

# Insights into Multiphase Reactions during Self-Discharge of Li-S Batteries

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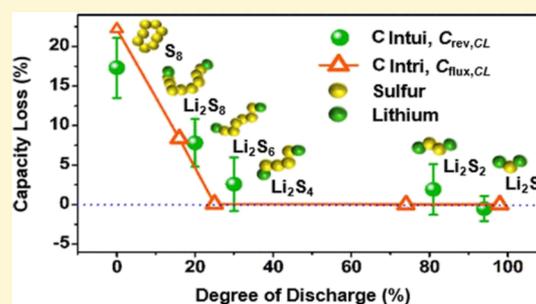
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Supporting Information

**ABSTRACT:** Lithium-sulfur (Li-S) batteries are promising next-generation rechargeable energy storage systems due to their high energy density and use of abundant and inexpensive materials. However, rapid self-discharge and poor cycling stability due to the solubility of intermediate polysulfide conversion products have slowed their commercialization. Herein, we provide a detailed account of the multiphase reactions occurring during the self-discharge of a Li-S battery held at various depth of discharge (DOD) through both simulation and experiment. For the first time, self-discharge of a full Li-S battery is simulated using a 1D model to describe reactions at both the anode and cathode. The model accurately describes experimentally derived results obtained over the longest durations of self-discharge studied to date (140 h).

This validated model was used to follow the reversible and irreversible capacity loss caused by shuttling and precipitation of insoluble  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  as a function of DOD. While the most rapid self-discharge is observed at low DOD, this also leads to the smallest irreversible loss. The results suggest that resting a Li-S battery near 2.1 V minimizes both reversible and irreversible losses.



## 1. INTRODUCTION

The lithium-sulfur (Li-S) battery is one of the most promising battery systems owing to its high theoretical specific capacity of 1672 mAh/g and specific energy of 2600 Wh/(kg active material only).<sup>1–3</sup> Unlike intercalation compounds, the transformation of sulfur to  $\text{Li}_2\text{S}$  takes place via the formation of a series of intermediate lithium polysulfides (PSs), i.e.,  $\text{Li}_2\text{S}_n$  (where,  $n = 2 - 8$ ).<sup>4,5</sup> The long chain PSs are soluble in the ether-based electrolytes typically used. Consequently, they migrate across the cell and participate in parasitic reactions at the anode or elsewhere in the cell leading to reversible or irreversible capacity loss via chemical conversion or precipitation of shorter chain PSs.<sup>6,7</sup> This problem, caused by the mobility of sulfur-containing species, is generally referred to as the PS shuttling phenomena. Depending on the conditions, this shuttling can either passivate or corrode the lithium anode and contribute to self-discharge and low Coulombic efficiency.<sup>2,8,9</sup> To mitigate this, different strategies have been investigated such as the use of additives<sup>10,11</sup> or coatings to protect the lithium surface,<sup>12,13</sup> metal oxide adsorbents<sup>14–19</sup> to capture the PSs, modified separators<sup>20</sup> and cathode designs, which aim to stabilize and retain PSs.<sup>21–23</sup> Although the cycle-life improvement associated with these aforementioned strategies is well documented,<sup>13</sup> the time-scale associated with cycling is on the order of a few hours (cycling is typically carried out at 0.5 or 1C for practical reasons), and few studies focus on self-discharge, which can occur over days or months when a battery is stored between uses.<sup>24</sup> To accelerate the

commercial development of Li-S batteries, it is necessary to gain a deeper understanding of the shuttling phenomenon and its impact on self-discharge rates over long periods and different resting conditions so that such capacity losses can be minimized.

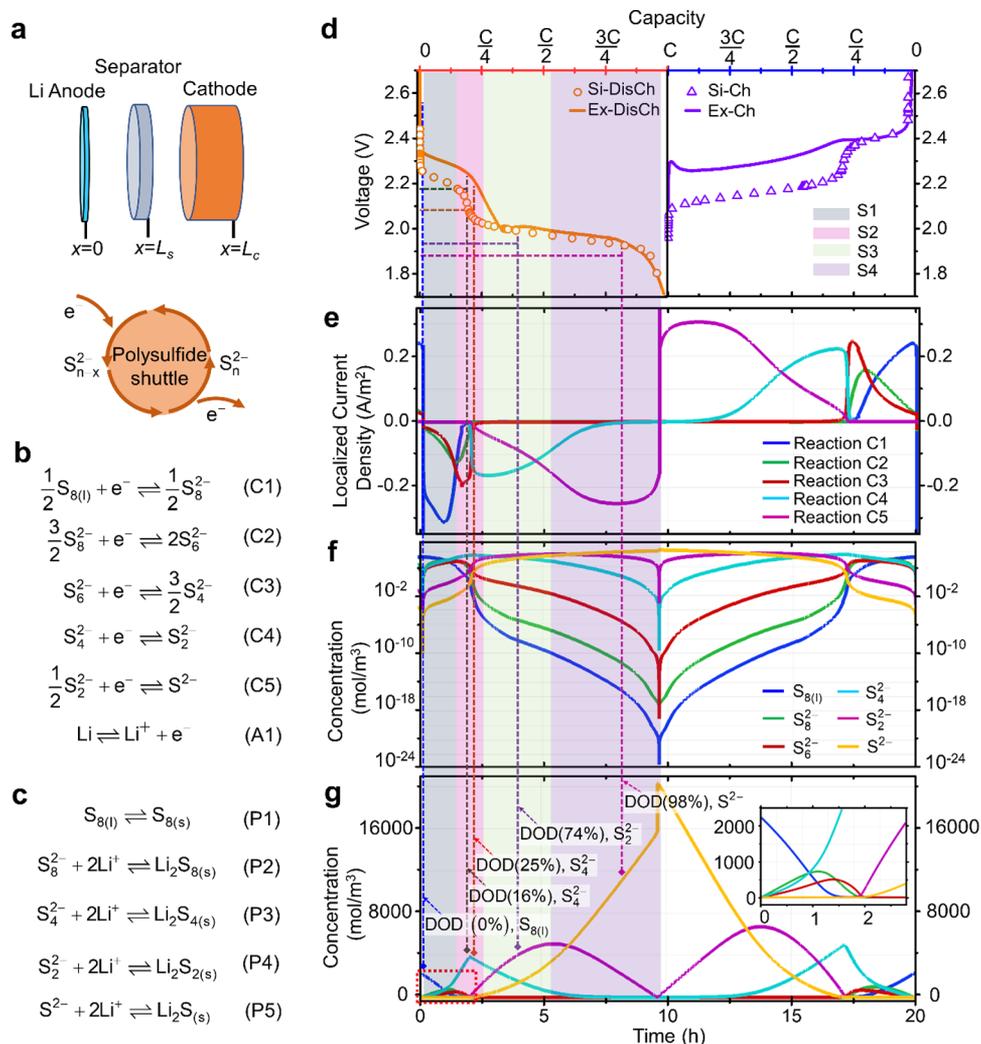
Self-discharge is a major obstacle for the development of Li-S batteries. Mikhaylik and Akridge have studied the experimental self-discharge rates for Li-S batteries by quantitatively analyzing the shuttle phenomenon.<sup>25</sup> They reported that the primary cause of self-discharge is the migration of soluble PSs ( $\text{Li}_2\text{S}_n$ ,  $8 < n < 3$ ) at the higher voltage plateau ( $\sim 2.33$  V vs Li). Knap et al. investigated the dependence of the self-discharge behavior on the depth of discharge (DOD), resting time, and operational temperature.<sup>26</sup> These works have demonstrated that Li-S batteries suffer a capacity fading of over 50% in a month or less. In contrast, commercial Li-ion batteries exhibit extremely low self-discharge (less than 3% per month).<sup>27–29</sup> While self-discharge is generally thought to be a result of shuttling, the mechanisms, which control the rates and reversibility of the capacity loss are not well understood. While cycling a real battery takes weeks

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**Figure 1.** (a) Schematic illustration of the Li-S battery model setup and the PS shuttle effect. (b) Electrochemical reactions in the sulfur cathode and the lithium anode. (c) Phase change reactions considered in the model. (d) Comparison of experimental (Ex) vs simulated (Si) voltage profiles during one discharge–charge cycle of Li-S batteries. (e) Simulated localized current density profiles of multireactions in the cathode and simulated concentration variations of PS during one discharge–charge cycle: (f)  $y$ -axes are in a logarithmic scale; (g)  $y$ -axes are in linear scale. Five representative DOD levels were chosen. The discharge profile was divided into four sections in (d–f): S1-dominated by Reaction C1; S2-dominated by Reaction C2 and C3; S3-dominated by Reaction C4; and S4 dominated by Reaction C5. The dashed lines correspond to the indicated DOD.

to months, a numerical model can be run in a fraction of the time to provide a useful understanding of the key chemical processes and performance. Thus, there is a strong incentive to develop rigorous models of Li-S batteries.

Recent studies have identified the presence of multifaceted physicochemical interactions during capacity fading, such as precipitation/dissolution dynamics, interfacial kinetics, concentrated solution effects, and poromechanical progression to name a few.<sup>4,30–33</sup> Hofmann et al. presented a mechanistic model to provide insights into the key mechanisms with a focus on the shuttling phenomena. However, their model did not take into account the nucleation and growth of solid precipitates.<sup>34</sup> The mathematical models by Busche et al.<sup>35</sup> and Marinescu et al.<sup>36</sup> studied the correlation between the state of discharge and the cell kinetics using a shuttle constant,  $k_s$ , which was determined by time-consuming experiments. However, they could not accurately estimate the self-discharge resulting from PS reduction at the anode. A more complete model was considered by Kumaresan et al.<sup>37</sup> who developed a

one-dimensional model of a Li-S cell involving five electrochemical conversion steps in the cathode and precipitation/dissolution reactions that form insoluble PSs. However, they were only able to simulate one charge and one discharge. Unfortunately, the complexity of the Li-S system requires not only the assumption of many parameters but also the consideration of the cycling and resting behaviors. After reviewing a range of analytical studies and physical models, it is clear that the state-of-the-art models lag behind experimental understanding.<sup>30</sup> The knowledge about mechanisms at the core of Li-S battery models is incomplete compared to the latest thinking based upon experimental results. More effort is needed to verify these results and update the models. Thus, there is a significant need to develop an improved model and to validate against the latest experimentally derived data.

Here, we present the first numerical 1D model of the Li-S battery that takes into account the speciation of PSs from the cathode to the anode over long cycling periods, including idling over various depths of discharge. The model provides a

deeper insight into the reversible and irreversible capacity loss experienced during self-discharge. Importantly, for the first time, simulation data is compared to extensive experimental data obtained from long cycling and resting periods and the results provide close agreement.

## 2. EXPERIMENTAL METHOD AND MODEL DESCRIPTION

**2.1. Synthesis of Acid-Modified Graphene.** Commercial graphene nanoplatelet powder (GNP) was obtained from Nano-Xplore Inc. (grade DMP-4). Prior to use, this material was modified via an acid treatment to increase the level of exfoliation and to provide some oxygen-containing functional groups, which are known to interact with polysulfides and somewhat reduce the shuttling phenomena.<sup>38</sup> In a typical synthesis procedure, 1 g of GNP powder and 10 mM sodium dodecyl sulfate (SDS micropellets, molecular biology grade, Fisher bioreagents) were mixed with 500 mL of 18 MΩ deionized (DI) water then sonicated for 1 h at 50% power. After sonication, the dispersion was vacuum-filtered and washed with 500 mL of DI water. To prevent aggregation of the GNPs, the filter cake was not allowed to dry, and this filter cake was added to 130.4 mL of concentrated sulfuric acid (Sigma Aldrich, 95–98%) and 113.23 mL nitric acid (Sigma Aldrich, 70%) (3:2 ratio (vol/vol)), which was heated at 50 °C for 24 h under stirring. The resulting mixture was separated from the residual acids by centrifugation. The supernatant was discarded, and the pellet was washed by filtration with 500–700 mL of DI water. The sample was dried and collected for electrode fabrication.

**2.2. Synthesis of Graphene Nanoplatelets/Sulfur Composites.** The modified GNP/sulfur composite was prepared by mixing 40:60 (mass/mass) of GNP to sulfur using a mortar and pestle for 15 min. The mixture was transferred to an Ar-filled glovebox (<1 ppm air and water) and placed within an autoclave that was sealed within the Ar-filled environment. The autoclave was heated to 160 °C for 12 h, which was sufficient to melt the sulfur and draw liquid into the pores of the graphene-based material via capillary action as molten sulfur is known to wet carbonaceous materials.<sup>39</sup>

**2.3. Fabrication of the Electrode and Electrochemical Measurement.** Sulfur cathodes were prepared by mixing 80 wt % of active materials (GNP/S), 10 wt % carbon black powder (carbon super P, MTI), and 10 wt % of polyvinylidene fluoride (PVDF, Sigma Aldrich, MW ~ 534,000) dissolved in *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich 99.5%) thoroughly to make a slurry. The slurry was then cast onto one side of a carbon paper (AvCarb P50 - 40 × 40 cm) and dried in a vacuum oven at 50 °C for 12 h for the evaporation of NMP. The sulfur loading was 3.2–5.5 mg cm<sup>-2</sup> and the electrolyte volume was 90 μL (electrolyte to sulfur ratio of ~16:1).

GNP/S cathodes were tested using CR2032-type stainless steel coin cells assembled in an Ar-filled glovebox. The cathode was separated from a lithium metal anode (Sigma-Aldrich, thickness 0.75 mm, width 45 mm, 99.9% trace metal basis) using a polypropylene membrane (25 μm, Celgard 2325). Prior to crimping, 90 μL of an ether-based electrolyte (1:1 (vol/vol) 1,3-dioxolane (DOL) and 1,2-dimethoxyethane ((DME), containing 0.2 M lithium nitrate (LiNO<sub>3</sub>) and 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) (all from Sigma-Aldrich 99.9%)) were added to the cell. Galvanostatic cycling was carried out between limits of 1.7 and 2.7 V (vs Li/Li<sup>+</sup>) on a Neware Battery Tester (0 to +5 V, 0.1 A). Based on the mass of elemental sulfur, a gravimetric current density of 1672 mA/g was used to define the C-rate.

The test protocol comprised five steps and the cells were charged and discharged between 2.7 and 1.7 V. Step 1 corresponds to a precondition cycle of charge and discharge. Step 2 involved charging the cell to 2.7 V by a current of 0.1C and discharging to a predetermined depth of discharge (DOD\*, the \* indicates that it is the experimental DOD as opposed to the one defined by the modeling below) by the same current. The cell was held under open circuit conditions (OCV) for 48 h during step 3 and then in step 4 it was fully discharged to 1.7 V. We chose five representative potentials

to investigate the behavior at rest because it took several months to finish one experiment. The DOD\* chosen for self-discharge measurements were specified by the potentials of 2.04 V (~81%, 8th discharge), 2.1 V (~30%, 14th discharge), 2.7 V (~0%, 21st discharge), 2.25 V (~22%, 27th discharge), and 1.95 V (~94%, 33th discharge). The order of the self-discharge measurements was changed in some experiments to confirm there is no cycle number dependence on the self-discharge behavior.

To investigate the precipitation of Li<sub>2</sub>S<sub>2</sub>(s) and Li<sub>2</sub>S(s) within the cell, ex-situ X-ray diffraction (XRD, Rigaku Miniflex II, CuK<sub>α</sub> radiation) on the components of a cell (cathode, anode, and separator) was carried out. Cells were disassembled after the 11th cycle when the cell was held for self-discharging at ~22% DOD (2.1 V) for 48 h and then completely discharged to 1.7 V. The XRD samples were prepared inside a glovebox, covered with a Kapton film to slow the diffusion of air/moisture, which would react with Li<sub>2</sub>S and Li<sub>2</sub>S<sub>2</sub> to form products such as H<sub>2</sub>S.

**2.4. Model Description.** Figure 1a shows the geometry considered in the study. An attempt was made to include a rigorous treatment of precipitation and polysulfide shuttling. A 1D model was used since it is more practical as computational complexity increases, as does the number of assumed parameters. To match the experimental conditions, the thickness of the separator was set to 25 μm, denoted as *L<sub>s</sub>*, while the thickness of the cathode was 36 μm, denoted as *L<sub>c</sub>*. To reduce the model complexity, the anode was considered a point. This assumption was acceptable because lithium was in excess (a thick Li foil is used).

As shown in Figure 1b, five electrochemical reactions were considered to take place at the cathode (C1–C5), while one occurred at the anode surface (A1) during charge and discharge per single electron transfer step. Although there was evidence to suggest that charge was not the exact reversal of discharge, the assumption can be made in this case for numerical simplicity.<sup>36,37,40–42</sup> Figure 1c shows the precipitation/dissolution reactions forming solid PSs that were considered to take place. Depending on the local concentrations of ionic species, one or more of the following precipitates may be formed: Li<sub>2</sub>S<sub>8</sub>, Li<sub>2</sub>S<sub>6</sub>, Li<sub>2</sub>S<sub>4</sub>, Li<sub>2</sub>S<sub>2</sub>, and Li<sub>2</sub>S. However, previous experimental and simulation studies indicate that all lithium sulfides except Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S are substantially soluble in the electrolyte.<sup>37,43–46</sup> In addition to precipitation of Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S, the model also includes the precipitation of Li<sub>2</sub>S<sub>8</sub> and Li<sub>2</sub>S<sub>4</sub> for illustration purposes.

The governing equations of the mathematical model are outlined below. A list of the stoichiometric coefficients of species in reactions is given in Table S1 of the Supporting Information. The current density is given by the Butler-Volmer equation:<sup>37</sup>

$$I_j = I_{0,ref,j} \left[ \left( \frac{c_{Re,j}}{c_{Re,ref,j}} \right)^{s_{Re,j}} \exp \left( \frac{\alpha_{an} F \eta_j}{RT} \right) - \left( \frac{c_{Ox,j}}{c_{Ox,ref,j}} \right)^{-s_{Ox,j}} \exp \left( \frac{-\alpha_{ca} F \eta_j}{RT} \right) \right] \quad (1)$$

where *I<sub>j</sub>* is the current density of the reaction *j*, *I<sub>0,ref,j</sub>* is the reference exchange current density, as shown in Table 1, *c<sub>Re</sub>* and *c<sub>Ox</sub>* are the concentration of reduced (Re) and oxidized (Ox) species (Ox + *ne*<sup>-</sup> → Re), respectively, *c<sub>ref</sub>* is the reference concentration, which is also

**Table 1. Kinetic Parameters for Each Reaction**

reactions	<i>I<sub>0,ref,j</sub></i> (A/m <sup>2</sup> )	<i>U<sub>j</sub><sup>0</sup></i> (V)
A1	1	0.0
C1	1.972	2.39
C2	0.019	2.37
C3	0.019	2.24
C4	1.97 × 10 <sup>-4</sup>	2.04
C5	1.97 × 10 <sup>-7</sup>	2.01

the initial concentration of the species in the electrolyte when beginning discharge for the first time,  $s$  is the stoichiometric coefficient of reduced or oxidized species,  $\alpha$  is the anodic (an) and cathodic (ca) transfer coefficients (both set equal to 0.5), and  $\eta_j$  is the overpotential given by:

$$\eta_j = \varphi_l - \varphi_s - U_{\text{ref},j} \quad (2)$$

where  $\varphi_l$  and  $\varphi_s$  are the liquid and solid phase potentials. The liquid phase current density is related to the flux of ionic species, while the solid phase potential is governed by Ohm's Law.  $U_{\text{ref},j}$  is the open circuit potential given by:

$$U_{\text{ref},j} = U_j^0 - \frac{RT}{n_j F} [s_{\text{Re},j} \ln c_{\text{Re},\text{ref}} - s_{\text{Ox},j} \ln c_{\text{Ox},\text{ref}}] \quad (3)$$

where  $U_j^0$  is the formal potential<sup>47</sup> of the reaction  $j$ , which is a fitting parameter that encompasses both the standard potential and the activity coefficients of the species;  $n_j$  is the number of electrons transferred in the reaction  $j$ . Equation 3 is valid only when the concentrations are expressed in moles per liter.<sup>37</sup> The sensitivity analyses of  $I_{0,\text{ref},j}$ ,  $U_j^0$ , and reference concentrations were performed to validate the values (Figures S1–S3).

For a multicomponent electrolyte in a porous electrode the conservation of each charged species  $i$  ( $i = \text{Li}^+$ ,  $\text{S}_{8(\text{l})}$ ,  $\text{S}_8^{2-}$ ,  $\text{S}_4^{2-}$ ,  $\text{S}_2^{2-}$ ,  $\text{S}^{2-}$ , and  $\text{A}^-$ , here,  $\text{A}^-$  denotes the anion of the lithium salt used in the electrolyte) is given by the Nernst-Planck equation:

$$\frac{\partial \varepsilon c_i}{\partial t} = -\nabla N_i + r_i - R_i \quad (4)$$

where  $c_i$  is the concentration,  $\varepsilon$  represents the pore volume fraction of the porous cathode or separator,  $N_i$  is the flux due to diffusion and migration in the potential field,  $r_i$  is the electrochemical reaction rate, and  $R_i$  is the precipitation/dissolution rate. Flux is given by:

$$N_i = -D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \varphi_l \quad (5)$$

where  $D_i$  is the effective diffusion coefficient of species  $i$  with the bulk electrolyte species, which can be related to the porosity of the material using the Bruggeman relation. (Table S2 and eq S1 of the Supporting Information).

The electrochemical reaction rate for the reaction  $j$  is given by:

$$r_i = -S_a \sum_{j=C1}^{C5} \frac{s_{i,j} I_j}{n_j F} \quad (6)$$

where  $S_a$  is the electrochemically active surface area per unit volume,  $s_{i,j}$  is the stoichiometric coefficient of species  $i$  in the reaction  $j$ . The surface area is assumed to vary with porosity, which changes over time as elemental sulfur dissolves and PSs precipitate, according to the following relation:

$$S_a = S_{a,0} \left( \frac{\varepsilon}{\varepsilon_0} \right)^\chi \quad (7)$$

where  $\chi$  is the empirical parameter describing the morphology of the precipitate and is assigned a value of 1.5 in this work.

The third term in eq 4,  $R_i$ , describes the rate of precipitation of species  $i$  to form solid salts and is important to the present study, which considers cycles and periods of rest and is given as:

$$R_i = \sum_{k=P1}^{P5} \gamma_{i,k} R'_k = \sum_{k=P1}^{P5} \gamma_{i,k} v_k \varepsilon_k \left( \prod_i c_i^{\gamma_{i,k}} - K_{\text{sp},k} \right) \quad (8)$$

where  $R'_k$  is the rate of precipitation reaction containing solid species  $k$  (P1–P5 as shown in Figure 1c),  $\gamma_{i,k}$  is the number of moles of species  $i$  in the precipitation reactions,  $v_k$  is the rate constant,  $\varepsilon_k$  is the solid volume fraction of the precipitation  $k$ . The precipitation rate ( $R'_k$ ) is assumed to depend on the solubility product and concentration of related species. The precipitation parameters are shown in Table S3. A sensitivity analysis of the precipitation rate (Figure S4) revealed

that the volume fraction of  $\text{Li}_2\text{S}_2$  increased rapidly and led to unphysical behavior when increasing the precipitation reaction rate.

The change in total porosity of the electrode is impacted by the precipitation/dissolution rate and the molar volume of the precipitating and dissolving species,  $\tilde{V}_k$ :

$$\frac{\partial \varepsilon}{\partial t} = - \sum_{k=P1}^{P5} \frac{\partial \varepsilon_k}{\partial t} = - \sum_{k=P1}^{P5} \tilde{V}_k R'_k \quad (9)$$

The polysulfide shuttle is essentially composed of two distinct events: shuttling of sulfur species in the electrolyte and their subsequent chemical reduction at the anode. The species shuttling in the electrolyte has two transport mechanisms: diffusion and migration. Concentration gradients lead to diffusion while potential gradients drive migration of PSs. Thus, the species shuttling in the electrolyte is strongly related to the species concentration. These PSs species accept electrons from the Li metal at the anode and are reduced, but the electron is not exchanged in the external circuit. In order to quantify the reactivity of PSs at the anode, Mistry et al.<sup>48</sup> proposed to use a chemical overpotential ( $\eta_{\text{ch}}$ ) as a fitting parameter, which is analogous to the definition of an electrochemical overpotential. Although the reduction at the anode is different from the electrochemical reduction of sulfur at the cathode, the chemical reactivity (reaction rate,  $v_{\text{an}}$ ) of the anode characterized by a chemical overpotential ( $\eta_{\text{ch}}$ ) might be an acceptable strategy:

$$v_{\text{an},j} = \frac{i_{0,\text{ref},j}}{F} \exp\left(\frac{-F\eta_{\text{ch}}}{2RT}\right) \left(\frac{c_{\text{Ox},j}}{c_{\text{Ox},\text{ref},j}}\right)^{s_{\text{Ox},j}} \quad (10)$$

where  $i_{0,\text{ref},j}$  is the reference exchange current density, which is the same as the definition at the cathode, and  $\eta_{\text{ch}}$  is the chemical overpotential. As  $\eta_{\text{ch}}$  approaches zero, the anode surface reactions are thermodynamically favored and in turn faster. When larger than 0.5 V, the PS reduction reactions at the anode become slow, which differs from the experimental observations. A sensitivity analysis of  $\eta_{\text{ch}}$  on the model output revealed that 0.45 V is a reasonable value that led to the best fit to our experimental data as discussed further in the main text below (Figure S5).

The other parameter values used in the model are listed in Table S4 and the equations of charge conservation are shown in eqs S2–S5. The set of differential and algebraic equations were solved using a finite element solver (COMSOL Multiphysics). A mesh sensitivity study was performed to determine the necessary amount of mesh refinement. Dynamic discharge–charge cycling periods and resting periods were simulated by the *event interface module*. The model predicted the evolution of the species concentrations, together with changes in the porosity of the separator and the cathode, and the volume fraction of the different precipitates across an electrode pair (anode–separator–cathode).

**2.5. Definition of Capacity Loss.** To provide a clear understanding of capacity loss (CL), a proper understanding of reversible and irreversible capacity fading during resting periods is needed. In terms of the experimental data, the CL can only be estimated via coulomb counting. On the other hand, simulations provide the species distribution over each simulation step and enable us to directly quantify the state of each species in the battery. Thus, two different kinds of definitions are provided based on the experimental and simulation results, respectively. The following sections discuss each of these.

**2.5.1. Intuitive Definition of CL.** From an experimental point of view, the CL of the cell or self-discharge behavior is quantified as follows, where the various capacities are obtained from coulomb counting:<sup>26</sup>

$$C_{\text{t,CL}} = \frac{(C_{\text{ini}^*} - C_{\text{dod}^*} - C_{\text{rem}})}{C_{\text{ini}^*}} \quad (11)$$

$$C_{\text{rev,CL}} = \frac{(C_{\text{rch}} - C_{\text{dod}^*} - C_{\text{rem}})}{C_{\text{ini}^*}} \quad (12)$$

$$C_{ir,CL} = \frac{(C_{ini}^* - C_{rch})}{C_{ini}^*}, \quad (13)$$

$$C_{t,CL} = C_{rev,CL} + C_{ir,CL}, \quad (14)$$

where  $C_{ini}^*$  is the initial capacity determined during the preconditioning cycle (again the \* indicates the experimentally derived value);  $C_{dod}^*$  is the discharge capacity to the specific DOD\* level;  $C_{rem}$  is the remaining discharge capacity after resting the cell at a specified voltage;  $C_{rch}$  is the capacity exhibited by the cell during recharge after the resting condition;  $C_{t,CL}$  represents the total CL during the resting condition; the reversible CL is  $C_{rev,CL}$ ; and  $C_{ir,CL}$  is the irreversible CL.

**2.5.2. Intrinsic Definition of CL.** The model can provide a detailed description of the species, which have been lost in the cycle and also the inefficiency of the cycling capacity due to self-discharge. Through counting the amount of precipitate directly and, from that, calculating a reduction in total working capacity and the amount of self-discharge current, the relevant losses can be calculated as follows:

$$C_{precip,CL} = \frac{[2F \cdot (c_{Li_2S} + 2c_{Li_2S_2})]}{C_{ini}}, \quad (15)$$

$$C_{flux,CL} = \frac{[FA_C(16\nu_{S_8} + 14\nu_{S_8^{2-}} + 10\nu_{S_6^{2-}} + 6\nu_{S_4^{2-}} + 2\nu_{S_2^{2-}} + \nu_{S^{2-}})]}{C_{ini}}, \quad (16)$$

where  $C_{precip,CL}$  is the precipitation CL due to the formation of  $Li_2S$  and  $Li_2S_2$ , which precipitates in the electrolyte and at the anode side;  $c_{Li_2S}$  and  $c_{Li_2S_2}$  are the total number of moles of  $Li_2S$  and  $Li_2S_2$ , respectively;  $C_{ini}$  is the theoretical initial capacity based on species concentration;  $C_{flux,CL}$  is the total self-discharge CL due to the shuttle flux and reduction of  $S_{8(1)}$ ,  $S_8^{2-}$ ,  $S_6^{2-}$ ,  $S_4^{2-}$ , and  $S_2^{2-}$  species toward the anode;  $\nu_{S_8}$ ,  $\nu_{S_8^{2-}}$ ,  $\nu_{S_6^{2-}}$ ,  $\nu_{S_4^{2-}}$ , and  $\nu_{S_2^{2-}}$  represent the self-discharge flux rate of each species, and the unit is  $mol/(m^2 s)$ .

### 3. RESULTS AND DISCUSSION

**3.1. Model Validation, Current Density, and Concentration Distribution.** Figure 1d compares the cell voltages during both discharging and charging measured experimentally with the simulation results. The model qualitatively reproduces essential features of a typical Li-S cell discharge–charge profile. However, there are some noticeable mismatches between the simulated and experimental profiles in the finer details. The mismatch of the voltage profiles might be due to lack of a detailed treatment in the model of nucleation and growth of solid particles. Besides this, the model still reproduces essential features of a Li-S cell well, such as two discharging plateaus and the long experimental cycling capacity losses and satisfies the latest experimentally derived mechanisms. Therefore, the proposed Li-S model provides a significant advancement compared to the state-of-the-art models but requires further detail to be added in future work to capture all the mechanistic aspects. However, this will also require more unknown parameters. Future experimental work is needed to help validate some of the many kinetic and thermodynamic parameters required.

In order to simulate the species distribution under the same resting states as the experiments, we chose the specific simulation voltages ( $V_{rest}^*$ ) to keep the simulation DOD levels close to the experimental DOD\* levels. Due to differences in the voltage profiles between simulation and experiment, it was not possible to match DOD\* and  $V_{rest}^*$  in the simulation and thus intermediate values were chosen to match characteristic

points in the discharge curve (Figure 1d). The detailed experimental and simulation values are shown in Table 2.

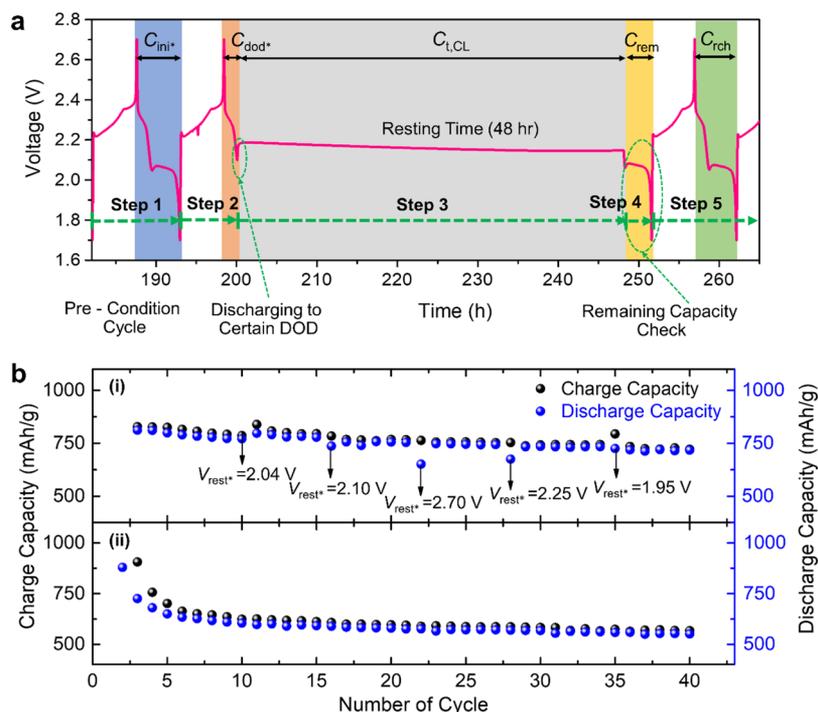
**Table 2. DOD Chosen for Self-Discharge Measurements<sup>a</sup>**

experiment		simulation	
DOD* (%)	$V_{rest}^*$ (V)	DOD (%)	$V_{rest}$ (V)
0	2.70	0	2.65
22	2.25	16	2.20
30	2.10	25	2.10
81	2.04	74	1.95
94	1.95	98	1.90

<sup>a</sup>DOD\* and  $V_{rest}^*$  means the experimental results; DOD and  $V_{rest}$  come from the simulation data.

The localized current density of five separate cathodic reactions are shown in Figure 1e. Reaction C1 occurs first and is followed by the conversion from longer PSs to shorter PSs. As shown in Figure 1d, there are four distinct sections on discharging voltage profile, labeled as S1–S4. In region S1, the discharge profile is dominated by Reaction C1, corresponding to the reduction of  $S_8$ . Region S2 involves Reaction C2 and C3 representing further reduction of  $S_8$  to  $S_6^{2-}$  and  $S_4^{2-}$ . Region S1 and S2 are related to the dissolution of PSs and it delivers 1/4 of the theoretical capacity ( $418 \text{ mA g}^{-1}$ ) due to 1/2 electron transfer per sulfur atom. Reaction C4 and C5 control discharging in S3 and S4 regions and contribute to the precipitation reaction of the solid phase reaction. The concentration variations further uncover the evolution of different PSs. Figure 1f,g shows the simulated concentration variations of PS during discharge–charge cycles under logarithmic scales and linear scales, respectively. The logarithmic scale more clearly displays the detailed concentration variations during the charge/discharge, while the linear scale gives us an intuitive idea of the concentration distribution of ionic species. Figures S6 and S7 further confirm the formation of PSs during one discharge–charge cycle and the spatial concentration distributions of  $Li_2S_2(s)$ ,  $Li_2S(s)$ , and  $S_8(s)$  through the simulation domain.

**3.2. Capacity Loss.** Figure 2a illustrates the procedure used to quantify CL as detailed above in Section 2.3. The plot of specific capacity as a function of cycle number exhibited by the a-graphene/S cathode at 0.1 C rested for 48 h at different DOD\* levels is shown in Figure 2b. It exhibits an initial discharge capacity of  $\sim 811 \text{ mAh/g}$ . As typical for Li-S batteries, the capacity decays more rapidly over the initial cycles. However, the capacity decay stabilized afterward and both the samples (Figure 2b (i) and (ii)) with and without self-discharge shows a similar average capacity decay of  $\approx 0.3\%$  calculated over the last 10 cycles. However, the drop-in discharge capacity is different at different DOD\* levels (as shown in Figure S8). When the cell was held for self-discharge during the eighth cycle (DOD\*  $\approx 81\%$  at 2.04 V), the capacity drops noticeably; however, this loss is recovered during the ninth cycle and  $C_{t,CL} \approx C_{rev,CL}$ . Similarly, resting the cell at  $\approx 30\%$  and  $\approx 0\%$  DOD\* causes an irreversible drop of the discharge capacity (values of the capacity drop are given in Table S5). Resting at  $\approx 22\%$  and  $\approx 90\%$  DOD\* results in negligible loss of  $C_{ir,CL}$ . As shown in Figure S9, the sequence (and thus cycle number) of these self-discharge measurements for one cell had little to no effect on the results.  $C_{rev,CL}$  is close to zero after the higher voltage plateau because the diffusion



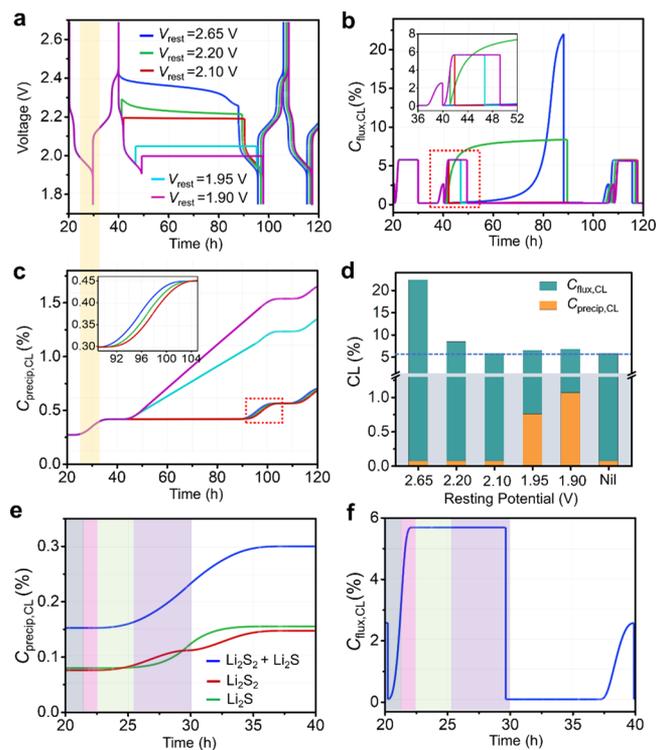
**Figure 2.** (a) Systematic protocol for self-discharge measurement (b) Variation of specific capacity as a function of cycle number (i) over different self-discharge periods of 48 h at certain voltages and (ii) without self-discharge periods.

and reaction kinetics at the anode are very slow for the lower order PS (in the simulation). The  $C_{ir,CL}$  is due to the precipitation, and this is shown to be irreversible by the monotonic increase in the precipitation of  $Li_2S_2$  and  $Li_2S$ .

The full capacity of the Li-S battery was estimated by complete discharge of the battery immediately after fully charging at  $C/10$ . However, as self-discharge is taking place, the obtained capacity is less than the total expected capacity.

Figure 3a depicts the simulated voltage profiles during rest and over the simulated charge and discharge carried out before and after the resting to mimic the experimental process. For example, as shown in Figure 3b,  $C_{flux,CL}$  which accounts for these shuttling species, is 22.3% when resting at 2.65 V. This shuttle phenomenon leads to high rates of self-discharge, so the cell voltage decreases quickly during idling. However, the CL is reversible at these cell voltages, so this form of self-discharge does not cause irreparable battery degradation. On the other hand, resting the cell at lower voltages is problematic because the shorter chain PSs are the dominant species in the cell at these states of charge ( $C_{precip,CL}$ , Figure 3c) and these precipitate to form  $Li_2S_2$  and  $Li_2S$  in the electrolyte and at the anode side. Ex-situ XRD (Figure S10) was carried out that provided some support for the formation of  $Li_2S_2$  on the Li anode. The potentially amorphous nature and low concentration make  $Li_2S_2$  and  $Li_2S$  difficult to observe experimentally. Figure 3d shows the predicted values of  $C_{flux,CL}$  and  $C_{precip,CL}$ . When resting the Li-S battery at 2.1 V, both reversible and irreversible CL is minimized, thus this is the suggested resting potential for Li-S batteries.

The degradation model contains the accumulation of precipitates and evolution of self-discharge. The last column in Figure 3d is the variation of  $C_{flux,CL}$  and  $C_{precip,CL}$  during one continuous charge/discharge cycle without resting the cell, which are 5.71 and 0.075%, respectively. The CL resulting from self-discharge due to the shuttle flux ( $C_{flux,CL}$ ) during one



**Figure 3.** Simulated (a) voltage profiles, (b) self-discharge CL ( $C_{flux,CL}$ ) profiles, and (c) precipitation CL ( $C_{precip,CL}$ ) profiles during cycling and resting. The legends in (b) and (c) are as the same as in (a). The yellow color bar highlights the discharge–charge cycle at the lower voltage plateau. (d) CL profiles during different resting potentials. Nil: CL during one discharge–charge cycle. (e) Precipitation CL profiles and (f) self-discharge CL profiles during one charge/discharge cycle. The color map in (e) and (f) is the same as Figure 1d–g.

cycle is significantly larger than the irreversible precipitation CL ( $C_{\text{precip, CL}}$ ). The detailed evolution of these two CL is depicted in Figure 3e,f.  $C_{\text{flux, CL}}$  is fast at the higher voltage plateau, while  $C_{\text{precip, CL}}$  keeps increasing at the lower voltage plateau during a charge/discharge cycle.

Figure 4 is the comparison of experimentally observed CL due to self-discharge and the simulated behavior during resting.

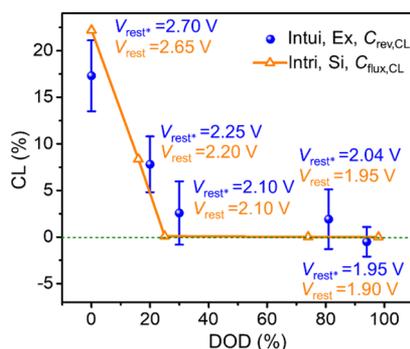


Figure 4. Comparison of CL between the simulation and experimental data.

The experimental data is calculated using coulomb counting, while the modeled result used the intrinsic approach. Error bars for  $C_{\text{rev, CL}}$  represent the standard deviation in reversible capacity loss of four different self-discharge tests. An inverse relation between DOD and self-discharge can be observed (with increasing the DOD the self-discharge is decreasing). This qualitative trend has also been reported by the experimental work of Knap et al. who looked at the self-discharge of Li-S pouch cells.<sup>26</sup>  $C_{\text{flux, CL}}$  is the total self-discharge CL and related to the shuttle flux and reduction reactivity of  $S_{8(1)}$ ,  $S_8^{2-}$ ,  $S_6^{2-}$ ,  $S_4^{2-}$ ,  $S_2^{2-}$ , and  $S^{2-}$  species at the anode. The values of  $C_{\text{flux, CL}}$  used in Figure 4 were reduced by 5%, meaning CL due to self-discharge during the rest period. The self-discharge flux during one discharge–charge cycle is 5%, Nil case in Figure 3d. At the higher DOD, the shorter PSs, especially  $S_2^{2-}$  and  $S^{2-}$ , were the predominant species in the cell. The low-chain PSs lead to precipitation, which cannot be recovered during the following cycles.<sup>49</sup>

#### 4. CONCLUSIONS

In this work, a 1D Li-S battery model was presented to investigate reversible and irreversible capacity losses for long periods of cycling and especially during resting over a large voltage range. An extensive set of experiments and sensitivity analysis was conducted to validate the model parameters. The study provides insights into a key relationship among the rate of self-discharge, polysulfides shuttling, and the resting voltages. Based on the simulation data, an intrinsic definition of self-discharge capacity loss is proposed, which is more accurate than the intuitive definition typically used based on coulomb counting. It uncovers that resting the cell at the higher voltage plateau suffers rapid self-discharge losses due to fast reduction of longer-chain PS at the anode, while resting at the lower voltage plateau results in precipitate formation. Our model suggests Li-S batteries should be better held at around 2.10 V where  $S_4^{2-}$  is the predominate species. Noticeably, the model suggests that the focus to avoid self-discharge should be on suppressing the reduction of PSs on the anode instead of controlling the shuttling in the electrolyte during the rest state.

With a firmer grasp of the key parameters required to accurately model long-term cycling, the study provides a useful basis for further engineering of these parameters. The model can be applied to other phenomena in future studies and with other sizes and types of cells.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c00235>.

Details model descriptions including the procedure of parameters fittings; supporting tables of stoichiometries for each species, transport properties and reference concentrations, precipitation parameters, other constant parameters, and reversible and irreversible capacity losses calculated using the eqs 11–14; supporting figures of the sensitivity analyses of the formal potential, exchange current densities, reference concentration, precipitation reaction rates, and chemical overpotentials; supporting figures of simulated concentration variations of PSs during one discharge–charge cycle and spatial concentration distributions of  $Li_2S_2(s)$  and  $Li_2S(s)$ ; experimental voltage profiles of the interrupted discharge plot at various resting voltages and the next immediate charge, variation of specific capacity as a function of cycle number over different self-discharge periods for different cycles; and XRD patterns of various battery cell components (PDF)

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## Notes

The authors declare no competing financial interest.

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