Analysis of Polysulfide Shuttle Currents in Lithium-Sulfur Cells

D. Moy[1], A. Manivannan[2] and S. R. Narayanan[1]

[1]Loker Hydrocarbon Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089

[2]US Department of Energy, National Energy Technology Laboratory, Morgantown, WV 26507

The development of a rechargeable lithium-sulfur battery has been of considerable interest due to its potential to have two to three times the energy density of commercial lithium-ion batteries. The high theoretical specific capacity of the lithium and sulfur electrodes coupled with the low cost and non-toxicity of sulfur make lithium-sulfur batteries very attractive for many applications.

One of the major drawbacks of the lithium-sulfur system, however, is its poor cycle life. Typically 20-50% of the capacity is lost in about 100 cycles. This poor cycleability results from the parasitic reaction known as the polysulfide shuttle.[1,2] There have been numerous efforts to slow down this parasitic process to improve the cycle life of the cells.[2-6]

In lithium-sulfur cells, higher order polysulfides will diffuse from the positive sulfur electrode and travel to the negative lithium electrode where they will be reduced to lower order polysulfides. These polysulfides must diffuse back to the positive electrode and be reoxidized, thus creating a shuttle.[1] In lithium-sulfur cells with an unprotected lithium electrode, some of the insoluble Li_2S_2 and Li_2S reduced at the lithium electrode will be trapped, resulting in an irreversible capacity loss. A direct measurement of the polysulfide shuttle at different cell voltages can be used to predict the degradation of lithium-sulfur batteries.

We have studied 2032 coin cells with a carbon-sulfur composite cathode, lithium foil anode and electrolyte prepared from 0.5M lithium bistrifluoromethyl sulfonimide salt in dioxolane/dimethoxyethane (1:1) solvent. We have measured the currents by first discharging a cell to a target voltage and then holding the cell at that voltage. When the cell is held at a chosen cell voltage, current flow occurs due to the diffusion and reduction of polysulfides occurring via the shuttle mechanism. The observed current under these conditions is related to the concentration gradient of polysulfides in the cell and the shuttle process. We call this the "shuttle current". Shuttle currents are found to vary with depth of discharge, the cell voltage and the history of the cell. These variations are due to the different polysulfide species and the concentration gradients present at different cell voltages (Figure 1).

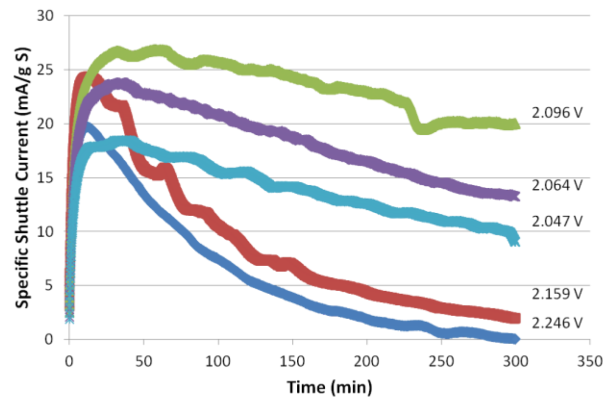

Figure 1. Shuttle current measurements for a Li/S cell with 0.5M $LiN(CF_3SO_2)_2$ in 1:1 DOL:DME electrolyte

This poster presentation will provide analysis of the shuttle currents and its relationship to the state of the cell.

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