Investigation of polysulfide transport in lithium sulfur batteries via optical transmission spectroscopy

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UV-vis in LiS batteries

Attraction:
• Absorbance measurements can enable quantitative estimation of species concentration (Beer Lambert law $A = c \varepsilon d$)

Ideally we would like to:
• Probe electrolyte composition…
  …as a function of state of charge…
  …spatially resolved

Speciation/calibration of UV-vis measurements

Reference spectra in TEGDME:

i) $S_8$ and $Li_2S$ (powder) dissolved in TEGDME

ii) Intermediate polysulfides obtained by reaction of $S_8$ with $Li_2S$

- Very similar peak positions
- Disproportionation of polysulfides makes it difficult to isolate individual species.

Speciation/calibration of UV-vis measurements

**Figure S-3.** On the left side, UV-visible absorption spectra obtained for a solution of lithium polysulfides (10^3 mol.L^-1 equivalent Li_2S_8 dissolved in TEGDME). The measurements were carried out during one day each 10 minutes, so as to detect the disproportionation reactions. The black arrows represent the bands’ evolution over time. On the right side, the possible UV band attribution supported by experimental and literature data.\(^{1-2,3}\)
Ex situ UV-vis and calculated spectra

- Ex situ measurements (Cathode immersed in 1 ml DME before UV-vis measurement)
- Calculated UV-vis spectra with DFT, GIAO, TD-DFT

In operando UV-vis reflectance

UV-vis in LiS batteries

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Challenges:
• Disproportionation, concentration dependence extinction coefficients, spectral overlap make it hard to perform systematic calibration
• Impossibility to discriminate phenomena happening at the two electrodes
• Ex-situ transmission measurements have limited validity
In operando UV-vis spectroscopy and UV-vis mapping
Electrolyte: “Li$_2$S$_8$” 0.5w% (18mM)

Estimated ratio of solvent/sulfur molecules ~ 2:1, (4:1 if for example only 50% cathode volume is involved)

Estimated cell capacity is in the order of 1mAh (or less)

Optical thickness tuned to enable optical transmission measurements

Very large separation between electrodes
Absorption spectrum of electrolyte in lateral LiS

Absorption peaks from Gaussian fit
\( \lambda_1 = 355 \text{ nm} \)
\( \lambda_2 = 478 \text{ nm} \)

Consistent with presence of \( \text{S}_6^{2-} , \text{S}_8^{2-} (\text{S}_4^{2-}? ) \)

In operando measurements

\[ V = 2.47 \text{ V} \]

\[ V \sim 2.15 \text{ V} \]

\[ \sim C/500 \]
In operando UV-vis: discharge

\[ t = 0s \]

\[ I = -2 \, \mu A \]
In operando UV-vis: discharge

\( t = 400 \text{s} \)

\[ I = -2 \, \mu\text{A} \]
In operando UV-vis: discharge

\[ t = 3600s \]

\[ I = -2 \mu A \]
**In operando UV-vis: discharge**

\[ t = 6800\text{s} \]

\[ I = -2\ \mu\text{A} \]
In operando UV-vis: discharge

$V \sim -3 \text{ V}$

$I = -8 \text{ } \mu \text{A}$
In operando UV-vis mapping
In operando UV-vis in LiS batteries

Resolution ~ 50 – 100 μm

Absorbance mapping at time 0 s

Absorbance

0 – 2.46 mm

Wavelength (nm)
$t = 500\text{s}$
Discharging

$t = 1000\text{s}$
Discharging

\[ t = 1500\text{s} \]
Discharging

$t = 2000\text{s}$

Absorbance mapping at time 2000 s
Discharging

$t = 2500\text{s}$
Discharging

$t = 3000$ s
Discharging

t = 3500s

Absorbance mapping at time 3500 s
Discharging

$t = 4000\text{s}$

Absorbance mapping at time 4000 s

\[ V(V) \]

\[ \text{Time (s)} \]

\[ \text{Absorbance} \]

\[ \text{Wavelength (nm)} \]
Discharging

$t = 4500\text{s}$

Absorbance mapping at time 4500 s
Discharging

\[ t = 5000 \text{s} \]
Discharging

\[ t = 5500\text{s} \]

Absorbance mapping at time 5500 s

\[ V(V) \]

Time (s)

Absorbance

Wavelength (nm)
Discharging

\[ t = 6000 \text{s} \]
Discharging

$t = 6500s$

Absorbance mapping at time 6500 s
Discharging

$t = 7000\text{s}$
Discharging

$t = 7500$ s

Absorbance mapping at time 7500 s
Discharging

\[ \text{Time (s)} \]

\[ V(V) \]

\[ t = 8000 \text{s} \]

Absorbance mapping at time 8000 s
$t = 8500\text{s}$
Discharging

$t = 9000s$

Absorbance mapping at time 9000 s
Discharging

\[ t = 9500 \text{s} \]

Absorbance mapping at time 9500 s

\[ V(V) \]

Time (s)
Discharging

$t = 10000\text{s}$

Absorbance mapping at time $10000\text{ s}$

![Graph showing voltage vs. time and absorbance mapping](image-url)
Discharging

$t = 10500\,\text{s}$

Absorbance mapping at time $10500\,\text{s}$

![Graph showing voltage (V) over time (s) and absorbance mapping.](Image)
Discharging

$t = 11000\text{s}$

Absorbance mapping at time $11000\text{ s}$
Discharging

$t = 11500\text{s}$

Absorbance mapping at time 11500 s
Discharging

$t = 12000\text{s}$

Absorbance mapping at time $12000\text{s}$
Discharging

$t = 12500\text{s}$
Peak fitting
Absorption peak evolution during discharging

Homogeneous distribution
Activity detected at both sulfur and lithium electrode: increase in absorption and blue shift.
Absorption peak evolution during discharging during:

- $t = 0s$
- $t = 2000s$
- $t = 4000s$

Deviation from open circuit condition decreases at lithium electrode
Absorption peak evolution during discharging

Peak position in the visible

Peak Absorbance in the visible
Relaxation at open circuit

\[ t = 12500 \text{s} \]
Relaxation at open circuit

\[ t = 14500 \text{s} \]
Relaxation at open circuit

\[ t = 16500 \text{s} \]
Charging

\[ t = 16500 \text{s} \]
$t = 20500 \text{s}$

Absorbance mapping at time 20500 s
Charging

$t = 24500s$

Absorbance mapping at time 24500 s
Charging

\[ t = 27500 \text{s} \]
In operando UV-vis in LiS batteries: Summary

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- Impossibility to discriminate phenomena happening at the two electrodes
- Ex-situ measurements have limited validity
- Towards more practically relevant device design
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Thank you for your attention