Mathematical modeling of the charging process of Li-S batteries by incorporating the size-dependent Li$_2$S dissolution

C. Xiong, T.S. Zhao*, Y.X. Ren, H.R. Jiang, X.L. Zhou

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

**A R T I C L E   I N F O**

Article history:
Received 3 May 2018
Received in revised form 22 November 2018
Accepted 23 November 2018
Available online 24 November 2018

Keywords:
Lithium-sulfur battery
Mathematical model
Dissolution kinetics
Size effect
Redox mediation

**A B S T R A C T**

During the discharge process of lithium-sulfur batteries, the nucleation and growth of Li$_2$S precipitates result in a non-uniform Li$_2$S particle size distribution, significantly affecting the charging process. However, a uniform Li$_2$S distribution at the initial state of the charging process of the batteries is assumed in the models reported in the literature, leading to an unrealistic simulation of the charging process. To address this issue, we propose a one-dimensional transient mathematical model, which incorporates the size-dependent Li$_2$S dissolution and redox mediation reaction between dissolved polysulfides and Li$_2$S particles into the charging process. Simulation results show that the dissolution rate of large Li$_2$S particles is suppressed at a lower potential due to the small specific surface area, while the smaller Li$_2$S particles are electrochemically oxidized into dissolved polysulfides first, which further act as the redox mediators to promote the oxidation of larger Li$_2$S particles. Capturing these effects enables an excellent agreement between the predicted and measured charging voltage profiles. Moreover, the effects of particle sizes and redox mediation reaction rates are studied. It is revealed that the optimal amount of smaller-sized Li$_2$S particles and suitable redox mediation reaction rate allow for a lower charging over-potential. Furthermore, it is shown that the effect of redox mediation rates on the dissolution of Li$_2$S large particles exerts a significant influence on the charging process.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

In recent decades, the exhaustion of fossil fuel has gained considerable attentions from the society and triggered unceasing research focus for developing electric vehicles (EV) and sustainable energy storage [1–3]. However, because of the limited specific energy density (~200 Wh kg$^{-1}$), lithium-ion batteries meet the bottleneck for the further development of EV and energy storage systems [4–7]. On the contrary, the rechargeable lithium-sulfur (Li-S) battery with a lithium metal anode and sulfur conversion cathode stands out as an excellent choice due to the high theoretical energy density (~2600 Wh kg$^{-1}$) and the earth-abundance of sulfur [8–10].

However, due to the multiple-phase conversion reactions in the cathode, the development of Li-S batteries is currently hindered by several serious issues, including polysulfide shuttle effect, sluggish Li$_2$S precipitation, and dissolution [11–13]. In particular, the sluggish dissolution of Li$_2$S during charging, which is mainly caused by its intrinsic electronically insulating property, greatly increases the charging over-potential and decreases the utilization of active materials [14–16]. It has been disclosed that the micro Li$_2$S particles with Li metal anode were difficult to be electro-oxidized completely even with much higher over-potential [17]. To solve this issue, two approaches have been proposed to decrease the high charging over-potential. One is to lower the over-potential by reducing the Li$_2$S particle size, such as adopting nano-sized Li$_2$S particles proposed by Sun et al. [18]. However, this approach is very expensive and hard to be scale-up. The other solution is to use a cost-effective redox mediator to lower the over-potential via facilitating the dissolution of large particles with a fast chemical reaction [19–21]. Many redox mediators have been investigated as additives, such as lithium iodine, decamethyferrocene and ferrocene [20]. Recently, Peng et al. found the self-healing of polysulfides on the dissolution of heterogeneous precipitated Li$_2$S in conventional Li-S batteries by playing a redox mediator role [22]. Gasteiger’s group also identified the redox mediation function of polysulfide intermediates during the charging process of Li/Li$_2$S batteries [23]. All of the results indicated that the redox mediation of polysulfides significantly affected the dissolution of large Li$_2$S...
particles during the charging process in lithium-sulfur batteries and activated the insulating Li$_2$S by dragging it into the electrolyte.

Although experimental characterizations are able to qualitatively speculate the mechanisms behind the battery engineering, they cannot quantitatively describe what happens in the practical battery system. As an effective method, theoretical modeling is capable of studying this process by providing insights into the mass transport and electrochemical/chemical reactions. Based on the previous simulations investigating the Li-S batteries' discharge process, Marinescu et al. proposed a zero-dimensional model to study the charge/discharge process [24]. In their model, they described the Li$_2$S decomposition process using a dissolution-oxidation mechanism instead of the widely adopted triple-phase (electrolyte/conductive substrate/Li$_2$S particles) oxidation, and they also ignored the impacts of mass transfer, polysulfides' redox mediation and particle size [25]. After that, Yoo et al. considered the existence of Li$_2$S$_2$ in their model, with which a better agreement with experiment was found compared with that without Li$_2$S$_2$ [26]. However, the specific influence of particle sizes and redox mediation on the charging process has been overlooked in their works.

Thus, to gain insight into the charging mechanism, in this work, we proposed a multi-scale one-dimensional model by incorporating the rate-dependent Li$_2$S dissolution and redox mediation phenomena. As demonstrated in Fig. 1, small particles and large particles are assumed to be evenly distributed on the conductive substrate after discharge as the initial situation for charging process. Because of the larger specific surface area, the dissolution rate of small particles is faster than large ones. Therefore, the small particles will be oxidized firstly by electrochemical reactions with minor oxidation of large particles, and the formed intermediates will act as the redox mediators to promote the large particles dissolution as illustrated in Fig. 2(a). In addition, mass transport and electrochemical reactions are combined into this model to quantitatively describe the whole system in detail, which is outlined below.

2. Methodology

Based on the discharge situation, we simply assume the bimodal particle sizes considering the coexistence of small particles and large particles to investigate the polysulfides redox mediation effect on large particles in this model [13,27]. During the charging process, we will track temporal evolution of the particle sizes and ions concentration incorporating the mass transport and multiple-step electrochemical and chemical reactions. Specifically, the kinetics of redox mediation chemical reaction for Li$_2$S large particles oxidation is explored to understand the charging mechanisms. After that, different volume ratios and various particle size combinations between small and large particles are respectively adopted to model the size-dependent Li$_2$S particles dissolution.

2.1. Computational model

As illustrated in Fig. 1, the model is established based on the configuration of conventional Li-S batteries, with lithium metal as the anode, sulfur/carbon composite as the cathode (90 μm) and porous polymer membrane as the separator (25 μm). All of the components are immersed into the DOL (1,3-dioxolane)/DME (1,2-dimethoxyethane) (1:1) electrolyte with low dielectric constant. During the charging process, Li$_2$S and other polysulfides are electro-oxidized on the positive side, Li$^+$ ions are electrodeposited on the lithium metal surface and the electrons transfer from cathode to anode to finish the whole charging process. For simplicity, some assumptions are made for better describing the systems and clarifying the main factors in the theoretical modeling work, which are detailed as below:

(i) All of the precipitated Li$_2$S particles, which are assumed to have hemispherical shapes [28], are distributed uniformly on the conductive substrate;
(ii) Statistical average will be done for the Li$_2$S size evolution after each computation steps;
(iii) Redox mediation reactions only occur on the large particles' surface [22];
(iv) The electrochemical oxidation of Li$_2$S happens on the triple phase boundary, and the triple phase boundary is simplified as the ring area of Li$_2$S particles as illustrated in Fig. 2(b) [22];
(v) Li$_2$S$_6$ is considered as the mixture of Li$_2$S$_4$ and Li$_2$S$_8$, and Li$_2$S$_2$ is not considered [29].

2.1.1. Electrochemical reactions

As the reversible reactions between the charging and discharge processes, the elementary electrochemical reactions have been
explored extensively [30], which are listed as below in equations (1)–(3). In addition, sulfur precipitation reaction and redox mediation reaction are described in equations (4) and (5), respectively [27,31]. At the positive electrode, the oxidation starts from the release of Li$^+$ on the small particles’ triple phase boundary to form Li$_2$S$_4$ firstly. Then, part of the formed lithium polysulfides Li$_2$S$_8$ from the electro-oxidation of Li$_2$S$_4$ without considering the formation of Li$_2$S$_6$ [24] transport to the surrounding of large particles’ surface, and react with large particles to form dissolved Li$_2$S$_4$ as demonstrated in Fig. 2(a). In this model, we assume that only Li$_2$S$_8$ is able to react with Li$_2$S particles [14]. The other part of Li$_2$S$_8$ will be electro-oxidized into saturation sulfur S$_8$, which will precipitate on the uncovered carbon surface. The chemically formed Li$_2$S$_4$ further participates in the redox mediation cycle to accelerate the large particles dissolution until the depletion of active materials occurs.

Cathode: \[
\frac{4}{3} \text{Li}_2\text{S} \rightarrow \text{2Li}^+ + 2e^- + \frac{1}{3} \text{Li}_2\text{S}_4 \quad (1)
\]

\[2\text{Li}_2\text{S}_4 \rightarrow \text{2Li}^+ + 2e^- + \text{Li}_2\text{S}_8 \quad (2)
\]

\[\text{Li}_2\text{S}_8 \rightarrow \text{2Li}^+ + 2e^- + \text{S}_8(\text{gas}) \quad (3)
\]

\[\text{S}_8(\text{gas}) \rightarrow \text{S}_8(\text{s}) \quad (4)
\]

\[\text{Li}_2\text{S}_8 + \frac{4}{3} \text{Li}_2\text{S}_4(\text{p}) \rightarrow \frac{7}{3} \text{Li}_2\text{S}_4 \quad (5)
\]

Anode: \[\text{Li}^+ + e^- \rightarrow \text{Li} \ (E_a = 0V) \quad (6)
\]

In this model, the electrochemical reaction rates in the positive electrode are expressed by the local current density according to the Butler-Volmer equation [32]:

\[
j_j = j_j^{\text{lim}} \left\{ k_j \prod_i \left( \frac{c_i}{c_{i,\text{ref}}} \right)^{\gamma_i} \exp\left( \frac{\alpha_{ij}F}{RT} \eta_j \right) 
- k_{j} \prod_i \left( \frac{c_i}{c_{i,\text{ref}}} \right)^{\gamma_i} \exp\left( - \frac{\alpha_{ij}F}{RT} \eta_j \right) \right\} \quad (7)
\]

where $c_i$ is the concentration of species $i$, $c_{i,\text{ref}}$ is the reference concentration of species $i$, $\gamma_i$ is the activity coefficient of species $i$, which is defaulted as 1 in our modeling, $\gamma_{ij}$ expresses the stoichiometric coefficient of species $i$ in reaction $j$, $k_j$ and $k_{j}$ are the forward rate constant and backward rate constant, respectively, and $\alpha_{ij}$ and $\alpha_{ij}$ are the anodic and cathodic charge transfer coefficient, respectively, $j^{\text{lim}}$ is the limiting current of reaction $j$, and $\eta_j$ is the electrostatic overpotential between electrolyte phase and electrode phase, which is equal to $\psi_{\text{electrode}} - \psi_{\text{electrolyte}} - E_{\text{eq}}$. For each electrochemical reactions, the electrolyte phase potential is spatially different because of the difference in ion mobility, but the electrode potential is almost the same around the whole cathode due to the high electronic conductivity provided by the carbon matrix. Moreover, the equilibrium potential can be described by the Nernst equation [32]:

\[E_{\text{eq}} = E_{\text{eq},j}^0 + \frac{R \bar{F}}{nF} \sum_j s_{ij} \ln \left( \frac{c_i}{c_{i,\text{ref}}} \right) \quad (8)
\]

where $n$ is the number of transferred electron in reaction $j$, $E_{\text{eq},j}^0$ is the thermodynamic equilibrium potential without the concentration difference.

And the cell voltage can be expressed as below:

\[U_{\text{cell}} = \psi_{\text{pos}} - \psi_{\text{neg}} \quad (9)
\]

where $\psi_{\text{pos}}$ is the positive electrode potential, and $\psi_{\text{neg}}$ is the negative electrode potential.

Under the galvanostatic condition, the overall input current is the sum of the local current density of all electrochemical reactions occurring on the positive side:

\[I_{\text{total}} = \sum_j \frac{A_j}{V} I_j dV \quad (10)
\]

where $A_j$ is the active surface area of the electrochemical reaction $j$, $j$ refers to the electrochemical reaction, as shown from equations (1)–(3), and $V$ is the positive electrode volume. As shown in Fig. 1(b), the value of $A_j$ is different from one reaction to another due to the different phases of active materials. For the solid Li$_2$S particles, the active surface areas of electrochemical reaction (1) for small particles and large particles are different, which refer to the triple phase boundary of particles, respectively, as shown in Fig. 2(b), where the triple phase area can be expressed below:

\[A_1 = A_i = 2\pi r_i N_i V_d \quad (11)
\]

\[A_2 = A_s = 2\pi r_s N_s V_d \quad (12)
\]
where \( r_l \) and \( r_s \) are the radii of the large particles and small particles, \( N_l \) and \( N_s \) refer to the number density of the large particles and small particles, and \( d \) is the lattice constant of Li\(_2\)S crystal as reported in the literature \([33,34]\).

However, for the soluble electrochemical active species, like Li\(_2\)S\(_4\) and Li\(_2\)S\(_8\), the dissociated polysulfide anions have high mobility and their electro-oxidation reactions will proceed on the uncovered conductive substrate surface. Therefore, the corresponding active surface areas for reaction (2) and (3) are the same as below:

\[
A_3 = A_4 = A_c - \pi r_l^2 N_l V - \pi r_s^2 N_s V
\]

where \( A_c \) is the total surface of conductive carbon substrate.

2.1.2. Redox mediation reactions

There are two chemical reactions involved in our model, one is the redox mediation reaction and the other is the sulfur precipitation. For the thermodynamically favored redox mediation reaction (5) \([17]\), we do not consider the electro-potential influence on the chemical rate and assume the chemical rate only associates with the large particles volume ratio and the dimensionless concentrations of Li\(_2\)S\(_4\) and Li\(_2\)S\(_8\). The chemical reaction rate can be expressed:

\[
v_6 = k_6 \varepsilon_{LiS} \left( \frac{c_{LiS_4}}{c_{LiS_4}^{ref}} \right)^{\frac{1}{2}} \left( \frac{c_{LiS_8}}{c_{LiS_8}^{ref}} \right)^{\frac{1}{2}}
\]

where \( k_6 \) is the redox mediation coefficient determined from the reaction rate, and \( \varepsilon_{LiS} \) is the large particles volume ratio in the whole cathode. And the active surface area for this chemical reaction is the large particles' surface area as below:

\[
A_6 = 2\pi r_l^2 N_l V
\]

2.1.3. Sulfur precipitation

Furthermore, the precipitation kinetics of sulfur is referred from the previous work \([31]\), and it is assumed to be related to the sulfur saturation limitation and the porosity of cathode. Therefore, the precipitation rate of equation (4) is able to be expressed as:

\[
v_5 = R_5 = k_5 \varepsilon \left( \prod_{i} c_i^{K_{sp,i}} \right) - k_{sp,5}
\]

where \( k_5 \) is the precipitation coefficient, \( \varepsilon \) is the porosity of the cathode, and \( K_{sp,5} \) is the sulfur solvation limitation \([31]\).

2.1.4. Species and charge transport

Although the shuttle effect is serious in the lithium-sulfur battery during the full cycles, many reported experimental methods have mitigated the issue effectively \([8]\). Therefore, we don’t consider the shuttle effect of long-chain polysulfides in our model. The migration and diffusion of soluble active materials, including S\(_4^2^-\), S\(_8^2^-\), and S\(_{8(\text{sol})}\) (solvated sulfur), are only considered in the cathode except for the lithium ions. Therefore, the transport of soluble species \( i \) is described by the typical conservation equation:

\[
\frac{\partial c_i}{\partial t} = -\nabla N_i + S_i
\]

where the term \( N_i \) refers to the average molar flux of species \( i \) across the whole cross-sectional area in this one-dimensional model, \( S_i \) is the source term of species \( i \), which results from the electrochemical and chemical reactions, and \( c_i \) is the molar concentration of the soluble species.

The fluxes of dissociated ions are mainly dominated by the mass diffusion and electromigration, the first part is associated with the diffusion coefficient and concentration gradient, and the latter is related to the electrolyte phase potential gradient as listed below:

\[
N_i = -D_i^{eff} \frac{\partial c_i}{\partial x} - \frac{F}{RT} \frac{c_i}{c_i^{ref}} \frac{\partial \phi_{electrolyte}}{\partial x}
\]

where \( z_i \) is the charge number of species \( i \). Different from the concentrated electrolyte theory, the effective diffusion coefficient obeys the Bruggeman correlation in dilute electrolyte regardless of the interactions between dissolved ions:

\[
D_i^{eff} = D_i^0 \varepsilon^{-\beta}
\]

where \( D_i^0 \) refers to the bulk diffusion coefficient, and \( \beta \) is the Bruggeman coefficient in the carbon skeleton. And the bulk diffusion coefficients of soluble species are clearly demonstrated in other articles by experimental methods.

The source term \( S_i \) stands for the generation or consumption rates of species \( i \), which can be obtained from the sum of the consumption/formation rates in each reaction:

\[
S_i = \sum_j S_{ij} v_j
\]

where \( v_j \) is standing for the rate of reaction \( j \). As for electro-oxidation reactions (1)–(3), the reaction rates are correlated with local current density:

\[
v_j = \frac{A_{ij}}{V_{Li} F}
\]

For the chemical reactions (5) and (4), the reaction rates are directly given in equations (14) and (16).

For the charge transport, the sum of the charge induced by the electrolyte and electronic solid is zero, and their values are determined by each reactions’ active surface areas and the local current source \( I \), obtained from the Butler-Volmer equation in the electrochemical reactions:

\[
\nabla_{electrode} = -\nabla_{electrolyte} = A_{ij}
\]

From Neman’s previous work, the current densities of electrode and electrolyte are related to the current density as below \([32]\):

\[
i_{electrolyte} = -\sigma_1^{eff} \nabla \phi_{electrolyte} - \frac{2RT \sigma_1^{eff}}{F} \left( 1 - t_s \right) \left( 1 + \frac{\partial \ln \sigma_1^{eff}}{\partial \ln \sigma_{Li^+}} \right) \ln \sigma_{Li^+}
\]

\[
i_{electrode} = -\sigma_{s,eff} \nabla \phi_{electrode}
\]

where \( \sigma_1^{eff} = \varepsilon^2 \sigma_{1,0}, \sigma_{s,eff} = (1 - \varepsilon)^2 \sigma_{s,0}, \) and \( \sigma_{1,0}, \sigma_{s,0} \) represent the ionic conductivity and electronic conductivity, respectively. \( I \) refers to liquid, \( s \) refers to solid.

2.1.5. Porosity and particle size evolution

For the immobile material Li\(_2\)S, the nano-dimensional particle size evolves with the time under the isotropic volume change assumption. Firstly, the evolution of the Li\(_2\)S particles’ volume
during the charging is given below:

\[ V_k(t) = V_{k,0} + \frac{\xi_{Li,S}}{N_k V} \int_0^t v_k(t) \, dt \]  

(25)

where \( k \) represents the small particle or large particle, \( V_{k,0} \) is the initial volume value, \( \xi_{Li,S} \) is the molar volume of Li\(_2\)S, and \( v_k(t) \) refers to the dissolution rate of particles by electrochemical and chemical reactions. Moreover, with the assumption that the particle size evolution of Li\(_2\)S is isotropic along the whole cathode, the particles size evolves following mass conservation:

\[ r_k(t) = \left( \frac{3}{2\pi N_k V} V_k(t) \right)^{\frac{1}{3}} \]  

(26)

where \( N_k \) refers to the number density of particles, and subscript \( k \) represents large particles and small particles.

### 2.1.6. Boundary conditions

The electric ground condition is employed on the lithium metal and separator interface (point 1), where Li\(^+\) ions are electro-reduced into lithium:

\[ \frac{\partial C_{Li^+}}{\partial \xi} = -(1 + t_i) \frac{\partial \text{app}}{\partial F} \]  

(27)

where \( t_i \) is the transference number of Li\(^+\).

For the cathode/separator interface (point 2), \( l_{\text{electrode}} = 0 \) and \( l_{\text{electrolyte}} = \text{app} \). The closer to the current collector, the larger of electric current. And at the interface of current collector and cathode, \( l_{\text{electrode}} = \text{app} \) and \( l_{\text{electrolyte}} = 0 \).

All soluble active species are localized in the positive electrode except the lithium ion and no-flux boundary condition will be applied on the cathode/separator interface for soluble sulfur materials:

\[ \vec{N}_j = 0 \]  

(28)

### 2.1.7. Computational details

To better validate the model with experimental results, the kinetics and thermodynamic parameters of electrochemical/chemical reactions are adjusted. All the conservation equations and the boundary conditions described above are iteratively solved through finite element method, and all the parameters are provided in later Table 1. In addition to the micron domain for describing the mass transfer and electrochemical/chemical reactions, an extra nanometer dimension is added into the cathode domain to depict the size evolution during Li\(_2\)S dissolution. In our model, there are 101 domain elements in the whole system, the length of each element is about 1.14 \( \mu m \), which is microscopically large for describing charging process, and the relative error tolerance is set to 1.0 \( \times \) 10\(^{-7} \), the calculation time step is 0.1s for ensuring the computational accuracy. All the governing equations were solved numerically using COMSOL Multiphysics.

### 3. Results and discussion

During the charging process, the discharge product Li\(_2\)S will be electro-oxidized into sulfur eventually, and the intermediated product polysulfides will accelerate the large Li\(_2\)S particles dissolution via the redox mediation reactions. Therefore, a systematic study of size-dependent effect and redox mediation rate is presented in this section. Firstly, we present experimentally validated simulation results for galvanostatic charging process at different rates, as demonstrated in Fig. 3, where the particle size, reaction kinetics, and thermodynamic parameters are fitted for the different charging current densities, and the detailed experimental processes are described in the Supporting information. Unlike the charging process of the lithium-oxygen battery, the lithium-sulfur battery has minimal size-dependent plateau because of the redox mediation reactions [35,36]. Although the experimental results have smoother charging voltage curves, which may result from the much wider size distribution of Li\(_2\)S particles and the specific material properties (e.g., the transport coefficients), the complex experiment situation can be simplified into bimodal size simulation to only consider two main parameters: particle size and redox mediation reactions. In addition, the activation process at the beginning is attributed to the limited surface area for electrochemical reactions, and we find that if the particle size is large, the spiky at the beginning of the charging process will appear. However, the charge transfer through Li\(_2\)S and Li\(_2\)S\(_2\) is complex, which is complicated with nanoscale electron and polaron formation and transportation through the insulating layer [37]. Therefore, to obtain the completed matched spiky is difficult. Moreover, for different rate currents, the particle sizes are different, we validate the experimental results with the same particle sizes (200 nm & 400 nm).

Secondly, the particle size distribution is non-uniform after discharge. As reported by Ren et al. [28], the particle size distribution is between tens to hundreds of nanometers. Therefore, we choose 500 nm as the initial particle radii for the large particles and 50 nm for small particles respectively. Moreover, the volumes of the large and small particles are the same at first and the redox mediation coefficient \( k_0 \) is equal to the standard coefficient \( k_0 = 4 \times 10^{-3} \text{ mol m}^{-3} \text{s}^{-1} \). The simulated charging voltage profile and Li\(^+\) concentration evolution of this combination are presented in Fig. 4. As shown in Fig. 4, Li\(^+\) concentration evolution is associated with the dissolution of the Li\(_2\)S particles, and it reaches the highest concentration when small particles are entirely decomposed, which is also congruent with the polysulfides concentration evolution as shown in Fig. 5(c). With the charging proceeding, the Li\(^+\) ions are released from the small particles firstly leading to the increase of lithium ion concentration. After that, as the increase of over-potential, more and more polysulfides are electrochemically oxidized into sulfur, which can be reflected on the decreased lithium ion concentration. Moreover, because of the difference between electron transfer and ion conductivity, the Li\(^+\) ion concentration has different spatial values, where the Li\(^+\) ion concentration is much higher at the interface of the cathode and the current collector than the lithium metal surface, suggesting that the electro-oxidation of Li\(_2\)S near the current collector occurs firstly.

After that, the charging voltage profiles with different redox mediation rates of 50 nm/500 nm size combination are compared in Fig. 5(a), and the size evolutions with and without redox mediation are presented in Fig. 5(b). For the case without the redox mediation, there are two obvious voltage plateaus because of the much smaller specific surface area of large particles, leading to the much higher overpotential comparing with small particles. Moreover, as illustrated in Fig. 5(b), the small particles are electro-oxidized firstly with a slight decomposition of large particles, after the depletion of small particles, the electro-oxidation of large particles proceeds with much higher over-potential. However, with different redox mediation rates as demonstrated in Fig. 5(a), the high voltage plateau disappeared with the increase of redox mediation rates. After reaching the redox mediation rate \( k_0 \), the voltage profiles have no obvious difference, in contrast to the strong difference between small and large particles without redox...
Li2S8 will play the redox mediator role to accelerate the dissolution of small particles, more and more Li2S4 are electrochemically mediated reactions. For the charging process with standard redox mediation reaction and sulfur precipitation, the proportion of Li2S4 is higher than Li2S8. From the comparison between electrochemical dissolution and redox mediation dissolution of large particles in Fig. 5(d), only a small portion of large particles are dissolved by the electrochemical reaction, and almost large particles are decomposed by redox mediation, indicating the redox mediation plays a role in the dissolution of large particles.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbols</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium potential</td>
<td>( E^\circ_{i,j} ) (j = 1, 2, 3, 4)</td>
<td>{2.05, 2.05, 2.25, 2.30} V</td>
<td>[39]</td>
</tr>
<tr>
<td>Limiting currents</td>
<td>( I_j^{lim} ) [1, 2, 3, 4]</td>
<td>( 9.6845 \times 10^4 \text{A m}^{-2} )</td>
<td>[40]</td>
</tr>
<tr>
<td>( I_j^{lim} = n^*F/2j - 1, 2; I_j^{lim} = n^*F(j - 3, 4) )</td>
<td></td>
<td>( 1.9297 \times 10^4 \text{A m}^{-2} )</td>
<td></td>
</tr>
<tr>
<td>Charge transfer coefficient</td>
<td>( a_{ij} ) (j = 1, 2, 3, 4)</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Forward rate constant</td>
<td>( k_f(j = 1, 2, 3, 4) )</td>
<td>{2.5 \times 10^{-5}, 2.5 \times 10^{-3}, 2.56 \times 10^{-4}, 2.68 \times 10^{-5}} \text{mol m}^{-3}\text{s}^{-1}</td>
<td></td>
</tr>
<tr>
<td>Backward rate constant</td>
<td>( k_b(j = 1, 2, 3, 4) )</td>
<td>{2.45 \times 10^{-5}, 2.45 \times 10^{-3}, 3.48 \times 10^{-4}, 5.36 \times 10^{-5}} \text{mol m}^{-3}\text{s}^{-1}</td>
<td></td>
</tr>
<tr>
<td>Electric and dissolved species properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric conductivity</td>
<td>( \sigma )</td>
<td>1000 m\text{s}^{-1}</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficients of polysulfide anions</td>
<td>( D_{Li} ) (k = 8, 4)</td>
<td>{6 \times 10^{-11}, 1 \times 10^{-10}} m\text{^2}\space\text{s}^{-1}</td>
<td>[30]</td>
</tr>
<tr>
<td>Diffusion coefficient of Li(^{+})</td>
<td>( D_{Li^{+}} )</td>
<td>1000 m\text{s}^{-1}</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of sulfur S(_{8})</td>
<td>( D_{S_8} )</td>
<td>2 \times 10^{-10} m\text{^2}\space\text{s}^{-1}</td>
<td>[30]</td>
</tr>
<tr>
<td>Transference number of Li(^{+})</td>
<td>( t_+ )</td>
<td>0.2594</td>
<td></td>
</tr>
<tr>
<td>Derivative of natural logarithm of Li salt activity to Li(^{+}) concentration</td>
<td>( \delta \ln(n_{Li^{+}}) / \delta \ln(c_{Li^{+}}) )</td>
<td>-1.03</td>
<td></td>
</tr>
<tr>
<td>Reference concentration of Li(^{+}) ion</td>
<td>( c_{Li^{+}}^{\infty} )</td>
<td>1007.64 \text{mol m}^{-3}</td>
<td></td>
</tr>
<tr>
<td>Lattice constant</td>
<td>( d )</td>
<td>0.572 nm</td>
<td></td>
</tr>
<tr>
<td>Electrode properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td>( A )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity of the Naion®/Celgard 2500 separator</td>
<td>( \epsilon_{sep} )</td>
<td>2.8 \times 10^6 m\text{^2}\space\text{m}^{-3}</td>
<td></td>
</tr>
<tr>
<td>Volume fraction of carbon in cathode</td>
<td>( \varepsilon_{C,C} )</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Sulfur mass density</td>
<td>( \rho_{C} )</td>
<td>2070 kg m\text{^-3}</td>
<td></td>
</tr>
<tr>
<td>LiS molar volume</td>
<td>( \rho_{LiS} )</td>
<td>2.768 \times 10^{-3} m\text{^{3}} \text{mol}^{-1}</td>
<td></td>
</tr>
<tr>
<td>LiS mass density</td>
<td>( \rho_{LiS} )</td>
<td>1660 kg m\text{^-3}</td>
<td></td>
</tr>
<tr>
<td>Chemical reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur solubility</td>
<td>( K_{sp,S} )</td>
<td>1 \times 10^{-4} \text{mol m}^{-3}</td>
<td>[24]</td>
</tr>
<tr>
<td>Precipitation rate</td>
<td>( k_p )</td>
<td>40 s(^{-1})</td>
<td>[24]</td>
</tr>
<tr>
<td>Redox mediation rate</td>
<td>( k_r )</td>
<td></td>
<td>Assumed</td>
</tr>
<tr>
<td>Standard redox mediation rate</td>
<td>( k_0 )</td>
<td>4 \times 10^{-3} \text{mol m}^{-3}s(^{-1})</td>
<td>Assumed</td>
</tr>
</tbody>
</table>

Fig. 3. Comparison between simulated cell voltage curves and experimental results at 1C (1.875 Am \text{^-2}), 1.5C, and 2C.

Fig. 4. Simulated charging curve and temporal evolution of Li\(^{+}\) ion concentration at 1C (500 nm and 50 nm for Li2S\(_{4}\) and Li2S\(_{8}\) respectively), and the mass loading is about 1 mg cm\text{^-2} based on the sulfur.

\text{transformed into Li2S\(_{4}\) with the increased cell voltage and Li2S\(_{8}\) are electro-oxidized into solvated sulfur S\(_{8}^\text{(R)}\) [23]. Because of the redox mediation reaction and sulfur precipitation, the proportion of Li2S\(_{4}\) is higher than Li2S\(_{8}\). From the comparison between electrochemical dissolution and redox mediation dissolution of large particles in Fig. 5(d), only a small portion of large particles are dissolved by the electrochemical reaction, and almost large particles are decomposed by redox mediation, indicating the redox mediation plays a role in the dissolution of large particles.}
much more important role in the decomposition of large particles with certain redox mediation reaction rate.

It is known that the portion of large particles will increase under the small discharge current densities [13]. To better understand the effect of volume ratio on the charging process, the impact of volume ratio of large particles to small particles is studied and the simulated results are provided in Fig. 6. As shown in Fig. 6(a), in the presence of the redox mediation (kₐ), no obvious voltage profile change is observed among different volume ratios; whereas the charge curves vary significantly against the volume ratio without redox mediator, as depicted in Fig. 6(b). Specifically, the more volume fraction of large particles, the longer duration of high voltage plateau is. As shown in Fig. 6, the volume ratio effect on the charging profile is negligible with fast redox mediation rate, which is in contrast to lithium-oxygen batteries [38]. However, if the redox mediation reaction rate is slow, the volume ratio is supposed to affect the charging voltage greatly. Moreover, the volume ratios have seldom influence on the over-potential of small particles because of the negligible decrease of active surface area for reaction (2).

Finally, the particle size distributions are different under different discharge operations. With the small discharge current density, the large particle size will increase, and vice versa. Therefore, to comprehensively understand the particle size effect, we changed the large particles size for comparison under two situations: with redox mediation and without redox mediation. For the case without the redox mediation, a larger over-potential is detected with a larger particle size at a volume ratio of 1:1, which is attributed to the decreased active surface area, as shown in Fig. 7(b). However, for the situation with the standard redox mediation rate, the difference of over-potentials between large particles and small particles is negligible. Moreover, if the redox mediation rate is smaller than the standard redox mediation rate k₀, we can speculate that the difference of over-potential will become more obvious as the increase of large particles size.

Although no studies on the redox mediation rate have been reported, Peng et al. indicated that the redox mediation rate between polysulfides and Li₂S was not weak [22,27]. Therefore, it is important to incorporate the redox mediation reaction into the charging model. Furthermore, previous research works have reported various redox mediators for accelerating the Li₂S dissolution in the Li₂S-Li batteries, and the redox mediation reaction rates for those additives are different, so it is meaningful to compare different redox mediation rates in the charging model.

Fig. 5. (a) Simulated charging voltage curves with different redox mediation reaction rates (relative to standard redox mediation reaction rate k₀ = 4 × 10⁻¹⁴ mol m⁻³ s⁻¹); (b) simulated temporal evolution of different particle sizes with and without redox mediation reaction (50 nm for small particles rₛ, 500 nm for large particles rᵢ); (c) simulated temporal evolution of polysulfide anions relative concentration over the whole charging process with redox mediation reaction; (d) comparison between redox mediation reaction and electrochemical reaction on large particles dissolution (1C).
From the above results, the size effect and volume ratio have non-negligible impact on the charging profile without redox mediation or with slow redox mediation rates. It is well known that the particles of Li$_2$S in Li$_2$S-Li batteries are micro-sized, and the overpotential is extremely high with the red oxidation reactions of polysulfides, so our model is an indication that there should be more small particles, like nano-size Li$_2$S, and more efficient redox mediator additives, like I$_2$ [16,22].

Because the size distribution after discharge in the experiment is more complex than the bimodal size distribution adopted in our model, the charging voltage profiles in our model cannot meet the experimental results perfectly. In addition, it is demonstrated that the spiky at the beginning will appear if the particle size is larger than we discussed above, as shown in the Supporting information Fig. 1 with only 100 nm particles, but the spiky is not only related with the particle size, but also associated with the charge transfer through insulated Li$_2$S and Li$_2$S$_2$ layer, so there is a little error with the experimental result as we mentioned. However, the simplified model describes the phenomenon of size-dependent effect and redox mediation effect existing along the whole charging process first time. Moreover, this innovative multi-scale model incorporates these mechanisms into the traditional model considering mass transport and elementary reaction kinetics.

In this model, besides the stepwise electrochemical reactions from Li$_2$S to soluble polysulfides, and finally precipitated solid sulfur, it reproduces the impact of different sizes distribution and volume ratio with and without redox mediation reaction on charging process. The results in our model demonstrate that the charging process is different from the discharge process, where there are no obvious two plateaus because of the fast redox mediation reaction. Especially, the decomposition of large particles is mainly caused by the redox mediation reactions instead of the electro-oxidation reactions with certain redox mediation rate. Therefore, optimizing the size distribution and adding more useful redox mediation additives, like iodide/triiodide, instead of the intrinsic polysulfide redox mediator can be an effective approach to

**Fig. 6.** (a) Simulated charging curves of different volume ratios between small particles and large particles with standard redox mediation reaction rate ($k_0 = 4 \times 10^{-3} \text{ mol m}^{-3} \text{s}^{-1}$); (b) simulated charging curves of different volume fractions of large and small particles without redox mediator reaction.

**Fig. 7.** (a) Simulated charging curves of different size combinations of large particles and small particles with standard redox mediation rate ($k_0 = 4 \times 10^{-3} \text{ mol m}^{-3} \text{s}^{-1}$); (b) simulated charging curves of different size combinations of large and small particles without redox mediation reaction.
improve the utilization of active materials in the lithium-sulfur batteries and decrease the activation overpotential for Li-based batteries assembled with a Li$_2$S electrode. In the future, the insufficient initial situation comparing with the real case can be further developed to more comprehensively describe the charging process.

4. Conclusions

Overall, to understand the charging process of Li-S batteries through theoretical modeling is able to guide the experimental exploration. Controlling different parameters can be an approach to achieve better performance of battery engineering, and theoretical modeling provides the effective pathways to mimic the physico-chemical processes that occur in the lithium-sulfur battery system to better manage the polysulfides. We can further develop the full cycle model by considering the discharge process and shuttle effect into this model, where the size distribution can be extracted from the discharge process directly.

Acknowledgements

The work described in this paper was fully supported by a grant from the Research Grant Council of the Hong Kong Special Administrative Region, China (Project No. T23-601/17-R).

Nomenclature

\( A \)  
specific surface area, \( \text{m}^{-1} \)

\( c \)  
molar concentration, \( \text{mol} \cdot \text{m}^{-3} \)

\( D \)  
diffusion coefficient, \( \text{m}^2 \cdot \text{s}^{-1} \)

\( F \)  
Faraday constant, \( 96,485 \text{ C} \cdot \text{mol}^{-1} \)

\( R \)  
Gas constant, \( 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \)

\( n \)  
number of transferred electrons

\( N \)  
number density of Li$_2$S particles

\( r \)  
particle radius, \( \text{nm} \)

\( i \)  
current density, \( \text{A} \cdot \text{m}^{-2} \)

\( i' \)  
current source, \( \text{A} \cdot \text{m}^{-2} \)

Greek letters

\( \alpha \)  
charge transfer coefficient

\( \gamma \)  
activity coefficient

\( \varepsilon \)  
porosity or solid species fraction

\( \eta \)  
over-potential, \( \text{V} \)

\( \theta \)  
electrode surface coverage fraction

\( k \)  
reaction rate constant, \( \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \)

\( \sigma \)  
electronic conductivity and ionic conductivity, \( \text{S} \cdot \text{m}^{-1} \)

\( \rho \)  
density, \( \text{kg} \cdot \text{m}^{-3} \)

\( \phi \)  
electrolyte potential, \( \text{V} \)

\( \psi \)  
electrode potential, \( \text{V} \)

Subscripts

\( \text{app} \)  
carbon and cathode

\( \text{eq} \)  
equilibrium

\( \text{eff} \)  
effective

\( \text{i} \)  
species

\( \text{j} \)  
electrochemical reduction reactions and chemical reactions

\( \text{l} \)  
large particles

\( \text{ref} \)  
reference value

\( \text{s} \)  
small particles

\( \text{sep} \)  
separator

\( \text{0} \)  
initial

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2018.11.159.

References


