Novel Chemistry: Lithium Selenium and Selenium Sulfur Couple

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DOE merit review

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Project ID: ES280

Overview

Timeline

- Start - October 1st, 2015.
- Finish - September 30, 2018.
- 60% Completed

Barriers

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

Budget

- Total project funding
  - DOE share: $1000K
- Funding received in FY15: $500K
- Funding for FY16: $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. X. Cheng, Dr. L. Curtiss (ANL)** DFT calculation.

Relevance and project Objectives

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

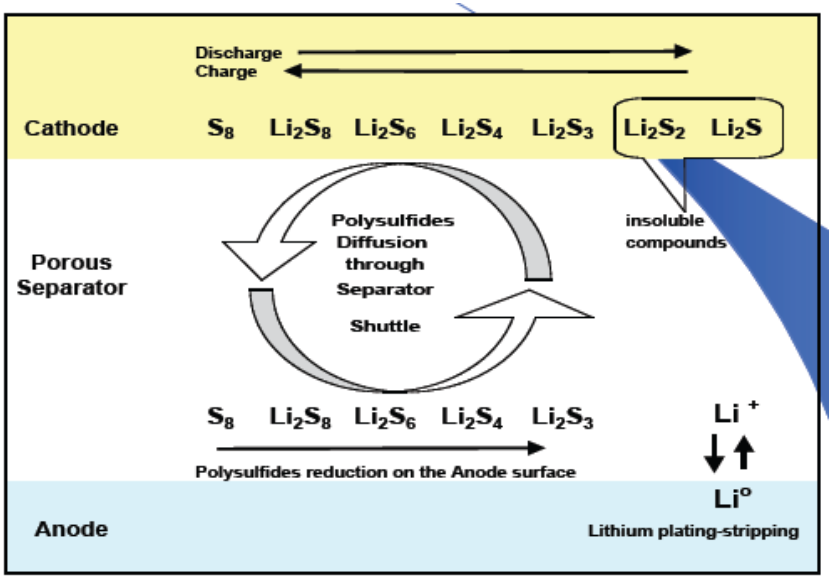
- **This technology, If successful, will lead to:**
  - A cell with nominal voltage of 2 V and energy density of 600 Wh/kg
  - A battery capable of operating for 500 cycles with low capacity fade.

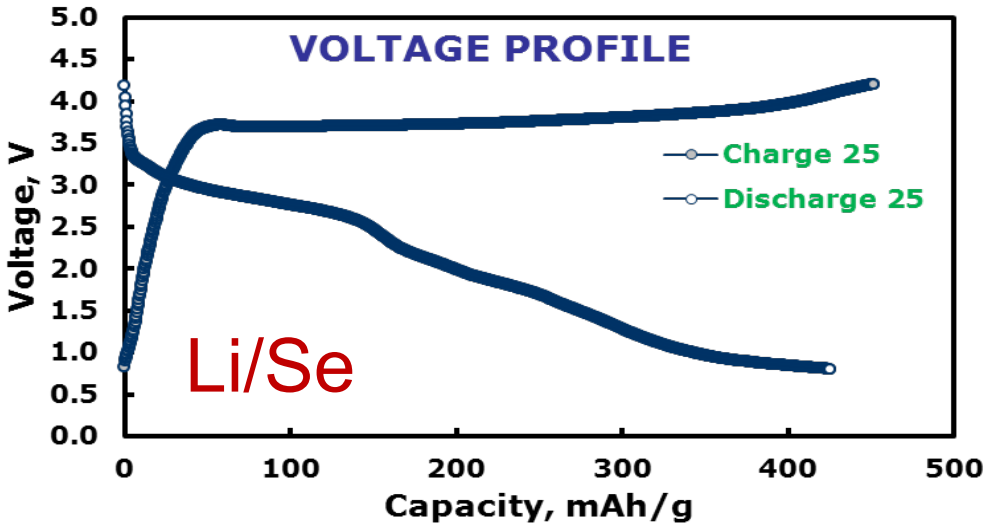
Milestones

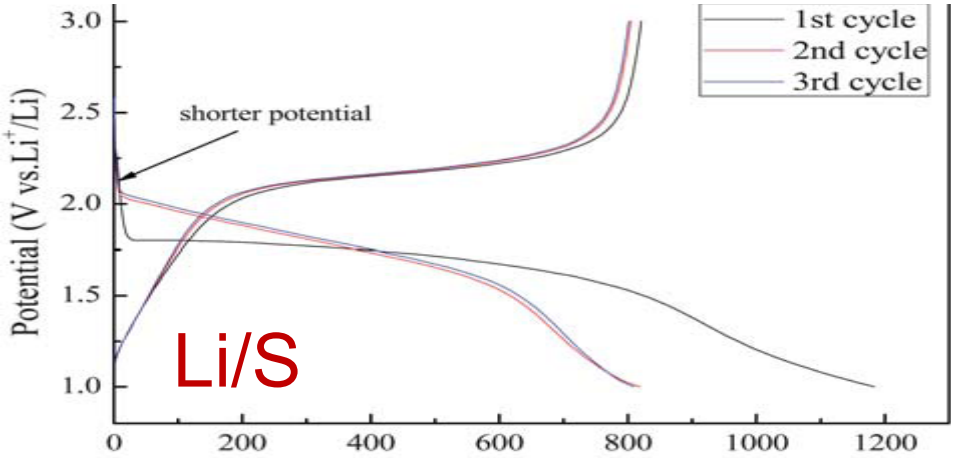
- Investigate the lithium storage mechanism of Se using in situ synchrotron probes (completed).
- Investigate the performance of S_5Se_2 in ether-based electrolyte (completed).
- Investigating the potential use of carbonates for Li/Se cell (completed).
- Exploring the phase diagram of S_xSe_y (ongoing).
- Encapsulate S_xSe_y in porous carbon matrix (ongoing).
- Investigate the alloying mechanism between S and Se (ongoing).

Motivation

Redox shuttle effect of dissolved lithium polysulfides.

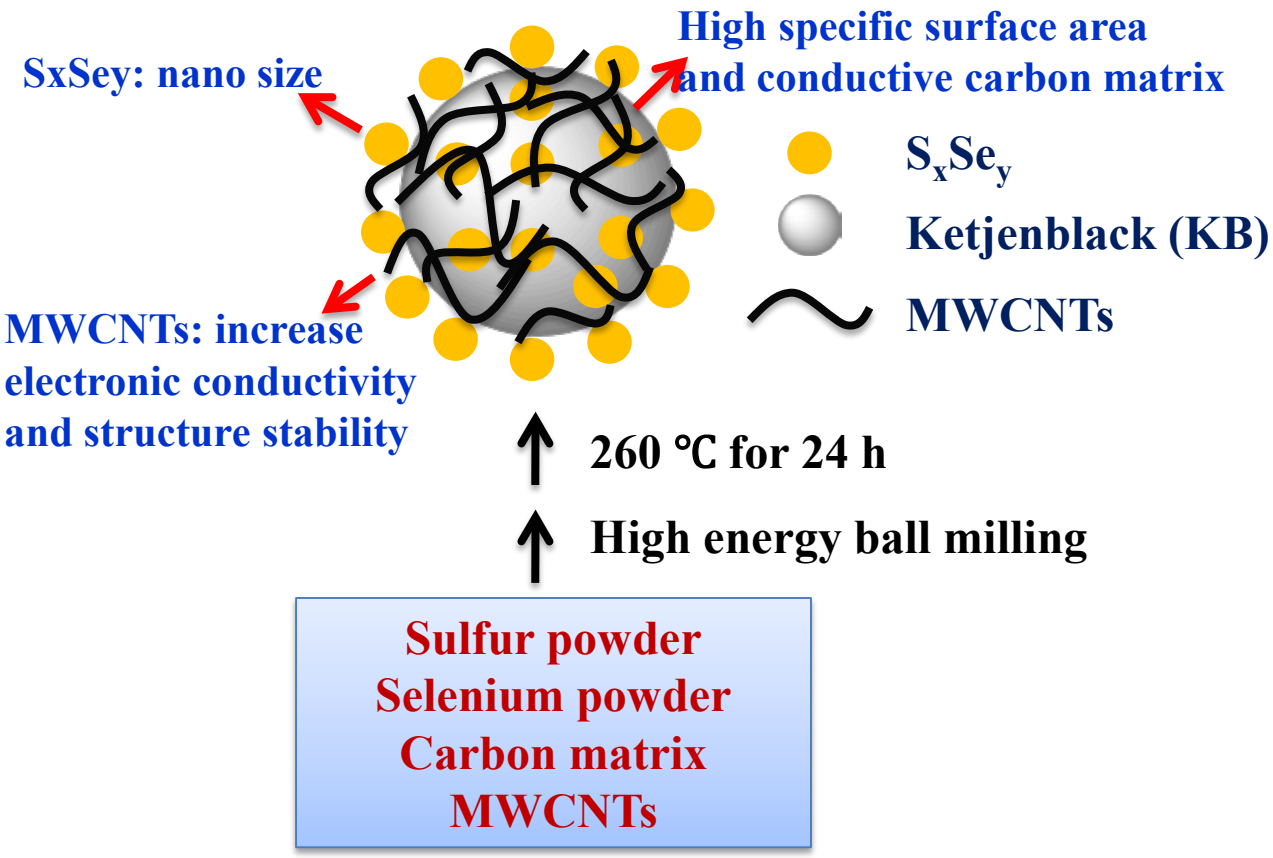






Li/Se can be charged to 4.5 V without any shuttle effect.

Approach

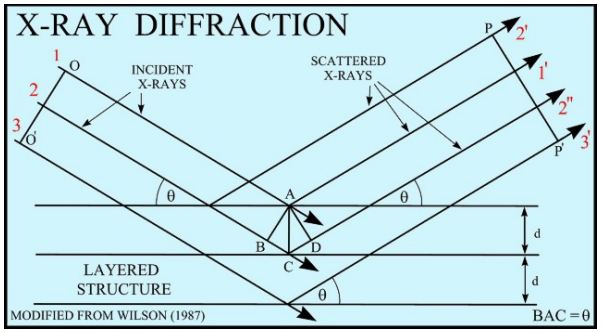


- Micro-porous and meso-porous carbons will be designed to replace carbon black for better encapsulation and higher loading of the active material.
- The electrolyte composition will be optimized based on the composition of S_xSe_y.
- In situ synchrotron probes will be used to identify the capacity fade mechanism.

Approach: advanced characterization

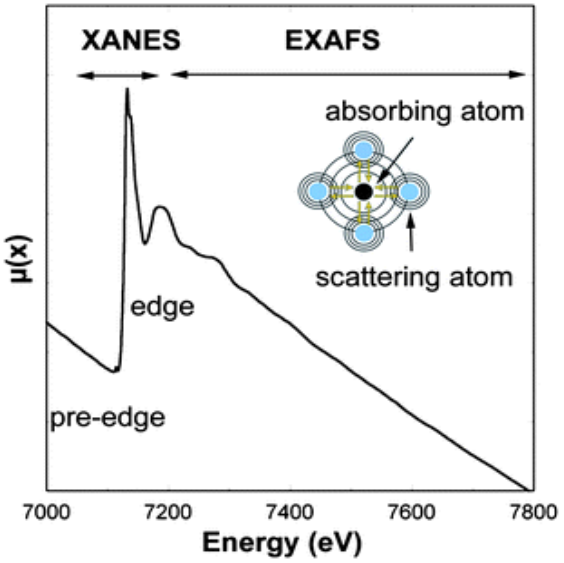
❑X-ray Diffraction

- Powerful and fast, need good **crystals**, no solutions



❑X-ray Absorption Spectroscopy

- XAFS uses the X-ray photoelectric effect and the wave nature of the electron to determine local structures around selected atomic species in material
- Precise local structural information (distances, numbers of atoms, types, disorder) in **crystalline or noncrystalline** systems e.g. metalloprotein active sites, liquids, amorphous materials
- Information on **charge state**, **orbital occupancy** may be available by studying XANES depending on system and edge



Technical accomplishments

- Electrical conductivity of cathode improved significantly by adding Se to Sulfur
- Lithium storage mechanism of Se cathode was investigated using synchrotron probes.
- Lithium storage mechanism of S_5Se_2 cathode was investigated using synchrotron probes.
- Dissolution of polyselenide phases can be prevented depending on electrolyte choice
- Better compatibility between Se cathode and carbonate-based electrolyte was validated with no dissolution of polyselenide phases.

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. R. Yang (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using in situ HEXRD.
- Dr. X. Chen, and Dr. L. Curtiss (MSD, ANL)
  - DFT calculations.

Cost and toxicity consideration

Se :

60-70$/kg for 99.99 purity.

✓50mg/day is recommended by doctor as a supplement.

http://www.wisegeek.com/what-is-a-selenium-toxicity.htm

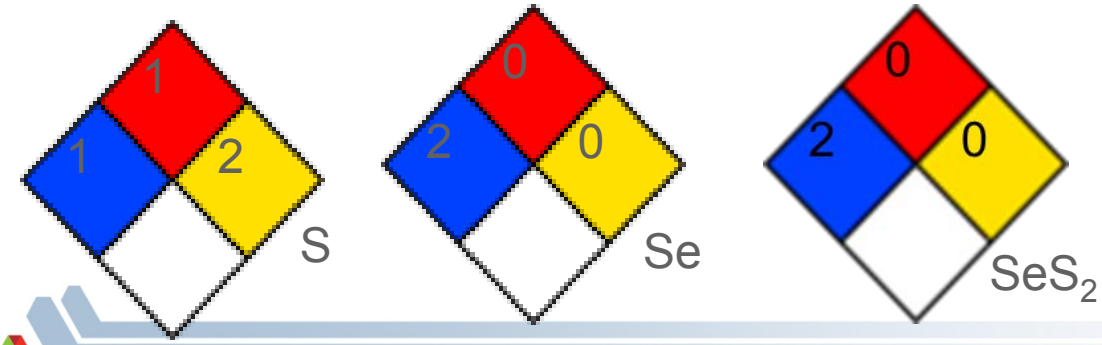
SeS_2 :

commercially called selenium disulfide is sold as an antifungal agent in shampoos for the treatment of dandruff and seborrheic dermatitis associated in the scalp with *Malassezia* genus fungi. At the 2.5% strength, selenium disulfide is also used on the body to treat tinea versicolor, a type of fungal skin infection caused by a different species of *Malassezia*.

* We are not going to use H_2 or any H_2 sources that can lead to the formation of H_2Se.

Selenium Powder 99.99 China USD/KG				
Date	Low	High	Avg.	Change
Current pricing available to subscribers				
24 Apr 09	63.0	70.3	66.66	.05
17 Apr 09	63.0	70.3	66.61	.01
03 Apr 09	62.9	70.3	66.60	-.01
27 Mar 09	63.0	70.3	66.61	.08
20 Mar 09	62.9	70.2	66.53	0
06 Mar 09	62.9	70.2	66.53	0
27 Feb 09	62.9	70.2	66.53	-2.99
13 Feb 09	65.9	73.2	69.52	0
06 Feb 09	65.9	73.2	69.52	2.94
19 Dec 08	62.9	70.2	66.58	4.77
Source - Reuters / Shanghai Nonferrous Metals Prices include VAT				

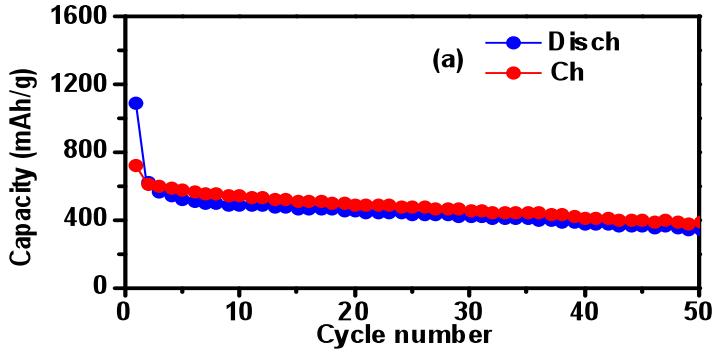
Selenium Sulfide 2.5% Anti-Dandruff Shampoo, 40 Oz (18.5$)

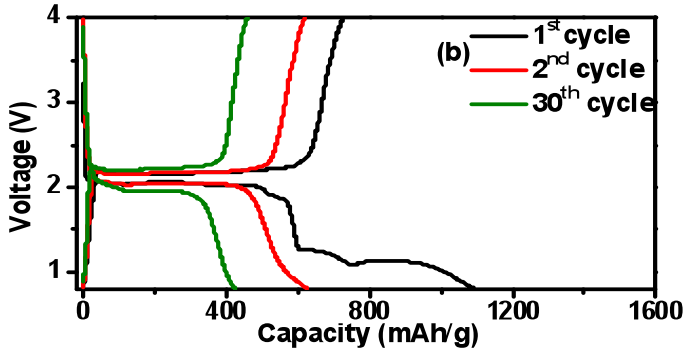


Li/Se battery performance: ether-based electrolyte

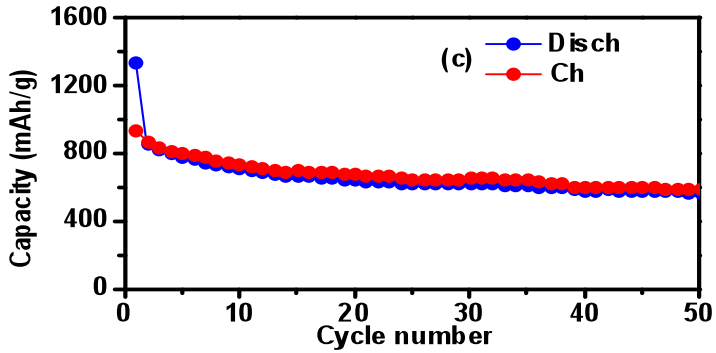
1M LiTFSI in DOL/DME

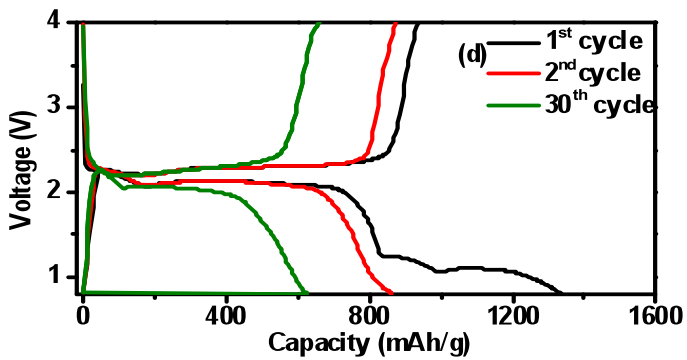
Li/Se



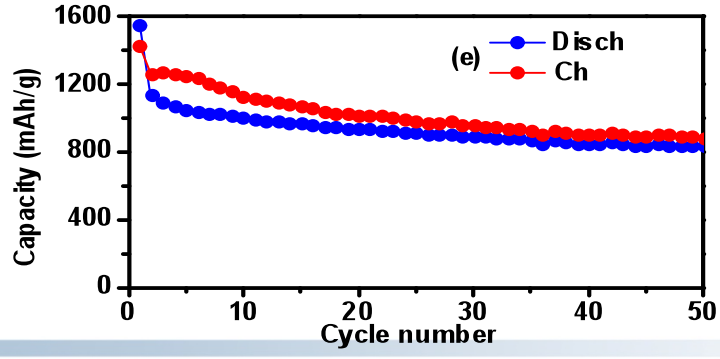


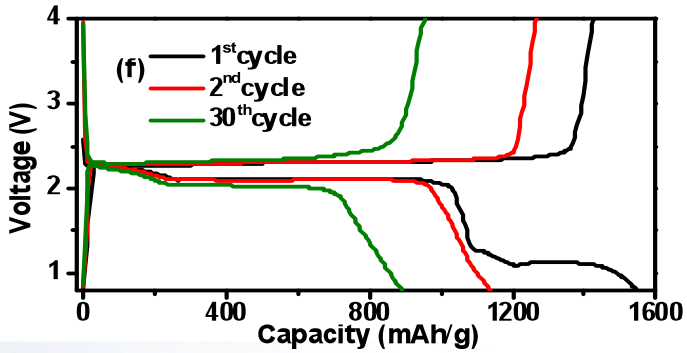
Li/SeS_2



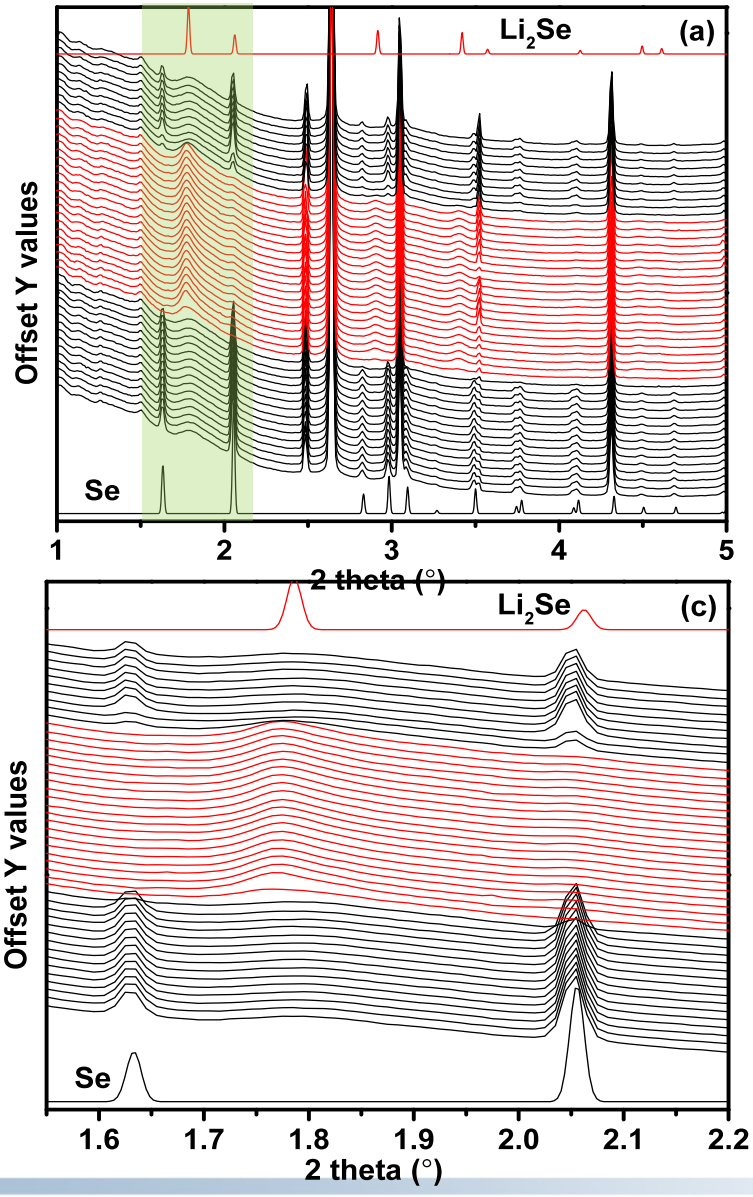


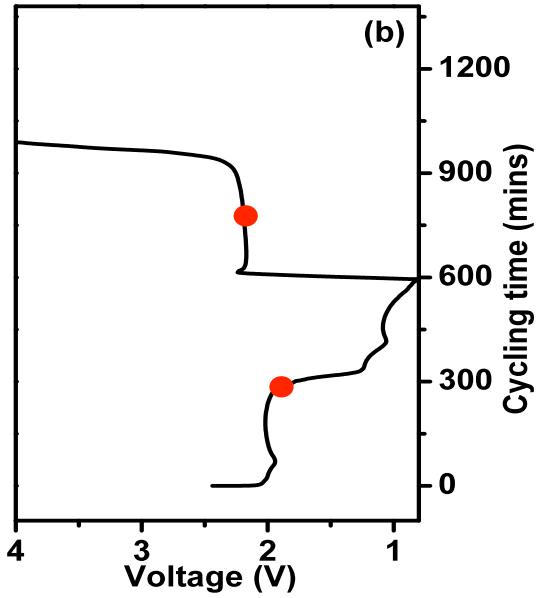
Li/SeS_7





Li storage in Se: in situ HEXRD



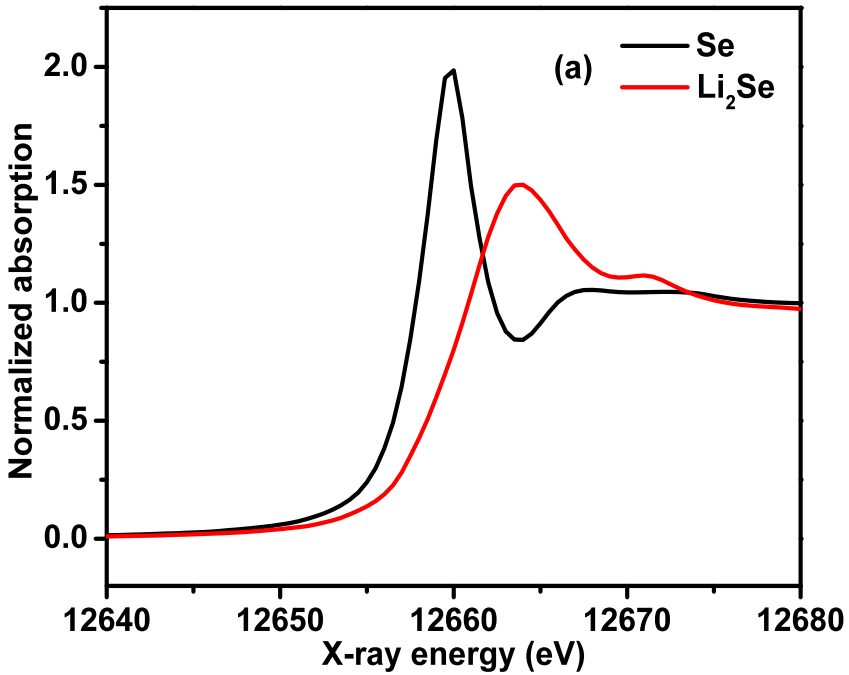


The compete conversion of Se to Li_2Se by the end of the discharge.

Changes of chemical environment during lithiation of Se

Se K-edge of standard end products:

XANES spectra

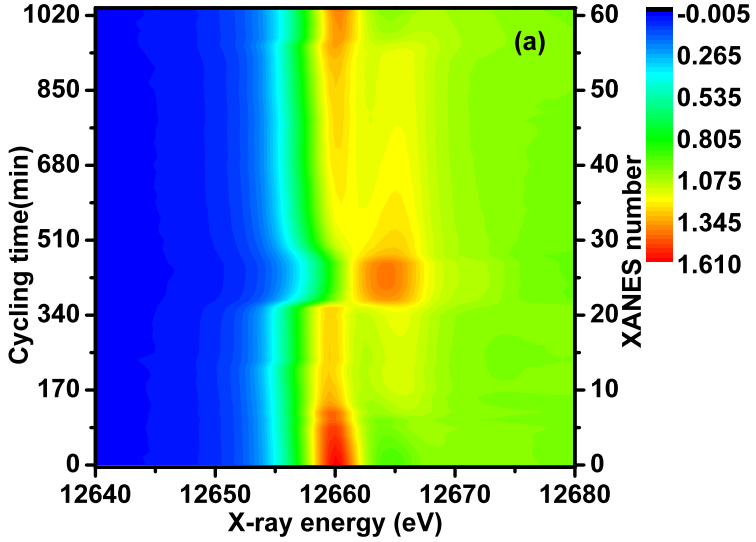


Se K-edge of Se^{2-} at a higher energy than atomic Se

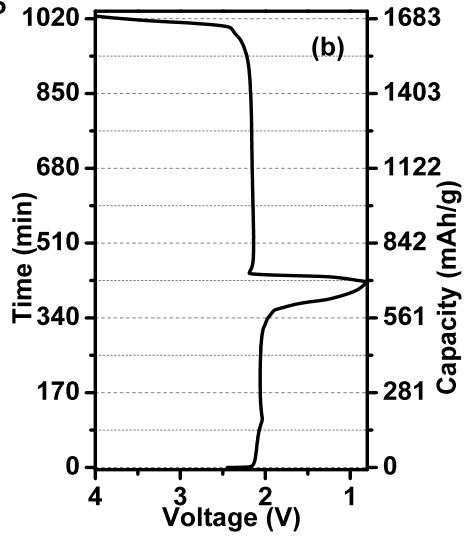
Se –edge of Li2Se at a higher energy than elemental Se. this is inconsistent with the commonly observed phenomenon that the edge shifts to higher energy with the increase in the oxidation states

Delithiation of Li_2Se to form Se – *in situ* XANES study

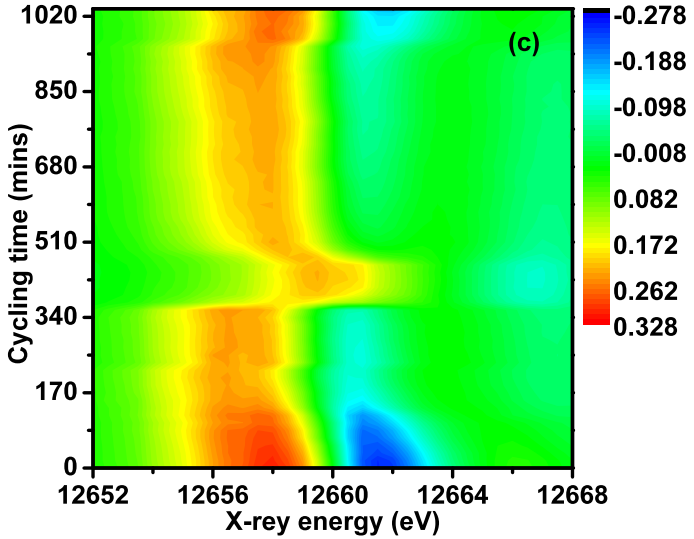
Se K-edge XANES Spectra



Voltage Profile

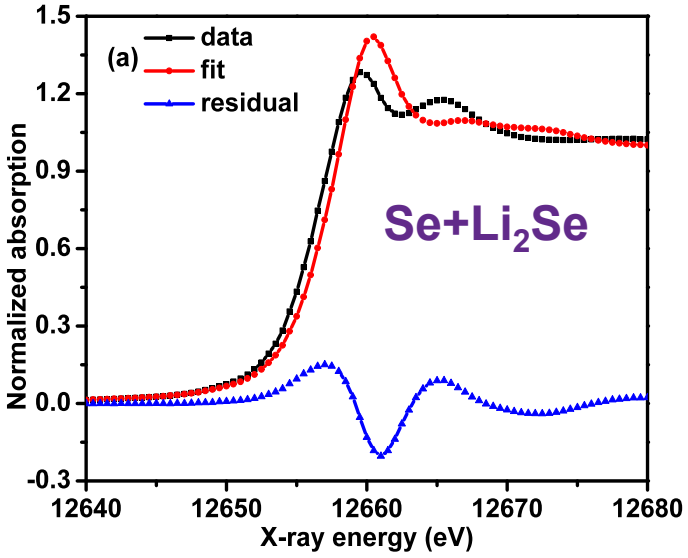


First Derivative of Se XANES



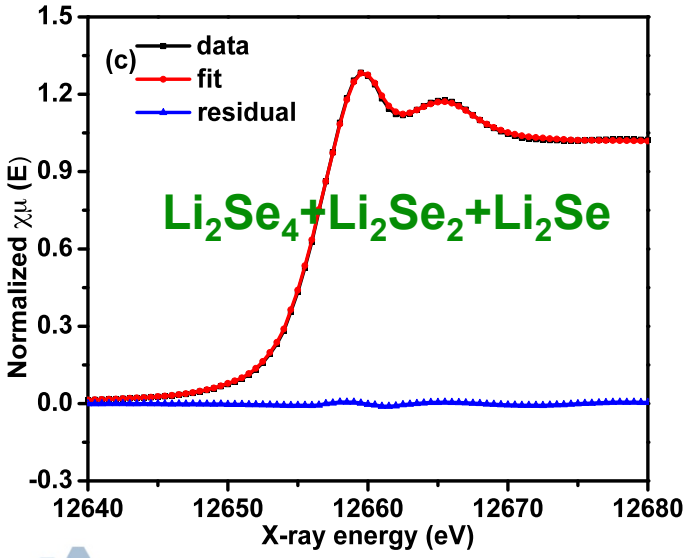
Se K-edge of Li_2Se shifted to high energy may be caused by the strong columbic interaction between Se^{2-} and surrounding lithium leading to reduction in the screening effect .

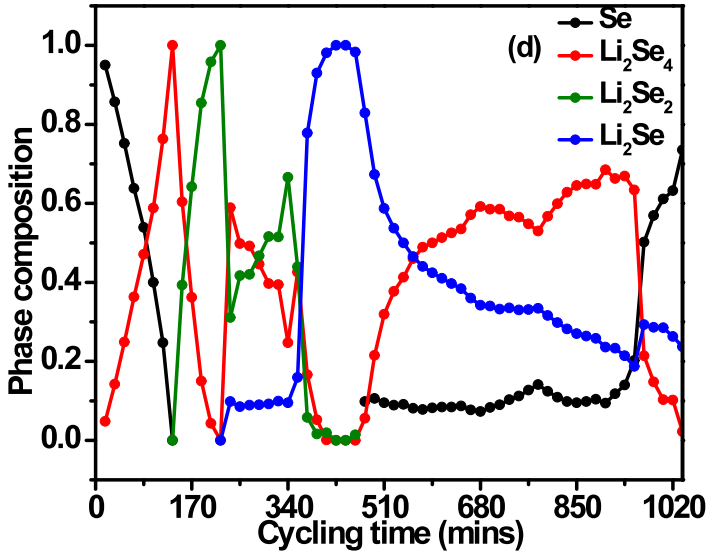
Identification of intermediate - Li_2Se_2



Se and Li_2Se two phase-transition is impossible.

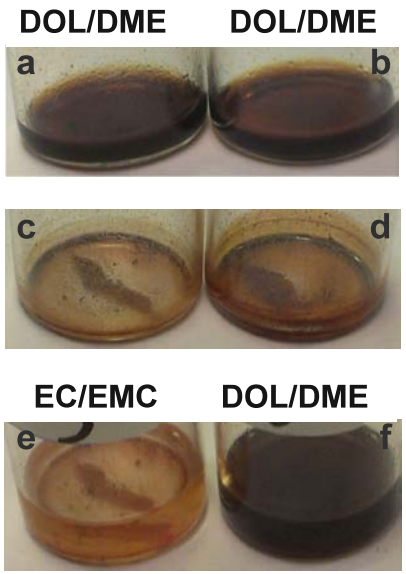
The presence of intermediate phases is plausible as shown by the good fits achieved with tiny residuals.





Confirmation of dissolved polyselenide in ether-based electrolyte

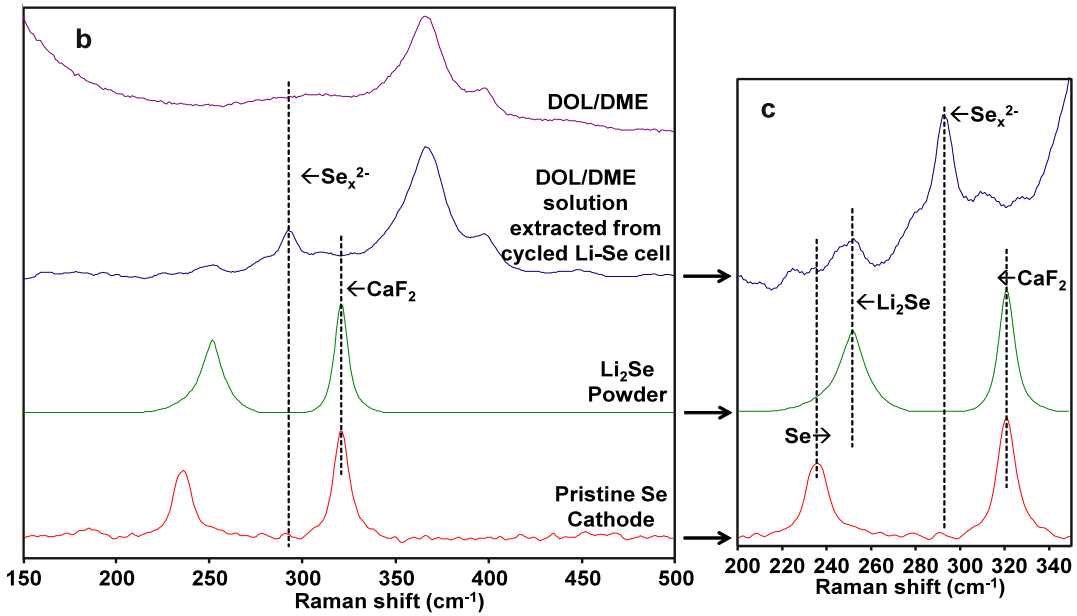
Disassemble cycled cells with 1 M LiTFSI in DOL/DME electrolyte and wash the parts with DOL/DME solvent



Li_2Se_n dissolved in DOL/DME solvent

Solvent evaporated

Added new solvent EC/EMC and DOL/DME respectively.



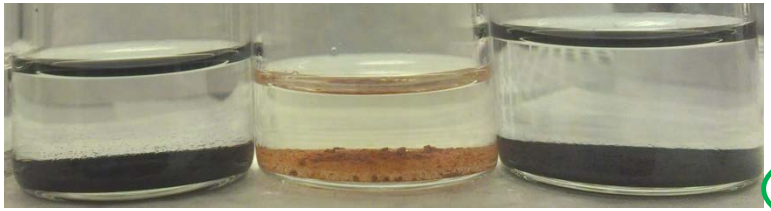
Raman spectroscopy of DOL/DME solvent, the Li-Se cell rinsing solution, Li_2Se powder and pristine Se cathode for comparison.

Li_2Se_n is insoluble in carbonate based electrolyte and soluble in the ether based electrolyte.

Potential of carbonates for Li/Se batteries

Carbonate based electrolyte :

Se Li_2Se Se+Li_2Se



Ether based electrolyte:

Se Li_2Se Se+Li_2Se

The solubility of redox products dominate the lithiation mechanism of a Li-Se cell.

Proposed Mechanism

(no dissolution of polyselenide phases)

$$Se + 2Li^+ + 2e \longleftrightarrow Li_2Se$$

Improvement on ion/electron transport kinetics: short solid-state diffusion length, large surface area…

$$nSe + 2Li^+ + 2e \longleftrightarrow Li_2Se_n$$

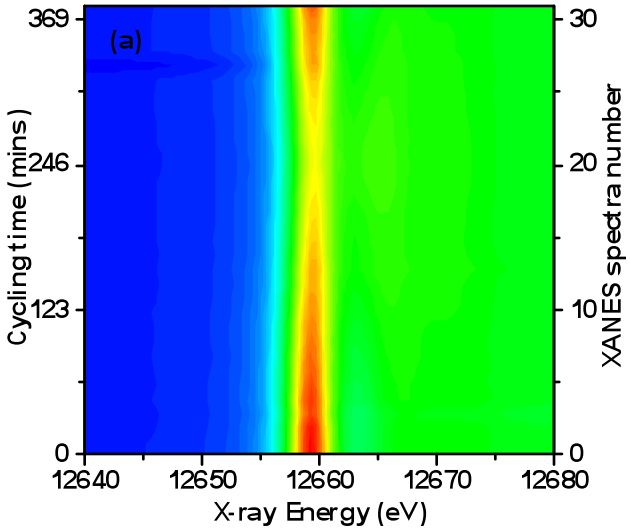
$$Li_2Se_n + (n-2)Li^+ + (n-2)e \longleftrightarrow n/2Li_2Se_2$$

$$Li_2Se_2 + 2Li^+ + 2e \longleftrightarrow 2Li_2Se$$

Reducing shuttle effect: material confinement, saturated electrolyte...

Se has a reversible lithiation/ delithiation in carbonate-based electrolyte

Se K-edge XANES Spectra



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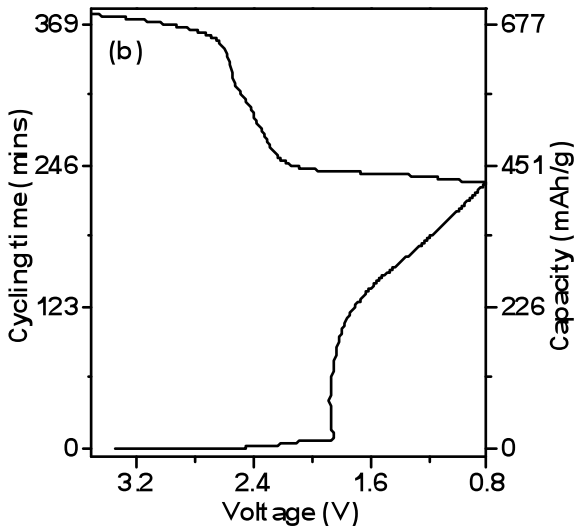
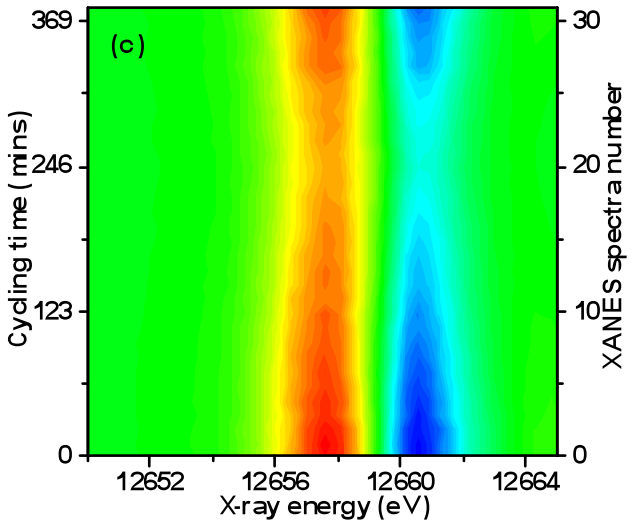


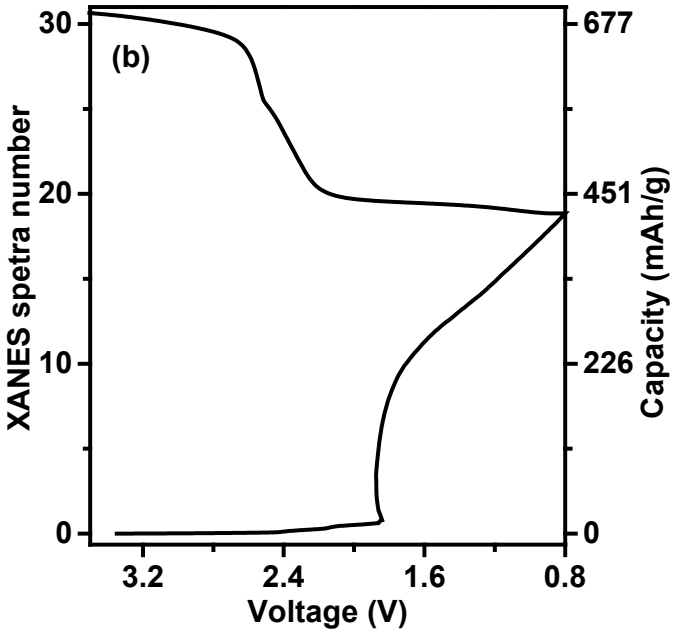
First Derivative of Se XANES



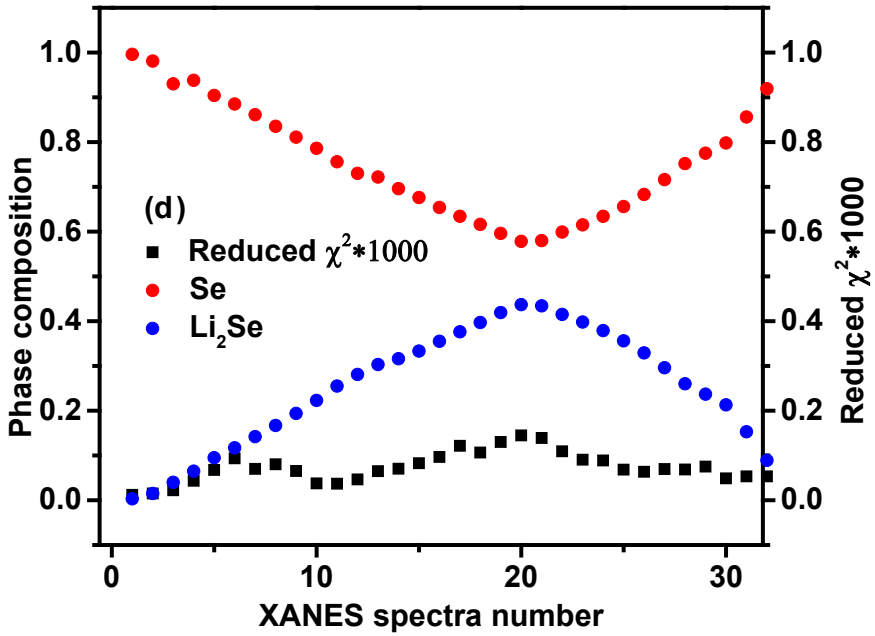
Se K-edge position did not show clear shifts, but the absorption intensity decreased with discharging.

Bypassing the formation of Li_2Se_x(X>1)

Voltage profile



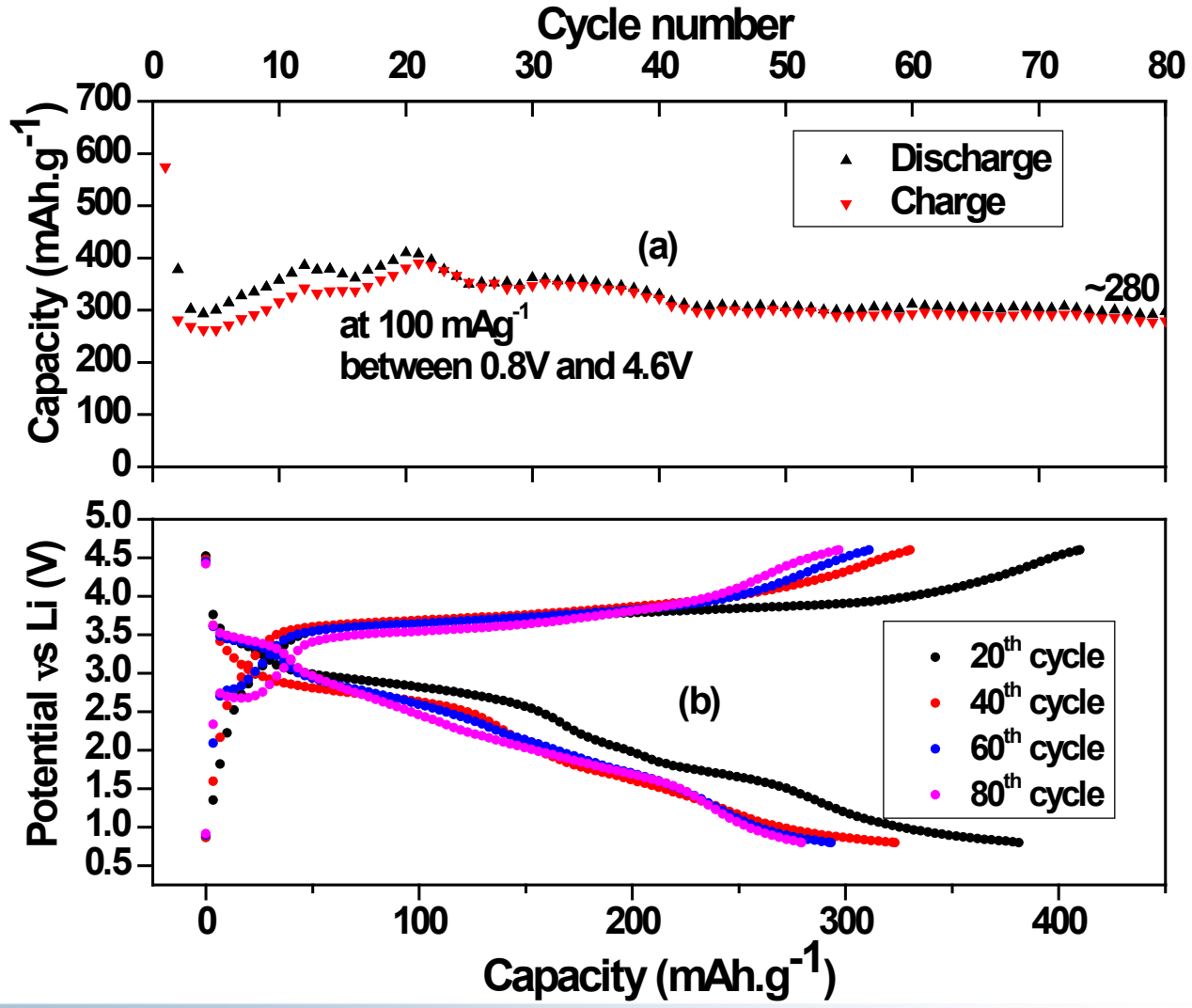
Linear combination fitting results of Se XANES



Li_2Se is formed and increasing in composition with discharge to 0.8V, then oxidized to Se with charge.

Se and Li_2Se two phase fitting leads to decent results.

New electrochemical behavior of Se in carbonate-based electrolyte



Proposed Future Work for FY 2016 and FY 2017

- FY 2016 Q3 Milestone:
  - Investigate the phase stability of S_xSe_y.
- FY 2016 Q4 Milestone:
  - Investigate the synergetic effect of S_xSe_y alloys and explore Encapsulating S_xSe_y in porous carbon matrix
- FY2017 work proposed
  - Finalize the optimization of S-Se-C composite.
  - Finalize the optimization of solvent.
  - Develop functionalized electrolyte additives for extended cycle life.

Summary

- In situ synchrotron probes were used to investigate the lithium storage mechanism of Se and S_xSe_y.
- A reversible lithiation/delithiation of Se in carbonated-based electrolyte was confirmed.
- The dissolution of polyselenides in carbonate-based electrolyte was suppressed.