Biomass-Templated Composite Solid-State Electrolytes and Their High Lithium-ion Transference

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NMT naturmaterialteknik

TAPPI NANO DIVISION

Content

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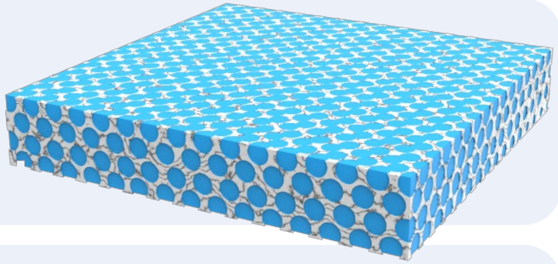
1 Introduction – structure design of solid-state electrolyte

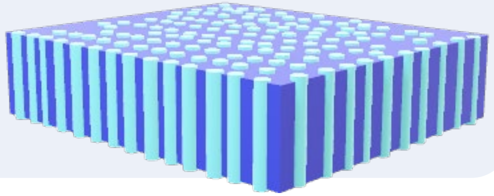
2 LNP-regulated CNF film templated LLZO/PEO CSE

— with uniform and controllable Li-ion pathways



3 Upright cellulose layer templated LLZO@PEO CSE

— with vertically aligned Li-ion pathways



4 Summary and outlook –SUSTEC (next generation of battery-SIB)

Introduction   Li-ion batteries: from liquid to solid

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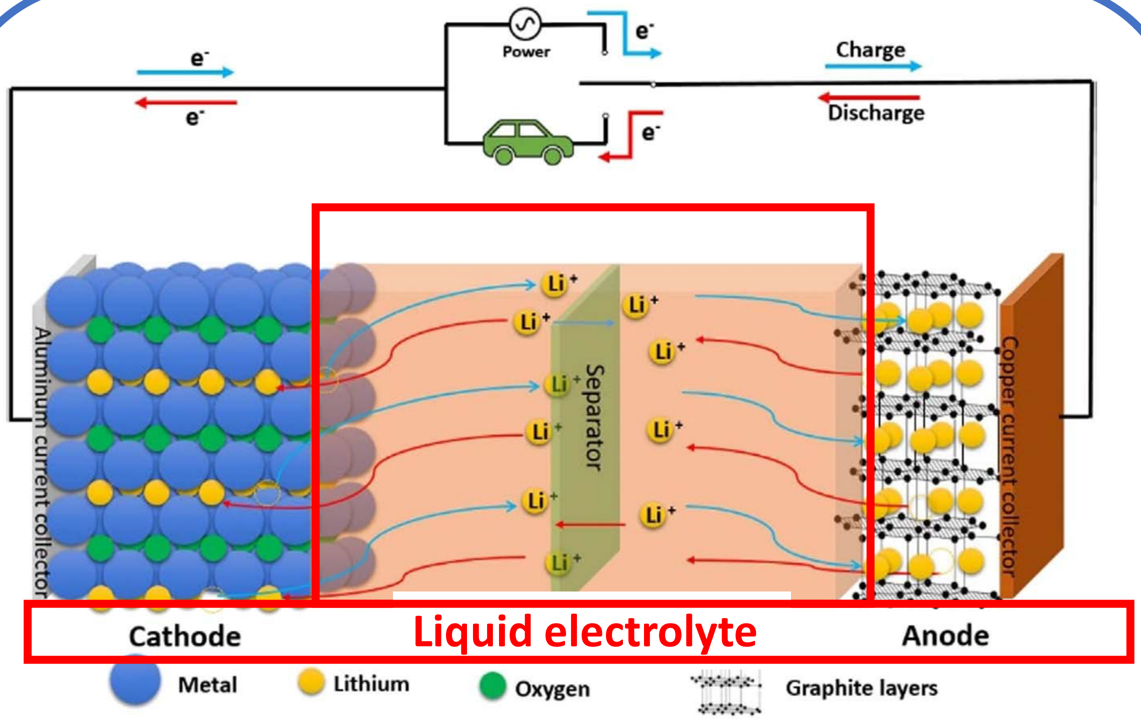
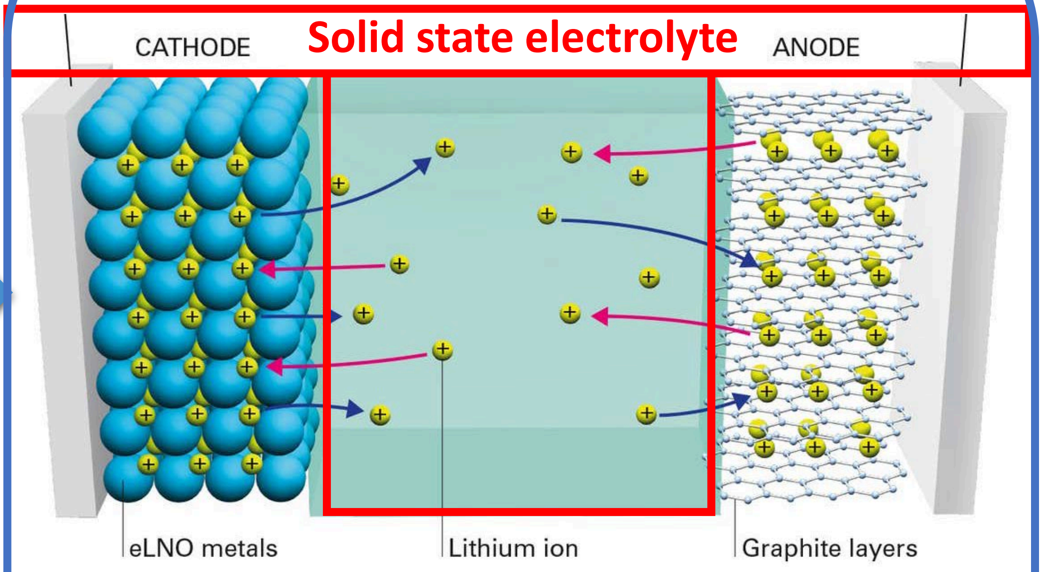


Traditional Li-ion battery (liquid state)



Solid-state Li-ion battery

Anode, Cathode, ***Liquid electrolyte***, Separator

Inflammable, Risk of combustion

Anode, Cathode, ***Solid-state electrolyte***

High safety, Easy assembly, Less side reaction

https://www.everexceed.com/blog/various-advantages-of-lithium-iron-phosphate-lifepo4-battery_b4

Introduction Composite solid-state electrolytes (CSE) design

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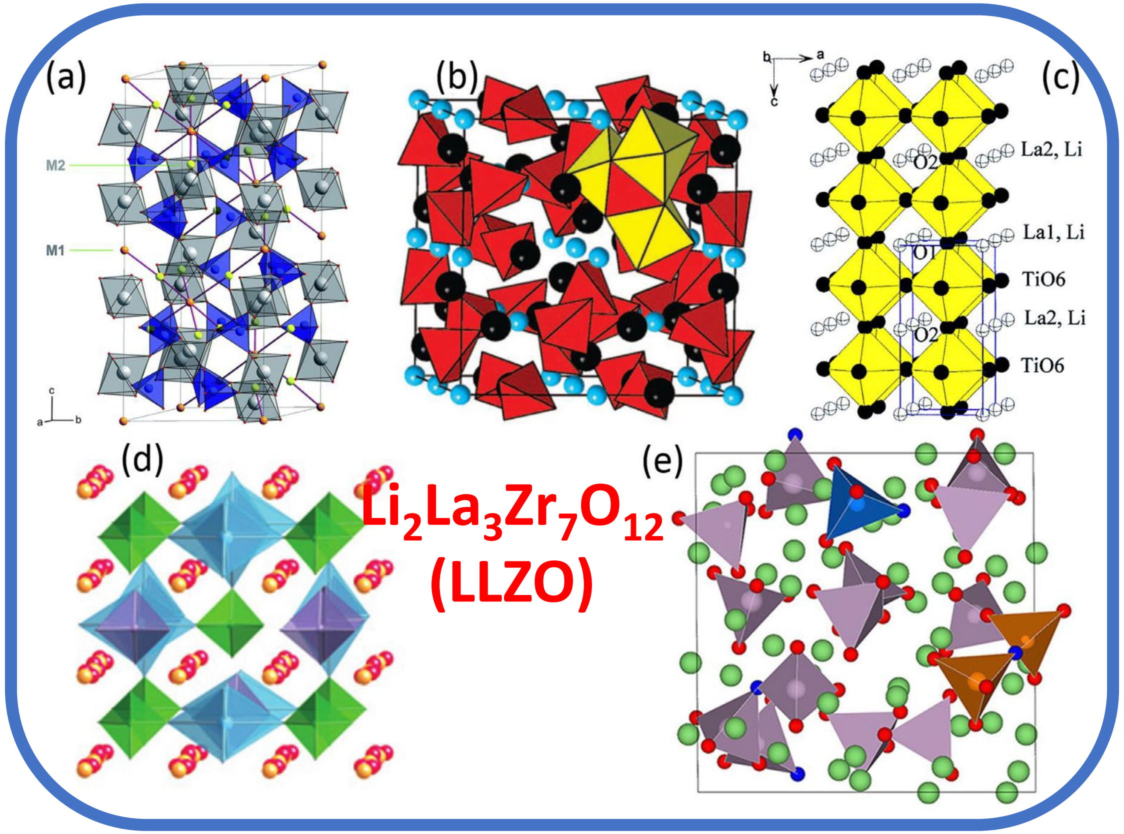

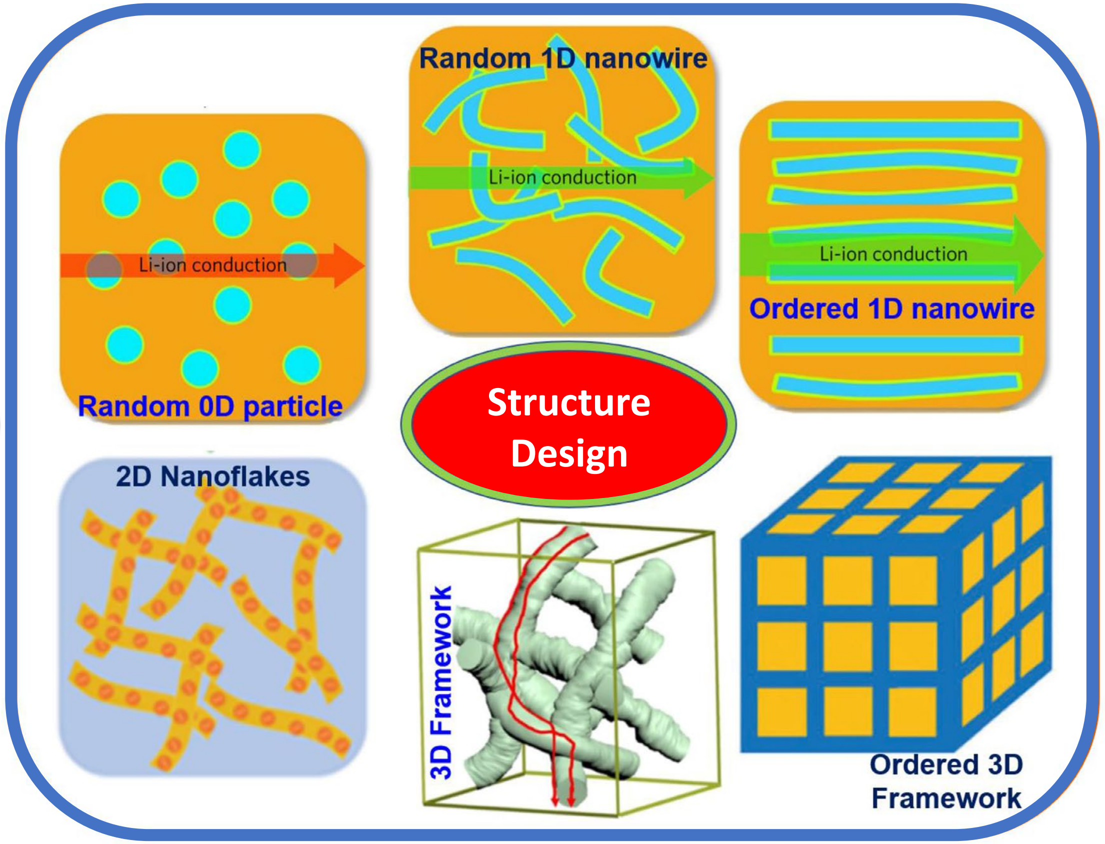

Solid Inorganic/ceramic electrolyte *(e.g.: LLZO):*

- High ionic conductivity
- Poor interface compatibility

Composite solid-state electrolytes (CSEs)

- Ceramic network/ framework
- Polymer electrolyte *(e.g.: PEO)*

Introduction Templated composite solid electrolyte (CSE)

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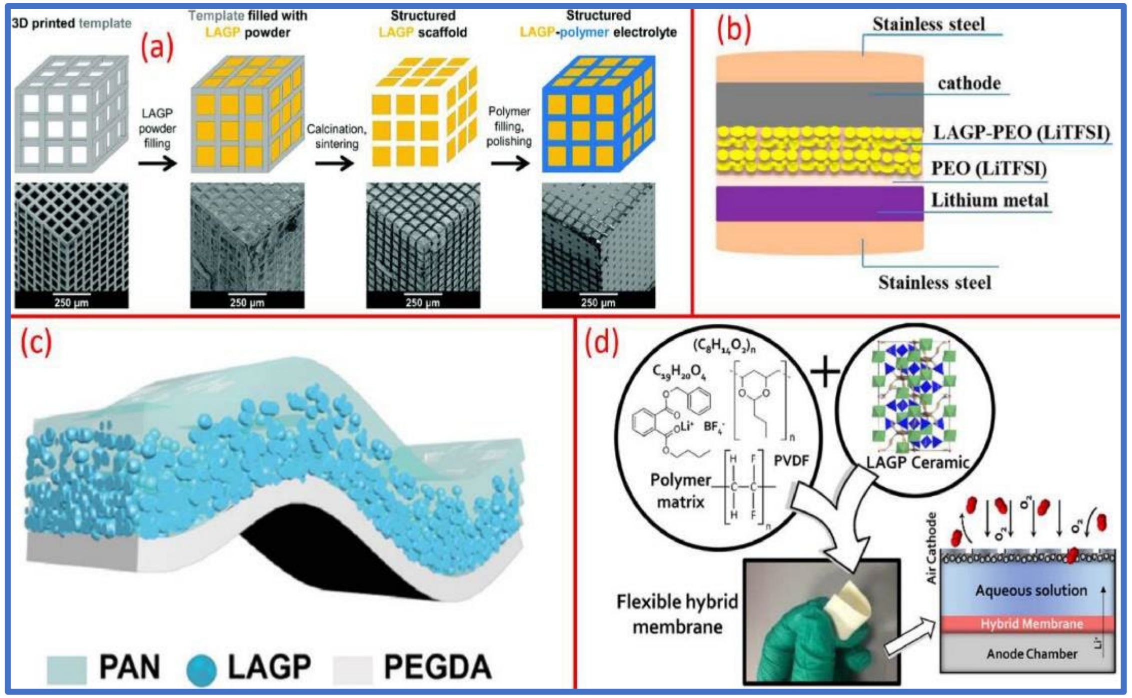
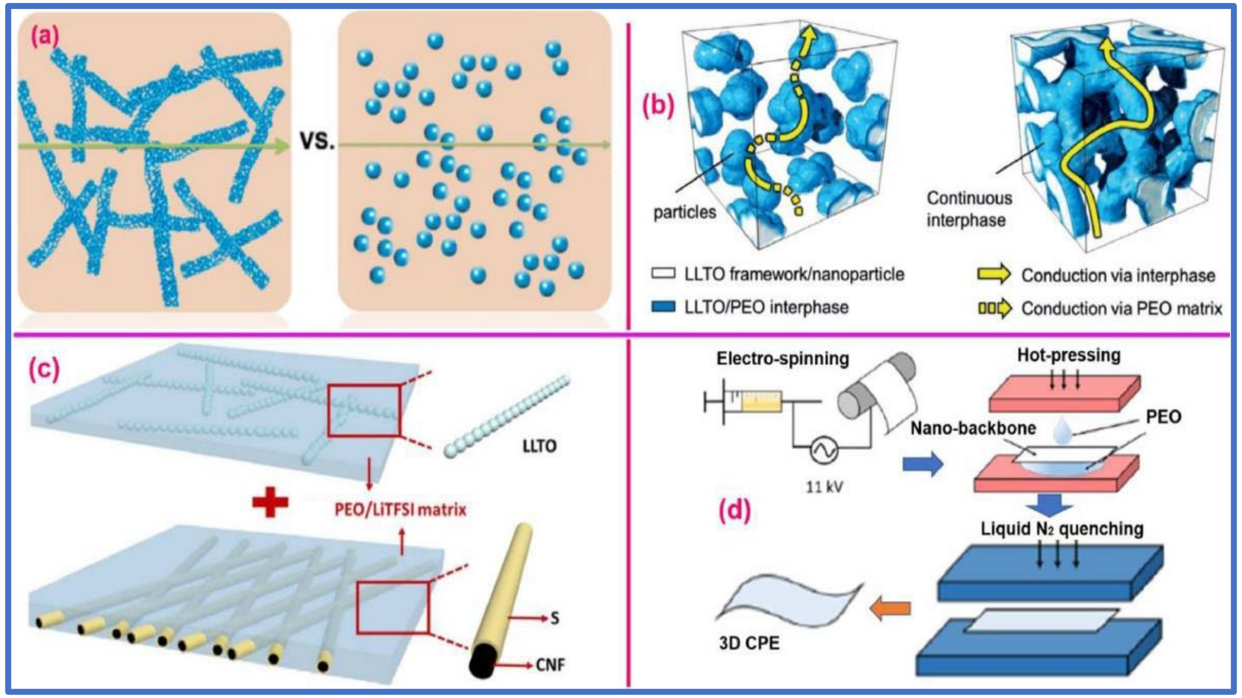




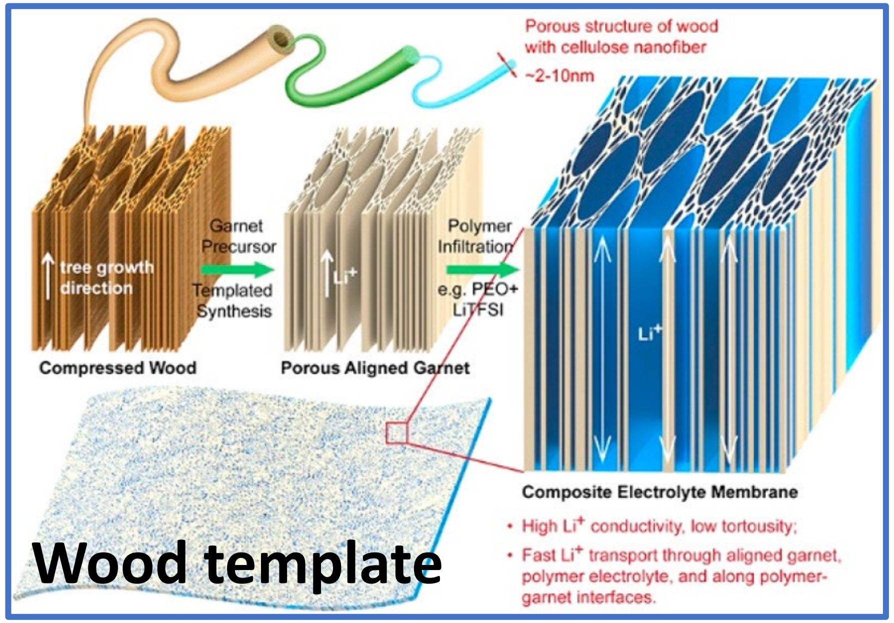
Template method:

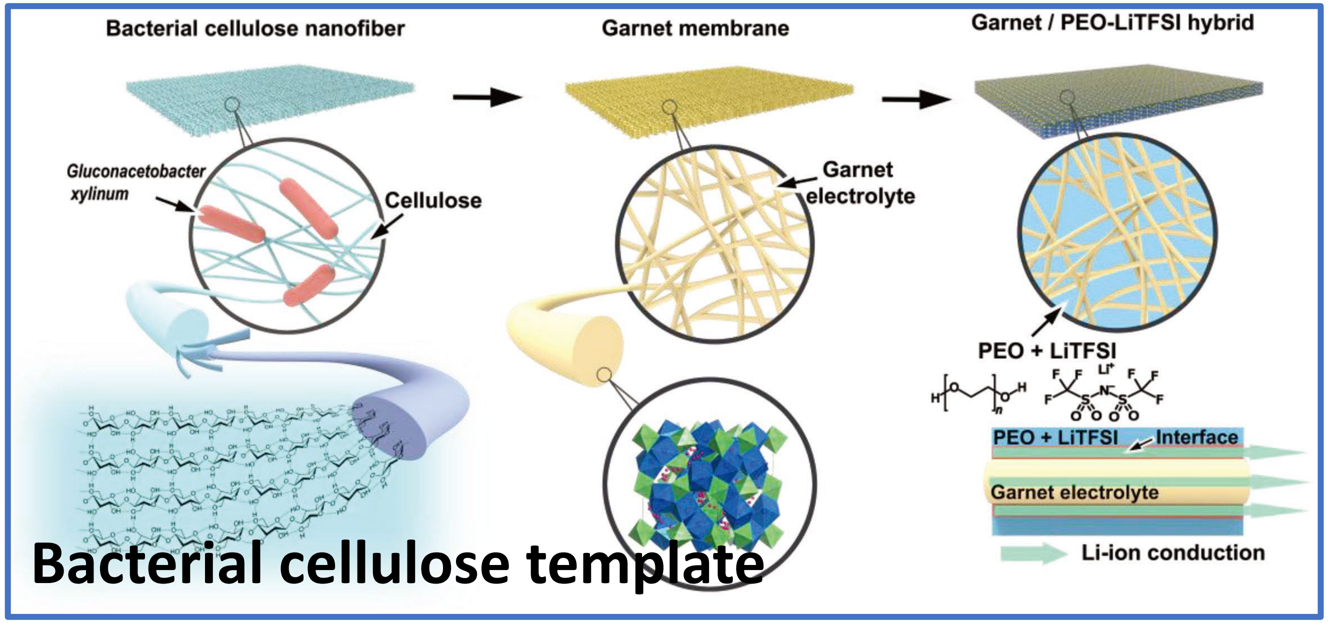
- Structure construction
- Sacrificial template

Templated CSE design：

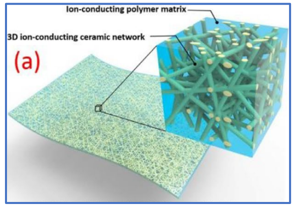
- Similar structure to a template
- Li-ion conductance pathways design

Introduction Application of biomass materials in CSE design





Bio-template



Templated CSE

- **Abundant functional groups**
- **Hierarchical framework**

- **Continuous and thin structure**
- **Uniform/ ordered/ aligned Li-ion pathways**

ACS Materials Lett. (2019) 1, 3, 354–361; Advanced Energy Materials (2018) 8, 18, 1703474

2 LNP-regulated CNF film templated LLZO-PEO CSE

——with uniform and controllable Li-ion conductance pathways

Thin, flexible, and conductive LLZO-PEO CSE

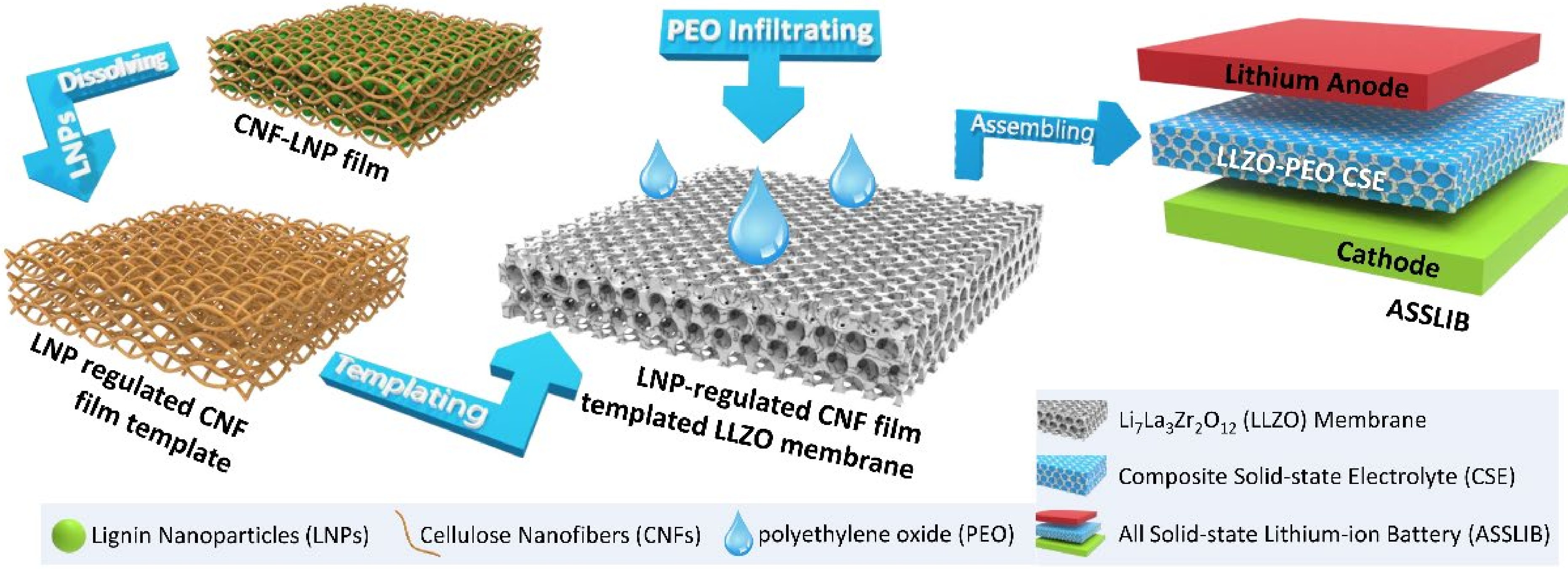
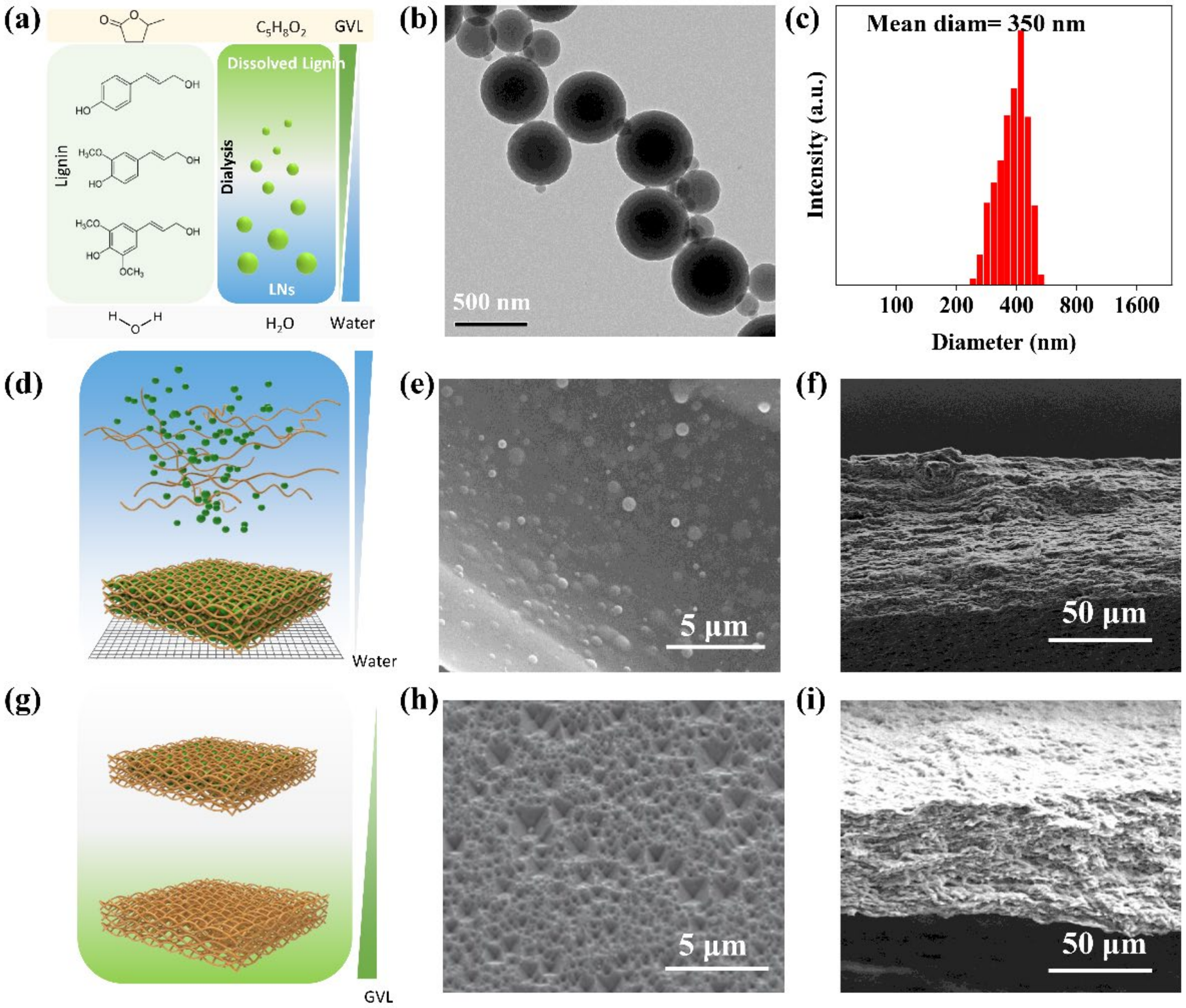


Figure 1: The illustration of CNF-LNP templated LLZO-PEO CSE fabrication.

Chem. Eng. J. 425 (2021) 130632

2.1 LNPs and LNP-regulated CNF film



Lignin nanoparticles (LNPs)

- Dialysis nanoprecipitation method
- average size of 350 nm

CNF-LNP composite film

- **Well distribution** of LNPs in CNF network

LNP-regulated CNF film

LNPs was dissolved from film

- **Uniform and porous structure was formed**
- Thin thickness of ~80 μm

Figure 2: characterization of LNPs and CNF-LNP template film. (a) The preparation schematic, (b) TEM images and (c) particle size distribution of LNPs. (d) and (g) The preparation schematic, (e) and (h) top surface, (f) and (i)cross-sectional SEM images of (f) CNF-LNP composite film and LNP-regulated CNF film.

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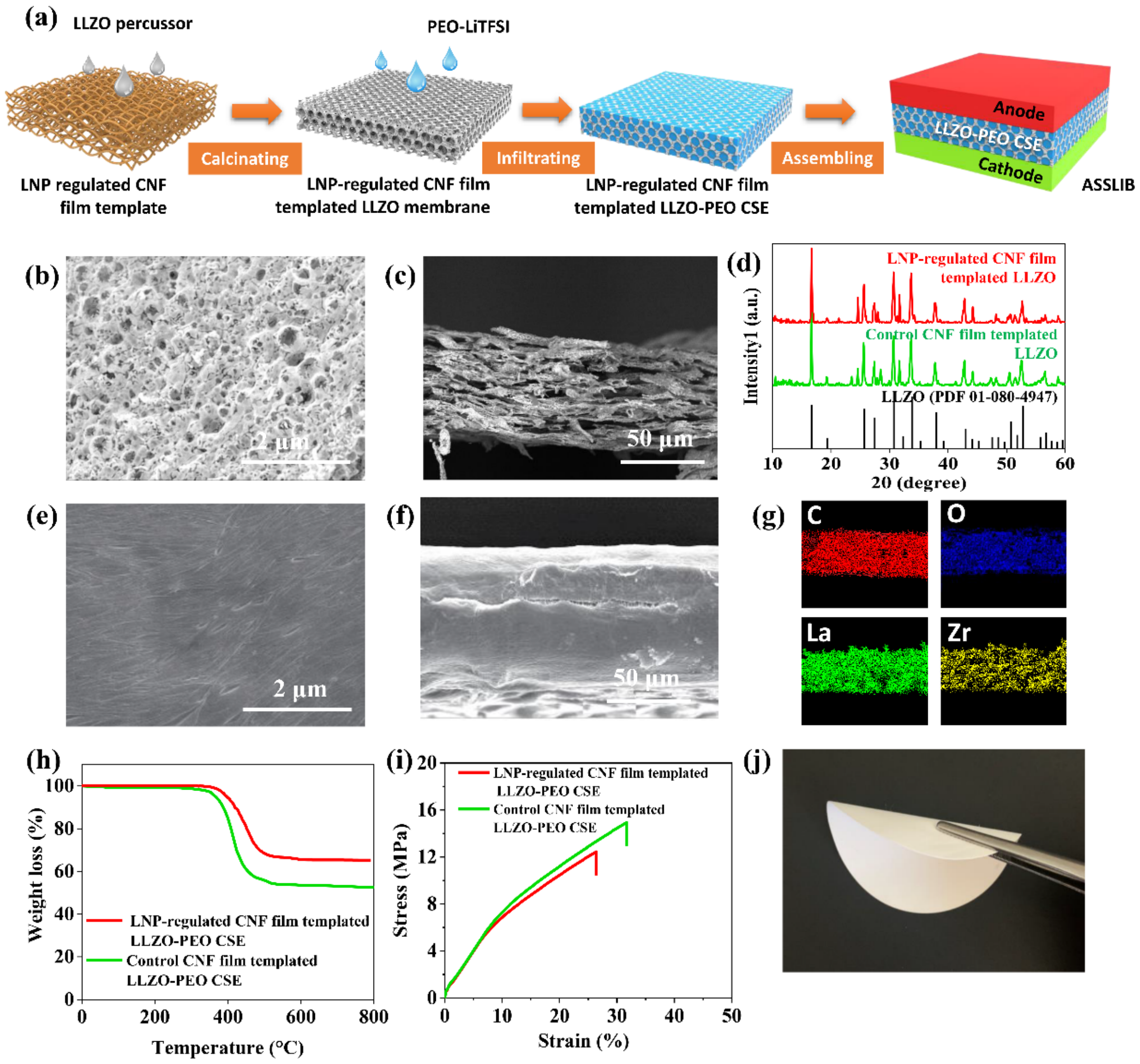
2.2 LNP-regulated CNF film templated LLZO and LLZO-PEO CSEs



LNP-regulated CNF film templated LLZO

- **Uniform and porous structure**
- Pores of hundreds of nanometers
- Thin thickness of ~70 µm

Templated LLZO-PEO CSEs

- Uniform penetration of PEO-LiTFSI
- Thin thickness of ~80 µm
- Excellent Thermal Stability
- High mechanical strength & flexibility

Figure 3: Characterization of LLZO membranes and CSEs.
(a) The preparation schematic, (b) top surface and (c) cross-sectional SEM images, (d) XRD patterns of LLZO membranes. (e) Top surface and (f) cross-sectional SEM images and (g) EDS element mappings, (h) TGA, (i) stress-strain curves and (j) Digital photographs of CSEs.

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2.3 Electrochemical performance of CSEs

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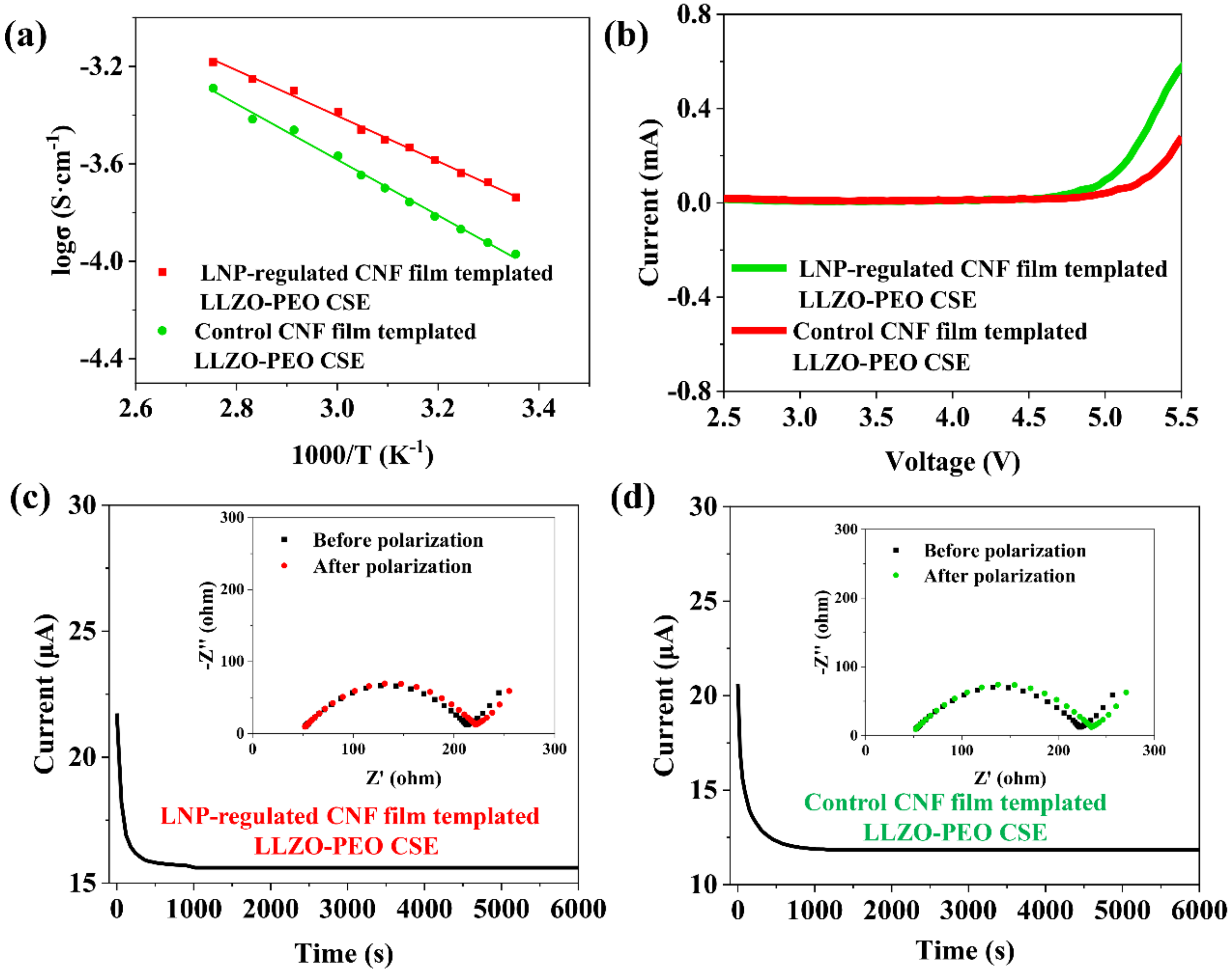

LNP-regulated CNF film templated LLZO-PEO CSE

vs. Control CNF templated LLZO-PEO CSE

Ionic conductivity

- **1.83×10^{-4} S·cm^{-1}** vs. 1.07×10^{-4} S·cm^{-1} (25°C)

Electrochemical window

- **5.0 V** vs. 4.8 V (25°C)

Lithium transference number t_{Li+}

- **0.65** vs. 0.48 (25°C)

Figure 4: Electrochemical properties of CSEs.
(a) Arrhenius plots of ionic conductivity, (b) LSV curves, (c) and (d) DC Polarization curve and the inset AC impedance spectra before and after the polarization for CSEs at 25 °C.

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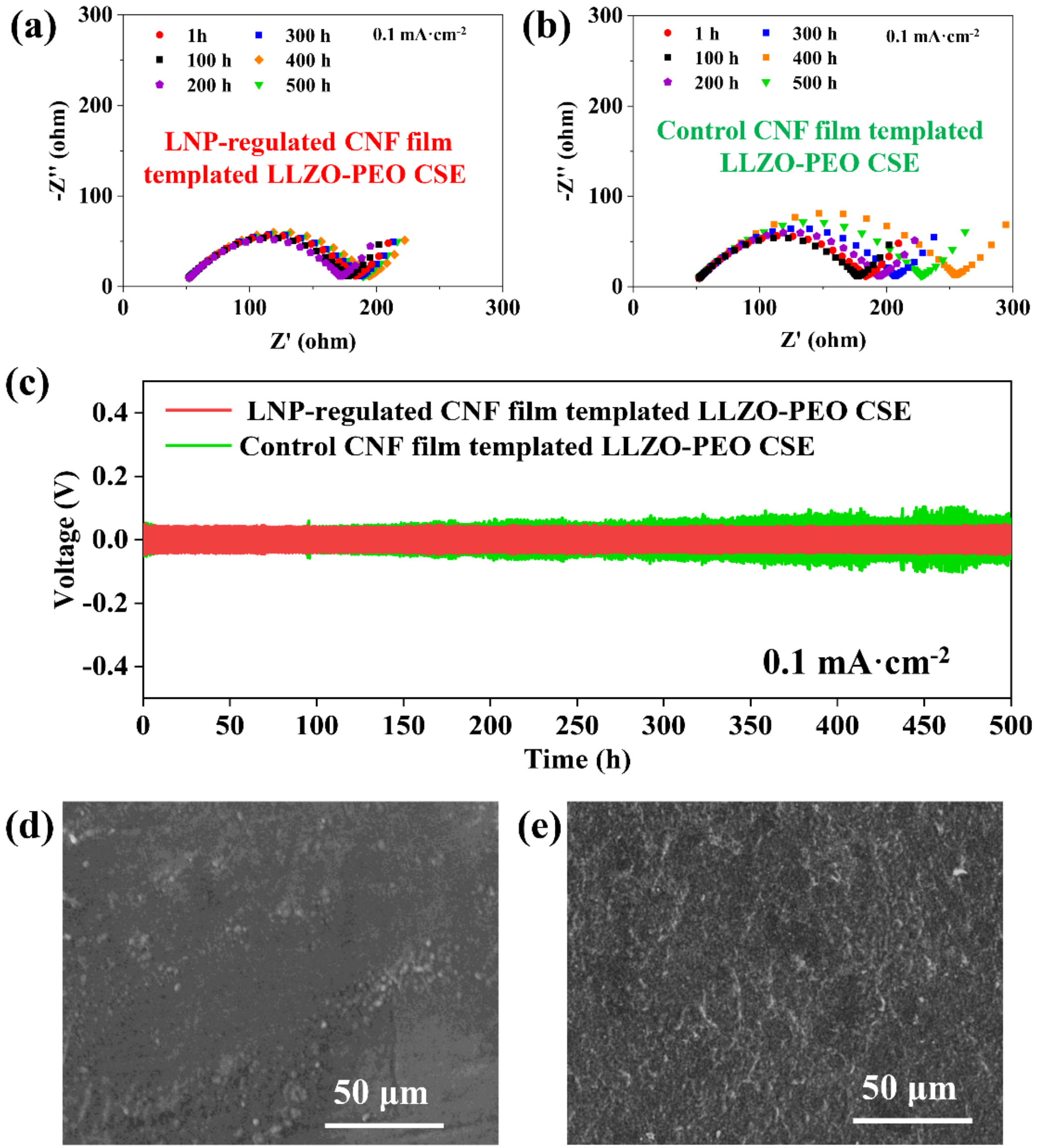
2.4 Interface compatibility of CSEs with Li anode



Stripping/plating behavior

LNP-regulated CNF film templated LLZO-PEO CSE

- **Outstanding interface stability**
- **Stable voltage (red line) in 500 h**
- **Uniform lithium deposition**

Control CNF templated LLZO-PEO CSE

- Obvious resistance changes
- Obvious increase (blue line)
- Obvious lithium dendrites on the Li surface

Figure 5: Interface compatibility between CSEs with Li anode.
(a) and (b) Nyquist plots, (c) Galvanostatic cycling curves of the symmetric Li batteries assembled with CSEs, (e) and (f) SEM images of lithium anode surface contacted with CSEs after cycling.

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2.5 Battery performance of CSEs— LFP batteries

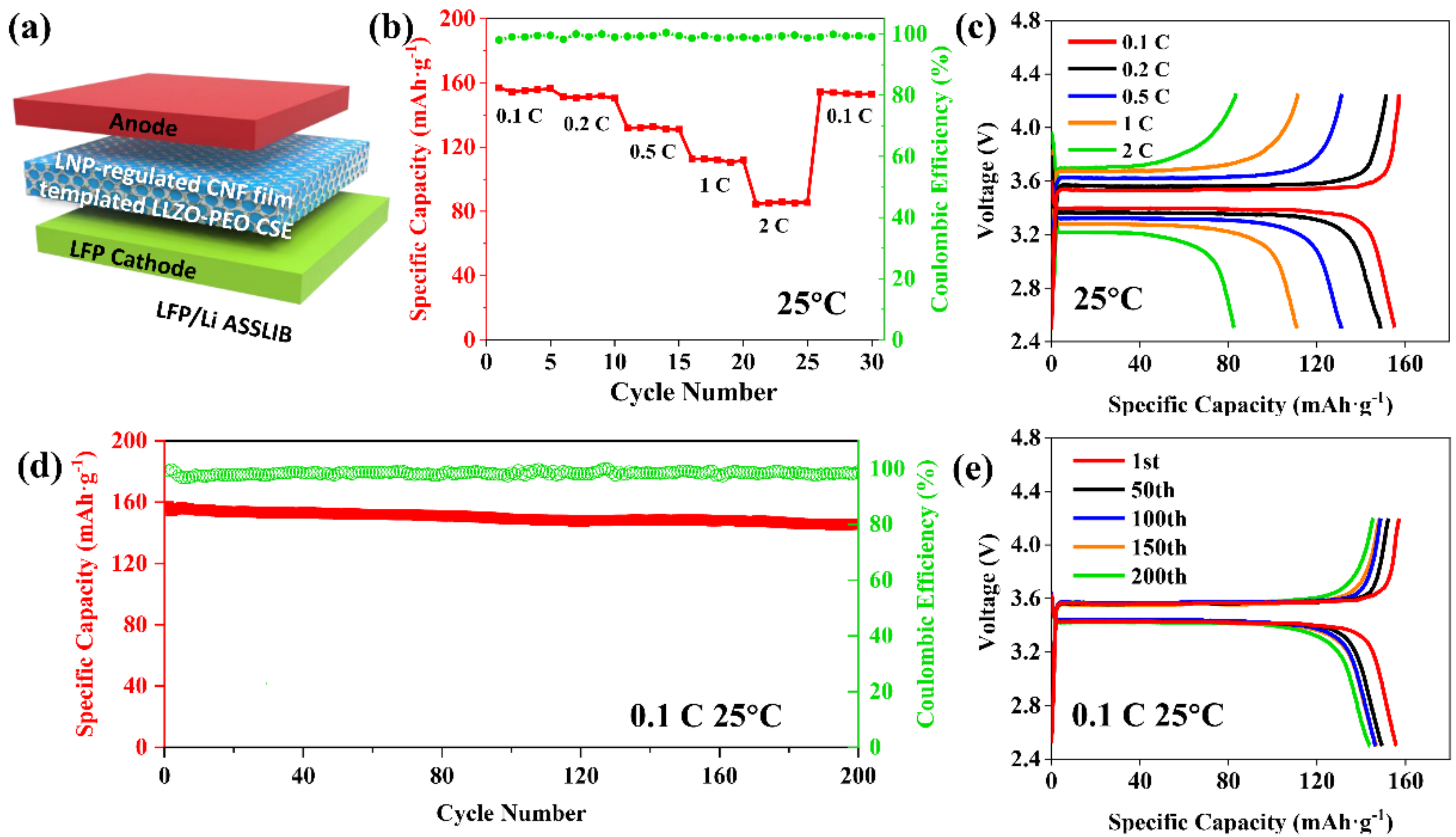

Figure 6: Electrochemical performance of LFP/CSE/Li batteries.
(a) Schematic diagram, (b) and (d) Charge and discharge voltage profiles,
(c) and (e) the cycling stability with coulombic efficiency of LFP/CSE/Li batteries under different rates and 25°C

Li/CSE/LFP batteries

Initial discharge capacity

157 mA h·g^{-1} at 0.1 C

C-rate performance:

98.5% capacity retention after high-rate cycles

Cycling performance

92.7% capacity retention after 200 cycles

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2.5 Battery performance of CSEs— NMC batteries

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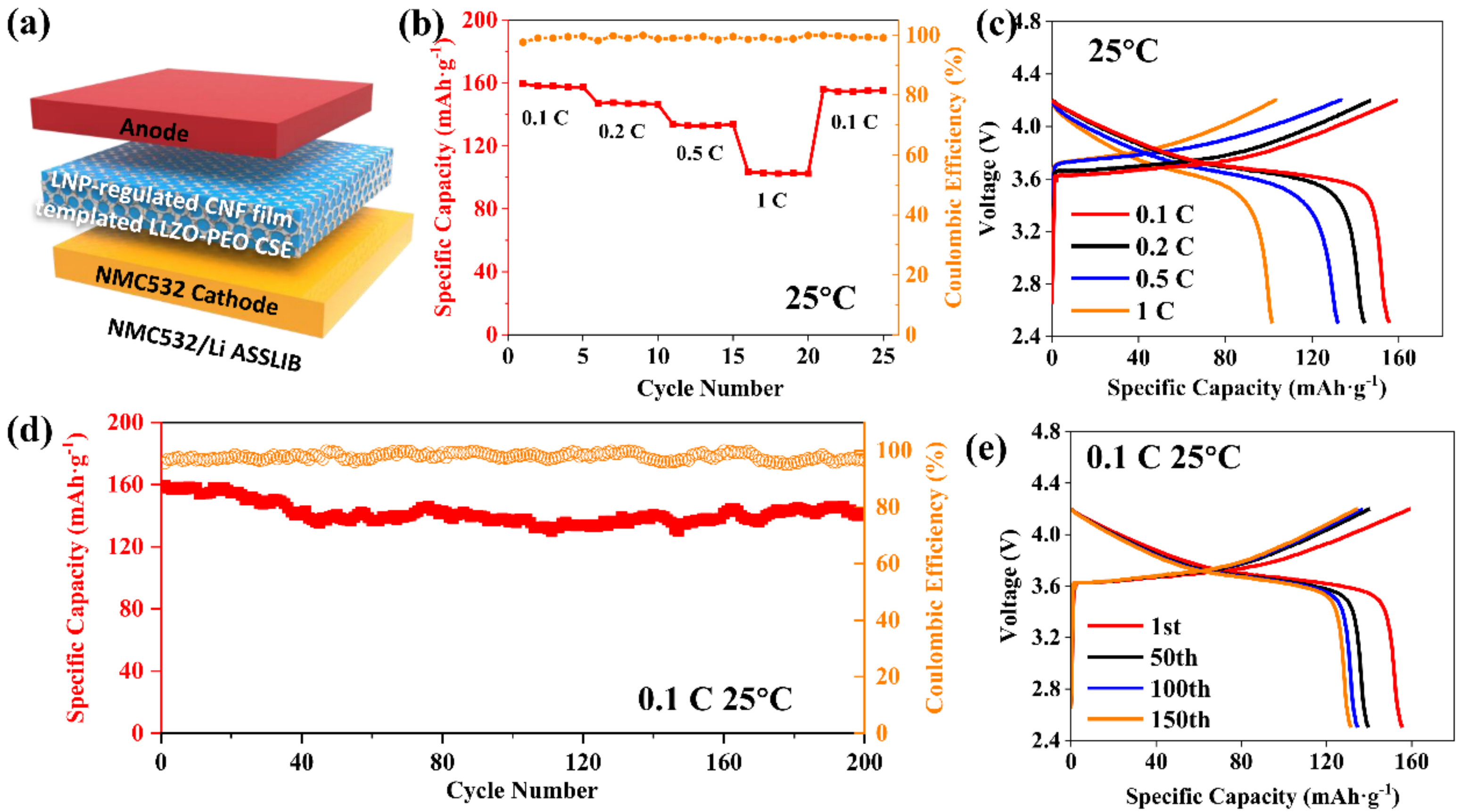

Figure 7: Electrochemical performance of NMC532/ CSE/Li batteries.
(a) Schematic diagram, (b) and (d) Charge and discharge voltage profiles,
(c) and (e) the cycling stability with coulombic efficiency of NMC532/ CSE/Li batteries under different rates at 25°C

Li/CSE/NMC532 batteries

Initial discharge capacity

159.5 mA h·g^{-1} at 0.1 C

C-rate performance:

96.7% capacity retention after high-rate cycles

Cycling performance

96% capacity retention after 200 cycles

3 Upright cellulose layer templated LLZO@PEO-LiTFSI CSE

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—— with vertically aligned Li-ion pathways

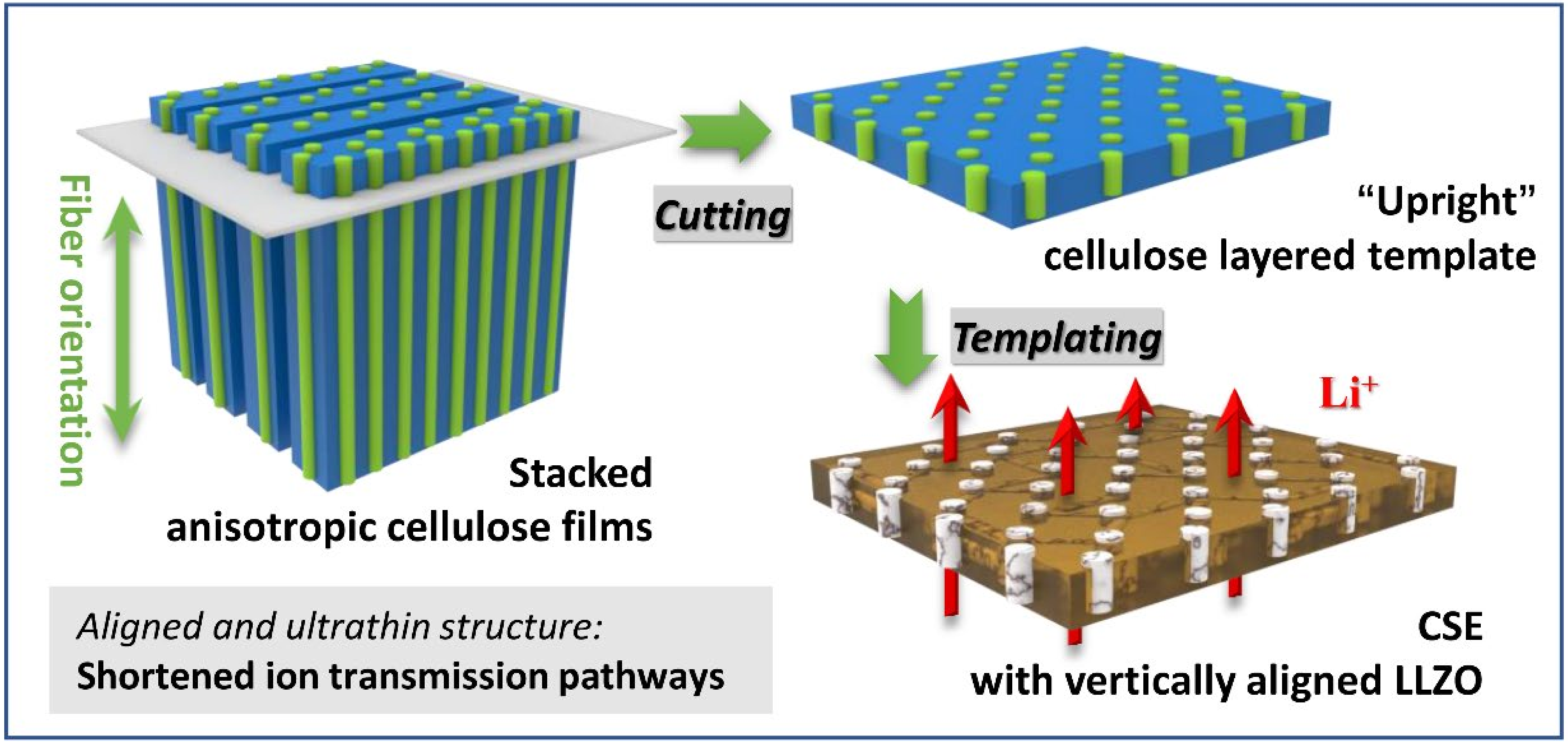

Figure 8: The illustration of Upright cellulose layer templated LLZO@PEO-LiTFSI CSE fabrication.

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3.1 Anisotropic cellulose film and cellulose layered template

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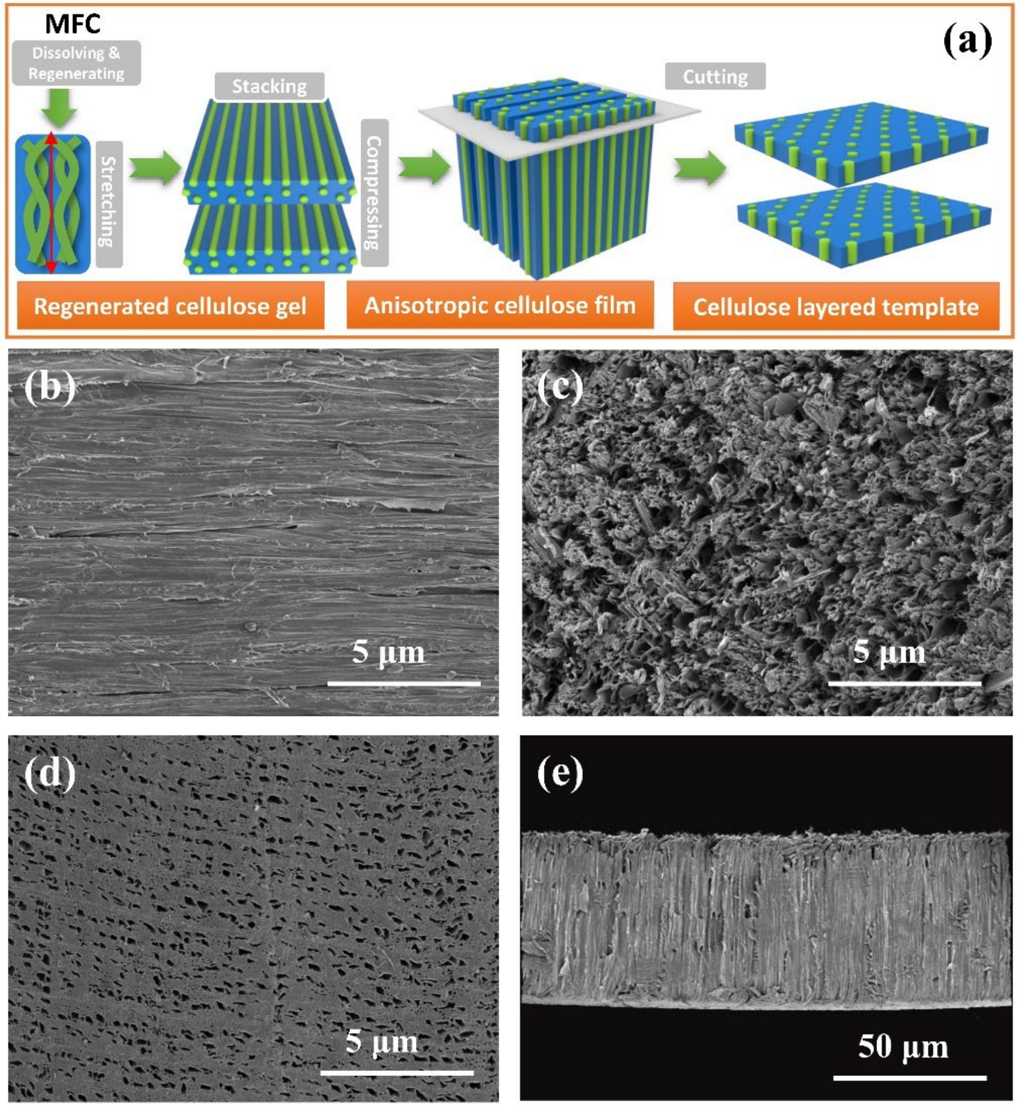

Figure 9: The fabrication and characterization of the anisotropic cellulose film and the cellulose layered template.

Fabrication

- Anisotropic cellulose film:

  MFC dissolving-Pre-stretching-Regeneration
- Cellulose layered template:

  Stacking-Compressing-Cutting

Anisotropic cellulose film

- Surface: vertically aligned fiber structure
- Cross section: highly oriented porous structure

Cellulose layered template

- Structure: highly aligned, closely packed
- Thickness: 40 µm

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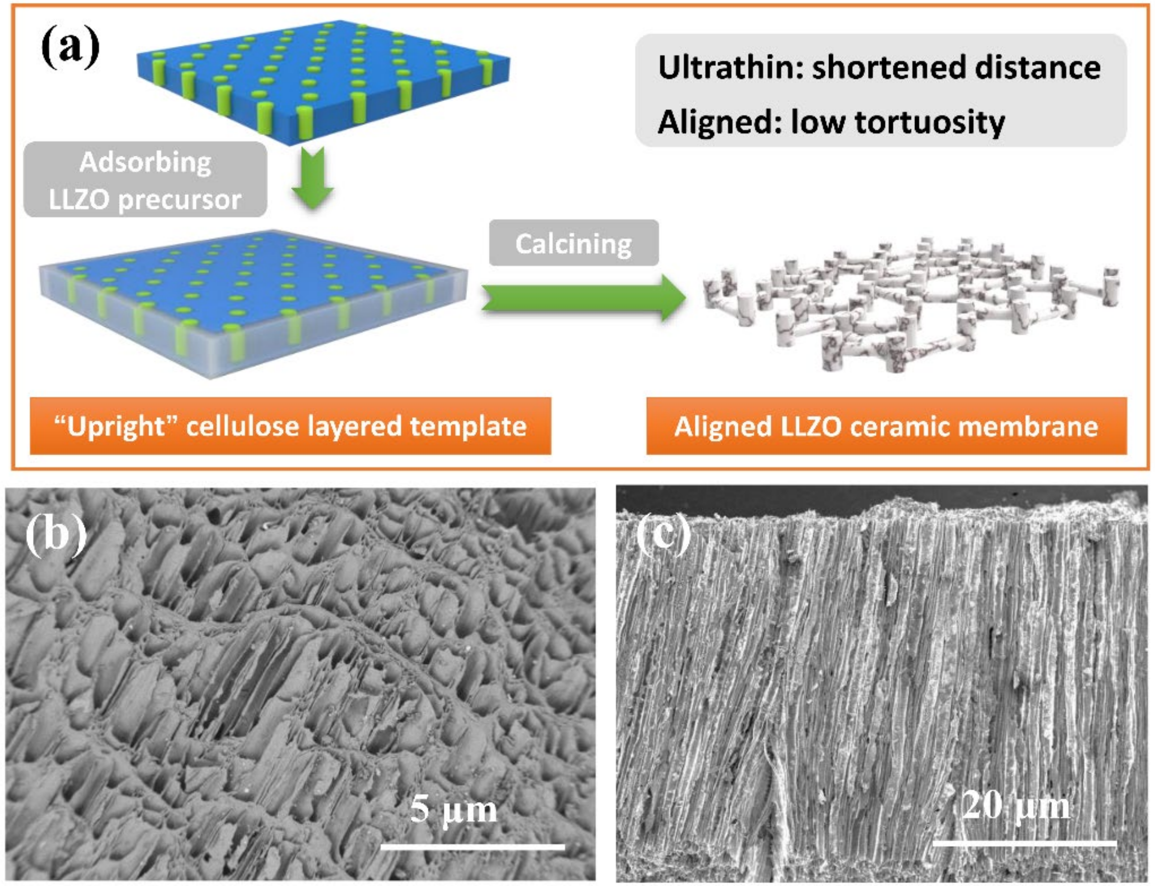
3.2 Vertically aligned LLZO ceramic membrane



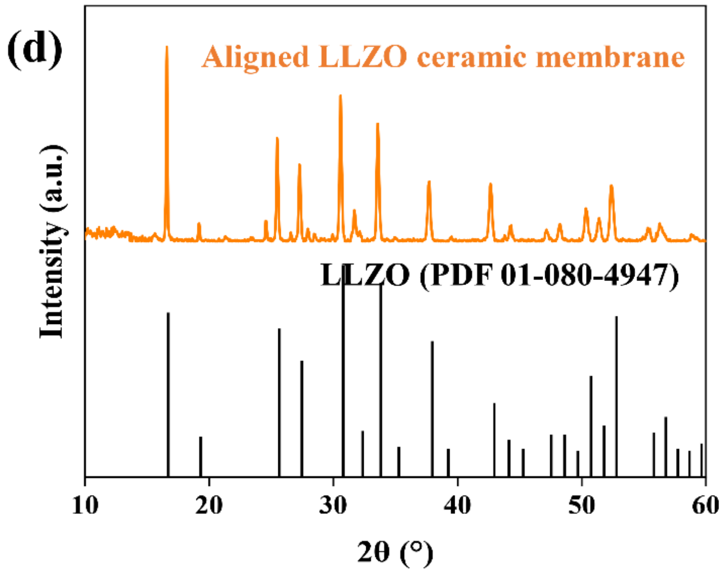


Figure 10: The fabrication and characterization of the LLZO ceramic membrane.
(a) Schematic, (b) Top view and (c) cross sectional view SEM images, (d) XRD pattern.

LLZO ceramic membrane

- Surface: low-tortuosity channels
- Cross section: **a vertically aligned whole**
- Thickness: 50 μm
- XRD: cubic-phase, garnet-type

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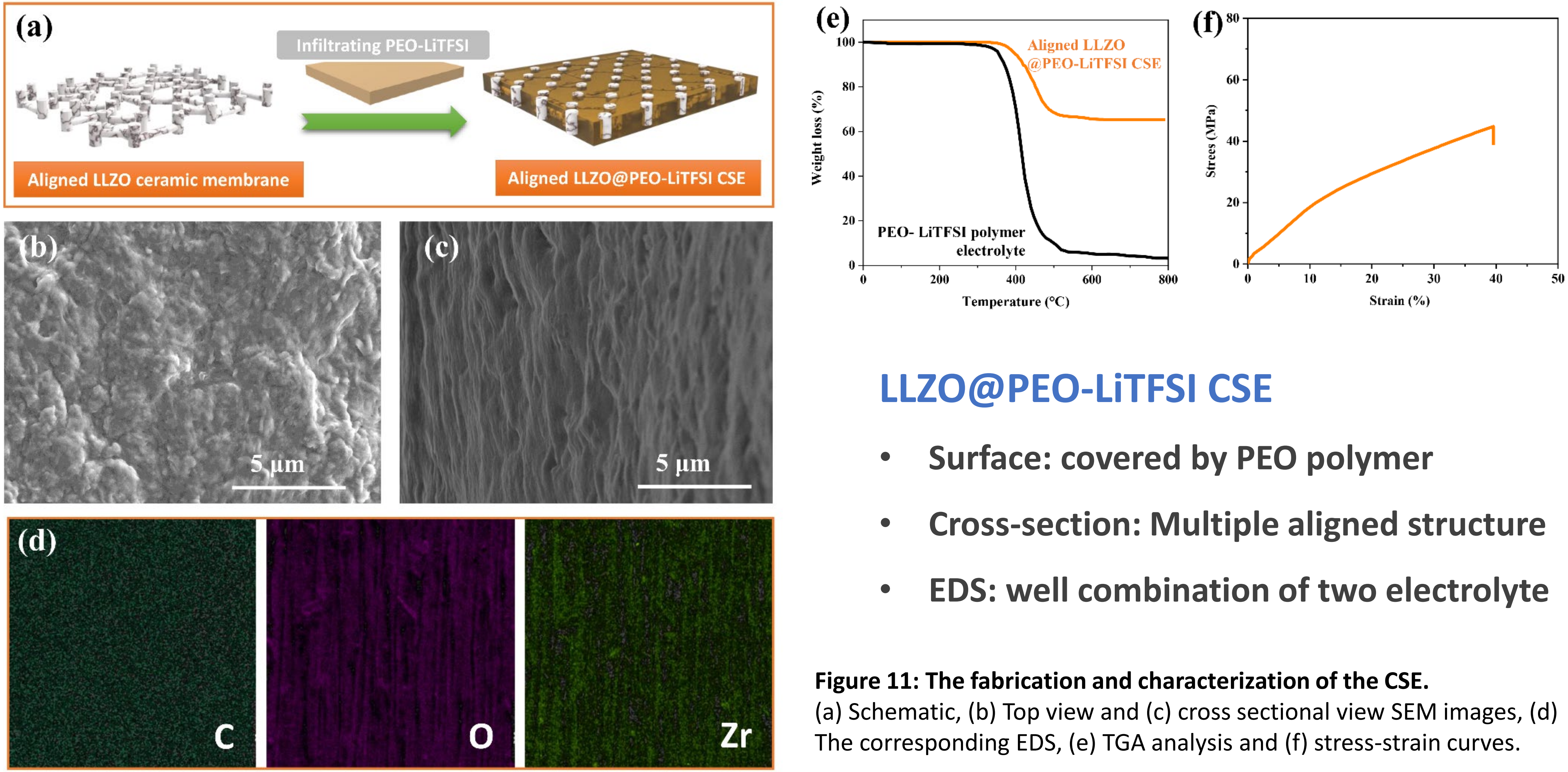
3.3 Multiscale aligned LLZO@ PEO-LiTFSI CSE



LLZO@PEO-LiTFSI CSE

- Surface: covered by PEO polymer
- Cross-section: Multiple aligned structure
- EDS: well combination of two electrolyte

Figure 11: The fabrication and characterization of the CSE.
(a) Schematic, (b) Top view and (c) cross sectional view SEM images, (d) The corresponding EDS, (e) TGA analysis and (f) stress-strain curves.

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3.4 Lithium transport hypothesis of aligned LLZO@ PEO-LiTFSI CSE

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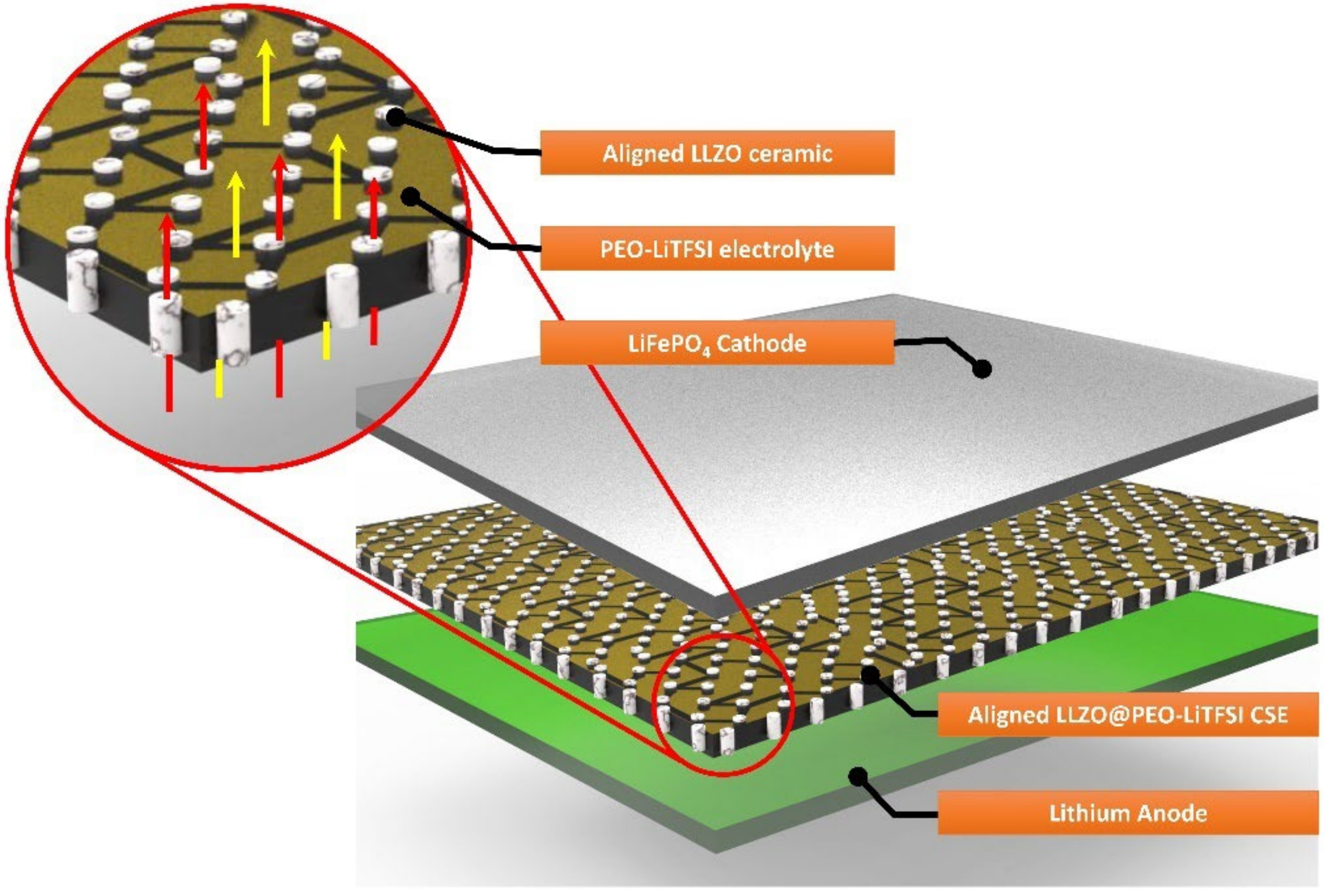

Figure 12 Schematic of ASSLIBs with the multiscale aligned LLZO@PEO-LiTFSI CSE showing fast lithium transport pathways with low tortuosity

Highly aligned channels

- Low tortuosity
- Short distance

Multiple Li- transport pathways

- LLZO ceramic (The fastest way)
- PEO-LiTFSI electrolyte (Low crystal)
- Ceramic/polymer interface (Low resistance)

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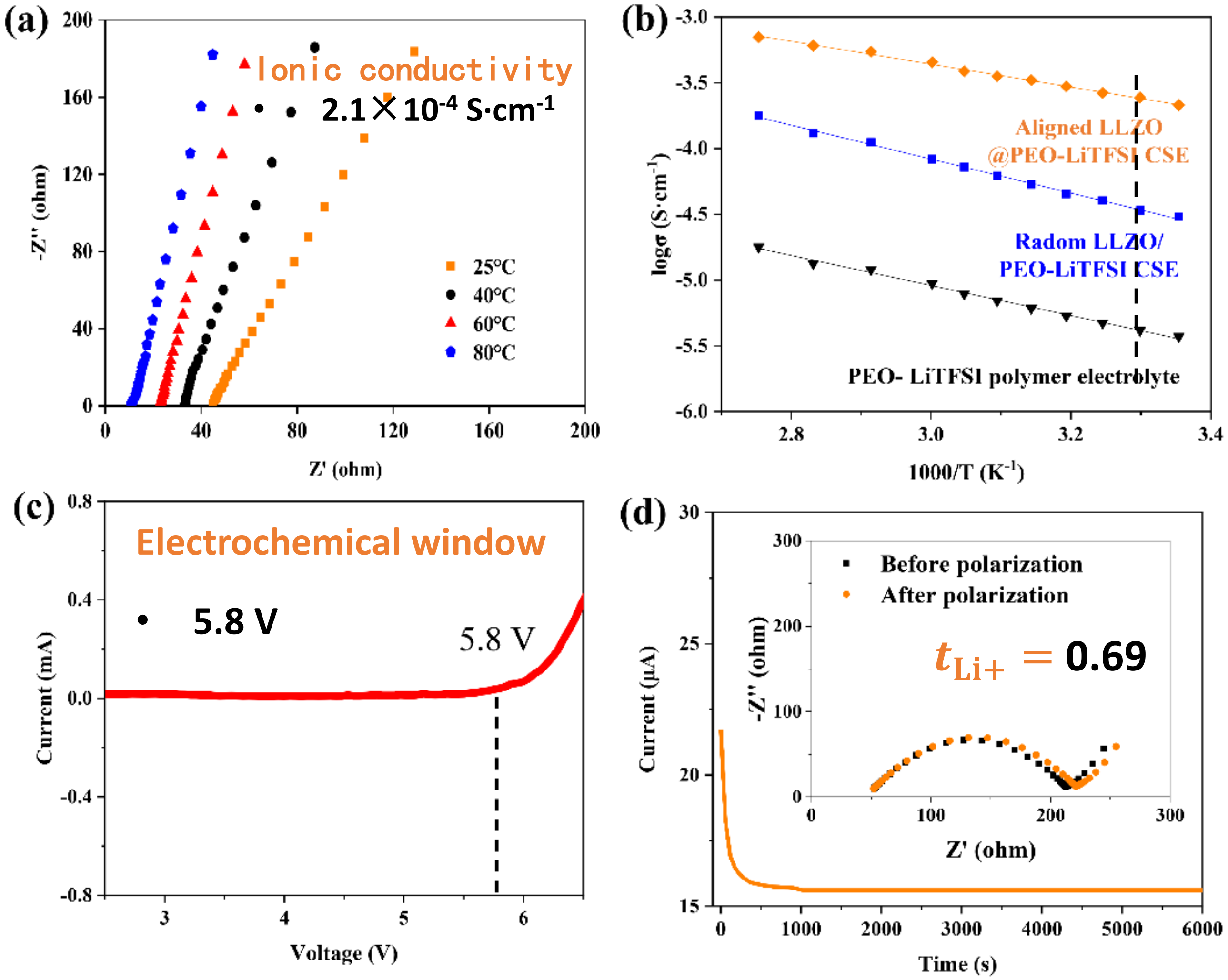
3.5 Electrochemical performance of CSEs



Aligned LLZO@ PEO-LiTFSI CSE

Ionic conductivity

- 2.1×10^{-4} S·cm^{-1}

Electrochemical window

- 5.8 V

Lithium transference number t_{Li+}

- 0.69

Figure 13: Electrochemical properties of CSEs.
(a) Nyquist plots, (b)Arrhenius plots of ionic conductivity, (c) LSV curves, (d) DC Polarization curve and the inset AC impedance spectra before and after the polarization for CSEs at 25 °C.

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3.6 Interface compatibility of CSEs with Li anode

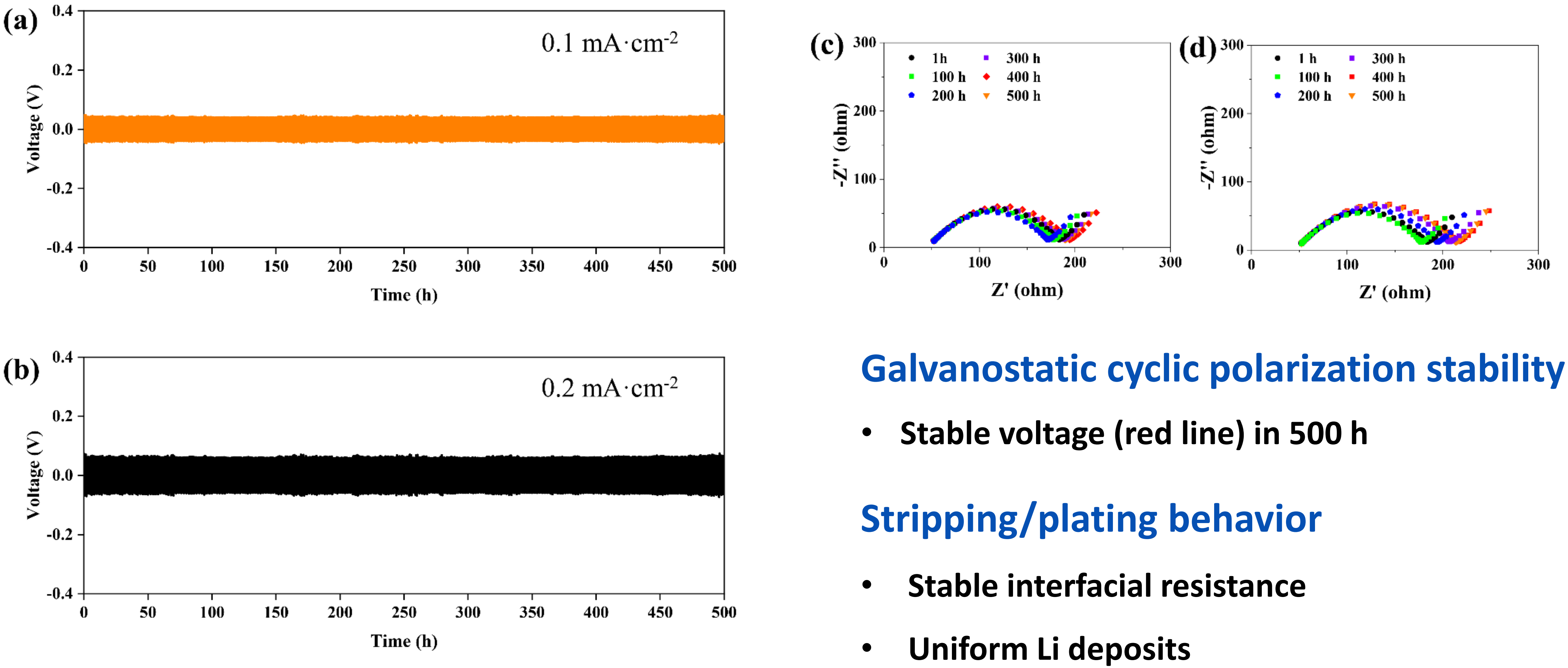

Figure 14: Interface compatibility of the CSEs in Li/Li symmetric cells at 25° C. (a) (b) Galvanostatic cycling curves and (c) (d) Nyquist plots of the symmetric Li batteries assembled with CSEs

Galvanostatic cyclic polarization stability

- **Stable voltage (red line) in 500 h**

Stripping/plating behavior

- **Stable interfacial resistance**
- **Uniform Li deposits**

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3.7 Battery performance of CSEs— LFP batteries

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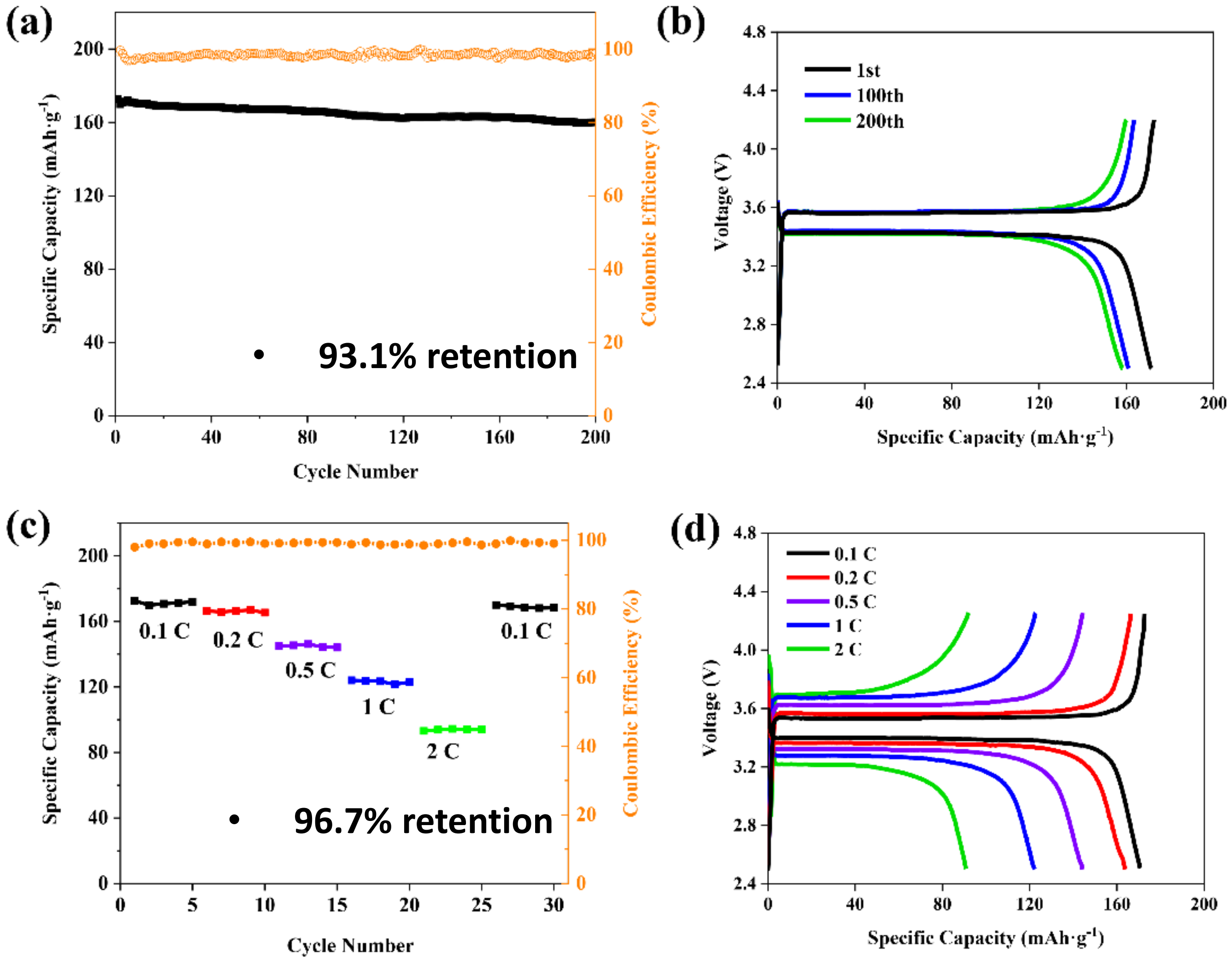

Li/CSE/LFP batteries

Initial discharge capacity

- **172.3 mA h·g^{-1} at 0.1 C**

Cycling performance

- 93.1% capacity retention after 200 cycles at 0.1 C

C-rate performance:

- 96.7% capacity retention after high-rate cycles

Figure 15: Electrochemical characterizations of CSEs in Li/LFP cells. (a) and (b) Charge and discharge voltage profiles, (c) and (e) the cycling stability with coulombic efficiency under different rates.

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3.8 Battery performance of CSEs—Extreme conditions

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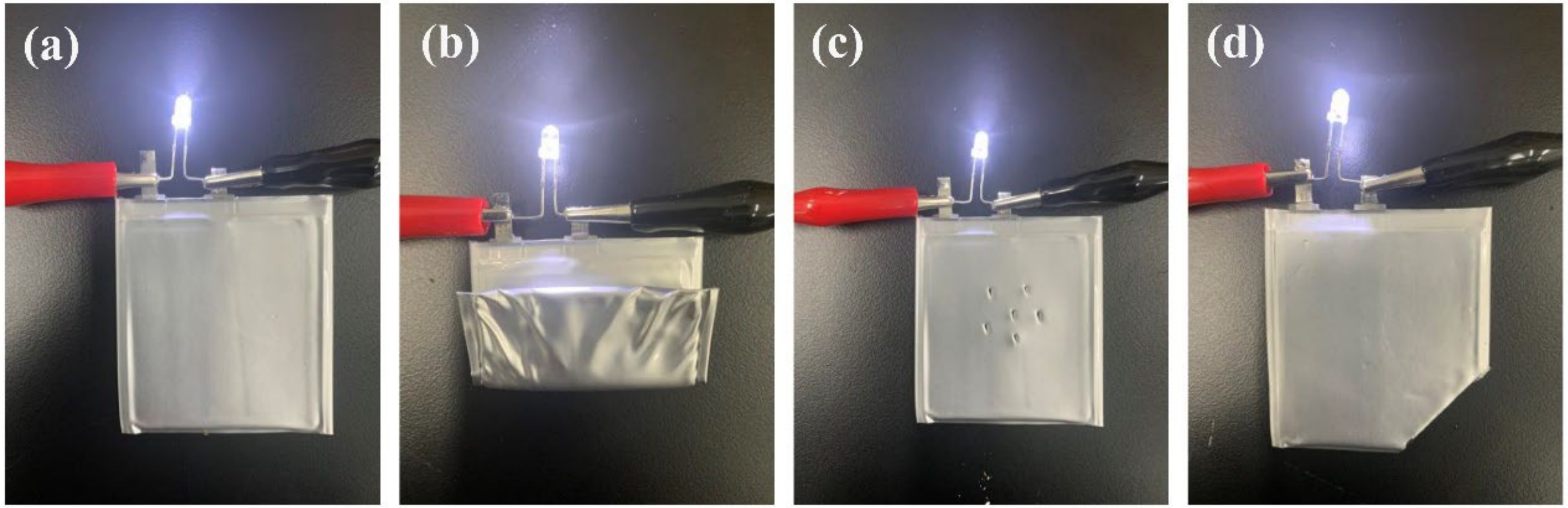

Figure 16: Digital photos of flexible pouch cells showing excellent performance by lighting up an LED bulb.
(a) in normal state, (b) under/after folding, (c) after nail test and (d) after cutting a corner.

The assembled pouch cells keep stable running

under/after folding, after nail test and after cutting a corner.

4 Summary

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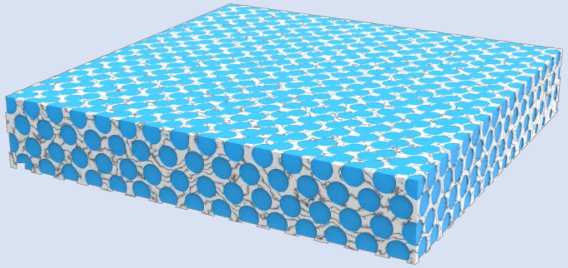
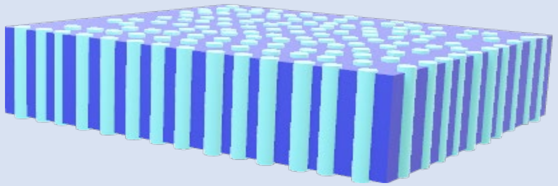
(1) LNP-regulated CNF film templated LLZO/PEO CSE

- Controllable template, porous LLZO membrane in CSE;
- Uniform and regular Li-ion conductance pathways.



(2) Upright cellulose layer templated LLZO@PEO-LiTFSI CSE

- Oriented template, aligned LLZO and PEO structure in CSE;
- Short and low-tortuosity Li-ion conductance pathways



4 Outlook

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Development of <u>sus</u>tainable <u>tec</u>hnologies for electrical energy storage based on biomaterials and 3D printing (SUSTEC)

To Manufacture of a new generation of *green solid-state sodium-ion batteries (SSIBs)*

https://www.innovationnewsnetwork.com/sustec-project-develops-sustainable-3d-printed-sodium-batteries/25794/

Project team

Åbo Akademi University

Laboratory of Natural Materials Technology (NMT)
Laboratory of Molecular Science and Engineering (MSE)

- **Supervisors:** Prof. Johan Bobacka, Prof. Chunlin Xu
- **Senior researcher:** Zekra Mousavi
- **Fresh researcher:** Hao Zhang
- **Doctoral researcher:** Angelo Robiños
- **Cooperation:** Prof. Leena Hupa, Tor Laurén

https://www.abo.fi/en/natural-materials-technology-research-and-personnel/
https://www.abo.fi/en/laboratory-of-molecular-science-and-engineering-research-and-personel/
https://jaes.fi/en/donations-granted/donations-granted-2022/

Project objectives

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Electrochemistry side:

to solve critical issues in battery

- electrode capacity,
- electrolyte ion transport efficiency,
- interface stability

Material side:

to further expand the application of sustainable wood-derived materials in battery components.

The research initiatives:

Nanostructures of sustainable materials

- Electron transport (electrode),
- ion transport (electrolyte),
- interfacial reactions.

Microstructures regulated by 3D printing

- Capacity of SSIBs,
- Energy/power density of SSIBs.

Using our expertise in natural materials, 3D printing and electrochemistry.

Project method

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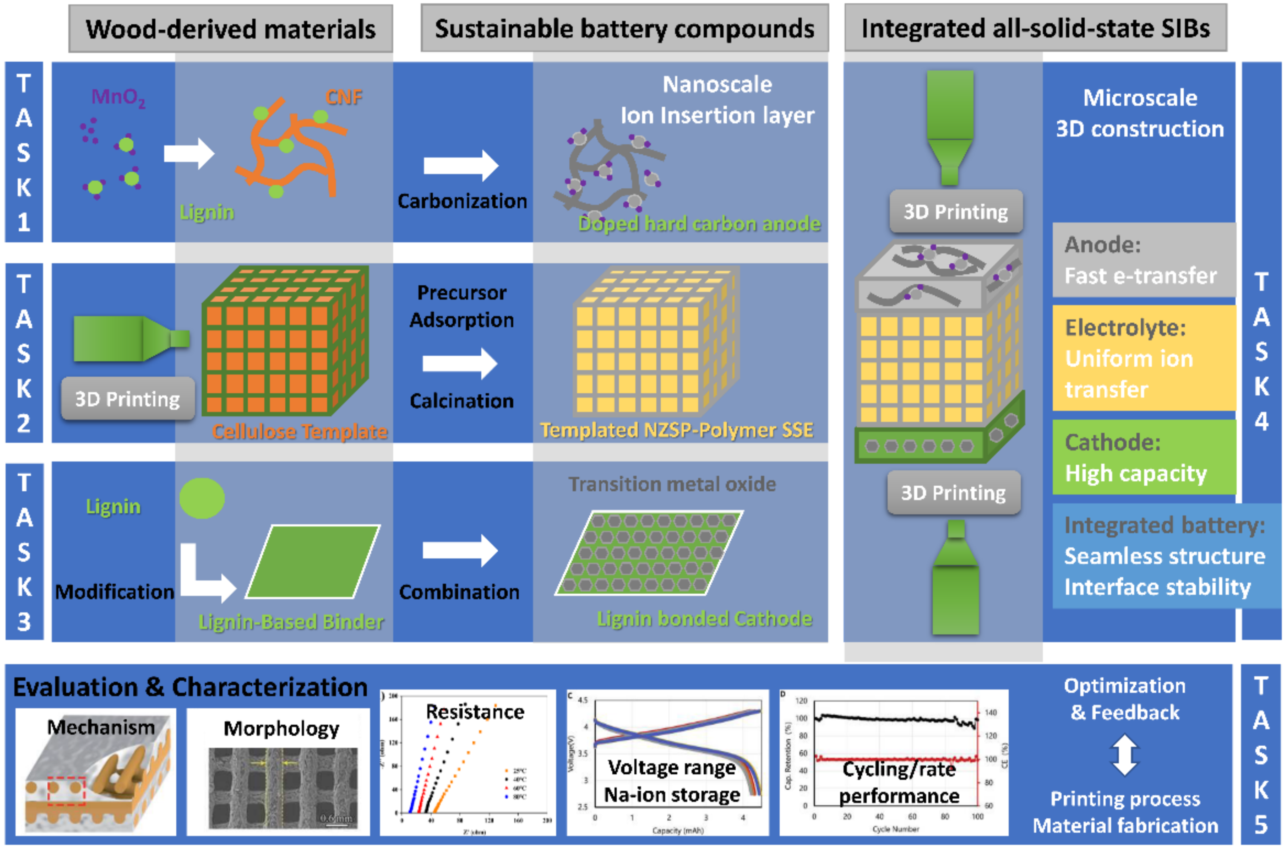
The end products:

- A wood-derived carbon anode
- A wood-derived templated electrolyte
- A bio-bonded cathode
- Their assembly into an integrated SSIB by 3D printing.



Technologies for a Sustainable Future

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University

- **We are highly in line with the research profile Technologies for a Sustainable Future at our university**
  - To develop new technology to replace fossil raw materials with renewable resources such as biomass and solar energy,
  - to find technical solutions that will slow down the ongoing climate change and to contribute to a clean environment and sustainable society.
- **A new generation of sustainable SIB components utilizing wood-derived materials in green energy storage devices will come true.**

EWLP 2024

17th European Workshop on Lignocellulosics and Pulp

26-29 AUGUST 2024

Åbo Akademi University, Finland

https://ewlp2024.fi/

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Thank you for your attention!

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