Keywords: Ambient operation, Scalable batteries, Lithium metal batteries, Multistage printing, Single-ion conductors, Soft electrolytes

Scalable Semi-Solid Batteries based on Hybrid Polymer-Liquid Electrolytes

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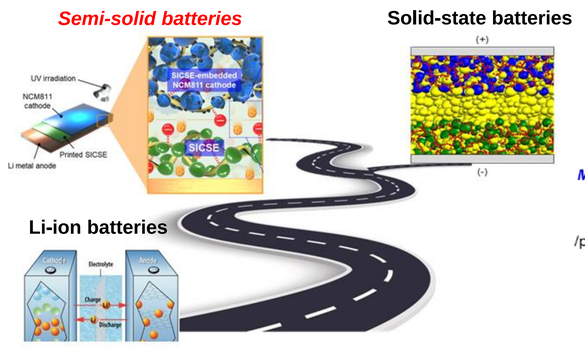
Abstract

Semi-solid Li metal batteries (SSLMBs) face challenges with electrochemical sustainability and ambient operation due to the lack of reliable solid-state electrolytes. A new class of quasi-solid-state soft electrolyte (SICSE) for semi-solid Li-metal batteries is presented. SICSE is single-ion conducting, composed of a nonflammable electrolyte and ion-rectifying compliant skeleton. Rheology-tuned SICSE pastes and UV curing-assisted multistage printing allow for seamless SSLMB fabrication. The single-ion conducting capability of SICSE improves electrode stability, resulting in stable cycling performance, tunable voltages, and high energy densities (476 Wh kg_{cell}^{-1}/1102 Wh L_{cell}^{-1} at 16.656 V). The SSLMB exhibits low-temperature performance, mechanical foldability, and nonflammability.

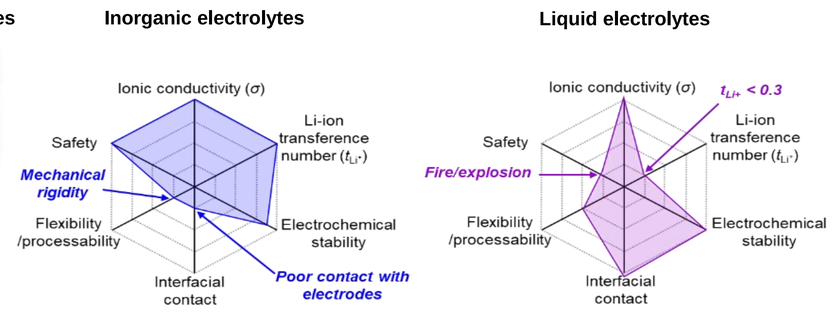
Keywords: Ambient operation, Scalable batteries, Li metal batteries, Single-ion conductors, Hybrid electrolytes, Bipolar configuration

Introduction

Advanced LIBs



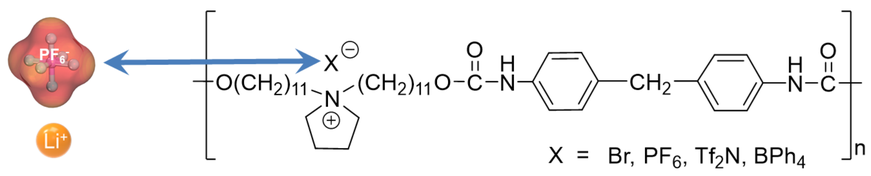
Drawbakcs of Previous Electrolytes



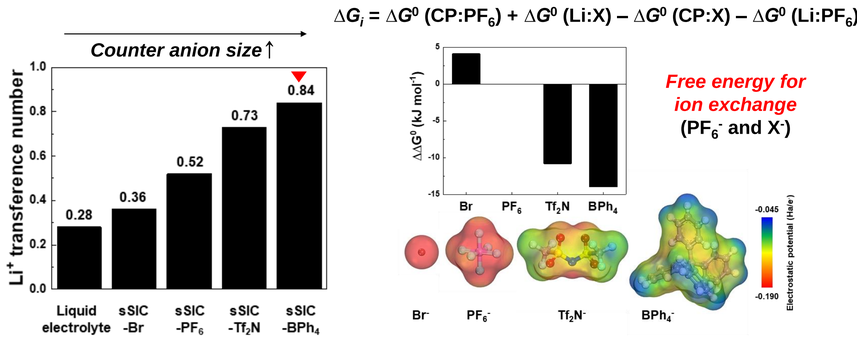
- Semi-solid lithium (Li)-metal batteries (SSLMBs) have recently garnered considerable attention as a promising candidate for post Li-ion batteries (LIBs) owing to their exceptional energy densities and safety.
- Despite their solid-state feature and ideal Li^+ transference number (t_{Li}^+ = 1), the inorganic electrolytes have suffered from interfacial/grain-boundary resistances, thickness issues, mechanical rigidity, and dendrite growth through interstitial voids.
- Counter anions and solvents of the liquid electrolytes tend to cause undesirable interfacial side reactions with the Li-metal anodes, resulting in low Coulombic efficiency, dendritic Li growth, and the formation of a passivation layer.
- Here, we present a hybrid polymer-liquid electrolyte as a new material strategy for practical semi-solid batteries that allow cell fabrication and operation under ambient conditions.

Strategy

Controlled Anion Exchange



$\Delta G_i = \Delta G^0$ (CP:PF_6) + ΔG^0 (Li:X) – ΔG^0 (CP:X) – ΔG^0 (Li:PF_6)



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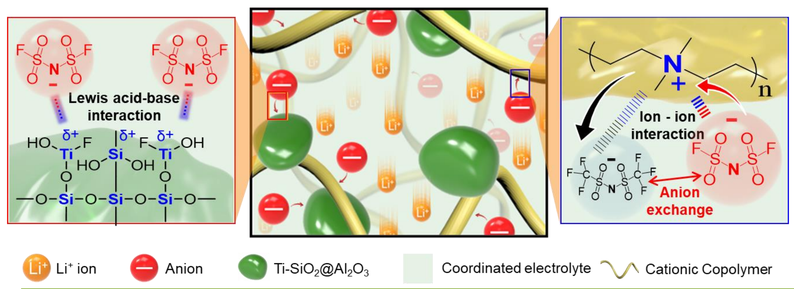
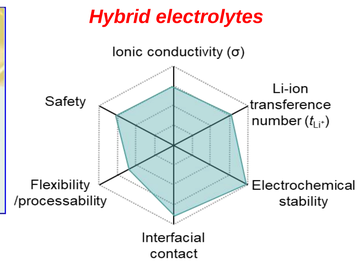
Result & Discussion

Design of SICSE by the Anion-Rectifying Compliant Skeleton

Anion-Trapping Effect (High t_{Li}^+)

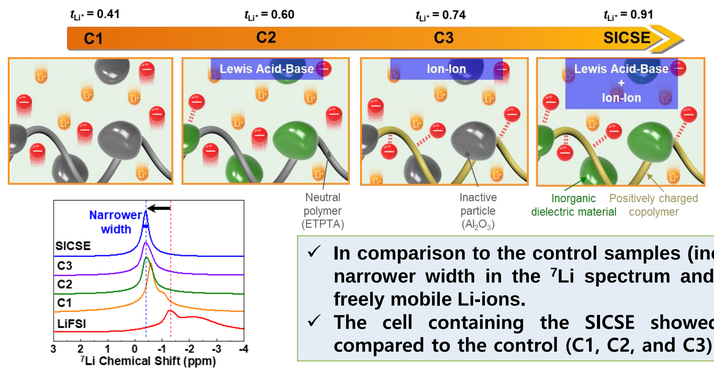


Hybrid electrolytes

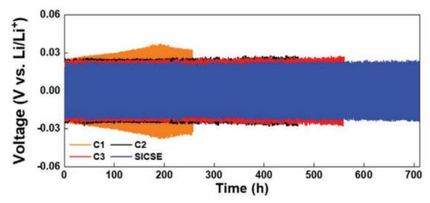


- ✓ The coupled effect of DADMA and Ti-SiO_2@Al_2O_3 nanoparticles
  : via controlled anion-exchange ([FSI^- from LiFSI] – [$TFSI^-$ from cationic polymer])
  : via Lewis acid-base interaction

Interfacial Stability with Li Metal



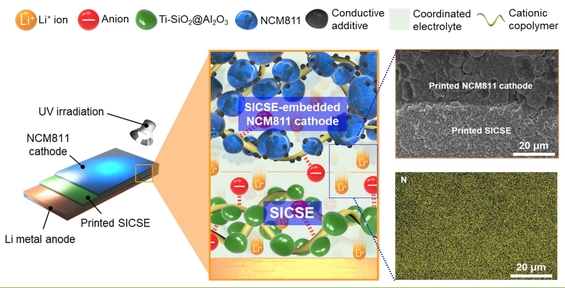
SICSE as a well-designed single-ion conductor



- ✓ In comparison to the control samples (including the bare LiFSI salt), the SICSE showed a narrower width in the ^{7}Li spectrum and a downfield shift, revealing the prevalence of freely mobile Li-ions.
- ✓ The cell containing the SICSE showed better Li plating/stripping cyclability when compared to the control (C1, C2, and C3) samples.

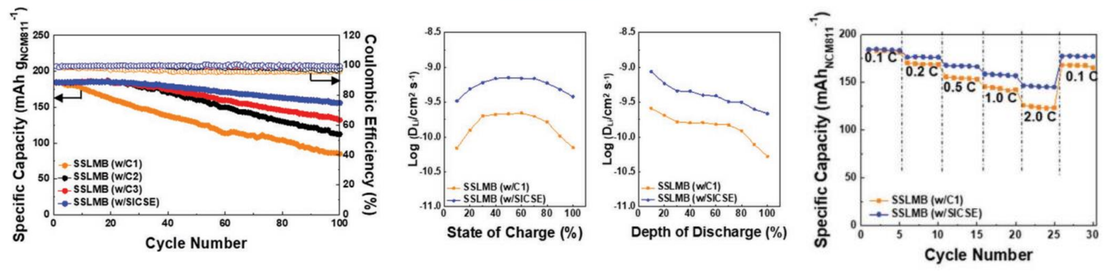
Electrochemical Performance of SSLMBs at Ambient Conditions

Cell Fabrication under Ambient Condition



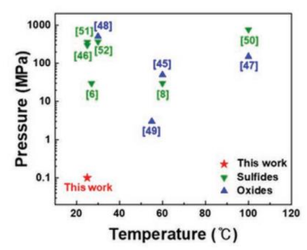
- ✓ The SSLMB full cell was featured with the seamless integration of the Li metal anode, printed SICSE, and printed NCM811 cathode.
- ✓ The identical hybrid electrolyte existed in both the NCM811 cathode and SICSE, thus acting as an ion-conducting interfacial glue.

Application to SSLMB Full Cells



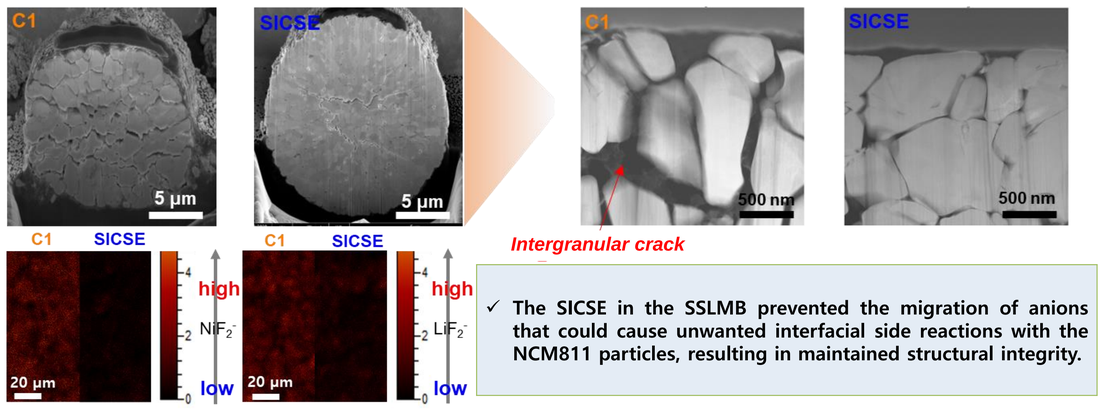
- ✓ The SSLMB with the SICSE exhibited higher cycling performance (capacity retention ≈ 84.5% after 100 cycles) compared to the SSLMBs with the control samples (C1, C2, and C3).
- ✓ The SSLMB with SICSE showed higher Li^+ diffusion coefficients than the SSLMB with C1 over the entire range of the state of charge (SOC) and the depth of discharge (DOD).

Cell Operation under Ambient Condition



- ✓ The solid-state LMBs should be fabricated and also operated under ambient conditions without relying on precisely defined pressing and high temperatures.

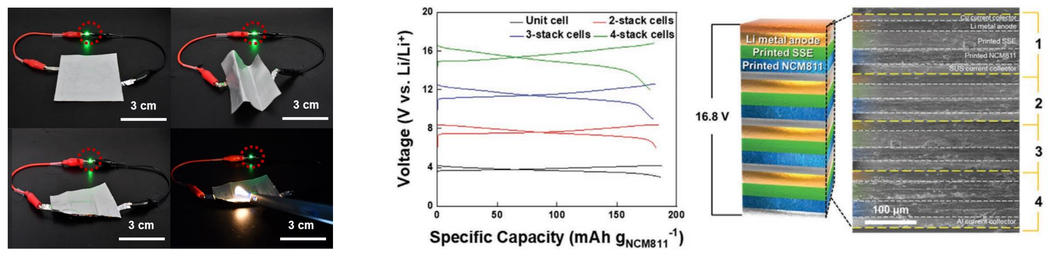
Effect of SICSE on NCM811 Cathodes



- ✓ The SICSE in the SSLMB prevented the migration of anions that could cause unwanted interfacial side reactions with the NCM811 particles, resulting in maintained structural integrity.

Beyond Traditional SSLMBs

Bipolar configuration



- ✓ After being horizontally cut in half, the SSLMB operated a LED lamp without explosion and structural disruption.
- ✓ The full-charge voltages of the bipolar SSLMBs were linearly proportional to the number of serially stacked cells, exhibiting facile control of cell voltages through the bipolar cell configuration. More notably, the bipolar SSLMB (4 cells stacked in-series) was achieved with high energy densities (476 Wh kg_{cell}^{-1}/1102 Wh L_{cell}^{-1} at 16.656 V).

Summary

- We have demonstrated the SICSE as a new hybrid polymer-liquid electrolyte strategy for practical SSLMBs that enable cell fabrication and operation under ambient conditions.
- The SICSE described herein can be suggested as a promising single-ion conducting hybrid electrolyte platform that can lead us closer to the scalable semi-solid batteries.
- This study was published as a Back Cover in the *Adv. Energy Mater.* and won the gold prize in the Samsung Electronics Paper Award.