Modeling of lithium-sulfur batteries incorporating the effect of Li$_2$S precipitation

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HIGHLIGHTS

- A transient discharge model for Li-S batteries is developed.
- Rate-dependent precipitation is depicted by the nucleation and growth kinetics.
- The precipitated Li$_2$S particle growth is suppressed at a higher discharge rate.
- Strategies to improve the surface precipitation are discussed.

GRAPHICAL ABSTRACT
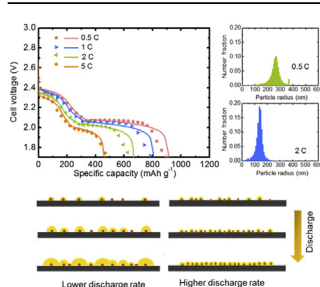
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ABSTRACT

In this work, we present a one-dimensional model for the discharge behavior of lithium-sulfur (Li-S) batteries. In addition to the consideration of multiple-step polysulfide dissolution and reductions, the surface nucleation and growth kinetics coupled with electrochemical reactions is particularly exploited for describing the Li$_2$S precipitation. Unlike previous models that overlook the rate-dependent precipitation phenomenon, our model reveals that discrete Li$_2$S particle growth becomes suppressed at higher rates, resulting in smaller Li$_2$S precipitates with a more uniform particle size distribution and a limited discharge capacity. Experimental discharge curves and discharge product observation adequately confirm our numerical results. It is further predicted that promoting the growth of Li$_2$S particles, including lowering the initial nucleation rate and providing a suitable amount of initial nucleation sites, can efficiently prolong the Li-S battery's discharge capacity.

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1. Introduction

Lithium-sulfur (Li-S) batteries are promising energy storage devices for next-generation electric vehicles and distributed grids owing to its high theoretical energy density (~2600 Wh kg^{-1}), natural abundance, and nontoxicity [1,2]. On the journey towards scaled-up applications, several challenges need to be addressed, including fast capacity degradation, incomplete sulfur utilization and low coulombic efficiency [3,4]. To address these challenges, one direction is to identify efficient electrode/electrolyte materials, which has undergone remarkable progress over the past few years [5,6]. The other emerging direction is to gain a better understanding of the battery's discharge characteristics, which further propels material research and battery engineering [7–11]. In consideration of the complex multiple-step phase transfer processes occurring in Li-S batteries, theoretical modeling in tandem with experimental investigations can be employed.

Currently, it is believed that the lithiation of sulfur involves both dissolution and precipitation during the discharge process of Li-S

batteries. Toward the higher voltage plateau where dissolution occurs, solid sulfur is initially reduced to a long-chain polysulfide anion (S_8^{2-}), which dissolves into the electrolyte and is subsequently reduced to lower order polysulfides (S_6^{2-} and S_4^{2-}) in the liquid phase [7,11]. Controlling the dissolution process is essential, because during discharge those dissolved polysulfides can be reduced onto the Li anode, leading to the active material loss and anode degradation (so called "shuttle effect"). Moreover, at the lower voltage plateau where precipitation occurs, S_4^{2-} is reduced to insoluble Li_2S, which precipitates from the electrolyte [11,12]. Intrinsically, the temporal and spatial distributions of dissolved polysulfides are found to have a direct impact on the subsequent precipitation process, which was confirmed by an in-operando optical imaging method [13]. In application, numerous strategies to effectively control polysulfide dissolution have been proposed to improve the battery's performance using strong polysulfide-binding cathode materials as well as ion selective membranes [14–18].

Beyond controlling the polysulfide dissolution, to obtain a high capacity in non-aqueous solvents, it is necessary to shed light on the precipitation process, as three quarters of the theoretical capacity comes from the precipitation of Li_2S from S_4^{2-}. However, this perspective is often overlooked. Using solid-state Li^+ ion conducting electrolyte as the separator to inhibit the shuttle effect, Lu et al. found that the capacity decreased considerably with an increase in the discharge current, whereby only the capacity at the lower voltage plateau diminished but that of the higher voltage plateau remained essentially constant [7,12]. Chiang et al. discovered that the precipitation of Li_2S on conductive substrates proceeded via nucleation, followed by a two-dimensional growth that occurred at the triple-phase boundaries among precipitate, substrate and electrolyte [19,20]. The precipitated Li_2S demonstrates a rate-dependent morphology, resulting in rate-dependent capacities, which shares similarities with the lithium peroxide formation in the cathode of non-aqueous Li–O_2 batteries [21]. In this regard, to gain insight into the rate-dependent precipitation phenomenon provide opportunities to improve the battery's performance.

Aside from experimental efforts, theoretical modeling serves to fill crucial roles in the exploration of these phenomena. Mikhaylik et al. developed the first lumped mechanistic model of Li-S batteries by taking account of the shuttle effect with an empirical shuttle constant [22]. A more comprehensive one-dimensional model has been proposed by Kumaresan et al., in which the multicomponent transport in dilute electrolyte and simplified precipitation kinetics are considered; however, the rate-dependent capacity has not been revealed [23]. More recently, limiting factors in Li-S batteries, including the shuttle effect, incomplete utilization of the active material and ionic conductivity limitation, have been intensively studied [8,24,25]. However, among the aforementioned studies, there is still a lack of explanation for the rate-dependent Li_2S precipitation phenomenon as observed in the experiment.

Motivated by this issue, we model the reaction and transport processes in Li-S batteries along a single direction, associated with a one-dimensional coupled domain to take account of the precipitation kinetics. The details of our model are outlined below as a combination of transport physics and chemical reactions. As the precipitation kinetics emerge as an essential limiting factor for the battery's practical capacity, the nucleation and growth of the final discharge product (Li_2S) is extensively considered. In addition, experimental investigation is conceived to validate the numerical results. Combined with the experimental findings, this model can depict a more realistic relationship between the current density and capacity.
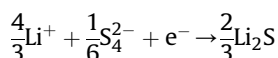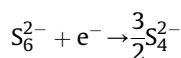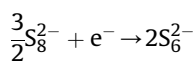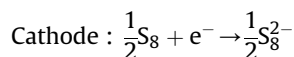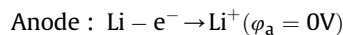
2. Methodology

In this section, we focus on presenting a realistic description of the Li-S battery's discharge behavior through a numerical model combined with experimental validations. First, we implement multiple-step electrochemical reactions including the dissolution and precipitation. Specifically, the kinetics of electrocrystallization from the nucleation and growth theory is exploited for an explanation of the rate-dependent precipitation phenomenon. Secondly, the electrode surface coverage induced by the accumulated precipitates is depicted via the Kolmogorov's phase transformation theory. Thirdly, multicomponent species transport is presented, along with boundary conditions and computational details. Moreover, to support the numerical results, we assembled Li-S batteries to test rate performance (0.1–5 C) and disassembled the batteries after discharge to characterize precipitates.

2.1. Computational model

As shown in Fig. 1a, a Li-S battery is composed of a lithium foil anode, a porous separator ($L_{sep} = 30 \ \mu m$), which insulates electron transfer and mitigates the polysulfide shuttle effect, and a sulfur/carbon cathode ($L_c = 90 \ \mu m$). Both separator and cathode are often saturated in the aprotic organic solvent with lithium salt additives. The liquid electrolyte systems for Li-S batteries is a mixture of DOL (1,3-dioxolane) and DME (1,2-dimethoxyethane) with low dielectric constants, which is widely applied in Li-S battery research [12]. For any theoretical models, the one proposed here is expected to work within a set of conditions, thereby the following general assumptions are made: (a) the battery system is operated under room temperature (298 K); (b) the sulfur content can be fully dissolved in the electrolyte, providing 100% sulfur accessibility; (c) long-chain polysulfides (Li_2S_x) with x = 8, 6 and 4 are dissolved and ionized in the electrolyte [7,26]; (d) Li_2S dissolution and comproportionation between S_4^{2-} and Li_2S to generate Li_2S_2 are neglected.

2.1.1. Electrochemical reactions

As mentioned, the typical Li-S battery discharge curves consist of two plateaus (Fig. 1b). During the first discharge, molecules of elemental cyclo-octasulfur sulfur (S_8) accept electrons, generating a chain of lithium polysulfides (Li_2S_x). Usually polysulfides with x = 8, 6 and 4 are generated at the high voltage plateau, and further polysulfide reduction takes place at a lower voltage plateau around 2.1 V [7]. Detailed electrochemical reactions occurring during discharge are as follows:

$$\text{Anode}: \ Li - e^- \rightarrow Li^+ \ (\varphi_a = 0V)$$

$$\text{Cathode}: \ \frac{1}{2}S_8 + e^- \rightarrow \frac{1}{2}S_8^{2-}$$

$$\frac{3}{2}S_8^{2-} + e^- \rightarrow 2S_6^{2-}$$

$$S_6^{2-} + e^- \rightarrow \frac{3}{2}S_4^{2-}$$

$$\frac{4}{3}Li^+ + \frac{1}{6}S_4^{2-} + e^- \rightarrow \frac{2}{3}Li_2S$$

Though the rate constant of the electrochemical reduction of S_8 might be obtained by the onset overpotentials at various discharge rates, the rate constants of the subsequent reactions need to be obtained via calibrating the model with measured discharge curves as conducted by Zhang et al. [8]. The model parameters and their