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Analysis of a Mathematical Model of Lithium-Sulfur Cells Part III: Electrochemical Reaction Kinetics, Transport Properties and Charging

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ABSTRACT

Sensitivity analysis of a mathematical model of a lithium-sulfur (Li-S) battery was performed by investigating the response of the model to variation of the exchange current densities, diffusion coefficients, and cathode thickness over a wide range; the results of the analysis were used to explain the some aspects of the behavior of the system which may be seen in experiments. In particular, among all the exchange current densities, the exchange current density of the elemental sulfur reduction has the most significant effect on the discharge capacity of the cell. The variation of the diffusion coefficients was also analyzed, providing information on the non-uniformity of precipitants in the cell after discharge. An optimum cathode thickness was presented to gain the highest capacity of the cell. Finally, the simulation of charging was studied, showing that the model needs a large solubility product of di-lithium sulfide to be able to simulate the charge process of a cell.

1. Introduction

Among the lithium-based batteries, lithium-sulfur (Li-S) batteries are of primary interest because of their high theoretical specific capacity, low cost, availability, and environmental friendliness [1]. Many experiments have been performed to assist in the development of a rechargeable Li-S battery, but there are several unresolved issues, such as the insulating nature of sulfur (and the consequent necessity of a conductive additive in the cathode) and the shuttle effect, which causes self-discharge [2,3]. Although the behavior of sulfur as the active material is complicated and remains unclear [4–6], some models have been proposed to simulate Li-S batteries [7,8].

This work is based on the model proposed by K. Kumaresan et al. [8], which includes a five-step chain of sulfur reduction and precipitation reactions. The authors used numerous parameters in the model, the values of which were mainly assumed. Determining the parameters experimentally is difficult due to the complexity of the system. Thus, a sensitivity analysis was performed on the model to clarify the different aspects of the model and better understand Li-S cells. A wide mathematical range was assumed for each parameter to clarify both the physical and mathematical abilities and the limits of the model.

The first part of the sensitivity analysis [9] investigated the response of the model to various discharge current rates to gain insight into the Li-S cell behavior and the various aspects of its discharge voltage plateau. Moreover, the effect of the cathode's electronic conductivity was studied, indicating that a conductivity threshold is required to functionalize the cell; increasing the conductivity further has almost no effect on battery performance [9]. A non-uniform distribution of the precipitants and of the diffusion to the separator is observed after discharge. The non-uniformity increases with an increasing discharge rate and varies according to the conductivity of the cathode.

In [10], the effect of the speed on the dissolution/precipitation of polysulfides on the model behavior was investigated. It was shown that, in particular, the ratio of the speed of the dissolution reaction of elemental sulfur to the speed of electrochemical reactions (controlled by applied discharge current) determines the shape of the voltage plateau. Sulfur content was also the subject of study, in an attempt to find its upper limit.

This part of the sensitivity analysis investigated the exchange current rates and diffusion coefficients. The effect of cathode thickness was also studied to determine an optimal value.

Following [8–10], the assumed reactions in the cell and governing equations are summarized in Tables 1 and 2. A schematic of the cell is presented in Fig. 1.

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Table 1
assumed reactions in the cell.

	Reaction	Anode	Separator	Cathode
Electrochemical reactions	(1) $Li \rightleftharpoons Li^{+} + e^{-}$	•		
	(2) $\frac{1}{2}S_{8(l)} + e^{-} \rightleftharpoons \frac{1}{2}S_8^{2-}$			•
	(3) $\frac{3}{2}S_{8(l)} + e^{-} \rightleftharpoons 2S_6^{2-}$			•
	(4) $S_6^{2-} + e^{-} \rightleftharpoons \frac{3}{2}S_4^{2-}$			•
	(5) $\frac{1}{2}S_4^{2-} + e^{-} \rightleftharpoons S_2^{2-}$			•
	(6) $\frac{1}{2}S_2^{2-} + e^{-} \rightleftharpoons 2S^{2-}$			•
Precipitation/dissolution	(7) $S_{8(s)} \rightleftharpoons S_{8(l)}$	•	•	•
	(8) $2Li^{+} + S_8^{2-} \rightleftharpoons Li_2S_{8(s)}$	•	•	•
	(9) $2Li^{+} + S_4^{2-} \rightleftharpoons Li_2S_{4(s)}$	•	•	•
	(10) $2Li^{+} + S_2^{2-} \rightleftharpoons Li_2S_{2(s)}$	•	•	•
	(11) $2Li^{+} + S^{2-} \rightleftharpoons Li_2S_{(s)}$	•	•	•

Our parameters are defined in Appendix A, and the proposed value for each parameter is provided in Tables I-IV in Appendix B.

2. Results and discussion

In order to determine the behavior of the model with respect to different situations, a range of variations is assumed for each parameter. It is obvious that the functionality of the model with respect to these parameters is not linear.

Following [9,10], we define the normalized current due to electrochemical reaction j in the cathode and use it to illustrate the kinetics of the system:

$$I_j^N = \frac{1}{I_{app}} \int_{x=L_s}^{x=L} a i_j dx \tag{12}$$

Table 2
governing equations of the model.

Process	Governing equation
Material balance of an individual species:	$\frac{\partial \varepsilon C_i}{\partial t} = -\nabla \cdot N_i + r_i - R_i$
Individual species flux:	$\frac{N_i}{\varepsilon} = -D_i \nabla C_i - z_i \frac{D_i}{RT} F C_i \nabla \varphi_l$
Bruggeman's expression:	$D_i = D_{i,0} \varepsilon^b$
The rate of production/consumption of species i due to the electro-chemical reactions: Butler-Volmer equation:	$r_i = a \sum_j \frac{s_{ij} i_j}{n_j F}$ $i_j = i_{0,jref} \left\{ \prod_i \left(\frac{C_i}{C_{i,ref}} \right)^{p_{i,j}} \exp\left(\frac{\alpha_{aj} F}{RT} \eta_j \right) - \prod_i \left(\frac{C_i}{C_{i,ref}} \right)^{q_{i,j}} \exp\left(-\frac{\alpha_{cj} F}{RT} \eta_j \right) \right\}$ $p_{i,j} = s_{ij}$: anodic species / $q_{i,j} = -s_{ij}$: cathodic species
The evolution of specific surface area of the cathode:	$a = a_0 \left(\frac{\varepsilon}{\varepsilon_{initial}} \right)^{\xi}$
Overpotential for the reaction j:	$\eta_j = \varphi_s - \varphi_l - U_{j,ref}$ $U_{j,ref} = U_j^{\theta} - \frac{RT}{n_j F} \sum_i s_{i,j} ln \left[\frac{C_{i,ref}}{1000} \right]$
The liquid phase current density:	$i_l = F \sum_i z_i N_i$
The solid phase current density:	$i_s = -\sigma \nabla \varphi_s$
Charge transfer at the liquid/solid interface:	$\nabla \cdot i_l = a \sum_j i_j$ $\nabla \cdot i_s + \nabla \cdot i_l = 0$
The rate of consumption or production of species i due to precipitation/dissolution:	$R_i = \sum_k \gamma_{i,k} R'_k$ $R'_k = k_k \varepsilon_k \left(\prod_i C_i^{\gamma_{i,k}} - K_{sp,k} \right)$
The porosity variation with time: The volume fraction of the precipitate, *k:*	$\frac{\partial \varepsilon}{\partial t} = -\sum_k \tilde{V}_k R'_k$ $\frac{\partial \varepsilon_k}{\partial t} = \tilde{V}_k R'_k$
Boundary conditions at the interface of the cathode and the current collector:	$N_i = 0$ $i_s = I_{app}$ $i_l = 0$
Boundary conditions at the cathode-separator interface:	$N_{i,seperator} = N_{i,cathode}$ $i_{l,seperator} = i_{l,cathode} = I_{app}$ $i_s = 0$
Boundary conditions at the surface of anode:	$\varphi_s = 0$ $N_i = 0$ $N_1 = i_1 / F$ $i_l = FN_1$