Novel Chemistry: Lithium Selenium and Selenium Sulfur Couple

Khalil Amine (PI)

Zonghai Chen and Gui-Liang Xu

Argonne National Laboratory

2018 DOE VTO Annual Merit Review

June 18th ~21st, 2018

Project ID: BAT280

Overview

Timeline

- Start - October 1st, 2015.
- Finish - September 30, 2020.
- 60% Completed

Barriers

- Barriers addressed
  - High energy
  - Long calendar and cycle life

Budget

- Total project funding
  - DOE share: $2500K
- Funding received in FY16&17: $1000K
- Funding for FY18: $500K

Partners

- Project lead: Khalil Amine
- Interactions/collaborations:

- **Prof. C. S. Wang (UMD)** **Encapsulating S_xSe_y in carbon matrix**
- **Dr. C. J. Sun (ANL)** **Mechanism study using in situ XANES**
- **Dr. Y. Ren (ANL)** **Mechanism study using in situ HEXRD**
- **Dr. L. Cheng, Dr. L. Curtiss (ANL)** **DFT calculation**

Relevance and project Objectives

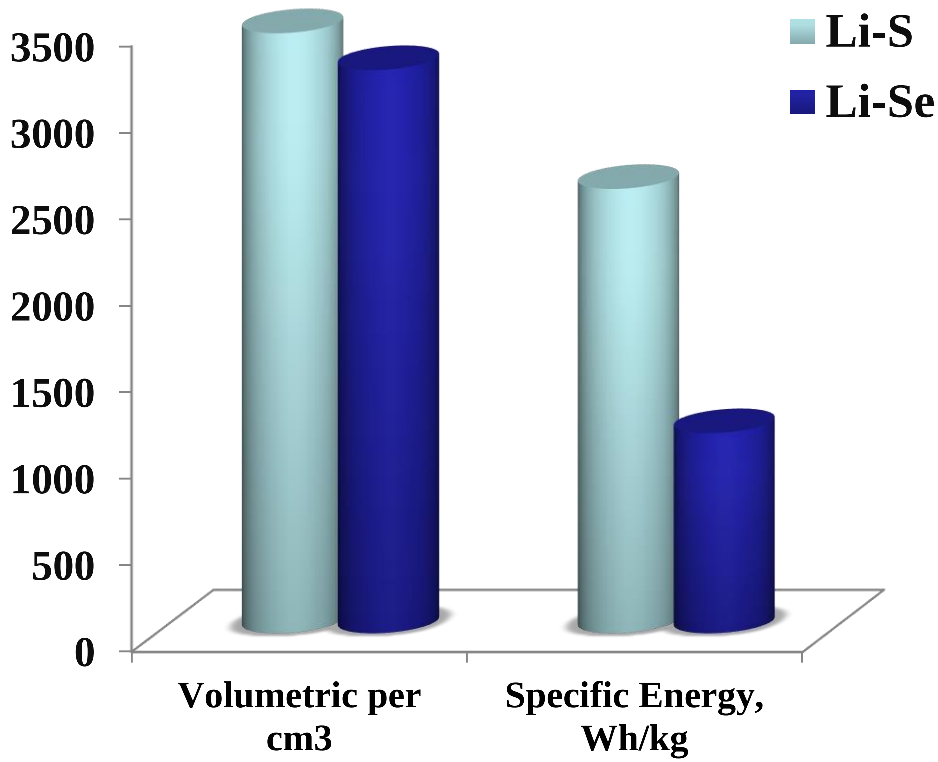
- **Objective:** develop novel S_xSe_y cathode materials for rechargeable lithium batteries with high energy density and long life as well as low cost and high safety.

- **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

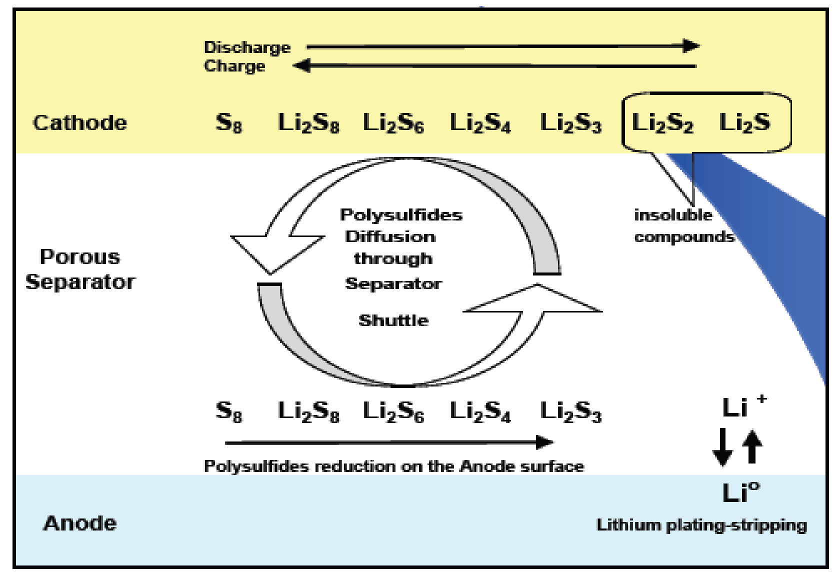
Milestones

- Investigate the alloying mechanism between S and Se (completed)
- Encapsulate S_xSe_y in porous carbon matrix (completed)
- Investigate the performance degradation mechanism of space-confined S_xSe_y cathodes in ether-based electrolytes (completed)
- DFT calculation study on the interaction between polyselenides and carbon host (completed)
- Explore novel electrolytes to suppress the polysulfides/polyselenides dissolution in ether-based electrolytes (on going)
- Parasitic reactions study of various S_xSe_y cathodes in different electrolytes (on going)
- Investigate the pore selection of carbon host towards different electrolytes for S_xSe_y cathodes (on going)

Motivation



Redox shuttle effect of dissolved lithium polysulfides



Selenium

- **Comparable high volumetric capacity to Li-S battery**
- **High gravimetric density (>1000 Wh/kg)**
- **High electrical conductivity (1E^{-3} vs. 5E^{-28} S/m for S)**

Approach

- Investigate the impact of carbon pore structure host on the active material loading and performance
- Develop novel electrolyte to suppress dissolution of polysulfide & polyselenide species
- Use in-operando synchrotron X-ray and spectroscopy probes to understand failure mechanism
- Deploy advanced modeling capability to complement diagnostic activities

Technical accomplishments

- Electrical conductivity of cathode improved significantly by adding Selenium to Sulfur
- Performance degradation mechanism of S_xSe_y cathodes in ether-based electrolytes was elucidated
- Novel electrolytes to suppress the dissolution of polysulfides/polyselenides was explored
- The (de)/lithiation mechanism of S_xSe_y cathodes in the fluorinated ether electrolytes was understood by in-situ NMR and Operando X-ray probes
- High performance S_xSe_y cathodes with good cycle stability and rate capability was developed

Responses to Previous Year Reviewers' Comments

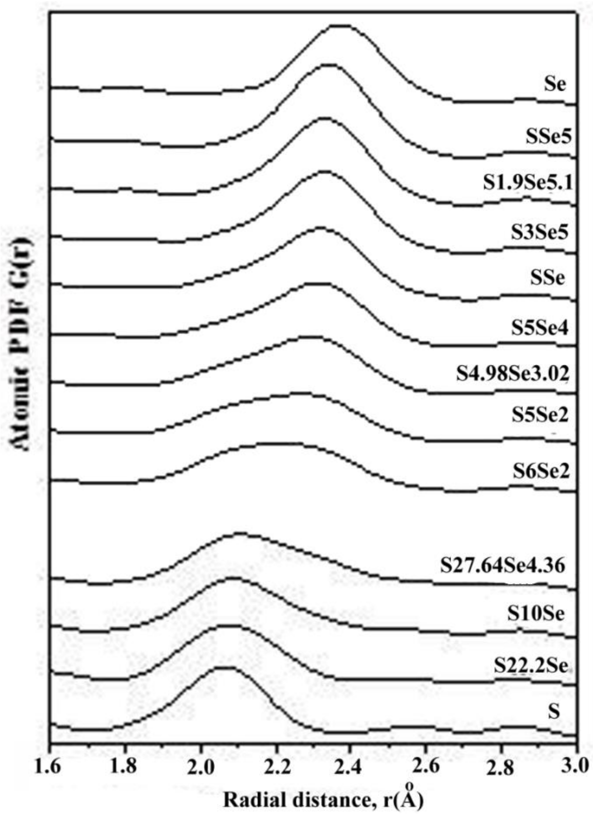
- This project was not reviewed last year

Collaborations

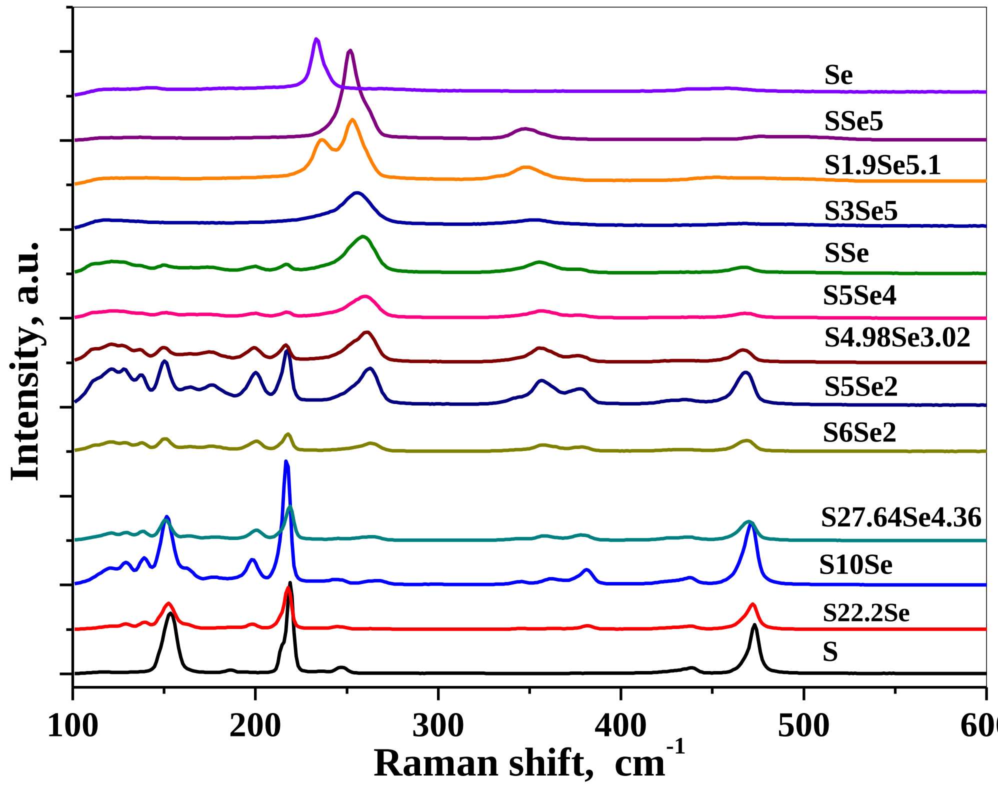
- Prof. C. S. Wang of University of Maryland at Collage Park
  - Encapsulating S_xSe_y in carbon matrix.
- Dr. C. J. Sun (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using in situ XANES.
- Dr. Y. Ren (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using in situ HEXRD.
- Dr. L. Cheng, and Dr. L. Curtiss (MSD, ANL)
  - DFT calculations.

Numerous Sulfur-selenium compounds (S_xSe_y) were investigated

Paid distribution function analysis

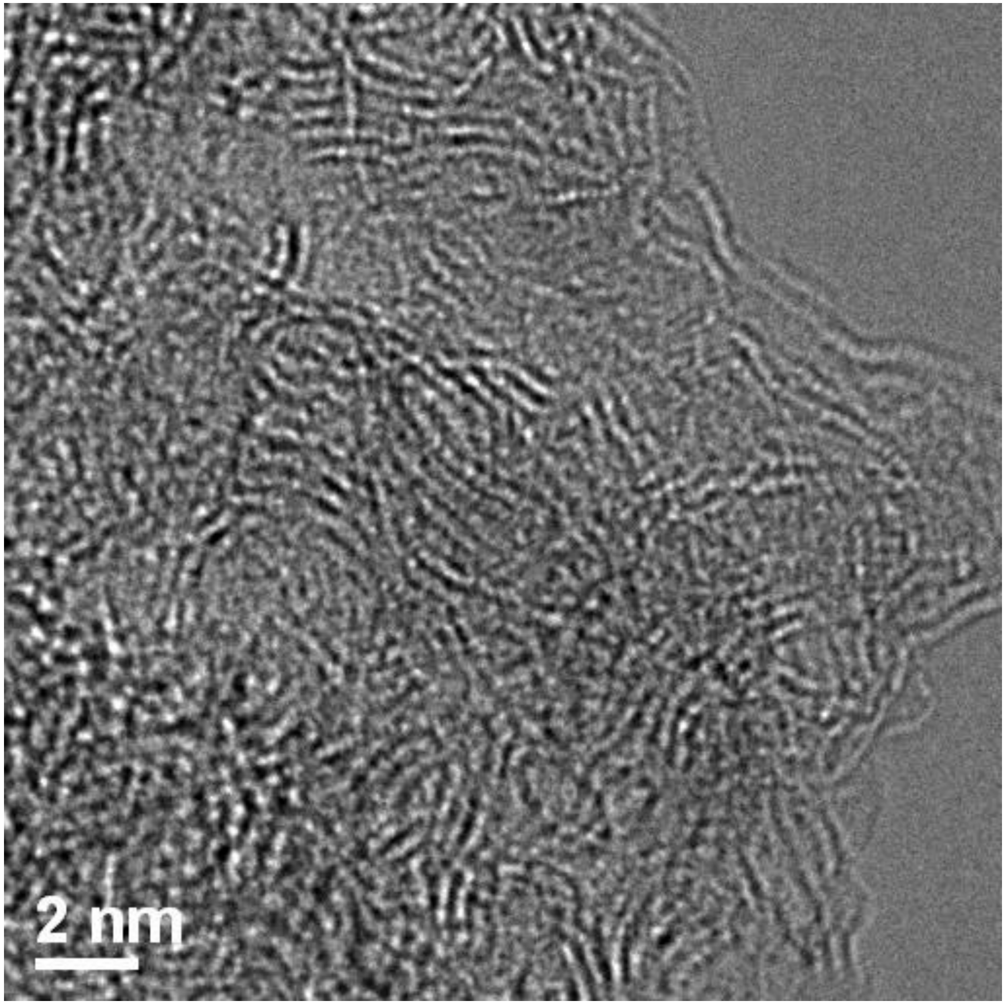


Raman spectra



PDF and Raman show that selenium and sulfur formed new compound and not a physical mixture

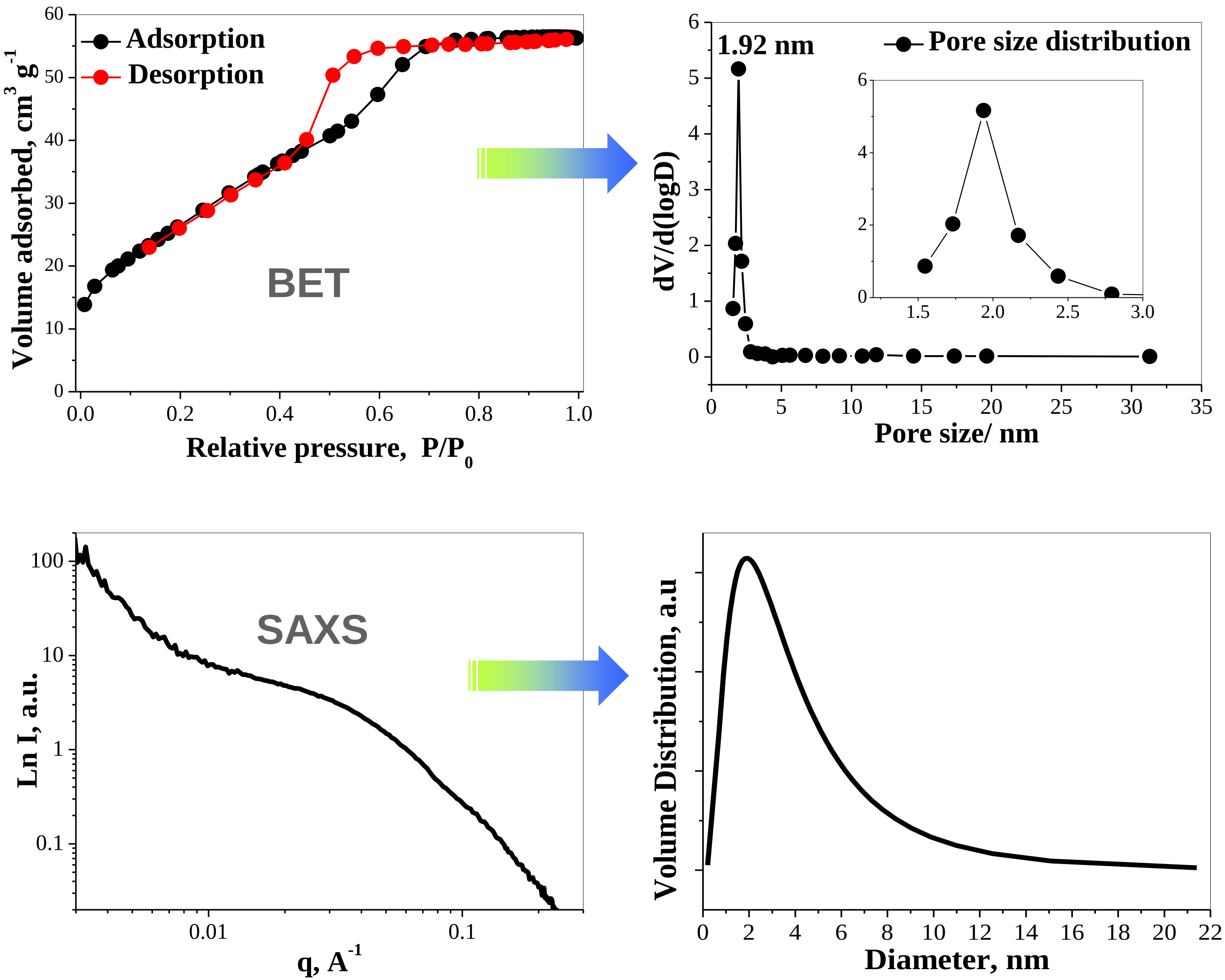
Structure of micro-porous carbon as host for S_xSe_y



TEM image of micro-porous carbon

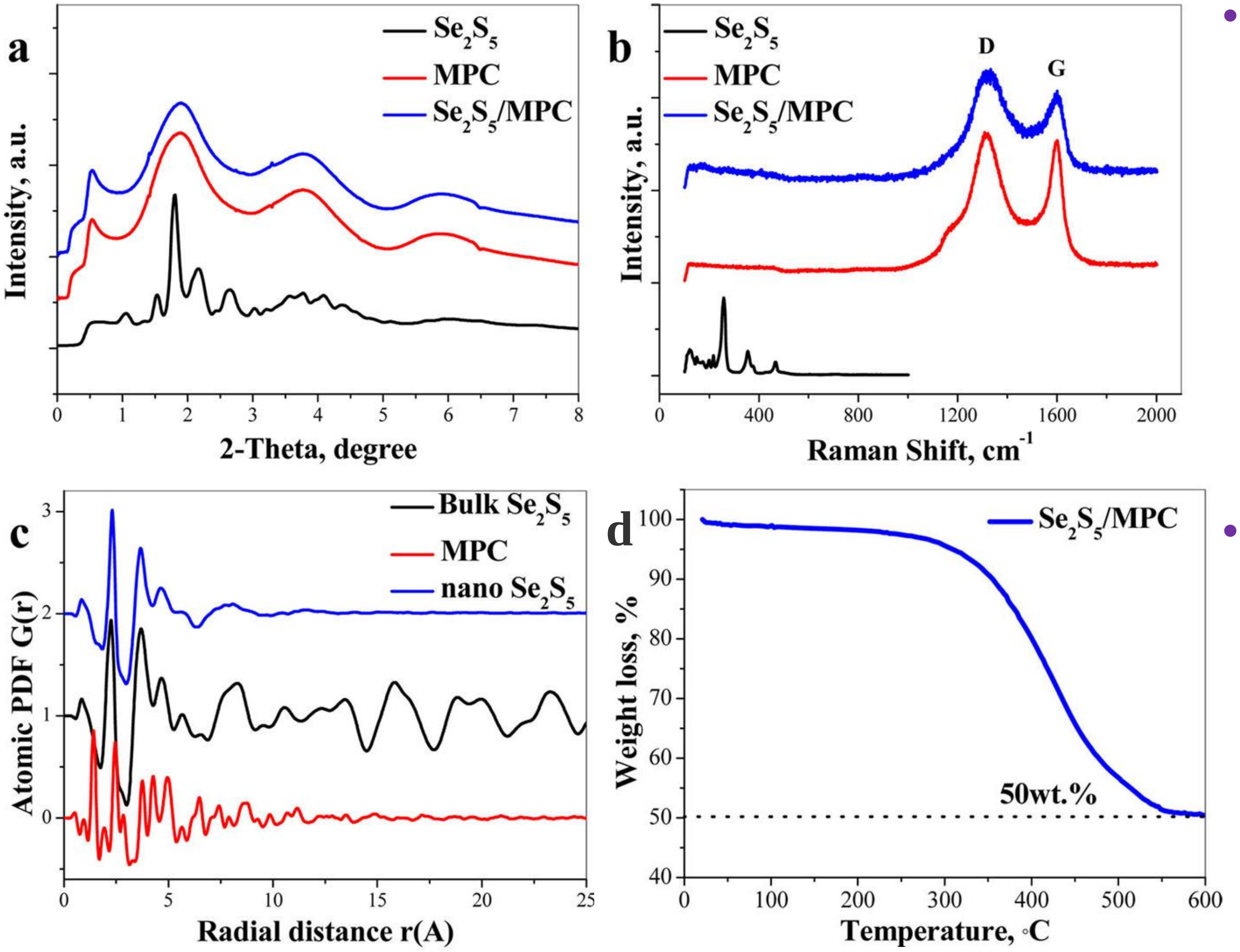
- Dominated by micro-porous of about 2 nm.
- Some bigger pores of 4-5 nm can also be observed.

Pore size of synthesized micro-porous carbon



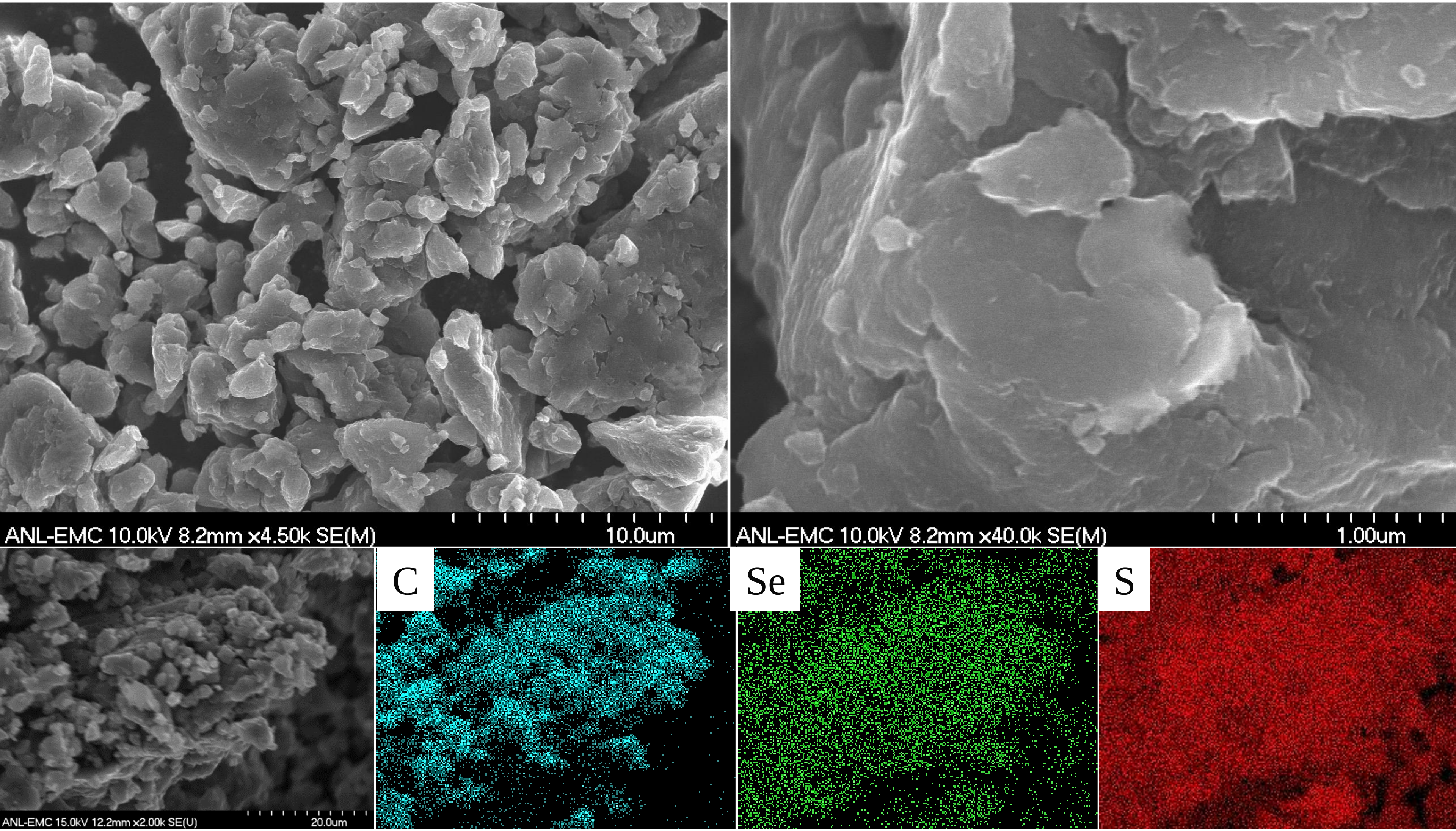
Both BET and SAXS confirmed a pore size of about 2 nm.

XRD (a), Raman (b), PDF (c) and TGA (d) of Se_2S_5/Microporous carbon (MPC) composite



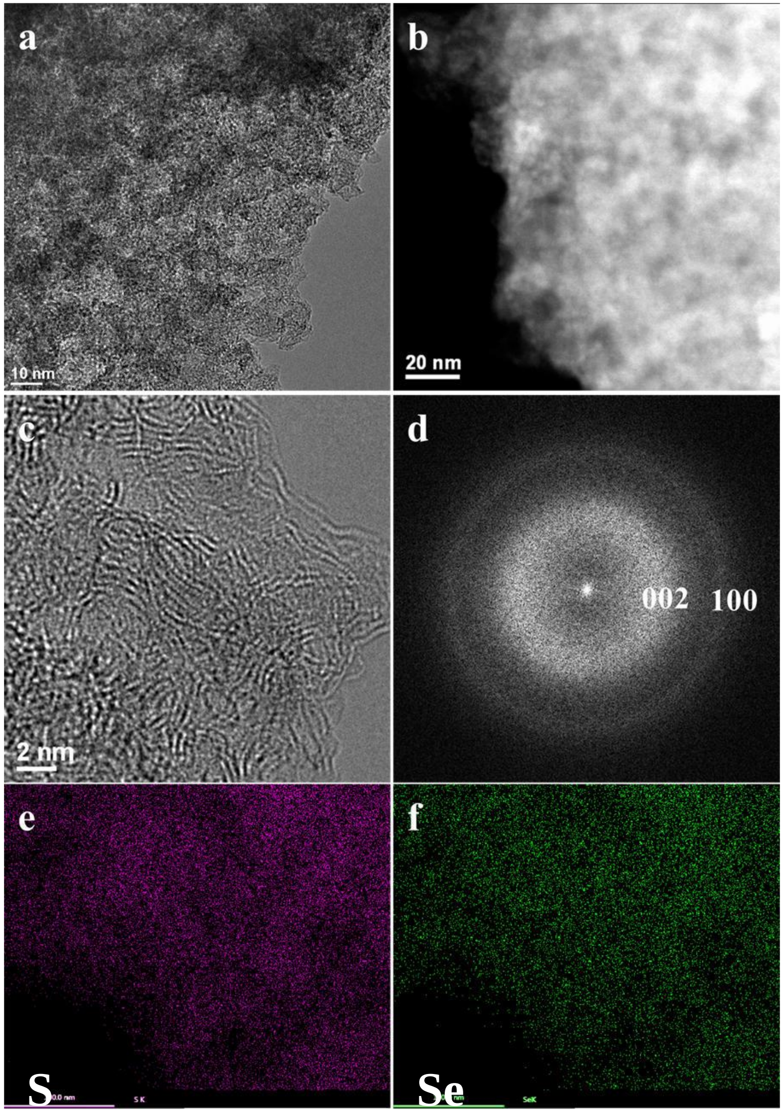
- XRD, Raman and PDF confirmed that Se_2S_5 existed in an amorphous state
- TGA analysis under argon showed that the Se_2S_5 loading in the composite is ca. 50 wt.%

Typical SEM images of Se_2S_5/C composite-50 wt.%



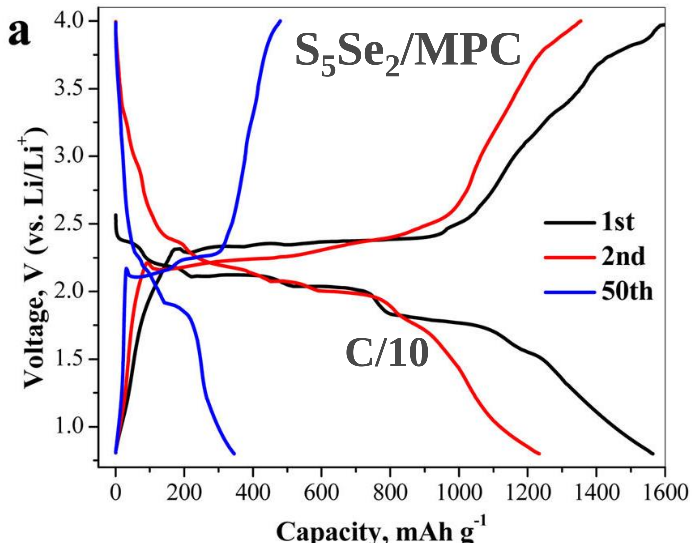
Micro-sized secondary particles with uniform Se, C and S distribution.

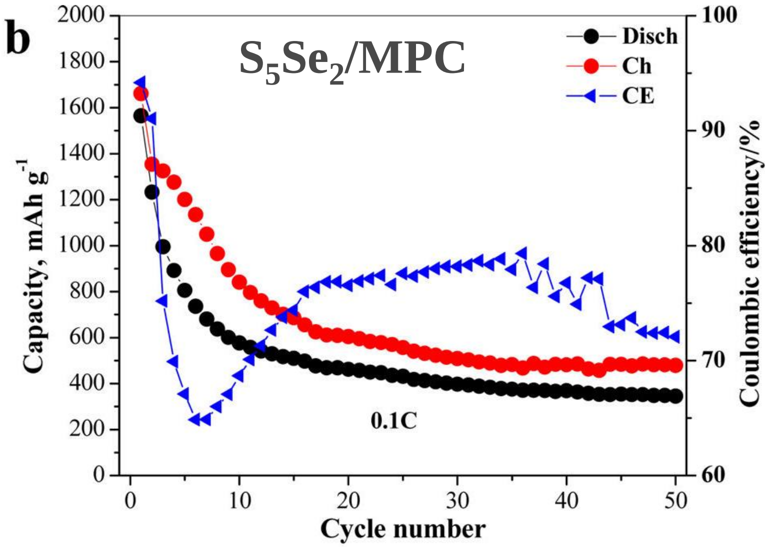
TEM characterization of Se_2S_5/MPC composite

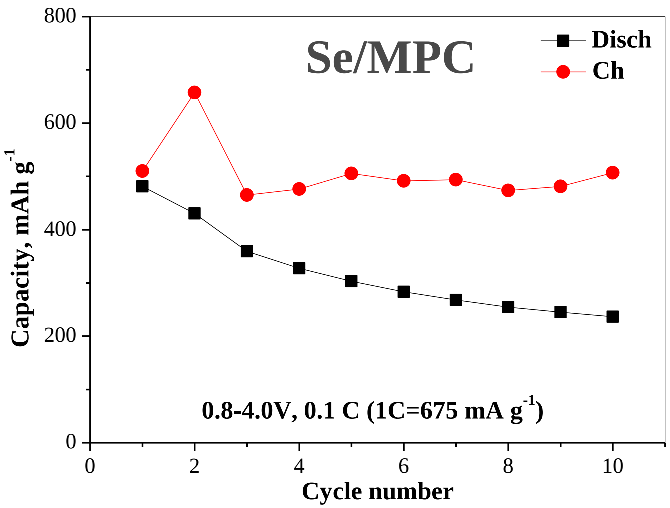


- Small brighter particles of 1-2 nm could be observed in the HAADF image (No aggregation of large particles)
- HRTEM shows only graphite lattice and FFT pattern shows only graphite ring (Se_2S_5 is amorphous)
- Uniform distribution of selenium and sulfur in the Se_2S_5/MPC composite

Space-confined S_5Se_2/MPC cathode in the commonly used DOL-DME electrolytes



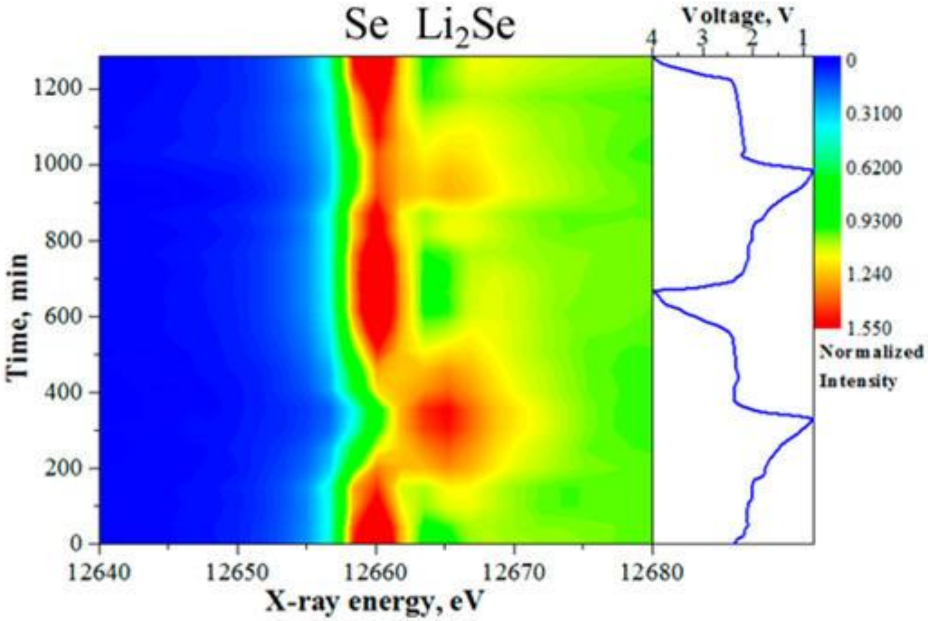


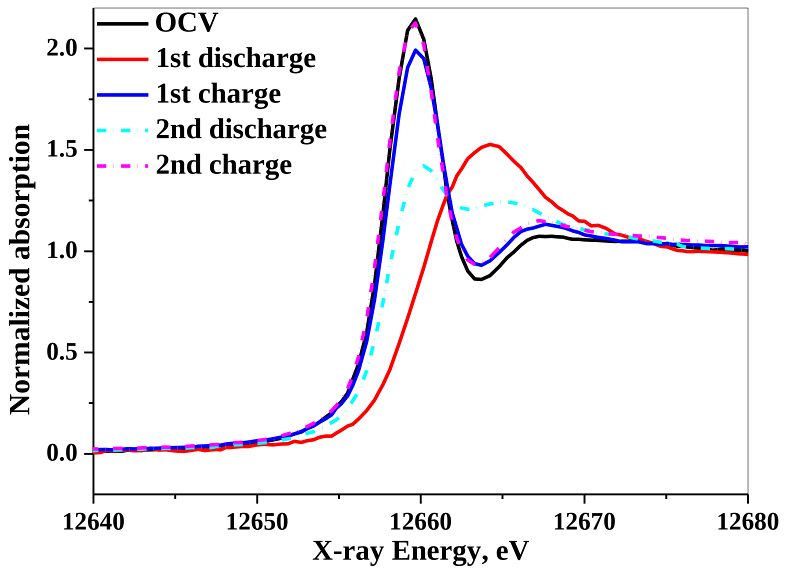


- Even with very good encapsulation, the Se_2S_5/MPC shows a rapid capacity fading with a severe shuttle effect;
- The Se/MPC shows similar results, confirming the capacity fade come from Se.

Electrolytes: 1M LiTFSI/DOL+DME(1/1,v/v) + 0.1M $LiNO_3$

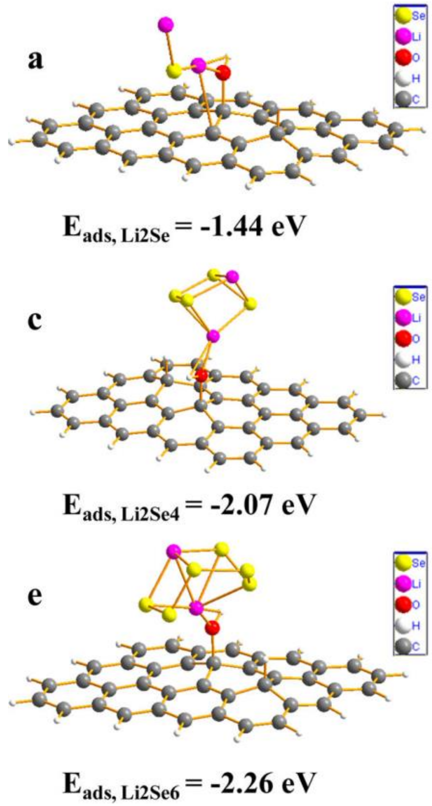
In-situ Se K-edge XANES showed that the performance degradation come from the loss of Li_2Se during cycling





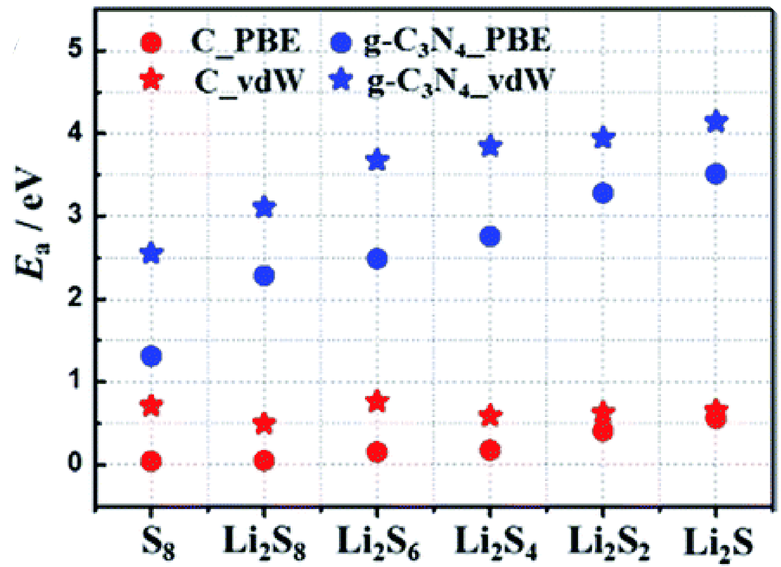
- Se K–edge of Li_2Se shift to high energy than elemental Se. This is inconsistent with the commonly observed phenomenon that the edge shifts to higher energy with the increase in the oxidation states (dissolution of polyselenides).
- The Se shows a highly reversible lithiation/de-lithiation process in the 1^{st} cycle;
- The reversible lithiation/de-lithiation of Se with Li decreased in the subsequent cycle;
- Preferred formation of long-chain polyselenides at the end of discharge (not fully lithiation)

Use of DFT calculation to understand the interaction between Li_2Se_n (Li_2S_n) with carbon host material



The binding energy of polyselenides with carbon host is as follow: Li_2Se_6> Li_2Se_4>Li_2Se_2;

Li_2S_n—carbon

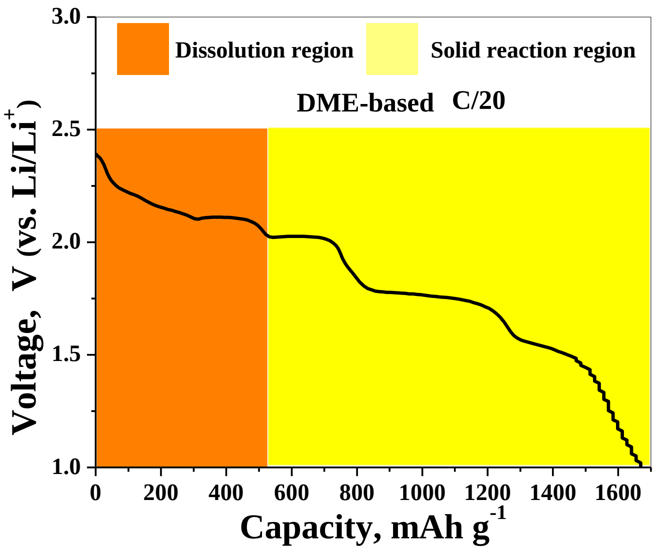


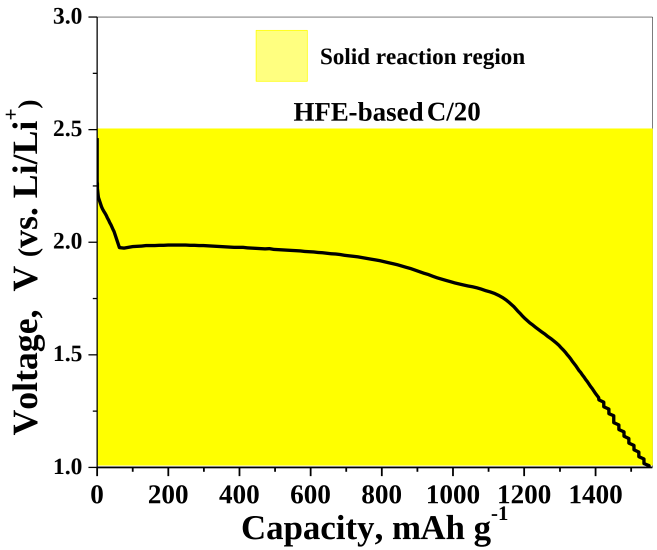
J. Mater. Chem. A, 2016, 4, 5406-5409

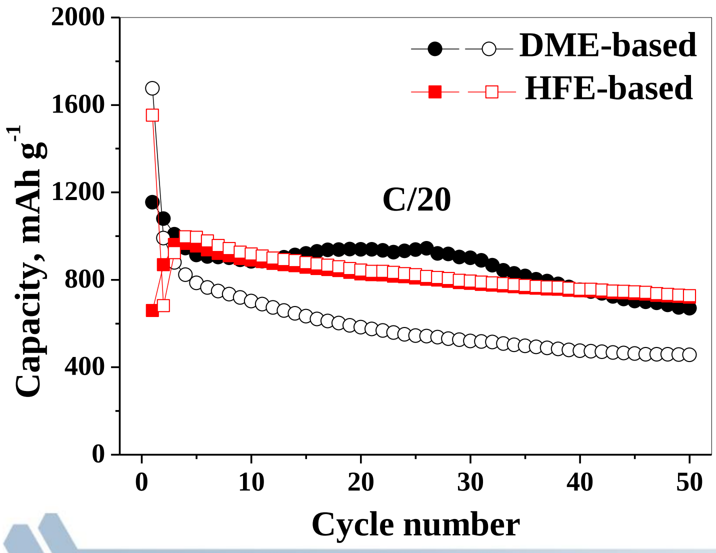
The vdW and PBE symbols refer to the DFT with and without vdW correction, respectively.

Polysulfides with host shows opposite trend

Use of Novel HFE electrolytes to suppress shuttle effect in Se_2S_5/C cathodes

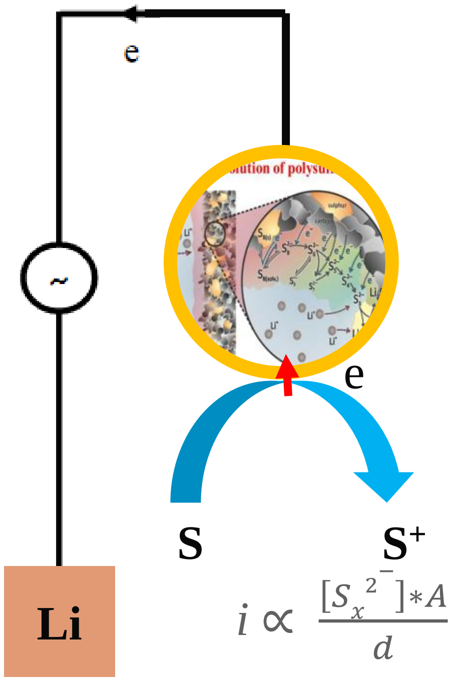


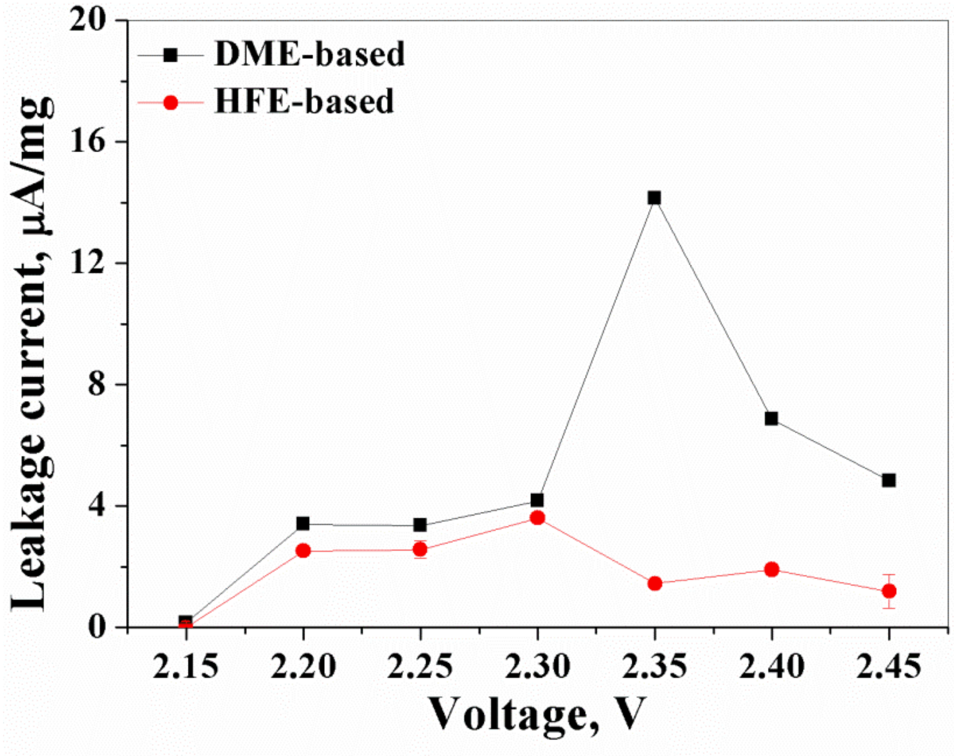




- The (de)/lithiation mechanism and cycle performance of Se_2S_5/C cathodes highly depend on the electrolytes
- With DME-based electrolyte, two-step lithiation process (solid-liquid-solid)
- With HFE-based electrolyte, one-step lithiation process (solid-solid)

Leakage current test showed that Se_2S_5/C cathode has higher parasitic reactions in DME-based electrolytes vs HFE electrolyte

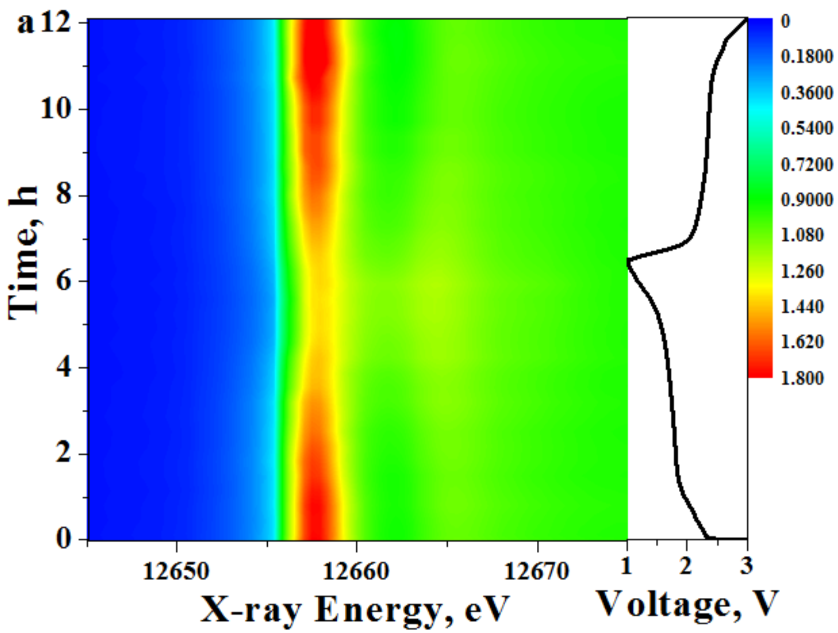




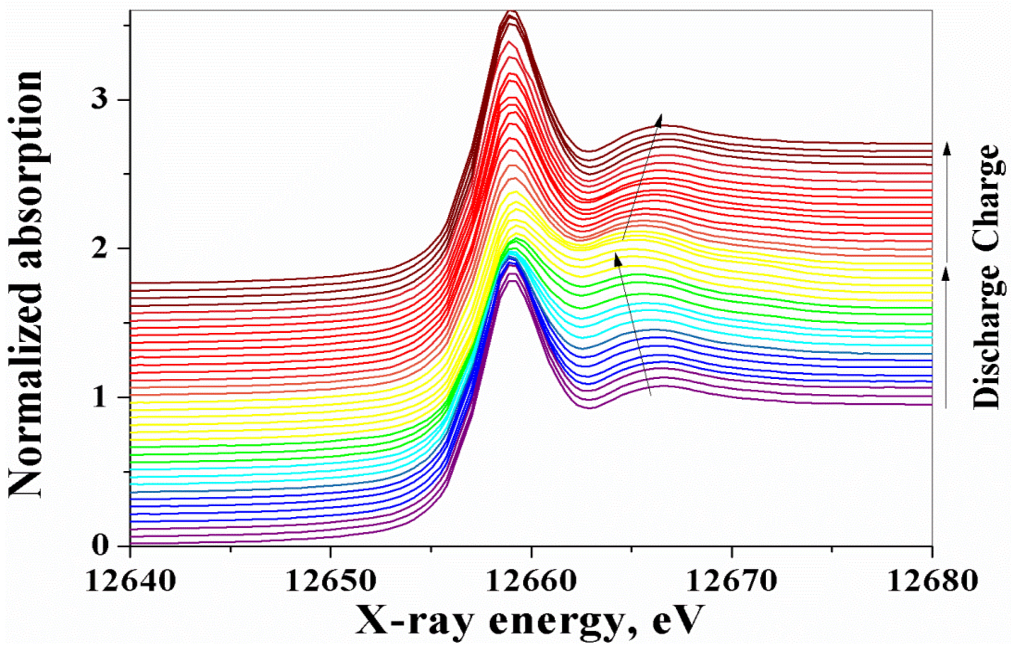
The cells were discharged/charged for 2 cycles and then charged to a different potential and held for 20 h to obtain the equilibrium current. The measured leakage current (*i*) is proportional to the reaction rate of the parasitic reactions between the polysulfides/polyselenides and Li anode during charge.

In-situ Se K-edge XANES characterization of Se_2S_5/C cathode in HFE-based electrolytes

2D contour plot



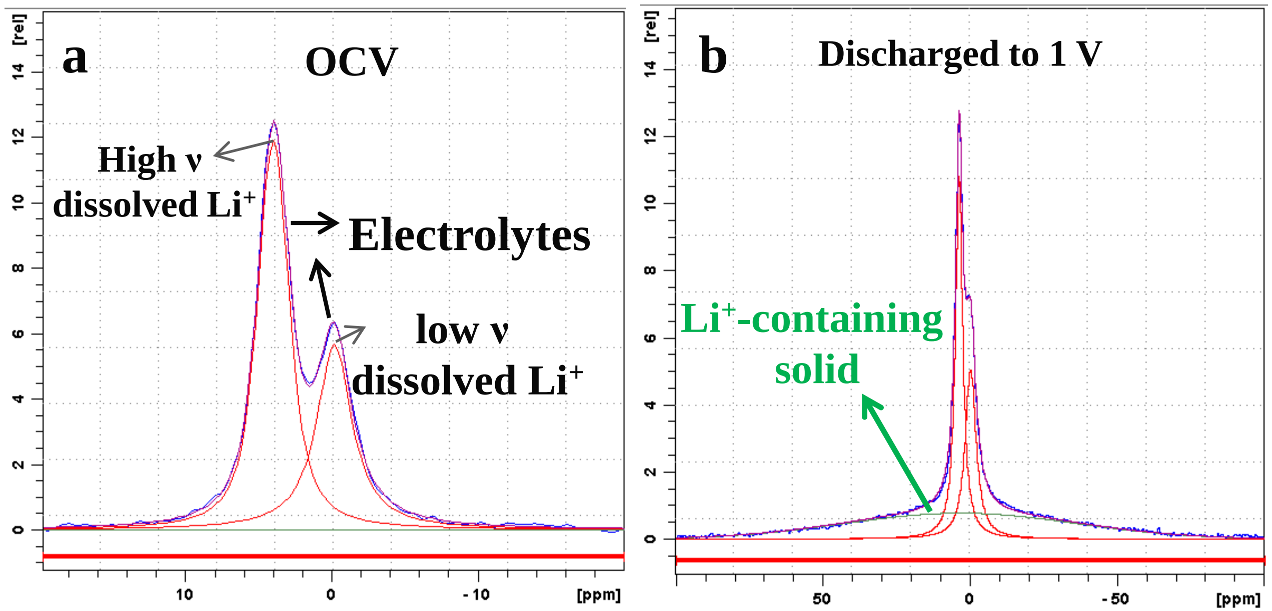
Typical Se K-edge Spectra



- Se K-edge position did not show clear shifts, but the absorption intensity decreased with discharging and recovered during charging
- The result confirmed that Se-S/C cathodes undergo a solid-state lithiation/de-lithiation process in the HFE-based electrolyte

In-situ ^{7}Li NMR characterization of Se_2S_5/C cathode in HFE-based electrolyte

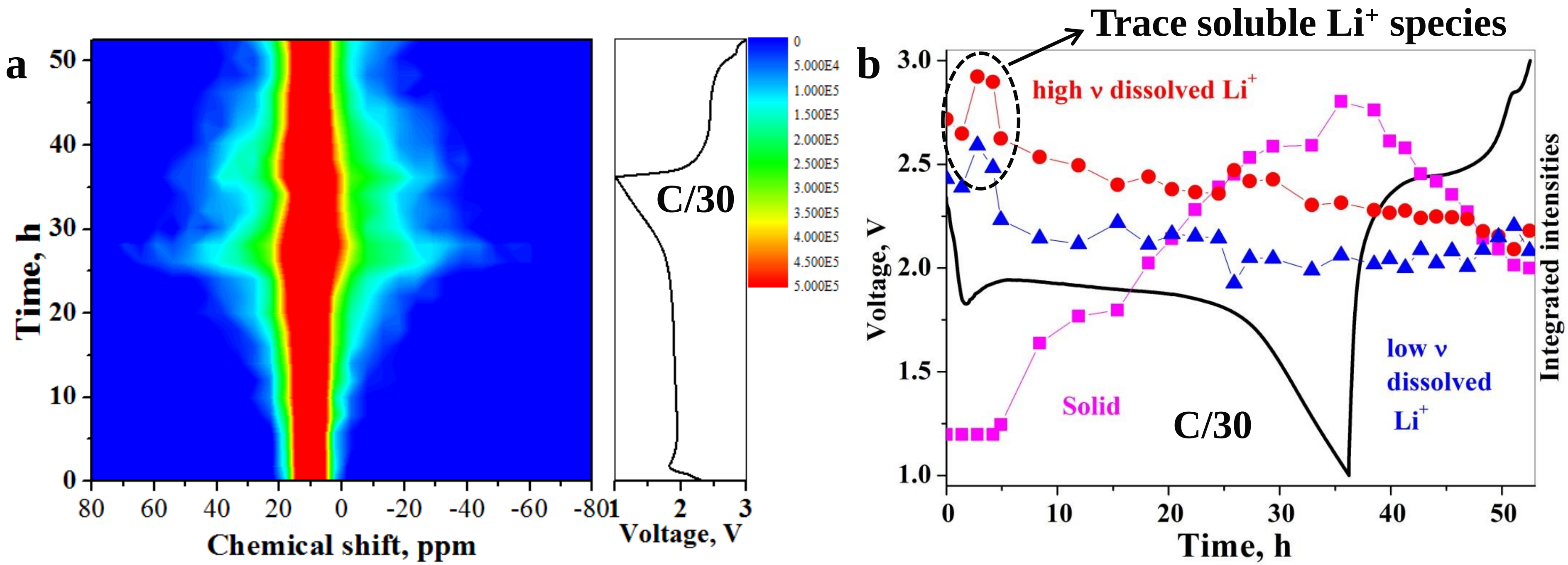
^{7}Li NMR spectra of Li/Se_2S_5 cell at different charge/discharge states



- a) Two sharp signals including one at higher frequency and one at lower frequency can be observed before charge and discharge, which are assigned to the soluble Li^+ species in the electrolyte.

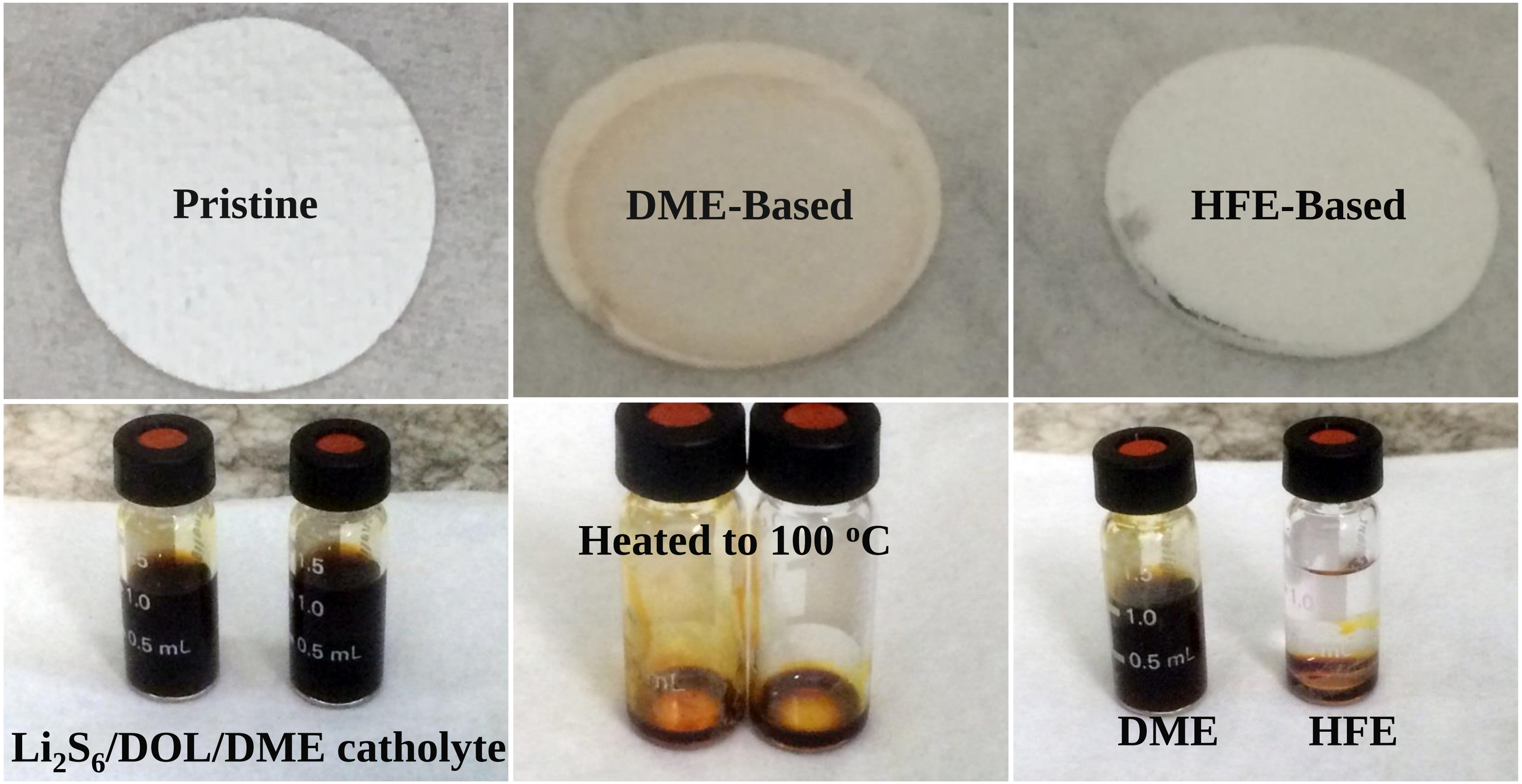
- b) During discharge, a weak and broad peak can be observed, which is related to the formation of a Li^+-containing solid such as Li_2S and Li_2Se

Quantification on the change of solid and liquid Li^+ species during charge/discharge using in-situ NMR



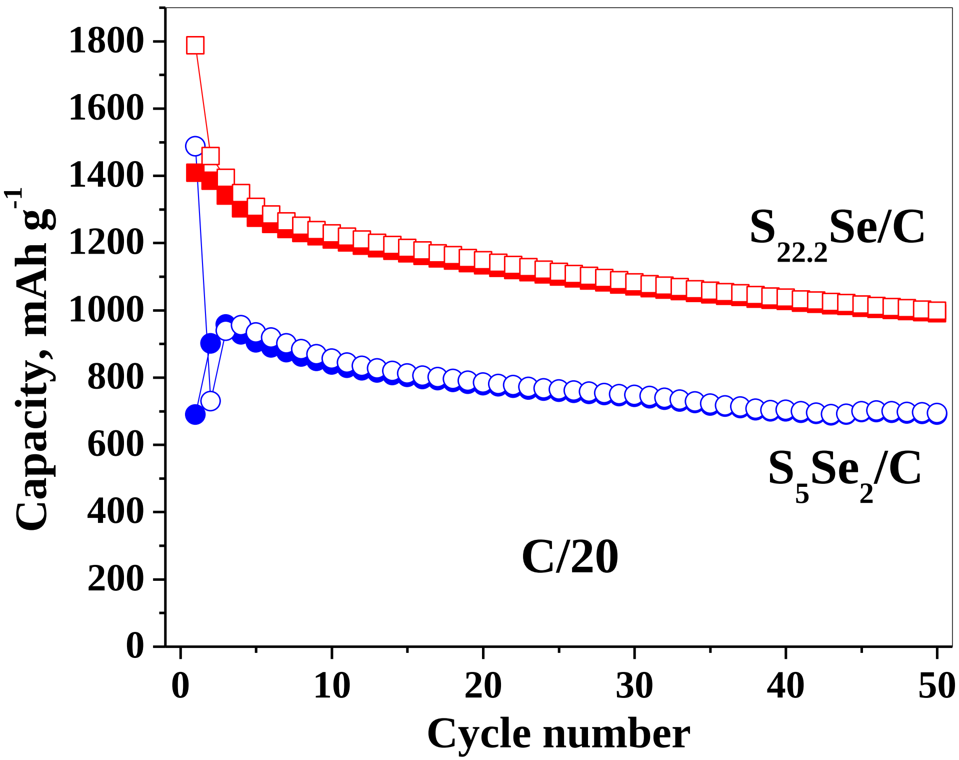
- In-situ NMR results revealed that the major (de)lithiation process of Se-S/C cathodes in HFE-based electrolytes is a solid-state reaction process;
- The integrated area of the Li^+-containing solid increased during discharge and decrease during charge process, while the lithium in liquid species remain (lithium from the electrolyte) relatively stable during the whole charge/discharge process.

Solubility test showed suppressed polysulfides dissolution in the HFE-based electrolytes



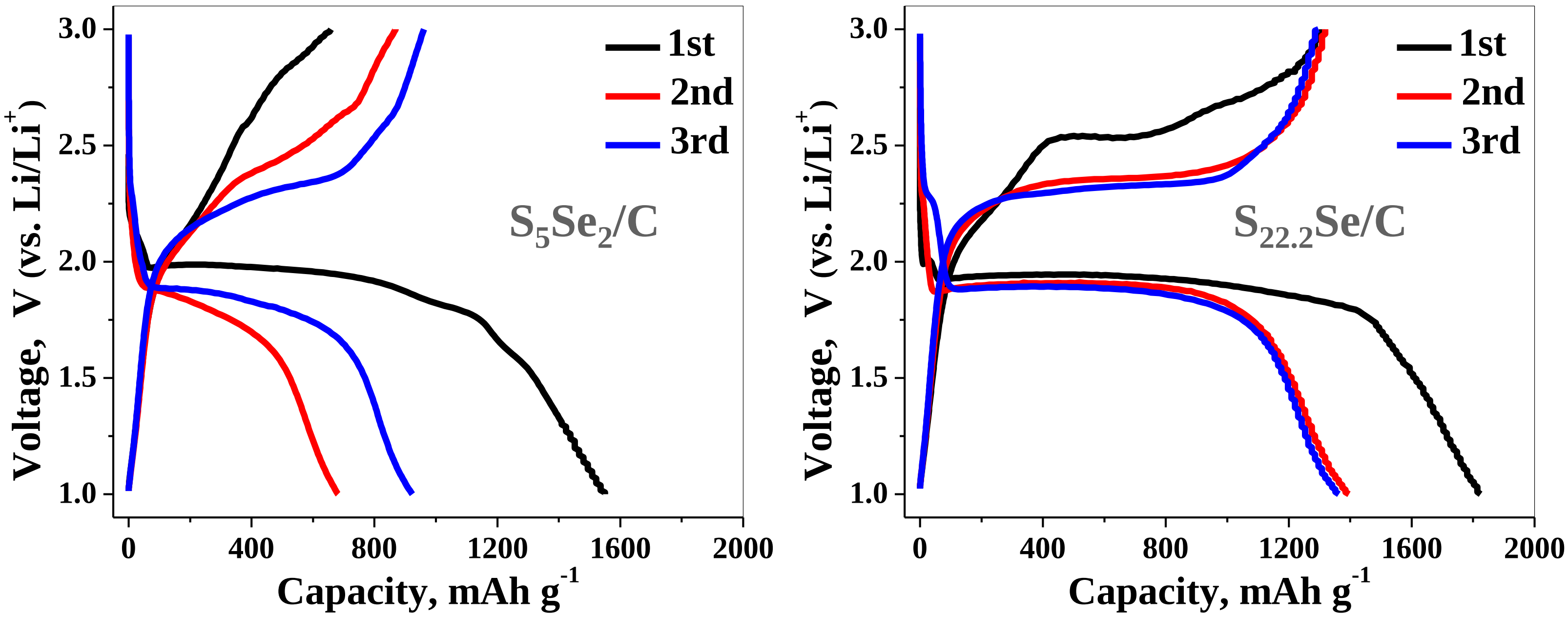
Polysulfides can be well dissolved in the DME-based electrolytes, but not dissolved in the HFE

Lowering Se content in selenium-sulfur system to reduce cost ($S_{22.2}Se/C$)



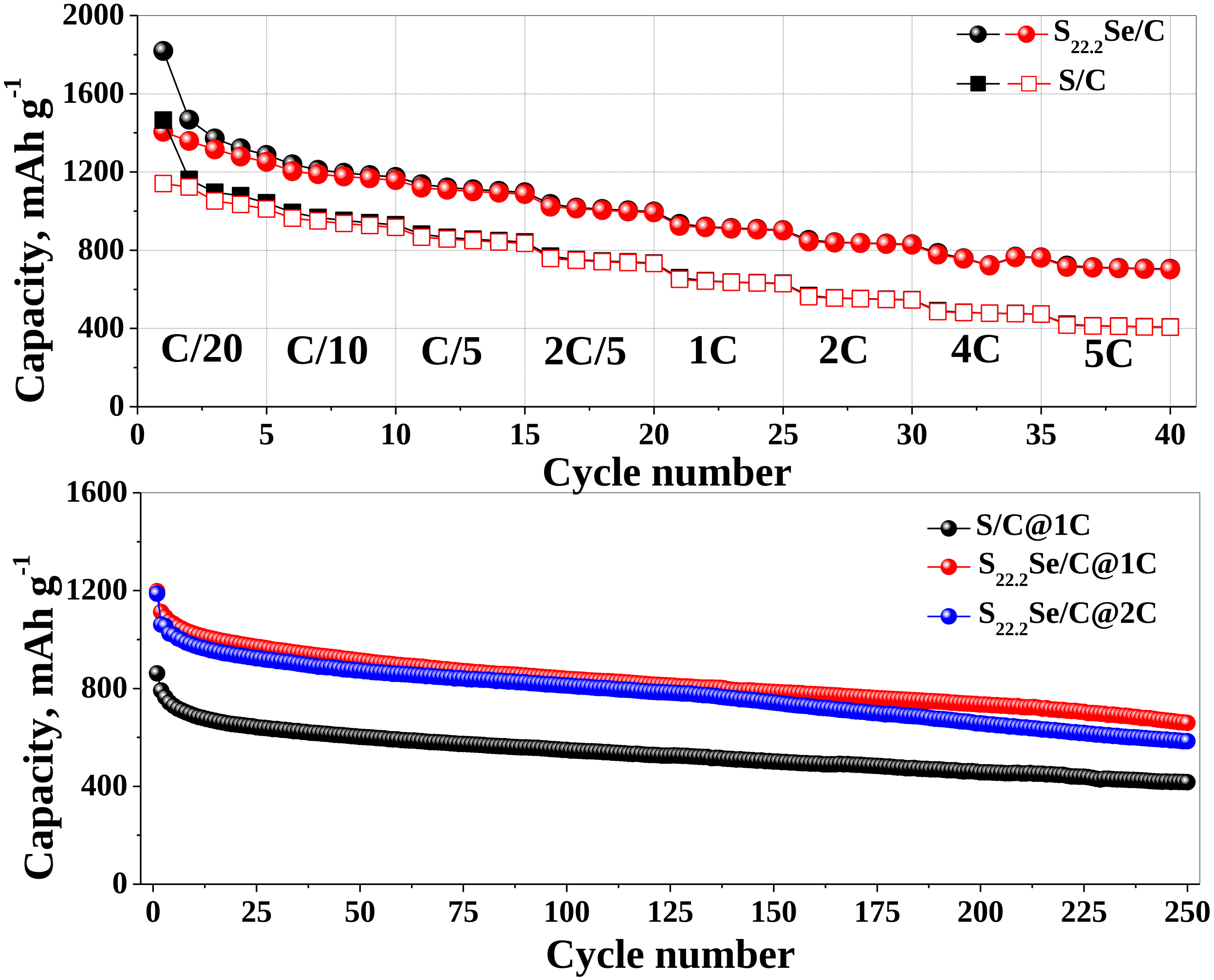
- Cell capacity increased with increasing content of S
- All the Se-S/C cathodes present high coulombic efficiency. No gap between charge and discharge capacities, indicating no shuttle effect.

Charge/discharge curves of Se-S/C composite-50 wt.% cathodes in HFE-based electrolytes



All the Se-S cathodes present single voltage plateaus, indicating solid-state lithiation process

$S_{22.2}Se/C$ composite shows high rate capability and long cycle stability compared to Sulfur alone



Se-doped S cathode present higher reversible capacities and better rate capability than S cathode due to better electronic conductivity provided by the Se doping

Proposed Future Work for FY 2018 and FY2019

- FY 2018 Q3 Milestone:
  - In operando X-ray probes study on the (de)/lithiation mechanism of Se-S cathodes in novel electrolytes.
  - Parasitic reactions of Se-S/C cathodes in novel electrolytes
- FY 2018 Q4 Milestone:
  - Computational modeling on the on the (de)/lithiation mechanism of Se-S cathodes in novel electrolytes
- FY2019 work proposed
  - Develop functionalized electrolyte additives for extended cycle life.
  - Develop high electrode areal loading Se-S systems in novel electrolyte

Summary

- The performance degradation of space-confined Se-S cathodes in ether-based electrolytes come from the preferred binding sequence of long-chain polyselenides over short-chain polyselenides with carbon host

- New HFE electrolytes could enable a solid-state (de)lithiation process for Se-S/C cathodes, thus suppressing the shuttle effect and improving the electrochemical performance

- Se-doped S cathodes ($S_{22.2}Se$) could present better lithium storage performance than S cathodes due to significantly improved electronic conductivity.