Rechargeable Lithium Air Batteries

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Project ID #bat517

Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 90%

Budget

- Total project funding:
  - DOE Share: 100%
- Funding for FY20: $200k
- Funding for FY21: $200k

Barriers and Technical Targets

- **Short cycle life**: Need functional electrolytes and Li metal protection to stabilize electrode/electrolyte interphase (SEI).
- **Low coulombic efficiency**: Need functional catalysts and soluble additives to decrease large overpotential during charging.

Partners

- U.S. Army Research Laboratory

Relevance/Objectives

Relevance

Design and understand electrolytes and electrode/electrolyte interfaces in Li-oxygen batteries (LOBs) are critical for the development of LOB technology as the next-generation of high energy density battery systems for practical applications.

Objectives

- Develop innovative electrolytes, air electrodes with catalysts and Li metal protection concepts for stable cycling of LOBs.
- Develop air electrodes with uniform pore structure and dual catalysts.

Milestones

Milestone Name/Description	Milestone End Date	Status
Develop binder-free electrocatalysts on the surface of air electrode with polymer-supported SEI and redox mediators	12/31/20	Completed
Develop polymeric colloidal localized high-concentration electrolytes (PC-LHCEs) using osmosis effect	3/31/21	Completed
Understand the interphase properties of PC-LHCE/electrode	6/30/21	On track
Develop new solvents that are stable against oxidation and singlet oxygen species for reversible Li-O_2 batteries	9/30/21	On track

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Approaches

1. Develop highly stable electrolytes, including novel PC-LHCEs to protect Li-metal anode and
2. Develop effective catalysts (both liquid and solid) to prevent the irreversible parasitic reactions at the electrodes (cathode and anode).
3. Evaluate the stability of the electrolyte and the artificial SEI layer.
4. Synthesis new solvents to stabilize the electrolyte system; identify the key parameters for suitable electrolytes in Li-O_2 batteries.

Stabilization of electrolyte and Li metal anode

Development of air electrodes and catalysts

Development of colloidal LHCEs

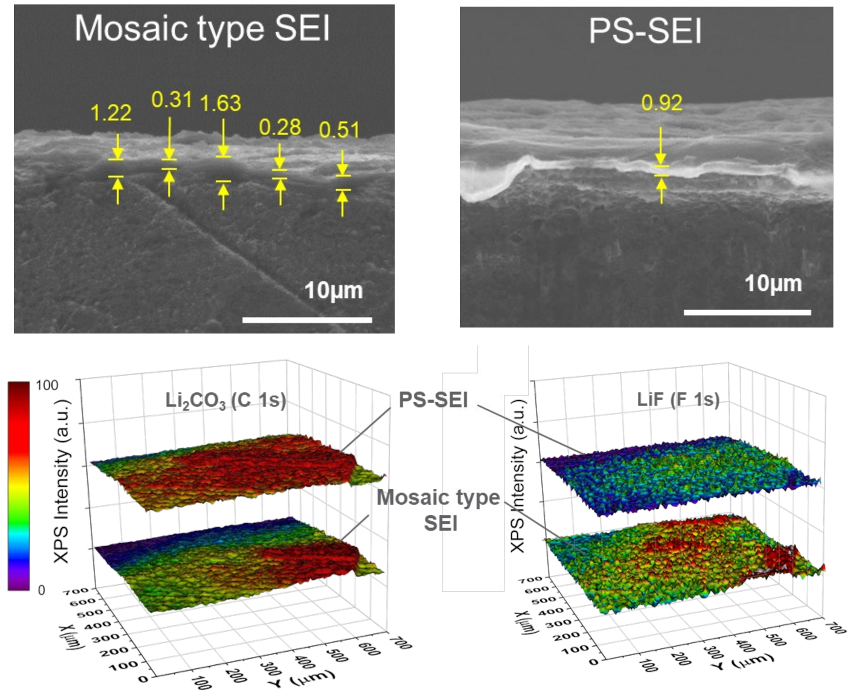
Synthesis of new solvents

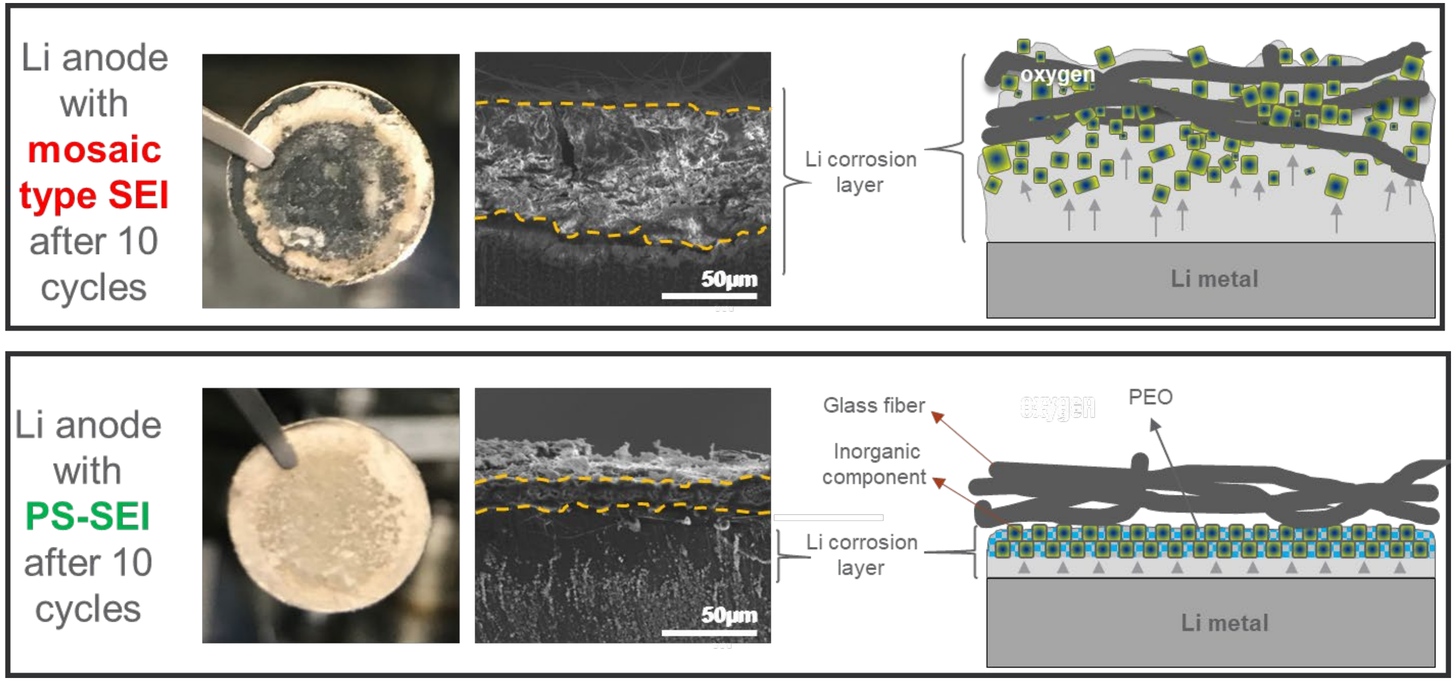
LABs with longer cycle life

Technical Accomplishments

1. Polymer supported SEI layer (PS-SEI) formed by electrochemically pre-treated PEO coating on Li metal anode

PS-SEI: PEO supported SEI layer formed by electrochemical pre-treatment; Mosaic-type SEI (MT-SEI): SEI formed by electrochemical treatment without polymer

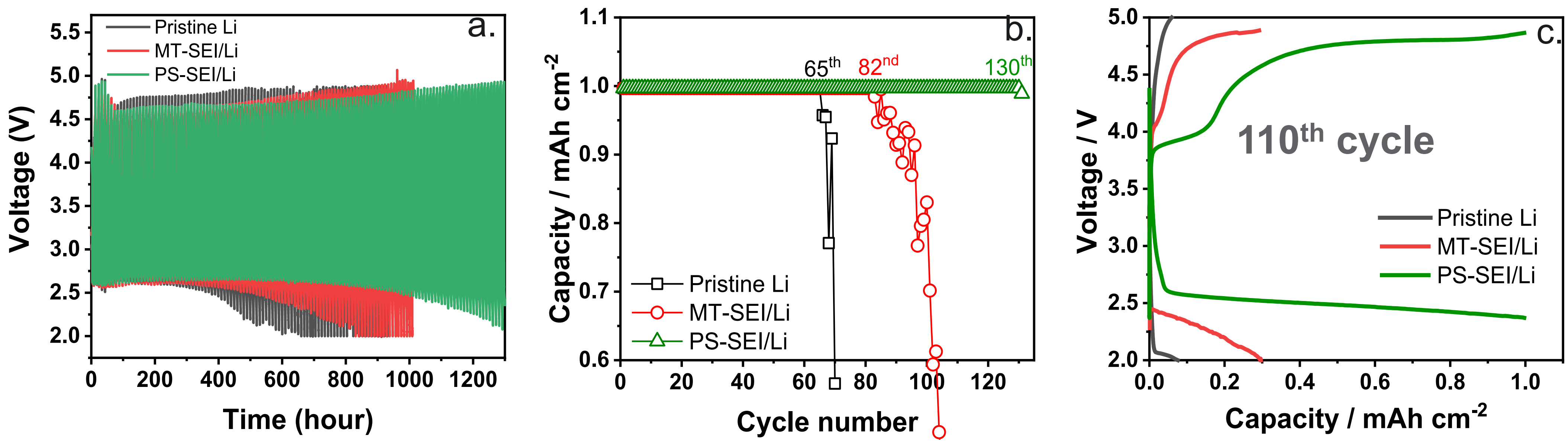




- A uniformly distributed inorganic layer (rich in Li_2CO_3 & LiF) was formed on PEO coated Li metal surface after pretreated by electrochemical pre-charging process under O_2.
- Cross-sectional SEM and EDX map (oxygen) images show that the Li metal anode with PS-SEI layer is much more stable than that with mosaic type (MT) SEI layer due to the uniformly distributed stiff inorganic components in the flexible polymer phase.

Technical Accomplishments

Cycling performance of LOBs with PS-SEI or mosaic type SEI



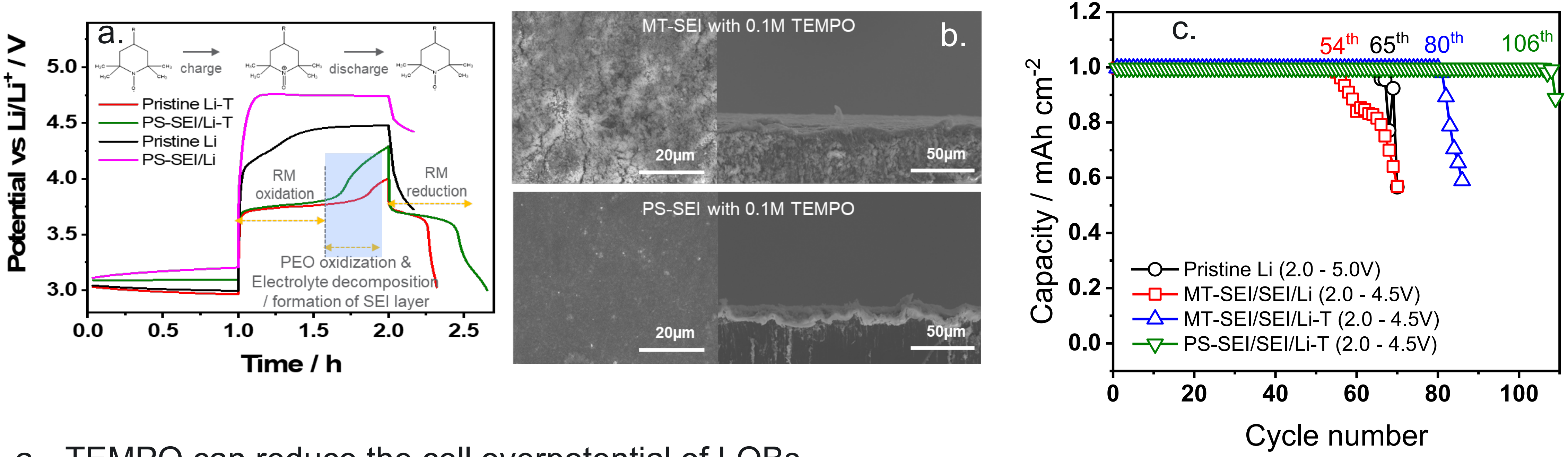
Li: pristine Li anode; PLi-Ar: mosaic type SEI; PPG5Li-O_2: polymer supported SEI (PS-SEI)

a. PS-SEI protected anode leads to more stable voltage profiles of LOBs.
b. PS-SEI protected anode leads to longer cycle life of LOBs.
c. LOBs with PS-SEI layer exhibit better cycling stability and smaller over potential than those with natural SEI or MT-SEI layer.

Technical Accomplishments

2. Applying mobile catalyst (redox mediator, RM) with PS-SEI

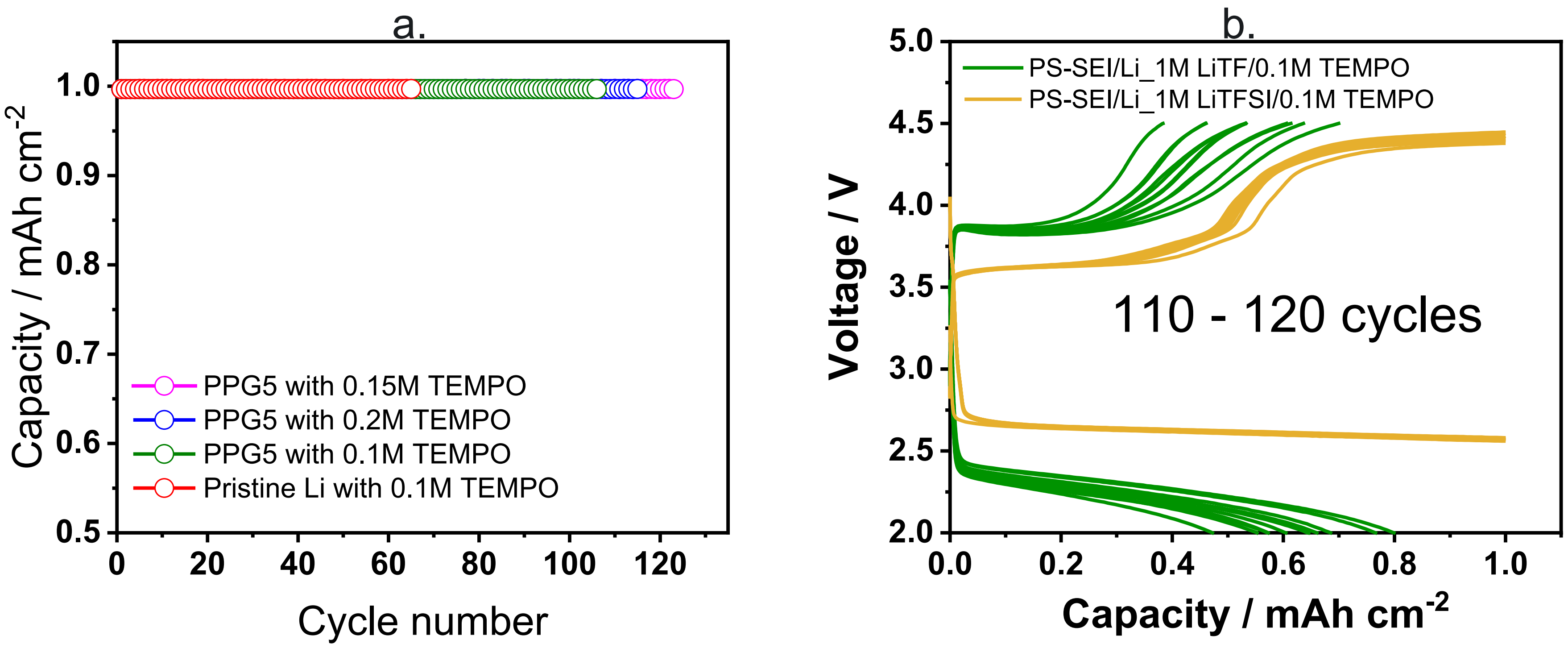
Liquid catalyst: TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl



a. TEMPO can reduce the cell overpotential of LOBs.
b. PS-SEI forms a continuous uniform film to protect Li metal anode.
c. LOB cell with TEMPO catalyst and PS-SEI layer on Li anode shows much better cycling performance than those with pristine Li anode.

Technical Accomplishments

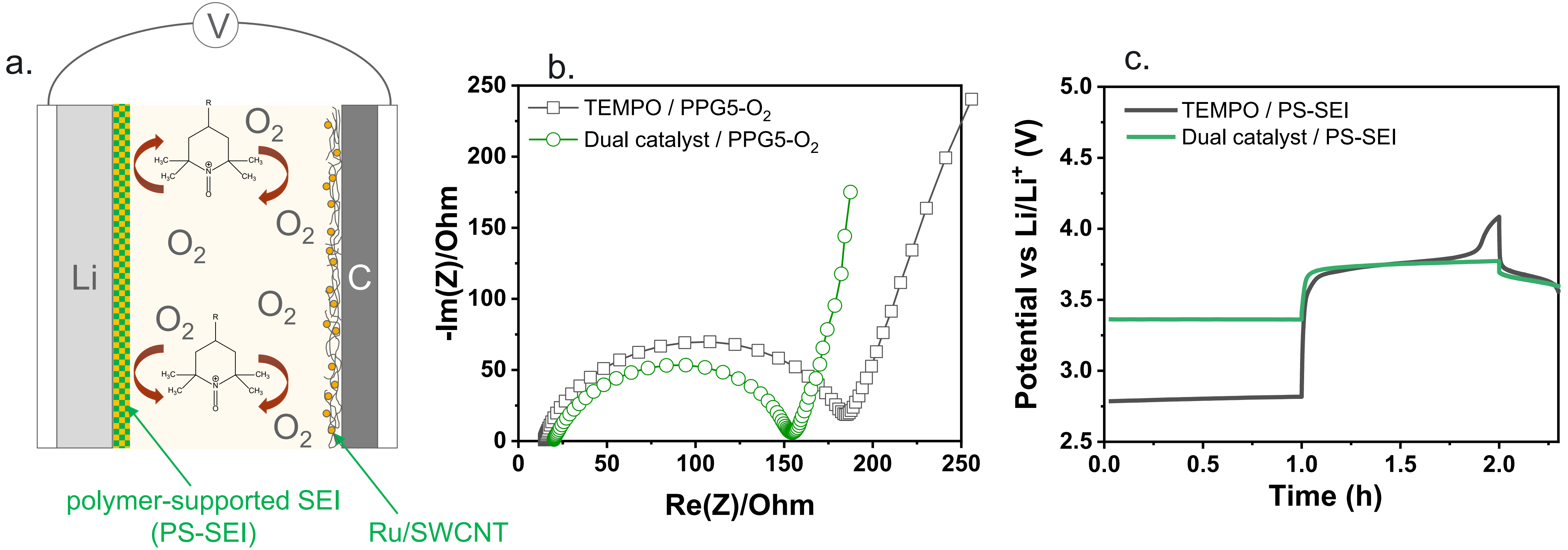
Optimization of Catalyst concentration and Li salt



a. Optimized TEMPO concentration in LiTF/G4 electrolyte is 0.1M.
b. LiTFSI salt based electrolyte leads to longer cycling of LOBs than those with LiTF salt.

Technical Accomplishments

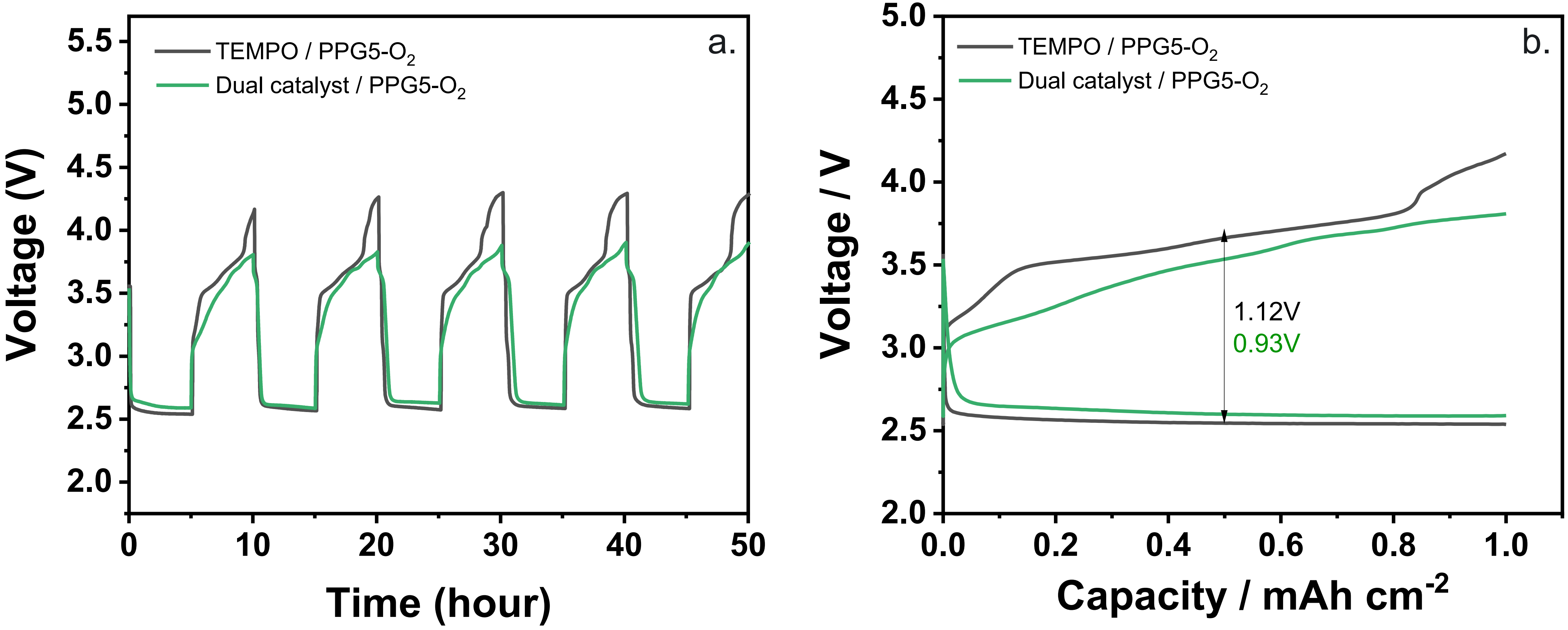
3. Dual catalyst (mobile + solid catalysts) system for long-term LOB operation



- Dual catalysts leads to lower cell-impedance and lower over-potential due to the oxidation of both mobile and solid catalysts at 3.75 V.

Technical Accomplishments

Effect of dual catalyst on LOB performance



- ➢ Dual catalysts further reduce the overpotential of LOBs.

Summary

- Electrochemically pre-formed PS-SEI stabilizes Li metal anode and leads to much longer cycling life of LOBs due to the uniformly distributed stiff inorganic components in the flexible PEO phase.
- Mobile catalyst effectively reduces the cell over-potential with PS-SEI layer during the long-term LOB cycling against highly reactive singlet oxygen and TEMPO molecules.
- Dual catalyst (mobile and solid) combined with pre-formed PS-SEI layer significantly reduces the cell over-potential for much longer cycle life of LOBs.

Proposed Future Research

- Systematically design and synthesis of stable solvents to minimize decomposition of electrode and electrolyte during long-term LOB operation.
- Development of new colloidal type electrolytes with low vapor pressure, high O_2 solubility, good mixability, and wide electrochemical redox potential.
- Development of air electrodes with unique pore structure and dual catalyst (mobile and solid) by evaluation of cycling performance of Li-O_2 batteries.

Any proposed future work is subject to change based on funding levels.

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Acknowledgements

- Financial support from the DOE/EERE/VTO/BMR program is greatly appreciated.

- DOE/BER/EMSL for microscopic and spectroscopic characterizations and computational calculations.

- Team Members: Hyung-Seok Lim, Won-Jin Kwak, Sujong Chae, Sungun Wi, Linze Li, Chongmin Wang

Responses to Previous Year's Reviewers' Comments

- This project was not reviewed last year.

Collaboration

- Dr. Jeffrey Read (U.S. Army Research Laboratory) for measurements of O_2 solubility in electrolytes and volatility of electrolytes.

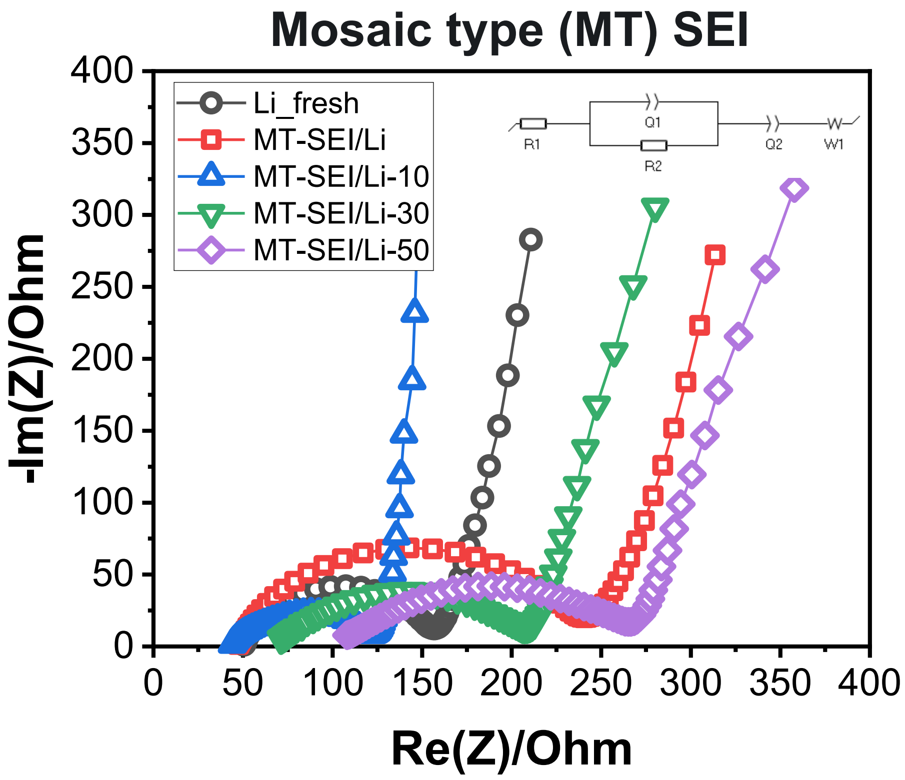
Remaining Challenges and Barriers

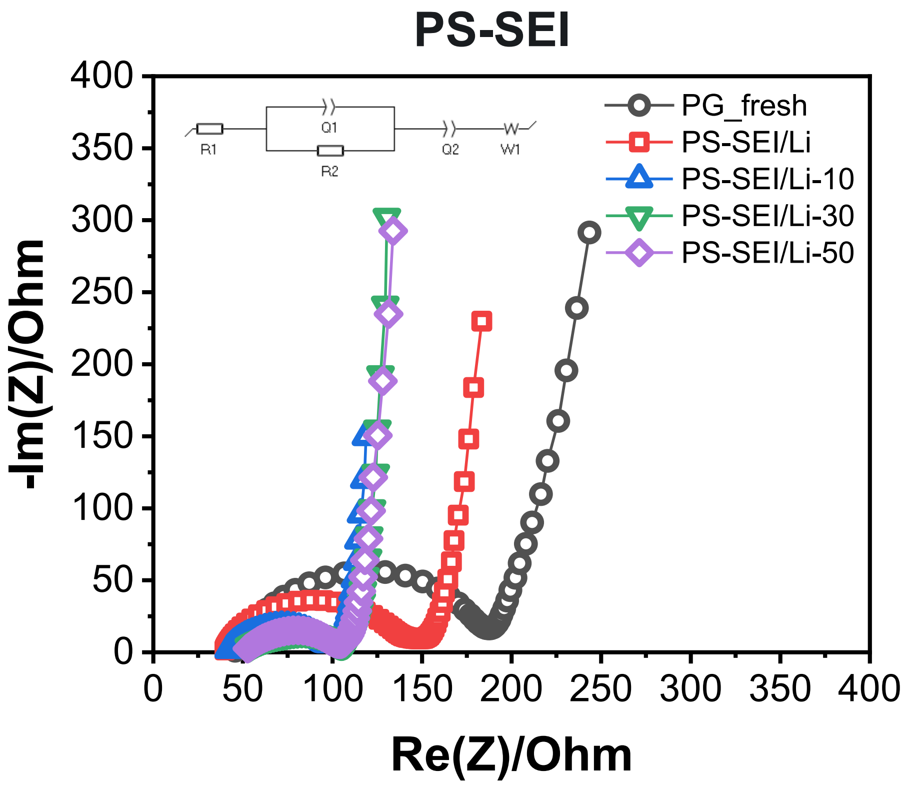
- Limited cycle life in narrow operation voltage.
- Poor rate capability resulting in low practical specific energy.
- Large voltage hysteresis during cycling resulting in significant degradation of electrodes and electrolyte decomposition.

Technical Backup Slides

Technical Accomplishments

Effect of PS-SEI on cell resistance in LOBs

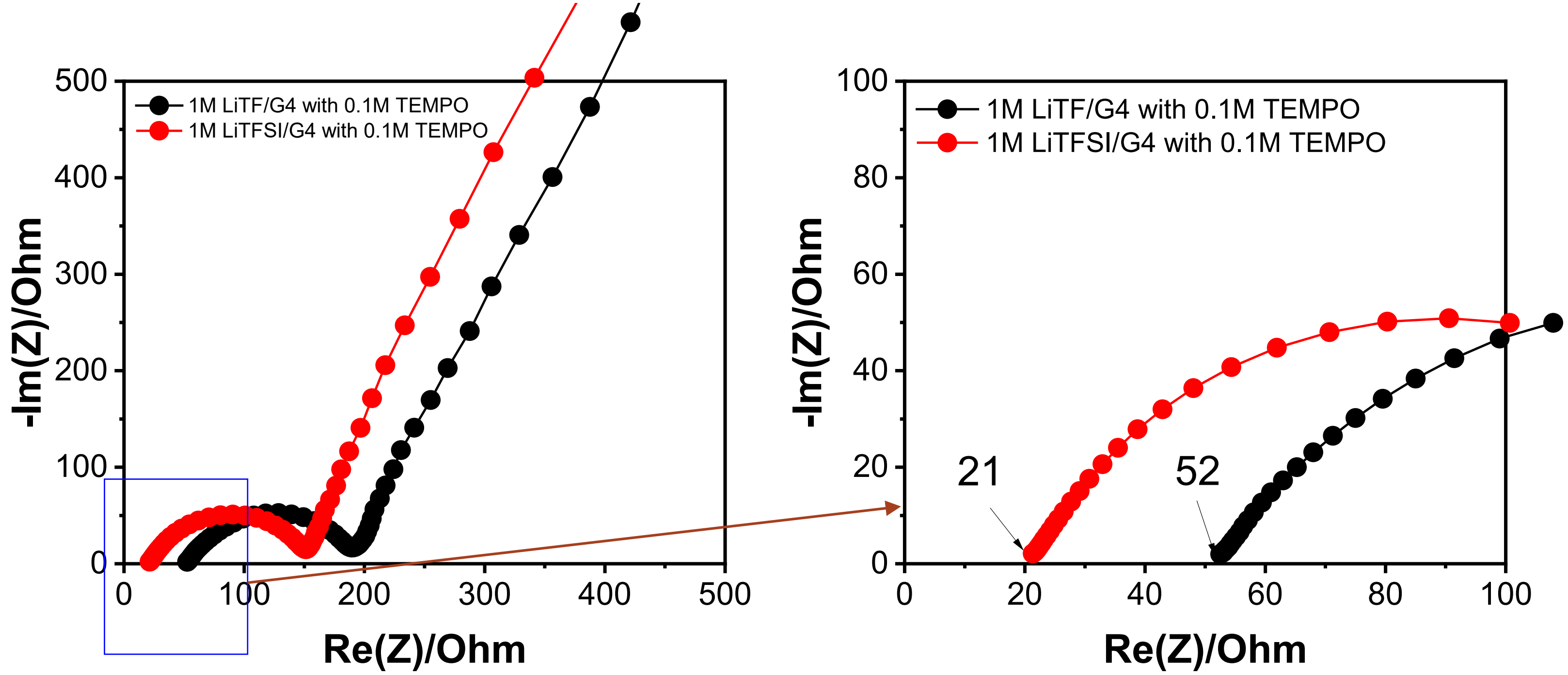


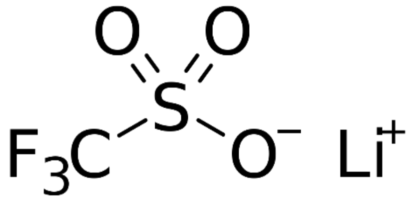


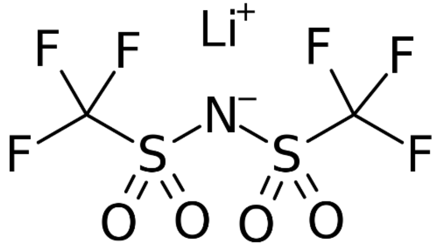
- **LOB with PS-SEI layer on Li anode exhibits smaller cell impedance than LOB with MT-SEI layer after 50 cycles.**

Technical Accomplishments

3. Optimization with different Li salt for long-term cycling in narrow operation voltage







- LOB cell with LiTFSI based electrolyte leads to smaller cell resistance (solution resistance + charger transfer resistance) than those with LiTF based electrolyte because LiTFSI has higher donor number and better ionic conductivity.