Overcharge Protection for PHEV Batteries

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Project ID: ES037

Overview

Timeline

- Start date: March 2009
- End date: ongoing
- Percent complete: ongoing

Barriers Addressed

- Cycle life
- Abuse tolerance for PHEV Li-ion batteries

Budget

- Total project funding
  - FY10 $190K
  - FY11 $240K
  - FY12 $240K

Partners

- ANL, BNL, INL, and SNL
- Berkeley program lead: Venkat Srinivasan

Objectives\Milestones

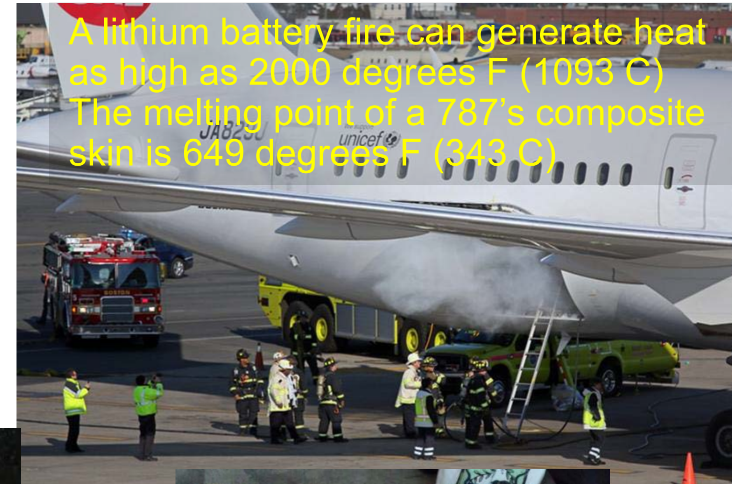
Objectives

- Develop a reliable, inexpensive overcharge-protection mechanism.
- Use electroactive polymers for internal, self-actuating protection.
- Minimize cost, maximize rate capability and cycle life of overcharge protection in high-energy Li-ion batteries for PHEV applications.

Milestones

- Investigate rate performance and cycle life of cells protected by electrospun electroactive-fiber composite separators (January 2013).
- Evaluate alternative placements of the fiber-composite membranes in battery cells (March 2013).
- Attend review meetings and present research results.

Lithium-ion Battery Safety Issues



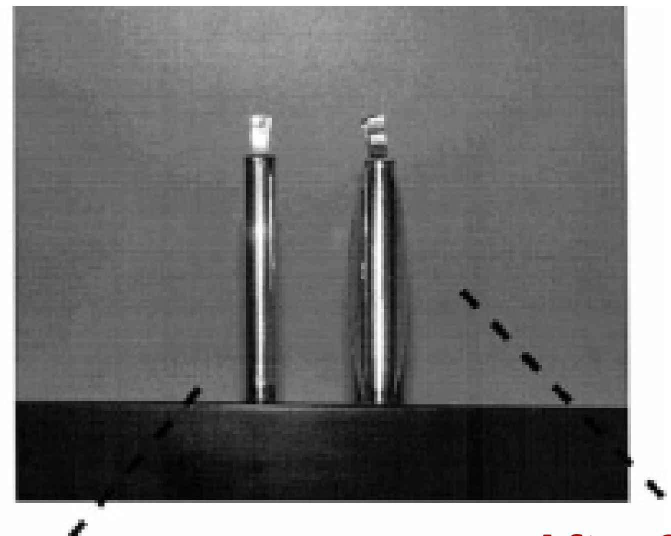
"Thermal runaway was found on all the 787 batteries that burned up"

Inherent thermal instability leads to battery safety issues – prevention measures needed.

Overcharge Major Concern for Safety and Lifetime

Why

- Cathode degradation, metal ion dissolution, O_2 evolution
- Electrolyte breakdown, CO_2 evolution
- Li deposition on anode, H_2 evolution
- Overheating, breakdown of anode SEI layer and thermal runaway
- Current collector corrosion
- Explosion, fire, toxics released
- Accelerated capacity/power fade, shortened battery life



Before

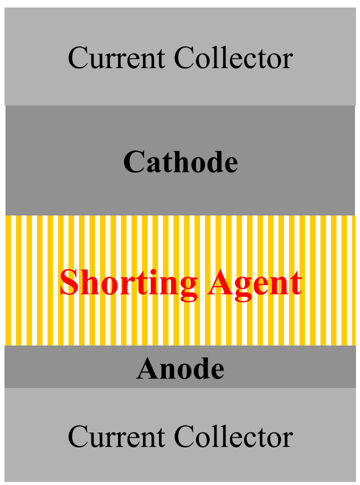
After 2C overcharge

What causes overcharge

- Over-voltage excursions
- Charging exceeding electrode capacity
- Cell imbalance in the battery pack
- Low-temperature operation at high internal resistance

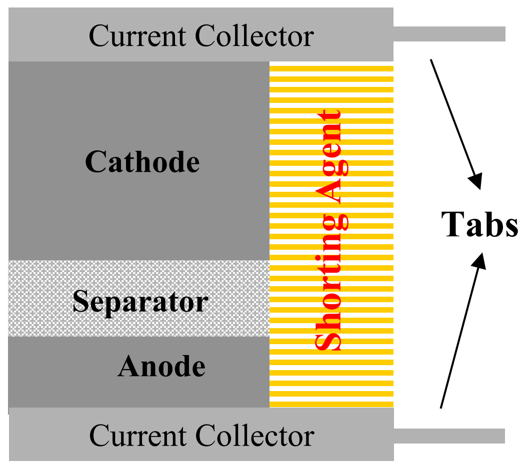
Approach – Reversible Soft-Shorting Activated by Cell Voltage

Sandwich



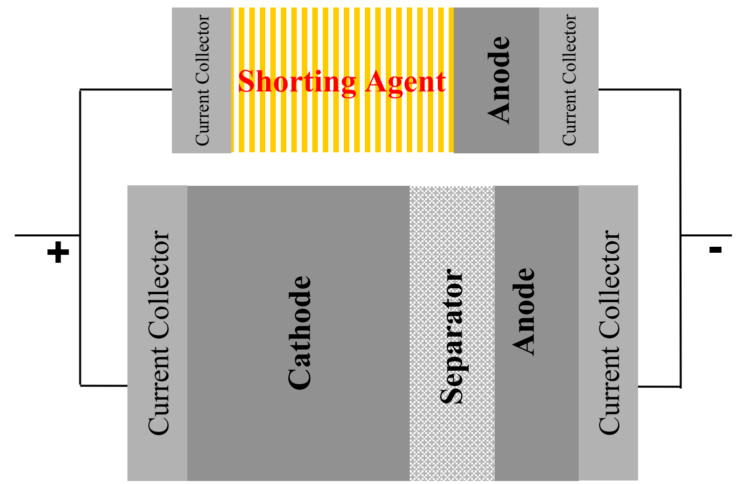
Shorting agent impregnated in the separator between the battery electrodes

Parallel



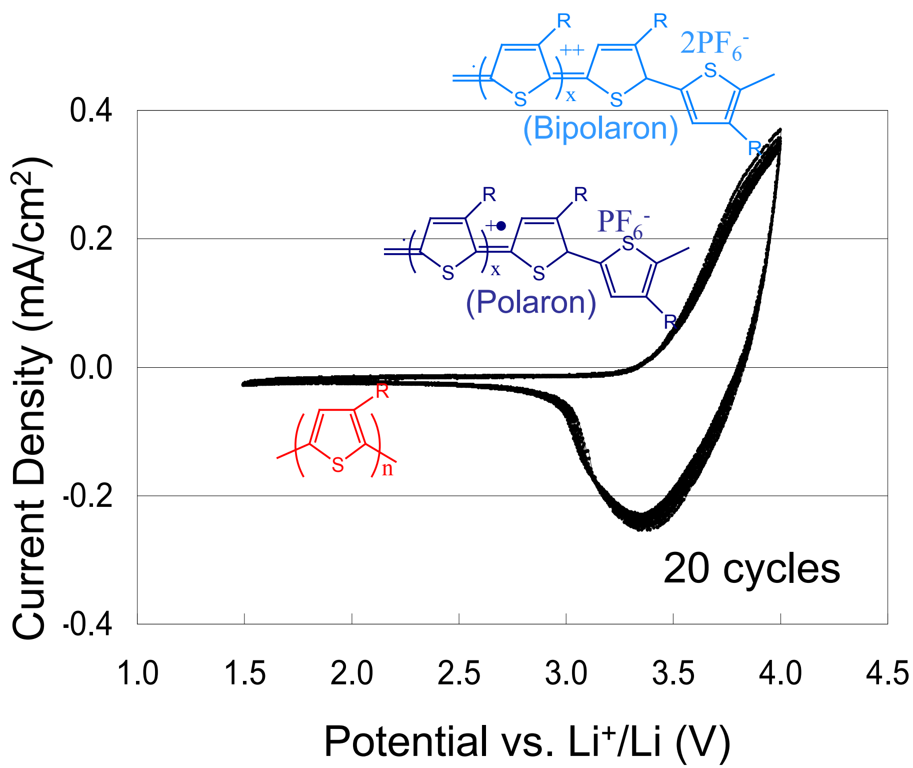
Shorting agent placed between the current collectors

External



Shorting agent used in an external component connected parallel to the battery cell

Electroactive Polymers As Shorting Agent



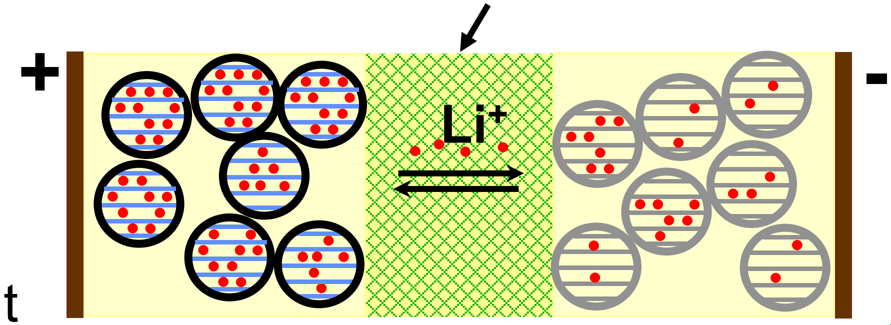
Anion doping level

SOC	Conductivity (S/cm)
0.25	1×10^{-1} (oxidized)
0.22	1×10^{-2}
0.19	3×10^{-3}
0.14	1×10^{-4}
0.11	1×10^{-5}
0.09	1×10^{-6}
0.07	3×10^{-7}
0.06	1×10^{-8}
0.04	7×10^{-9}
0.03	3×10^{-9}
0.02	2×10^{-9}
0	1×10^{-9} (neutral)

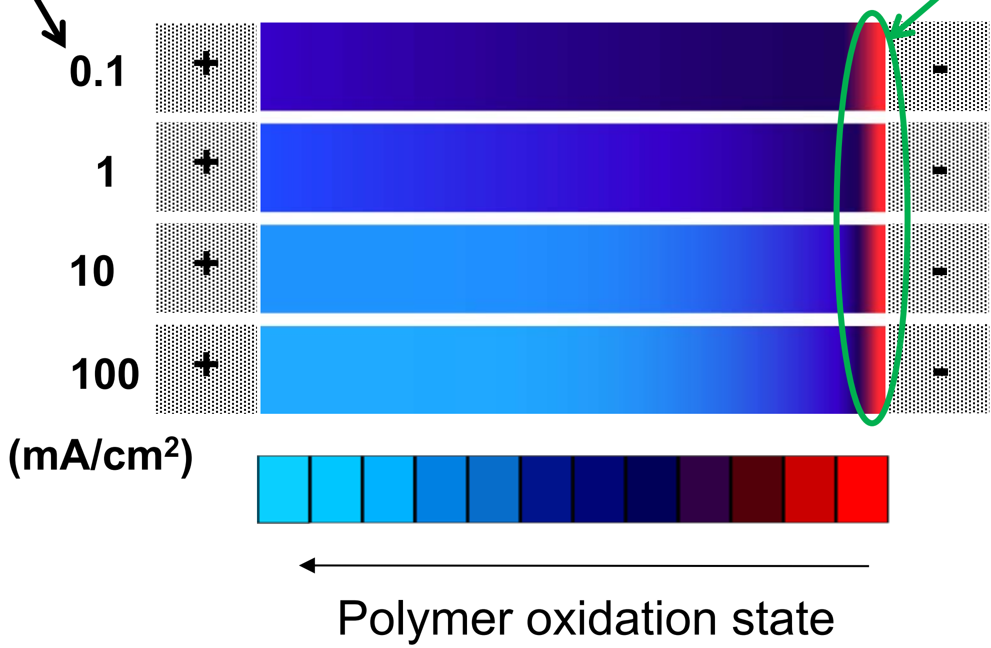
- Highly reversible redox reactions – capable of reversible, long-term protection.
- Rapid changes in electronic conductivity upon the redox reaction – cell voltage regulates the resistivity of the polymer shunt.

Protection Mechanism

Electroactive polymer impregnated separator



Intrinsic ability to carry large current



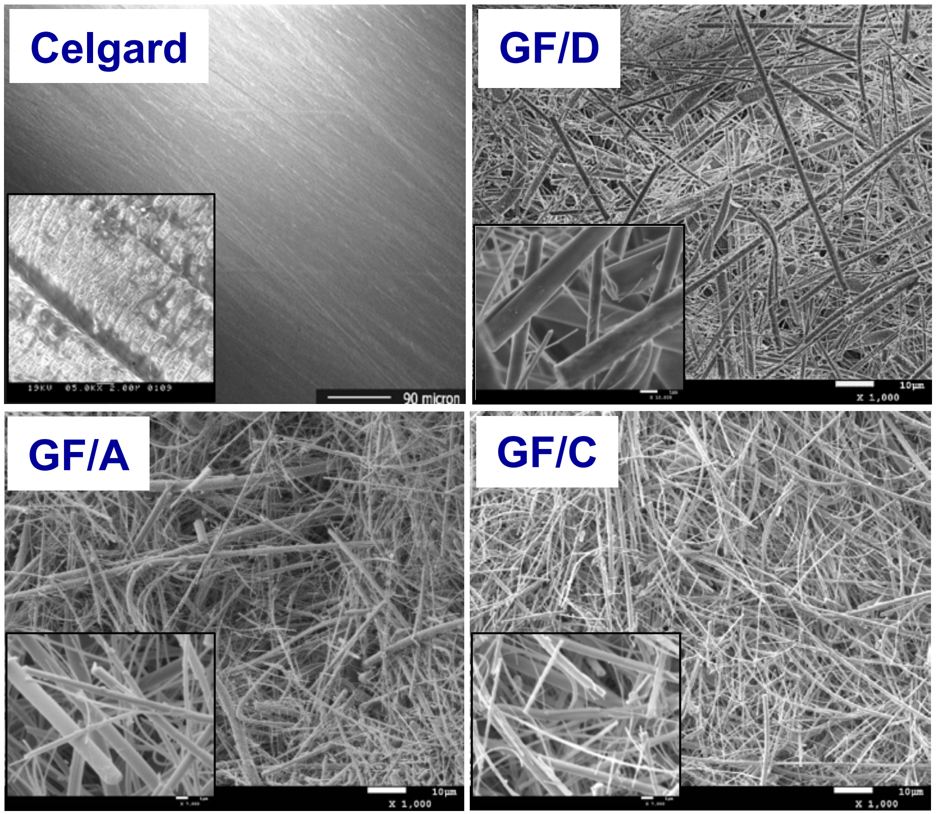
Most potential drop occurs at the small region close to the anode

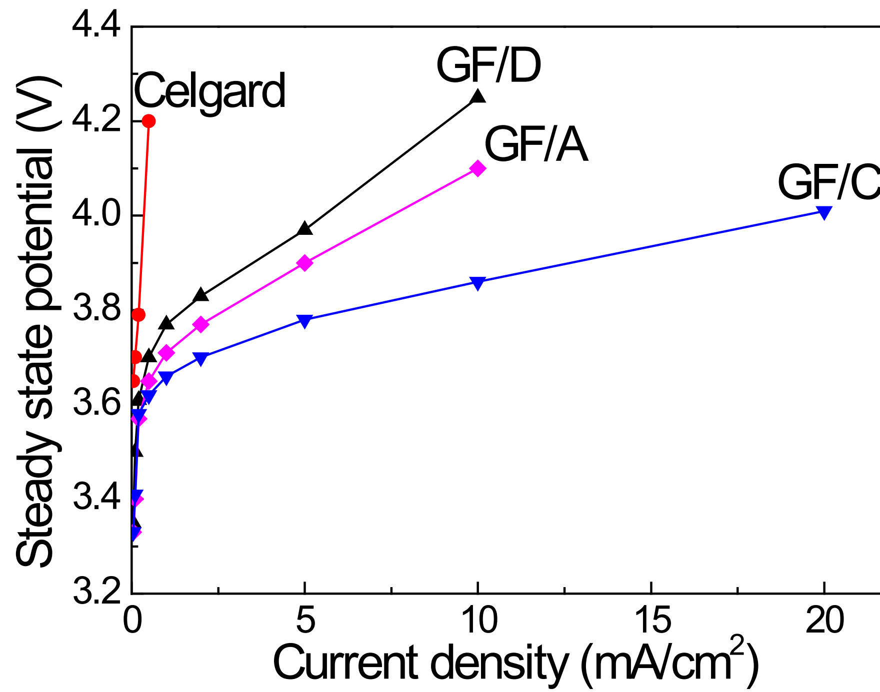
- Soft-shorting
- May benefit heat transfer

Technical Accomplishments

- Achieved 40-fold increase in sustainable current in glass fiber membrane supported electroactive polymer composites.
- Achieved protection for hundreds of high-rate, deep overcharged cycles in several cell chemistries. Demonstrated the most stable overcharge protection reported so far.
- Developed a low-cost electrospinning technique to prepare dense, single-layer or bilayer polymer-fiber composite separators. Demonstrated their excellent rate capability and stability for overcharge protection.
- Demonstrated stable protection in larger-sized pouch cells and the feasibility in scale-up.

Effect of Membrane Substrate



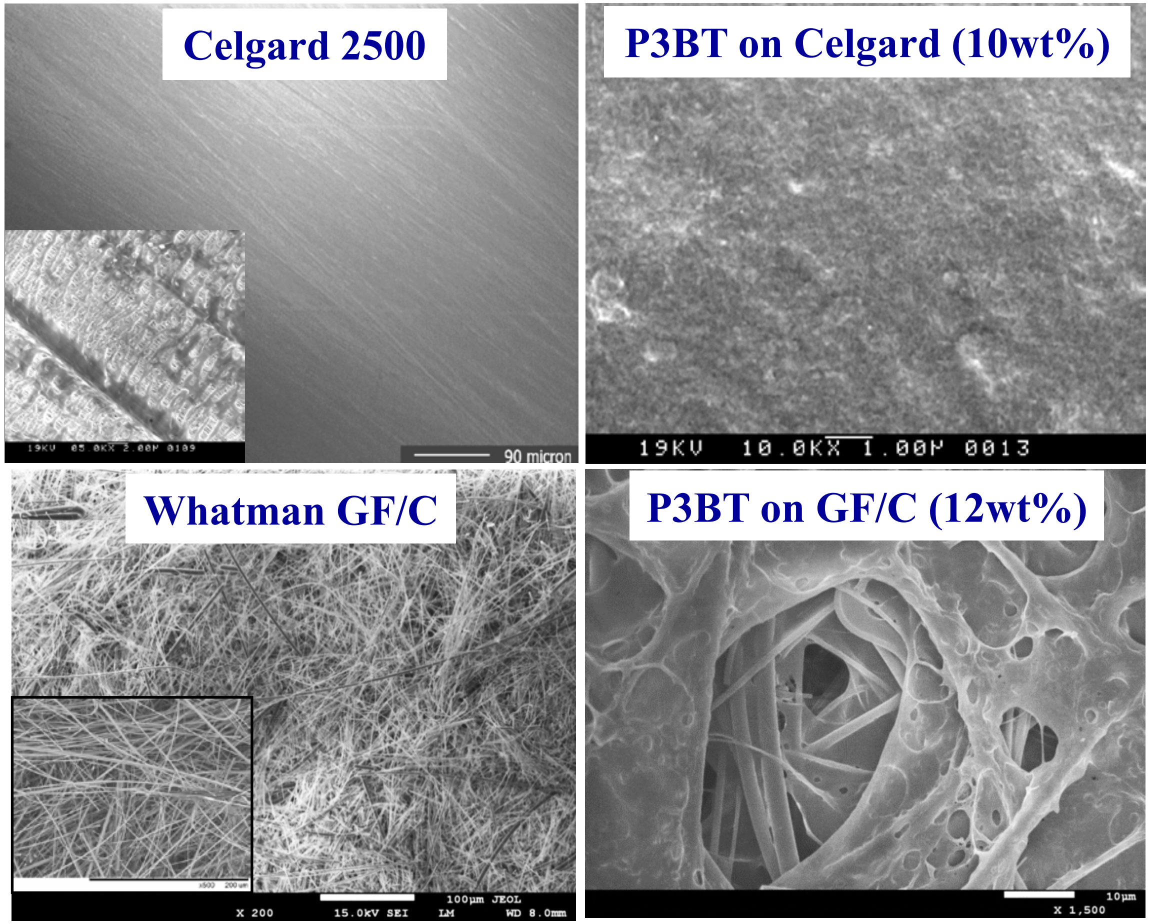


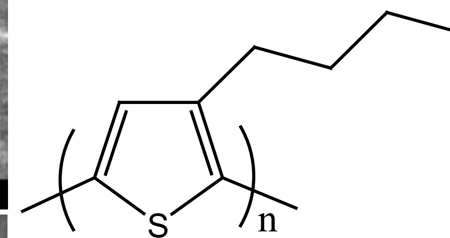
Smaller fiber diameter and higher surface area in the GF/C membrane led to improved performance in the composite.

Improved Polymer Distribution on Fiber-Membrane Substrates

Microporous membrane substrate (25µm, 55% porosity)

Glass fiber membrane substrate (85µm, ~75% porosity)

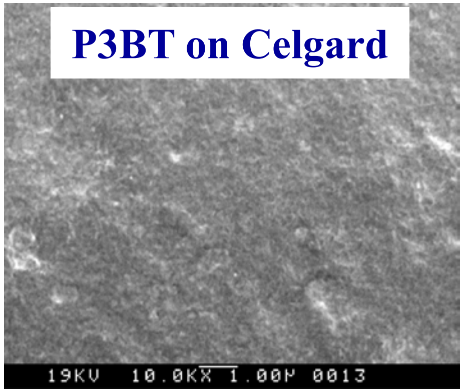


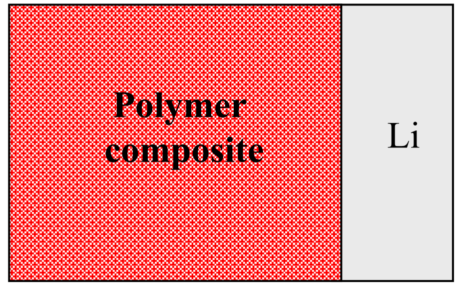


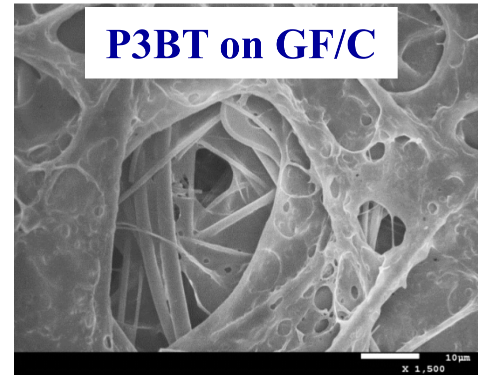
Poly(3-butylthiophene)
(P3BT)

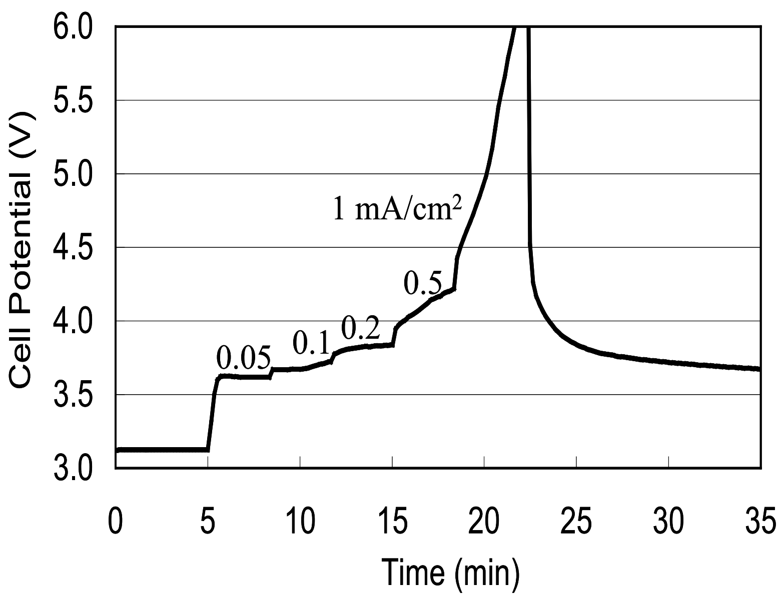
- Electroactive polymer composites prepared by solution impregnation.
- Large porosity and open pore structure in the glass fiber membranes promote more uniform polymer distribution and reduced surface deposit.

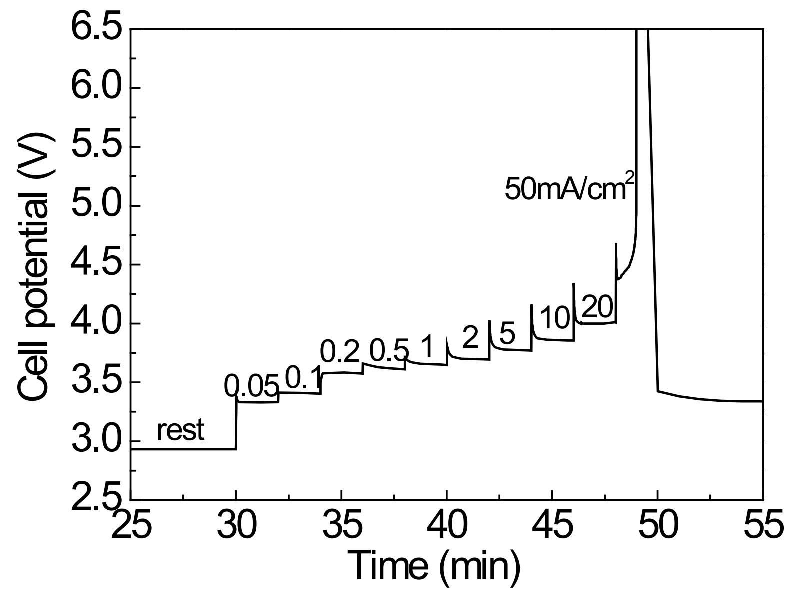
Improved Sustainable Current in Fiber-Membrane Composites





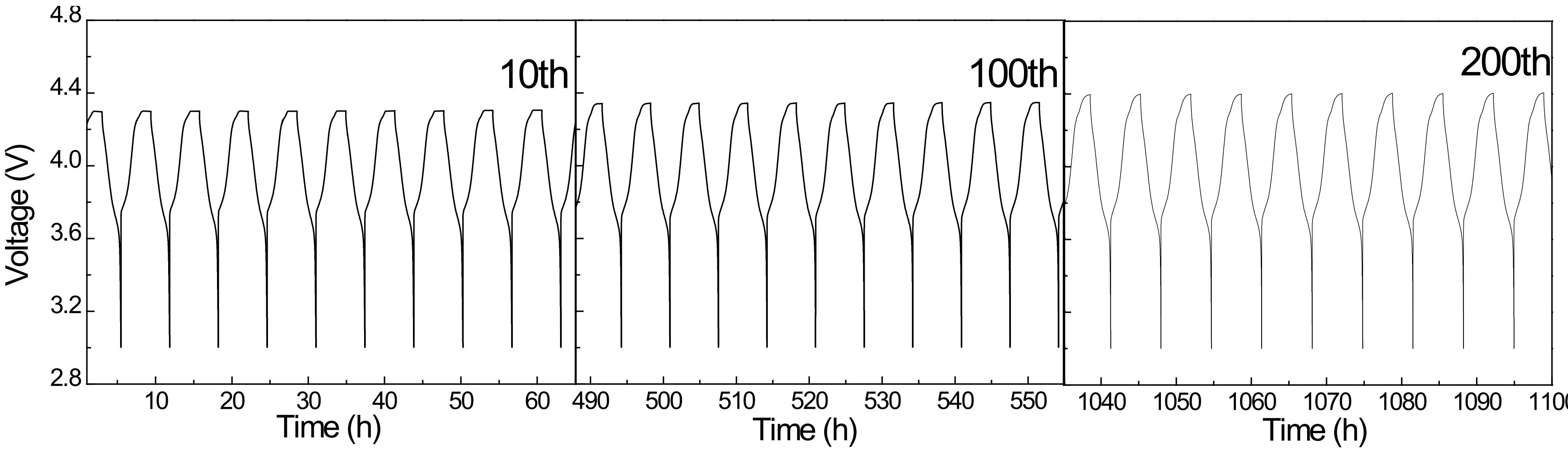


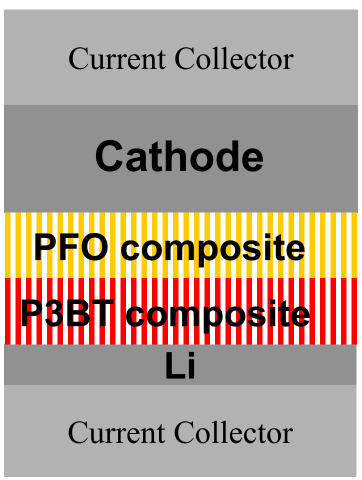


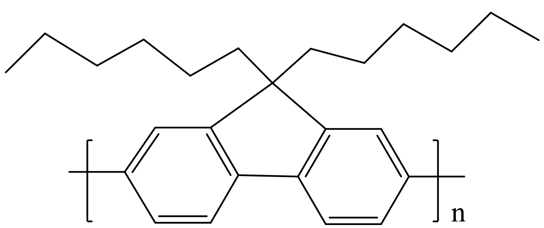


Improved polymer distribution and utilization in the fiber-membrane composite led to 40-fold increase in sustainable current.

Glass Fiber Composites – Long-term Protection



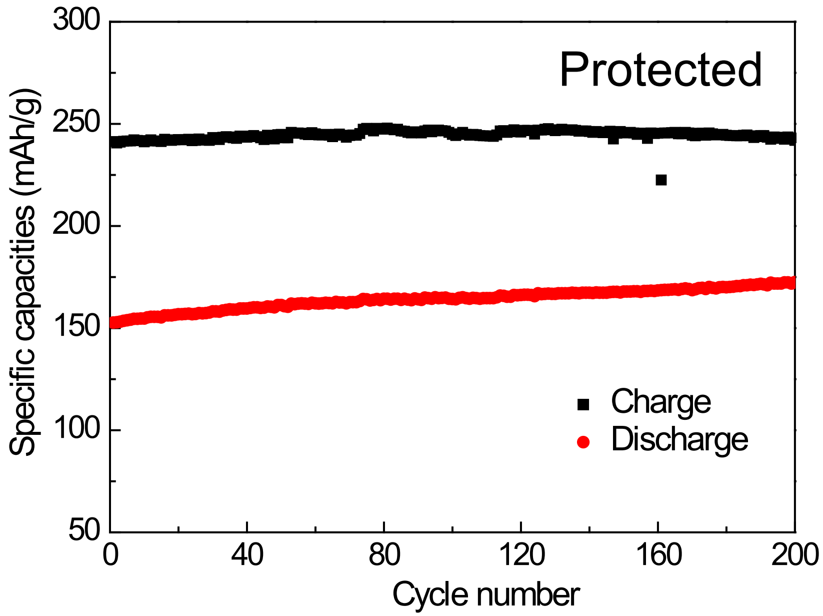


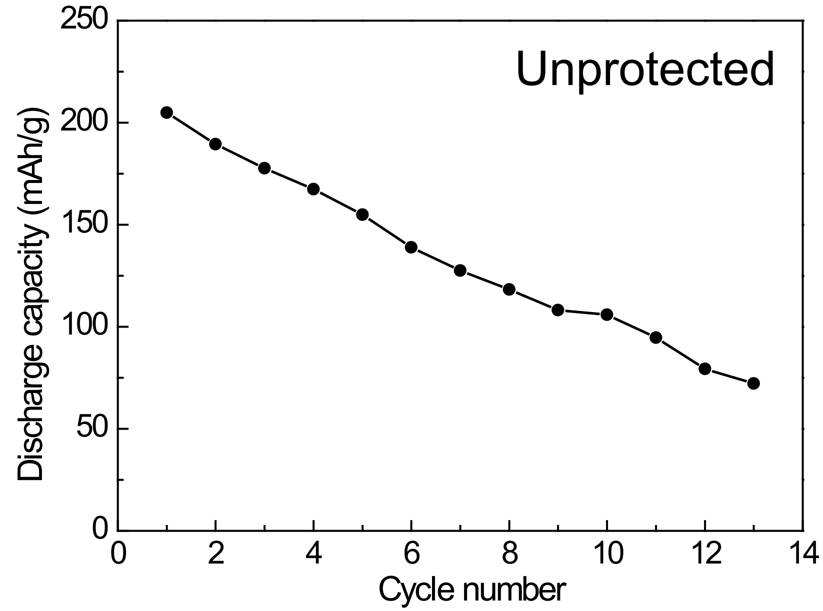


Poly(9,9-dioctylfluorene)
(PFO)

- Protection in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen 3) cell drastically improved from the previous microporous composites.
- Cell cycled at 0.5C and 60% overcharge for more than 200 cycles.
- Upper limiting voltage increased from 4.35 to 4.4 V. Instability suggests some polymer distribution issues remain in the glass fiber composites.

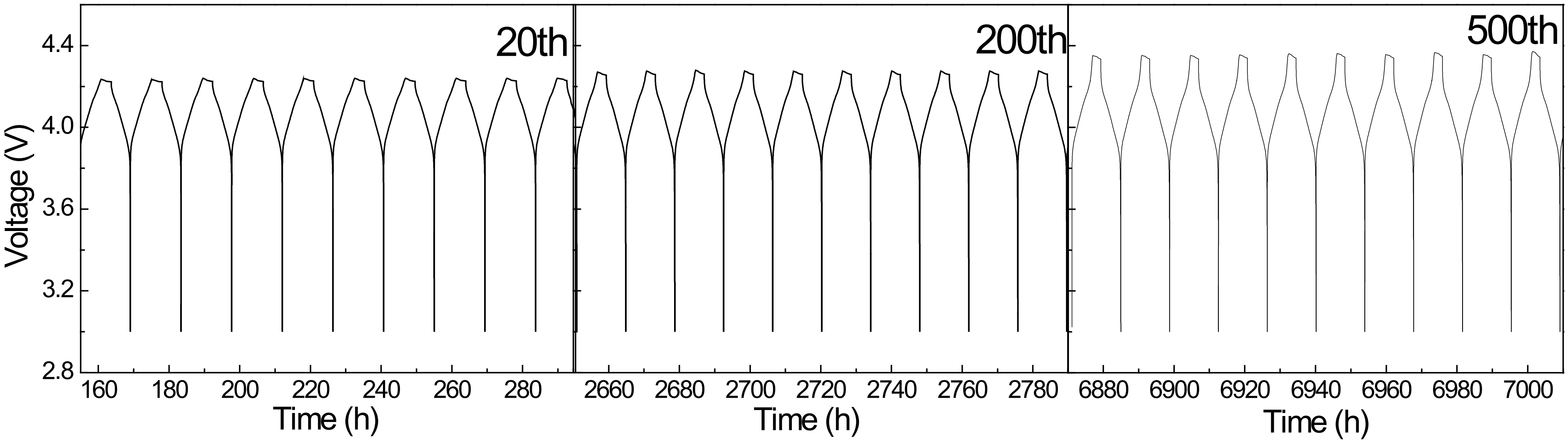
Glass Fiber Composites – Long-term Protection

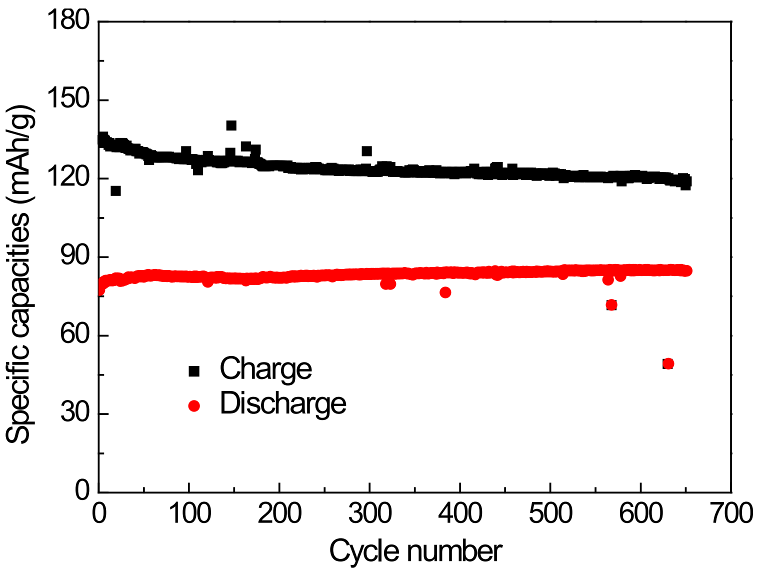




- Increase in upper limiting voltage leads to a slight increase in discharge capacity in the protected cell.
- In comparison, the discharge capacity in the unprotected cell rapidly decreased upon overcharge abuse.

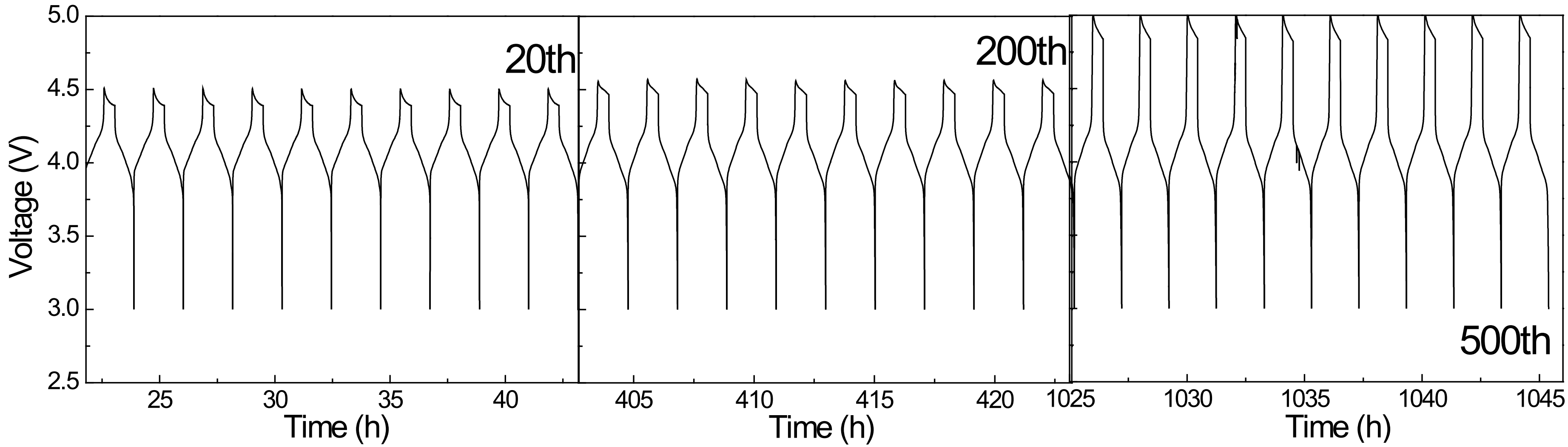
Glass Fiber Composites – Long-term Protection

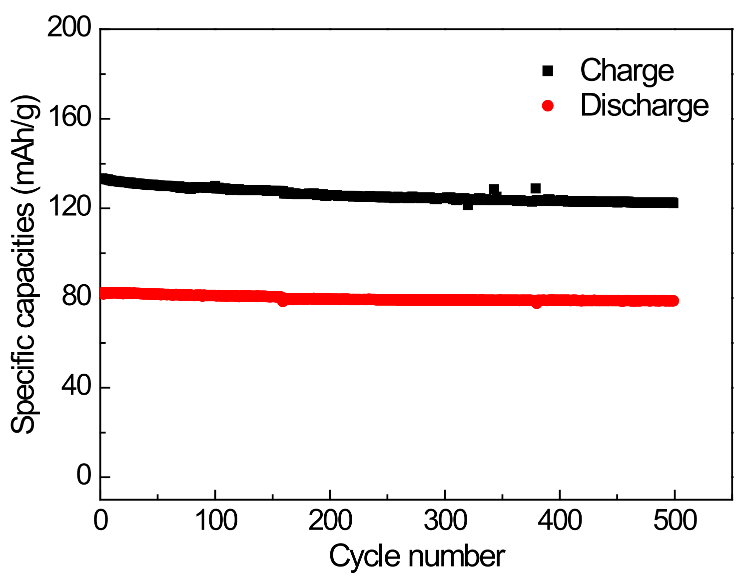




- Improved protection in $Li_{1.05}Mn_{1.95}O_4$ cell cycled at C/6 rate and 50% overcharge.
- Upper cell voltage increased from 4.25 to 4.35 V during the first 500 cycles.
- Stable discharge capacity for over 650 overcharged cycles so far.

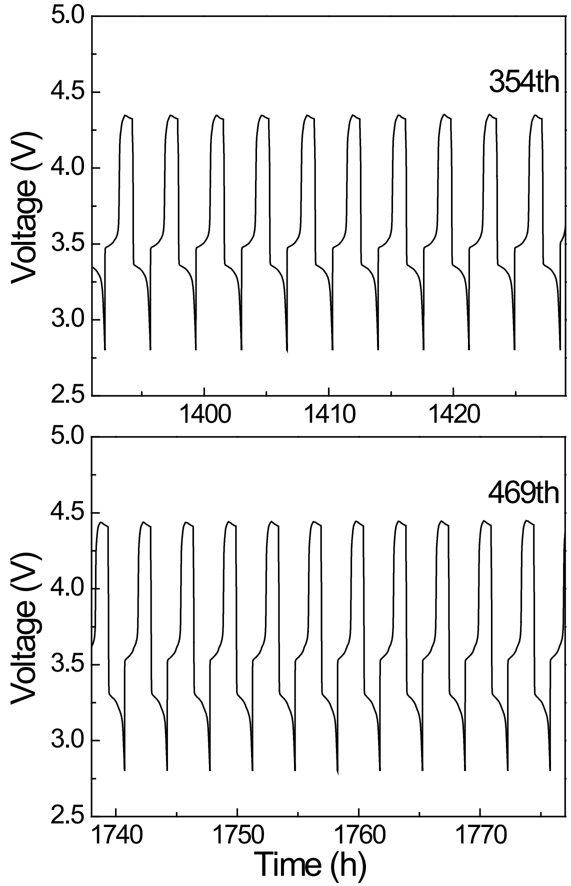
Glass Fiber Composites – High-Rate Protection

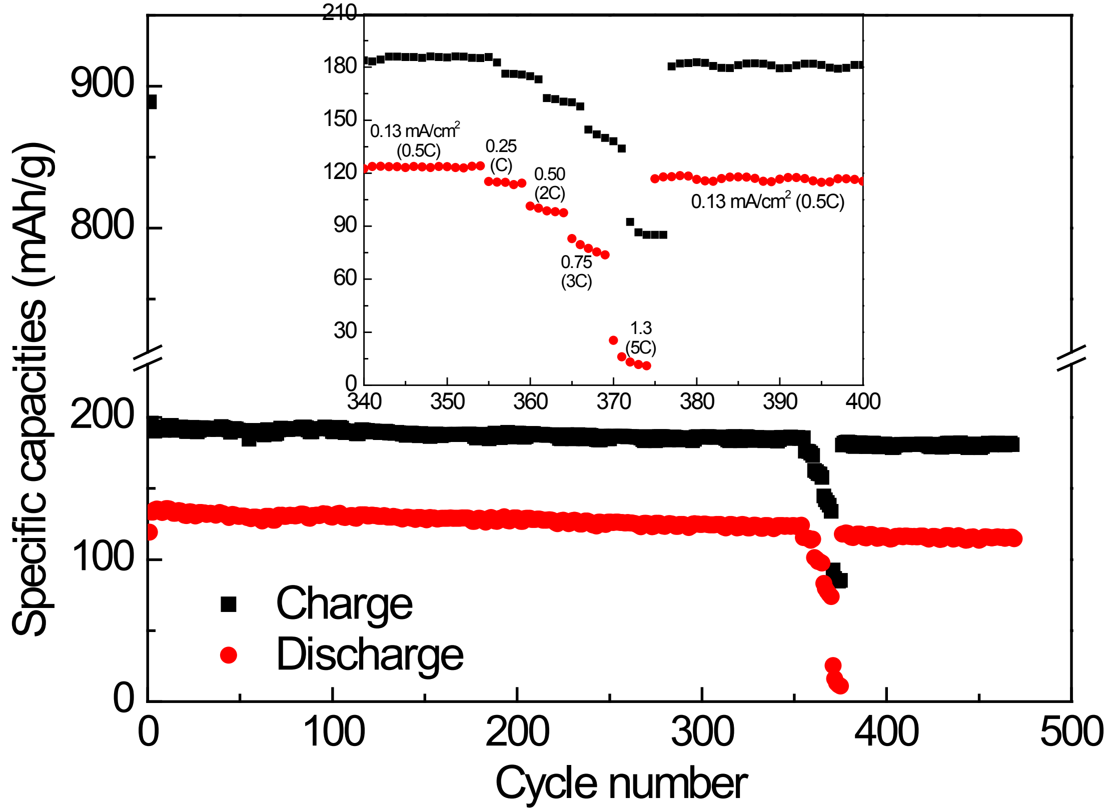




- $Li_{1.05}Mn_{1.95}O_4$ cell cycled at C rate and 60% overcharge. Improved rate capability compared to the previous microporous composites.
- Upper cell voltage limited at about 4.5 V for more than 300 cycles.
- High-rate overcharge protection maintained for more than 500 cycles.

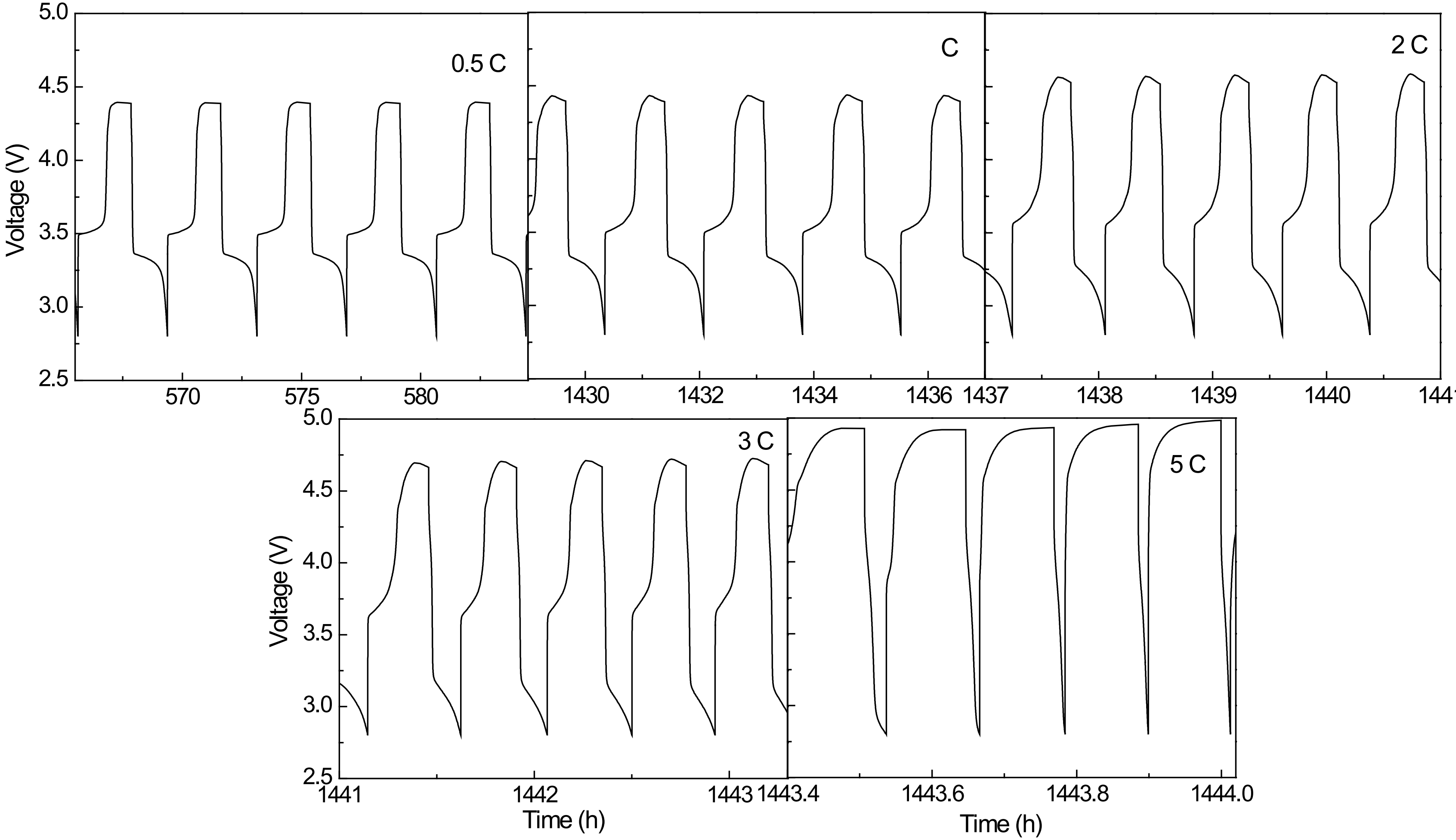
Glass Fiber Composites – Rate Capability





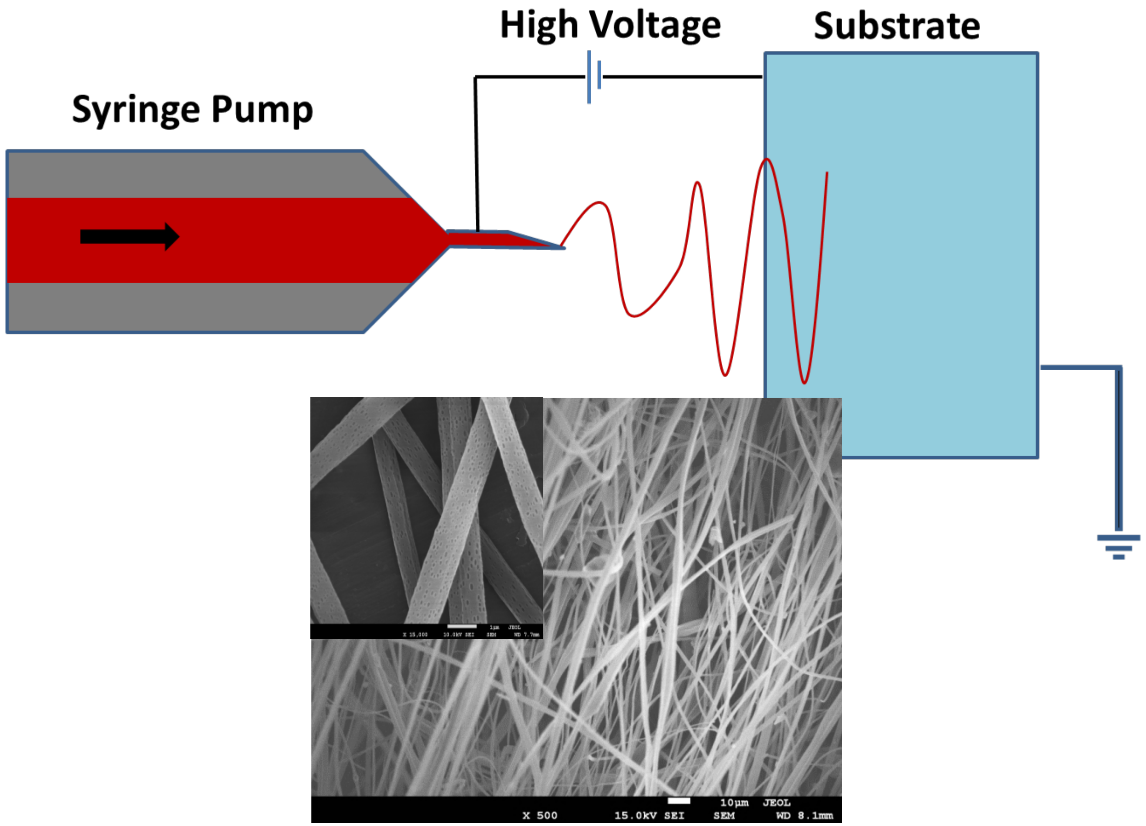
- Upper limiting voltage at 4.35 V when cycling the $LiFePO_4$ cell at 0.5C and 50% overcharge.
- 95% capacity retention after the first 350 overcharge cycles at 0.5C.
- Maintained for more than 470 overcharged cycles.

Glass Fiber Composites – Rate Capability



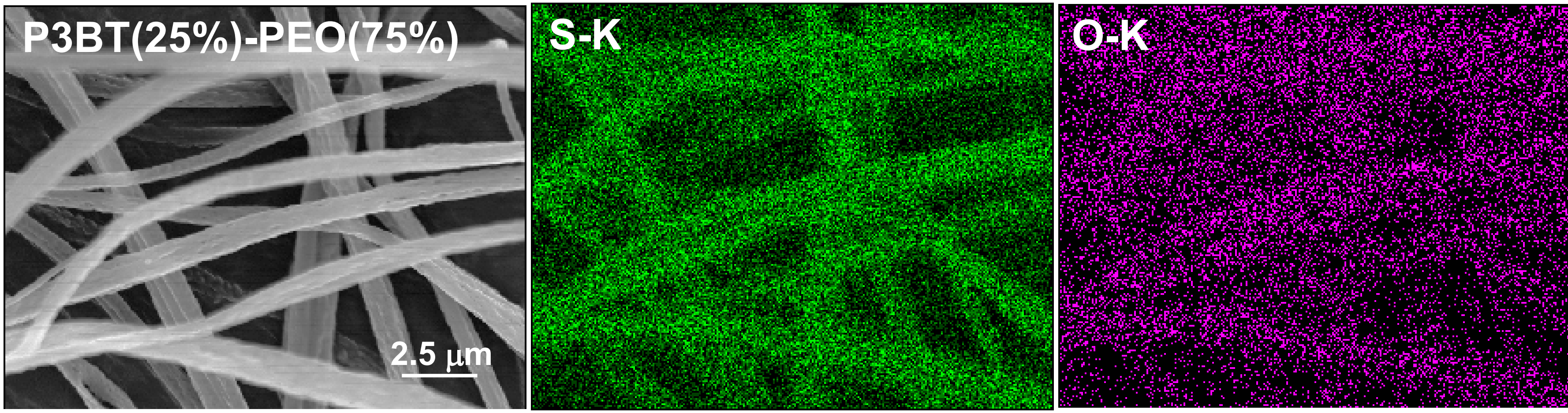
- Increased upper limiting voltage at higher cycling rates.
- Protection was effective even at 5C charging rate.

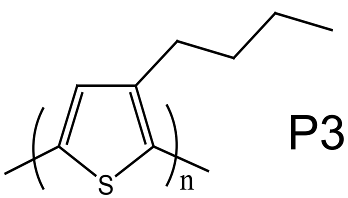
Electroactive Fibers Synthesized by Electrospinning



- Electrospinning technique used to prepare a range of electroactive fibers and fiber composites.
- Porous structure results from solvent evaporation beneficial for electrolyte absorption and wettability in the fiber composites.

Uniform Polymer Distribution in Electrospun Fiber Composites





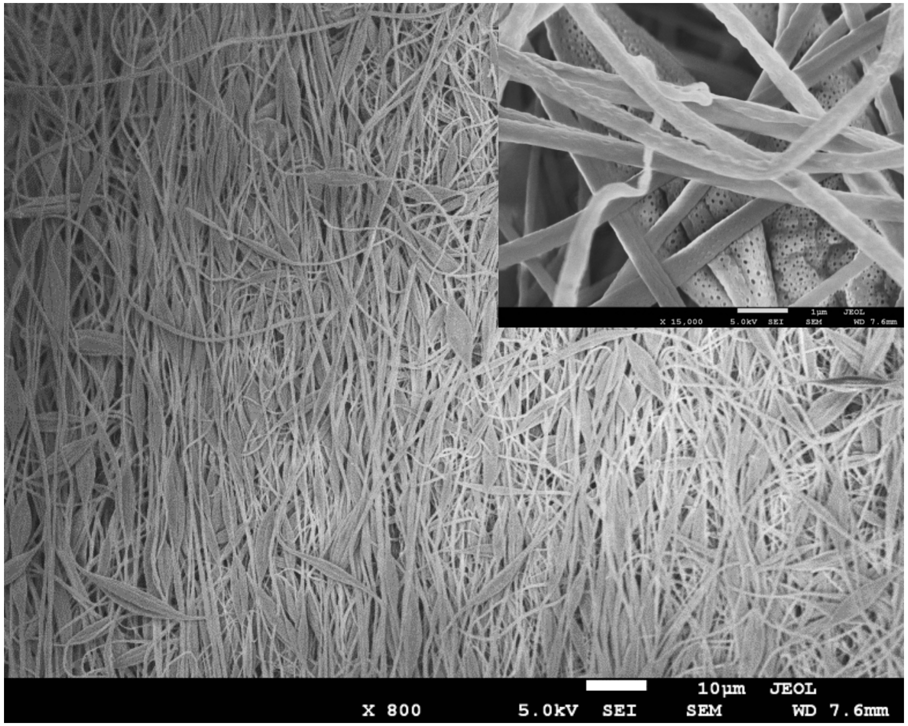
P3BT

$(\text{-}CH_2CH_2O\text{-})_n$ PEO

- Polymers are well mixed at individual fiber level - improved utilization of electroactive polymer and reduced cost for overcharge protection.

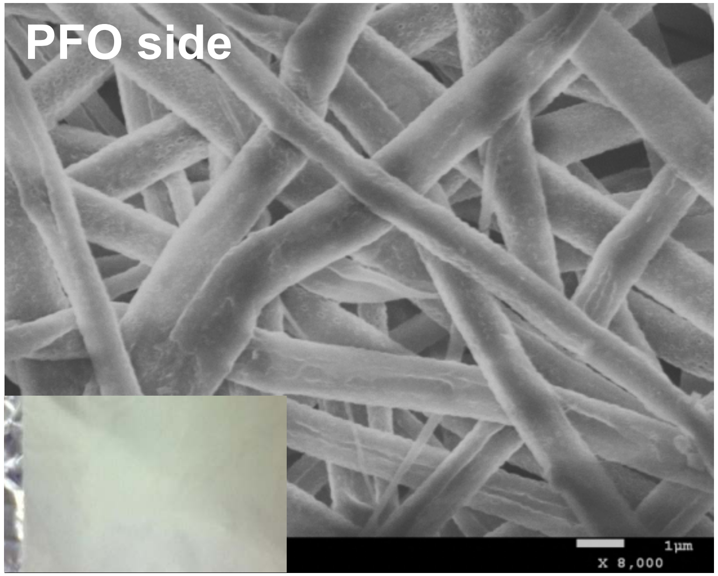
Dense Single-Layer Electroactive-Fiber Composite Membranes

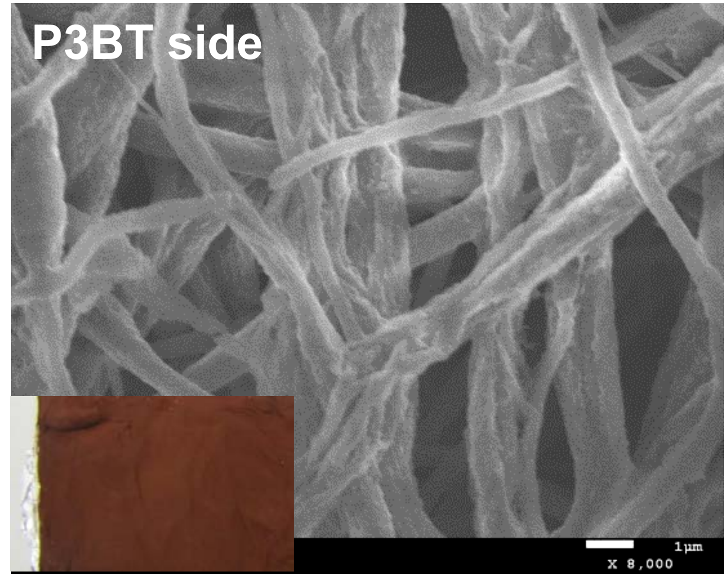
PFO (25%) - PEO(75%)



- Dense electroactive-fiber membranes made in varying compositions and film thicknesses.
- A simple, scalable, and cost-effective way to produce lithium-ion battery separators capable of voltage-regulated shunting.

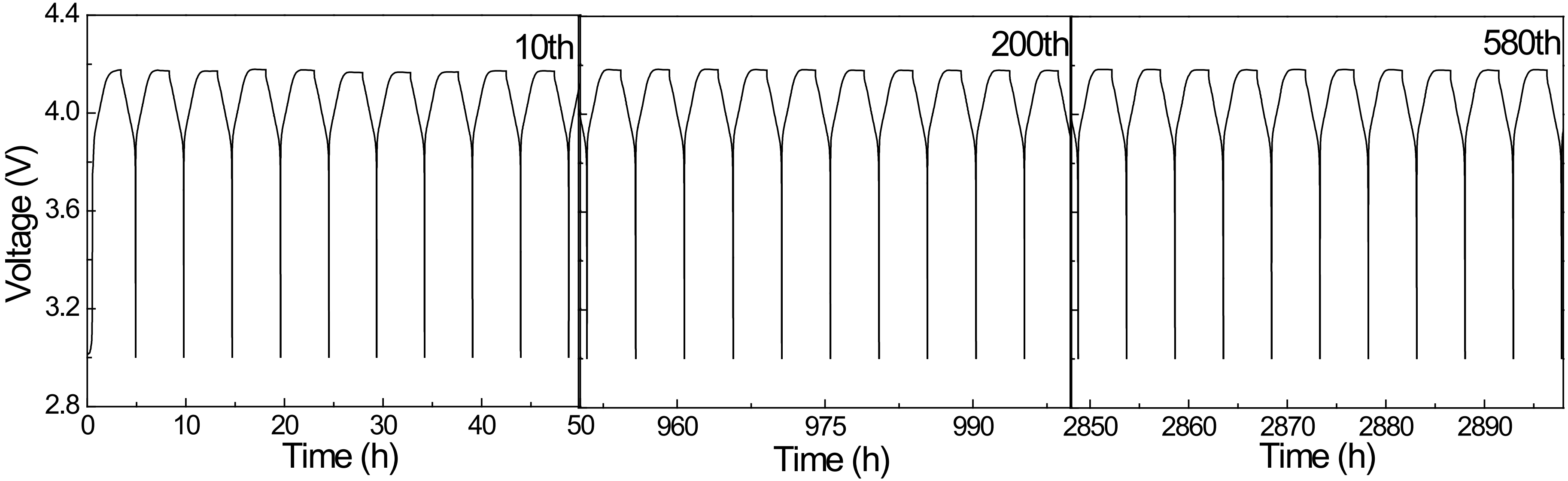
Dense Bilayer Electroactive-Fiber Composite Membranes

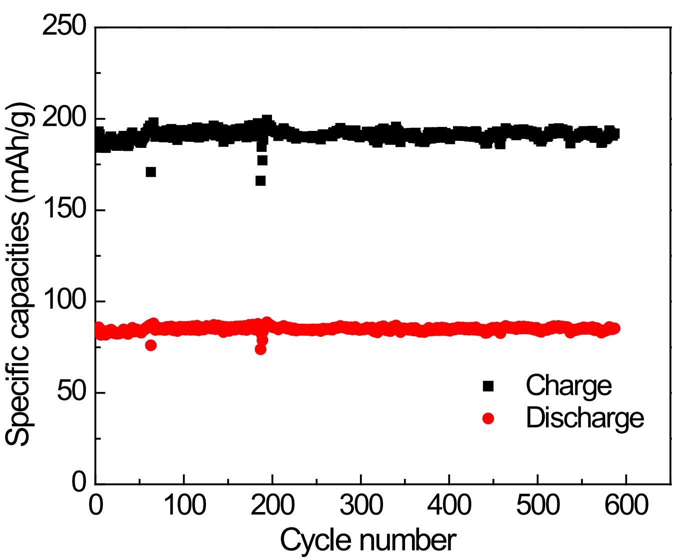




- Dense bilayer electroactive-fiber membranes made by direct deposition of the second polymer fibers on top of the first polymer fibers.
- Expansion of voltage window by placing the high-voltage polymer next to the cathode to set the protection potential and the lower-voltage polymer next to the anode to complete the reversible shunt and protect the high-voltage polymer from degradation at the anode potential.

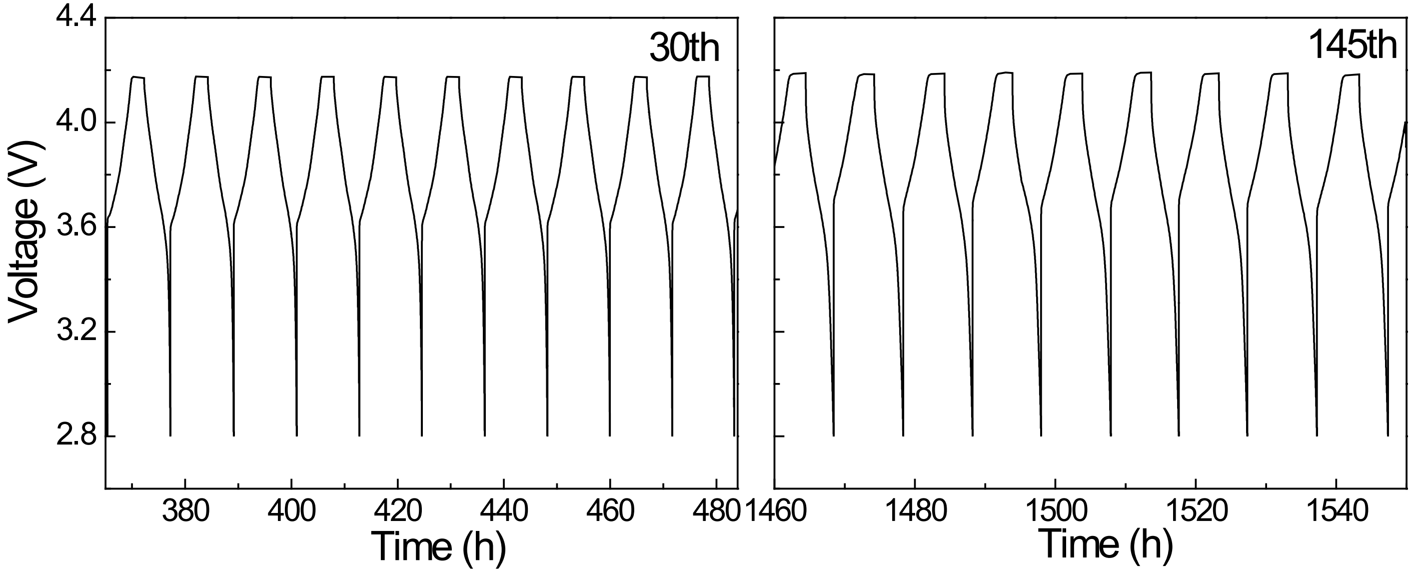
Improved Performance in Electroactive -Fiber Composite Membranes

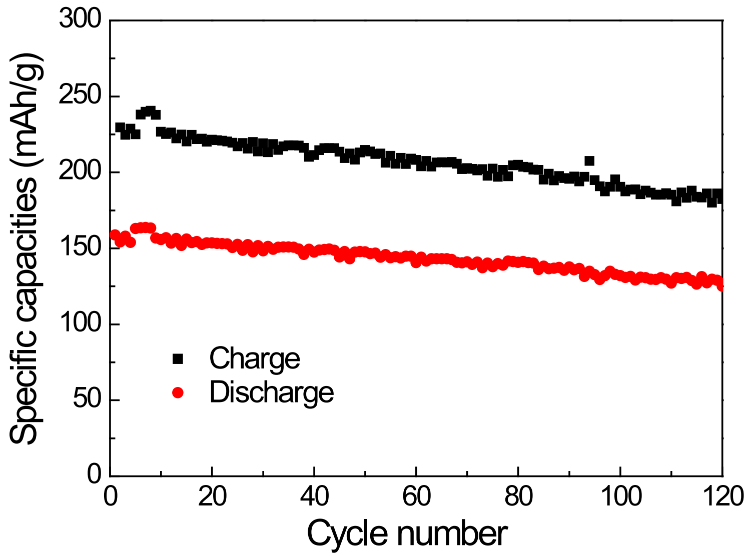




- $Li_{1.05}Mn_{1.95}O_4$ cell protected by a PFO/P3BT bilayer fiber composite. Cycled at C/2 rate and 125% overcharge.
- Improved polymer utilization and lowered internal resistance. Stable high-rate overcharge protection at 4.2 V for 600 cycles so far.

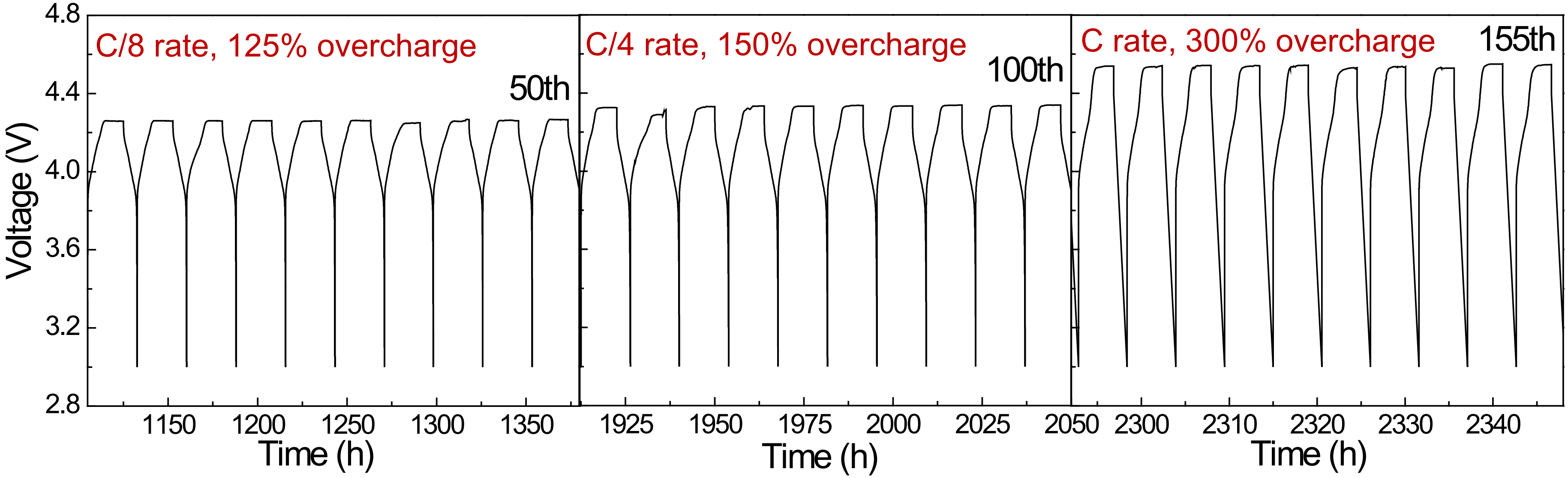
Improved Performance in Electroactive -Fiber Composite Membranes

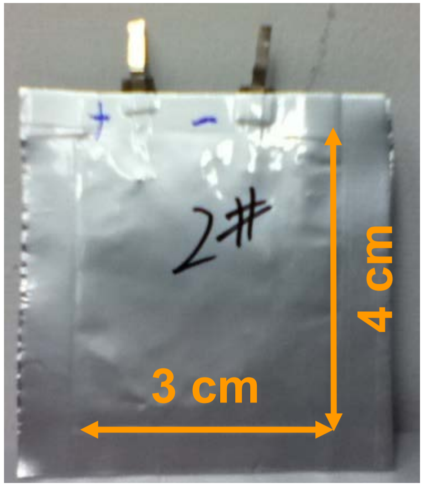




- $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen 2) cell protected by a PFO/P3BT bilayer fiber composite. Cycled at C/5 rate and 50% overcharge.
- Upper limiting voltage constant at 4.2 V, suggesting improved protection.
- The decrease in discharge capacity is likely due to the instability of Gen 2 cathode.

Feasibility in Scale-up





- Larger-sized $Li_{1.05}Mn_{1.95}O_4$ pouch cell protected by the PFO/P3BT glass fiber composite.
- The holding voltage increased with the current density. Stable protection achieved at all rates tested.

Collaborations

- Robert Kostecki (LBNL) – Raman and FTIR Spectroscopy
- Yuegang Zhang (Molecular Foundry) – Electrospinning techniques
- John Kerr (LBNL) – TGA and DSC, AFM
- Vince Battaglia, Marca Doeff, Gao Liu (LBNL) – Electrode fabrication
- Quy Ta, Brian Nguyen (American Dye Source, Inc.) – Electroactive polymer synthesis

Future Work

- Further evaluate the rate capability and cycle life of the cells protected by electrospun electroactive-fiber separators.
- Investigate alternative placement of electrospun electroactive-fiber membranes to improve cell protection performance and lower cost.
- Explore alternative high-voltage electroactive polymers that are suitable for overcharge protection in PHEV batteries. Prepare their polymer-fiber composite membranes and evaluate the performance.
- Investigate overcharge protection in cells with a high-capacity, Li and Mn rich $Li_{1+x}M_{1-x}O_2$-type cathode.
- Collaborate with industry and other national labs to continue the evaluation on scaling up the approach.

Summary

- The distribution of electroactive polymer in the composite membrane is critical in achieving efficient overcharge protection. Significant performance improvement was obtained on fiber composites.
  - The concept was first demonstrated on glass fiber composites made by solution impregnating an electroactive polymer into the Whatman membranes. A 40-fold increase in sustainable current density was obtained. High-rate protection for several hundreds of deep overcharged cycles in various cell chemistries was demonstrated for the first time.
  - A low-cost electrospinning method was developed to prepare dense electroactive-fiber composite membranes in a simple process. Protection performance was further improved due to more uniform electroactive polymer distribution, with stable and high-rate overcharge protection successfully demonstrated on both spinel and Gen 2 cells.
- Stable and high-rate overcharge protection in larger-sized pouch cells was achieved, demonstrating the feasibility in scale-up .