Enabling High-Voltage Solid-State Lithium Metal Batteries through Polymer Electrolyte Engineering

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1. Abstract

Within the framework of the HyLiST project, this work addresses the shift toward high-energy solid-state lithium metal batteries by developing polymer electrolytes derived from PMTFSI (SLIC, single lithium-ion conducting systems). To enable stable operation up to 5 V, compositional tuning is used to balance high ionic transport with structural robustness. The membranes are manufactured using dry-processing techniques, ensuring compatibility with sustainable and scalable production. Through a progressive evaluation methodology, key transport and stability phenomena are decoupled to establish fundamental design guidelines for next-generation, high-performance polymer electrolytes.

2. Results

2.1 Material selection

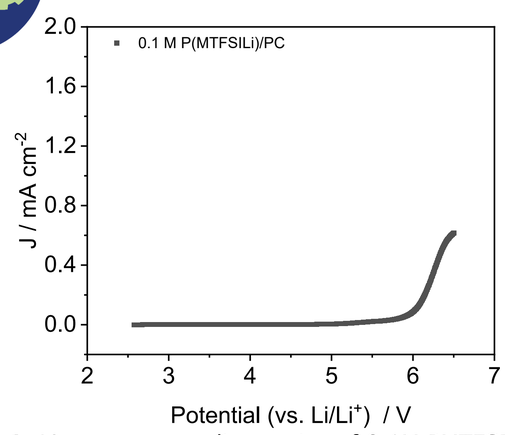


Figure 1. Linear sweep voltammetry of 0.1M PMTFSILi in PC. Three-electrodes setup was employed with Li chips as counter and reference electrode and platinum disc as working electrode with a scan rate of 0.1 mV/s

- ✓ PMTFSILi was selected as source of Li^+ due to its high anodic stability for SLIC preparation
- ✓ Sulfolane was identified as potential plasticizer because of its known wide electrochemical window as a compromise towards lithium metal and high voltage stabilities
- ✓ Additionally, alumina and PVDF-HFP were included in the formulation to bring self-standing properties and membrane robustness
- ✓ The selected ratios were identified in the seek for the best compromise between ionic conductivity and structural integrity

Table 1. Recipes of studied formulations in weight percent.

Component	CPE1	CPE2	CPE3
PMTFSILi (Mw 395 KDa)	49.50	47.15	41.25
Sulfolane	35	35	35
PVDF-HFP (Mw 400 KDa)	5.50	7.85	13.75
Al_2O_3 (5nm)	10	10	10

PMTFSI:PVDF-HFP: CPE1 (9) > CPE2 (6) > CPE3 (3)

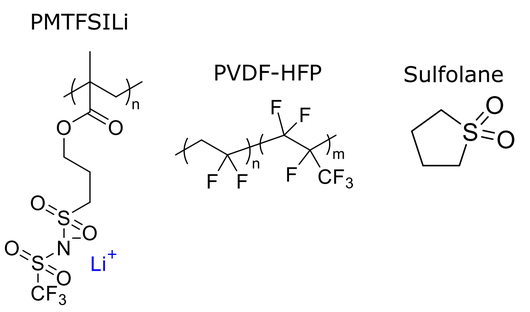


Figure 2. Chemical structure of the polymer electrolyte components: PMTFSILi, PVDF-HFP and sulfolane plasticizer

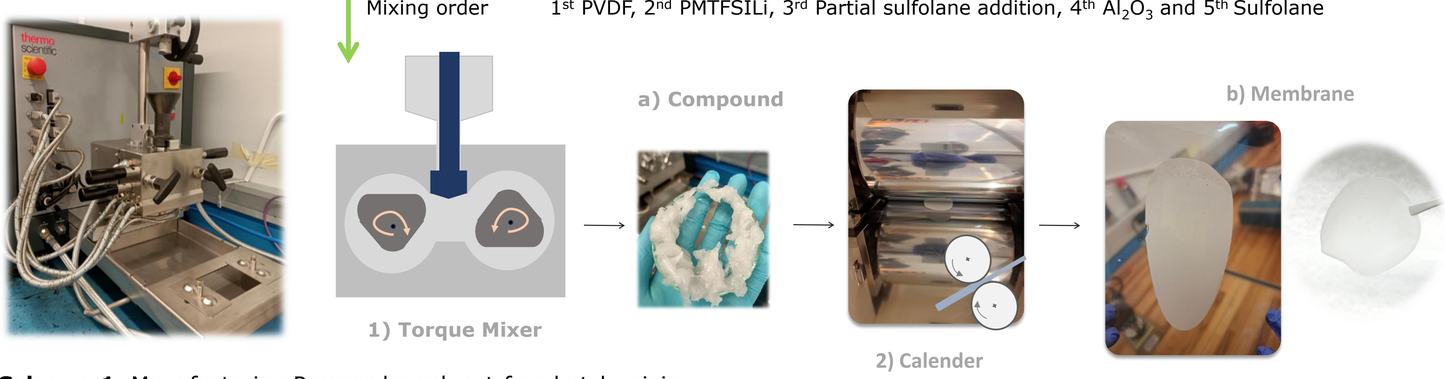
2.2 Processing of SLIC membranes

- ✓ The resultant formulations were manufactured by dry-processing technique in gram scale inside dry room (dew temperature -60 ºC)
- ✓ On this way, solvent removal step, which typically leads to plasticizer evaporation, is avoided in a highly scalable process
- ✓ 100 µm thick membranes were obtained in the range of 10 x 20 cm

Two step process:

1) Mixing of the materials with the torque mixer to obtain a homogeneous a) compound.
2) Calendering of the compound to obtain a b) membrane with the desired thickness

Temperature (ºC): 130ºC Based on TGA and DSC results.
Speed (rpm): fixed 30 rpm
Mixing order 1st PVDF, 2nd PMTFSILi, 3rd Partial sulfolane addition, 4th Al_2O_3 and 5th Sulfolane



Scheme 1. Manufacturing Process by solvent-free batch mixing

2.3 Transport properties

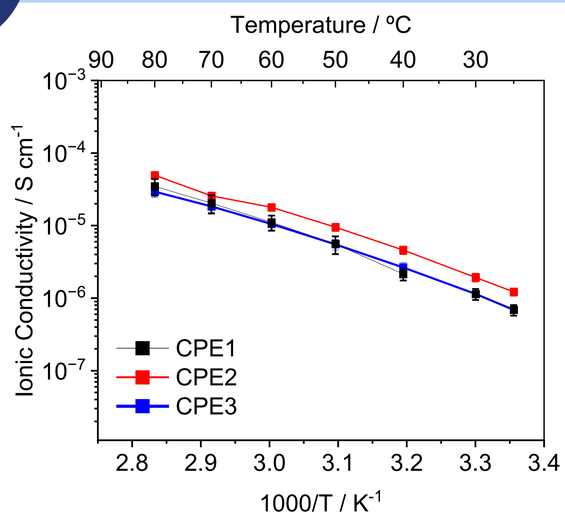


Figure 2. Ionic conductivity of HYl06, HYl07 and HYL08 in the temperature range of 25 to 80 ºC

- ✓ Conductivities of $1.8 \cdot 10^{-5}$ S/cm were reached with CPE2 at 60 ºC, while CPE1 and CPE3 remained slightly lower ($1.1 \cdot 10^{-5}$ S/cm)

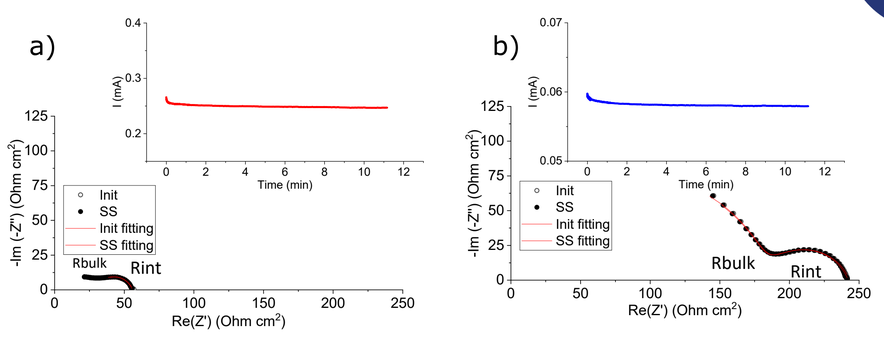


Figure 3. Electrochemical measurement of lithium transference number for a) CPE2 and b) CPE3 at 60 ºC

- ✓ Single-ion properties were confirmed by measuring lithium transference number employing Bruce-Vincent method.
- ✓ Flat chronoamperometries were obtained accompanied by low interfacial resistances, which is a sign of SLICs.
- ✓ As a result, reproducible values of 0.90 ± 0.02 (CPE2) and 0.95 ± 0.01 (CPE3) were obtained.

2.4 Cell cycling in Li||Li

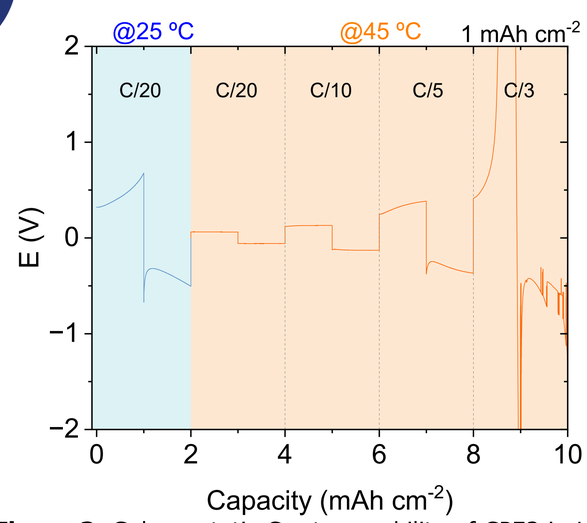


Figure 3. Galvanostatic C-rate capability of CPE3 in Li||Li cells at different temperatures considering 1 mAh cm^{-2}.

- ✓ CPE3 obtained the best compromise between mechanical properties and transport properties being able to cycle at C/5 at 45 ºC.

3. Conclusions

- Scalable production successfully validated by solvent-free dry process for manufacturing SLIC gel polymer electrolyte membranes, demonstrating a sustainable production route.
- Ionic conductivities in the range of 10^{-5} S/cm has been obtained, combined with exceptional single-ion selectivity for lithium carriers.
- As a proof of concept, the membrane with the best compromise between mechanical properties and ionic conductivity (CPE3) provided C/5 capability at 45ºC in Li||Li cells.

References

1. https://hylist.eu/

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