Overcharge Protection for PHEV Batteries

Guoying Chen and Thomas J. Richardson
Lawrence Berkeley National Laboratory

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Project ID: ES037

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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
  - FY09 $190K
  - FY10 $190K
  - FY11 $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 overcharge protection performance of polymer-fiber incorporated composite separators (Jun. 2012).
- Evaluate the property and performance of new high-voltage electroactive polymer candidates (Jul. 2012).
- Report overcharge protection for pouch cells and other large-scale battery cells (Sep. 2012).
- Attend review meetings and present research results.

The Need for Overcharge Protection

Causes of overcharge

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

Consequences of overcharge

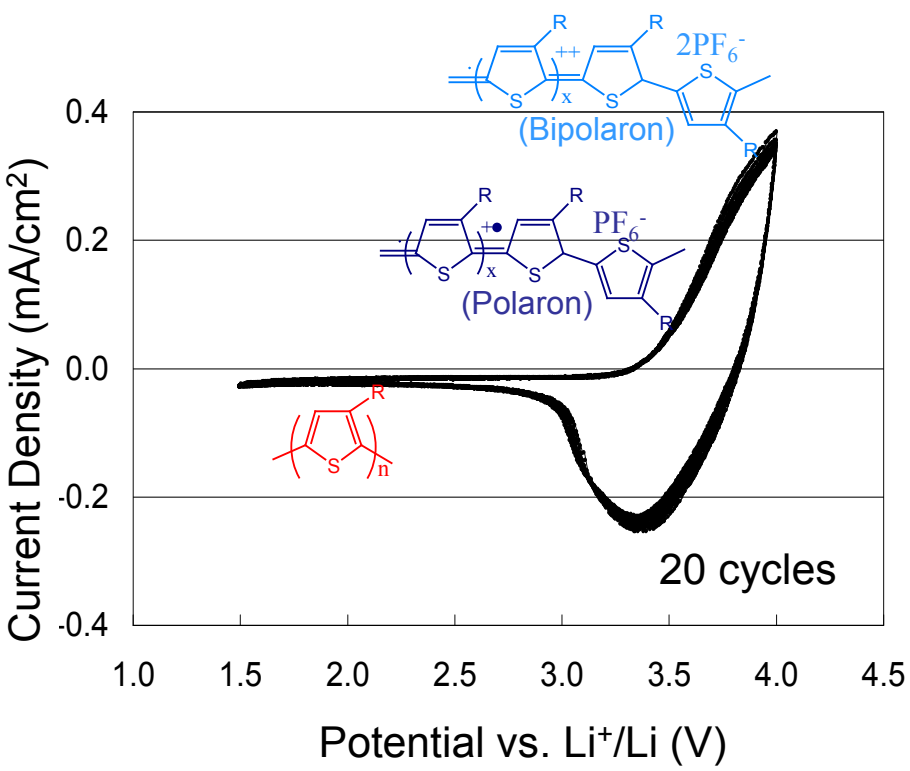
- Cathode degradation, metal ion dissolution, O_2 evolution
- Electrolyte breakdown, CO_2 evolution
- Li deposition on anode, H_2 evolution
- Overheating, breakdown of anode SEI layer and thermal runaway
- Current collector corrosion
- Explosion, fire, toxics released
- Accelerated capacity/power fade,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

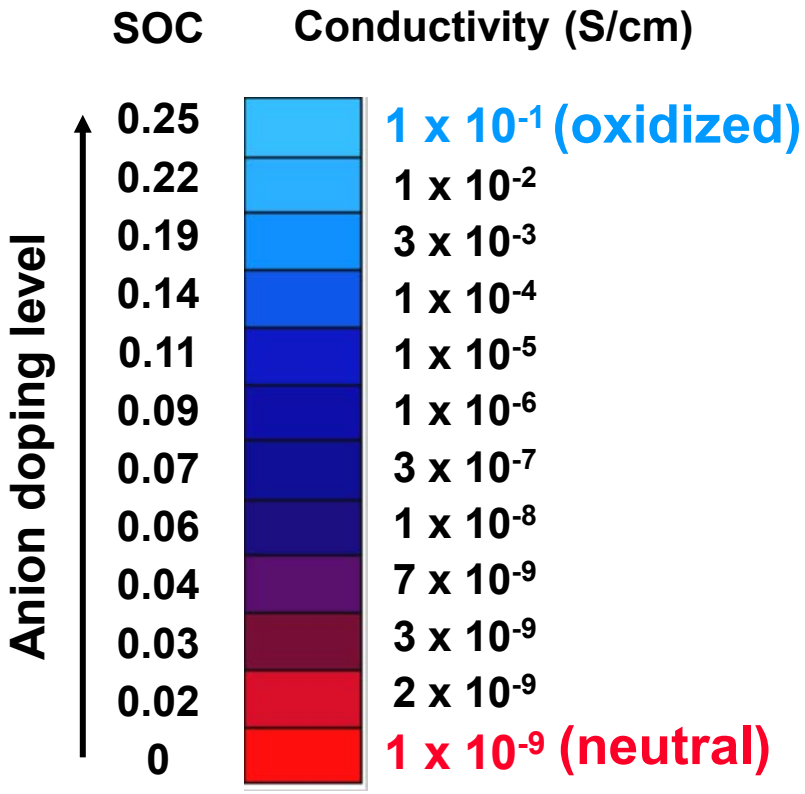
Series-connected $LiFePO_4$ battery pack

http://stores.headway-headquarters.com

http://www.rokemneedlearts.com

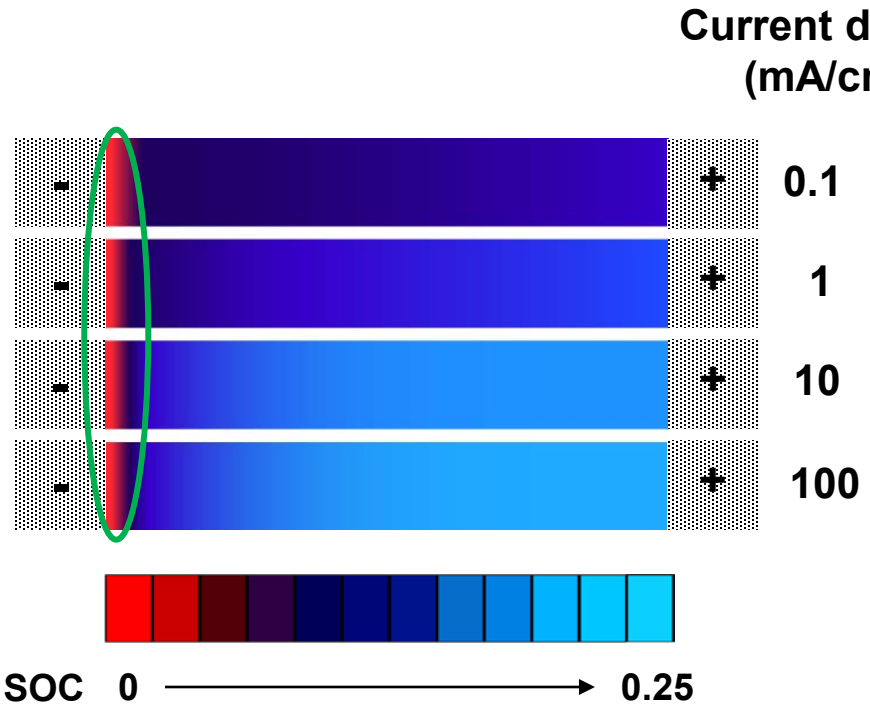
Our Approach – Electroactive Polymers





- 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.

Our Approach – Protection Mechanism

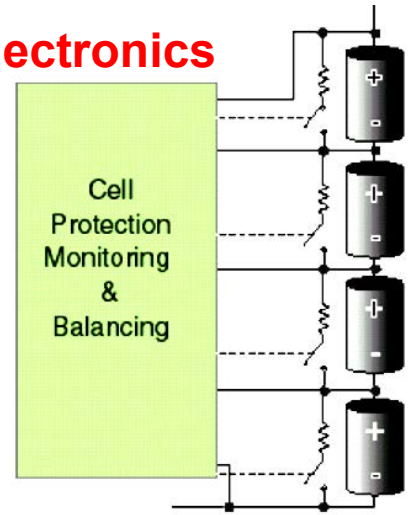


- Potential drop occurs at the small region close to the negative electrode
  - Provides soft-shorting
  - Good for heat transfer out of the cell
- Polymer is capable of carrying a large amount of current.
- System simulation validated by experimental observation.

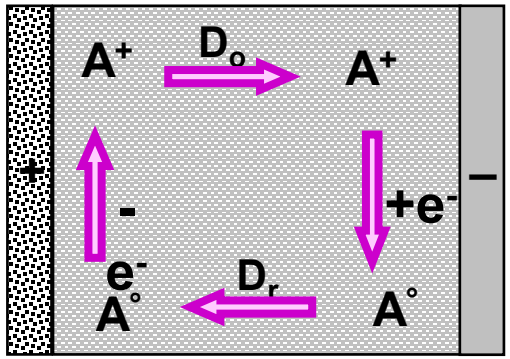
Our Approach – Advantages

External electronics

- Expensive
- Added weight and volume
- One bad cell kills the whole string

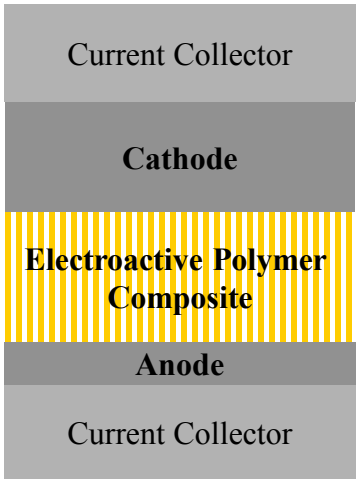


Redox shuttle method

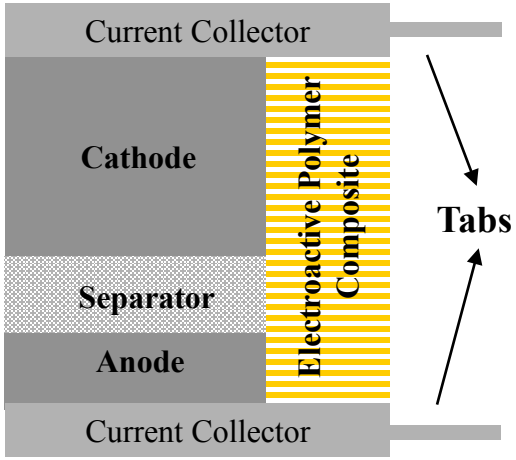


- Diffusion limited - low rate capability and poor low temperature performance
- Interference with the cell chemistry
- Solubility and volatility issues

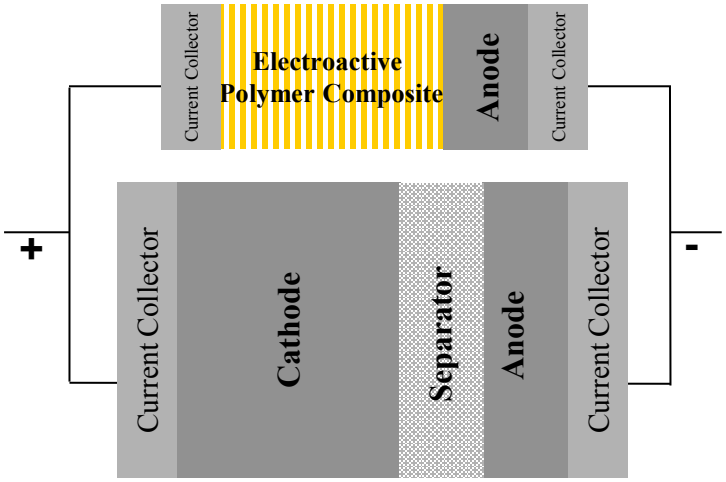
Versatility of the polymer approach – cell configuration



Sandwich



Parallel



External

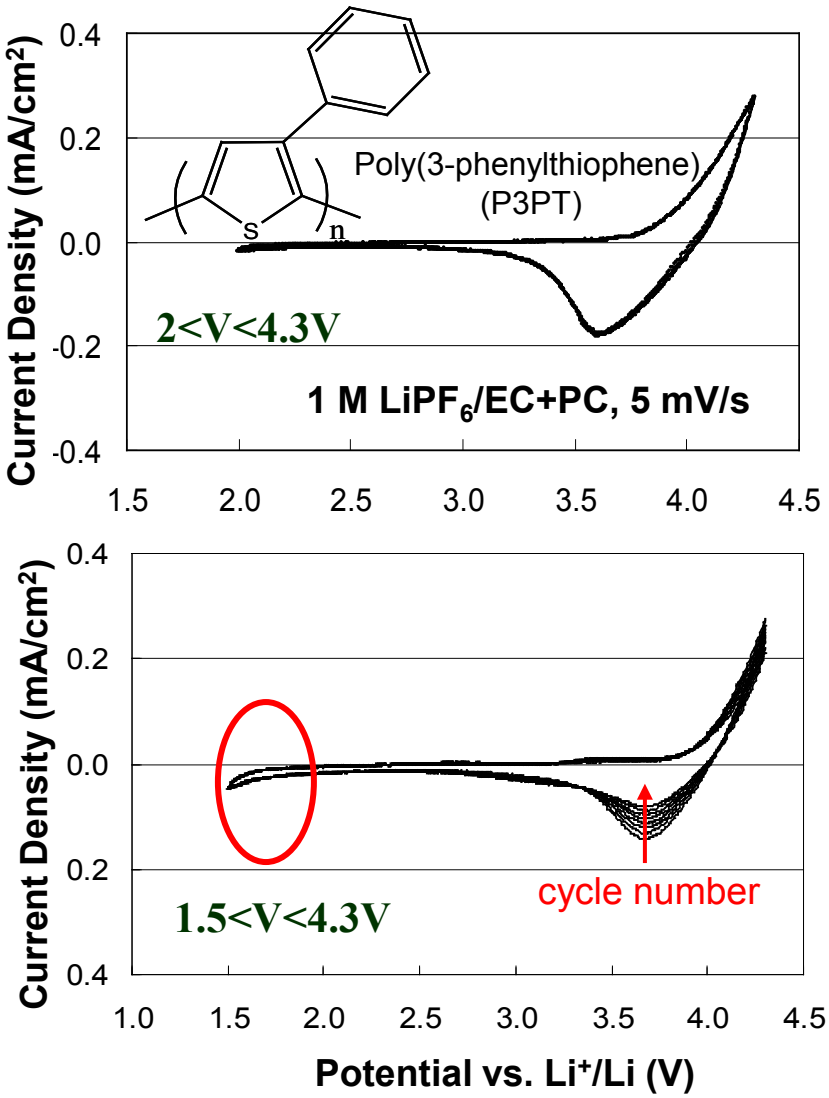
Technical Accomplishments

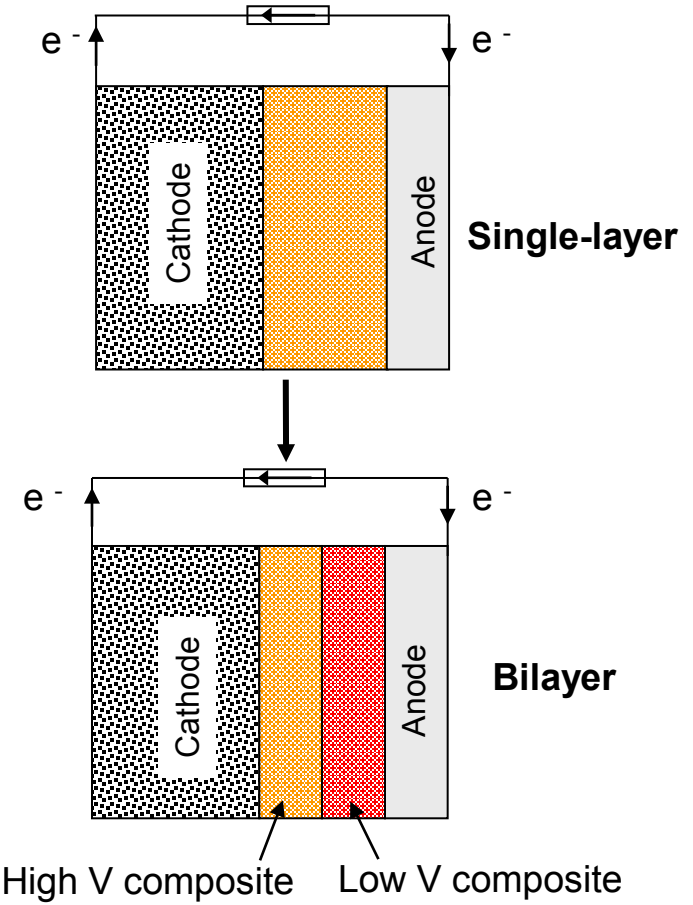
- PFOP was found to have an extended stability window in lithium battery electrolytes. Its ability to provide single-polymer overcharge protection was demonstrated.

- Modification on electroactive polymer composites led to 20x increase in sustainable current density and excellent long-term overcharge protections for several cell chemistries, including Gen2 and Gen3.

- Electroactive polymer-fibers and their composite mats were prepared by an electrospinning technique. The behavior of the fibers as charge carriers in Li-ion batteries was characterized in an *in situ* optical cell.

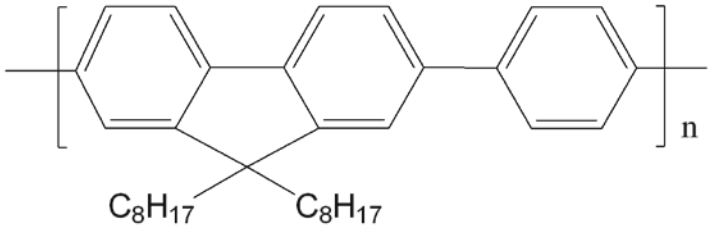
Polymer Stability Window



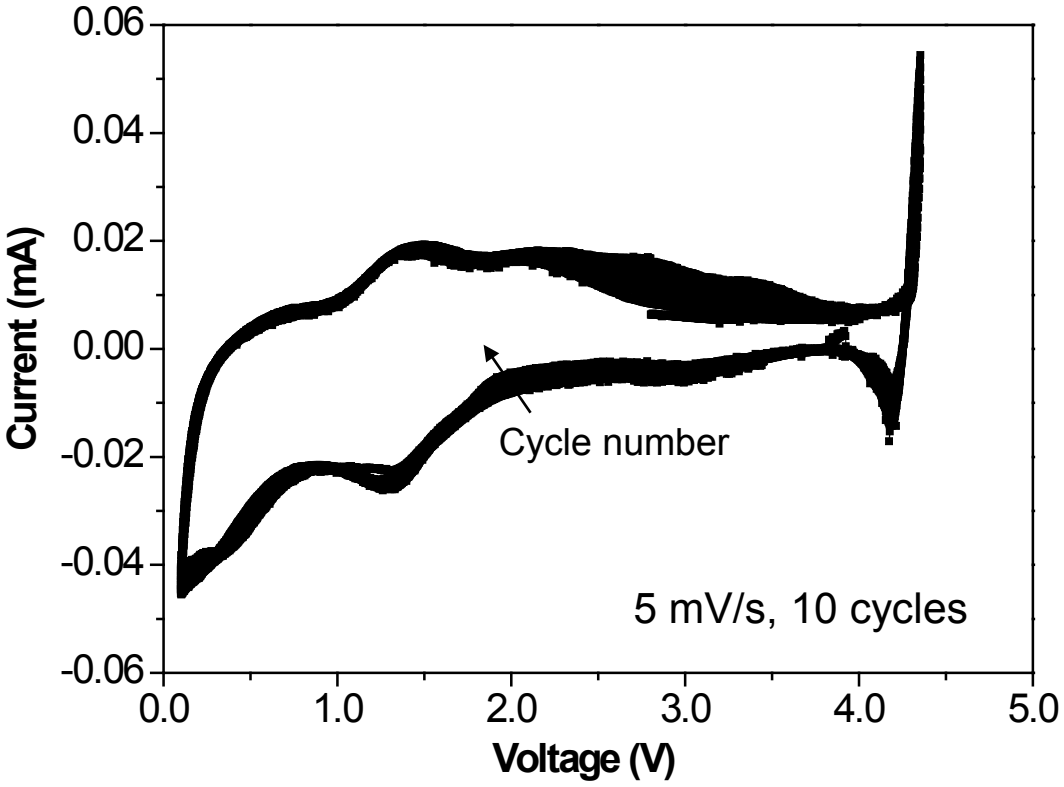


- A bilayer arrangement was previously adapted to protect the high-voltage polymer from degradation at the anode potential.

Extended Redox Window in PFOP

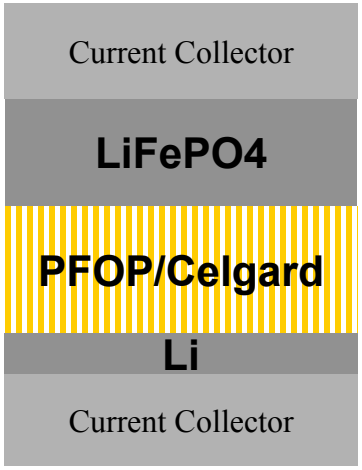


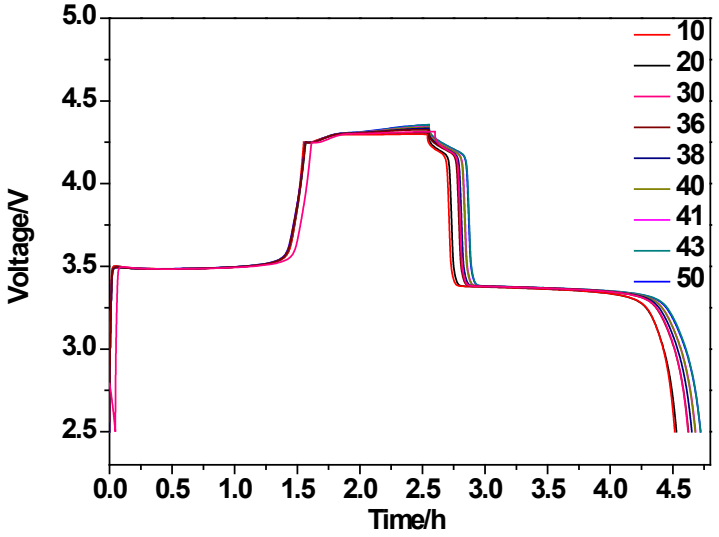
Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)] (PFOP)



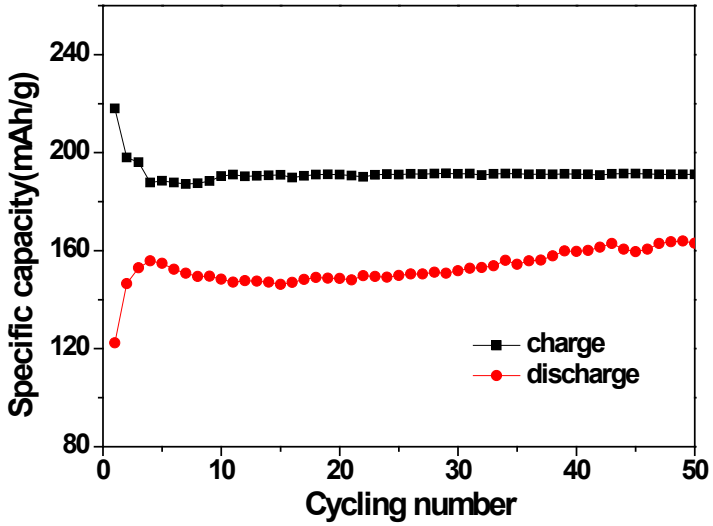
- PFOP has the highest onset oxidation voltage (4.25V) among the investigated electroactive polymers.
- Improved low-voltage stability at anode.

Single-polymer Protection Achieved





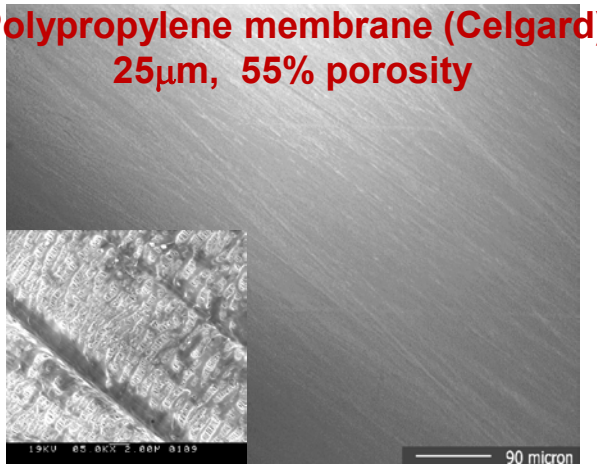
- Cell cycled at 0.5C and 40% overcharge.
- Improved low-voltage stability allows for stable single-polymer protection.
- Improved discharge capacity upon cycling may be a result of enhanced conduction in the electrode.

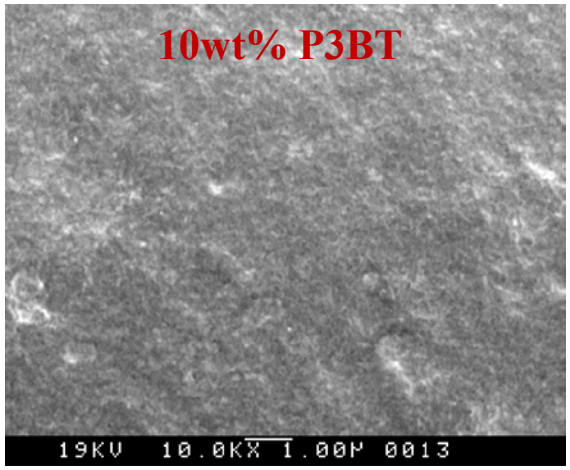


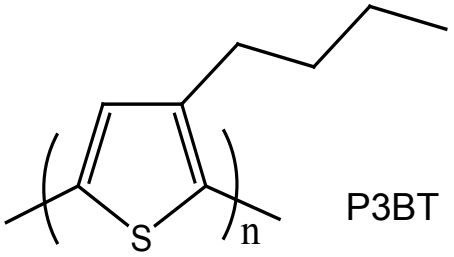
Composites Modified for Better Polymer Distribution

Membrane substrate **P3BT + membrane composite**

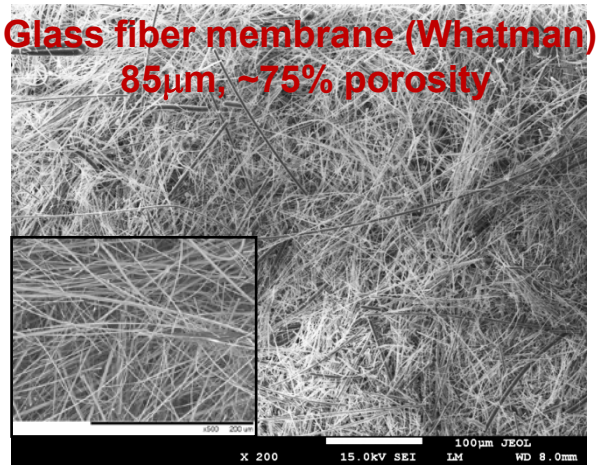
Polypropylene membrane (Celgard)
25μm, 55% porosity

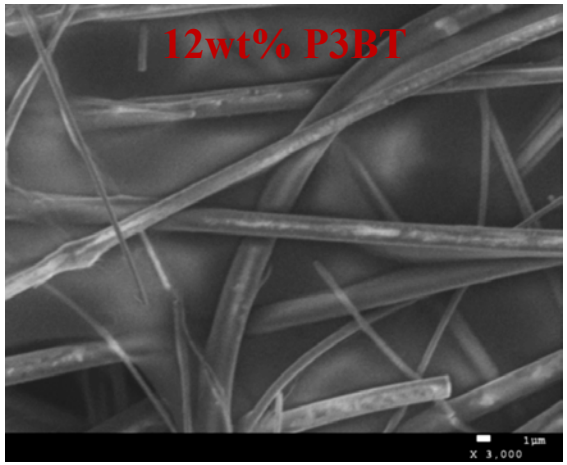






Glass fiber membrane (Whatman)
85μm, ~75% porosity

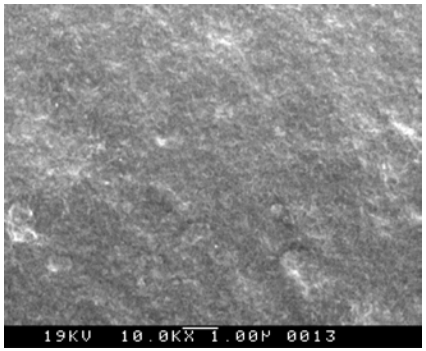


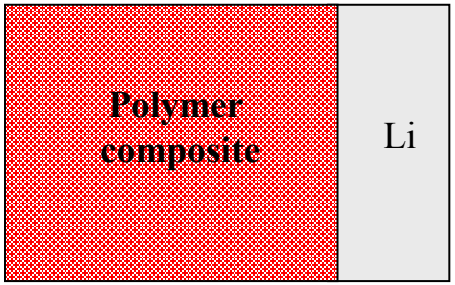


- Large porosity and open pore structure in the glass fibers led to more uniform polymer distribution in their composites.

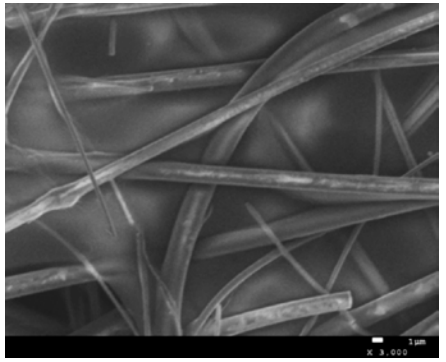
Improved Sustainable Current Density in Modified Polymer-composites

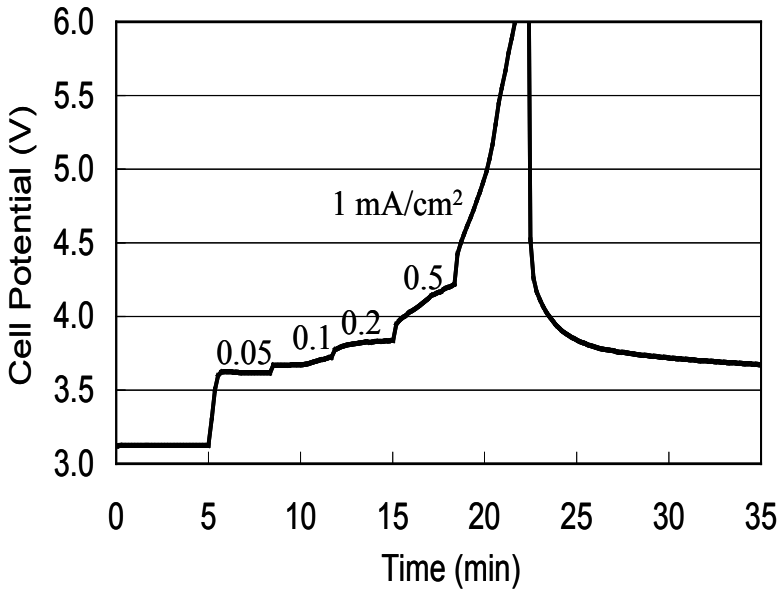
P3BT/Celgard composite

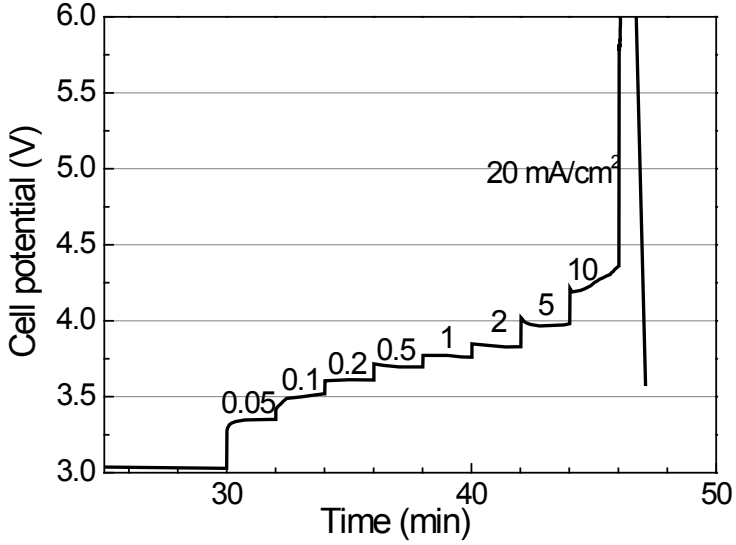




P3BT/glass fiber composite

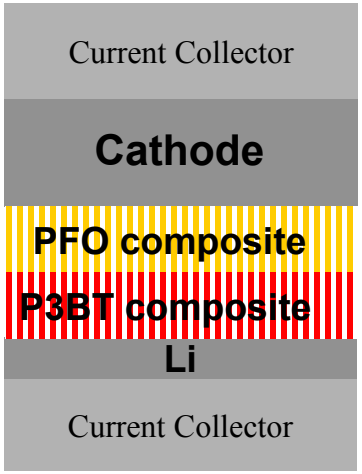


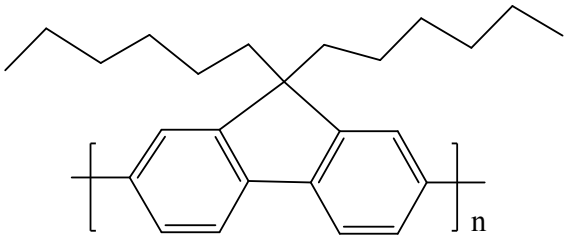




- Up to 20x improvement in sustainable current density.

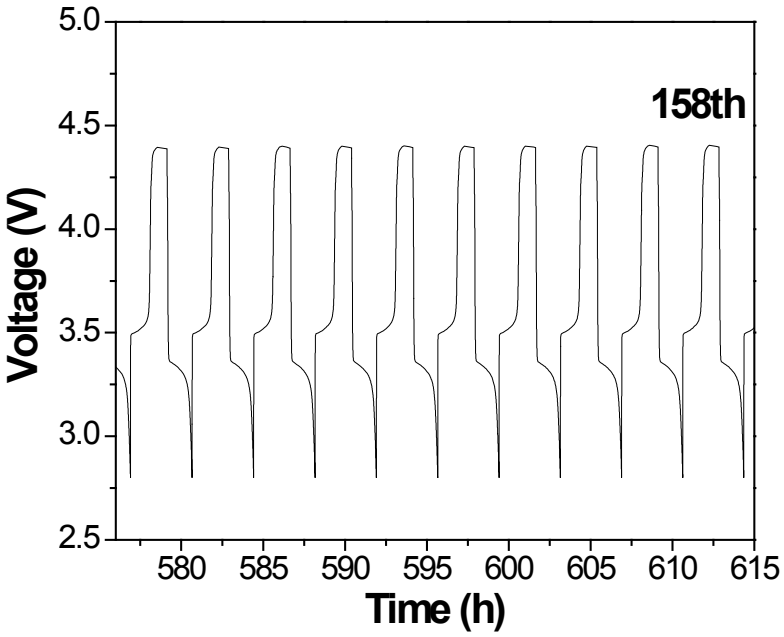
Long-term Overcharge Protection Achieved – $LiFePO_4$ Cell

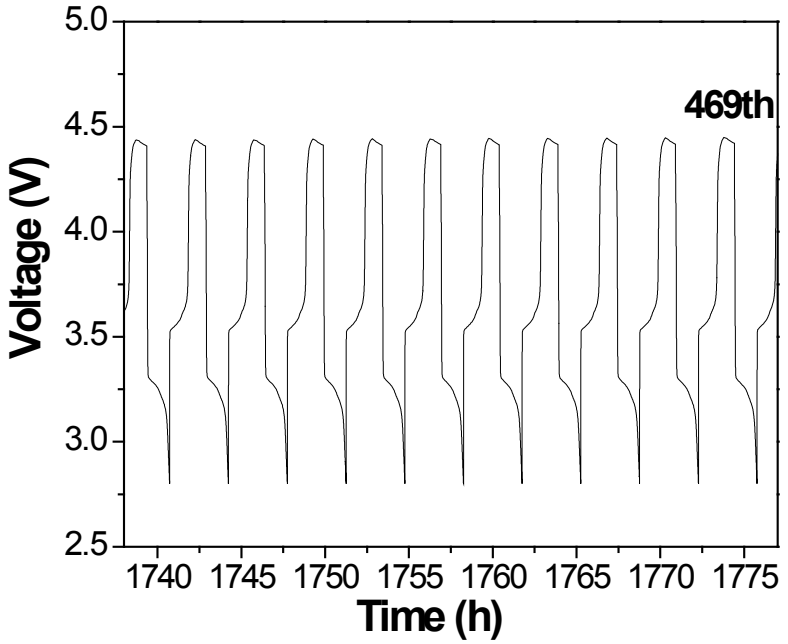




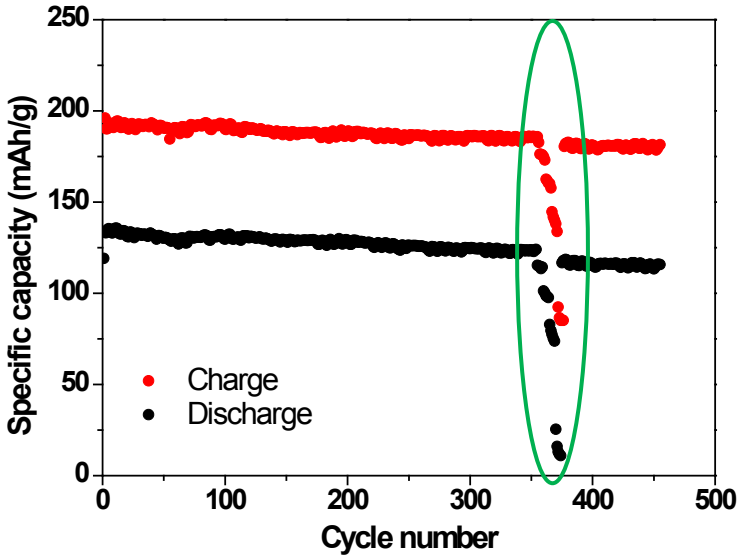
Poly(9,9-dioctylfluorene)
(PFO)

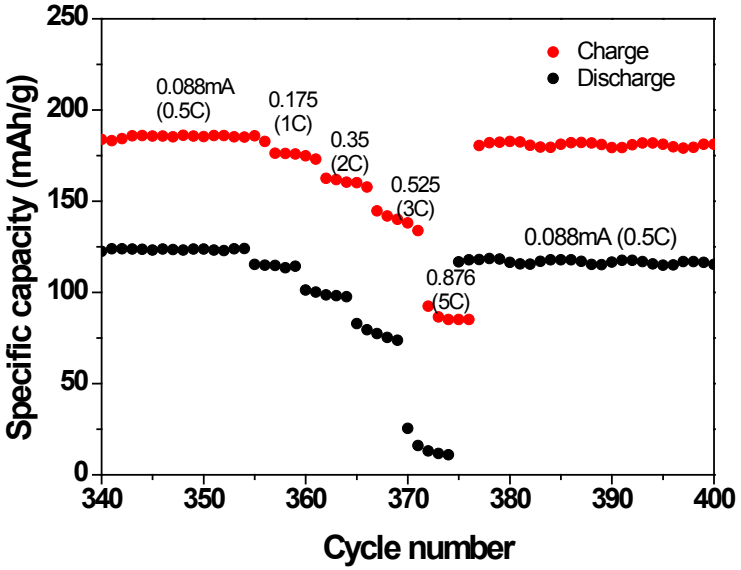
- Cycled at 0.5C rate and 50% overcharge.
- Upper cell voltage limit at 4.4V, maintained for more than 470 overcharge cycles.



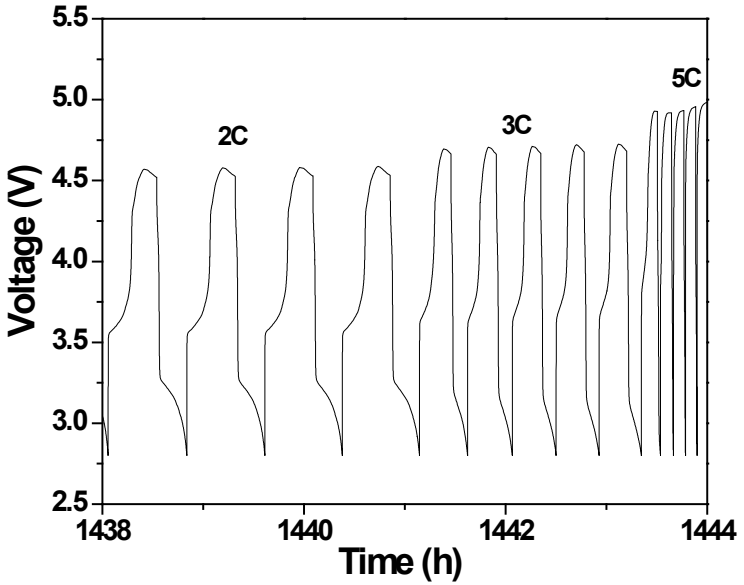


Long-term Overcharge Protection Achieved – $LiFePO_4$ Cell

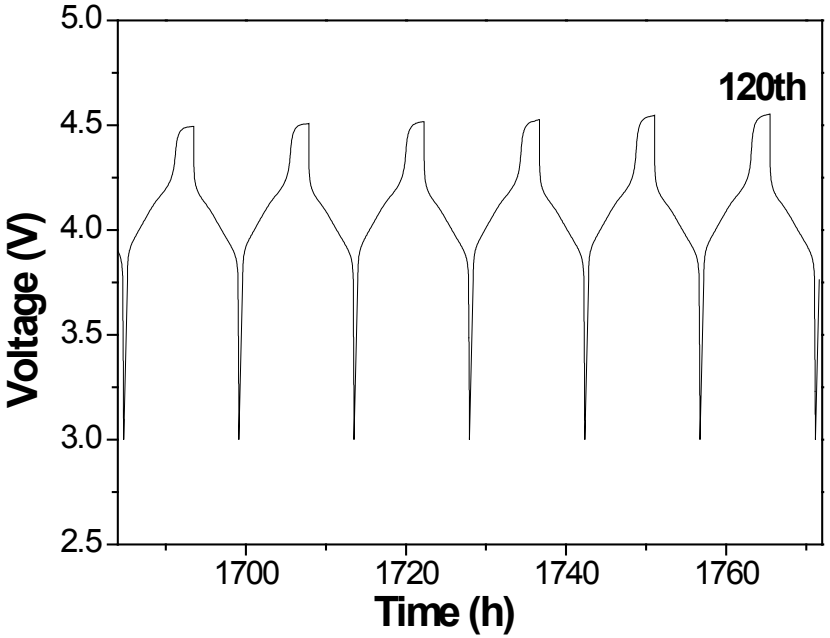


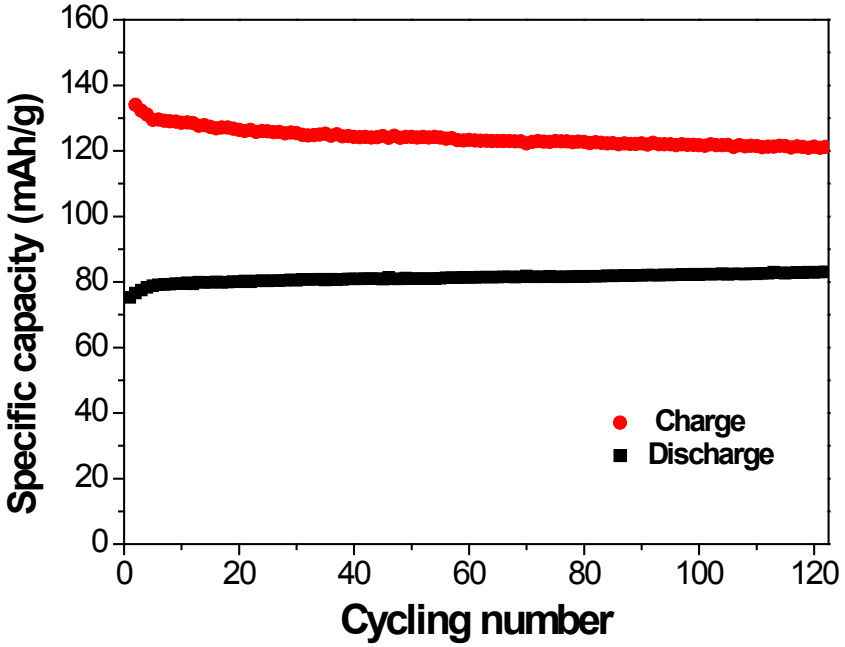


- Increased upper cell voltage limit at higher rates.
- Protection achieved even at 5C charging rate.
- 95% capacity retention after the first 350 overcharge cycles at 0.5C.



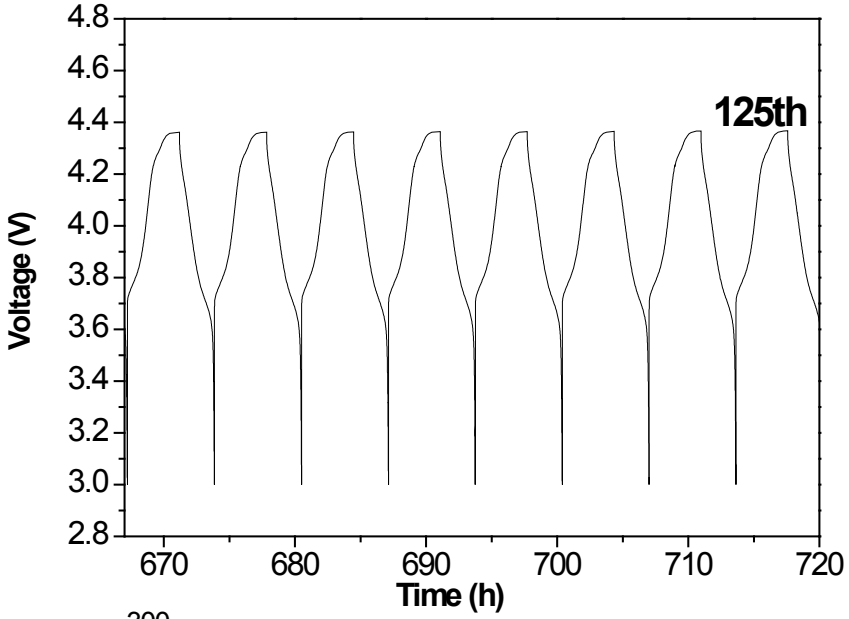
Long-term Overcharge Protection Achieved – Spinel $Li_{1.05}Mn_{1.95}O_4$ Cell

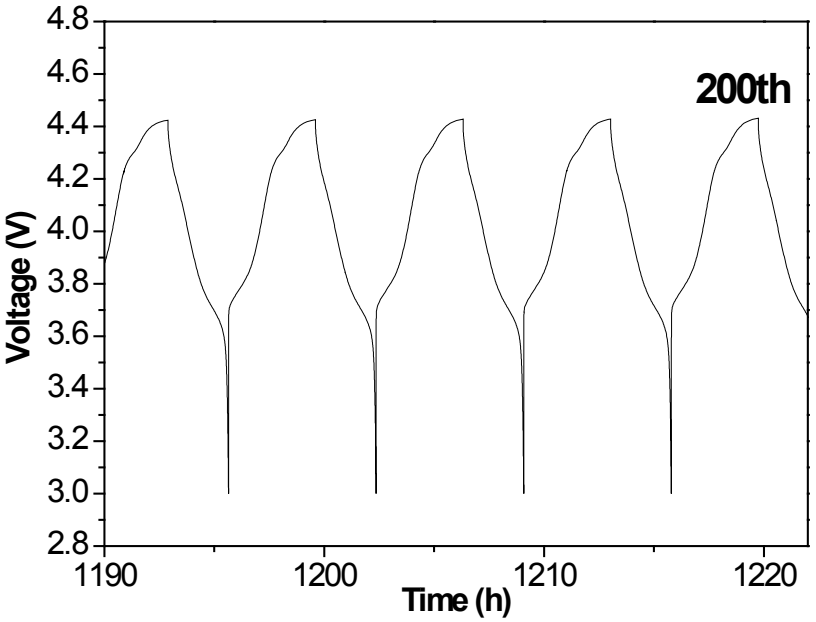


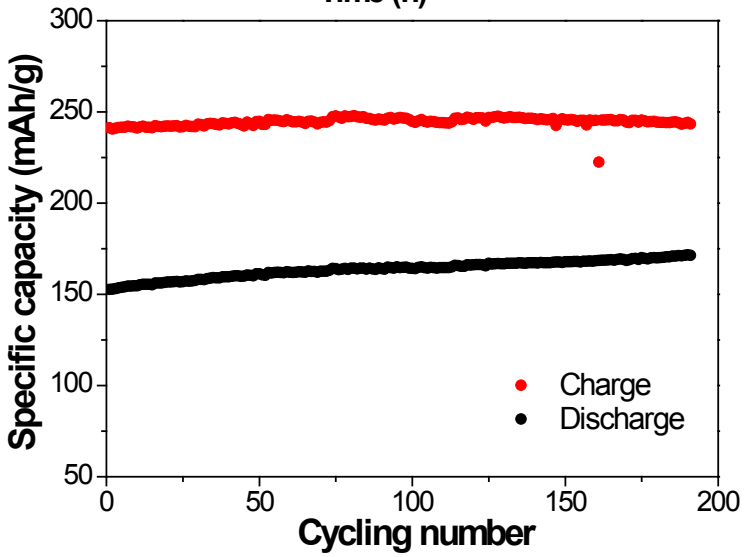


- Cycled at 0.2C rate and 60% overcharge.
- Upper cell voltage limit at 4.45V.
- Discharge capacity maintained for more than 120 overcharge cycles.

Long-term Overcharge Protection Achieved – $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cell

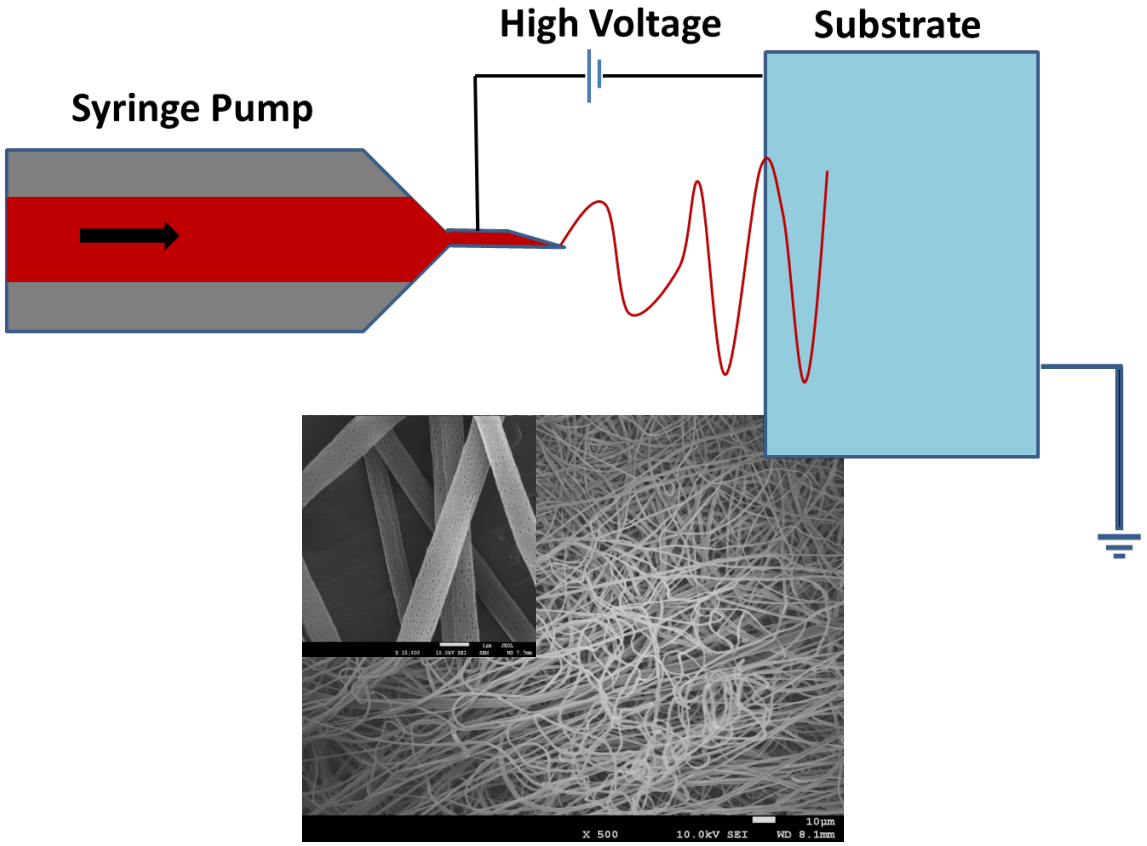






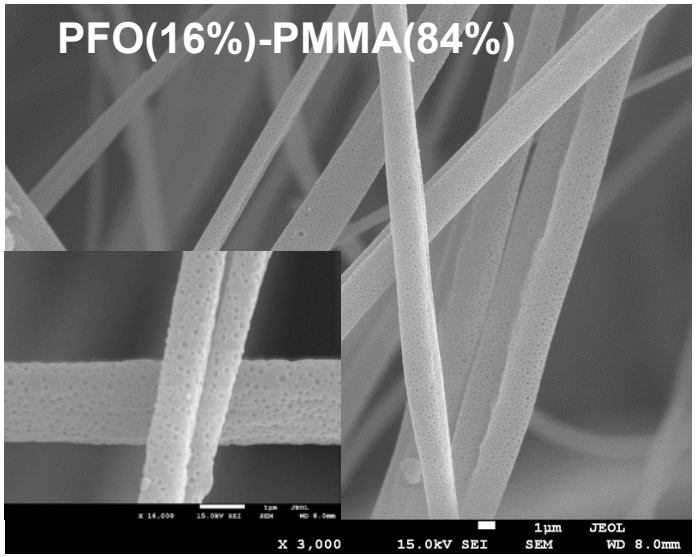
- Cycled at 0.5C and 50% overcharge.
- Upper cell voltage limit increased from 4.35 to 4.4V during the first 200 overcharge cycles, which results in a slight increase in discharge capacity.

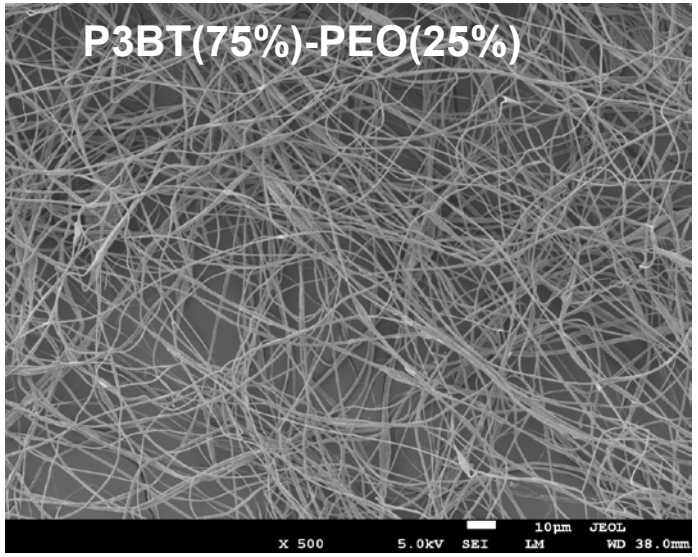
Electroactive-fibers Synthesized by Electrospinning

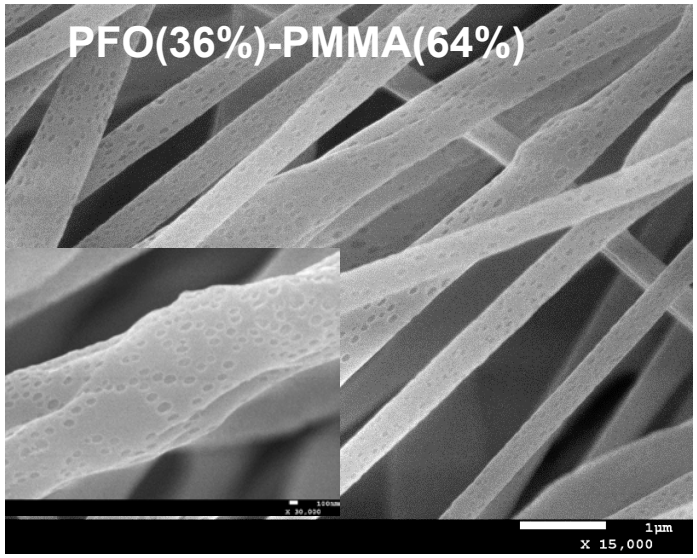


- Modification in electrospinning successfully made to produce polymer fibers from non-aqueous solution in a easily scalable manner.

Versatility of Electrospinning



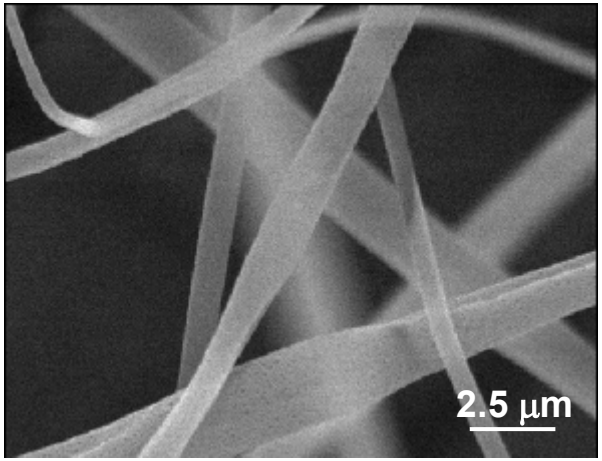


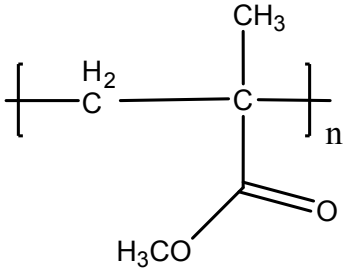


- The technique can be used to prepare a range of electroactive fibers and fiber-composites.
- Porous structure results from solvent evaporation may be beneficial for electrolyte absorption and wettability.

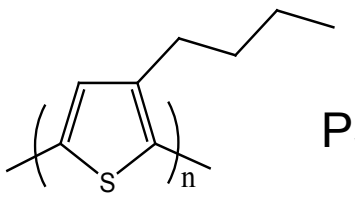
Uniform Polymer Distribution in Fiber-composites

P3BT(22%)-PMMA(78%)

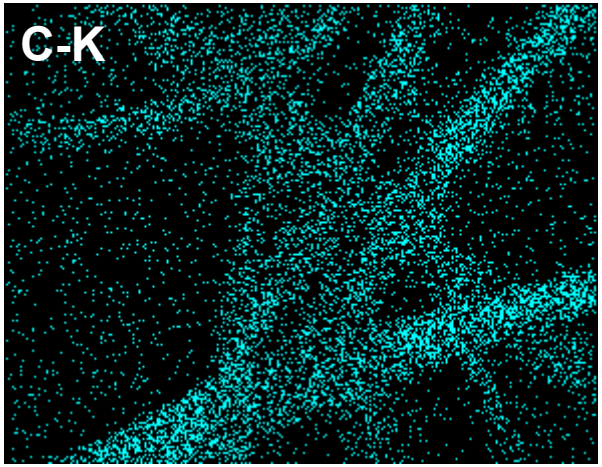


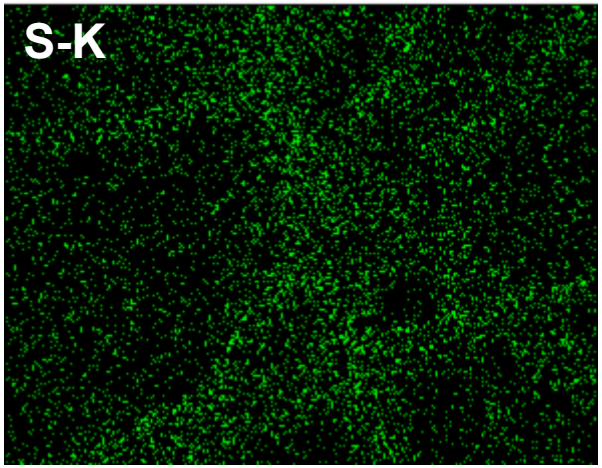


PMMA



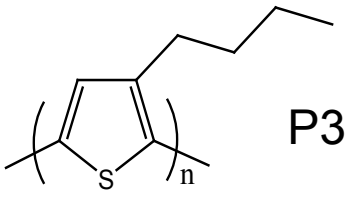
P3BT





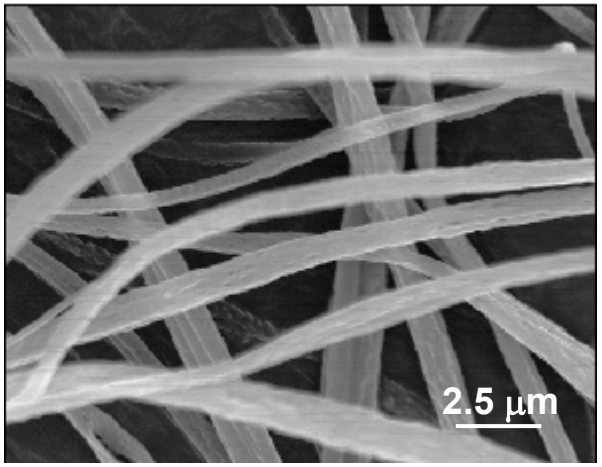
Uniform Polymer Distribution in Fiber-composites

$(-CH_2CH_2O-)_n$ PEO

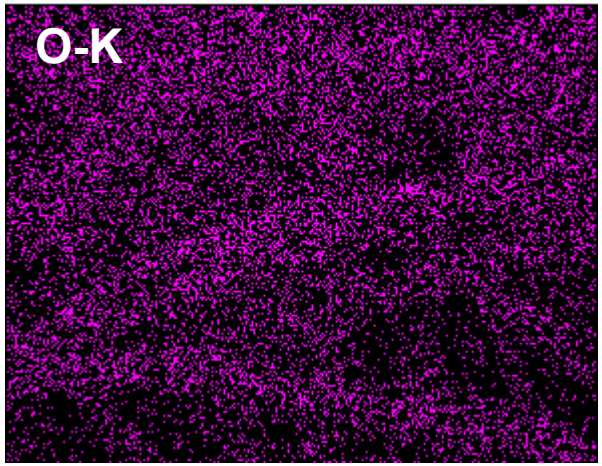


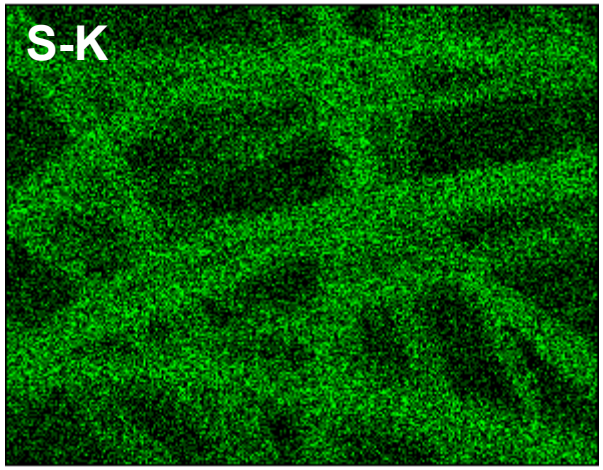
P3BT

P3BT(75%)-PEO(25%)

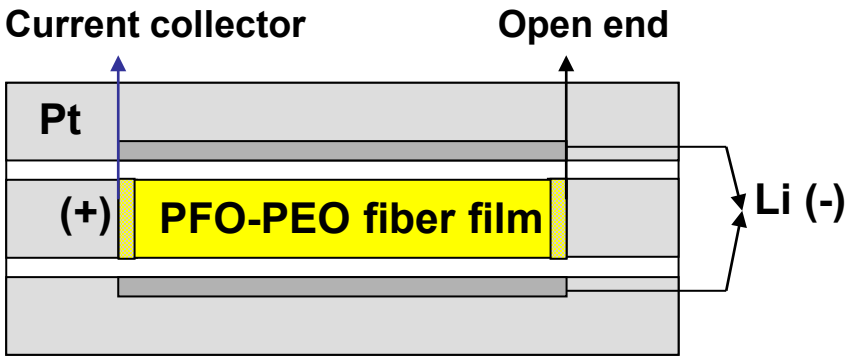


- Polymers are well mixed at individual fiber level.
- Electrospinning Improves utilization and efficiency of the electroactive polymer, and reduces the cost of overcharge protection.

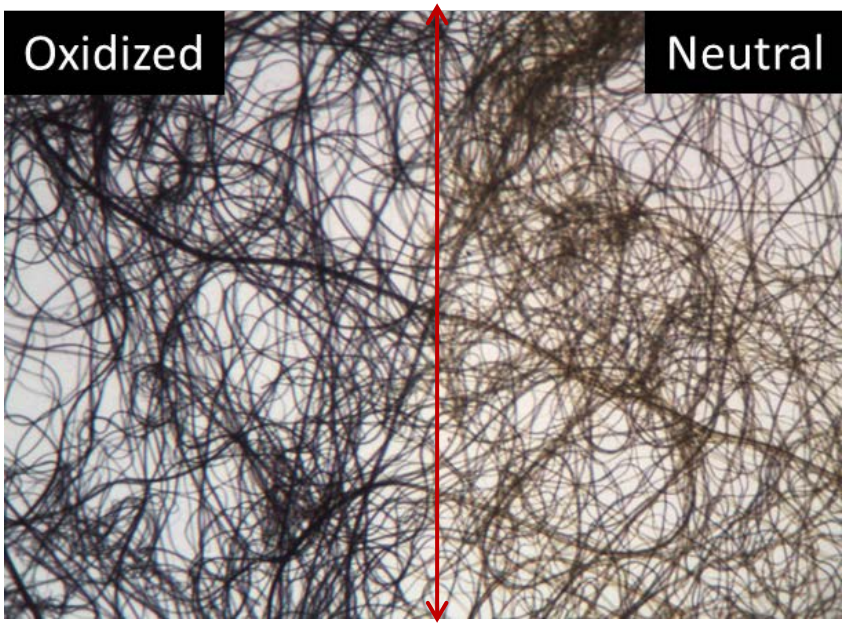




Current Passage in the Fiber-composite Film



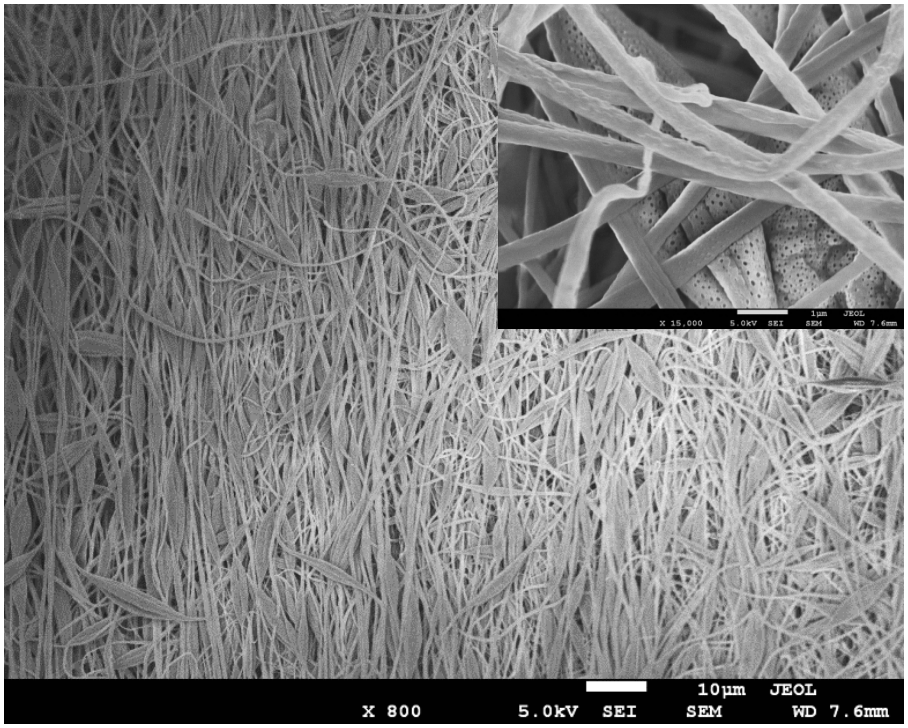
I=40mA/cm^2, V=4.25V



- Color changes from yellow to black upon oxidation.
- Distinct boundary between the oxidized and the neutral PFO suggests sufficient inter-connection between fibers for charge carriers to propagate across.

Electroactive-fiber-composite Membranes Made by Electrospinning

PFO (25%) - PEO(75%)



- Dense electroactive-fiber membranes can be made in various thickness.
- A cost-effective way to produce lithium-ion battery separators capable of voltage-regulated shunting.

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

- Evaluate rate capability and cycle life of the cells protected by electrospun electroactive-fiber-separators.
- Explore alternative polymer placement in the cells that may lead to improved protection and lowered cost.
- Continue to explore other high-voltage electroactive polymers that are suitable for overcharge protection for PHEV batteries. Optimize the morphology of their composites for maximum protection.
- Investigate overcharge protection for the cells with other high-voltage cathodes, particularly the Li and Mn rich $Li_{1+x}M_{1-x}O_2$-type cathodes.
- Collaborate with industry and other labs to “scaling-up” the approach.

Summary

- An electroactive polymer with extended stability window was discovered, which was found to be capable of single-polymer overcharge protection for lithium-ion battery cells.
- The distribution of polymer in the composite is critical for long-term overcharge protection. Protection for hundreds of cycles can be achieved by using the glass fiber composites with better distribution.
- Electroactive-fiber-composite membranes with uniform polymer distribution were made by electrospinning. This type of membranes are expected to provide improved protection with higher polymer utilization and efficiency, and they can be flexible in their placement in the cells.
- Electrospinning can be a cost-effective way to achieve overcharge protection using the electroactive polymer approach.