ELECTROACTIVE POLYMERS FOR OVERCHARGE PROTECTION IN LITHIUM BATTERIES

Guoying Chen, Karen E. Thomas, John Newman, and
Thomas J. Richardson

Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
Berkeley, California 94720, USA

Because of their very large energy densities and the potential for catastrophic failure, overcharge protection is a necessary feature in rechargeable lithium batteries. When the application requires high voltage, multicell stacks, designs are needed that permit current to flow through or around a damaged cell. While external electronic shunts are currently used for this purpose, they add weight, volume, and cost to the battery package. Redox shuttle additives [1], which provide internal protection by transferring charge through the electrolyte, have limited rate capabilities and can generate large amounts of heat at the charged anode.

An alternative approach is the use of electroactive polymers whose conductivity depends upon their state of charge [2]. These may be formed from a molecular precursor additive or they may be incorporated into the cell during manufacture. Figure 1 shows the current-voltage behavior of a cell containing a polypropylene separator impregnated with poly(3-methylthiophene) by *in situ* electropolymerization of 3-methylthiophene. The separator is resistive below 3.2 V. Behavior of a solution-impregnated separator in a Li-TiS_2 cell is shown in Fig. 2.

The charge capacities, conductivities and switching potentials of the polymers depend upon their compositions and morphologies, which in turn depend upon the methods used to produce them. Inhomogeneous charge distribution within the polymer may influence the switching behavior and current carrying capacity of a conducting polymer shunt. The current distribution within the conducting polymer is strongly affected by two factors: the extreme variation of electronic conductivity with degree of oxidation and the fact that the salt in the electrolyte is consumed during oxidation. Simulations were performed to examine these effects. Mathematically, the conducting polymer is treated similarly to a lithium-insertion electrode [3], except that the polymer reacts with the anion instead of the lithium ion, and the polymer's electronic conductivity varies with degree of oxidation. The simulations show that the reaction front proceeds from the positive current-collector interface inwards towards the negative electrode. The sharpness of the reaction front depends on how steeply the electronic conductivity and the open-circuit potential of the conducting polymer vary with degree of oxidation.

Experimental and theoretical efforts toward practical implementation of electroactive polymers for overcharge protection in lithium batteries will be described.

[1] T. J. Richardson and P. N. Ross, Jr., *Proc. Electrochem. Soc.*, **99-25**, 687 (2000).
[2] F. R. Denton, J. N. Howard, A. A. Anani, and J. M. Fernandez, US Patent 6,228,516 (Motorola).
[3] M. Doyle, T. F. Fuller, and J. Newman, *J. Electrochem. Soc.*, **140**, 1526 (1993).

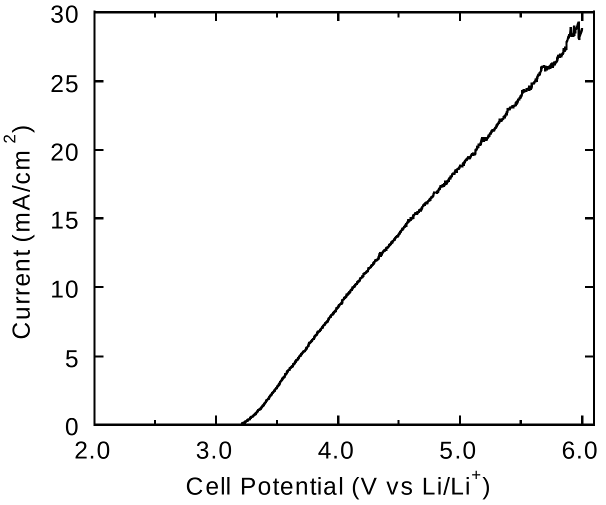

Fig. 1. Current response of a 1.6 cm^2 cell containing electropolymerized 3-methylthiophene, stainless steel vs. lithium foil, 1M $LiPF_6$ in EC:2DMC.

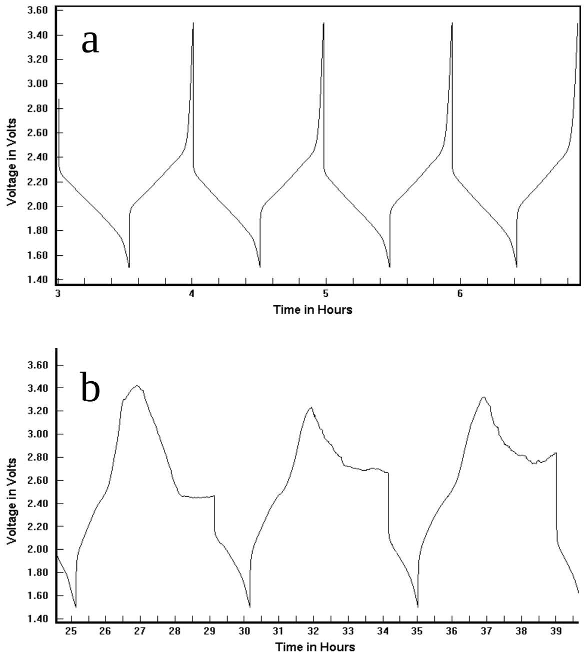

Fig. 2. Charge/discharge curves of TiS_2-Li cells in 1M $LiPF_6$ in EC:2DMC with a) plain Celgard separator; b) poly (3-butylthiophene-2,5-diyl)-coated separator.