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Sensitivity analysis of a mathematical model of lithium–sulfur cells: Part II: Precipitation reaction kinetics and sulfur content

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HIGHLIGHTS

- The discharge behavior of Li–S cells in wide range of rate constants for precipitation reactions is studied.
- Dissolution of elemental sulfur and precipitation of produced polysulfides play an important role in capacity performance.
- Optimum sulfur content is obtained to maintain the maximum capacity performance.
- Formulating the precipitation reactions and electrochemical reactions is needed to be modified in future works.

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ABSTRACT

A sensitivity analysis of a mathematical model of a lithium–sulfur (Li–S) battery was performed, focusing on the precipitation rate constants and sulfur content, by investigating the response of the model to the variation of these parameters over a wide mathematical range. The necessity of rapid dissolution of elemental sulfur and rapid precipitation of reduced sulfur is discussed in detail. The sensitivity analysis suggests modifying the reduction reaction steps of sulfur can improve the predictions of the model of Li–S battery. Furthermore, an upper limit on the sulfur content of the cathode exists to ensure optimal performance. Although the model provides valuable knowledge concerning Li–S batteries, a modification to the assumed five-step reduction of sulfur combined with the consideration of the insulating nature of the active material is required to improve the model.

1. Introduction

Sulfur (S) one of the favorite active materials for Lithium (Li) batteries due to its high theoretical specific capacity, low cost, high availability, and non-toxic nature [1]. However, several serious problems hinder the commercialization of rechargeable Li–S batteries. For example, the low electronic conductivity of sulfur and polysulfides necessitates the addition of conductive materials to the cathode, and the dissolution of polysulfides leads to a shuttle mechanism that causes self-discharging of the cell [2,3]. Despite the complex and not fully understood behavior of sulfur [4–6], attempts have been made to simulate Li–S batteries to provide insight into their mechanism of operation [7,8].

Continuing the work of Part I [9], this paper presents a sensitivity analysis of the model presented by K. Kumaresan et al. [8] on precipitation constant rates. The model considers a five-step electrochemical reduction reaction of elemental sulfur and also includes the dissolution and precipitation reactions of sulfur and polysulfides across the cell. However, the authors introduced numerous parameters whose values must be determined through the appropriate experiments. In the absence of such experiments, a sensitivity analysis can shed light on the different aspects of the model on and clarify Li–S cell behavior. To study the physical and mathematical abilities and limits of the model, a wide mathematical range is assumed for the parameters.

The behavior of the model at various discharge current rates was previously studied [9], and the details of the voltage plateaus at each current rate were explained. Furthermore, a sensitivity analysis of the cathode conductivity was performed, demonstrating the existence of an essential threshold of conductivity for a working cell [9]. After discharge, the distribution of the precipitants is not uniform; the degree of this non-uniformity depends on the discharge current rates and cathode conductivity. In addition, the precipitants diffuse in the separator, thus causing a fading cycle life.

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This part of the sensitivity analysis focuses on the rate constants of precipitation and the sulfur content.

2. Model development and governing equations

The model is based on the proposed model by K. Kumaresan, Y. Mikhaylik, and R.E. White [8]. Fig. 1 presents a schematic of the Li–S cell and summarizes the governing equations and boundary conditions of the model. Appendix B describes the model, and Appendix A defines its parameters. The values proposed for the parameters are provided in Tables 1–4 in Appendix C.

The reactions in the cell include Li metal oxidization at the anode surface during discharge [8]:

$$\mathrm{Li} \rightleftharpoons \mathrm{Li}^{+} + \mathrm{e}^{-} \tag{1}$$

It is assumed that during discharge, the elemental sulfur, which is initially in the solid phase, dissolves in the electrolyte and then goes through the following electrochemical reactions [8]:

$$\frac{1}{2}\mathrm{S}_{8(\mathrm{l})} + \mathrm{e}^{-} \rightleftharpoons \frac{1}{2}\mathrm{S}_8^{2-} \tag{2}$$

$$\frac{3}{2}\mathrm{S}_8^{2-} + \mathrm{e}^{-} \rightleftharpoons 2\mathrm{S}_6^{2-} \tag{3}$$

$$\mathrm{S}_6^{2-} + \mathrm{e}^{-} \rightleftharpoons \frac{3}{2}\mathrm{S}_4^{2-} \tag{4}$$

$$\frac{1}{2}\mathrm{S}_4^{2-} + \mathrm{e}^{-} \rightleftharpoons \mathrm{S}_2^{2-} \tag{5}$$

$$\frac{1}{2}\mathrm{S}_2^{2-} + \mathrm{e}^{-} \rightleftharpoons 2\mathrm{S}^{2-} \tag{6}$$

The following precipitation/dissolution reactions are also present:

$$\mathrm{S}_{8(s)} \rightleftharpoons \mathrm{S}_{8(l)} \tag{7}$$

$$2\mathrm{Li}^{+} + \mathrm{S}_8^{2-} \rightleftharpoons \mathrm{Li}_2\mathrm{S}_{8(\mathrm{s})} \tag{8}$$

$$2\mathrm{Li}^{+} + \mathrm{S}_4^{2-} \rightleftharpoons \mathrm{Li}_2\mathrm{S}_{4(\mathrm{s})} \tag{9}$$

$$2\mathrm{Li}^{+} + \mathrm{S}_2^{2-} \rightleftharpoons \mathrm{Li}_2\mathrm{S}_{2(\mathrm{s})} \tag{10}$$

$$2\mathrm{Li}^{+} + \mathrm{S}^{2-} \rightleftharpoons \mathrm{Li}_2\mathrm{S}_{(\mathrm{s})} \tag{11}$$

The details of the model and its governing equations can be found either in Appendix B or ref. [8]. The current densities due to the electrochemical reactions are given by the Bulter–Volmer equation.

3. Results and discussion

A range of variations is assumed for each parameter. This range is not bounded by a range of physical values. The goal is to determine the behavior of the model system with respect to different situations and to find a range for the parameters in which the Li–S cells are feasible. However, the functionality of the model with respect to these parameters was found not to be linear. Instead, we must choose a parameter each time and investigate the changes in the model from variations in this parameter while keeping the other parameters constant.

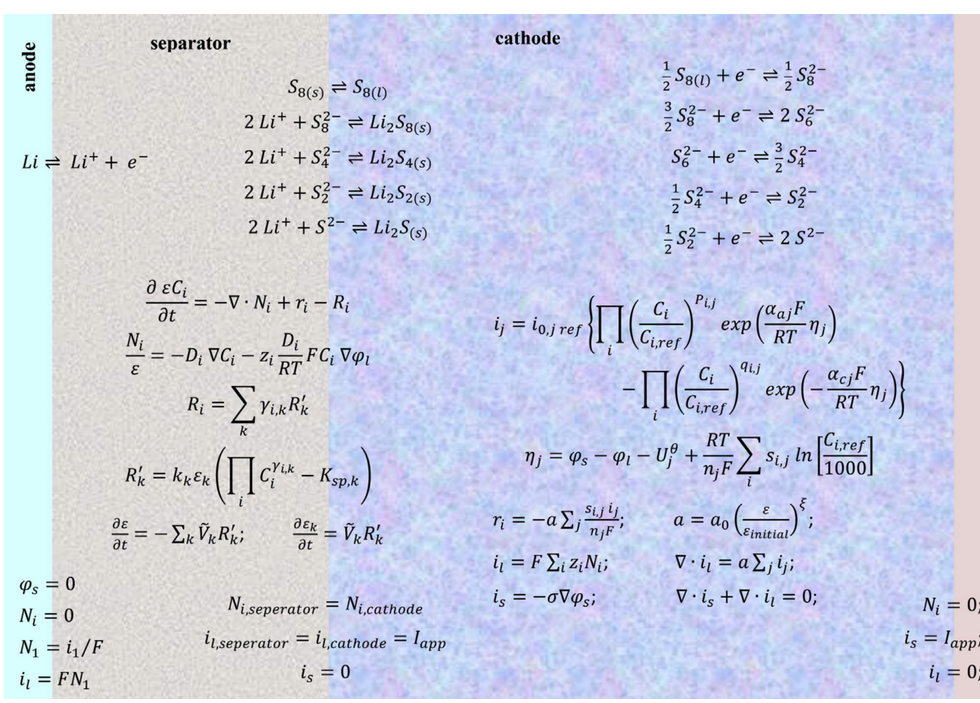

Fig. 1. Schematic of a Li–S cell and a summary of the governing equations and boundary conditions. Repeated from Ref. [9].