PhD Defense

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

16h30 - 17h30, Room 204 - Building 6

June 12, 2023

Ph.D. student: An-Giang Nguyen

Supervisor: Professor Chan-Jin Park

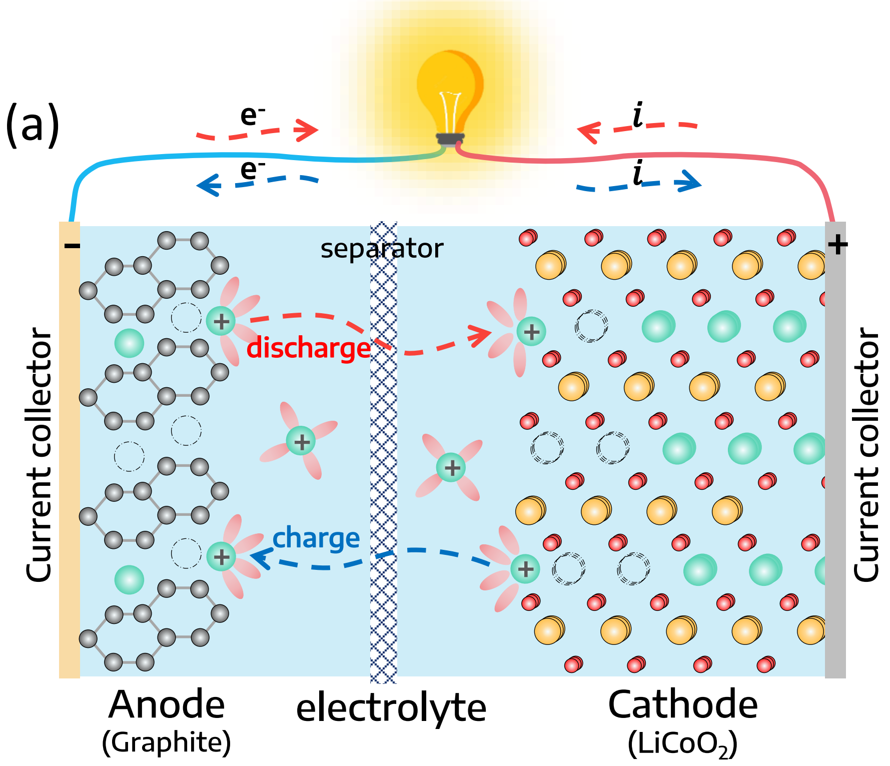
MElab

Content

Energy density of LIBs

Working principle of LIBs

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

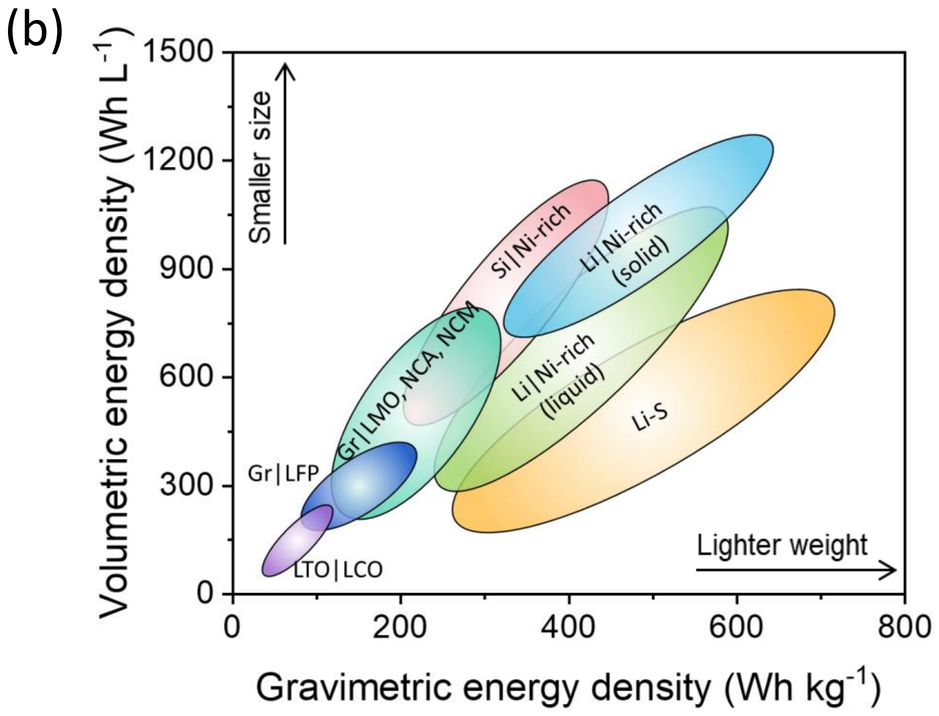


Portable to stationary (mW to MW)

Instant

How to increase Energy Density of LIBs?

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

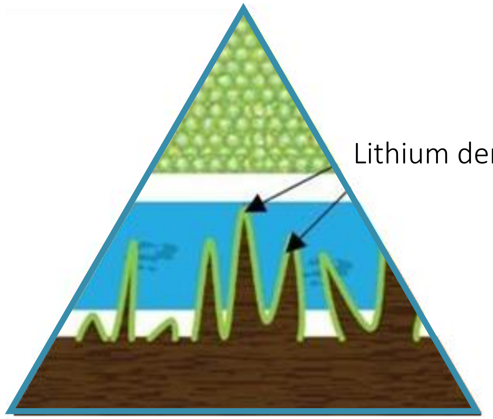


We need higher energy density batteries!

Safety issue

Graphite|LFP (HighTechLab)

Fuel
- Flammable electrolyte



Lithium dendrite

Oxygen
- Cathode decompose

Trigger Factor
- Internal: Overcharge
- External: Accident

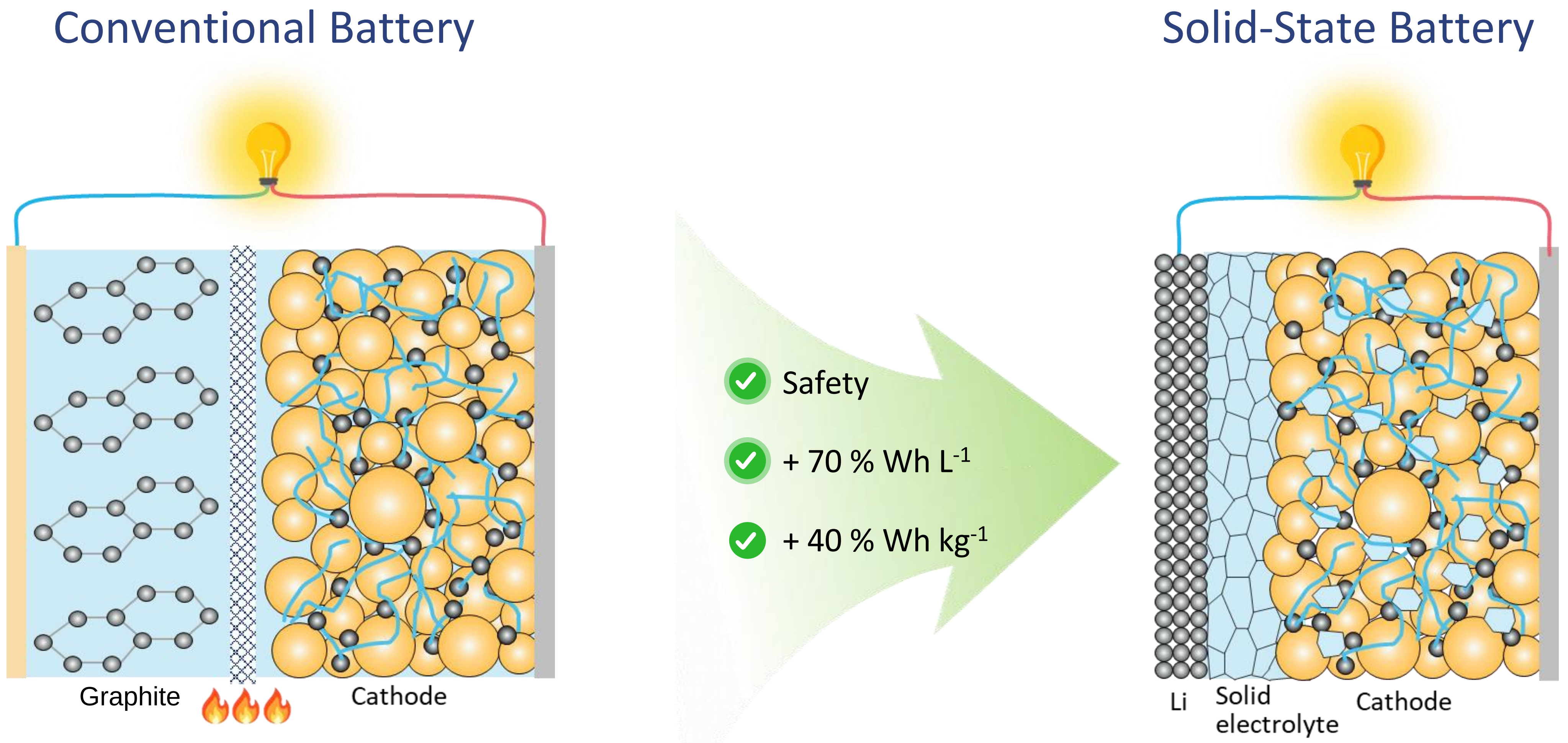
Initiation
- Battery temperature ~120 °C
- Exothermic decomposition of SEI
- Melt of the separator

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

Thermal runway

We also need safer batteries!

Why Solid-State Batteries?

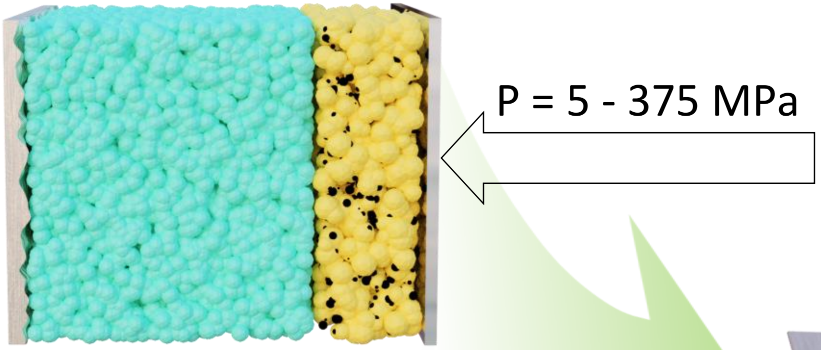


Solid-State Batteries (SSBs): safer and higher energy density

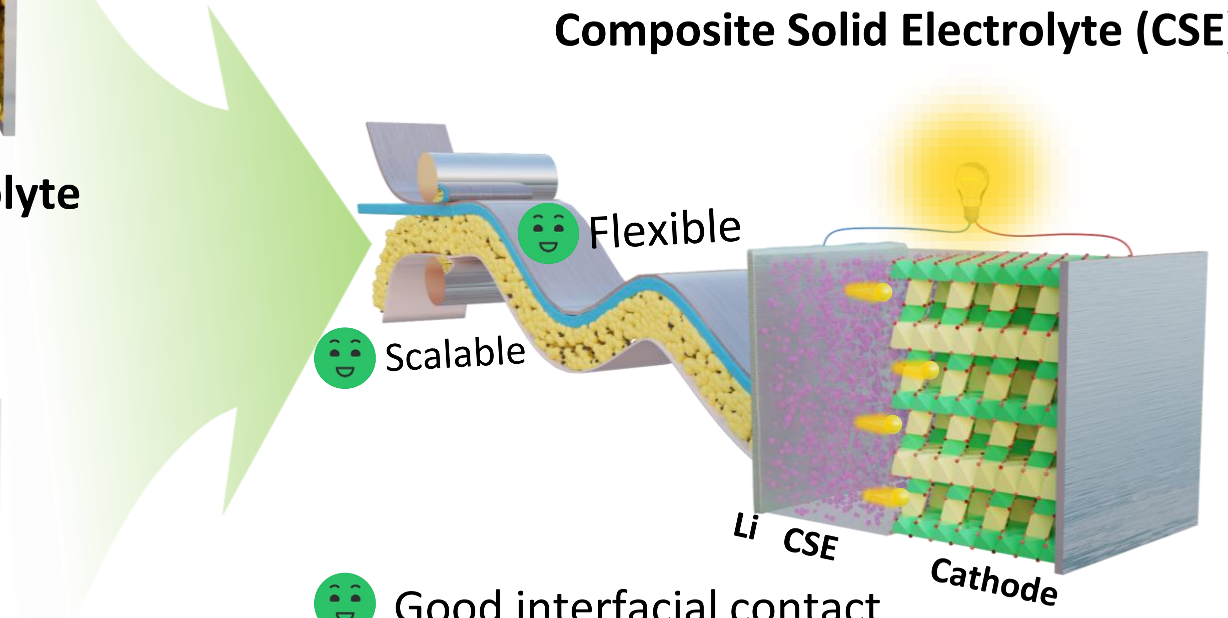
Why Composite Solid Electrolyte?

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



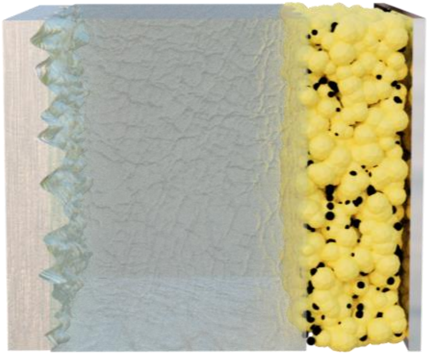
Inorganic Solid Electrolyte



Composite Solid Electrolyte (CSE)

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

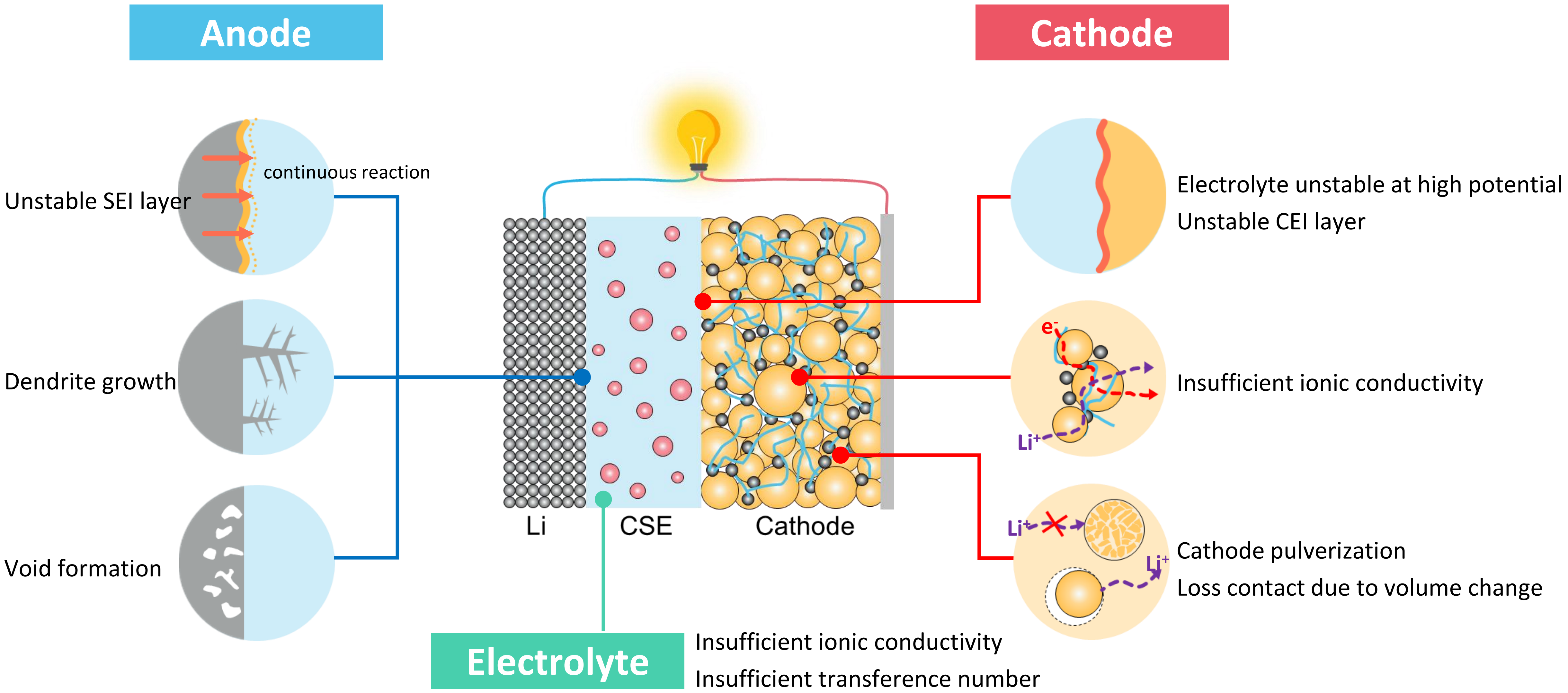
- Good interfacial contact
- Scalable
- Poor dedrite suppression
- Low ionic conductivity ($<10^{-5}$ S cm^{-1})



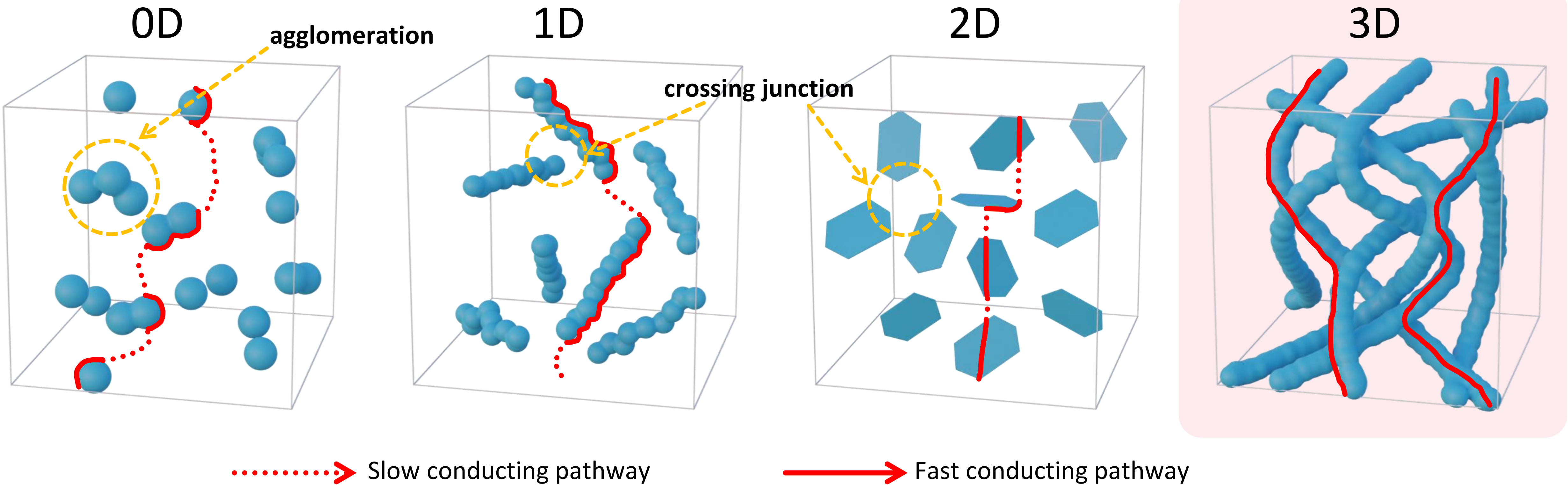
Solid Polymer Electrolyte

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

Issues in CSE-based SSBs



Effect of filler dimension in CSEs

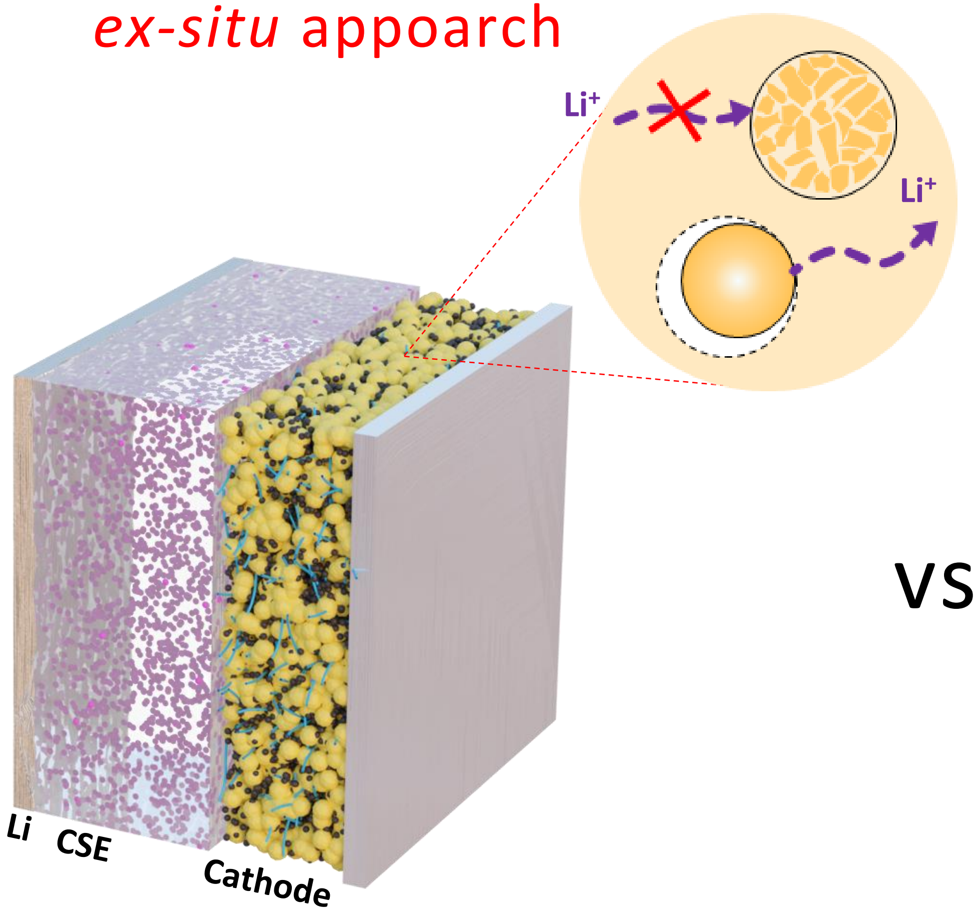


A.G. Nguyen *et. al.*, Journal of Membrane Science, 2023, 675, 121552

Control the filler dimension in composite solid electrolyte

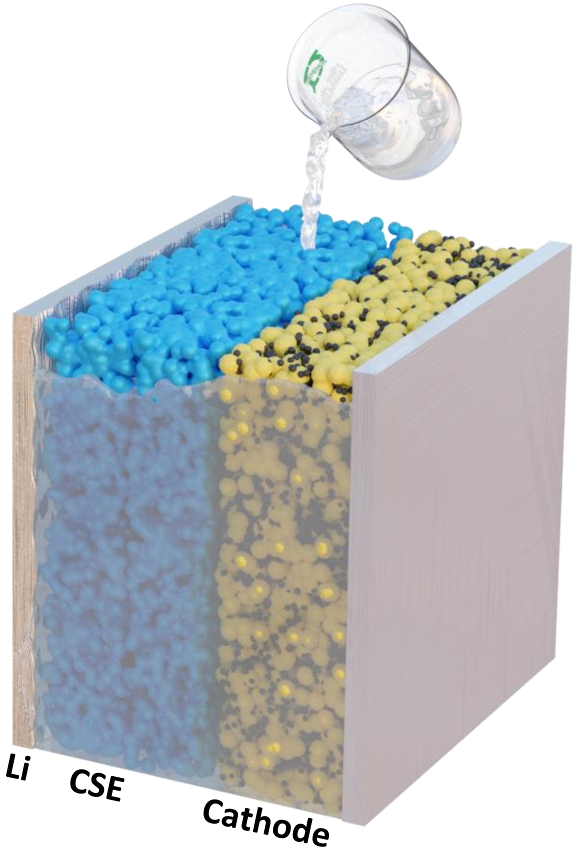
Improve the ionic conductivity on the cathode side

ex-situ appoarch



in-situ appoarch

vs.



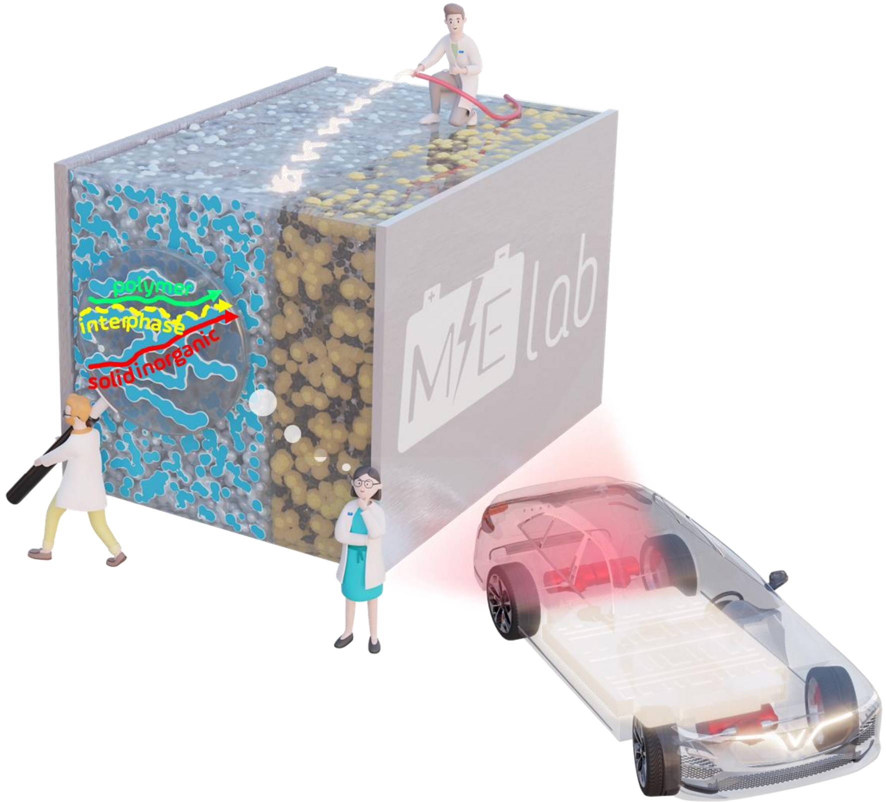
× Electrode-electrolyte interphase issue
× Insufficient ionic conduction on the cathode

✓ 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

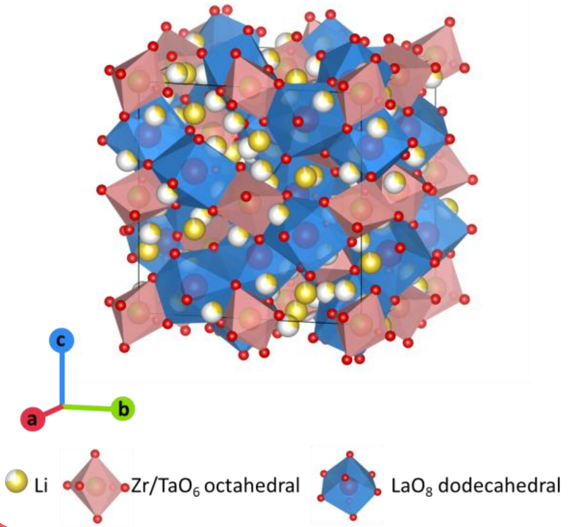
Objective

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

Ceramic

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

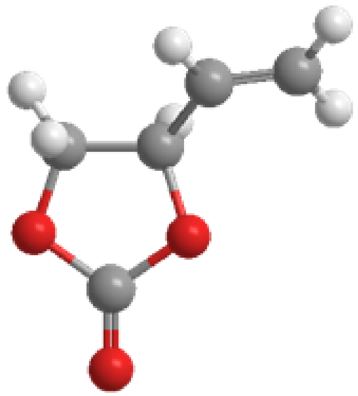
- ✓ Stability against electrodes
- ✓ High conductivity



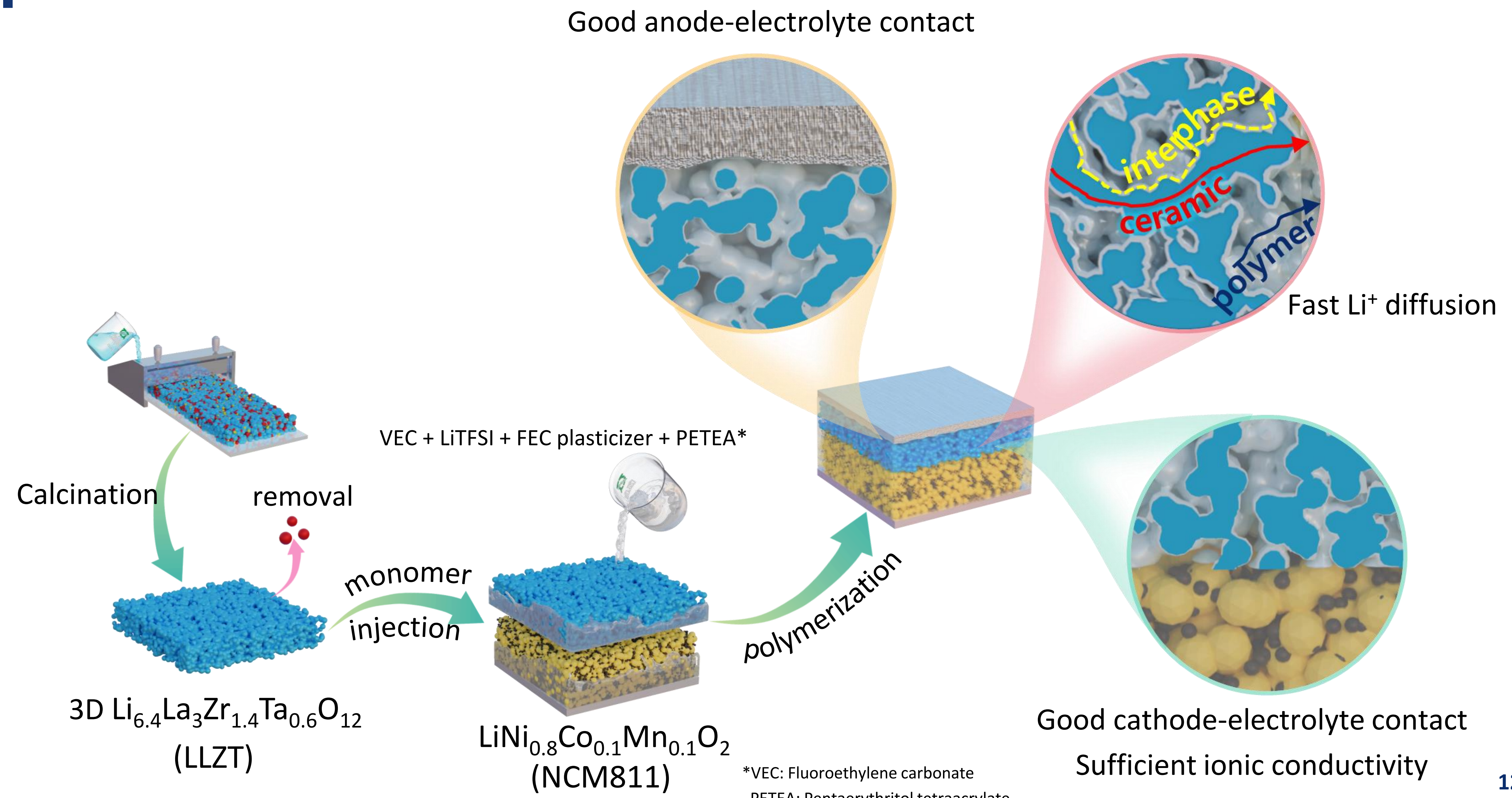
Polymer

Vinylene Ethylene Carbonate

- ✓ Can be polymerized
- ✓ Facilitate ions transportation



Preparation of CSE for Solid-State Lithium Batteries

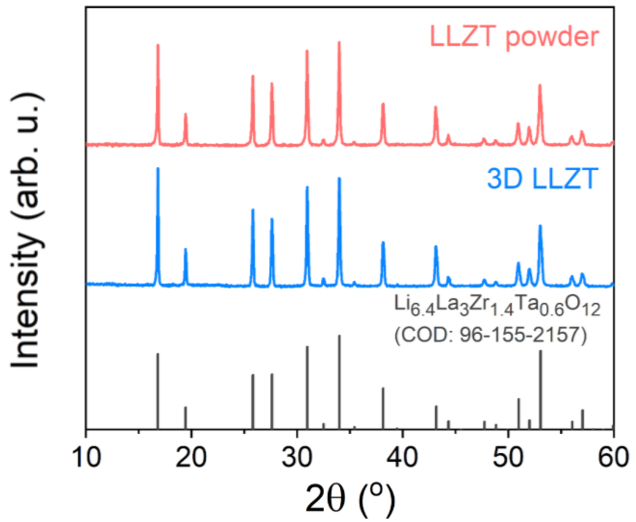


*VEC: Fluoroethylene carbonate
PETEA: Pentaerythritol tetraacrylate

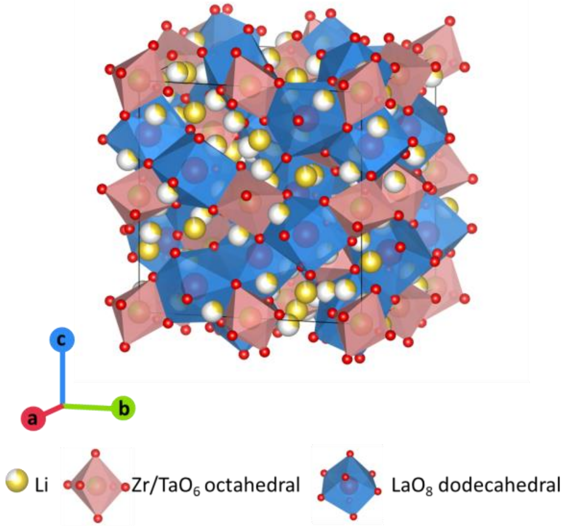
Crystal structure of 3D-LLZT

(a)

LLZT powder and 3D LLZT

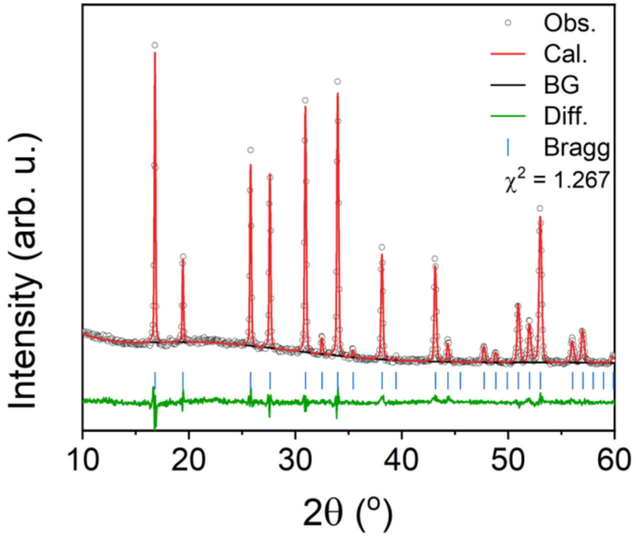


(b)

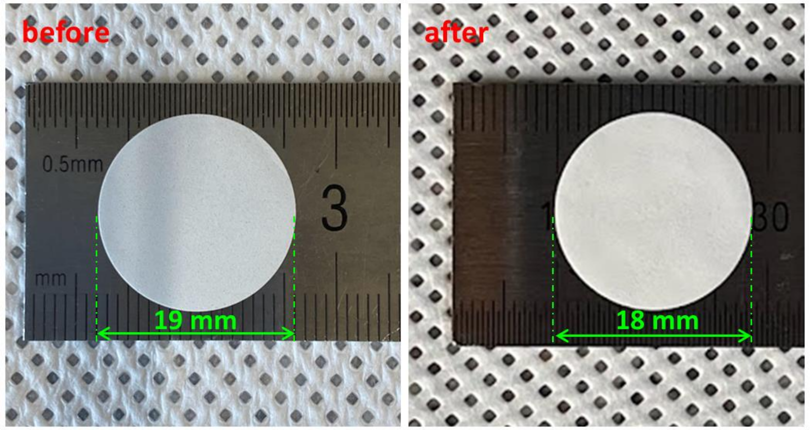


(c)

3D LLZT



(d)

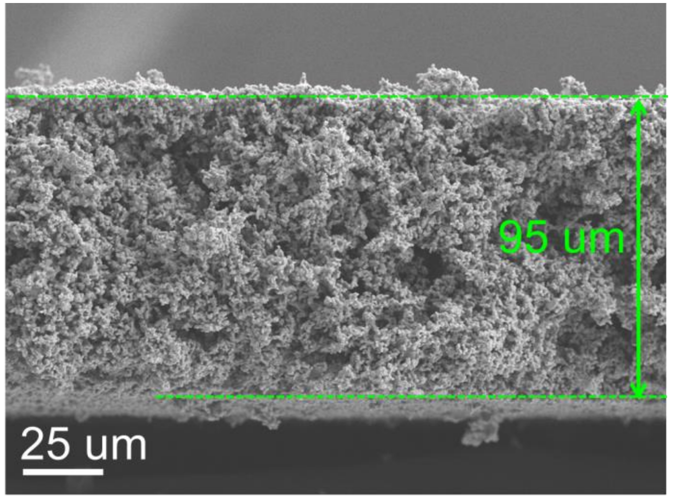


3D LLZT maintaine the cubic structure, which favor for good ionic conductivity at room temperature

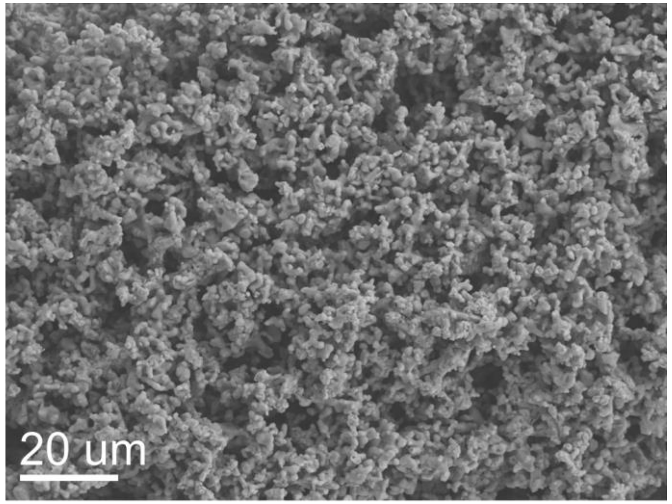
SEM images of 3D-LLZT and CSE

3D LLZT

(a)

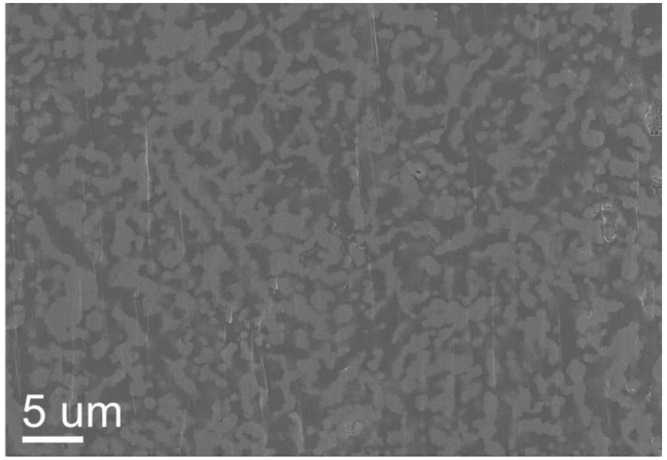


(b)

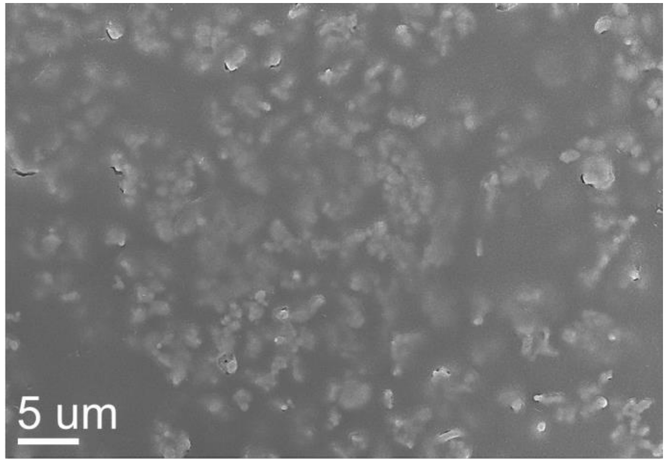


In-situ polymerization (3D-LLZT-CSE)

(c)



(d)

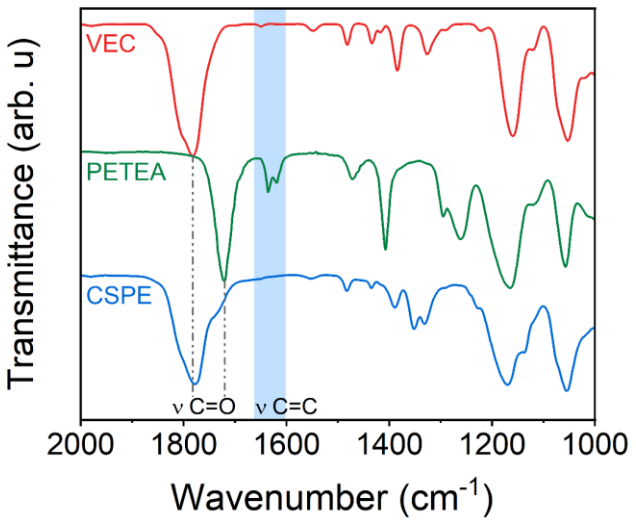


Polymer evenly occupy the pores of the 3D-LLZT framework

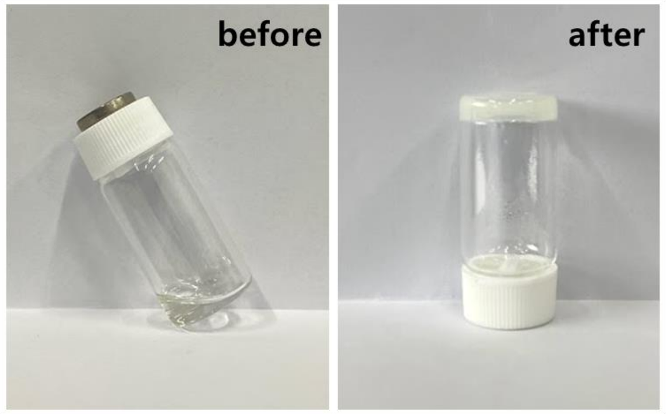
Generate continuous Li^+ transport channels

Polymerization mechanism

(a)



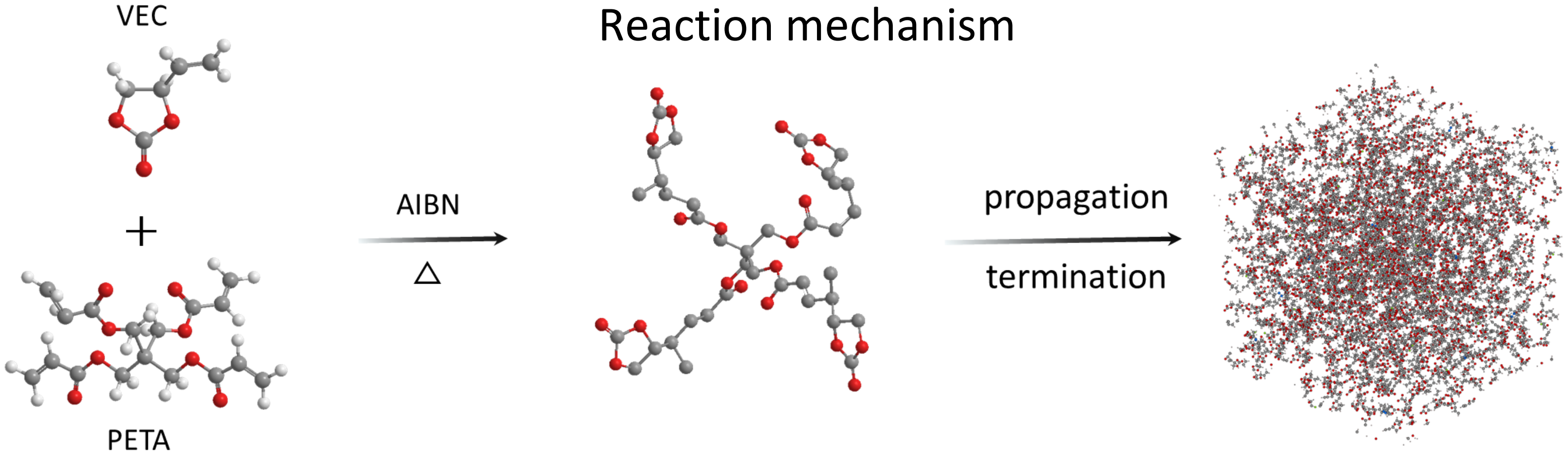
(b)



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

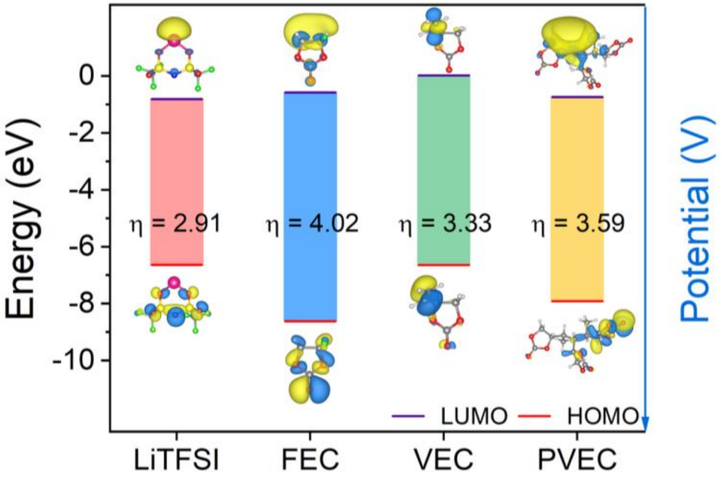
(c)

Reaction mechanism



Calculation

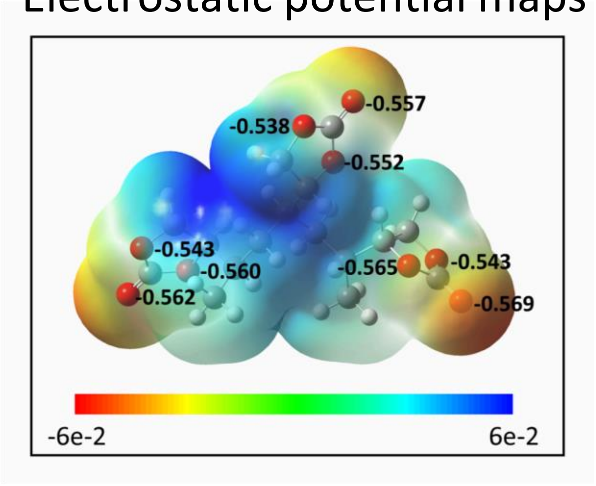
(a)



LiTFSI tends to decompose to form interphases

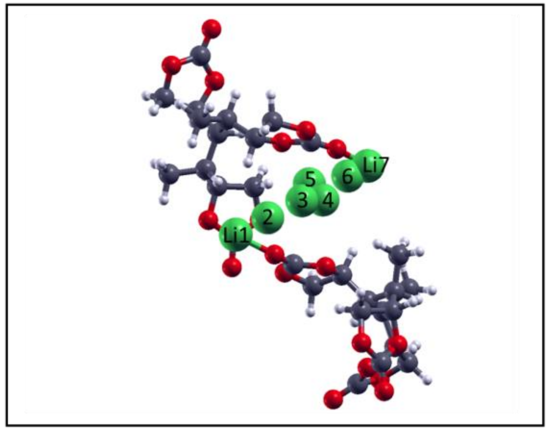
Electrostatic potential maps

(b)



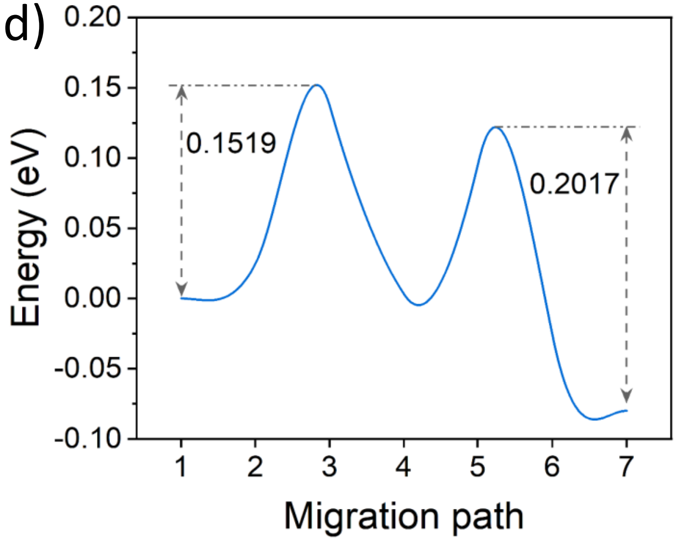
C=O group with electron-withdrawing effect, favor the interaction with Li^+

(c)



Activation energy

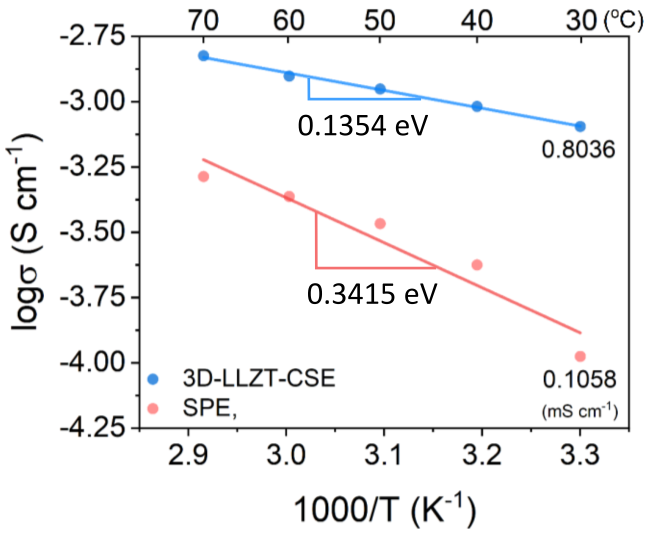
(d)



Electrochemical Analysis

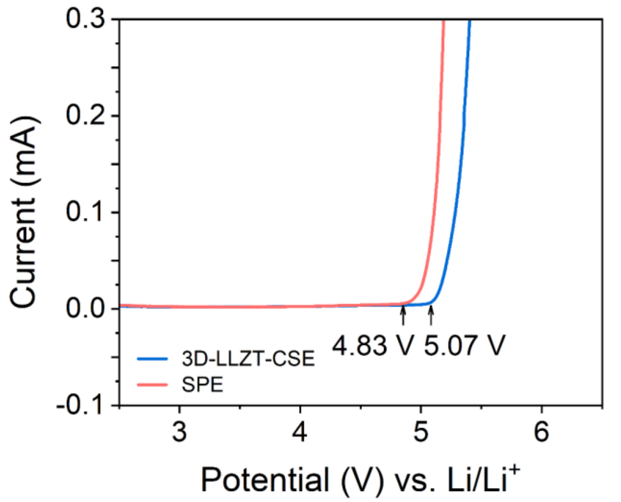
Ionic conductivity + activation energy

(a)



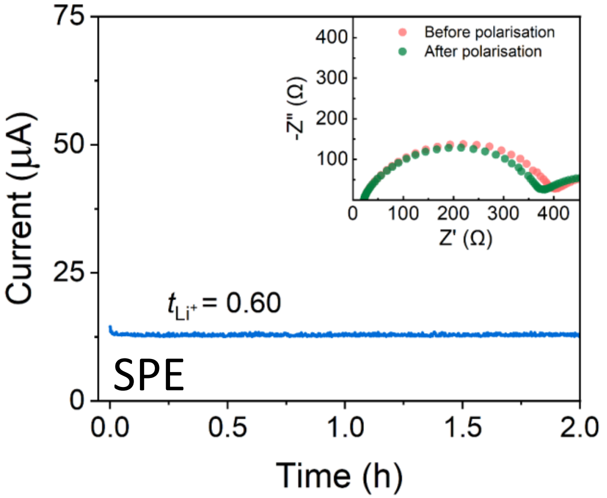
Linear sweep voltammetry

(b)

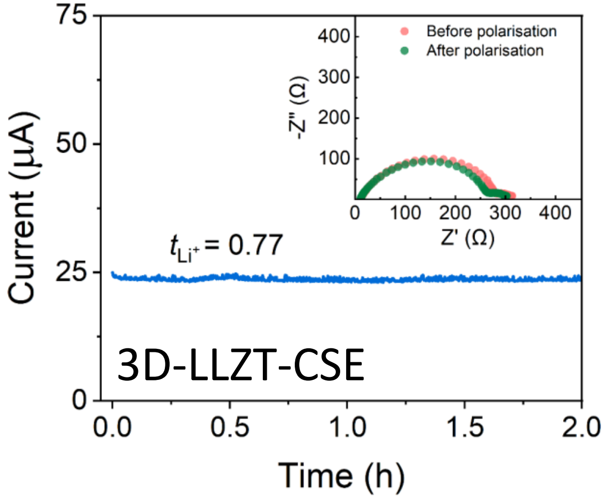


Lithium transference number

(c)

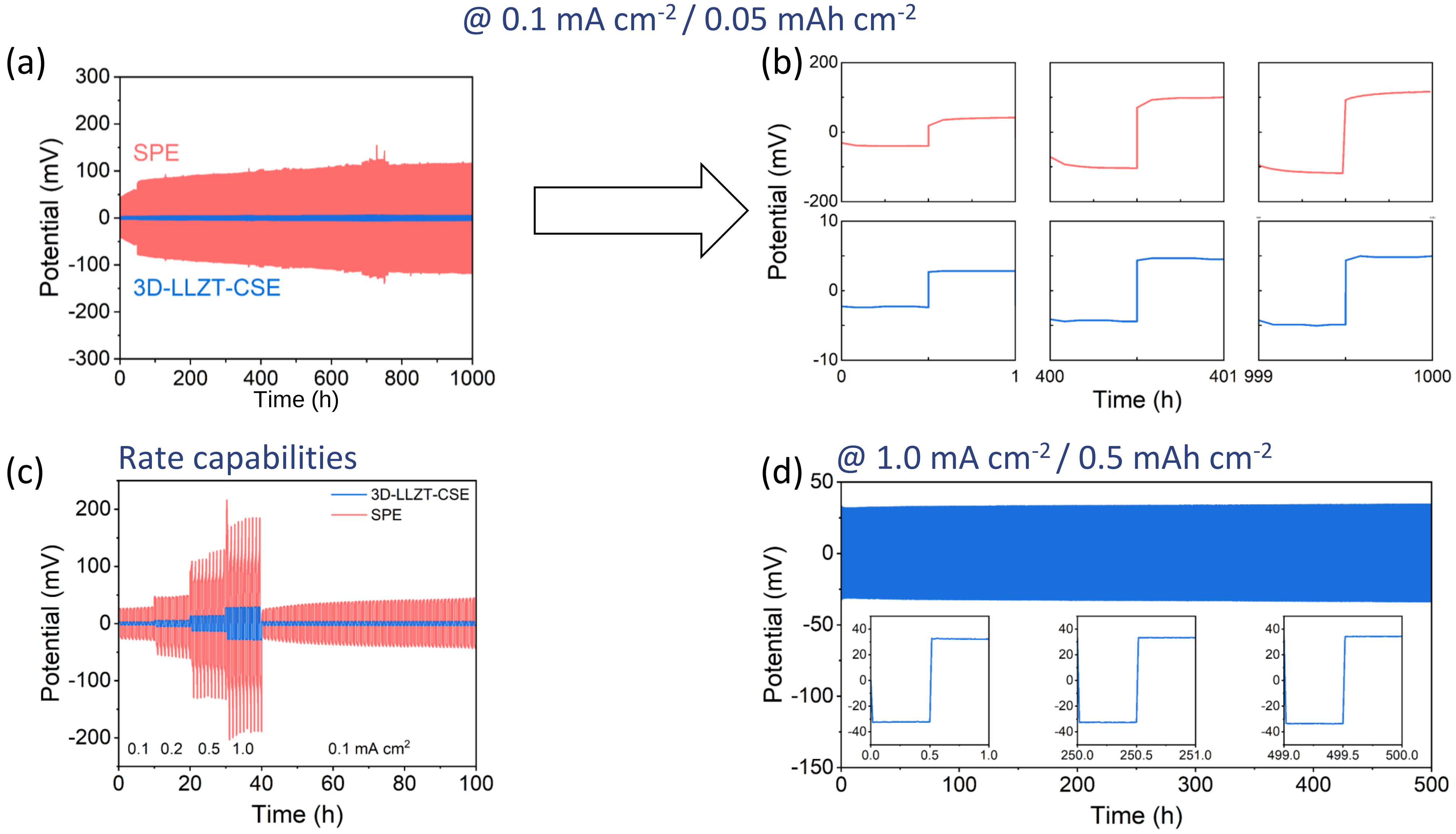


(d)



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

Li plating/stripping

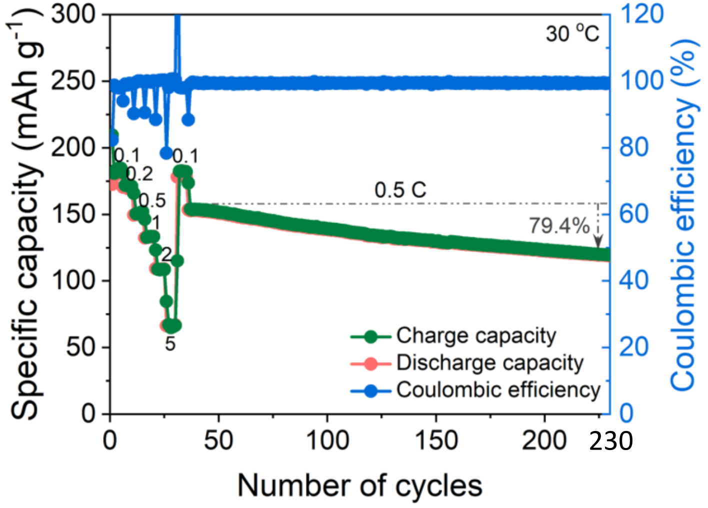


3D-LLZT-CSE exhibited square wave-like potential profiles with small overpotential values

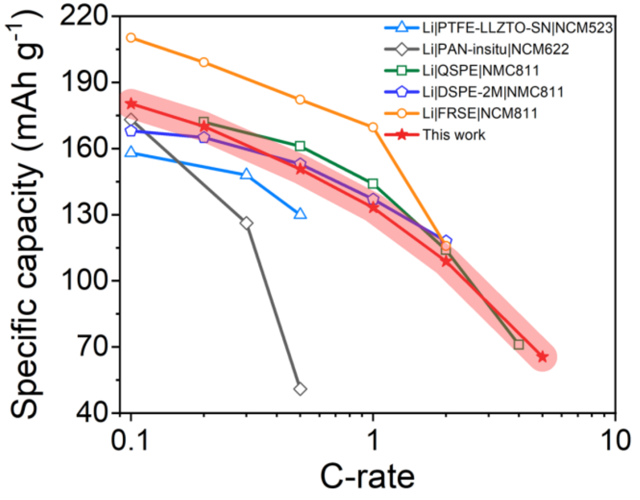
Solid-State Lithium Batteries

Coin-cell CR2032

(a)



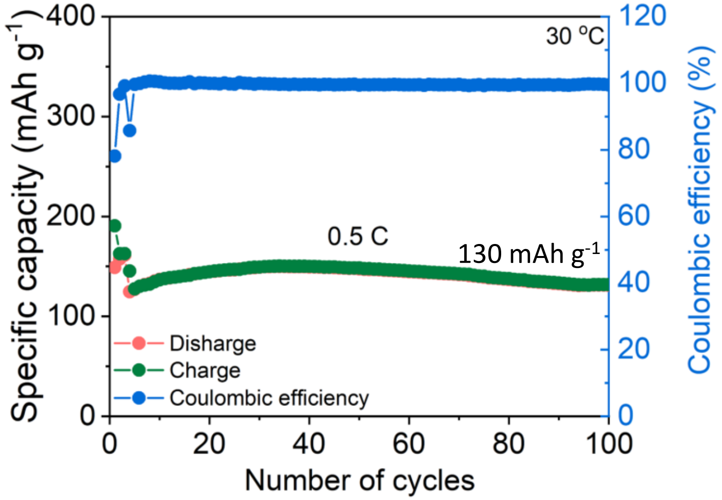
(b)

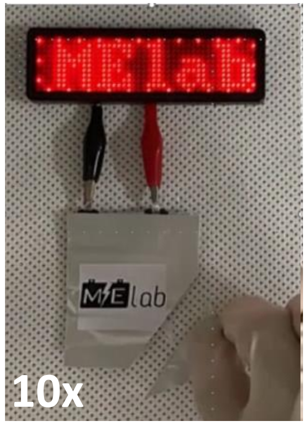


Li|3D-LLZT-CSE|NCM811 cell delivered specific discharge capacities of 180.3, 170.0, 150.7, 133.2, 108.8, and 65.5 mAh g^{-1} at the C-rates of 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively

(c)

Pouch cell (2.5 x 3.5 mm)



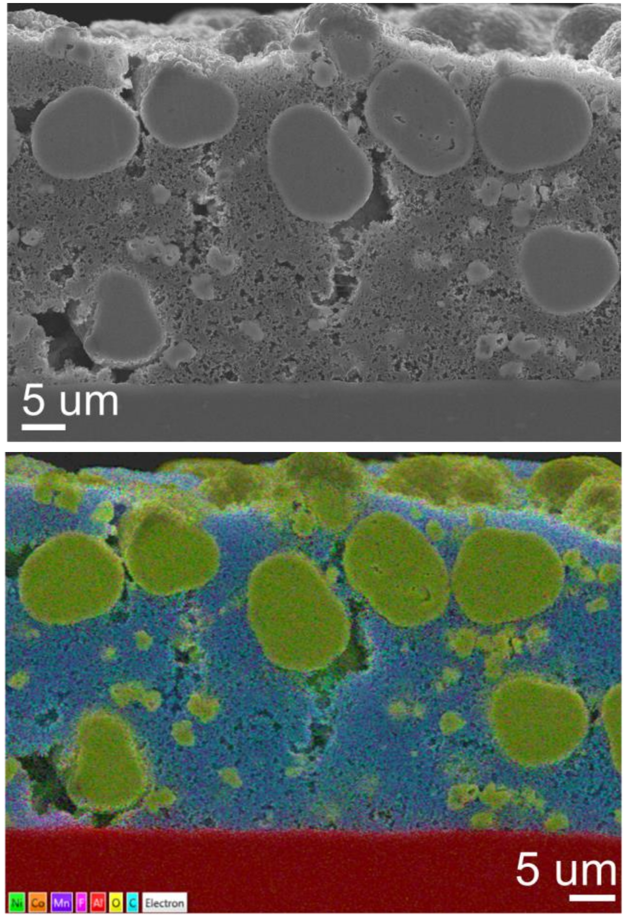


Pouch cell also exhibited the good cyclability

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

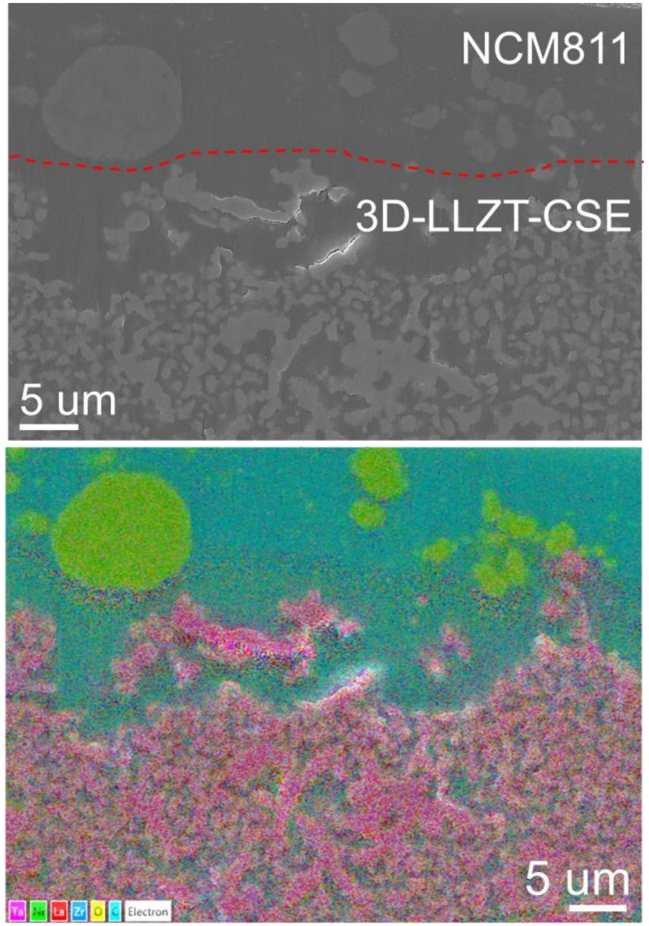
Cathode-Electrolyte contact

Bare NCM cathode



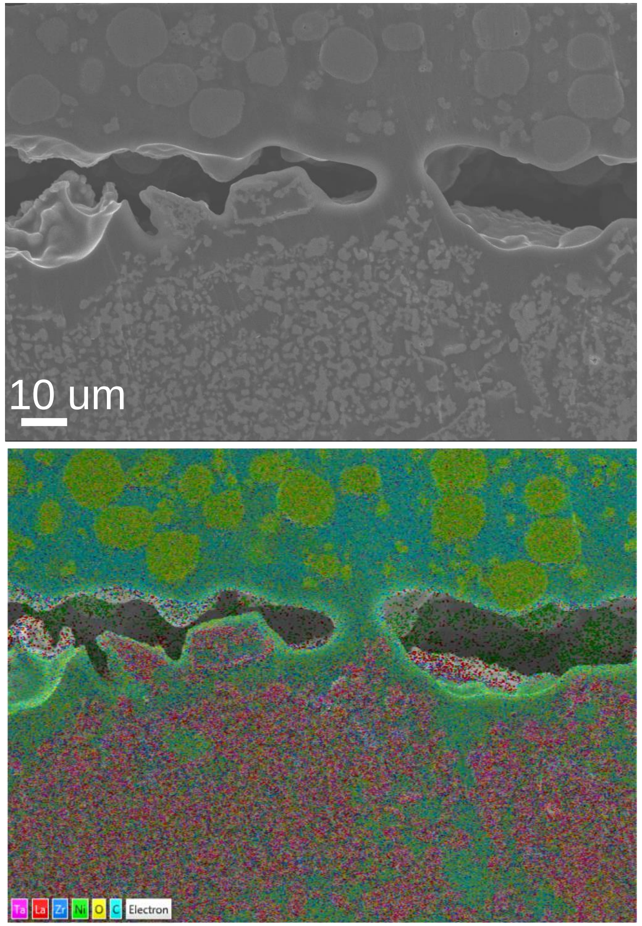
porous structure

in-situ CSE + NCM cathode



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

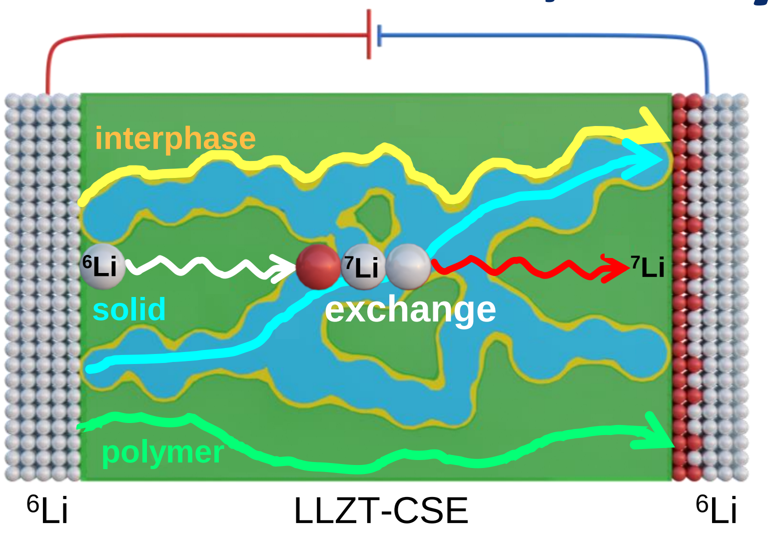
ex-situ CSE + NCM cathode



Gaps were exsited which induce the large interphase resistance

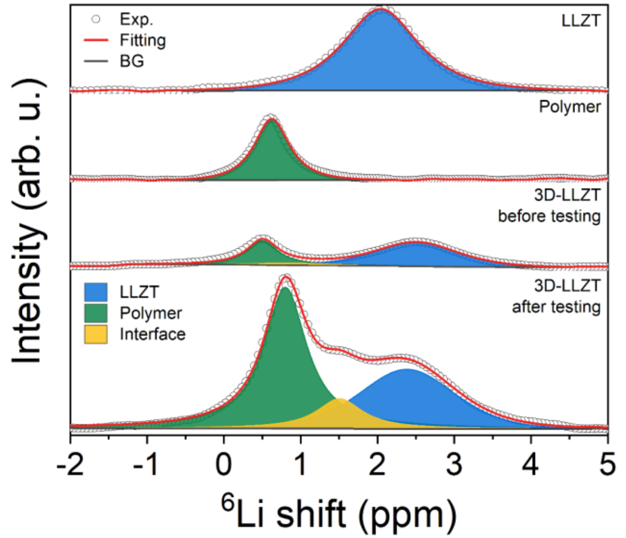
Contribution of LLZT, Polymer, and Interphase

(a)

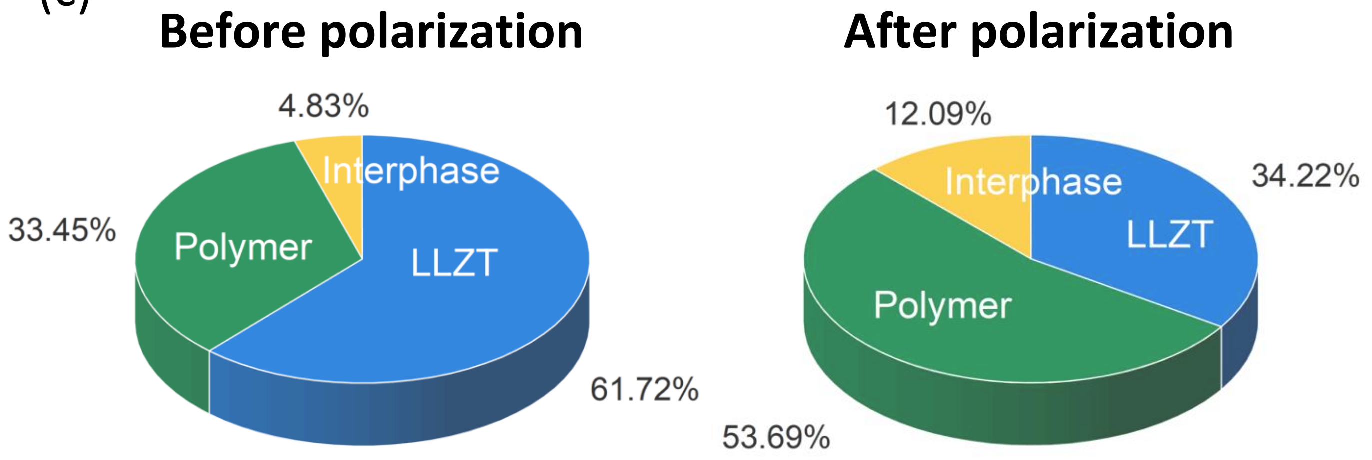


^{6}Li tracer-exchange mechanism + solid-state NMR

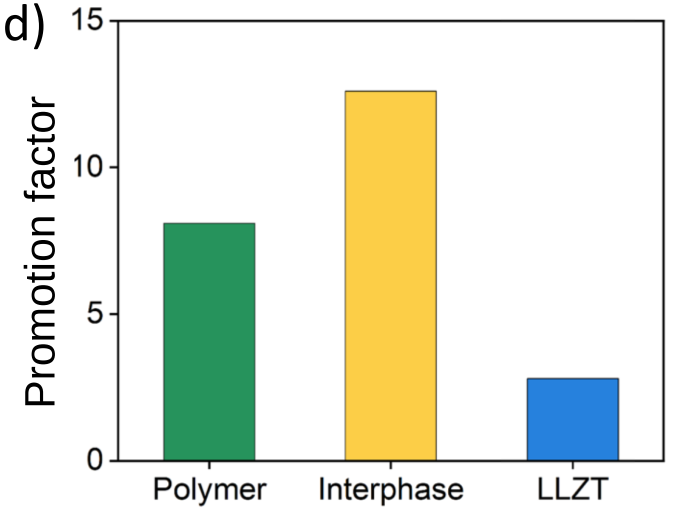
(b)



(c)



(d)



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

Conclusion 1

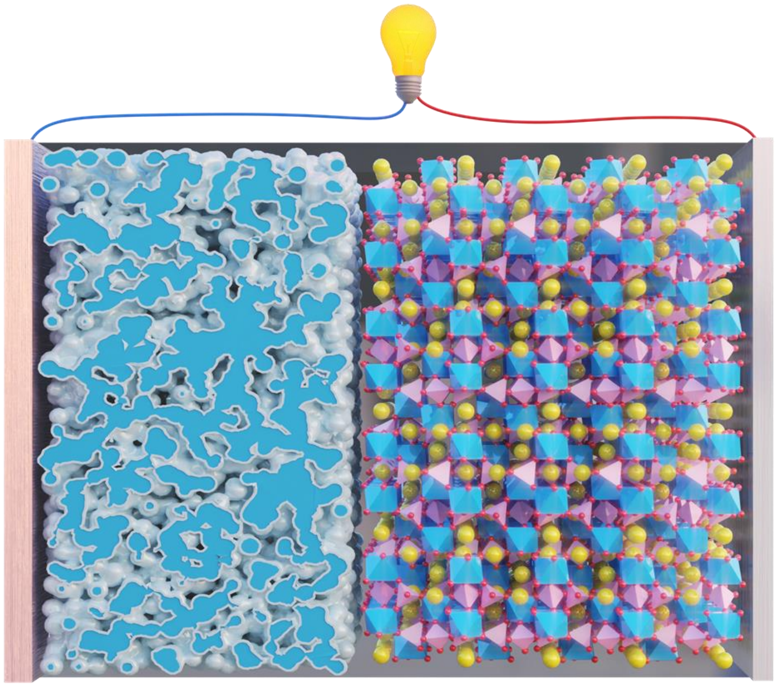
- In-situ CSEs were rationally designed and fabricated for solid-state lithium batteries with excellent electrochemical performance

- 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

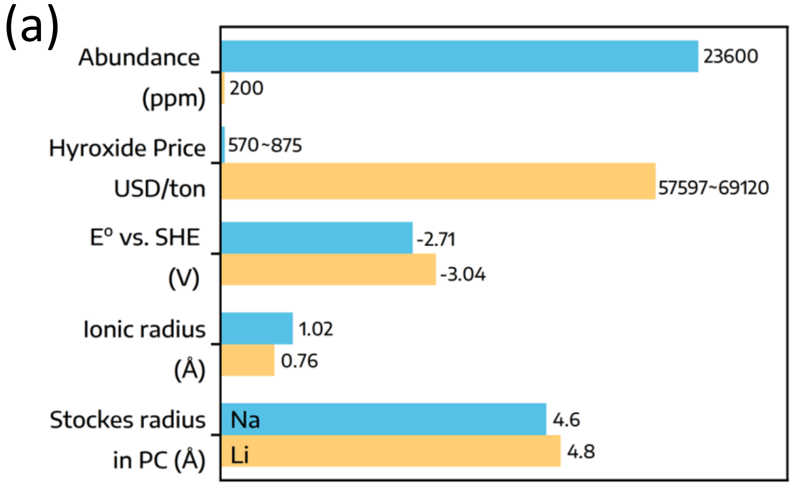
Part 2

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

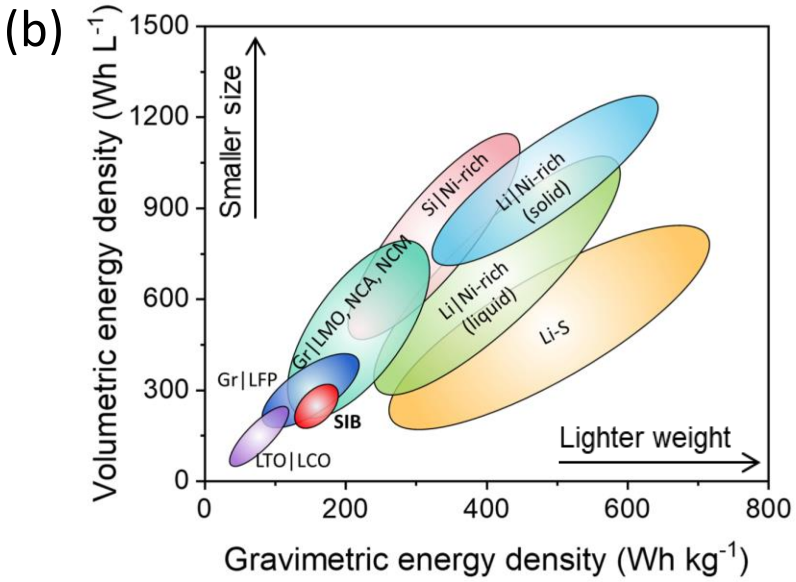


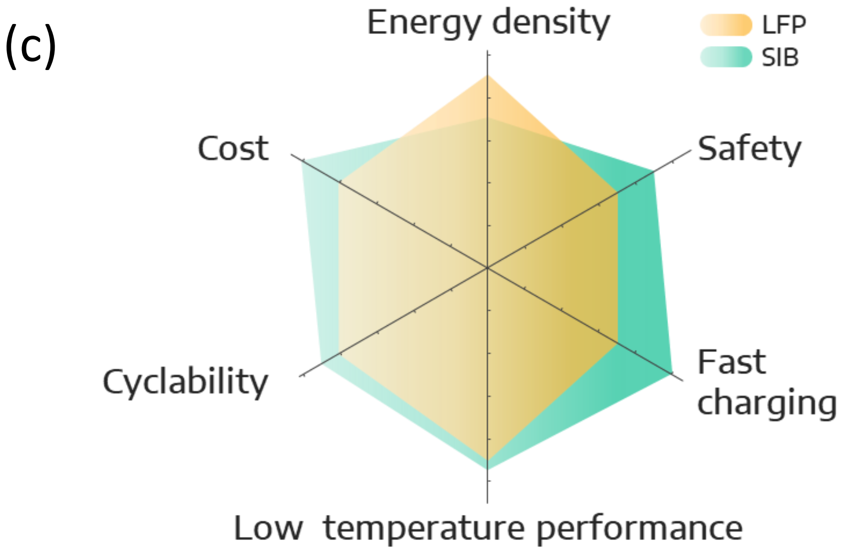
Na 3D-NZLSP-CSE NVMP@C

Why Sodium-ion batteries?



A.G. Nguyen *et. al.*, Energy Materials, 2023, 3





- 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

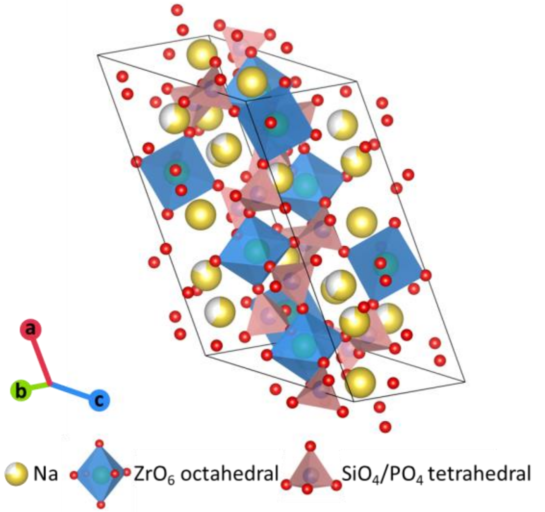
Objective

➢ Apply our strategy for Solid-State Sodium Batteries

Ceramic

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

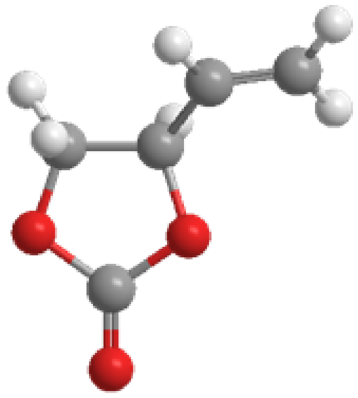
- ✓ Stability against electrodes
- ✓ High conductivity



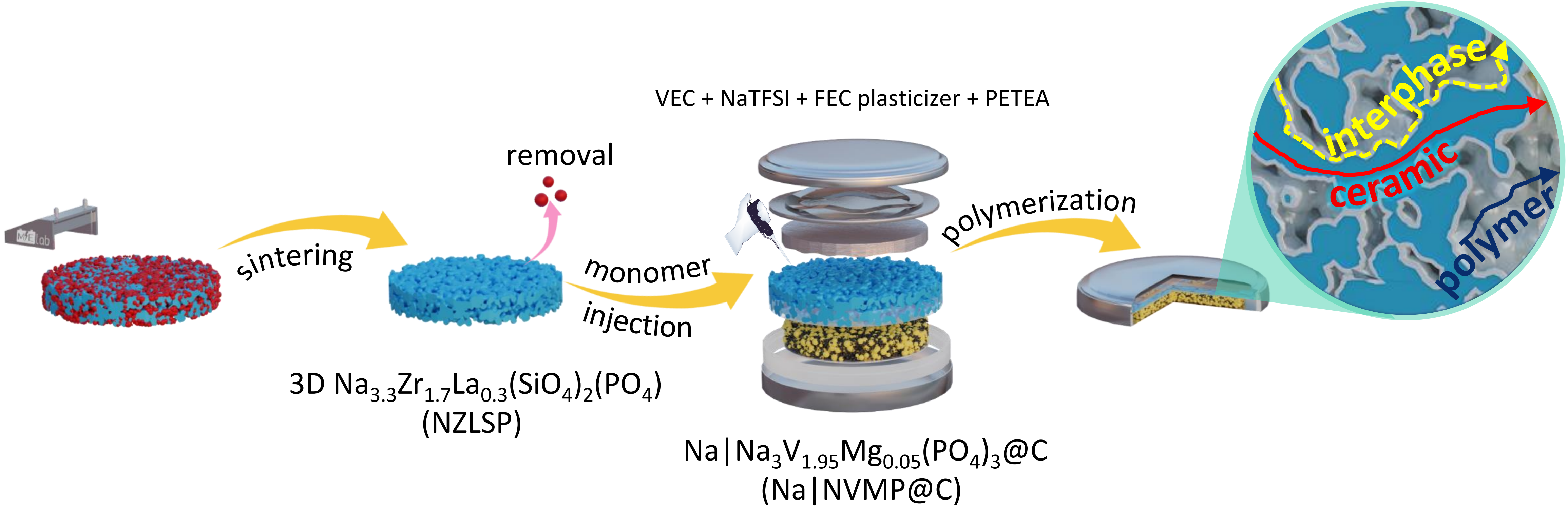
Polymer

Vinylene Ethylene Carbonate

- ✓ Can be polymerized
- ✓ Facilitate ions transportation

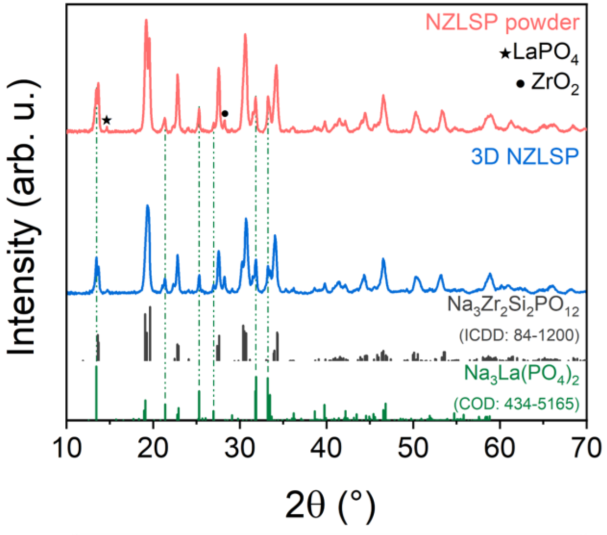


Preparation of CSE for Solid-State Sodium Batteries

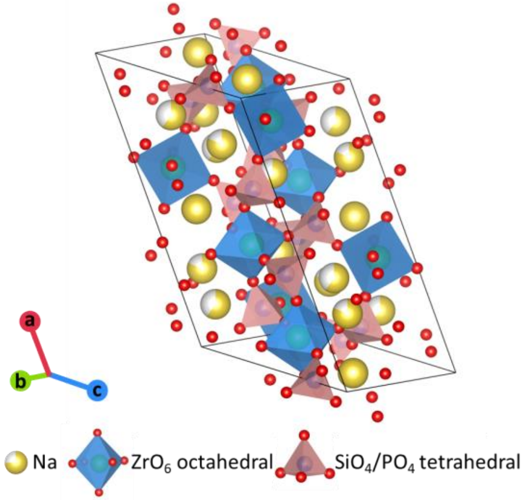


Material Characterization

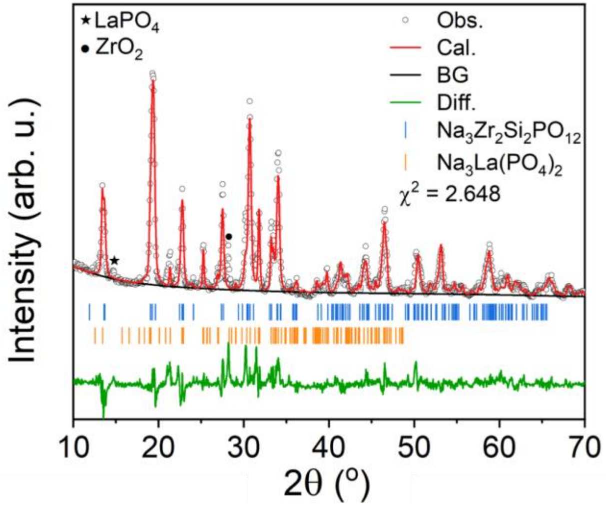
XRD (a)



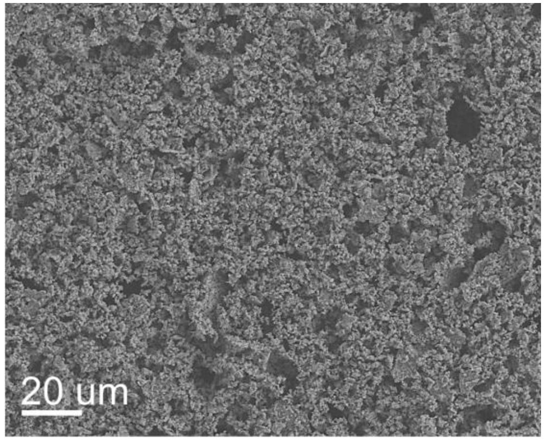
(b)



(c)



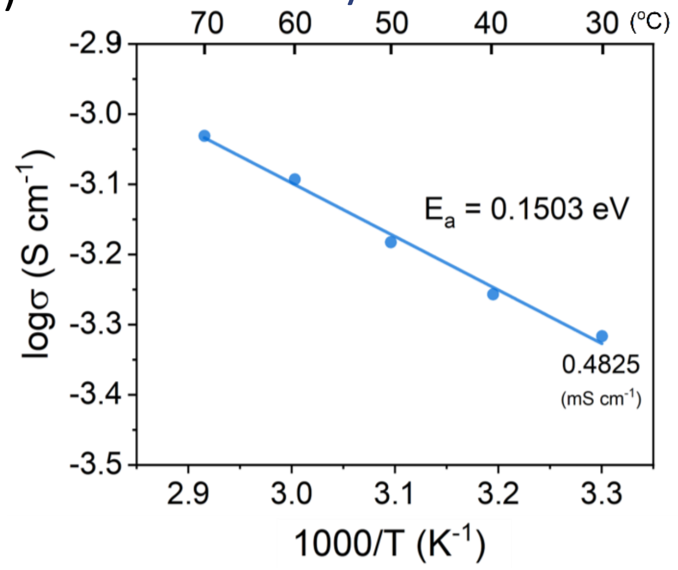
SEM (d)



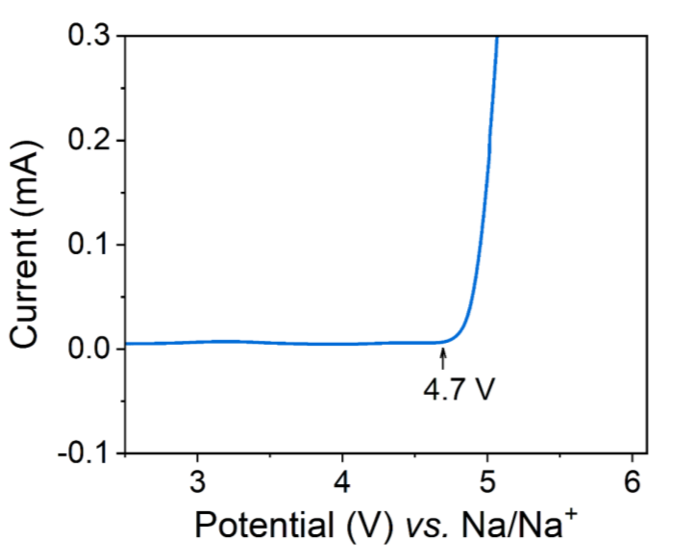
3D-NZLSP still maintains its structure after calcination and exhibits high porous morphology

Electrochemical Analysis

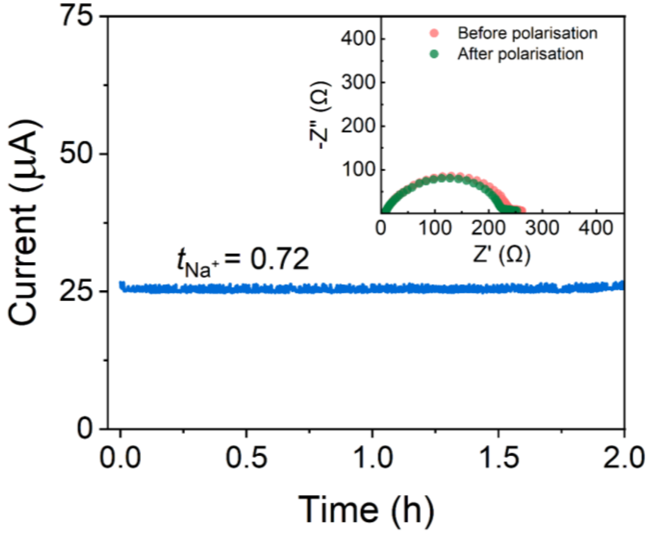
(a) Ionic conuctivity + activation energy



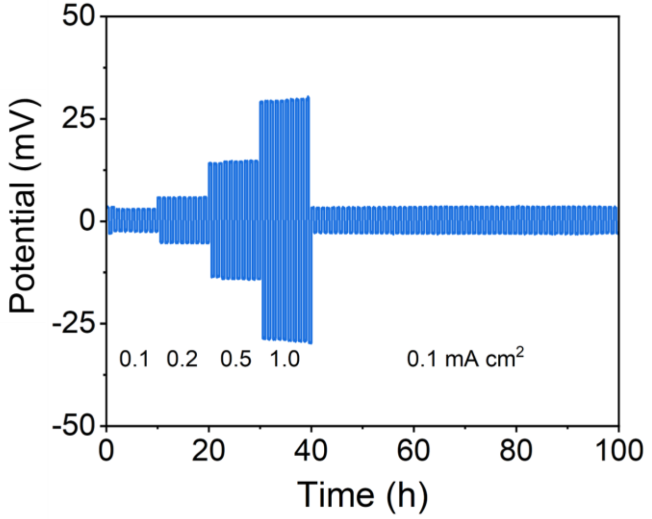
(b) Linear sweep voltammetry



(c) Lithium transference number

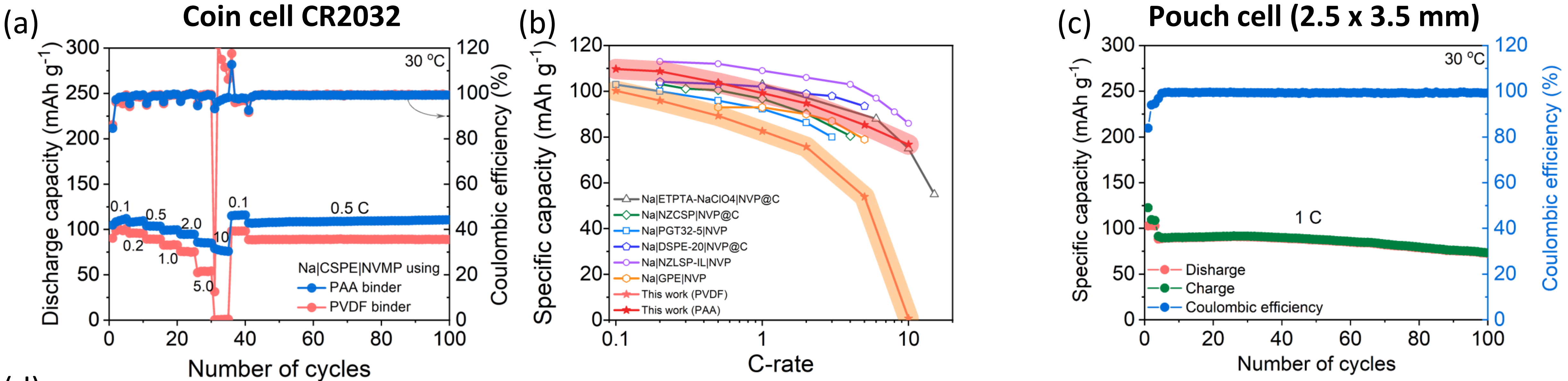


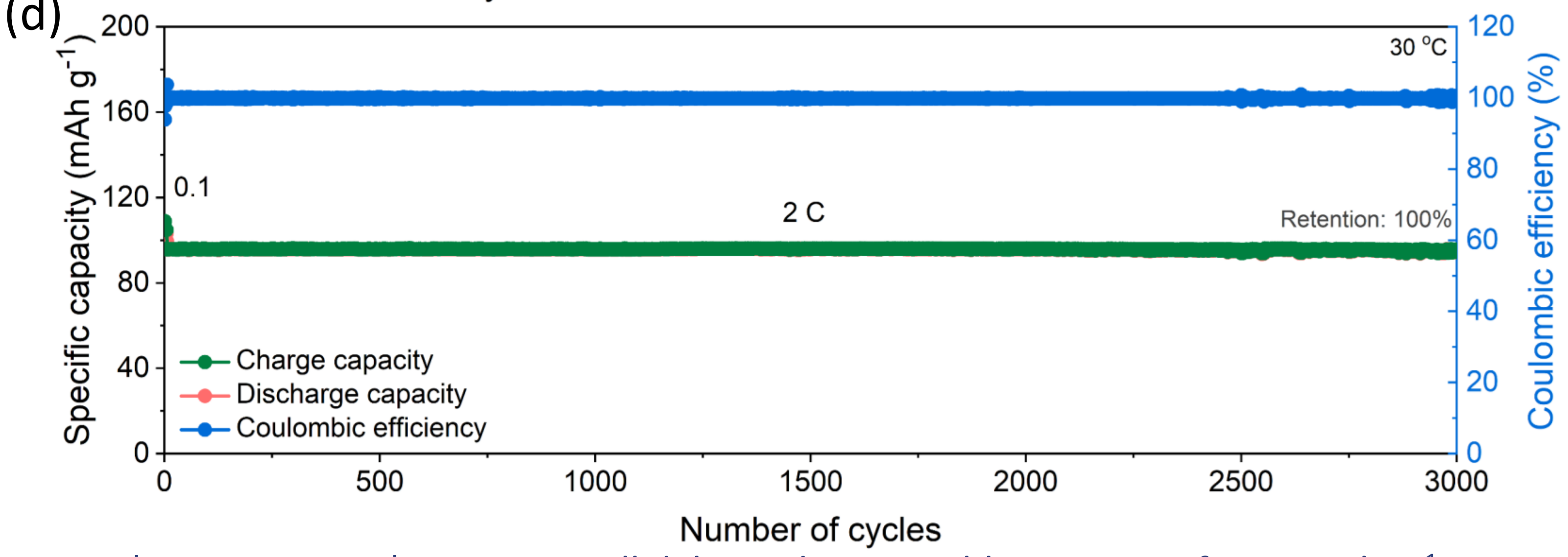
(d) Rate capability of CSE

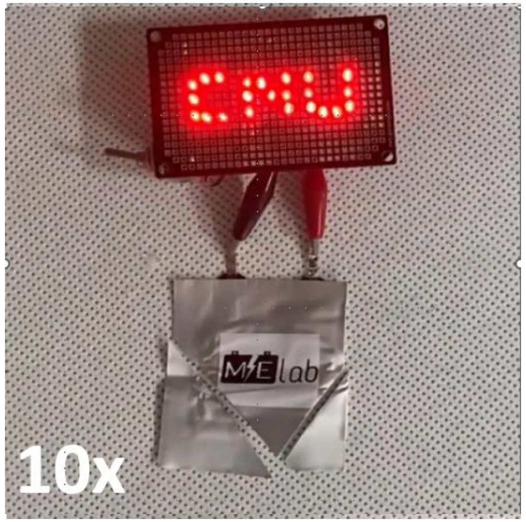


3D-NZLSP-CSE exhibited good ionic conductivity, high transference number and stability

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%

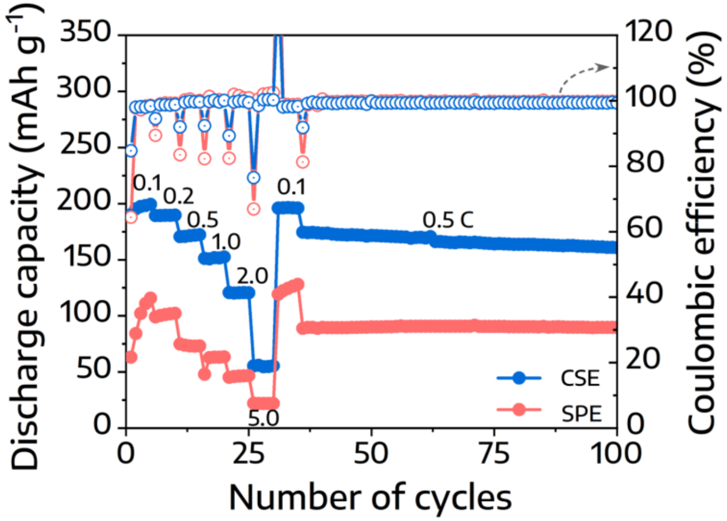
Part 3

Unpublished

Solid-State Lithium Batteries

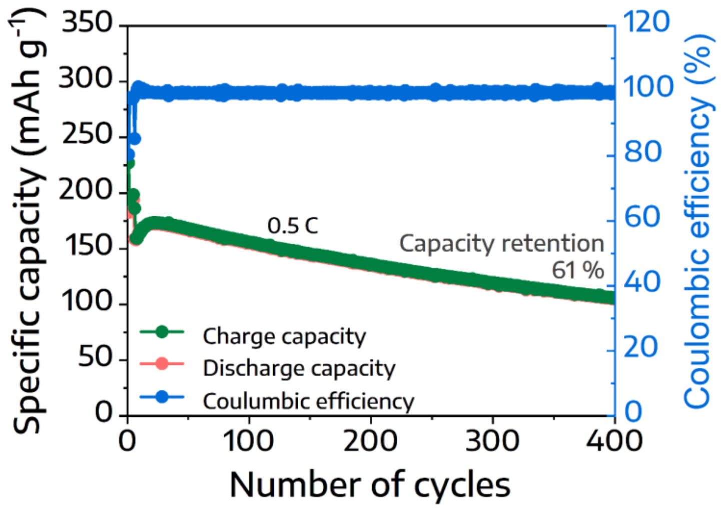
(a)

Coin cell



Li|CSE|NCM811 exhibited excellent rate capability

(b)

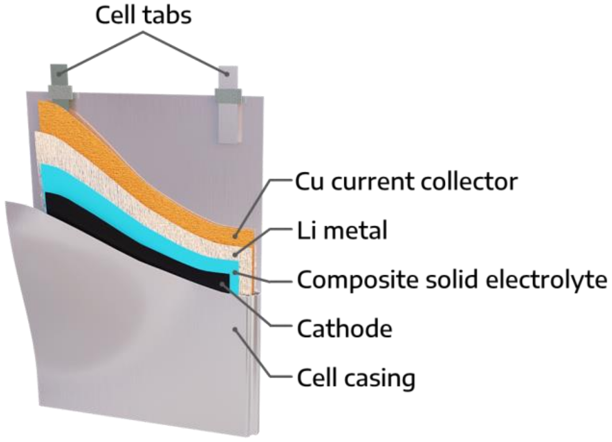


Discharge-specific capacity of 105.1 mAh g^{-1} after 400 cycles

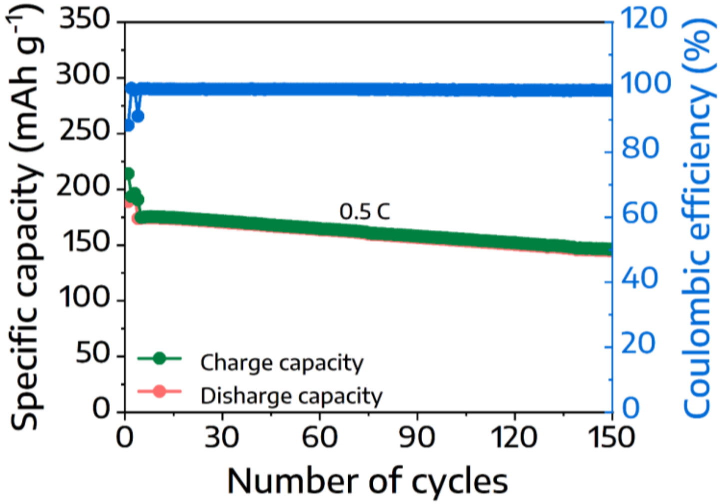
Capacity retention of 61%, average Coulombic efficiency > 99%

(c)

Pouch cell



(d)



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

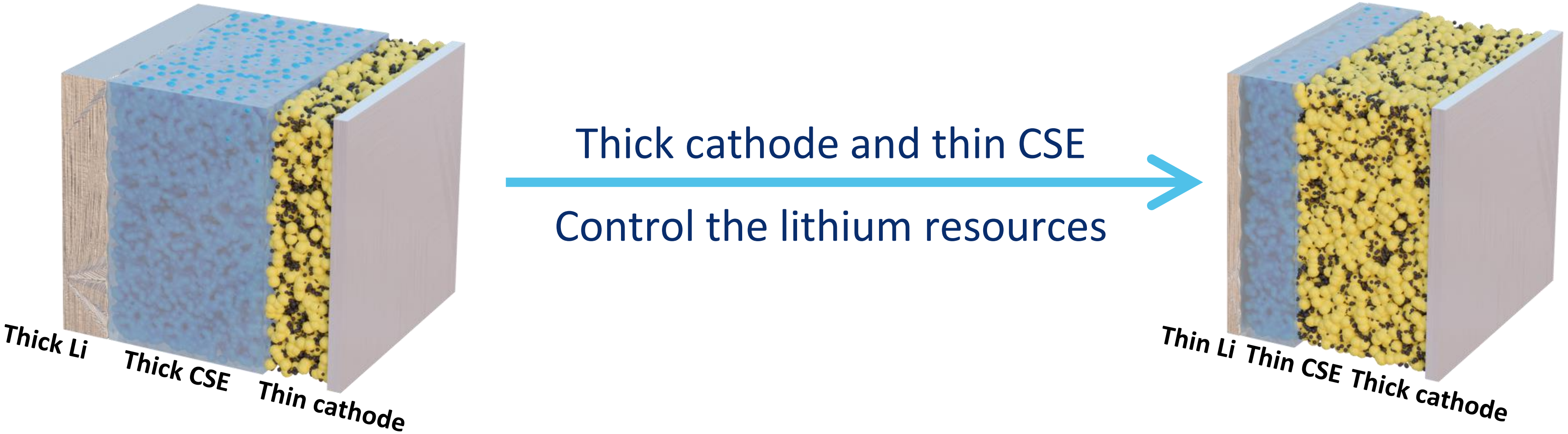
Conclusion 3

- 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

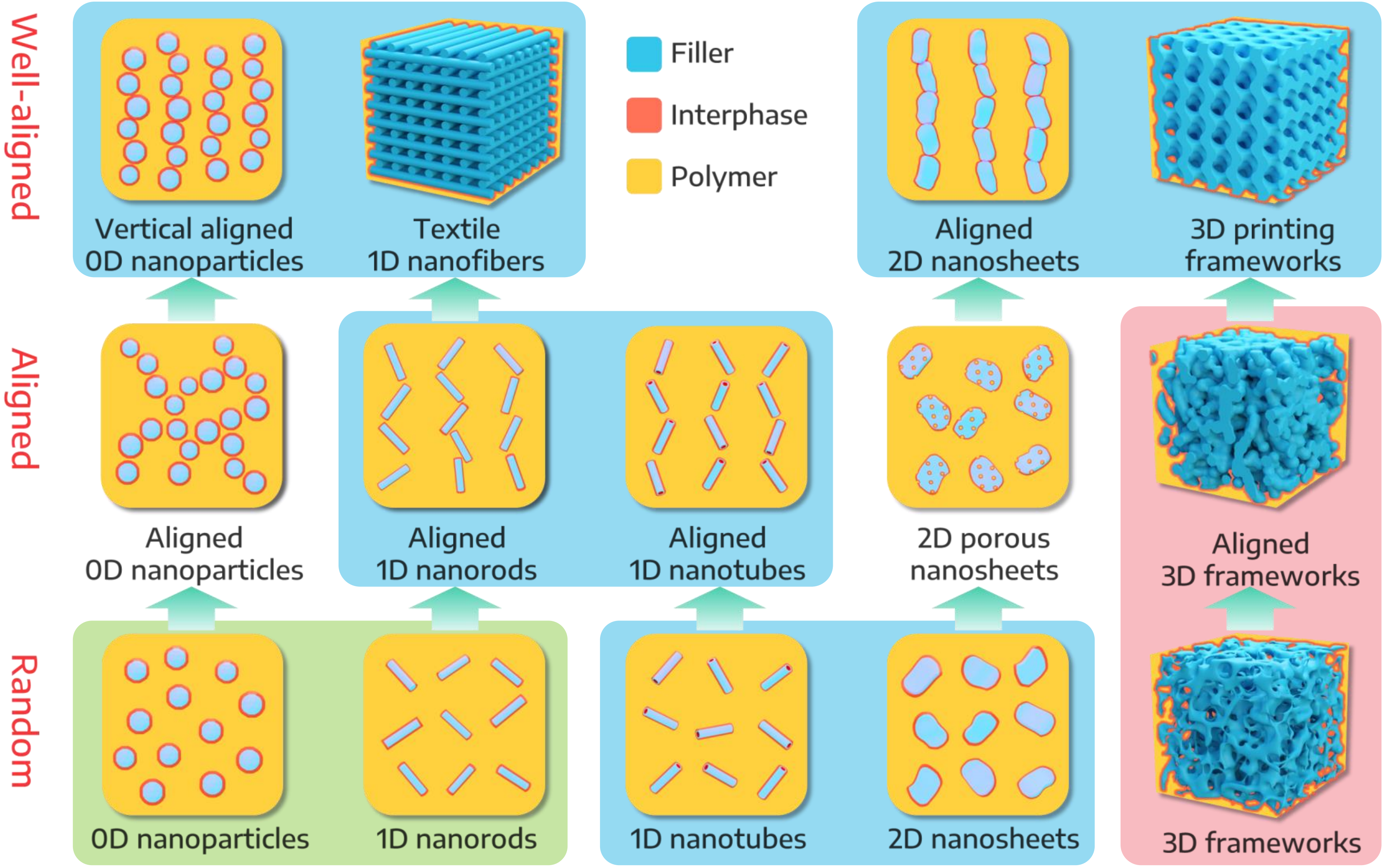
General Conclusion

- ➢ 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

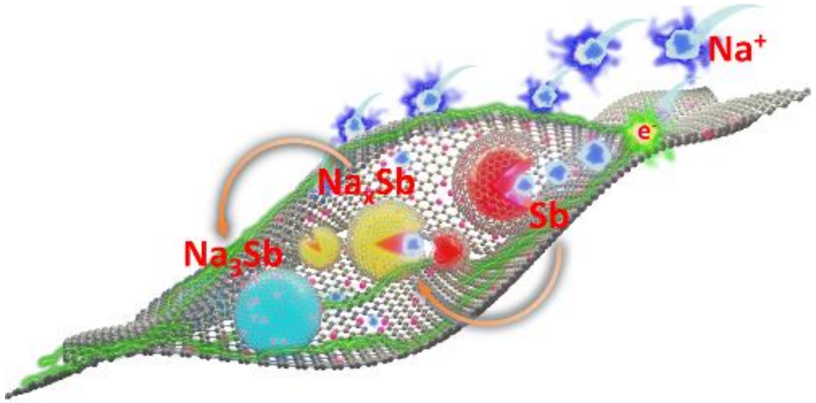


Perspective

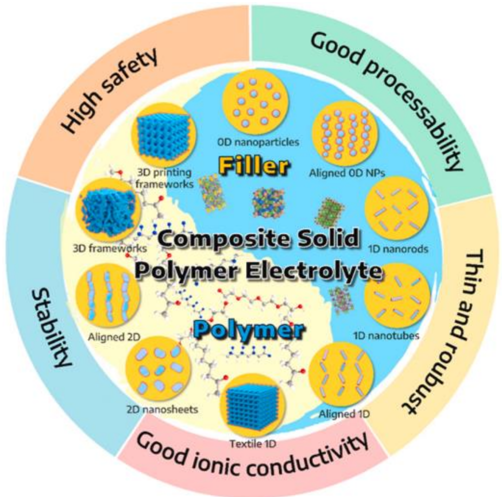


The type, size, surface properties, and dimension of the filler will have a significant impact on the ionic conductivity of composite solid electrolytes

Pubication

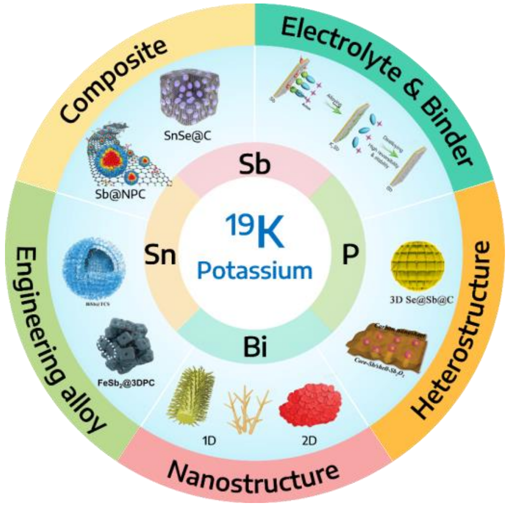


Chem. Eng. J., 429, 2022, 132359



J. Membr. Sci., 675, 2023, 121552

Adv. Sci., 2023, 2207744



Energy Mater., 2023

And 9 articles as a co-author

Acknowledgment

Advisor:

Prof. Chan-Jin Park

Committee:

Prof. Jong-Sook Lee

Prof. Sun-Ju Song

Prof. Won-Hee Ryu

Prof. Hyunjung Park

All the past and present MElab members

Dr. Le Thi Thu Hang

Dr. Ngo Duc Tung

Dr. Vu Duc Luong

Dr. Rakesh Verma

Dr. Yashabanta N. Singhbabu

Dr. Pravin N. Didwal

Mr. Hyeong-Seo Ki

Mr. Bong-Joon Sung

...