

STABLE REVERSIBLE OVERCHARGE
PROTECTION FOR HIGH-VOLTAGE
RECHARGEABLE LITHIUM BATTERIES

Bin Wang, Thomas J. Richardson and Guoying Chen*
Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
Berkeley, California 94720, USA

Lithium batteries are prone to energetic venting, ignition, and even explosion following severe overcharging [1]. Even slight overcharging reduces the discharge capacity of a cell, potentially causing overdischarging, increased impedance, and local heating [2]. Battery packs for consumer electronics are protected by electronic controls and by internal shutdown mechanisms like melting separators and pressure or temperature-activated disconnects. In a multi-cell stack capable of delivering several hundred volts, permanently shutting down a cell reduces the usable capacity of the stack and adds to the burden of the remaining cells in parallel circuit. Complex re-routing of current around overcharged cells is impractical in these stacks.

An approach was previously developed in our laboratory to address this issue [3-6]. Electroactive-polymers capable of forming a reversible resistive shunt between the current collectors were introduced to protect cells from overcharge damage. The process is self-activated by voltage, and it does not pose interference to normal cell charge and discharge. The polymer can be added to cells in a variety of configurations, opening the possibility for cell designs that best accommodate heat transfer during overcharging.

In this presentation, we report the recent progress in cell protection for high-energy lithium-ion batteries intended for PHEV and EV applications. An electrospinning technique was adopted to prepare dense non-woven composite membranes with the electroactive polymer well mixed with a matrix polymer at individual fiber level. This improves polymer utilization and reduces the cost of overcharge protection. Fig. 1 shows a 25 μm -thick electroactive-fiber-composite membrane composed of poly[(9,9-dioctylfluorenyl-2,7-diyl)] (PFO) and polyethylene oxide (PEO) in a weight ratio of 1:3. The excellent connection between the fibers, the high porosity and the open pore structure enable rapid transport of both ions and electrons within the membrane. A single-step process was also developed to prepare bilayer fiber composite membranes consisting of a high-voltage electroactive polymer on one side and a low-voltage polymer on the other. Fig. 2a shows the cycling performance of a spinel $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ half-cell overcharge-protected by an electrospun PFO and poly(3-butylthiophene) (P3BT) composite separator. The high-voltage PFO was placed next to the cathode to set the protection potential while the lower-voltage P3BT was placed next to the anode to complete the reversible shunt and protect the PFO from degradation at the anode potential. At C/2 rate and 125% overcharge, a steady state was reached at 4.2 V, which is significantly lower compared to that of the previous cells protected by similar PFO/P3BT composites prepared on microporous membranes. This suggests reduced internal resistance and improved power density in the cells with an electrospun fiber separator. The steady state potential as well as the charge and discharge capacities remained constant for over 600 cycles (Fig. 2b), demonstrating excellent

stability of the polymer protection. We will discuss the details on electroactive polymer properties, the impact of membrane substrate and polymer distribution on overcharge protection performance. Results on scaling up the approach for protection in large-format cells will also be presented.

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Fig. 1. SEM and digital (inset) images of a PFO-PEO fiber composite membrane prepared by the electrospinning technique.

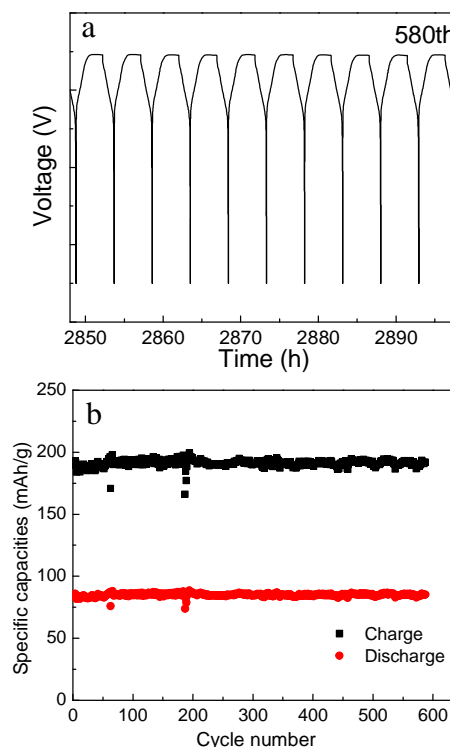


Fig. 2. a) Cycling profiles and b) charge and discharge capacities of a $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ -Li cell overcharge protected by a bilayer PFO-P3BT fiber composite separator membrane.

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