Lithium/Sulfur Rechargeable Cells: Effect of Carbon and Binder on Sulfur Electrode Performance

Joongpyo Shim, Kathryn A. Striebel,
and Elton J. Cairns

Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory, and
University of California
Berkeley,CA 94720

Elemental sulfur is very attractive as a cathode material for high-specific-energy rechargeable lithium cells because of high theoretical specific capacity (about 1675 mAh/g) and the fats that it is very low cost and non-toxic. Sulfur can react with lithium ions between 1.5 and 3.0V(vs. Li/Li^+) to produce several lithium polysulfides and Li_2S. The use of sulfur as cathode material in lithium cells has not been successful because of rapid capacity fade on cycling. The capacity fade has been attributed to the solubility of polysulfides in many organic electrolytes. Yamin and Peled reported on the electrochemical characteristics of sulfur and polysulfides in several organic solvents.[1,2] They also observed a capacity loss of the sulfur electrode at 60°C of 2-5% per month depending on solution composition.

Sulfur and lithium polysulfides are non-conducting materials. The inclusion of an electronic conductor such as carbon black is important for the achievement of good utilization at useful rates. We have found that at least 10 w/o carbon black is necessary for reasonable performance. In this work, we investigate the effect of carbon black content on cycling performance. We will report results from charge/discharge cycling, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry.

Experimental Procedures

Electrodes were prepared from a mixture of sulfur (99.7%, International Sulfur Inc.), carbon black (Shawinigan black) as electric conductor, and PEO (Aldrich, MW 5,000,000) as binder in acetonitrile. Electrochemical characteristics of the sulfur electrodes were stidied using a Swagelok cell three-electrode system. The working and reference electrodes were lithium foil, and separator was porous polypropylene (Celgard). Thje lithium salt for these experiments was lithium (bis)trifluoromethanesulfonate imide (LiTFSI, 3M) and the solvent was polyethyleneglycol dimethyl ether (PEGDME, MW 500). Lithium/sulfur cells were assembled in a glove box filled with argon gas. Cell assembly is described in detail elsewhere[3].

Cell performance was measured with an Arbin battery cycler with cut-off potentials of 1.5 and 3.0V vs. Li/Li^+. The cells were discharged and charged galvanostatically and the rest time between discharging and charging was 1 hour. To characterize oxidation/reduction of sulfur and polysulfide, and the variation of resistance for sulfur electrode on cycling, cyclic voltammetry and electrochemical impedance spectroscopy were carried out using an EG&G 273 and Solartron 1286, respectively.

Results

The cycling performances of sulfur electrodes were carried out in LiTFSI/PEGDME solution. PEGDME is structurally similar to polyethylene oxide (PEO) and has the same ether backbone as PEO. The molecular weight of PEGDME is much lower than that of PEO. A typical electrode composition was sulfur 70%, carbon 20% and PEO 10%. Fig. 1 shows the voltage profiles of the sulfur electrode on cycling at 0.05mA/cm^2. By the 100th cycle, the capacity increased significantly to about 280mAh/g. The capacity, however, decreased slowly after the 100th cycle. The capacity at the 300th cycle is still 180mAh/g(of electrode) which corresponds to 257mAh/g(of sulfur). The cell is overcharged slightly on each cycle except for the initial cycle. During overcharging, lithium polysulfides such as Li_2S_x (x>6) in the cathode can diffuse to the anode, where they are reduced. The reduced lithium sulfides can diffuse back to cathode, where they may be reoxidized. This sulfide redox shuttle mechanism exists in Li/S cell because Li_2S_x is soluble to some extent in the electrolyte.The capacity fading for first plateau at around 2.4V is smaller than that for second one at 1.8 - 2.0V. The upper plateau may be assigned to the formation of various lithium polysulfide such as Li_2S_4, Li_2S_6, Li_2S_8 etc and lower plateau may be assigned the formation of Li_2S as a separate phase.

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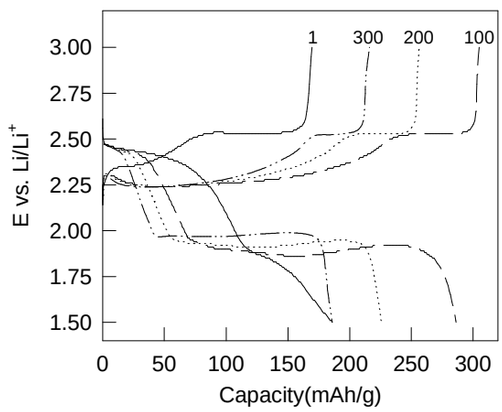

Fig. 1 Voltage profiles of the sulfur electrode on cycling. Cut-off voltages: 1.5 and 3.0V vs. Li/Li^+. Current density 0.05mA/cm^2.