Rechargeable Lithium Air Batteries

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Project ID # BAT443
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Overview

Timeline

- Project start date: Oct. 1, 2016
- Project end date: Sept. 30, 2020
- Percent complete: 89%

Budget

- Total project funding:
  - DOE Share: 100%
- Funding for FY19: $200k
- Funding for FY 20: $200k

Barriers and Technical Targets

- **Short cycle life**: Need functional electrolytes and Li metal protection to stabilize electrode/electrolyte interface.

- **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 understanding of electrolytes and electrode/electrolyte interface in Li-air batteries (LABs) are critical for the development of LAB technology as the next-generation of high energy density battery systems for practical applications.

Objectives

Develop innovative electrolytes and Li metal stabilization concepts for stable cycling of LABs.

- Develop efficient and reliable electrolytes to improve the efficiency and cycle life of LABs.
- Develop promising and facile concept to stabilize Li metal anode and air electrode for long-term cycle life of LABs.

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Milestones

Milestone Name/Description	Milestone End Date	Status
Develop stable electrolytes to minimize the parasitic reactions at the electrodes.	12/31/19	Completed
Protect anodes to prevent Li dendrite and LiOH formation.	3/31/20	Completed
Develop stable additives (solid or soluble) or methods for sustainable catalytic effect.	6/30/20	On track
Evaluate cycling performance of Li-O_2 batteries with optimized cell components and conditions.	9/30/20	On track

Approaches

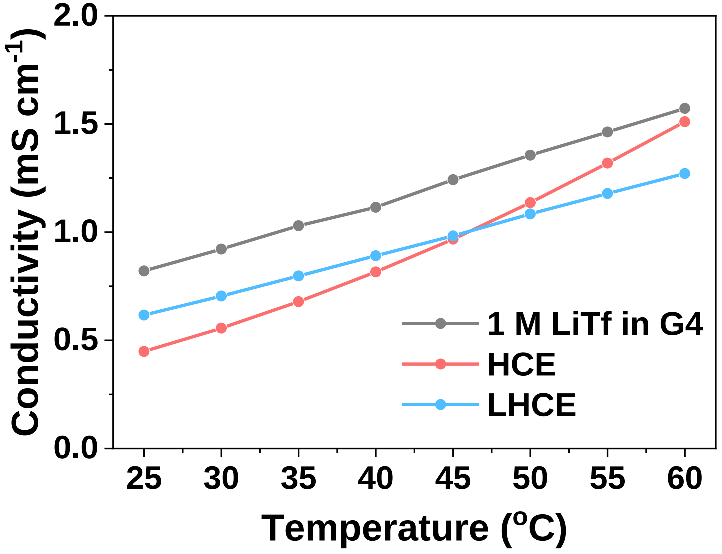
- Use a localized high-concentration electrolyte (LHCE) to enhance the stability of the electrolyte against singlet oxygen, which is the main cause of parasitic reactions in LABs using conventional typical 1 M Tetraglyme-based electrolyte.
- Investigate fundamental mechanism of LHCE as an effective electrolyte for LABs with comparison to a conventional electrolyte and high-concentration electrolyte (HCE).
- Study effect of different diluents in LHCEs to develop more suitable diluents and electrolytes for LABs.

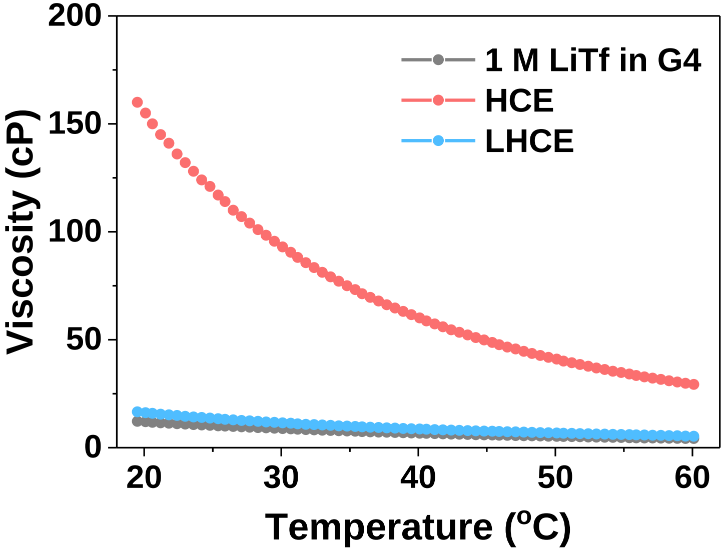
Stability against $^1O_2$ | **Stabilization of Li metal anode** | **Fluidity** | **O_2 & Li salt solubility**

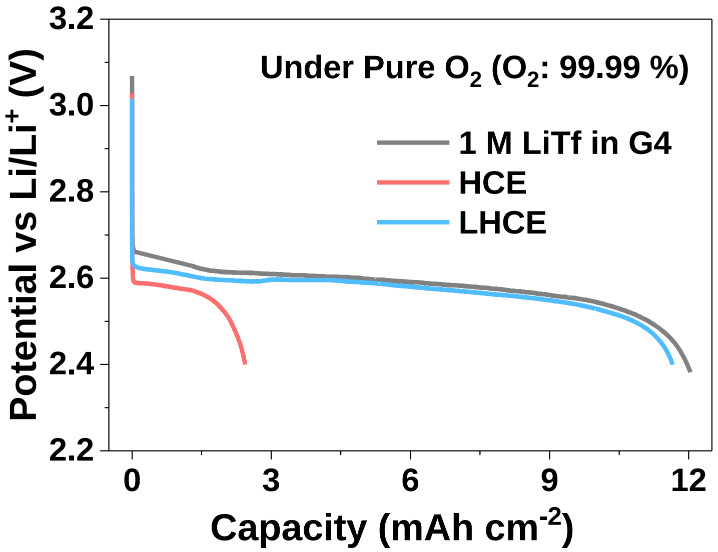
LABs with longer cycle life

Technical Accomplishments

Effects of conductivity and viscosity of electrolytes on discharge capacity of Li-O_2 batteries (LOBs)





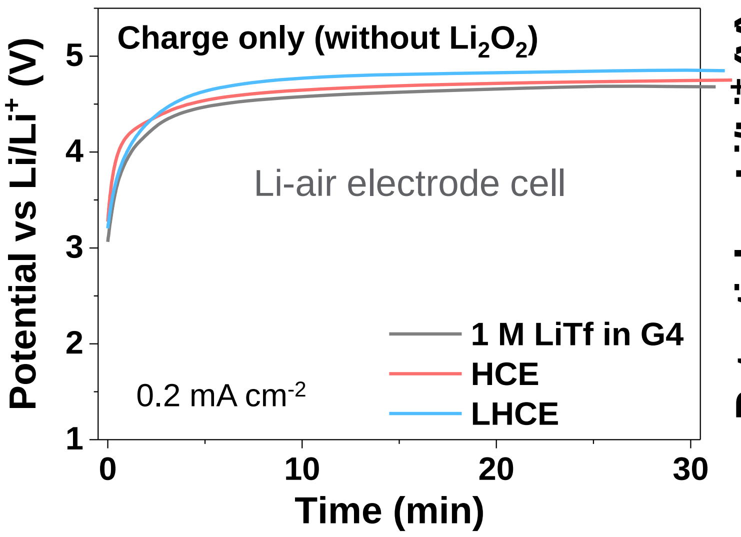


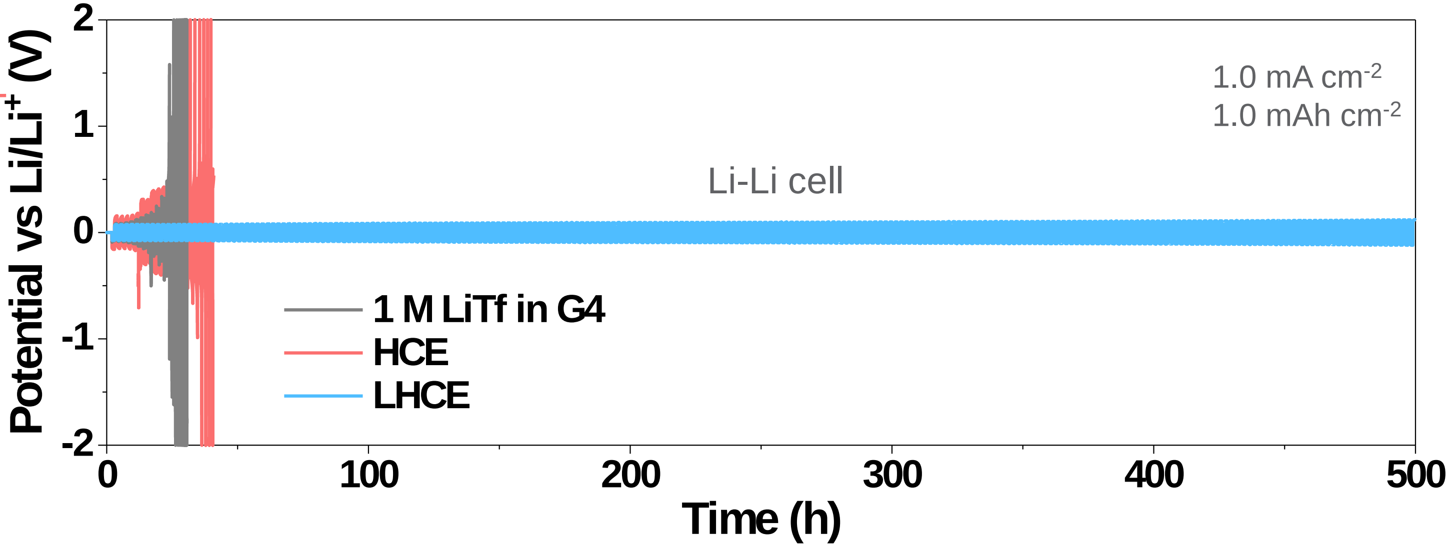
- Ionic conductivity at 25 °C: 1 M LiTf in G4 > OTE-LHCE > HCE
- Viscosity at 25 °C: 1 M LiTf in G4 < OTE-LHCE <<< HCE
- Discharge capacity at 25 °C: 1 M LiTf in G4 > OTE-LHCE >>> HCE
- **Viscosity of electrolyte is a critical factor for performance of LOBs.**

LiTf: Lithium trifluoromethanesulfonate
G4: Tetraethylene glycol dimethyl ether (Tetraglyme or TEGDME)
OTE: 1H,1H,5H-Octafluoropentyl 1,1,2,2-tetrafluoroethyl ether

Technical Accomplishments

Stability of LHCE against Li metal anode and high oxidation potential



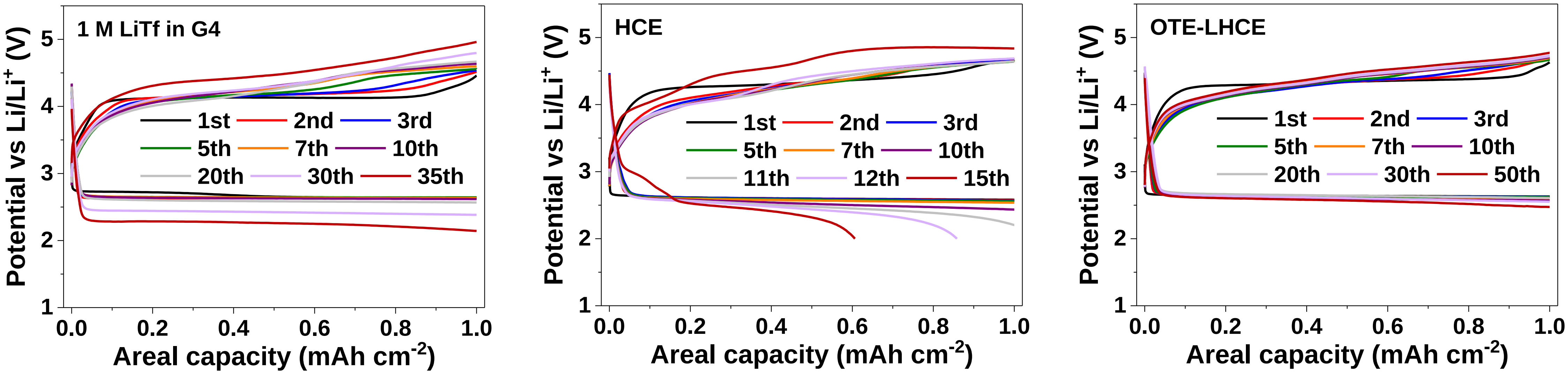


- Oxidation potential: OTE-LHCE > HCE > 1 M LiTf in G4
- Cycle life of Li-Li symmetric cell test: OTE-LHCE >>> 1 M LiTf in G4 > HCE

- **LHCE has the highest oxidation potential compared to other electrolytes, which is helpful for stable operation of LOBs and LABs during charging.**
- **LHCE stabilizes the Li metal anode, which is confirmed by stable stripping and plating processes in Li||Li cells.**

Technical Accomplishments

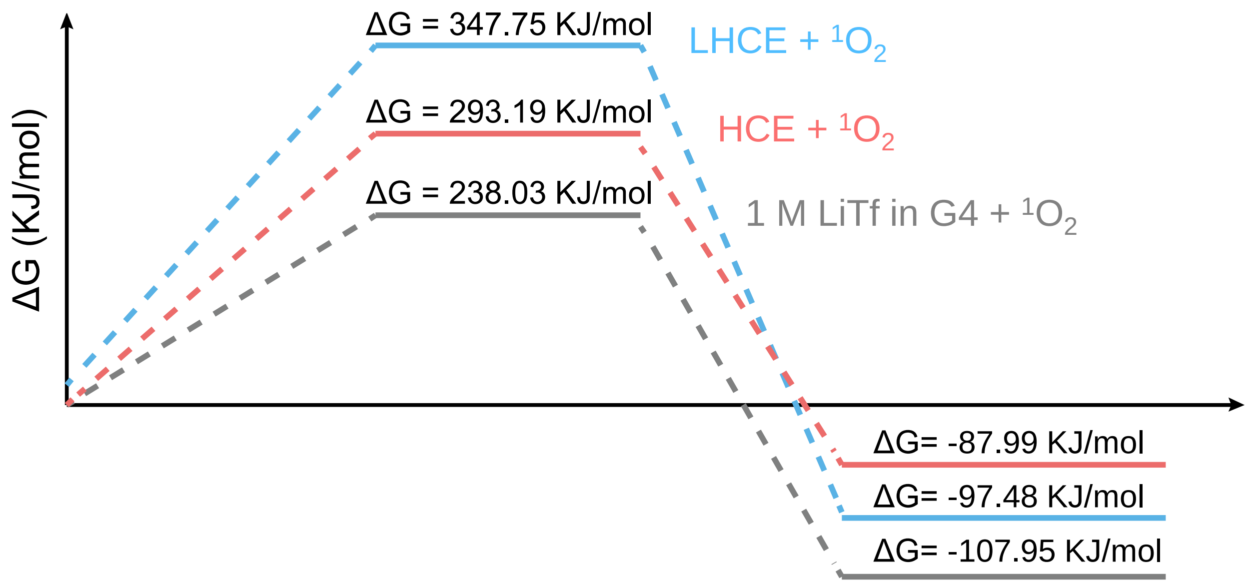
Cycling performance of LOBs using different electrolytes



- Cycle life of Li-O_2 batteries: OTE-LHCE > 1 M LiTf in G4 > HCE
- **LOBs using LHCE exhibit better cycling stability than those using other electrolytes.**

Technical Accomplishments

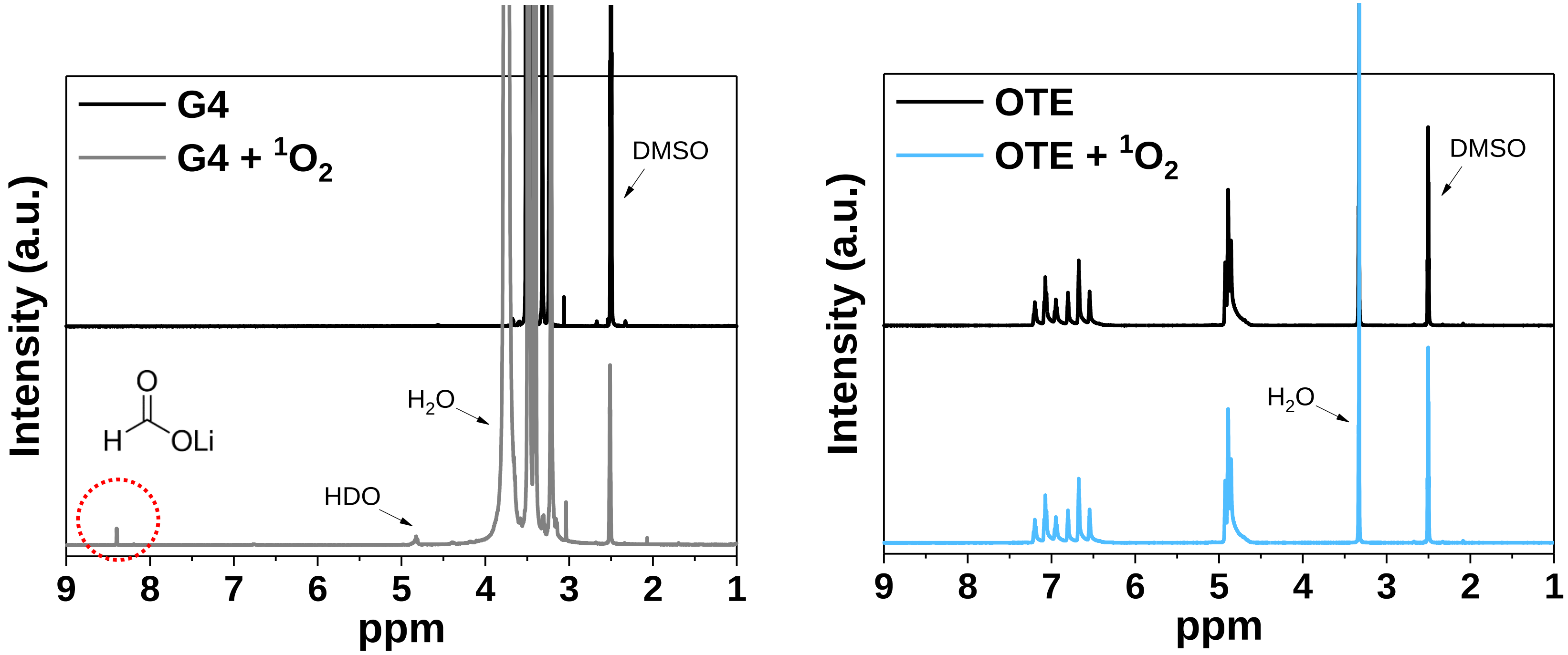
Calculation on the stability of electrolytes against singlet oxygen



- Calculated stability of electrolytes against $^1O_2$: OTE-LHCE > HCE > 1 M LiTf in G4
- **LHCE exhibits the highest stability against singlet oxygen attack.**

Technical Accomplishments

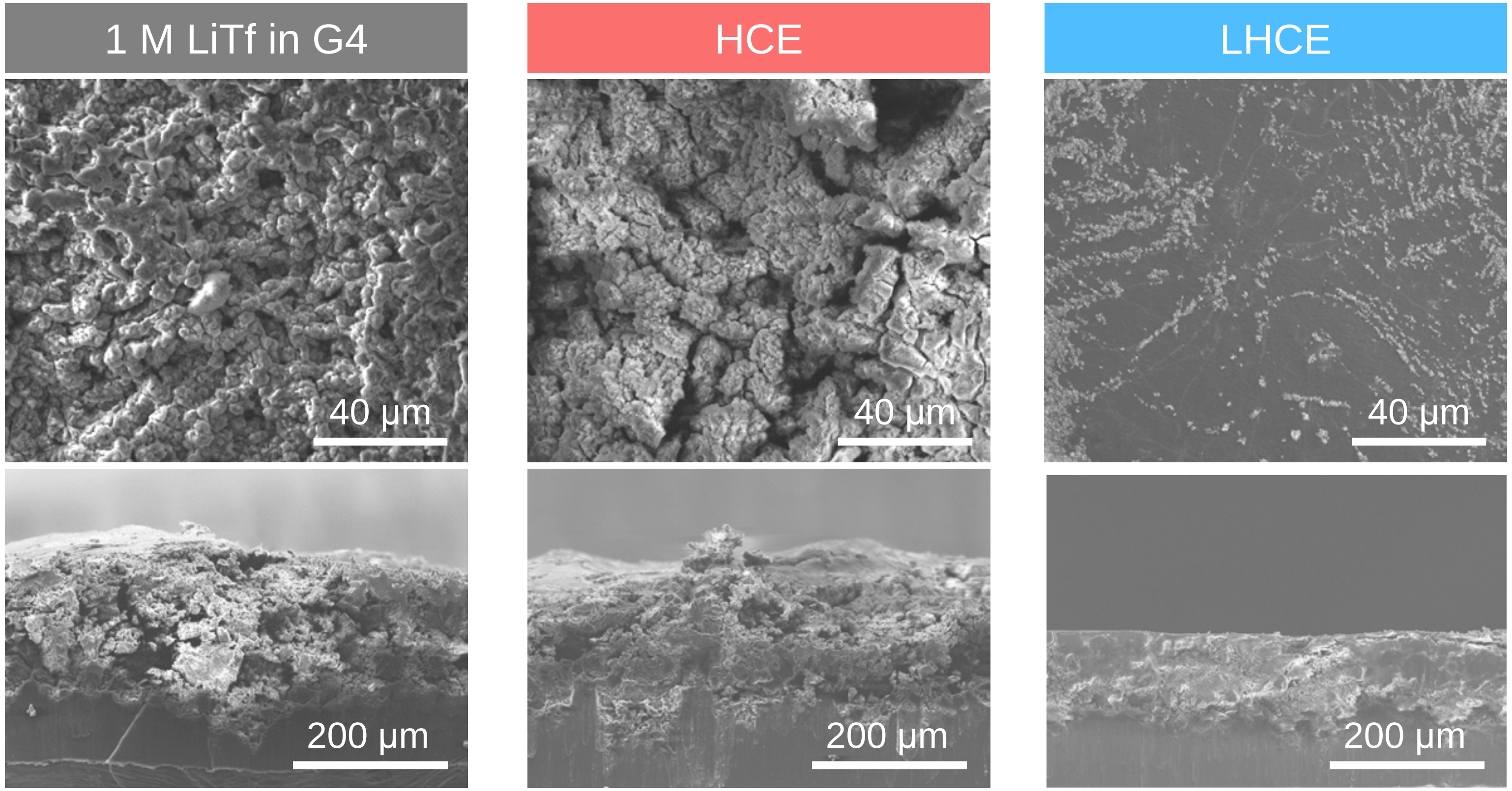
NMR analyses for stability of chemicals against singlet oxygen



- OTE (diluent) is stable against $^1O_2$, but G4 is decomposed by $^1O_2$ attack.
- It is consistent with the calculated results on the higher stability of OTE-LHCE than HCE and 1 M LiTf in G4.

Technical Accomplishments

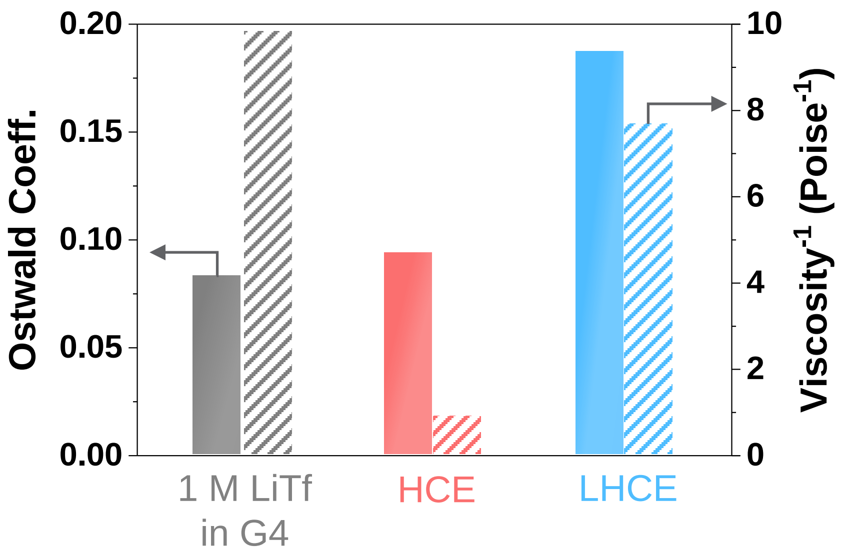
Li metal morphologies after cycling in LOBs

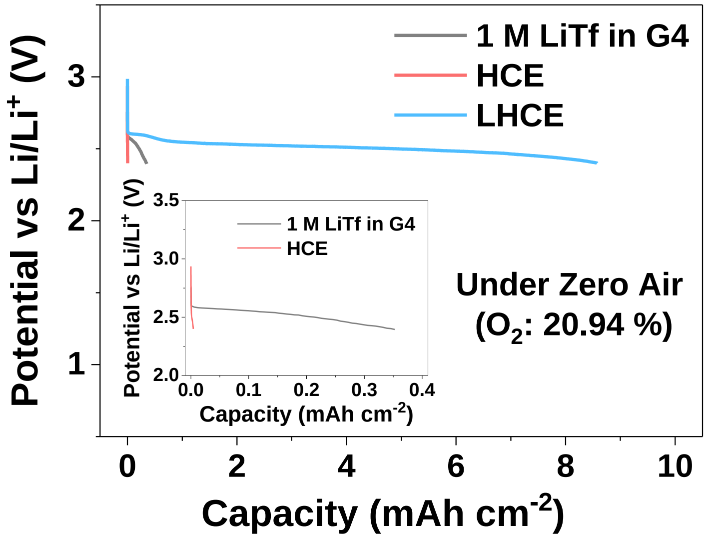


- **SEM images show that the Li metal anode is much more stable in LOB using LHCE than those using other electrolytes.**

Technical Accomplishments

Effects of O_2 solubility and viscosity of electrolytes on discharge capacity of LABs (21% O_2)



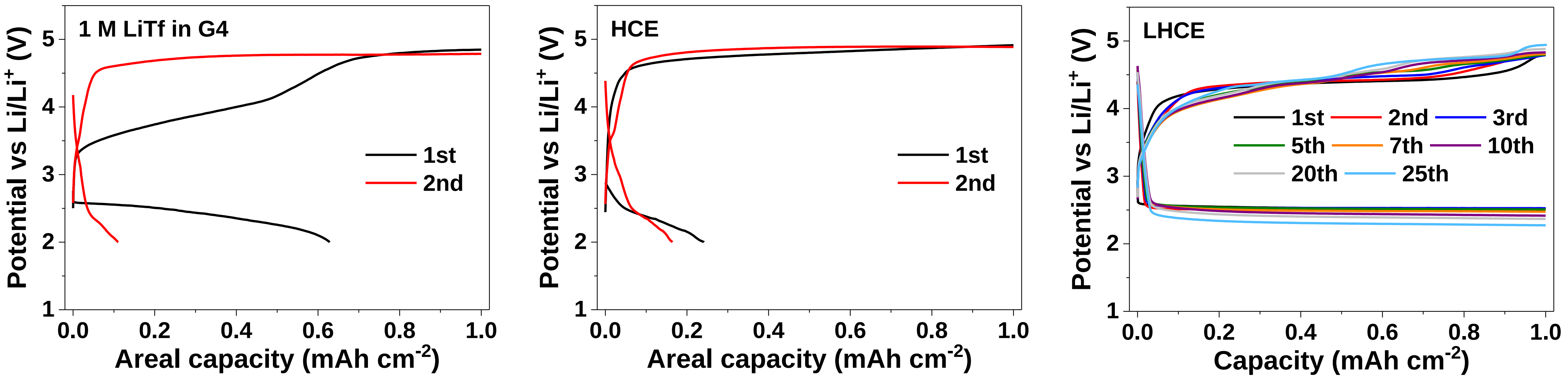


- O_2 solubility at 25 °C: OTE-LHCE >> 1 M LiTf in G4 > HCE
- Viscosity at 25 °C: 1 M LiTf in G4 < OTE-LHCE <<< HCE
- Discharge capacity at 25 °C: OTE-LHCE >>>> 1 M LiTf in G4 > HCE

- **O_2 solubility in electrolyte as well as viscosity of electrolyte become main limiting factors for performance of LABs in ambient air (21% O_2).**

Technical Accomplishments

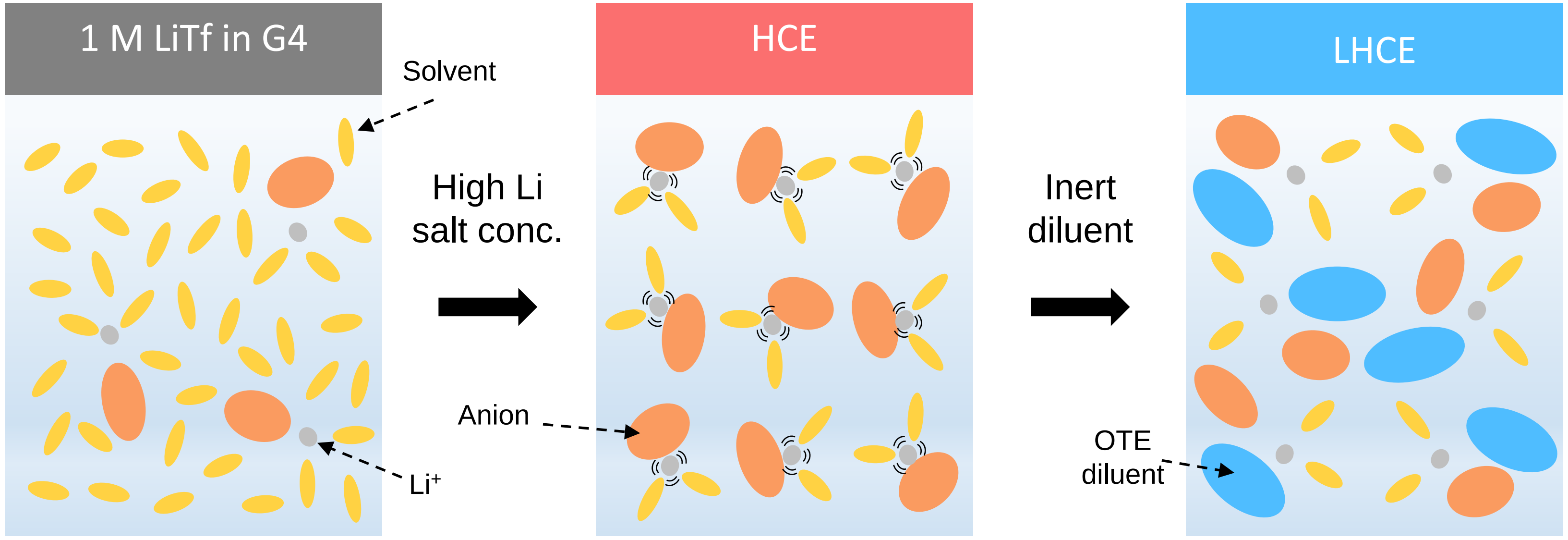
Cycling performance of LABs using different electrolytes

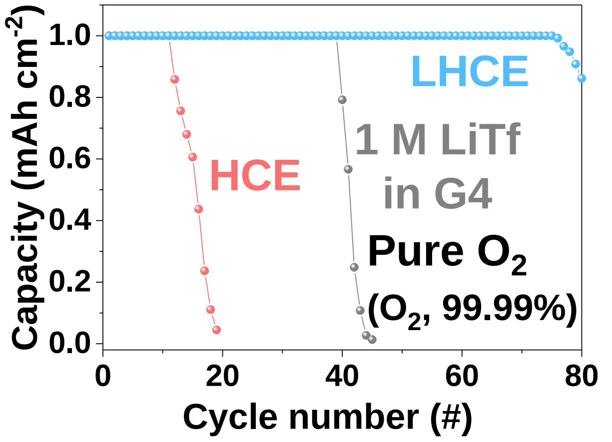


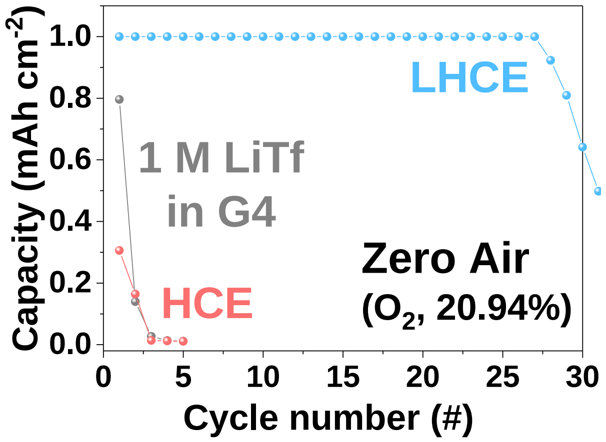
- Cycle life of LABs (21% O_2): OTE-LHCE >>> 1 M LiTf in G4 > HCE
- **LABs (21% O_2) with LHCE exhibit much better cycling performance than those using other electrolytes.**

Technical Accomplishments

Understand the advantages of LHCE for LOBs and LABs







1 M LiTf in G4:
- ▼ Unstable to Li metal
- ▼ Poor stability to $^1O_2$
- ▲ Low viscosity, good wetting, low cost

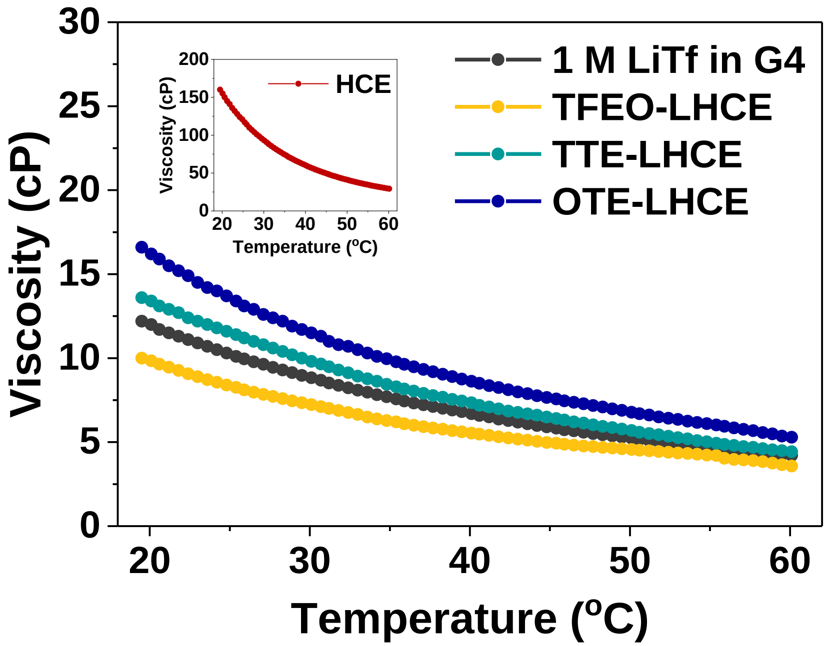
HCE:
- ▲ Stable to Li metal
- ▲ More stable to $^1O_2$ than 1M LiTf in G4
- ▼ High viscosity, poor wetting, high cost

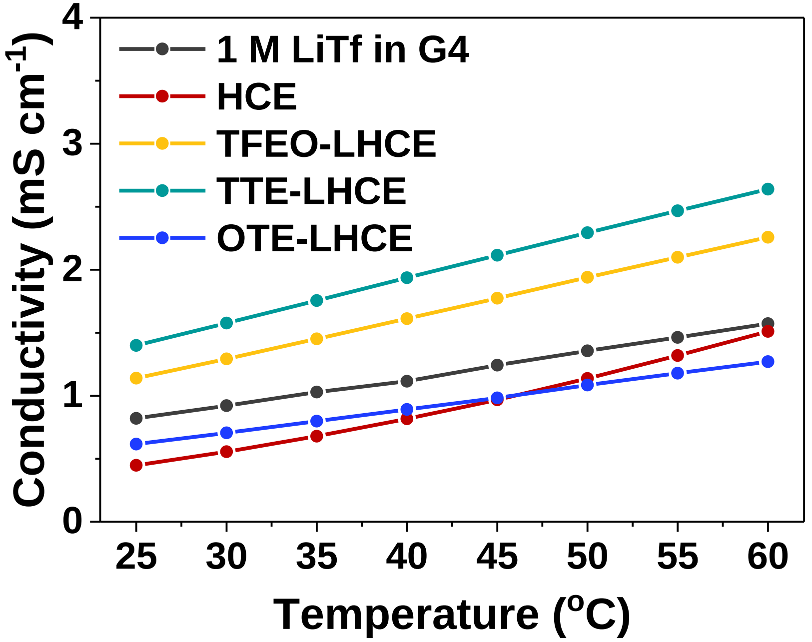
LHCE:
- ▲ More stable to $^1O_2$ and Li than HCE
- ▲ High oxygen solubility
- ▲ Low viscosity, good wetting, low cost

LAB or LOB is much more stable with LHCE electrolyte.

Technical Accomplishments

Temperature dependence of viscosity and conductivity of electrolytes

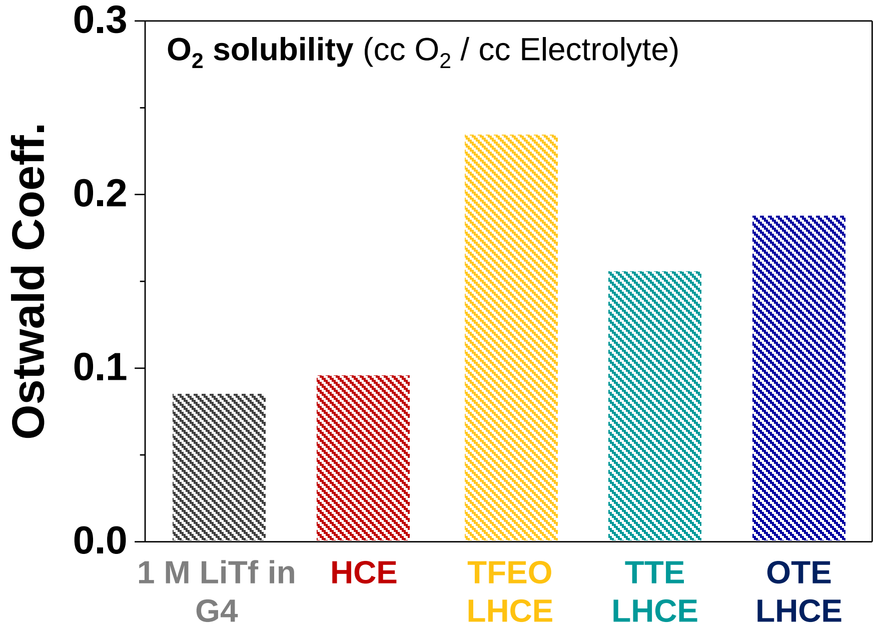


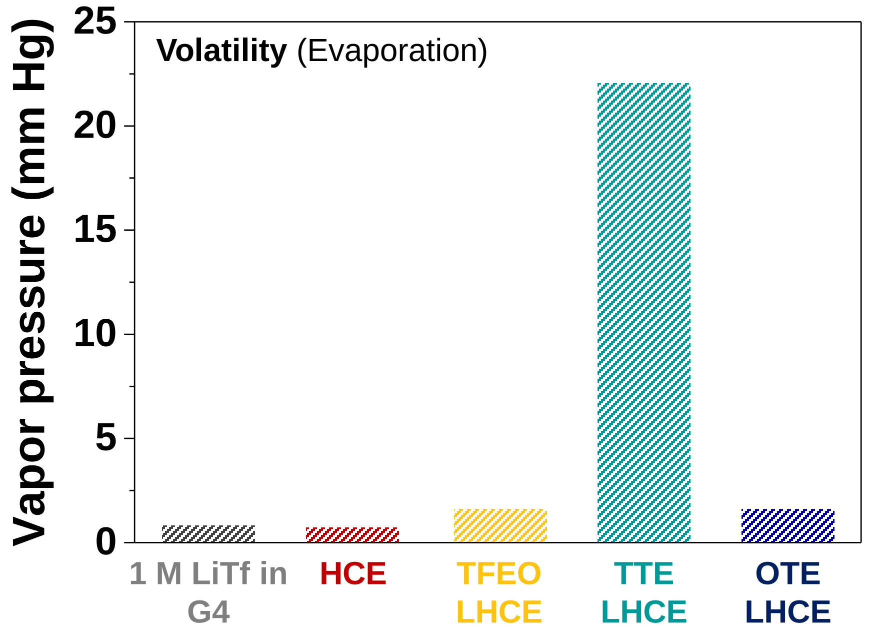


- Viscosity at 25 °C: TFEO-LHCE < 1 M LiTf in G4 < TTE-LHCE < OTE-LHCE <<< HCE
- Conductivity at 25 °C: TTE-LHCE > TFEO-LHCE > 1 M LiTf in G4 > OTE-LHCE > HCE

Technical Accomplishments

O_2 solubility and volatility of electrolytes

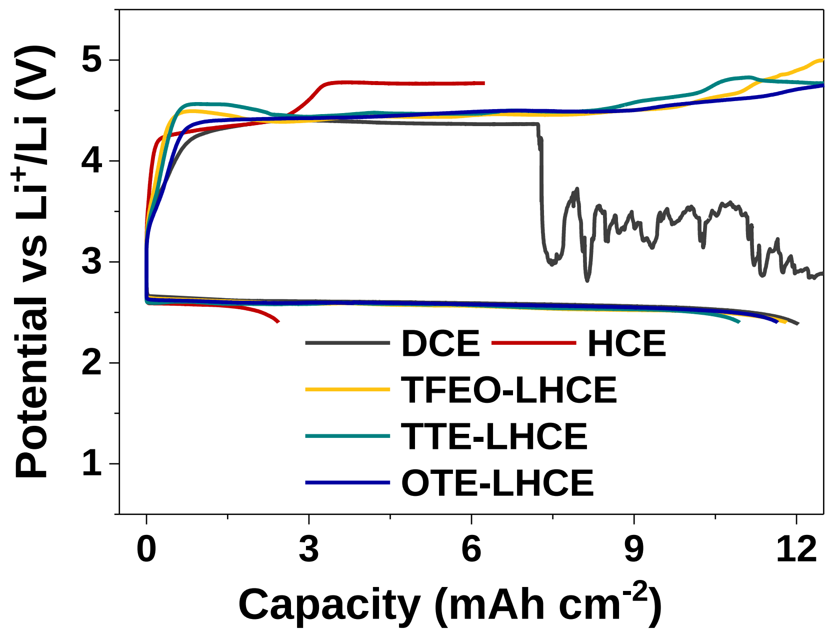


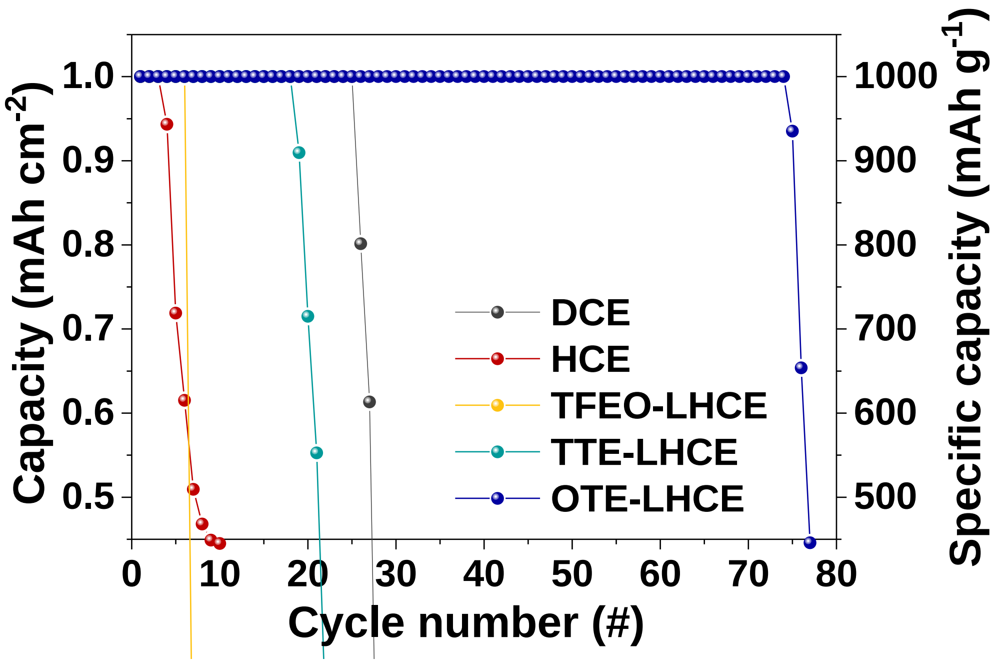


- O_2 solubility: TFEO-LHCE > OTE-LHCE > TTE-LHCE > HCE > 1 M LiTf in G4
- Volatility: HCE ≈ 1 M LiTf in G4 < TFEO-LHCE ≈ OTE-LHCE <<<< TTE-LHCE

Technical Accomplishments

Cycling performance of LOBs using different electrolytes

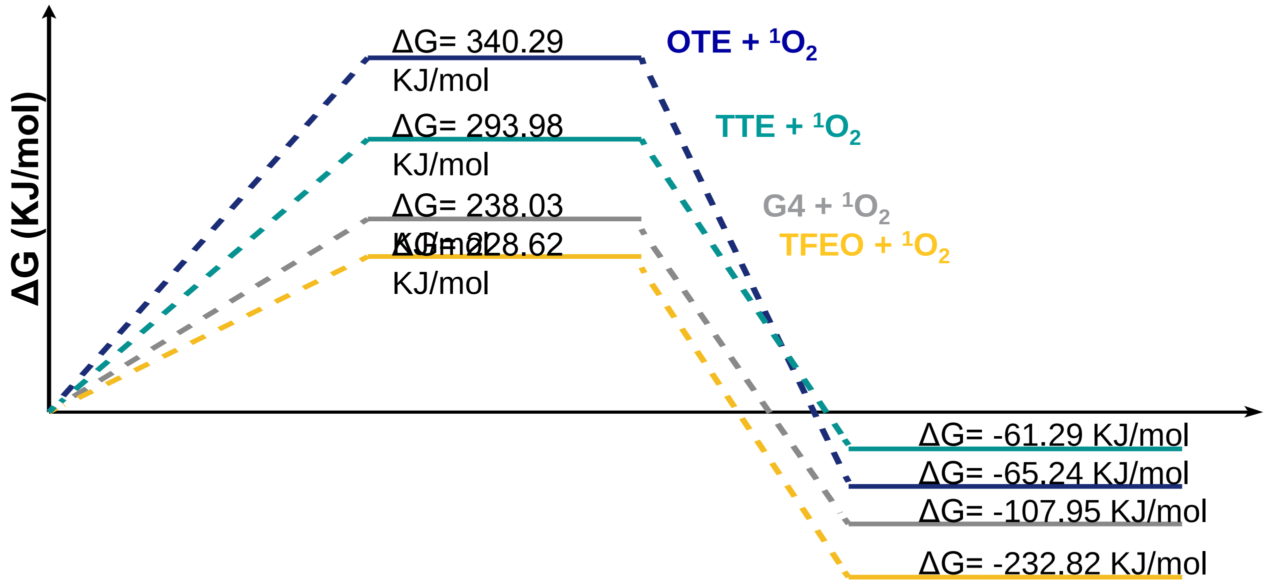




- Cycle life of LOBs: OTE-LHCE >>> 1 M LiTf in G4 > TTE-LHCE > TFEO-LHCE > HCE
- **LOBs using OTE-LHCE exhibit longer cycle life than those using other electrolytes.**

Technical Accomplishments

Stability of different diluents against singlet oxygen



Com-pound	DFT calculation		Molecular weight (mol/g)	Boiling point (°C)	Density (g/ml)
	HOMO (eV)	LUMO (eV)			
TFEO	-8.62	-0.18	310.11	143	1.457
TTE	-9.61	-0.21	232.07	92	1.532
OTE	-10.02	-0.68	332.09	133	1.616

- Calculated stability of chemicals against $^1O_2$: OTE > TTE > G4 > TFEO
- **OTE exhibits the highest stability against singlet oxygen attack.**
- **Stability of TFEO is worse than G4, which is the reason for the poor cycle life of LOBs using TFEO-LHCE.**

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

- Low energy efficiency due to extremely high overpotential during charge.
- The compatibility of LHCE with additives (solid or soluble).
- Evaporation of electrolyte due to relatively high volatility of diluents.

Proposed Future Research

- Suitable additives (solid or soluble) or methods for sustainable catalytic effects should be adapted.

- Optimization of electrolyte components (LHCEs and additives) by evaluation of cycling performance of Li-O2 batteries.

- Systematical design and synthesis of stable chemicals as solvents and diluents with low vapor pressure, high O2 solubility, good mixability, and wide electrochemical redox potential.

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

Summary

- LHCEs lead to much longer cycling performance for LOBs and LABs due to their lower viscosity, better stability with Li metal and reactive singlet oxygen, and their higher oxygen solubility.

- OTE is the best diluent for LHCE because of its lower volatility and higher stability against reactive singlet oxygen.

- Stability against singlet oxygen is a critical factor in stability of electrolyte and cyclability of LOBs and LABs.

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Acknowledgements

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- Team Members: Won-Jin Kwak, Sujong Chae, Hyung-Seok Lim, Ruozhu Feng, Peiyuan Gao, Mark H. Engelhard, Lirong Zhong