Towards thorough characterization of Li/S batteries using tomography techniques → Mechanisms & strategies

LIS-M³ 2017 | Céline Barchasz
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MULTIPLE issues of Li/S chemistry...

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- Sulfur solubility

- Li$_2$S$_n$ reactivity with carbonates

- Li$_2$S insulating behavior

- Sulfur thermal stability

- Multiple electrochemical / chemical equilibria

- Lithium corrosion (SEI) / dendrites


* Multiple electrochemical / chemical equilibria

S$_8$ + 2e$^-$ → S$_6^{2-}$
S$_6^{2-}$ → S$_8^{2-} + \frac{1}{4}$S$_8$
S$_6^{2-}$ → 3S$_2^{2-}$
2S$_2^{2-}$ → S$_4^{2-}$
2S$_8^{2-} + 2e^- → 3S_2^{2-}$
3S$_2^{2-}$ → S$_3^{2-} + 3$S$_1^{2-}$
3S$_2^{2-} + 2e^- → 4S_1^{2-}$
2S$_3^{2-} + 2e^- → 3S_2^{2-}$
S$_2^{2-} + 2e^- → 2S^{2-}$

No solid intermediate species

And how to take advantage of these issues…

- Sulfur solubility

→ Catholyte-based systems

Pros and cons of the solubility approach

...Whatever the strategy… Strong impact of carbon and electrolyte as compare to Li-ion

- Sulfur thermal stability

→ Sulfur infiltration into microporous carbon

Case study n°2

- Li$_2$S$_n$ reactivity with carbonates

→ Artificial SEI for confinement

Case study n°3

Pros and cons of the confinement

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And how to take advantage of these issues...

**Conventional Li/S\textsubscript{8} cell**

- Conventional cell design
- Easy cell activation (1\textsuperscript{st} discharge)
- **Sulfur easy to handle**
- Highest gravimetric energy density
- Need to use a Li\textsuperscript{0} electrode
- Cells initially charged
- Capacity fading

**Li-ion/sulfur cell**

- Conventional cell design
- Cells initially discharged
- **Positive electrode containing Li**
- Alternative electrode preparations
- Li\textsubscript{2}S not easy to handle (H\textsubscript{2}S)
- Difficult cell activation (1\textsuperscript{st} charge)
- Lower mean voltage / energy
- **Same capacity fading**
And how to take advantage of these issues…

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**Catholyte approach**
- No need of sulfur/Li\(_2\)S electrode
- Possible Li-ion/S configuration
- Improved cyclability
- Good rate capability

* C. Barchasz et al., J. Power Sources, 211 (2012) 19-26
* S. Liatard et al., Chem. Commun., 51 (2015) 7749
CASE STUDY N°1

- Polysulfides-based semi-flow batteries


~100 Wh/kg
~100 Wh/L

Y. Cui et al., Energy Environ. Sci., 6 (2013) 1552-1558
CASE STUDY N°1

- Catholyte-based Li/S batteries

Vertically-aligned carbon nanotubes

- Light, stable structure for S₈/Li₂S accommodation
- Good rate capability
- High capacity retention
- High areal capacity (~4.5 mAh/cm²)

<180 Wh/kg (assuming 7 M₃)

* S. Liatard et al., Chem. Commun., 51 (2015) 7749
And how to take advantage of these issues…

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### Catholyte approach

- No need of sulfur/Li$_2$S electrode
- Possible Li-ion/S configuration
- Improved cyclability
- Good rate capability
- **High sulfur concentrations needed**
- Challenges of soluble polysulfides
**CASE STUDY N°2**

- Microporous carbon (< 2 nm) for sulfur confinement

\[
\text{S}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}
\]

Solid-solid conversion

**Carbonate-based electrolytes can be used**

CASE STUDY N°2

Challenge: Lower cell voltage < 2V

High sulfur content Usually < 55 wt%

CASE STUDY N°3

- Chemically anchoring disulfide bonds on CNT

**Synthesis of disulfide precursor**

**Functionализation of MWCNT**

Challenge:
High surface capacity (S-S loading)
Solubility or not solubility?

Should we tune the system to more/less solubility?

* M. Wild et al., Energy Environ. Sci., 2015, 8, 3477-3494
* S. Walus et al., Adv. Energy Mater. 2015, 1500165

* J. Owen et al., Chem. Commun., 2016, 52, 12885
Towards low solubility systems

Required carbon architecture → Solid phases coexistence
- High surface area
- High pore volume

Use of polysulfides nonsolvents
- Fluorinated solvents
- Solvents-in-salt

Challenge: Capacity retention due to electrolyte depletion

*S. Kaskel et al., Carbon 107 (2016) 705-710
*M. Hagen et al., J. Power Sources, 264 (2014) 30-34
*S. Kaskel et al., Carbon 107 (2016) 705-710
*M. Watanabe et al., ACS Appl. Mater. Interf., 6 (2016) 27803−27813
*L. Chen et al., Nature Comm., 4 (2013) 1481
How to tune the Li/S system...

* J. Hassoun et al., ACS Appl. Mater. Interfaces 2015, 7, 13859–13865

DME
Dimethoxyethane \( n=1 \)

TEGDME
Tetraethylene glycol dimethylether \( n=4 \)

PEGDME
Polyethylene glycol dimethylether \( n=11 \)

**High solvation ability**

**Low viscosity solvents**

Need to select the suitable electrolyte for each positive electrode

CR2032, S/Li
C2400® + Viledon®
2.3 mg_sulfur/cm²

Towards high solubility systems

Challenge: High energy density (volume/mass)

1. Progressive consumption of soluble Li$_2$S$_x$
   - Formation of solid Li$_2$S

2. Progressive re-oxidation of solid Li$_2$S
   - Formation of soluble Li$_2$S$_x$

### Challenge: High energy density

- (volume/mass)

* S. Walus et al., Electrochimica Acta 211 (2016) 697–703

**Figures:**
- Top view and Bottom view of structures
- Cut views with scale markers: 100 µm and 30 µm
How to tune the Li/S system...

Tunability of carbon network

On-demand carbon loading, specific surface, porosity...
- Up to 7 mAh/cm²
- Up to 400-500 mAh/g\(_{\text{cathode}}\)

Trade-off between energy density and cyclability
Towards thorough characterization of Li/S system using tomography techniques

Ex situ tomography

Sulfur redistribution during first cycles

Comparison of morphological changes between Al and NWC paper
Towards thorough characterization of Li/S system using tomography techniques

- Ex situ tomography
- In situ tomography
- Operando tomography

* L. Zielke et al., Scientific Reports, 5 (2015) 10921

- Tomography on aged samples (including lithium)
- Identification of key mechanisms
- Tomography on the full cell during true operando conditions

Towards thorough characterization of Li/S system using tomography techniques

- **Operando** diffraction and absorption tomography

*G. Tonin et al., Scientific Report (2017)*
Towards thorough characterization of Li/S system using tomography techniques

- *Operando* absorption tomography

*G. Tonin et al., Scientific Report (2017)*
Towards thorough characterization of Li/S system using tomography techniques

- **Operando** absorption tomography

  - Sulfur mapping → mostly confined in the nano-carbon-binder domain

  ![Sulfur mapping graph]

  ![Lithium mapping graph]

- Lithium mapping

  *G. Tonin et al., Scientific Report (2017)*
Towards thorough characterization of Li/S system using tomography techniques

- **Operando** absorption tomography

- Sulfur mapping → mostly confined in the nano-carbon-binder domain

- Lithium mapping → thick and highly porous layer after 2 cycles

Towards thorough characterization of Li/S system using tomography techniques

- **Operando** X-ray diffraction and absorption tomography

**Ex situ** tomography  ➔  **In situ** tomography  ➔  **Operando** tomography  ➔  **Operando** tomography with control of pressure

**Representative characterization tool for materials design**

* Courtesy of M. Di Michiel

*D. Aurbach et al., Nature Review, 1 (2016) 16013*
To conclude, Li/S system is:

...An amazing and exciting system for chemists...

...A « nightmare » for R&D scientists...

...In any case, a tricky system with several limitations...

Still a long way to go...

But with major progresses and promising advances!
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Laura Boutafa
Rémi Vincent
Marco Bolloli

Yvan Reynier
Jean-François Colin
Jean Dijon
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