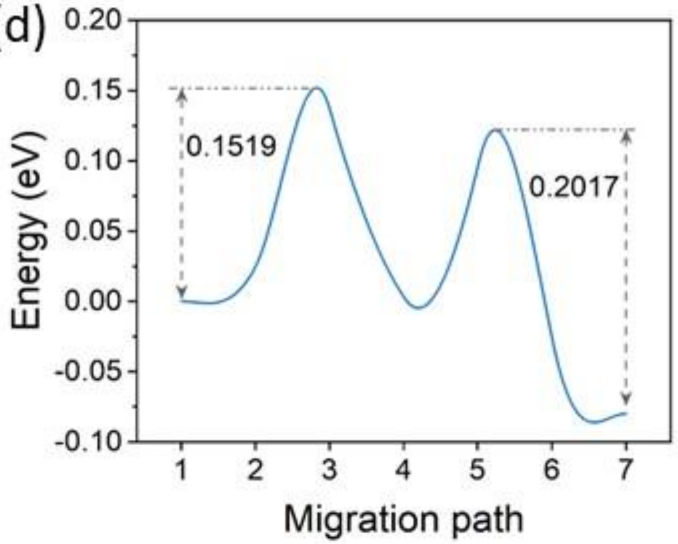
C=O group with electron-withdrawing effect, favor the interaction with Li^+

(c)



Activation energy

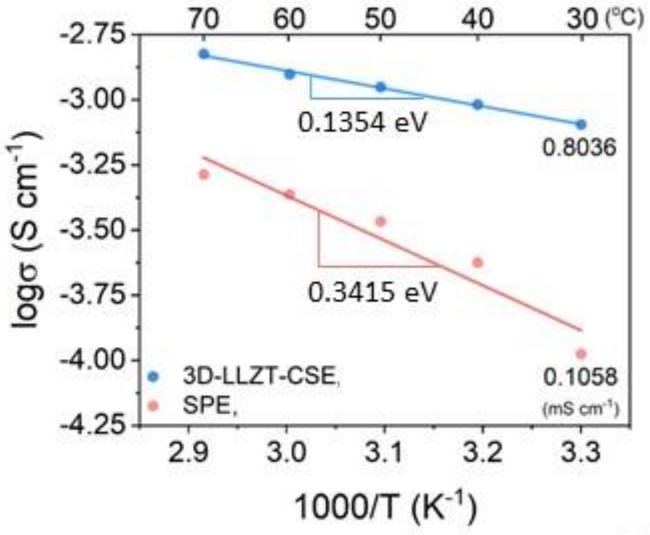
(d)



Electrochemical Analysis

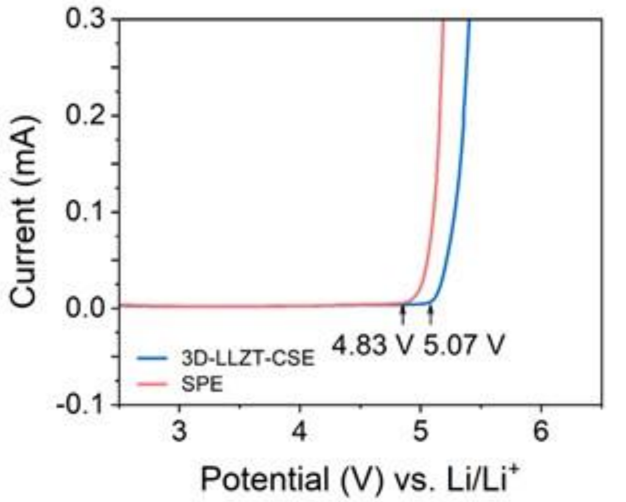
Ionic conductivity + activation energy

(a)



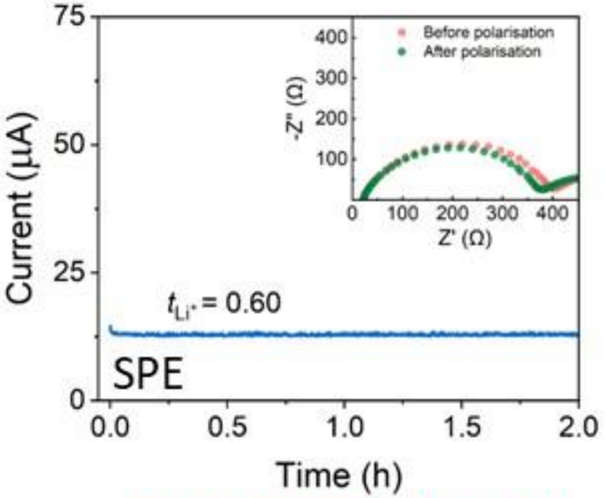
Linear sweep voltammetry

(b)

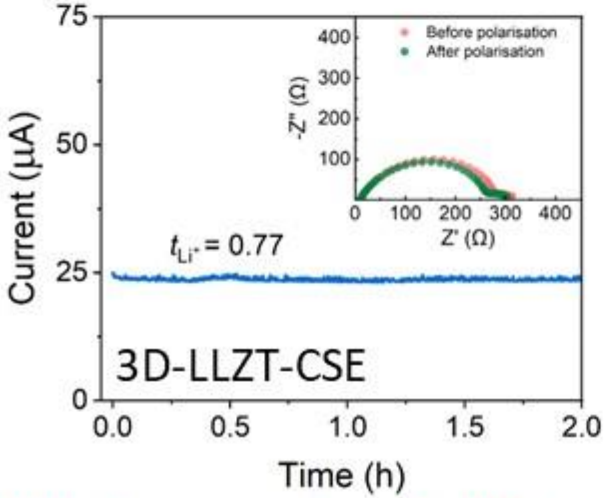


Lithium transference number

(c)



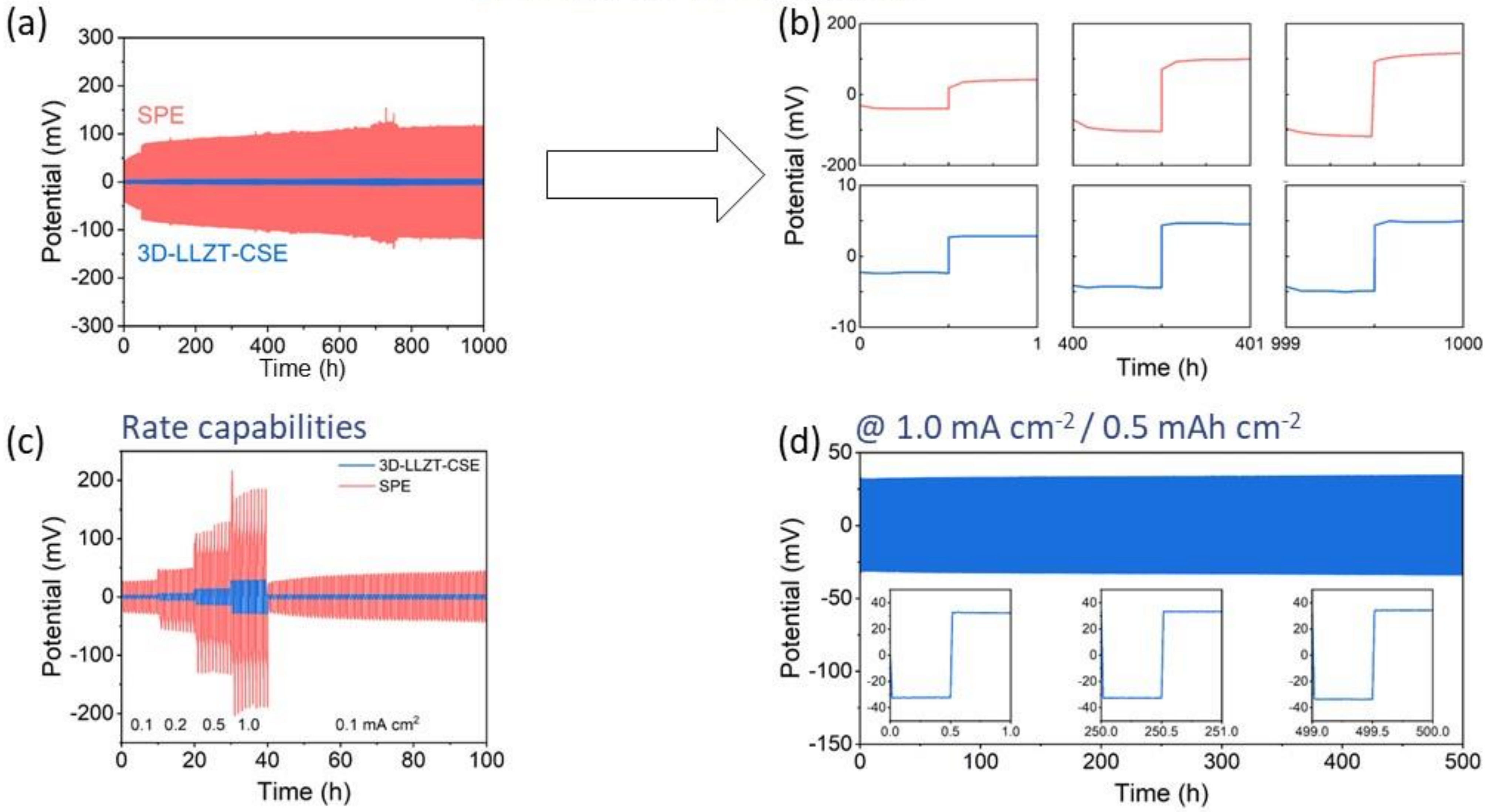
(d)



3D-LLZT-CSE exhibited superior properties and stability in comparison to SPE

Li plating/stripping

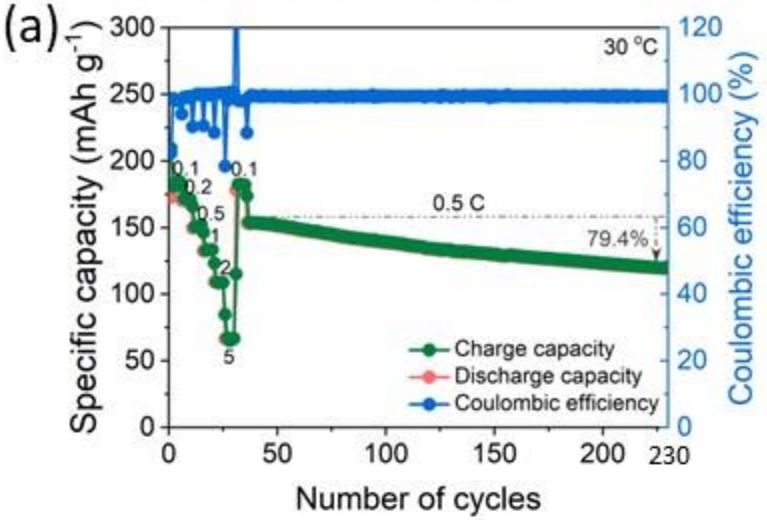
@ 0.1 mA cm^{-2} / 0.05 mAh cm^{-2}

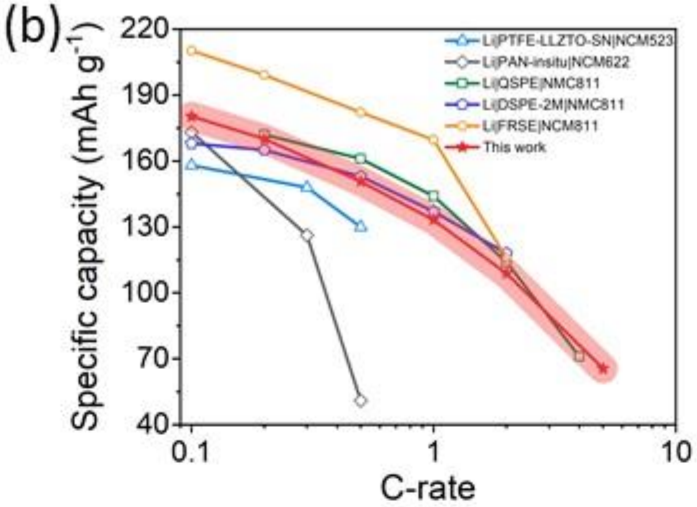


3D-LLZT-CSE exhibited square wave-like potential profiles with small overpotential values

Solid-State Lithium Batteries

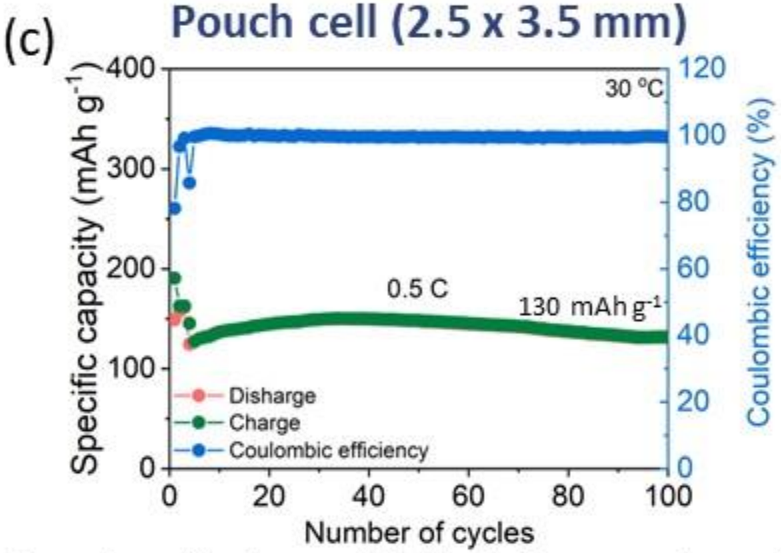
Coin-cell CR2032

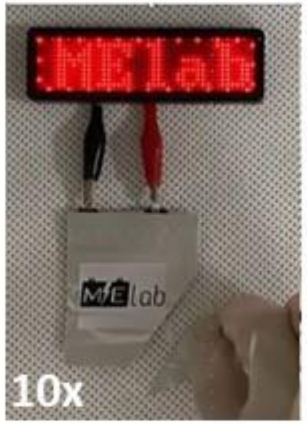




Li|3D-LLZT-CSE|NCM811 cell delivered specific discharge capacities of 180.3, 170.0, 150.7, 133.2, 108.8, and 65.5 mAh g^{-1} at the C-rates of 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively

Pouch cell (2.5 x 3.5 mm)



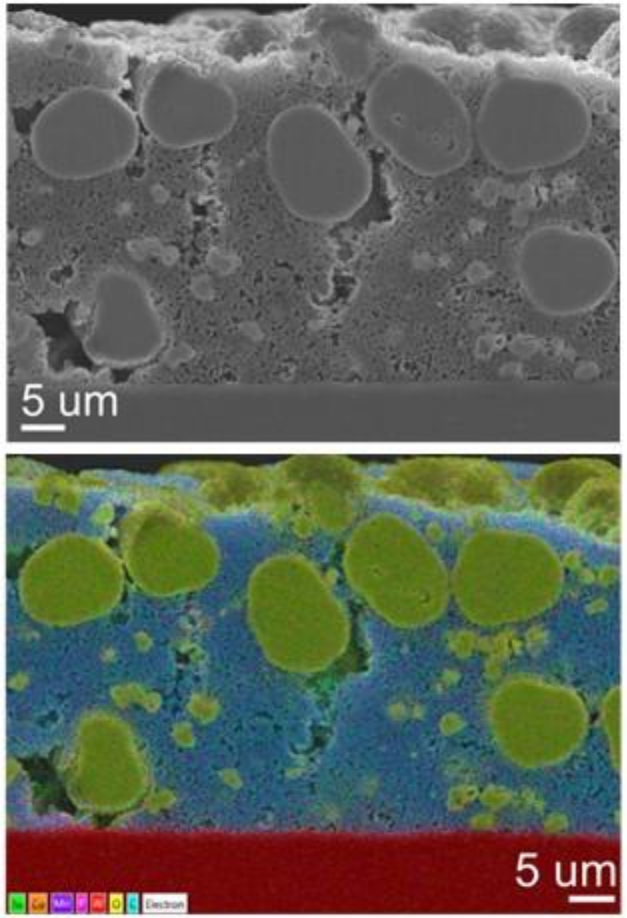


Pouch cell also exhibited the good cyclability

Can power a toy car and LEDs under folded or cut condition

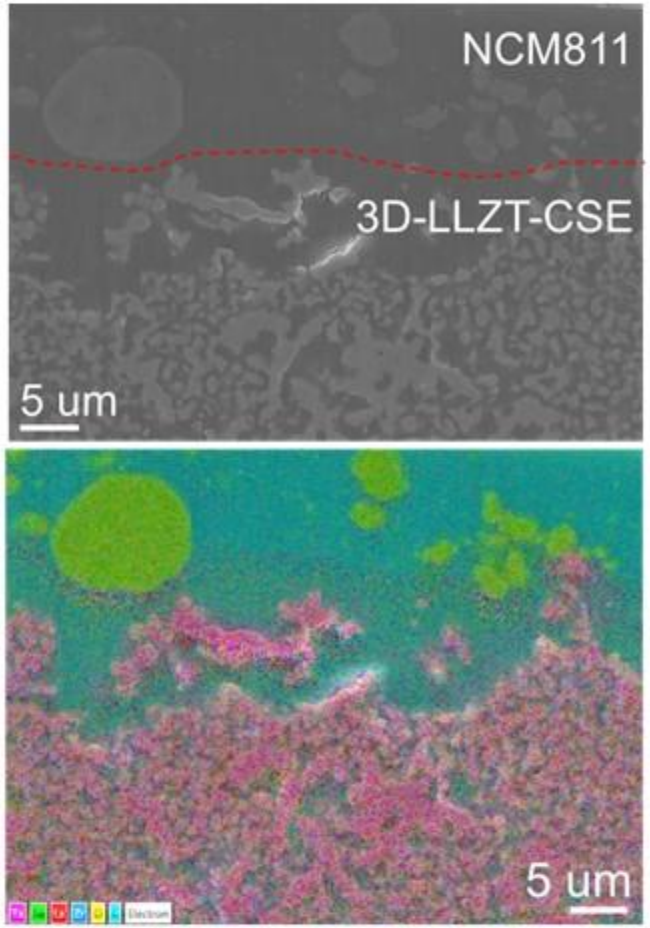
Cathode-Electrolyte contact

Bare NCM cathode



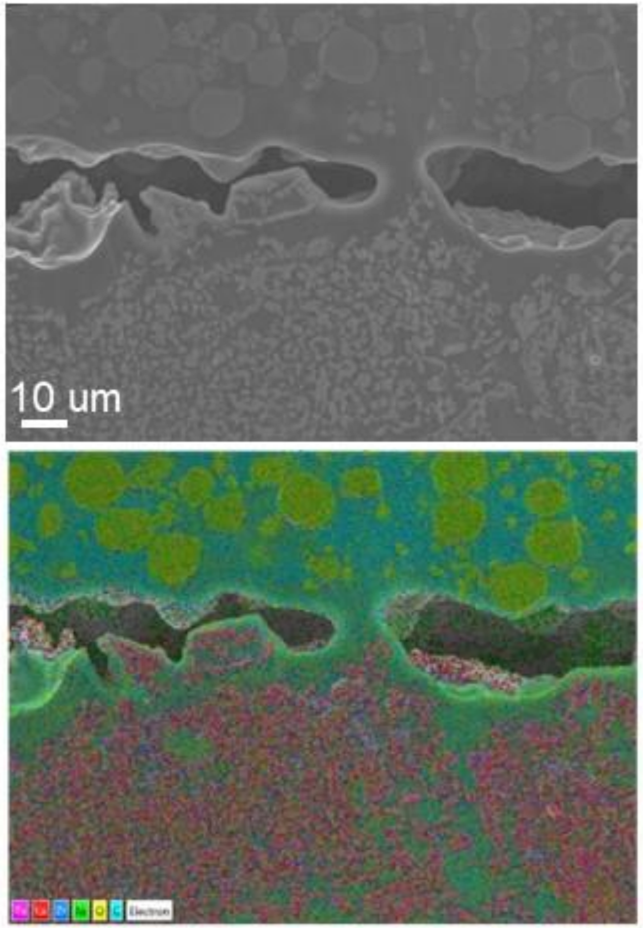
porous structure

in-situ CSE + NCM cathode



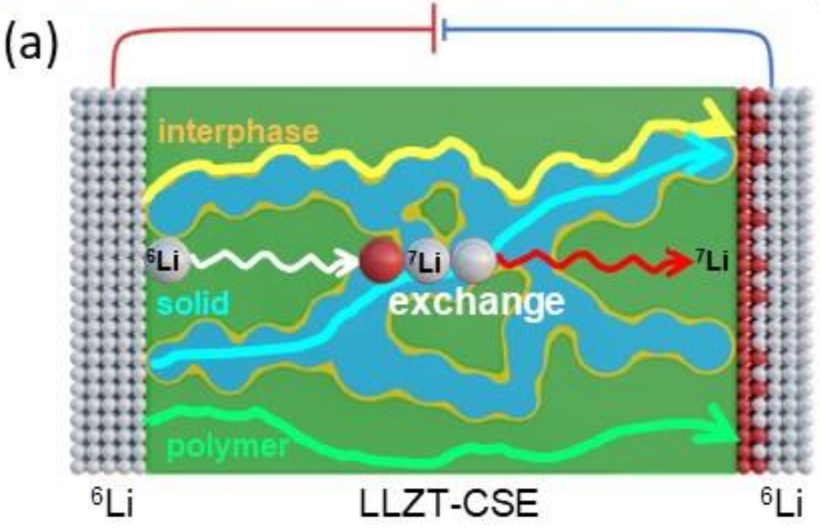
Pores in both NCM811 and 3D-LLZT were filled and integrated by the in-situ polymer

ex-situ CSE + NCM cathode

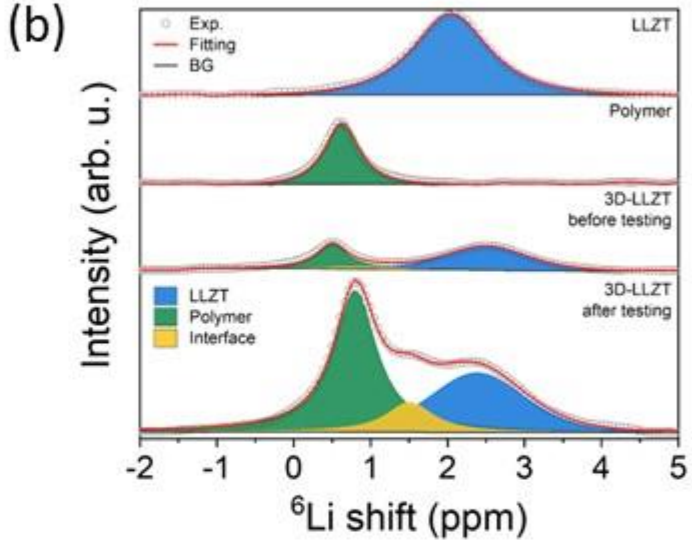


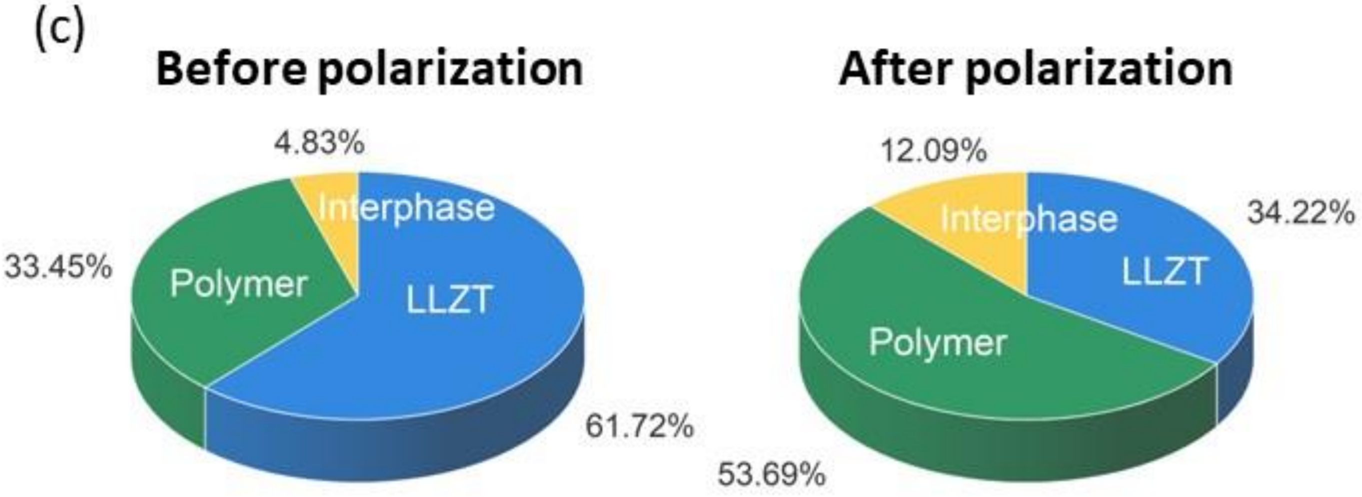
Gaps were exsited which induce the large interphase resistance

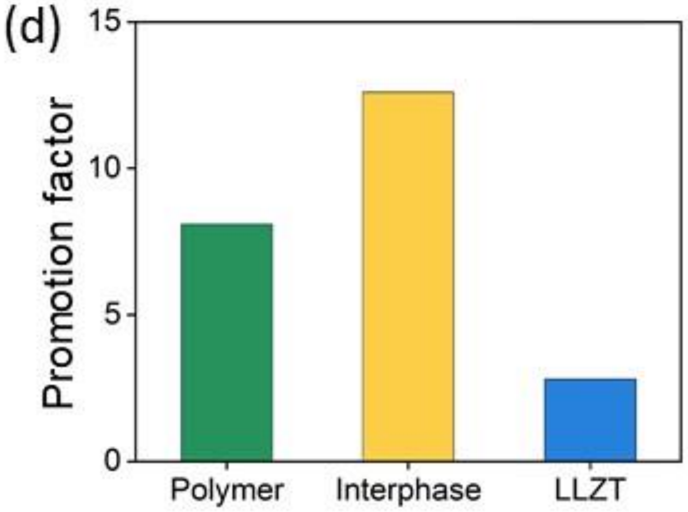
Contribution of LLZT, Polymer, and Interphase



^{6}Li tracer-exchange mechanism + solid-state NMR







Aligned polymer network and intephase in the 3D-LLZT-CSE serves as the most favorable Li^+ migration

Conclusion 1

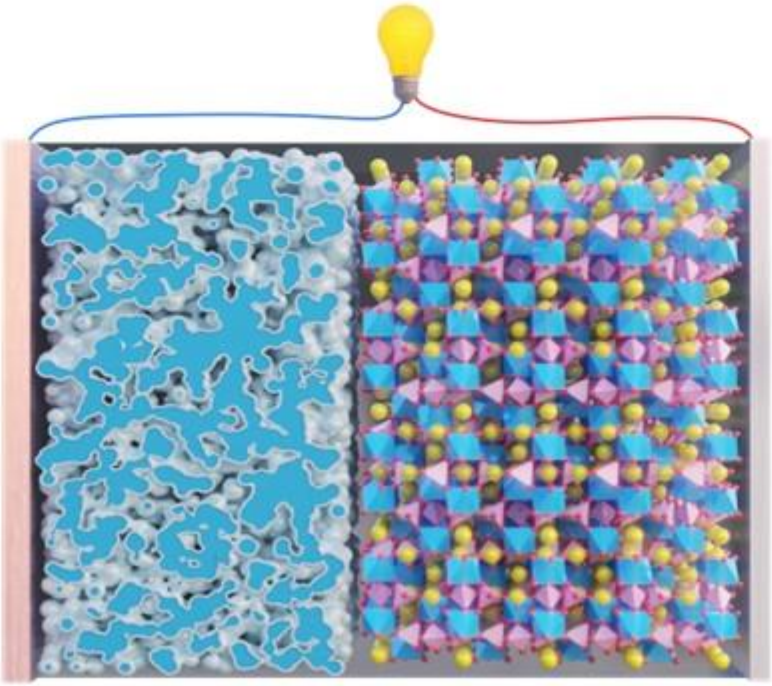
- In-situ CSEs were rationally designed and fabricated for solid-state lithium batteries with excellent electrochemical performance

- 3D-LLZT-CSE exhibited a high ionic conductivity of 0.8036 mS cm^{-1}, high t_{Li^+} of 0.77, and a wide electrochemical window up to 5.07 V *vs.* Li/Li^+ at 30 °C. The Li|3D-LLZT-CSE|NCM811 cell could be operated at up to 5 C at 30 °C with a reversible specific capacity of 65.5 mAh g^{-1} and still delivered a specific discharge capacity of 95.0 mAh g^{-1}, after 230 cycles at 0.5 C, which corresponds to a capacity retention of 79.4%

- The contribution of LLZT, polymer, and their interphase was identified by SS-NMR

Part 2

In-situ Polymerization on a 3D Ceramic Framework of Composite Solid Electrolytes for Room-Temperature Solid-State Sodium Batteries



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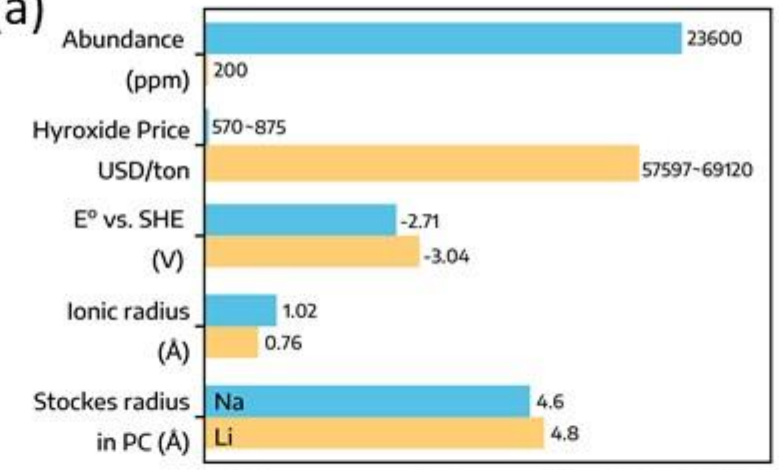
Why Sodium-ion batteries?

(a)



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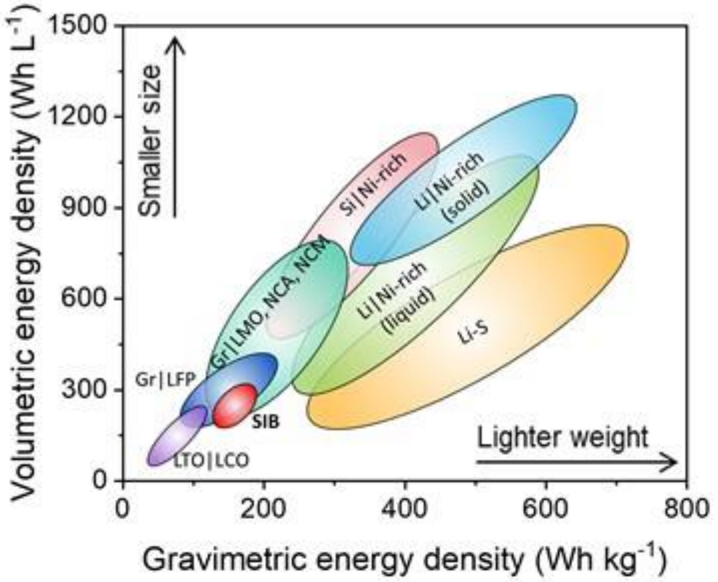
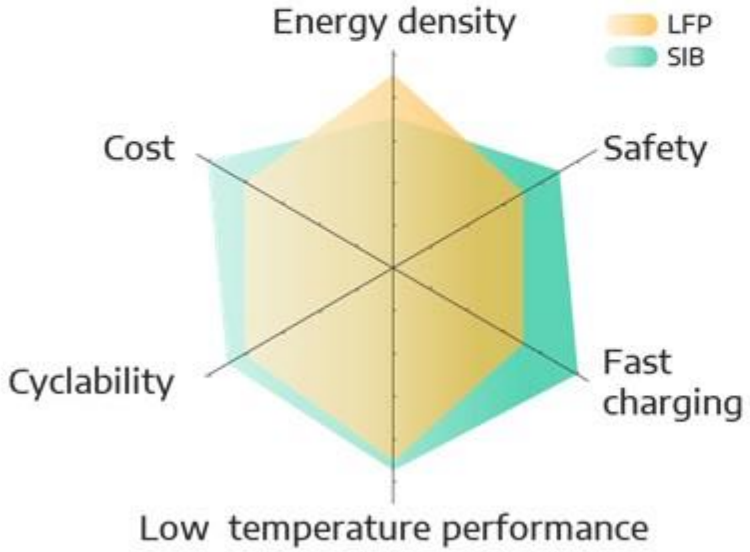
(b)



(c)



- Cheaper and more abundant than Li
- Similar chemistry to Li
- Compatible with current technologies
- Low energy density but comparable with LFP

Sodium-ion batteries: Game changer for low-cost application - But need to improve Energy Density

Complement rather than compete with lithium-ion batteries

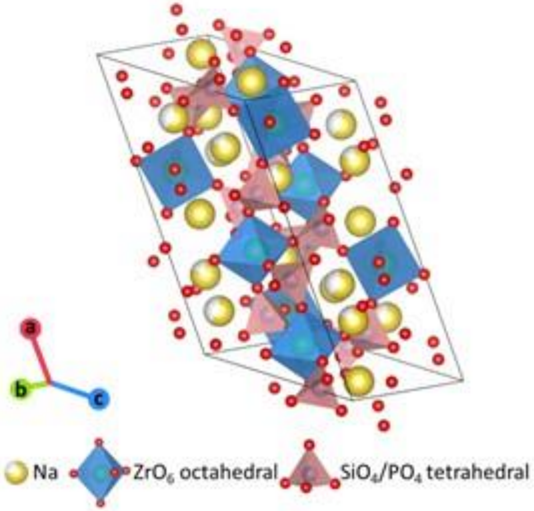
Objective

➢ Apply our strategy for Solid-State Sodium Batteries

Ceramic

$Na_{3.3}Zr_{1.7}La_{0.3}(SiO_4)_2(PO_4)$

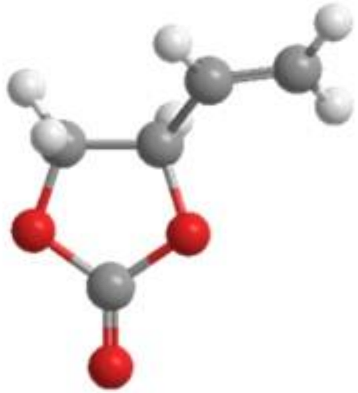
✓ Stability against electrodes
✓ High conductivity



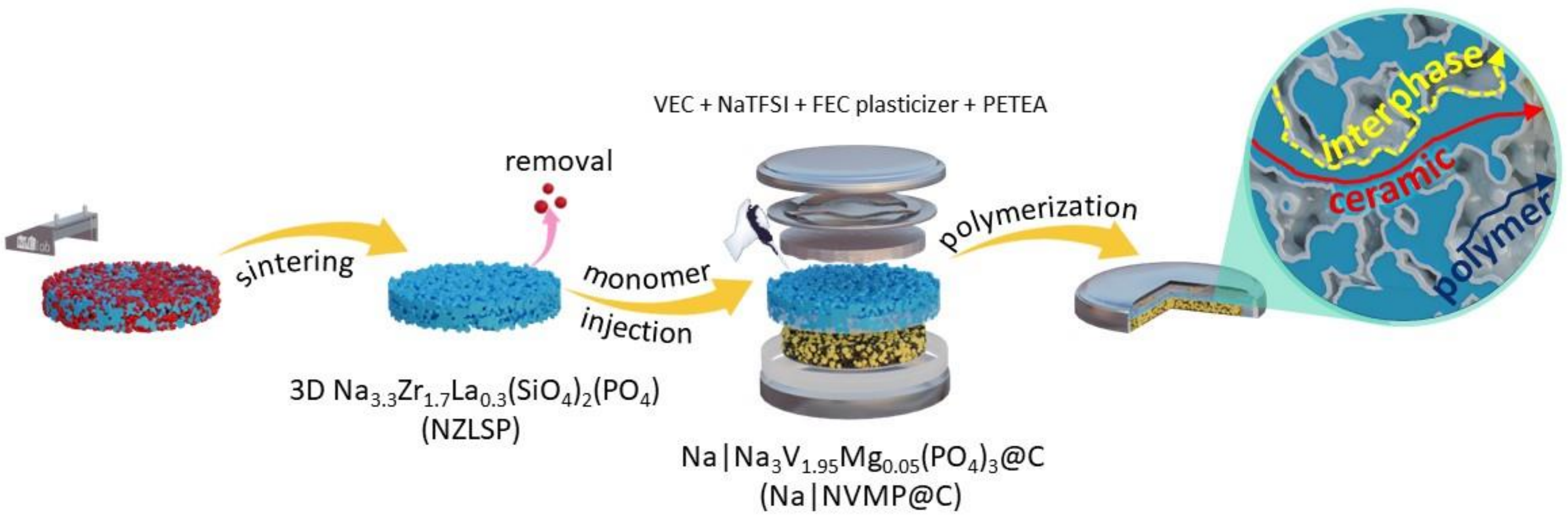
Polymer

Vinylene Ethylene Carbonate

✓ Can be polymerized
✓ Facilitate ions transportation

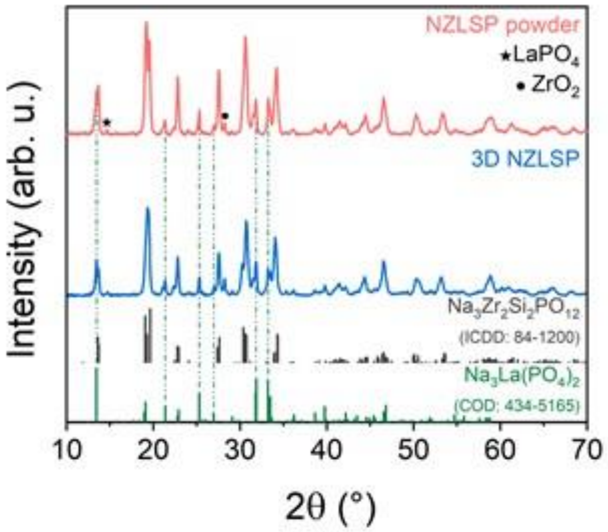


Preparation of CSE for Solid-State Sodium Batteries

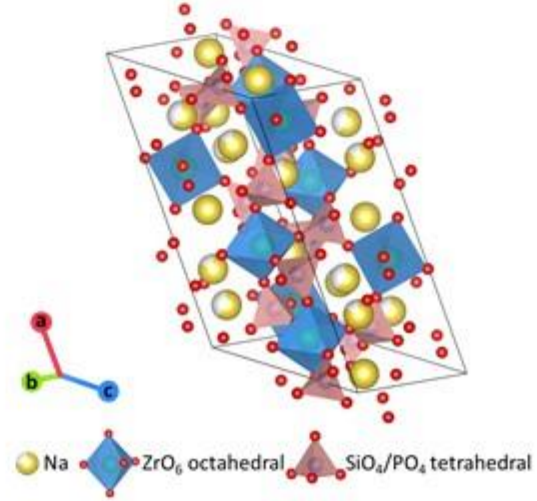


Material Characterization

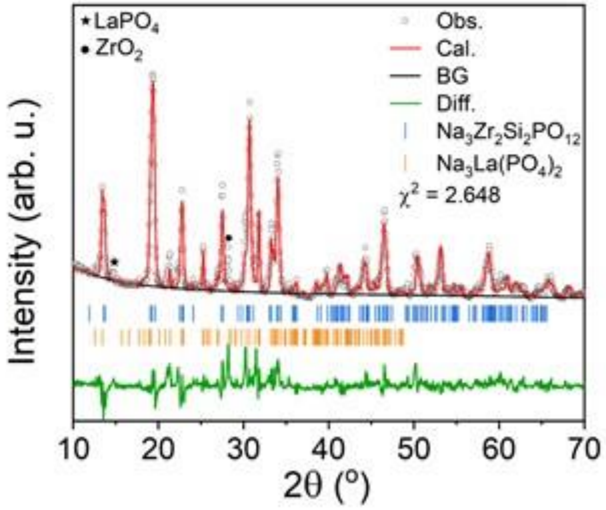
XRD (a)



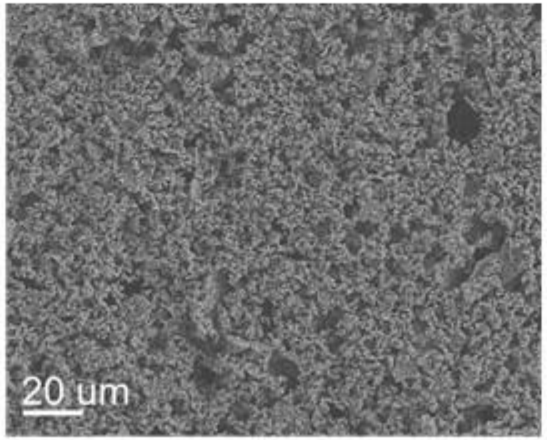
(b)



(c)

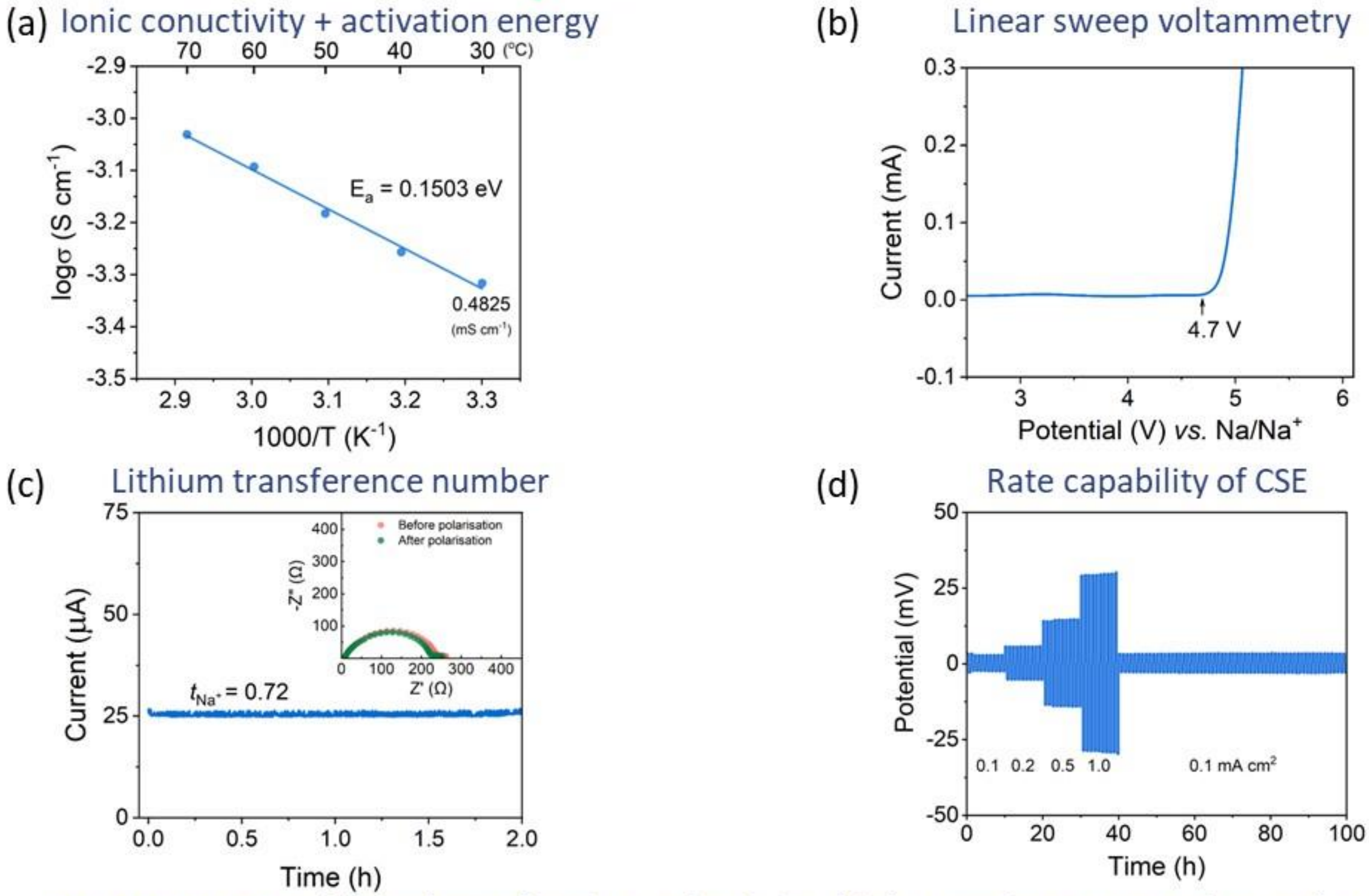


SEM (d)



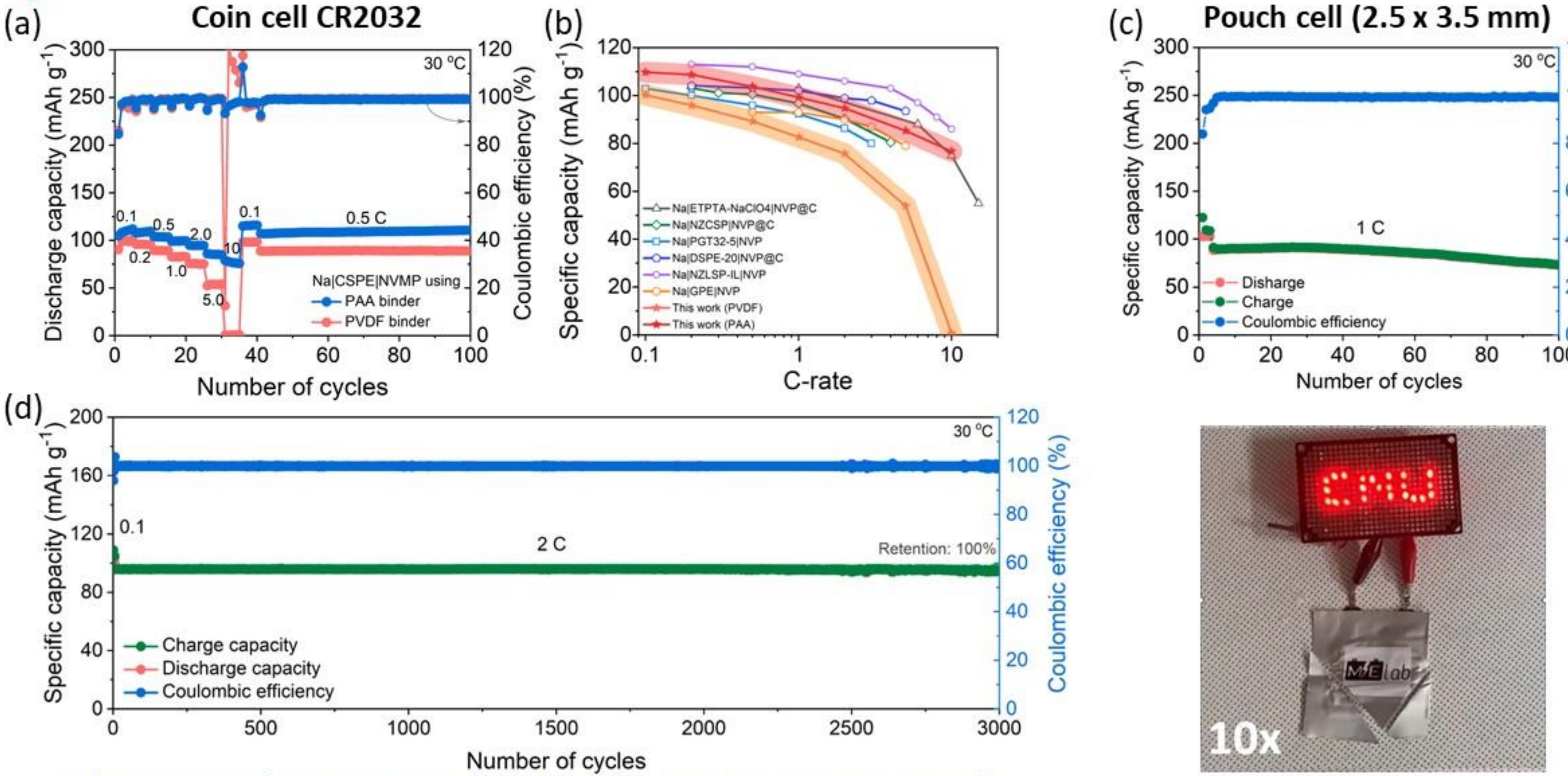
3D-NZLSP still maintains its structure after calcination and exhibits high porous morphology

Electrochemical Analysis



3D-NZLSP-CSE exhibited good ionic conductivity, high transference number and stability

Solid-State Sodium Batteries



Na|3D-NZLSP-CSE|NVMP@C cell delivered a reversible capacity of 95.0 mAh g^{-1} after 3000 cycles at a rate of 2 C with zero-fading

Conclusion 2

- In-situ CSEs were successfully applied to solid-state sodium batteries with excellent electrochemical performance

- 3D-NZLSP-CSE exhibited a high ionic conductivity of 0.4825 mS cm^{-1}, high t_{Na^+} of 0.72, and stability up to 4.7 V *vs.* Na/Na$^+$ at 30 °C.

- The Na|3D-NSLSP-CSE|NVMP@C cell delivered outstanding rate capability

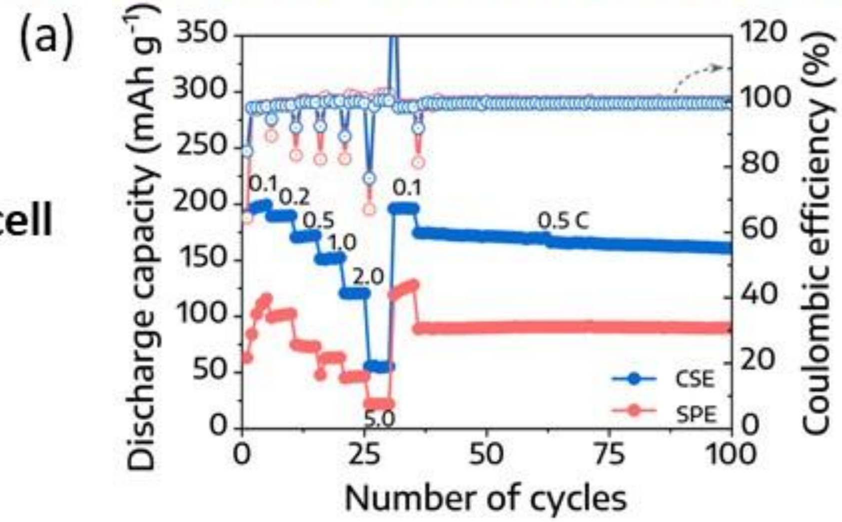
- In the long-term cycling test, the Na|3D-NZLSP-CSE|NVMP@C cell delivered a reversible capacity of 95.0 mAh g^{-1} after 3000 cycles at a rate of 2 C with zero-fading, as well as an average Coulombic efficiency of approximately 100.0%

Part 3

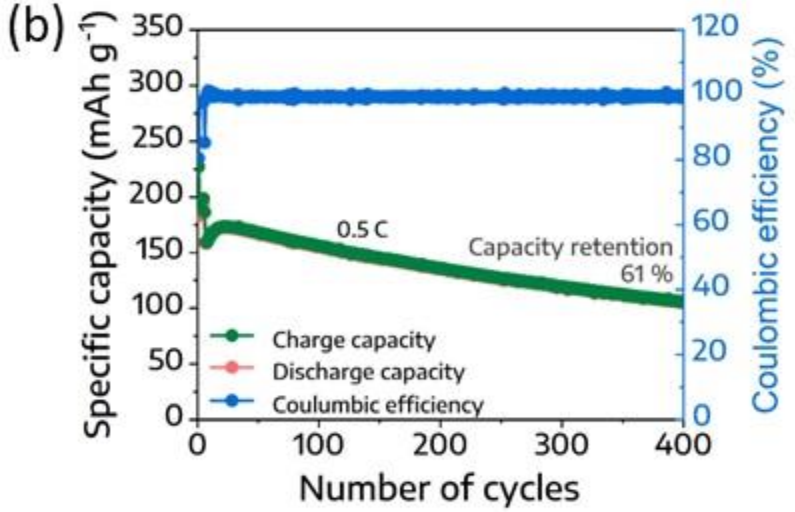
Unpublished

Solid-State Lithium Batteries

Coin cell



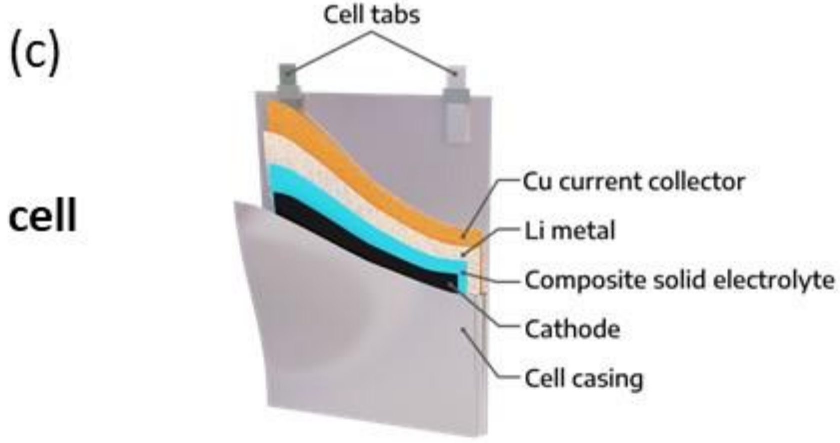
Li|CSE|NCM811 exhibited excellent rate capability

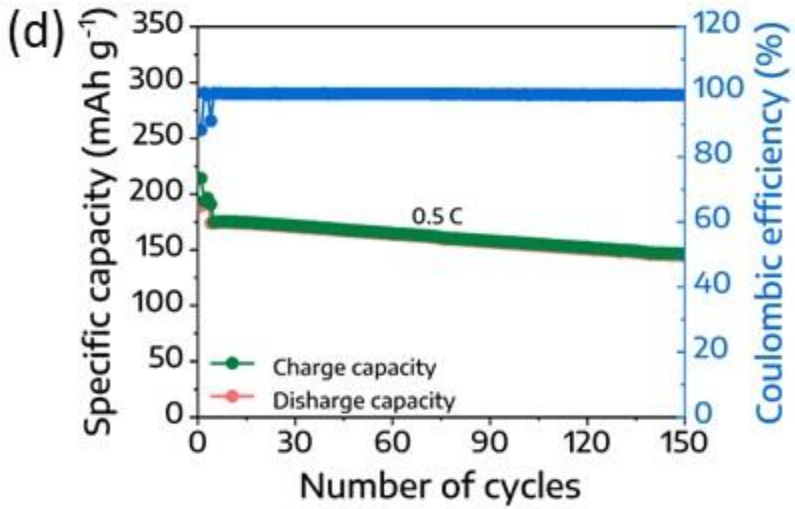


Discharge-specific capacity of 105.1 mAh g^{-1} after 400 cycles

Capacity retention of 61%, average Coulombic efficiency > 99%

Pouch cell





Single-layer pouch-type Li|CSE|NCM811 cell was also maintained a discharge capacity of 144.8 mAh g^{-1}

Capacity retention of 83.3% over 150 cycles at 0.5 C

Conclusion 3

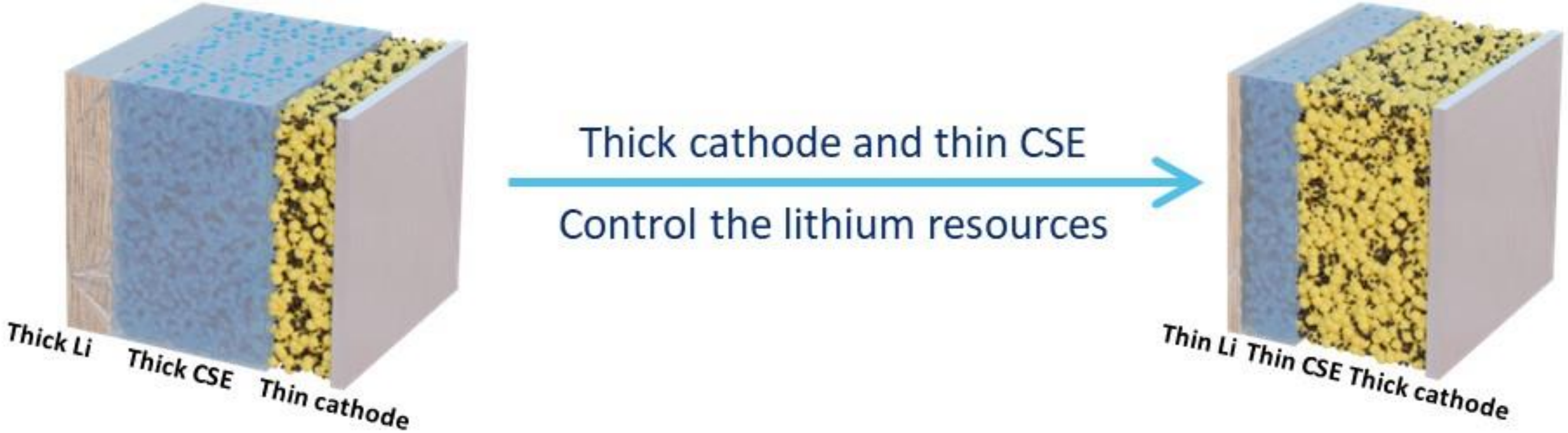
- The obtained CSE exhibited high ionic conductivity of 1.117 mS cm^{-1} at 30°C, high t_{Li^+} of 0.627, and a wide electrochemical window (5.06 V *vs.* Li/Li^+).

- Li|CSE|NCM811 full cell displayed exceptional rate capability, enabling operation at up to 5 C, as well as long-term cycling performance, retaining a discharge-specific capacity of 105.1 mAh g^{-1} after 400 cycles at 0.5 C and 30 °C

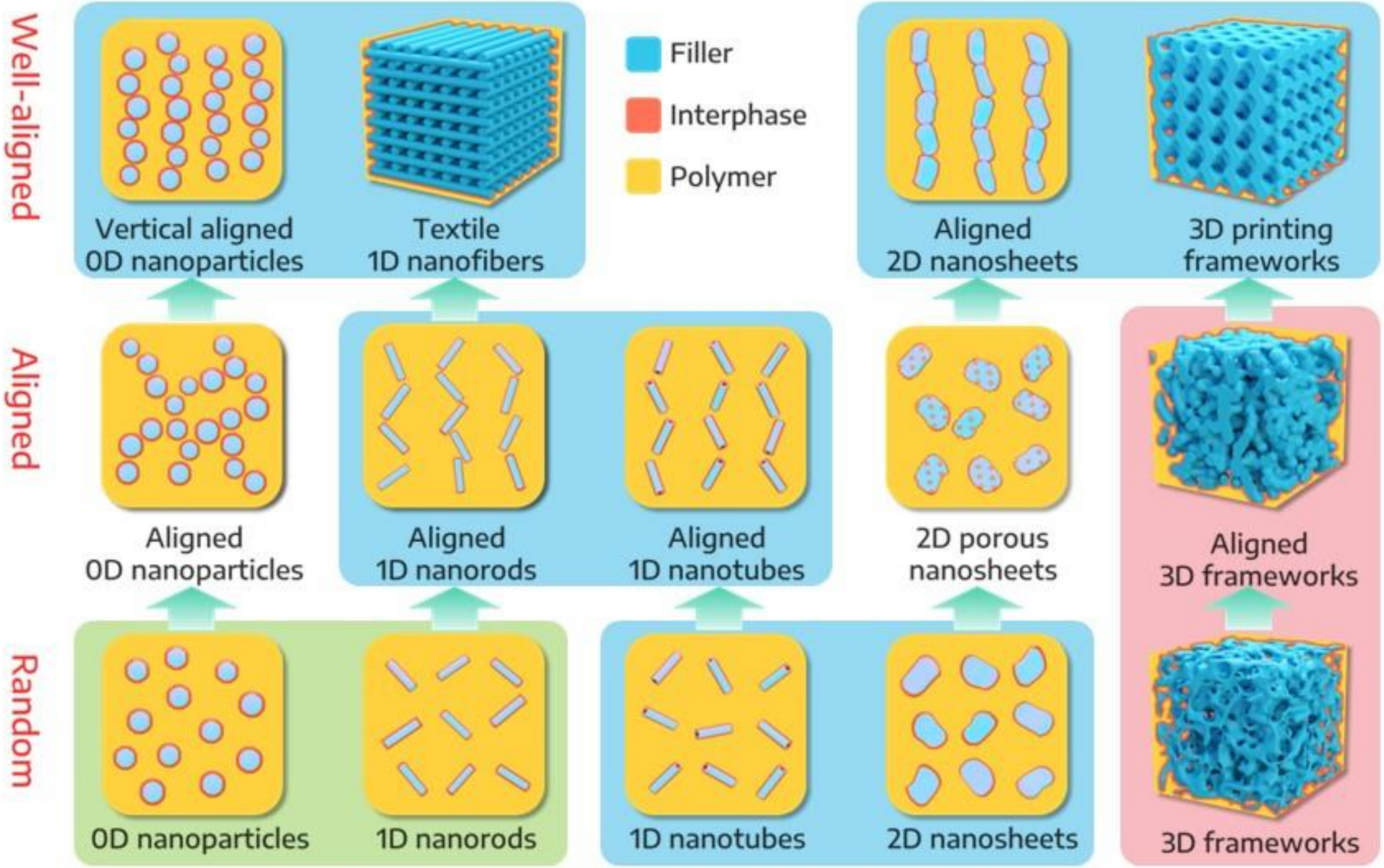
- Unpublished

General Conclusion

- ➢ The casting method offers a straightforward, cost-effective, and scalable approach for constructing a 3D ceramic architecture
- ➢ The in-situ polymerization in 3D framework approach can also be extended to other ceramic or polymer electrolytes and battery systems
- × The inherent fragility of 3D frameworks poses a challenge in maintaining their structural stability during the battery fabrication process
- × The current thickness of composite solid electrolytes remains in the range of 100 μm

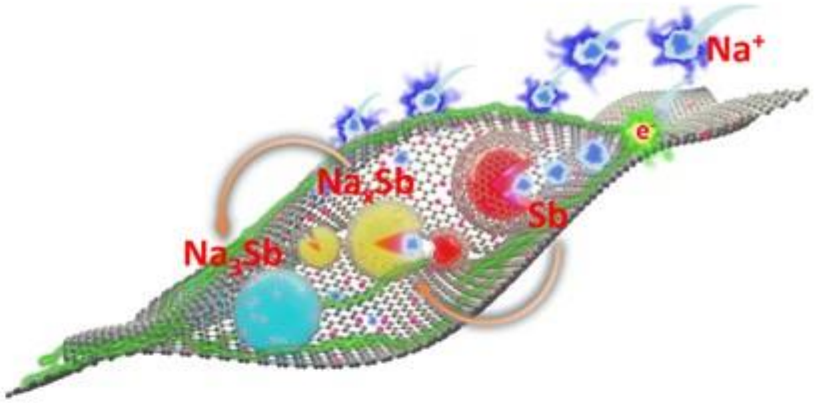


Perspective



The type, size, surface properties, and dimension of the filler will have a significant impact on the ionic conductivity of composite solid electrolytes

Pubication



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Energy Mater., 2023

And 9 articles as a co-author

Acknowledgment

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