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1 Discharge Mechanism in a Solid-State

2 Lithium-Sulfur Cell by Operando X-ray

3 Absorption Spectroscopy

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21

221. Abstract

23 The reduction of sulfur during discharge in a lithium-sulfur (Li-S) cell is
24 known to occur in a series of reaction steps that involve lithium polysulfide
25 intermediates. We present an operando study of the discharge of a solid-
26 state Li-S cell using X-ray absorption spectroscopy (XAS). In theory, the
27 average chain length of the polysulfides, $x_{\text{avg,cell}}$, at a given depth of discharge
28 is determined by the number of electrons delivered to the sulfur cathode.
29 The dependence of $x_{\text{avg,cell}}$ measured by XAS on the depth of discharge is in
30 excellent agreement with theoretical predictions. XAS is also used to track
31 the formation of Li_2S , the final discharge product, as a function of depth of
32 discharge. The XAS measurements were used to estimate rate constants of a
33 series of simple reactions commonly accepted in literature.

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372. Introduction

38 Lithium-sulfur (Li-S) batteries have been considered as attractive
39 alternative to current Li-ion batteries due to their large theoretical capacity
40 (1672 mAh/g) and theoretical energy density (2600 Wh/kg). Sulfur is a
41 particularly attractive cathode material for large format cells because it is
42 cheap and abundant.¹⁻⁴ While there are numerous practical problems that
43 have prevented the commercialization of rechargeable Li-S batteries, a
44 significant barrier is the lack of understanding of the reaction mechanism
45 that underlies this chemistry.⁵⁻¹⁰ The redox reactions in the sulfur cathode
46 occur in steps.¹¹ Some of the products in these steps are soluble lithium
47 polysulfides intermediates.¹²⁻¹⁴ The chemical formulae of lithium polysulfides
48 are generally expressed as Li_2S_x where x , the length of the sulfur chain in the
49 polysulfide is generally assumed to be between 2 and 8.¹⁵ The dissolution of
50 these species into the electrolyte is one of the primary problems that must
51 be overcome before rechargeable Li-S batteries are commercialized. It also
52 interferes with fundamental studies of redox reactions in the sulfur cathode.

53 The discharge reaction in the sulfur cathode of a Li-S cell can be written
54 as equation (1).

56 We define n_e as the moles of electrons delivered to the sulfur cathode per
57 mole of S_8 in the cathode. The discharge reaction is complete when $n_e = 16$
58 and the only product in the cathode is Li_2S . Our interest is to determine the
59 state of the cathode during the intermediate steps of the discharge process.

60 It is well known that numerous partially reduced sulfur species exist in the
61 cathode during these intermediate steps. Despite these complexities,
62 equation (1) must hold. In other words, the distribution of polysulfides
63 obtained at a particular value of n_e must be such that the average chain
64 length of the polysulfides, x_{avg} , is given by equation (2), which arises due to
65 mole balance of sulfur in equation (1).

$$66 \quad x_{avg} = \frac{16}{n_e} \quad (2)$$

67 To our knowledge, the validity of equation (2) has not been
68 experimentally established.

69 Many reactions have been proposed¹¹ for the stepwise reduction of sulfur.
70 We begin our discussion with a simple series of steps given below:

75 In the simplest case, the overall sulfur reduction reaction rate is governed
76 by the discharge rate imposed on the Li-S cell. This will be true if effects such
77 as transport limitations in the electrolyte and blocking of electrode surfaces
78 due to insulating products are negligible. The discharge rate is typically
79 expressed as C/τ where τ is the number of hours required to fully discharge
80 the cathode. The overall rate of the discharge reaction is controlled by $dn_e/$

81dt, which is held constant during a galvanostatic discharge. If we start with a
82sulfur cathode containing m grams of sulfur (0.171 mg), and discharge it
83with a current, i in mA (0.0143 mA), then n_e at a given time, t in hours, is
84given by equation (7).

85
$$n_e = \frac{16it}{1672m} \quad (7)$$

86where we have used the fact that the theoretical capacity of the sulfur
87cathode is 1672 mAh per g of sulfur.

88 The electrons delivered by the potentiostat to the cathode participate in
89all of the reactions (3)-(6). The distribution of polysulfides in the cathode at
90time t will be determined by the relative rate constants, k_0/k_1 , k_2/k_1 , and k_3/k_1 ;
91see reactions (3) –(6) for definitions of k_i . Our use of k_1 to normalize rate
92constants will be made clear shortly. Our objective is to estimate some of
93the relative rate constants that characterize reactions in a model sulfur
94cathode.

95 In the past decade, different techniques have been used to study the
96reaction mechanism in Li-S cells. Each technique has its own advantages and
97limitations.^{9,11} Electrochemical measurements such as cyclic voltammetry
98(CV)^{16,17} and rotating-ring disk electrode (RRDE)¹⁸ are powerful approaches
99for determining the state of discharge but lack of the ability to distinguish
100different reaction products. X-ray diffraction (XRD) can be used to detect the
101presence of crystalline species such as Li_2S and S_8 but it is insensitive to the
102presence of amorphous polysulfides.^{19,20} Uv-vis,²¹⁻²³ Raman,^{24,25} NMR^{26,27} and
103X-ray absorption spectroscopy (XAS)²⁸⁻³⁹ can, in principal be used to detect

104 polysulfides. In references 20-38, measured spectra are used to infer the
105 presence of certain specific polysulfide species. Such inferences rely on
106 spectral signatures of pure polysulfides. Unfortunately there is no consensus
107 on how polysulfides might be purified nor is there consensus on unique
108 spectral fingerprints of different polysulfides.

109 In this paper, we present results of an operando XAS study of a solid-state
110 Li-S cell. Our measurements enable independent measurements of x_{avg} and
111 n_e , thereby enabling a test of the validity of equation (2). The XAS data also
112 enable determination of the moles of Li_2S formed during discharge. These
113 measurements enable determination of relative rate constants that
114 characterize sulfur oxidation in the cathode, k_2/k_1 and k_3/k_1 .

115

1163. **Experimental Section**

117The separator/electrolyte and cathode were stored inside an argon-filled
118glove box (MBraun) with H₂O and O₂ concentrations maintained at less than
1190.1 ppm. Cell assembly was performed inside the same glovebox.

120**Separator/electrolyte film preparation.** The separator/electrolyte films
121were prepared using a block copolymer of polystyrene-b-poly(ethylene
122oxide) (SEO) synthesized using methods described in the work by
123Hadjichristidis et al.⁴⁰ and purified using methods described in the work by
124Teran et al.⁴¹ The molecular weights of polystyrene and poly(ethylene oxide)
125are 200 kg/mol and 222 kg/mol, respectively. Lithium perchlorate (LiClO₄,
126Sigma-Aldrich) was dried for 24 hours under vacuum at 90°C before use. The
127separator/electrolyte films containing SEO and LiClO₄ were prepared
128according to the method described in the work by Wujcik et al.⁴² The
129thickness of separator/electrolyte film used was 22 μm.

130**Cathode preparation.** Cathode slurries containing S₈ (Alfa Aesar), Li₂S
131(Sigma-Aldrich) carbon black (Denka), LiClO₄, and SEO (identical LiClO₄/SEO
132composition to that of the electrolyte separator) was mixed in n-
133methylpyrrolidone (NMP). The slurry was composed of 89 wt% of NMP. S₈ and
134Li₂S were mixed in a 256:46 weight ratio to produce Li₂S_x with an average x
135value of 8 as the starting material. Due to the insulating properties, both
136ionic and electronic, of S₈, Li₂S₈ was used as the starting material. Since Li₂S₈
137is soluble in the slurry, we expect a uniform distribution of the sulfur-
138containing species in the cathode (as opposed to insoluble S₈), and we posit

139that this leads to better contact between the active material, the electrolyte
140and carbon black in the dry cathode. The slurry was mixed overnight at 90°C
141and subsequently mixed using a homogenizer (Polytron) set to 15,000 RPM.
142Homogenization was done for five minutes and repeated three times, with
143two minute rests between each cycle to prevent the solution from heating up
144to undesirable temperatures. The resulting slurry was then casted onto an 18
145µm thick aluminum foil current collector using a doctor blade. The film was
146dried under Argon at 60°C for 10 hours and then placed under static vacuum
147overnight at room temperature. The resulting cathode had an average
148thickness of 16 µm, with the resulting composition: 12.8 wt% Li₂S₈, 51.4 wt%
149SEO, 5.5 wt% LiClO₄, and 30.3 wt% carbon. Our use of a relatively thin sulfur
150cathode with low sulfur loading was motivated by our desire to minimize self-
151absorption in the XAS experiments.

152**Cell Assembly and Cycling.** A pouch cell was prepared according to the
153method described in the work by Wujcik et al.³⁷ The electrolyte film was
154placed on the cathode. The lithium metal anode was then placed over the
155electrolyte film. The cathode-electrolyte-anode stack was tabbed and sealed
156in a pouch cell was kept at rest at room temperature in an argon
157environment for 48 hours before taking measurements. The cell was then
158taken out of the argon-filled glovebox and placed on a sample holder
159connected to a heating source. It was then held at a temperature of 90°C for
1601.5 hours to ensure good electrical contact between the cathode, electrolyte,
161and anode layers. The cell was then charged to partially form S₈, and then

162discharged at 90°C at a C/20 rate using a VMP3 Potentiostat (Bio-Logic).
163High temperature operation is necessary due to the limited conductivity of
164polymer electrolytes at low temperatures.⁴³ Figure 1 shows a schematic of
165the assembled cell. The discharge and charge rate was calculated using the
166measured mass of the cathode electrode, the known weight percent of sulfur
167in the cathode, and assuming a theoretical capacity of 1672 mA-h/g for
168sulfur. The voltage window was kept between 1.5 V and 3.0 V.

169**X-ray absorption spectroscopy.** XAS measurements were performed at
170beamline 4-3 of the Stanford Synchrotron Radiation Lightsource. Preliminary
171XAS experiments were performed at beamline 5.3.1 of the Advanced Light
172Source. Measurements were taken in fluorescence mode using a four
173element Vortex detector, with 0.1 eV energy resolution around the
174absorption K-edge. One scan took roughly 10 minutes to collect, equivalent
175to roughly 13.9 mA-h/g of capacity passed per scan. The beam spot size was
1762 mm² and was not moved during cycling. The cell holder was inside a
177helium-filled chamber during the in operando measurements. Calibration of
178the X-ray energy was performed using sodium thiosulfate (Sigma-Aldrich),
179setting the first peak maximum to 2472.02 eV.

180**XAS Spectra Analysis.** All spectra were analyzed using the Athena X-ray
181absorption spectroscopy program. Raw XAS spectra were used to calculate
182the “total sulfur” intensity based on methods described by our previous
183work.⁴² For peak deconvolution and product analysis, all spectra were
184normalized and self-absorption corrected using the Athena XAS analysis

185package. The initial spectra were fitted with 4 Gaussian peaks and a step
186function. After 50 mAh/g the spectra were fitted with 6 Gaussians to account
187for the increasing skewness in the main-edge peak due to blue shift of the
188main-edge peak for mid-chain and short-chain polysulfides. Example of
189fitting an experimental spectra with 6 Gaussian peaks and a step function is
190shown in Figure S1.

191

192

1934. Results and Discussion

1944.1 Theoretical XAS spectra analysis

195 Theoretical XAS spectra for different lithium polysulfides were presented
196by Pascal et al. in a previous publication,⁴⁴ and the results are summarized in
197Figure 2(a). In the inset of Figure 2(a), we show a typical molecular
198conformation of one of the polysulfides, Li_2S_8 . Polysulfides with chain length
199between 3 and 8 have two charged terminal sulfurs and the remainder of the
200internal sulfurs are uncharged. The two kinds of sulfurs give rise to two
201distinctive XAS features: a pre-edge peak corresponding to the two charged
202end-chain sulfurs and a main-edge peak corresponding to the internal
203sulfurs. The area under the theoretical pre-edge peak of each polysulfide is
204denoted by A_p^{Th} . Similarly the area under the theoretical main-edge peak of
205each polysulfide is denoted by A_m^{Th} . The spectral features of the polysulfides
206are approximated as a sum of Gaussian peaks and the areas under selected
207peaks were used to compute A_p^{Th} and A_m^{Th} as outlined in Figure S2. In Figure
2082(b) we plot the ratio, A_m^{Th}/A_p^{Th} , as a function of polysulfide chain length, x in
209 Li_2S_x ($3 \leq x \leq 8$). The line in Figure 2(b) is a least squares linear fit. We use
210this linear fit as a “calibration” to determine the average chain length of
211polysulfides in our cell, x_{avg} , using measured values of pre-edge and main-
212edge areas, A_p and A_m . The straight line in Figure 2(b) can be represented as

$$213 \quad x = 0.8732 A_m/A_p + 1.9326 . \quad (8)$$

214 In Figure 2(c) we plot the sum, $(A_p^{Th} + A_m^{Th})$, as a function of x in Li_2S_x ($4 \leq x$
215 ≤ 8). To a good approximation, $(A_p^{Th} + A_m^{Th})$ is 6.61, independent of x. The
216 theoretical spectrum of Li_2S contains a unique peak at 2476 eV that is not
217 present in any of the polysulfides. The area under this peak, A_s^{Th} , was
218 calculated by approximating the theoretical Li_2S spectrum by a sum of
219 Gaussian peaks as shown in Figure S3. The value of A_s^{Th} is 3.07.

220 Thus,

$$221 \quad \frac{A_s^{Th}}{A_p^{Th} + A_m^{Th}} = \frac{3.07}{6.61} = 0.46 . \quad (9)$$

222 We use this to estimate the moles of Li_2S . in our cell is determined by
223 estimating the area under the peak at 2476 eV, A_s .

224 **4.2 Total Sulfur signal**

225 The XAS cell was made with Li_2S_8 in the cathode. Our use of Li_2S_8
226 facilitated dispersion of the sulfur species in the cathode. Our main objective
227 is to determine the state of the sulfur-containing cathode as the cell is
228 discharged. We used a relatively thin cathode and adjusted the sulfur
229 content in the cathode to ensure that all of the sulfur-containing species in
230 the cell could be detected by XAS. The cell was prepared 48 hours before the
231 XAS experiment, stored at room temperature in an argon glovebox, placed in
232 the XAS sample stage, heated to 90 °C for 1.5 h, charged at C/20 until the
233 voltage reached 3.0 V, and then discharged at C/20. Figure 3(a) shows all of
234 the raw XAS spectra during these experiments. The magnitude of the high

235energy plateau attained between 2500 and 2575 eV is indicative of the total
236amount of sulfur detected. We define I_0 to be the average value of the raw
237XAS signal between 2500 and 2575 eV obtained just prior to discharge. We
238define I_n as the average value of the raw XAS signal in the same energy
239range obtained during other scans. The time dependence of the cell potential
240during these experiments is shown in Figure 3(b). The corresponding values
241of I_n/I_0 versus time shows are shown in Figure 3(c).

242 If our cell was perfectly designed, then I_n/I_0 would be independent of time.
243In our case, I_n/I_0 increased by about 12% during the heating step, and
244increased by about another 16% during the charging step. This is attributed
245to the dissolution of Li_2S_8 into the separator during the heating and charging
246steps. Because the anode side faces the incoming X-ray source, the incident
247intensity on the sulfur-containing species in the separator is higher than that
248on the sulfur-containing species in the cathode. Similarly, the fluorescence
249signal from the sulfur-containing species in the separator is more efficiently
250detected because the anode side also faces the detector. Thus, the diffusion
251of sulfur-containing species into the separator is expected to increase I_n/I_0 .
252During the discharge step, however, I_n/I_0 remained approximately constant,
253varying between 1.05 and 0.95. The constancy of I_n/I_0 during discharge
254indicates that all (or nearly all) of the products of sulfur reduction were
255detected by XAS experiment. We therefore conclude that there is no further
256change in the concentration of polysulfides in the separator during the
257discharge step.

2584.3 Discharge products from spectra

259 The raw spectra shown in Figure 3(a) were normalized and corrected for
260self-absorption. All of the normalized spectra exhibited a pre-edge peak
261around 2471 eV and a main-edge peak around 2473 eV. This enables
262calculation of the areas under the pre-edge, A_p , and main-edge peak, A_m .
263These areas can be used to determine the average polysulfide chain length
264in the cell, $x_{avg,cell}$ (x for Li_2S_x), using equation (8). After the heating step,
265 $x_{avg,cell}$ equals 7.0. After the charging step, $x_{avg,cell}$ reached 8.1.

266 An ideal cell would be one wherein all of the Li_2S_8 remained in the cathode
267during storage prior to the XAS experiment and during the heating step. In
268other words, $x_{avg,cell}$ would equal 8.0 in the ideal cell after the heating step. It
269is evident that our cell is not ideal as $x_{avg,cell}$ is 7.0 at the end of the heating
270step. This departure from ideality is attributed to the dissolution of Li_2S_8 into
271the separator, subsequent reactions with the lithium metal anode, and
272shuttling of the resulting shorter polysulfides back into the cathode. We posit
273that during storage and the heating step, 0.29 moles of Li from the anode
274per mole of Li_2S_8 is consumed to reduce the average chain length from 8 to
2757.0, as indicated in equation (10).

277 The cell with $x_{avg,cell} = 7.0$ was then charged at a C/20 rate. In an ideal cell,
278all of the sulfur-containing species would be converted to S_8 after charging. If
279this were true, $x_{avg,cell}$ would equal infinity after the charging step. Instead we
280find that the average chain length increased from 7.0 to 8.1 during the

281 charging step. During the charging step, 1.02 moles of electrons were
 282 delivered to the anode per mole of S_8 in the cell ($t = 1.27$ h in equation 7). If
 283 all of these electrons participated in the oxidation of $Li_2S_{7.0}$, then $x_{avg, cell}$ at the
 284 end of charging step would have been 14.2. The observed departure from
 285 ideality during the charging step is attributed to the reduction of polysulfide
 286 species at the anode/separator interface instead of complete conversion into
 287 Li metal. We conclude that these side reactions consume 0.73 moles of
 288 electrons per mole of S_8 . The remainder participated in the oxidation of $Li_2S_{7.0}$
 289 and the concomitant reduction of Li^+ to Li metal:

291 Figure 4(a) shows the self-absorption-corrected normalized spectra during
 292 discharge. Figure 4(b) shows the dependence of cell potential versus
 293 capacity, Q , during discharge. The XAS spectra in Figure 4(a) contain
 294 standard signatures of polysulfides: a main-edge peak with area A_m and a
 295 pre-edge peak with area A_p . Using methods described above and equation
 296 (8) we determined $x_{avg, cell}$ as a function of capacity, and the results are shown
 297 in Figure 4(c). (The spectra do not contain signatures of polysulfide radicals
 298 that are sometimes observed in Li-S cells.^{34,37,45}) The relatively low discharge
 299 capacity, 503 mAh/g, of our cell is due to non-idealities discussed above.
 300 During discharge, $x_{avg, cell}$ decreased monotonically from 8.1 to 3.0. In the
 301 early stage of discharge, $Q < 100$ mAh/g, $x_{avg, cell}$ decreases rapidly with
 302 increasing Q . In the late stage of discharge, $Q > 100$ mAh/g, $x_{avg, cell}$ decreases
 303 slowly with increasing Q .

304 The measured XAS spectrum at the end of discharge is shown in Figure
3055(a). In addition to the pre-edge and main-edge peaks at 2471 eV and 2473
306eV, an additional peak is observed at 2476 eV. The three dashed lines in
307Figure 5(a) correspond to the characteristic energies of these peaks. As
308discussed above, the theoretical spectra in Figure 2(a) show that the peak at
3092476 eV is a unique signature of Li_2S and it arises due to the crystalline
310nature of this compound.⁴⁴ In addition to determining A_p and A_m , we also
311determined A_s for each of the spectra shown in Figure 4(a). We define $m_{\text{Li}_2\text{S}}$
312as the moles of Li_2S formed per mole of polysulfides. In theory, $m_{\text{Li}_2\text{S}}$ is given
313by

$$314 \quad m_{\text{Li}_2\text{S}} = \frac{1}{0.46} \left(\frac{A_s}{A_p + A_m} \right) \quad (12)$$

315Where the constant 0.46 is based on analysis of the theoretical spectra and
316equation (7). Note that in this analysis, Li_2S is not considered as a

317polysulfide. In Figure 5(b), we plot $\frac{A_s}{A_p + A_m}$ on the left axis and $m_{\text{Li}_2\text{S}}$, on the
318right axis versus Q . The moles of Li_2S formed is low in the early stage of
319discharge, $Q < 100$ mAh/g, but increases rapidly in the late stage of
320discharge, $Q > 100$ mAh/g. Whether or not Li_2S forms in the early stage of
321discharge remains an interesting, open question. We suspect that the values
322we have obtained are due to limitations of our spectral fitting procedure. In
323our cell, $m_{\text{Li}_2\text{S}}$ remains small reaching a maximum value of 0.24 at the end of

324 discharge. Note that the theoretical spectrum of Li_2S contains a feature at
325 2474 eV. In principal, we should correct the measured values of A_m to
326 account for the fact that some of the signal at the main-edge peak is due to
327 Li_2S . This correction is small because $m_{\text{Li}_2\text{S}}$ remains small in our experiment.

328 **4.4 Relating average discharge products to n_e**

329 The dependence of $x_{\text{avg,cell}}$ on n_e during discharge is shown in the inset in
330 Figure 6. We have assumed that all of the electrons delivered to the cathode
331 are consumed by the Li_2S_8 molecules; side-reactions such as the formation of
332 the solid electrolyte interphase (SEI) are ignored. The curve in the inset
333 represents the theoretical predication, equation (2). The theoretical value of
334 n_e corresponds to a cathode that contains pure S_8 at the beginning of
335 discharge (see equation 1). In the experiments however, our cathode to a
336 good approximation contains Li_2S_8 at the beginning of discharge. The data
337 points in the inset in Figure 6 represent experimental values of $x_{\text{avg,cell}}$ and n_e .
338 $x_{\text{avg,cell}}$ was obtained from measurements of A_p and A_m using equation (8). To
339 account for the fact that the discharge begins with Li_2S_8 , we set n_e to a value
340 close to 2 at the beginning of discharge and it is incremented based on
341 equation (7). The actual value used was 1.97 to obtain a perfect match
342 between the experimental data and the theoretical prediction at the
343 beginning of discharge. It is evident that the decrease in the average chain
344 length of sulfur-containing species in the cell is in reasonable agreement with
345 equation (2).

Our analysis above indicates that some of the Li_2S_8 molecules located in the cathode when the cell was made diffuses into the separator and reacted with Li metal. This results in an average composition of $\text{Li}_2\text{S}_{7.0}$ before charging. The polysulfides in the separator not in contact with electronically conducting materials cannot participate in charge or discharge reactions. Their presence also affects our ability to detect the nature of the sulfur-containing species inside the cathode. We posit that these effects are responsible for the deviations between theory and experiment in the inset of Figure 6. We define $x_{\text{avg,cathode}}$ as the average length of sulfur-containing species in the cathode. We assume that the average length of the sulfur-containing species in the separator is fixed at 7.0 during the discharge process. Our cell thus contains two layers with different concentrations of sulfur. Given the agreement seen in the inset of Figure 6, we conclude that most of the sulfur is in the cathode. Specifically, in our model, we assumed that 90% of the sulfur atoms are in the cathode and 10% of the sulfur atoms are in the separator. This enables calculations of the transmission coefficients of the two layers of our cell based on the known absorption coefficients of sulfur and the other elements in our cell. These calculations indicate that the transmission coefficient of the separator layer, $T_{\text{sep}} = 0.623$, while that of the cathode layer, $T_{\text{cathode}} = 0.398$. The distance between the two layers is set to 19 μm based on the geometry of our cell. (We assume for simplicity that all of the sulfur-containing species are located in the middle of each layer.) The measured value of $x_{\text{avg,cell}}$ reflects the length of sulfur-

369containing species in both the cathode and separator ($x_{avg,cathode}$, $x_{avg,sep}$) with a
 370weighting function that depends on the sulfur content and the transmission
 371coefficient of each layer. This is quantified by equation (13).

$$372 \quad x_{avg,cathode} D_{cathode} + x_{avg,sep} D_{sep} = x_{avg,cell} \quad (13)$$

373where $D_{cathode}$ and D_{sep} reflect the weighting functions as shown in equations
 374(14) and (15).

$$375 \quad D_{cathode} = \frac{0.9 T_{cathode}}{0.9 T_{cathode} + 0.1 T_{sep}} = 0.852 \quad (14)$$

$$376 \quad D_{sep} = \frac{0.1 T_{sep}}{0.9 T_{cathode} + 0.1 T_{sep}} = 0.148 \quad (15)$$

377 Since $x_{avg,sep} = 7.0$, we can calculate $x_{avg,cathode}$ corresponding to each value
 378of $x_{avg,cell}$. Figure 6 shows the dependence of $x_{avg,cathode}$ versus n_e . The
 379agreement between theory and experiment reflects the fact that the data
 380are consistent with our assumption that 10% of the sulfur atoms are lost in
 381the separator and hence not available for redox reductions. Our analysis
 382indicates that $x_{avg,cathode}$ at the start of discharge is 8.28 while $x_{avg,cathode}$ at the
 383end of discharge is 2.28 (see Figure 6).

384 The XAS peak at 2476 eV enables detection of Li_2S . It is therefore helpful
 385to distinguish between Li_2S and other sulfur-containing species, namely
 386polysulfides (Li_2S_x , $2 \leq x \leq 8$). We define $x_{avg,PS}$ as the average length of
 387polysulfides. We calculate $x_{avg,PS}$ using the following equation:

$$388 \quad x_{avg,PS} = \left(1 + m_{Li_2S}\right) x_{avg,cathode} - m_{Li_2S} \quad (16)$$

389 We arrive at this equation based on the sulfur mole balance in the cathode.

390 For each mole of polysulfides ($Li_2S_{x_{avg,PS}}$) in the cathode we have m_{Li_2S} moles of

391 Li_2S , and together these compounds gives $(1+m_{Li_2S})$ moles of $Li_2S_{x_{avg,cathode}}$.

392 The final result of our analysis of the XAS data is given in Figure 7 where

393 $x_{avg,PS}$ and m_{Li_2S} are plotted as a function of n_e .

394 It is not possible to identify a particular pathway that is consistent with

395 the data in Figure 7. We used the principal of parsimony to interpret these

396 data. In particular we used a model presented in the introduction beginning

397 with equation (4) and ending with equation (6). We define C_8, C_4, C_2, C_1 to be

398 the molar concentrations of $Li_2S_8, Li_2S_4, Li_2S_2$, and Li_2S , respectively, and

399 assume that the reactions are limited by the concentrations of the sulfur-

400 containing species. We expect this to be true at extremely low C rates. The

401 simplest rate expressions for reactions (4) through (6) are given below:

$$402 \quad \frac{dC_8}{dt} = -k_1 C_8 \quad , \quad (17)$$

$$403 \quad \frac{dC_4}{dt} = 2k_1 C_8 - k_2 C_4 \quad , \quad (18)$$

$$404 \quad \frac{dC_2}{dt} = 2k_2 C_4 - k_3 C_2 \quad , \quad (19)$$

$$405 \quad \frac{dC_1}{dt} = 2k_3 C_2 \quad . \quad (20)$$

406 Since electrons are consumed in all three reactions,

$$407 \quad \frac{dn_e}{dt} = -2(k_1 C_8 + k_2 C_4 + k_3 C_2) \quad . \quad (21)$$

The measured quantities, $x_{avg,cathode}$, $x_{avg,PS}$, and m_{Li_2S} , are related to the molar concentrations of the sulfur-containing species:

$$x_{avg,cathode} = \frac{8C_8 + 4C_4 + 2C_2 + C_1}{C_8 + C_4 + C_2 + C_1}, \quad (22)$$

$$x_{avg,PS} = \frac{8C_8 + 4C_4 + 2C_2}{C_8 + C_4 + C_2}, \quad (23)$$

$$m_{Li_2S} = \frac{C_1}{C_8 + C_4 + C_2}. \quad (24)$$

Equations (17) through (24) were integrated numerically for specific values of k_1 , k_2 , and k_3 , with initial conditions $C_8 = 1$, $C_4 = C_2 = C_1 = 0$. The solved C_8 , C_4 , C_2 , C_1 at each t are used to predict $x_{avg,cathode}$, $x_{avg,PS}$, m_{Li_2S} , and n_e at each t . The symbols in Figure 8 show the experimentally determined values of $x_{avg,cathode}$, $x_{avg,PS}$, m_{Li_2S} , and n_e , respectively, as a function of time, t . The experimental values of m_{Li_2S} in Figure 8c were subtracted by a constant so that m_{Li_2S} at $t = 0$ is zero. This subtraction is necessary as the spectral signal at any given energy is not identically zero even if the species is absent due to factors such as contributions from neighboring excitations and background subtraction inaccuracies. The curves in Figure 8 show results of the numerical integration for $k_1 = 0.368 \text{ h}^{-1}$, $k_2 = 3/4 k_1$, and $k_3 = 1/6 k_1$. It is evident that the measurements are consistent with the proposed model. Our analysis indicates that the rate of reduction of sulfur-containing species decreases with decreasing chain length. To our knowledge, these are the

first estimates of reaction rate constants for discharge reactions in the cathode of a Li-S cell.

Figure 9 plots the predicted concentrations of Li_2S_8 , Li_2S_4 , Li_2S_2 , and Li_2S versus discharge capacity, based on our model, equations (17)-(21).

The results presented in Figures 8 and 9 represent the first step in quantifying the rates of reactions that occur in a sulfur cathode. Our simple discharge reaction models is also consistent with the reaction mechanism proposed by Hagen et al.²⁴ Most other studies suggest that the reduction of sulfur in the cathode during discharge is likely to follow more complex schemes. For example, Barchasz et al.²¹ have proposed the following reaction for the reduction of Li_2S_4 :

Such reactions require concerted action on several reactant molecules. In the example above, three Li_2S_4 molecules must react with two Li^+ and two e^- to yield the stated product. In contrast, the proposed reaction for Li_2S_4 (equation 5) only involves one reactant molecule. The additional complication with equation (25) is the fact that the reaction must involve many steps wherein the Li_2S_4 molecules are cleaved and then recombine to give four Li_2S_3 molecules. For these reasons, equation (5) is more likely to proceed than equation (25).

The reaction rates that we present are only applicable to the regime $0 \leq Q \leq 500 \text{ mAh/g}$ (the discharge range covered by our experiments). It is likely that these rates will change as Li_2S becomes the dominant species in the

450cathode. The shorter-chain polysulfides such as Li_2S_2 are insoluble⁴⁶⁻⁴⁸ and
451thus their concentration near reaction sites in the cathode may be
452significantly different from the bulk concentration. In addition to
453electrochemical reactions, polysulfides can interconvert through chemical
454reactions. Sophisticated models that include transport are needed to account
455for complications arising from polysulfide dissolution and concomitant
456shuttling effects. Further work is needed to explore the effects.

457 The subject of reaction mechanisms in sulfur cathode is of considerable
458current interest.^{21,27,51-57,28,31,32,35,38,42,49,50} Our detection of Li_2S at the very early
459stage of discharge (as seen in Figure 8c) is consistent with the findings of
460Waluś et al.^{20,58}, Cuisinier et al.³³, and Conder et al.⁵². Similarly, the formation
461and subsequent consumption of Li_2S_4 up to 500 mAh/g of discharge in Figure
4629 is similar to the findings of Dominko et al.³⁶, Zhang et al.⁵⁵ and Zheng et
463al.⁵¹. Our results in Figure 9 also indicated a significant amount of Li_2S_2 inside
464the cathode at a depth of discharge of 500 mAh/g, which is consistent with
465the results of Kawase et al.⁵⁴ Reaction mechanisms in the sulfur cathode
466have also been studied using computational simulations by Burgos et al.⁵⁹
467They found that a variety of radical and dianion species were formed in their
468simulation cell. However, S_8^{2-} dianions were formed at the early stage of
469discharge, S_4^{2-} dianions dominated the intermediate stage of discharge, and
470 S_4^{2-} dianions dominated the late stage of discharge at low applied current
471density. Our experimental findings and approach are consistent with these
472results.

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474

4755. Conclusion

476 In this work, we presented an operando XAS study of a solid-state Li-S
477cell. The use of a block copolymer electrolyte enabled the construction of an
478all solid-state Li-S cell that could readily be probed by XAS. Li_2S_8 was used as
479the active material inside the cathode instead of S_8 to facilitate dispersion of
480the sulfur-containing species in the electrode. The main objective of the
481operando XAS experiment was to study the discharge process. By using a
482thin cathode with relatively low sulfur content, we demonstrated that the
483XAS signal reflected all of the sulfur-containing species located throughout
484the depth of the cell. The average chain-length of sulfur-containing species,
485 $x_{\text{avg,cell}}$, was determined from the ratio of the areas under the main-edge and
486pre-edge XAS peaks located at 2473 and 2471 eV. The measured values of
487 $x_{\text{avg,cell}}$ at a given depth of discharge was in excellent agreement with
488predictions based on the number of electrons delivered to the cell as
489measured by the potentiostat. In addition, the production of Li_2S as a
490function of depth of discharge was monitored by tracking the area under a
491unique XAS peak located at 2476 eV. The XAS measurements were used to
492estimate rate constants of discharge reactions presented in the introduction
493(equations 4-6 where we introduced rate constants k_1 , k_2 and k_3). While the
494overall rate of reaction in the cathode is controlled by the current density
495used to discharge the cell, the relative rate constants, k_2/k_1 and k_3/k_1 , depend
496on the electronic structures of the polysulfides participating in the reactions.

497To our knowledge, this work presents the first estimate of relative rate
498constants for discharge reactions in Li-S cells.

499 It is well established that the rate at which Li-S cells can be charged and
500discharged is compromised by dissolution of polysulfides and the insulating
501nature of the reactants and products. In addition to these factors, the
502relative reaction rates may present fundamental limitations on the practical
503power density of Li-S batteries. The present study is only a step towards
504understanding these limitations.

505

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677
678

Figure 1. Schematic of a Li-S cell used for operando XAS study

683

684 Figure 2. (a) Theoretical XAS spectra from Pascal et al.⁴⁴, (b) linear relationship between x for
 685 Li_2S_x ($3 \leq x \leq 8$) and the area ratio of main-edge peak to pre-edge peak, A_m/A_p , and (c) sum of
 686 pre-edge and main-edge peak areas per mole of Li_2S_x ($4 \leq x \leq 8$) from theoretical spectra
 687

688

691 Figure 3. (a) All raw XAS spectra, (b) time dependence of voltage and (c) time dependence of I_n/I_0

692 I_0 before and during cycling

693

696 Figure 4(a) Normalized and self-absorption corrected

697 in operando XAS spectra and (b) voltage profile and

698 average polysulfide chain length during discharge

699

700

701 Figure 5 (a). Illustration of peaks with areas A_p , A_m , and A_s for a discharged spectrum, and (b)
 702 ratio of 2476 eV peak, A_s , to sum of peak areas for pre-edge and main-edge, $A_p + A_m$, on the left

703 axis and moles of Li_2S formed per mole of polysulfides, m_{Li_2S} , on the right axis versus discharge

704 capacity

705

706

707 Figure 6. Theoretical and experimental average chain length of sulfur-containing species in the

708 cathode, $x_{avg,cathode}$ and in the cell $x_{avg,cell}$, vs number of electrons delivered per S₈ molecule, n_e

709

710

711 Figure 7. Average polysulfide chain length inside the cathode, $X_{avg,PS}$, on the left axis, and molar

712 ratio of Li_2S to polysulfides, m_{Li_2S} , vs number of electrons delivered per S_8 molecule, n_e

713

Figure 8. Comparing experimental measures and the predicted values of (a) $X_{avg,cathode}$, (b)

$X_{avg,PS}$, (c) m_{Li_2S} , and (d) n_e versus t , time in hours, using the three-reaction model fitted with k_1

$$= e^{-1}, k_2 = \frac{3}{4}e^{-1}, \text{ and } k_3 = \frac{1}{6}e^{-1}.$$

Figure 9. Concentration profile of Li_2S_8 , Li_2S_4 , Li_2S_2 , and Li_2S predicted by model