

Modeling Degradation in Lithium-Sulfur Batteries

R. Purkayastha¹, G. Minton¹, L. O'Neill¹, S. Walus¹, M. Wild¹, M. Marinescu², T. Zhang², G. Offer²

¹Oxis Energy Ltd, Culham Science Centre, Abingdon, Oxfordshire, United Kingdom

²Mechanical Engineering Department, Imperial College, London, United Kingdom

Abstract

Lithium Sulfur batteries, with a theoretical gravimetric energy of 2700 Wh/kg are the next leap forward in battery technology. However, due to various degradation processes [1], the practical limit is closer to 350 Wh/kg. The battery itself operates due to a series of cascading reduction reactions, which can cause fluctuations in capacity and cycle life that are not fully understood. Analysis of these mechanisms using experimental techniques is limited, as most of the reactions occur simultaneously in solution. Modeling of the lithium sulfur system affords insights into the effects of different parameters and is particularly useful in replacing expensive and time consuming life-cycle testing. In this work we present a basic model of degradation processes at the anode and the effect over time. We build on previous 1-D models [2] which treated the anode as an ideal lithium conductor, and instead model the anode discretely. The cathode is modeled as a homogenized porous electrode with reacting sulfur species. The precipitates are accounted for using the general form of the Ordinary Differential Equation module.

The lithium anode reacts with the electrolyte to form a Solid Electrolyte Interphase (SEI) which causes a charge transfer resistance. Using the Electrochemistry Module in COMSOL it is possible to model the voltage reduction that occurs, which is depicted in Figure 1. In this example a fixed resistance was used, but it is possible to use a time-dependent resistance which would show a gradual increase in resistance, and a concomitant decrease in capacity over time.

In addition, the lithium sulfur battery undergoes a 'shuttle mechanism', wherein higher order polysulfides get reduced at the anode surface during charging (which being oxidized at the cathode), which causes a parasitic current within the battery. This leads to an increase in temperature within the battery. Using a previously developed model for shuttle [3] we look at cooling conditions required for these batteries. In the simulations, the battery cells are heated through the shuttle process until 1.5×10^4 s and are then cooled. As shown in Figure 2, forced convective cooling is required in order to prevent a rise in temperature in an affected cell, which can also help in prevention of thermal runaway.

Reference

1. M.Wild, et. al. , ‘Lithium Sulfur Batteries, A Mechanistic Review’, Submitted, (2015)
2. K. Kumaresan, et. al. ‘A Mathematical Model for a Lithium-Sulfur Cell’, Journal of the Electrochemical Society, 155(8), A576-A582, (2008)
3. Y.V. Mikhaylik, J.R. Akridge, ‘Polysulfide Shuttle Study in the Li/S Battery System’, Journal of the Electrochemical Society, 151 (11), A1969-A1976, (2004)

Figures used in the abstract

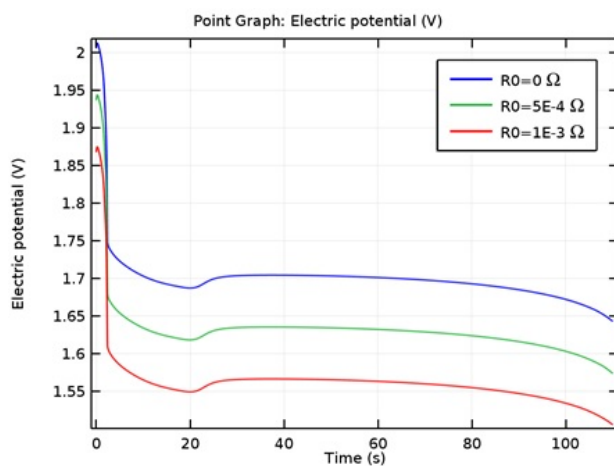


Figure 1: Discharge curve of a Lithium Sulfur battery plotted for different values of Solid Electrolyte Interphase resistance across the anode interface.

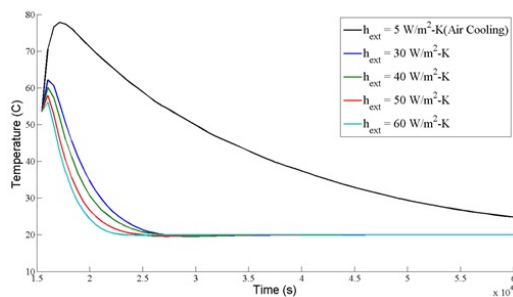


Figure 2: Batteries undergoing shuttle are cooled at different rates from air cooling to forced convection. The forced convection is able to cool the battery cell at a much quicker rate than if left to air cool.



Figure 3



Figure 4