2021 DOE VTO Annual Merit Review

Novel Chemistry: Lithium Selenium and Selenium Sulfur Couples

PI: Khalil Amine

Presenter: Gui-Liang Xu

Argonne National Laboratory

June 21-25, 2021

Project ID: bat280

Overview

Timeline

- Start - October 1st, 2015.
- Finish - September 30, 2023.
- 87% Completed

Barriers

- Barriers addressed
  - Shuttle effect
  - Low electronic conductivity and low active material loading
  - Lithium dendrite and safety
  - Cycle life

Budget

- Total project funding
  - DOE share: $2500K
- Funding received in FY16-FY20: 2500K
- Funding for FY21: $440K

Partners

- Project lead: Khalil Amine
- Interactions/collaborations:
  - **Dr. C. J. Sun (APS, ANL)** XAFS Characterization
  - **Dr. Y. Ren (APS, ANL)** HEXRD characterization
  - **Dr. A. Ngo, Dr. L. Cheng and Dr. L. Curtiss (ANL)** Computational modeling
  - **Prof. Andy Sun (Western University)** Surface coating

Relevance and project objectives

- **Objective:** develop novel S_xSe_y cathode materials for rechargeable lithium batteries with high energy density and long life as well as low cost and high safety.
- **Impact**

This technology, if successful, will lead to:

- A cell with nominal voltage of 2 V and energy density of 600 Wh/kg
- A battery capable of operating for 500 cycles with low capacity fade

Milestones

Time	Description (status)
July 2020	Interface understanding on the effect of fluorinated ether electrolytes on the cycled SeS_x cathode using TOF-SIMS and XPS (*Completed*)
Oct 2020	Interface understanding on the effect of fluorinated ether electrolytes on the cycled lithium metal using TOF-SIMS and XPS (*Completed*)
Jan 2021	Building in-house Li-S pouch cell fabrication line and demonstration of > 100 mAh pouch cells performance using Se-doped sulfur cathode and fluorinated ether-based electrolytes (*Completed*)
Apr 2021	Design of novel cathode host for high-loading Li-S and Li-Se/S batteries to further increase energy density (*on-going*)

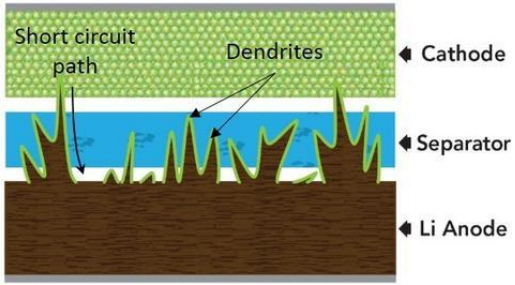
Approach

- Doping Se on S to improve electronic conductivity and increase active material loading
- Investigate the impact of carbon pore structure on the active material loading and performance
- Develop novel electrolytes to suppress dissolution of polysulfide & selenide species and prevent lithium dendrite formation
- Use in-operando synchrotron X-ray and spectroscopy probes to understand failure mechanism
- Deploy advanced modeling capability to complement diagnostic results

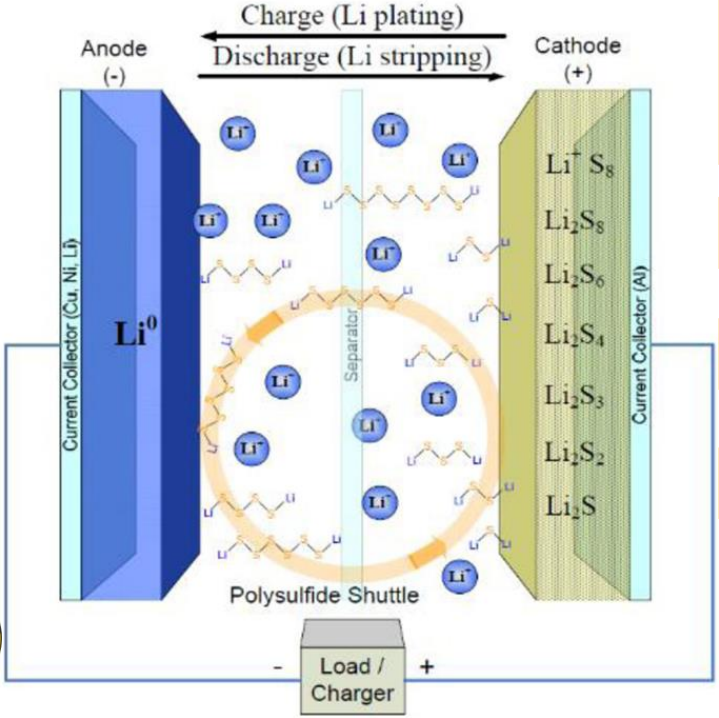
Technical accomplishments

- Unravelling the effect of fluorinated ether electrolytes in stabilizing lithium metal
- Unravelling the effect of fluorinated ether electrolytes in suppressing shuttle effect
- In-house Ah-level Li/Se-S pouch cell fabrication and testing using fluorinated ether electrolytes and Se-doped S cathode

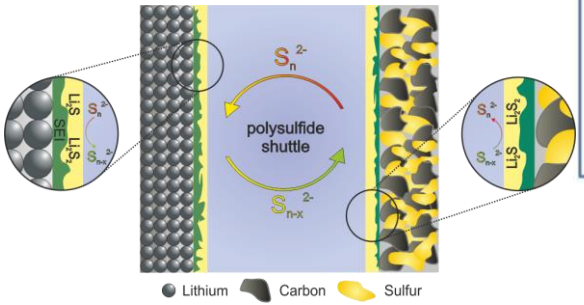
Challenges of lithium/sulfur batteries



Lithium dendrite growth



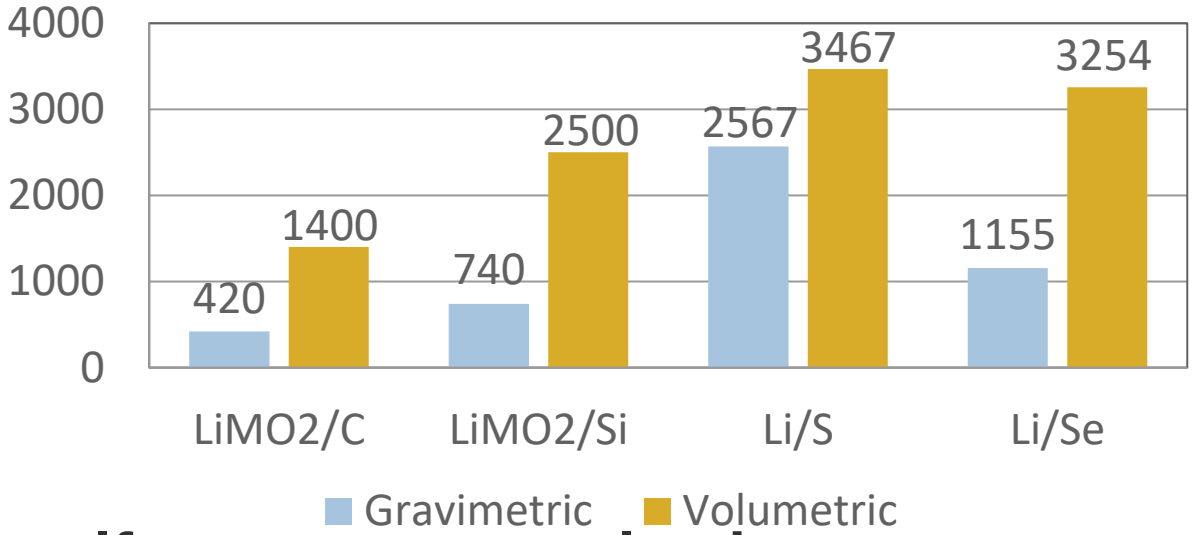
Polysulfides shuttle



Nat. Commun. 2013, 4, 1331.
Chem. Rev. 2014, 114, 11751.
Nat. Commun. 2014, 5, 4759.
Adv. Energy Mater. 2015, 5, 1500408

- Low electronic conductivity of sulfur (~10^{-30} S cm^{-1}) and Li_2S_2/Li_2S.
- Low mass-loading of sulfur
- Self-Discharge
- Volume changes

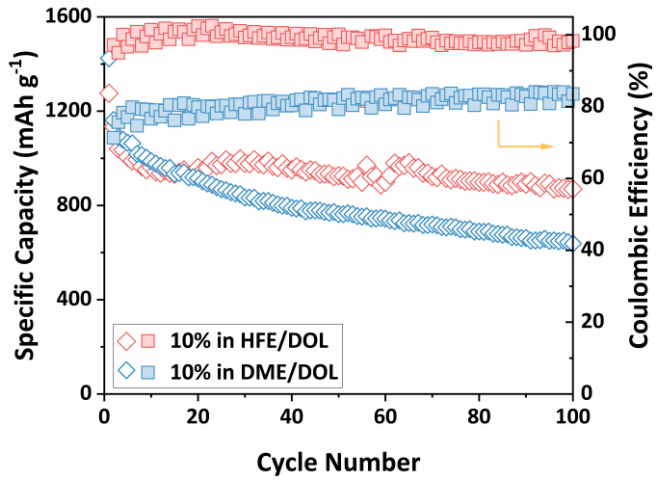
Motivation for selenium-sulfur chemistry

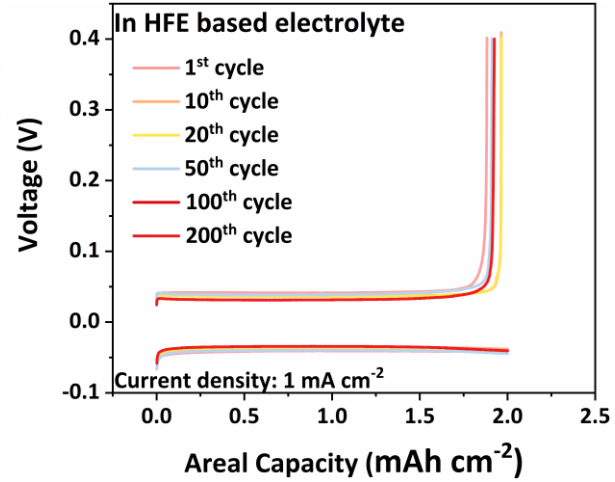


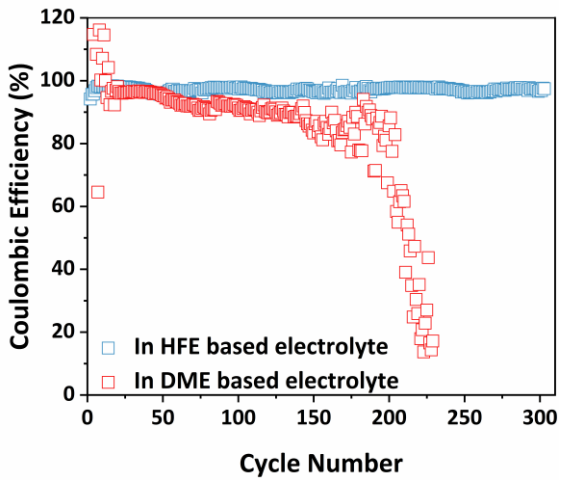
Selenium sulfur systems can lead to:

- Comparable energy density to Li/S battery
- High electrical conductivity ($1E^{-3}$ vs. $5E^{-28}$ S/m for S), leading to high utilization
- High active material loading, leading to high volumetric energy density

Argonne's fluorinated ether electrolytes can eliminate the shuttle effect and Li dendrite simultaneously







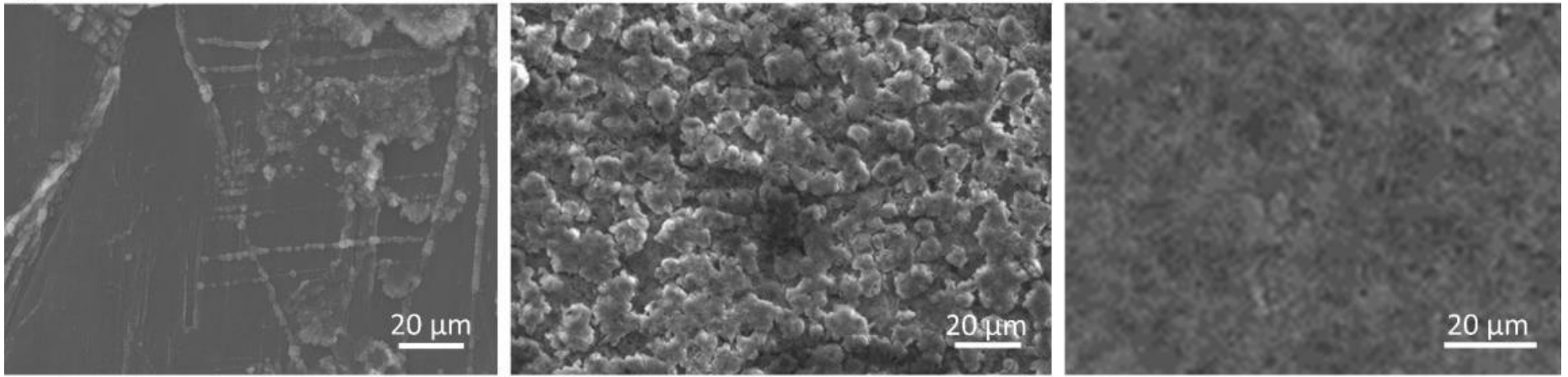
- Fluorinated ether (HFE) electrolytes demonstrated better cycle stability and no shuttle effect than conventional ether (DME)-based electrolytes
- Fluorinated ether electrolytes exhibited better Li stripping/plating reversibility than DME-based electrolytes

SEM confirmed that the cycled Li metal is smoother and more homogeneous in the HFE-based electrolytes

Pristine Li metal

Cycled Li metal of Li/Cu cell in DME-based electrolytes

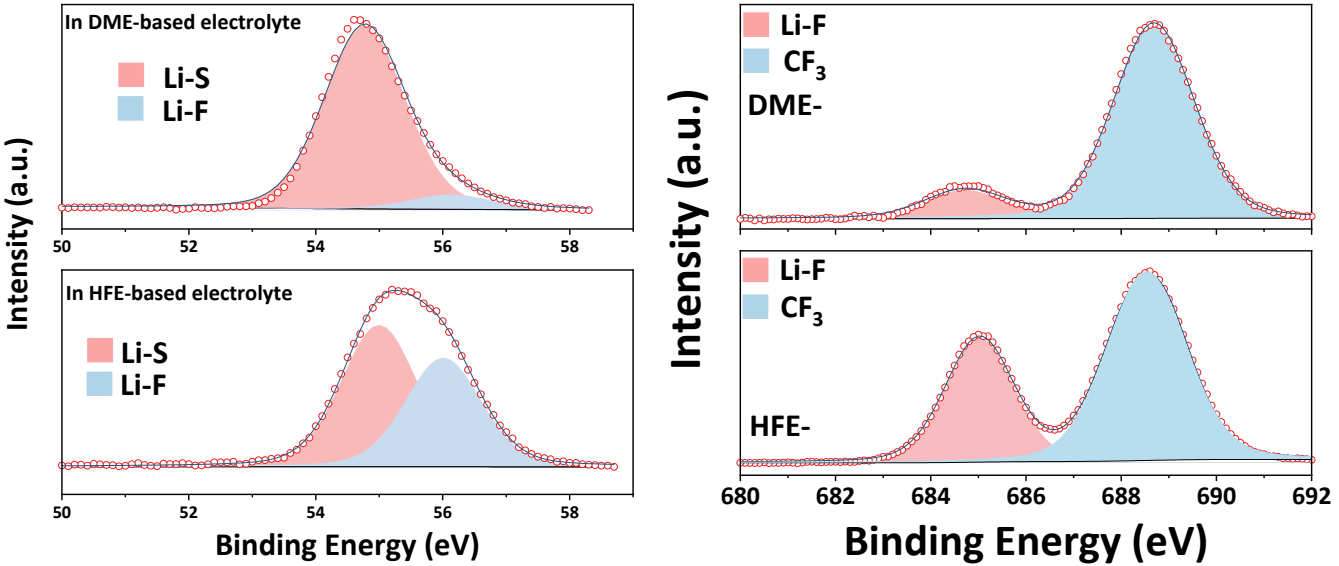
Cycled Li metal of Li/Cu cell in HFE-based electrolytes



Isolated metallic Li formed on the surface of the Li foil

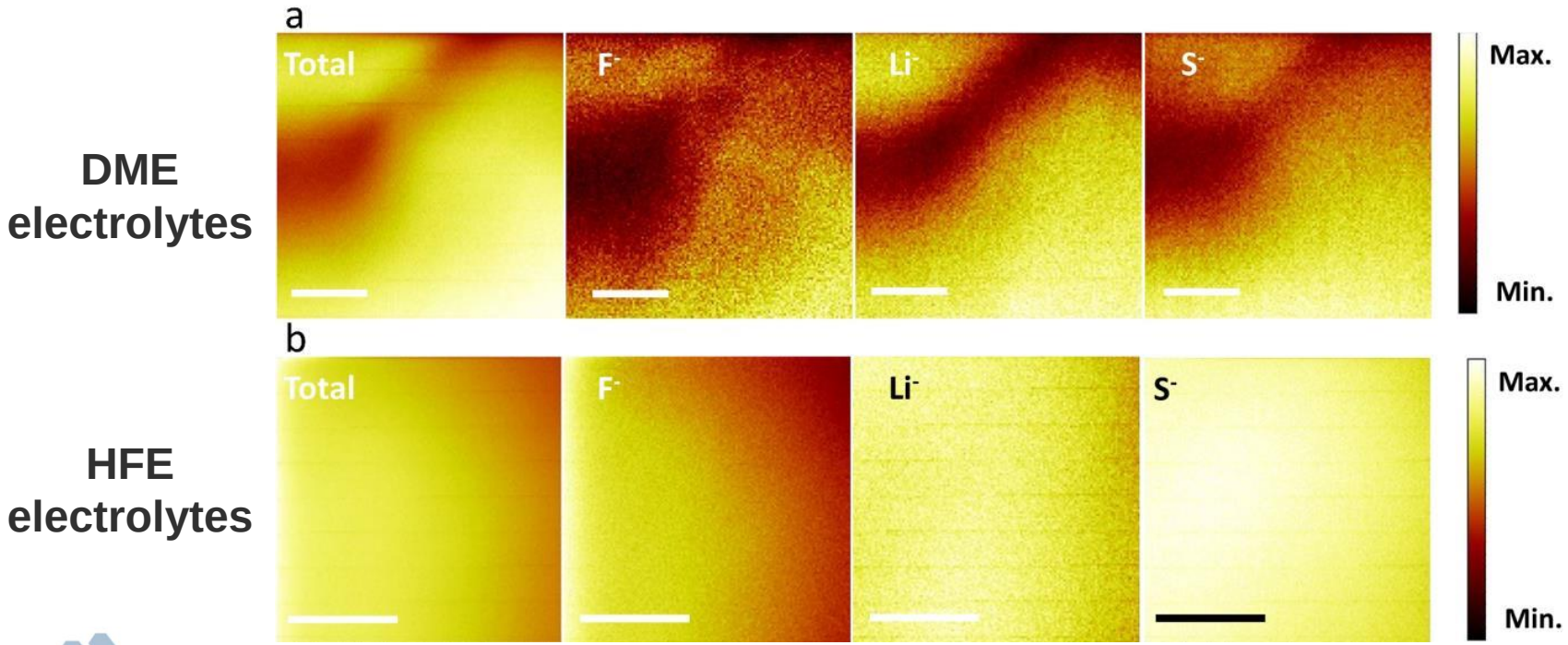
Homogeneous and uniform surface

X-ray Photoelectron Spectroscopy (XPS) showed that HFE electrolytes lead to formation of SEI with higher LiF content on Li metal



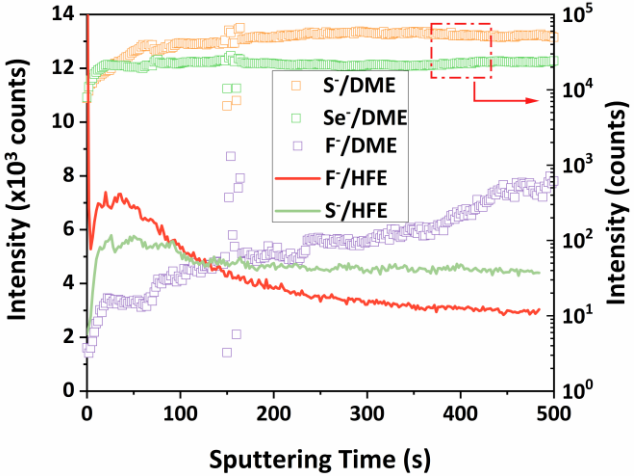
LiF was formed via the decomposition of salts and solvents, which was considered as a vital component to enable reversible Li stripping/plating

TOF-SIMS characterization on the cycled Cu foil of Li/Cu cells showed that the Li^- and F^- signals exhibit more homogeneous distributions in the HFE-based electrolyte

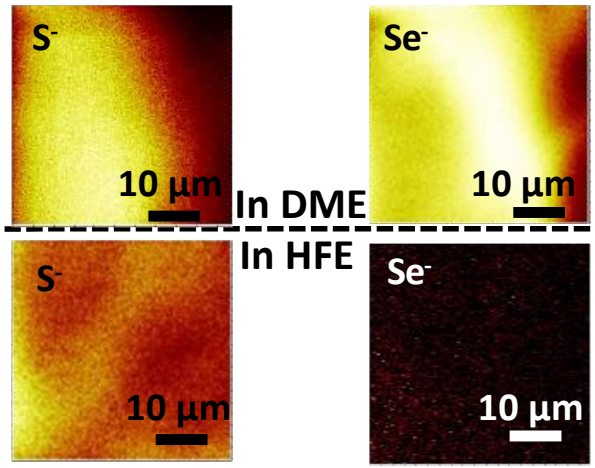


TOF-SIMS characterization on the cycled Li foil of Li/Se-S cells showed that the cycled Li metal exhibited a uniform and homogeneous morphology in HFE electrolytes

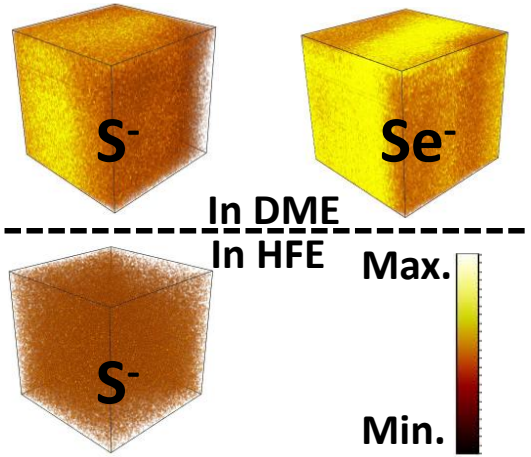
Depth profile of cycled Li metal in Li-Se/S cells



ToF-SIMS mapping (S^- and Se^-) of cycled Li metal in Li-Se/S cells



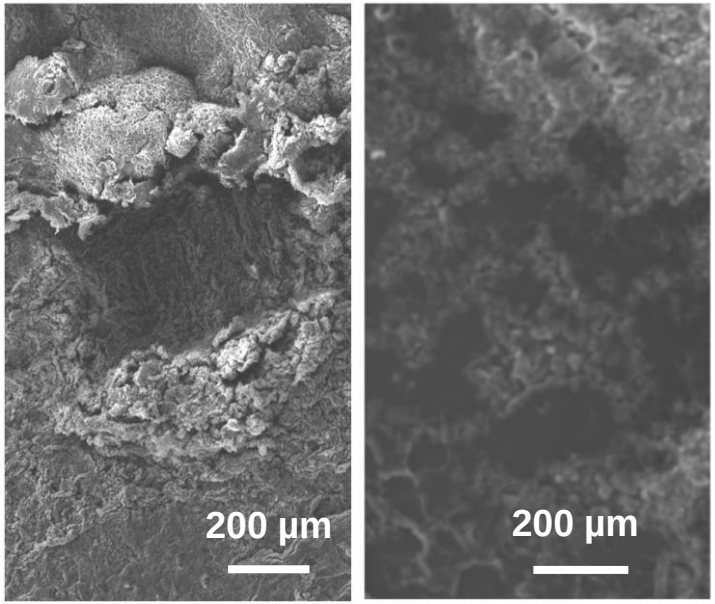
3D reconstruction (S^- and Se^-) of cycled Li metal in Li-Se/S cells



- Large amount of S and Se elements was found in DME electrolyte, indicating severe shuttle
- Only weak S from SEI and no Se can be detected in HFE electrolytes, indicating no shuttle

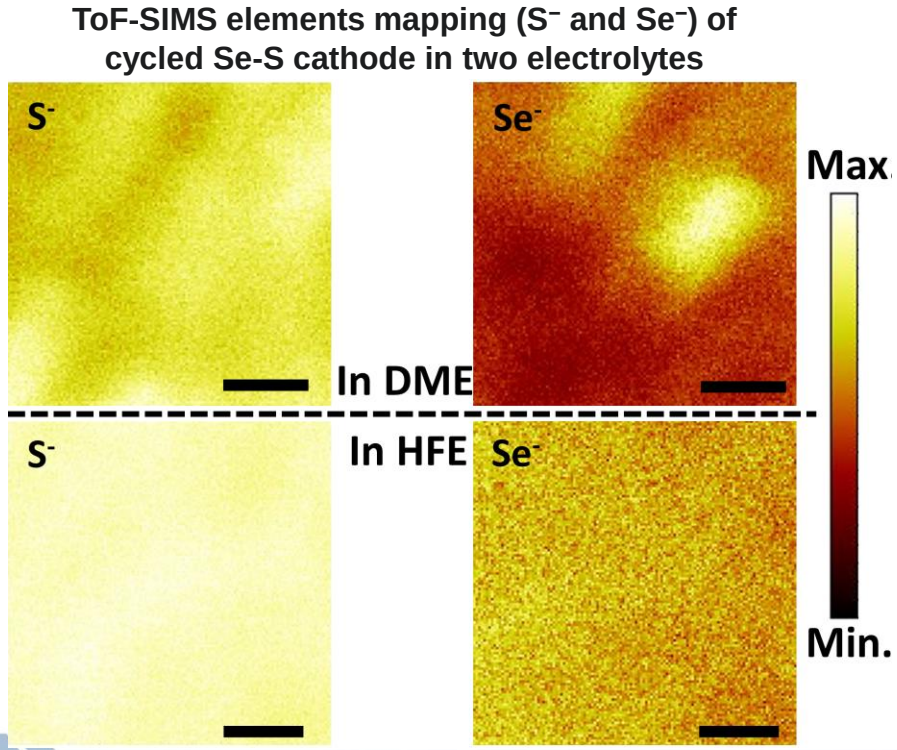
SEM confirmed that the morphology of cycled Li metal in Li/Se-S cells using HFE electrolytes is well maintained

DME: many irregular deposition products were found on the surface of the cycled Li foil



HFE: homogeneous and smooth

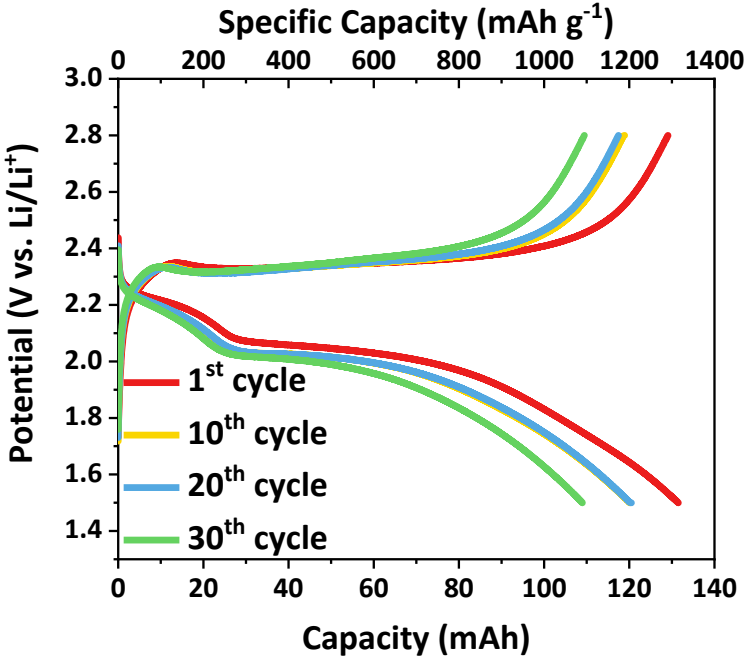
TOF-SIMS characterization on the cycled Se-S cathode confirmed much less polysulfides/polyselenides dissolution and re-deposition

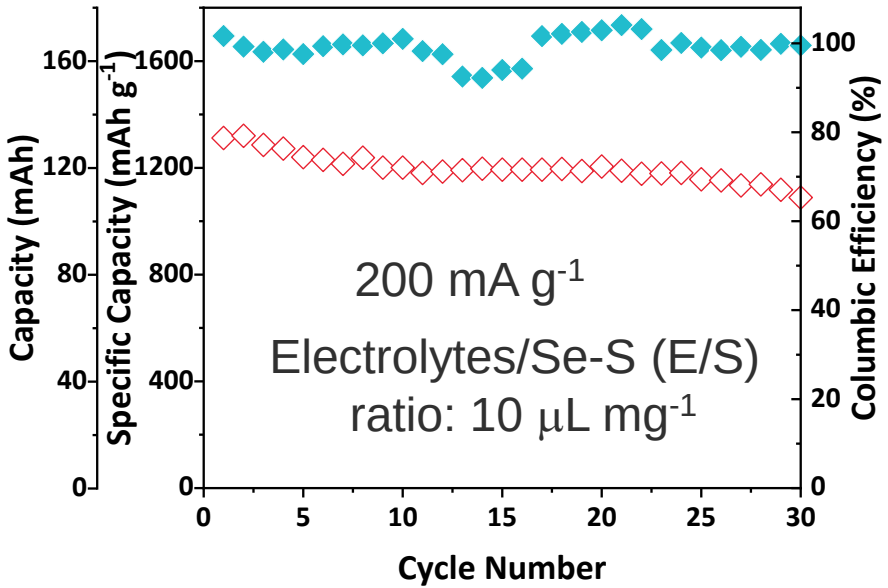


DME: Several isolated sulfur and selenium species were identified on the cycled cathode in DME-based electrolyte

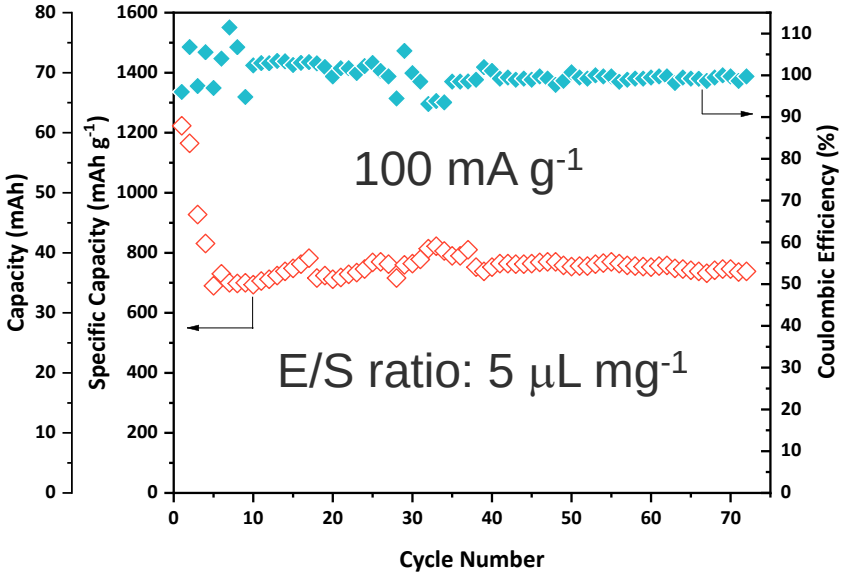
HFE: both S^- and Se^- were uniformly and homogeneously distributed on the cathode

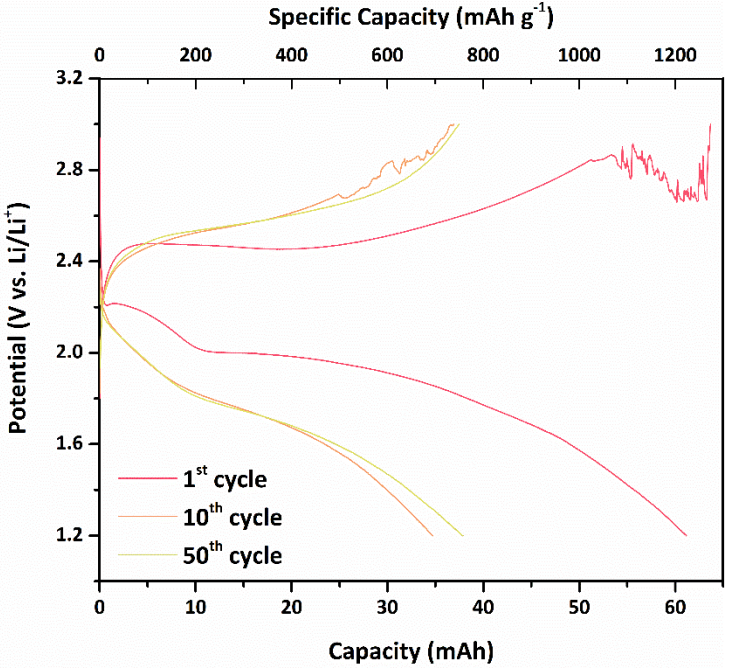
Li/Se-S pouch cell (>100 mAh) using Se-S cathode and fluorinated ether electrolytes showed stable cycle life and high sulfur utilization



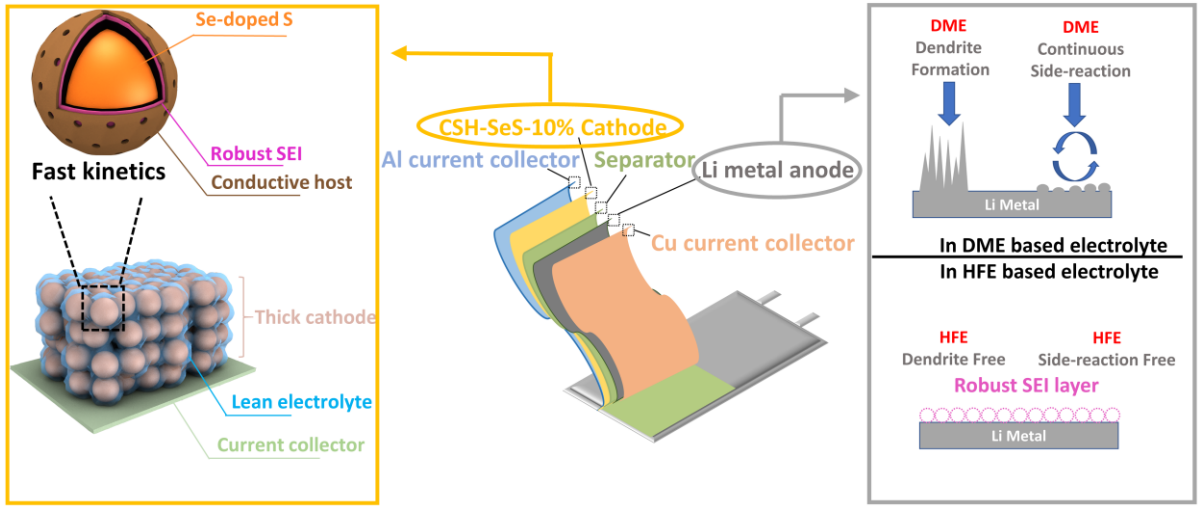


Sulfur utilization was decreased, and voltage polarization was increased with decreased E/S ratio





The working principle of Se-S cathode and fluorinated ether electrolytes



- The robust SEI forms in situ on the surface of the Se/S cathode, can act as a protective layer to suppress polysulfides dissolution
- The robust SEI forms in situ on the surface of Li metal surface can effectively eliminate the parasitic reactions between Li metal and electrolyte molecules, significantly improving the cycling stability and Coulombic efficiency.

The flammability test showed that the fluorinated ether electrolytes are nonflammable, leading to improved safety

DME electrolytes

HFE electrolytes

Responses to Previous Year Reviewers' Comments

- No comments from the reviewers

Collaborations

- Dr. C. J. Sun (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using operando XAFS.
- Dr. Y. Ren (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using operando HEXRD.
- Dr. A. Ngo, Dr. L. Cheng and Dr. L. Curtiss (MSD, ANL)
  - Ab initio molecular dynamics simulation and DFT calculation.
- Prof. Andy Sun (Western University)
  - ALD and MLD surface coating

Remaining Challenges and Barriers

- The areal S loading (capacity) need to further increased to > 6 mg cm^{-2} (6 mAh cm^{-2});
- The sulfur utilization under low electrolytes/sulfur ratio (< 3 μl mg^{-1}) need to be improved;
- Lithium stripping/plating reversibility need to be further improved to ensure long-term cycling stability
- The cell energy density of Li/Se-S pouch cells remain insufficient

Proposed Future Work for FY 2021 and FY2022

- FY 2021 Q3 Milestone:
  - Validate electrochemical performance of new cathode host
- FY 2021 Q4 Milestone:
  - Conduct operando and ex situ characterization on developed cathodes during charge/discharge
- FY2022 work proposed
  - Developing high electrode areal loading Se-S systems (> 6 mAh cm^{-2}) by designing new cathode structures
  - Electrolyte (additives, salts, co-solvents, etc.) modulation to further stabilize long-term cycling of Lithium metal
  - Demonstration of Li/Se-S pouch cells with a cell density of > 350 Wh kg^{-1}

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

Summary

- Fluorinated ether-based electrolytes can enable robust LiF-rich solid-electrolyte interphase on both Se-S cathode and lithium metal, thus eliminating shuttle effect and lithium dendrite simultaneously;
- Li/Se-S pouch cell using Se-S cathode and fluorinated ether electrolytes showed stable cycle life with high sulfur utilization;
- Fluorinated ether electrolytes showed lower flammability than conventional ether electrolytes, leading to better safety;
- The cell energy density of Li/Se-S pouch cell requires further improvement by improving lean electrolytes performance