Overcharge Protection for PHEV Batteries

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Project ID: ES037

Overview

Timeline

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

Budget

- Total project funding
  - FY09 $190K
  - FY10 $190K
  - FY11 $250K

Barriers Addressed

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

Partners

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

Objectives\Milestones

Objectives

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

Milestones

- Report the properties of alternative high-voltage electroactive polymer candidates (July 2011).
- Report overcharge protection performance of modified polymer composite separators and cell configurations (September 2011).

Why Overcharge Protection

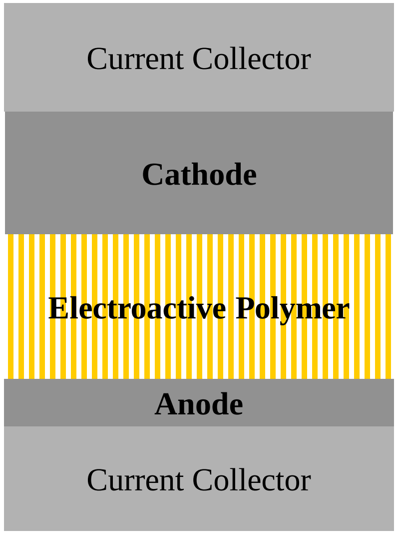
- Batteries are overcharged for a variety of reasons:
  - Cell imbalance due to manufacturing inconsistencies or temperature/ pressure variations during cycling
  - Charging at normal rates exceeding electrode capacity
  - Charging at a rate too high for one electrode (commonly the anode) without exceeding the maximum voltage
  - Over-voltage excursions for short or long periods
  - Low-temperature operation under high internal resistance

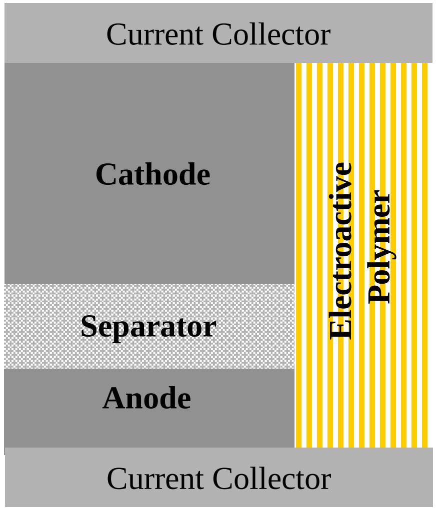
- Overcharging Li-ion batteries can lead to:
  - Cathode degradation, metal ion dissolution, O_2 evolution
  - Electrolyte breakdown, CO_2 evolution
  - Li deposition on anode, H_2 evolution
  - Overheating, breakdown of anode SEI layer and thermal runaway
  - Current collector corrosion
  - Explosion,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

Approach

Incorporating a reversible, resistive polymer shunt regulated by cell voltage

- “Sandwich-type” configuration – electroactive polymer impregnated in the separator between the battery electrodes
- Parallel configuration – Electroactive polymer placed between the current collectors, outside the electrode assembly





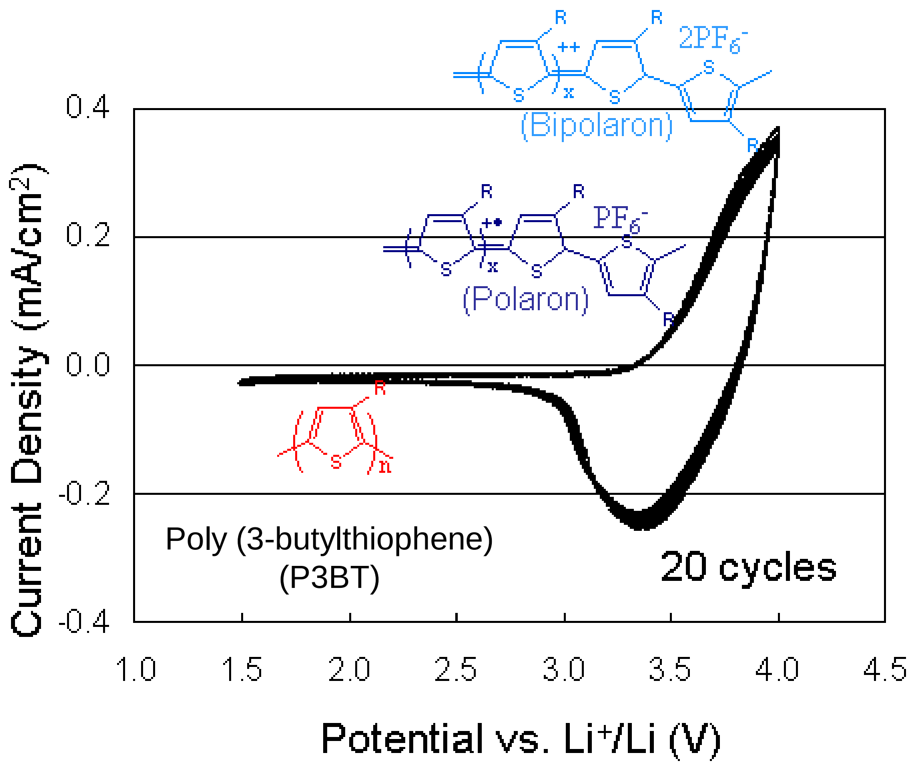
Advantages of Our Approach

- **Advantages over external methods (such as integrated control circuits)**
  - Inexpensive as only a small amount of polymer needed
  - Minimum weight and volume
  - Self-actuated internally for cell balancing

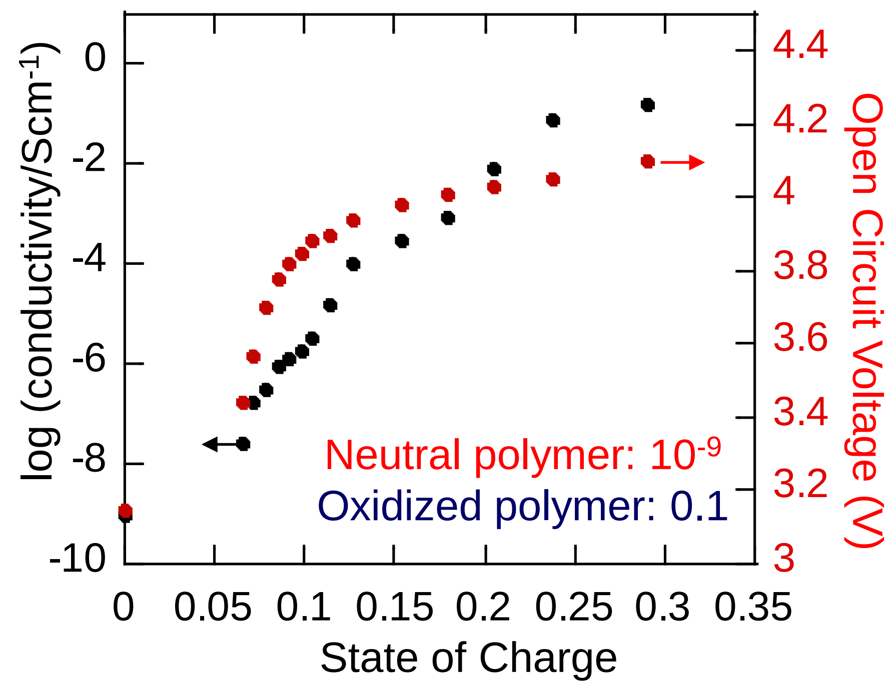
- **Advantages over internal methods (such as redox shuttles)**
  - Good rate capability
  - No interference with the cell chemistry
  - No solubility and volatility issues
  - Versatile as cell holding potential is varied by the choice of polymer, polymer morphology and distribution, system configuration
  - Capable of low temperature protection, no diffusion limitation

Electroactive Polymers

Reversible redox couple

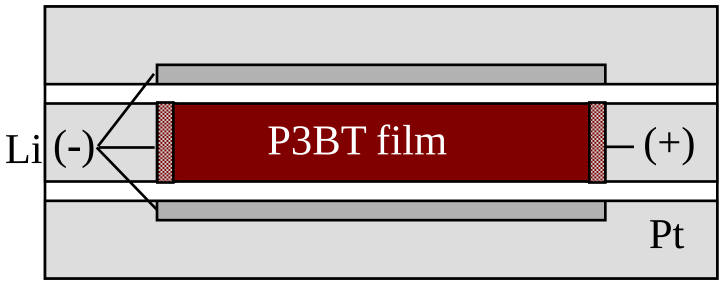


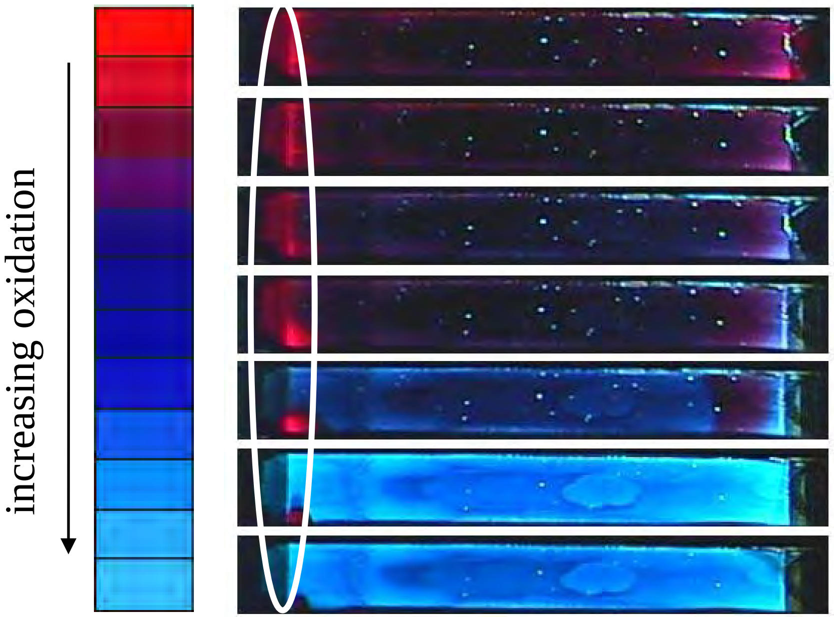
SOC dependent conductivity

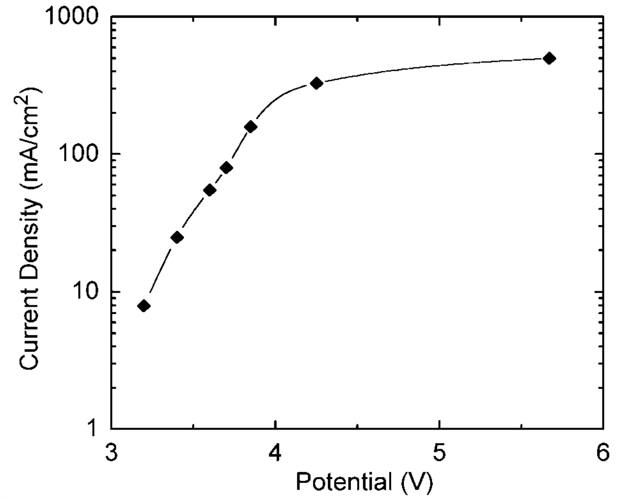


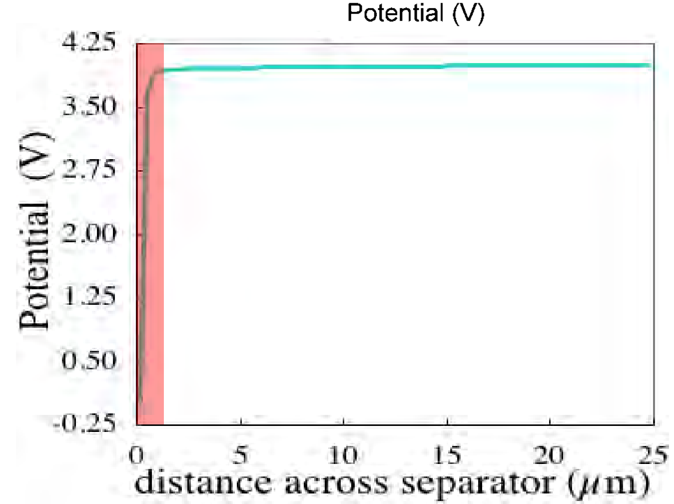
- Unique properties of electroactive polymers make them suitable for overcharge protection.

Overcharge Protection Mechanism







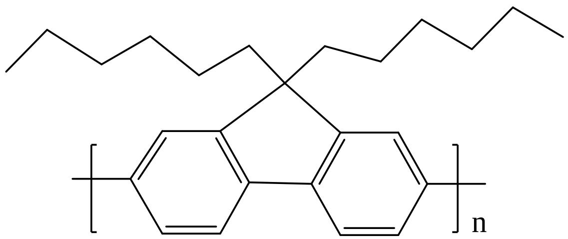


- At positive electrode, polymer is not fully oxidized but highly conductive.
- At negative electrode, polymer remains in neutral state, where most of the potential drop occurs.
- Polymer is capable of carrying a large amount of current.

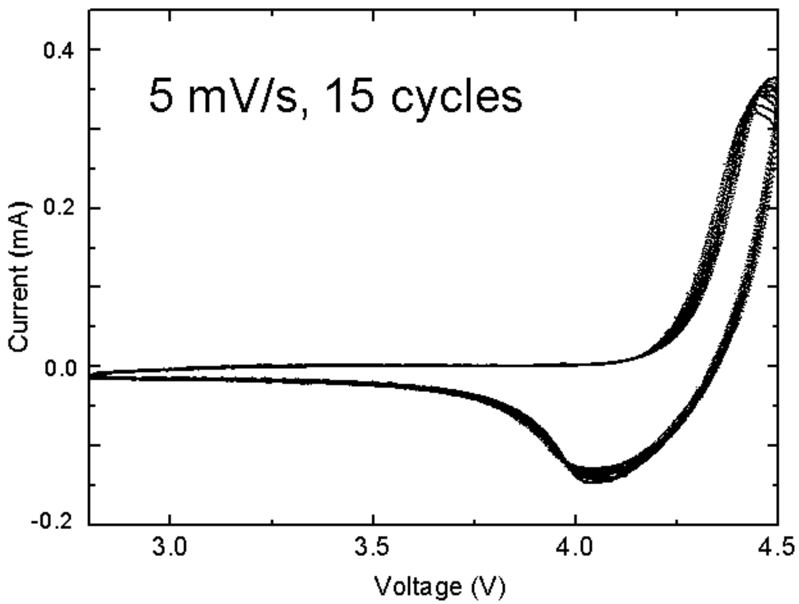
Polymer Requirements for PHEV Protection

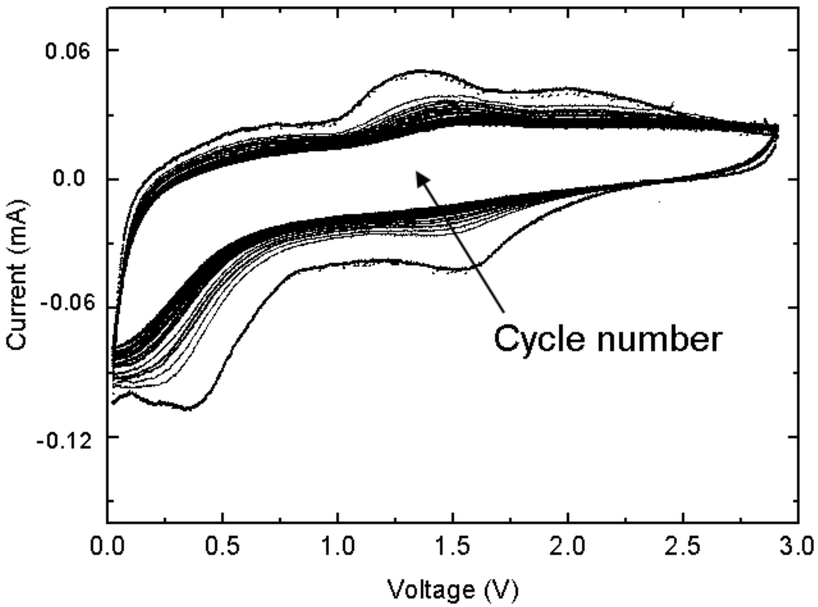
- Highly reversible redox couple situated above the end-of-charge voltage of 4 V class cathodes
- Rapid change in electronic conductivity during the redox process to establish a steady state potential and create negligible self-discharge
- High conductivity at oxidized state for high rate capability (2C and above)
- Compatible with cell chemistry, no side reactions
- Stable under aging and cycling conditions for long battery life (15 year life, 300,000 Cycles)
- Low cost

Redox Potential and Stability



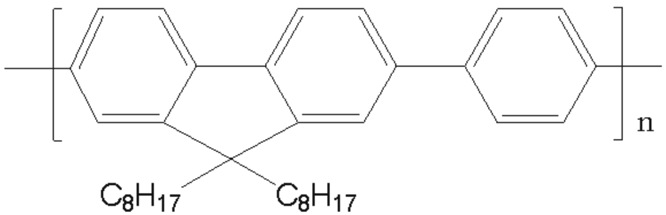
Poly(9,9-dioctylfluorene)
(PFO)



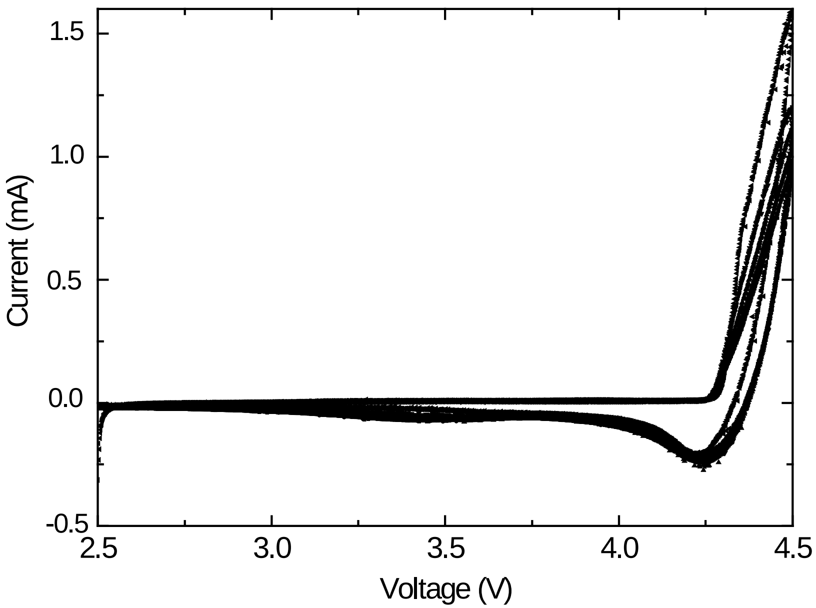


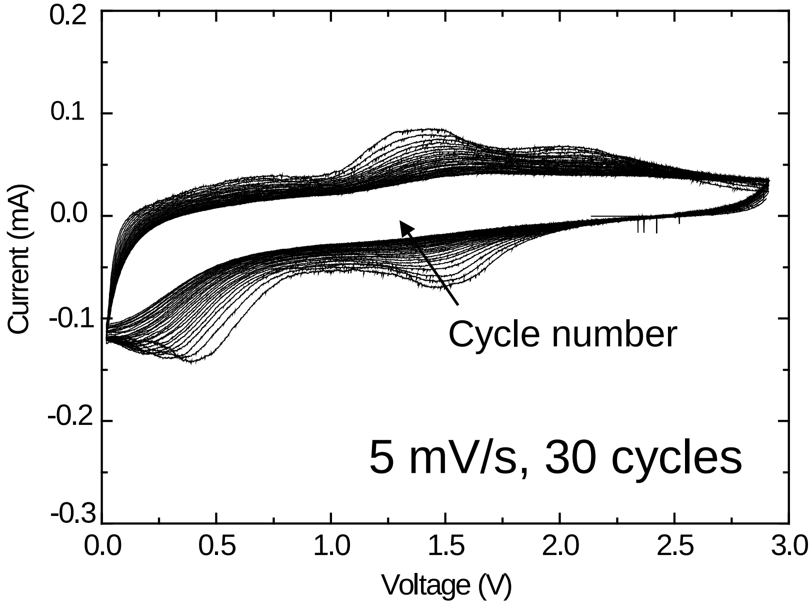
- Onset oxidation voltage is 4.1 V.
- Good reversibility at high voltage.

Redox Potential and Stability



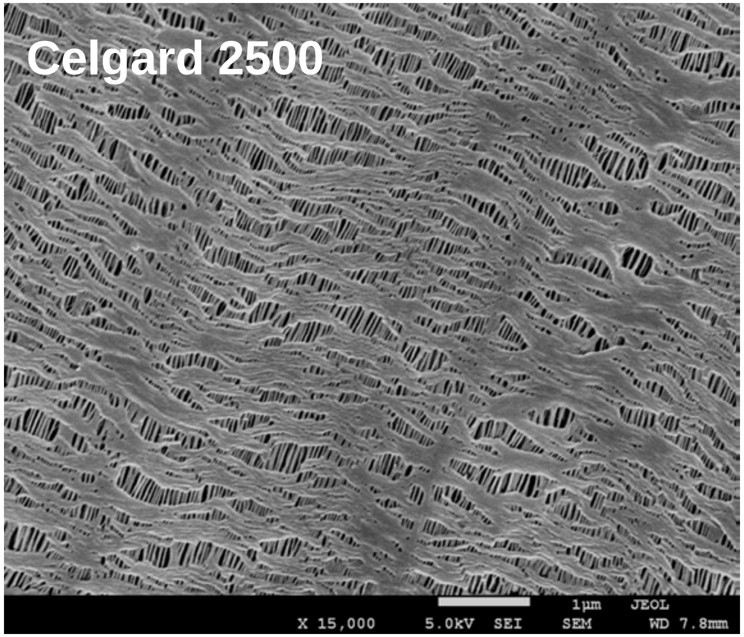
Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)]
(PFOP)

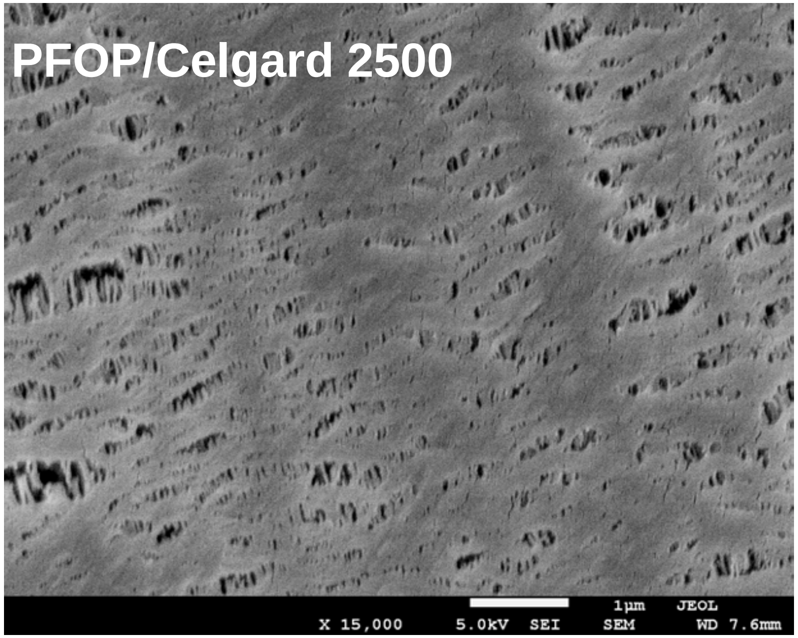




- Onset oxidation voltage is 4.25 V.
- Slightly improved stability at low voltage.

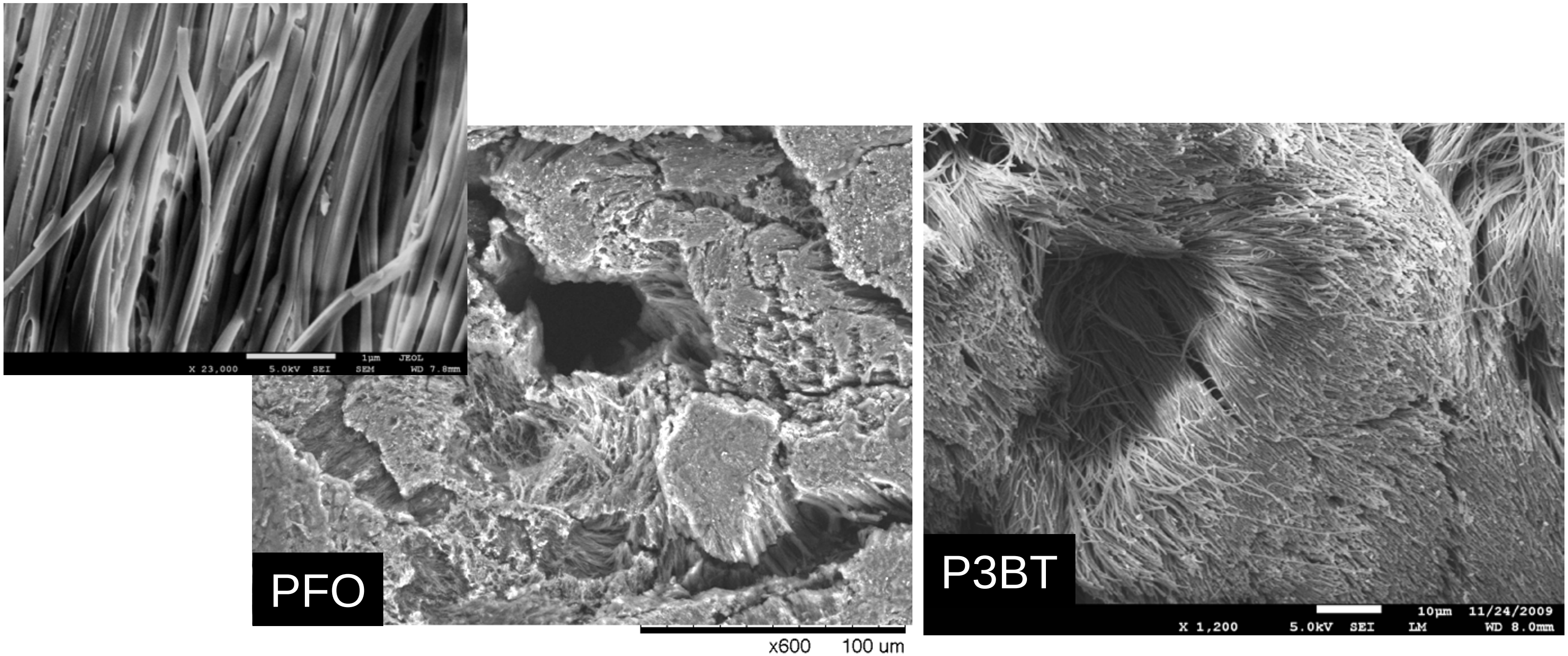
Morphology and Rate Capability





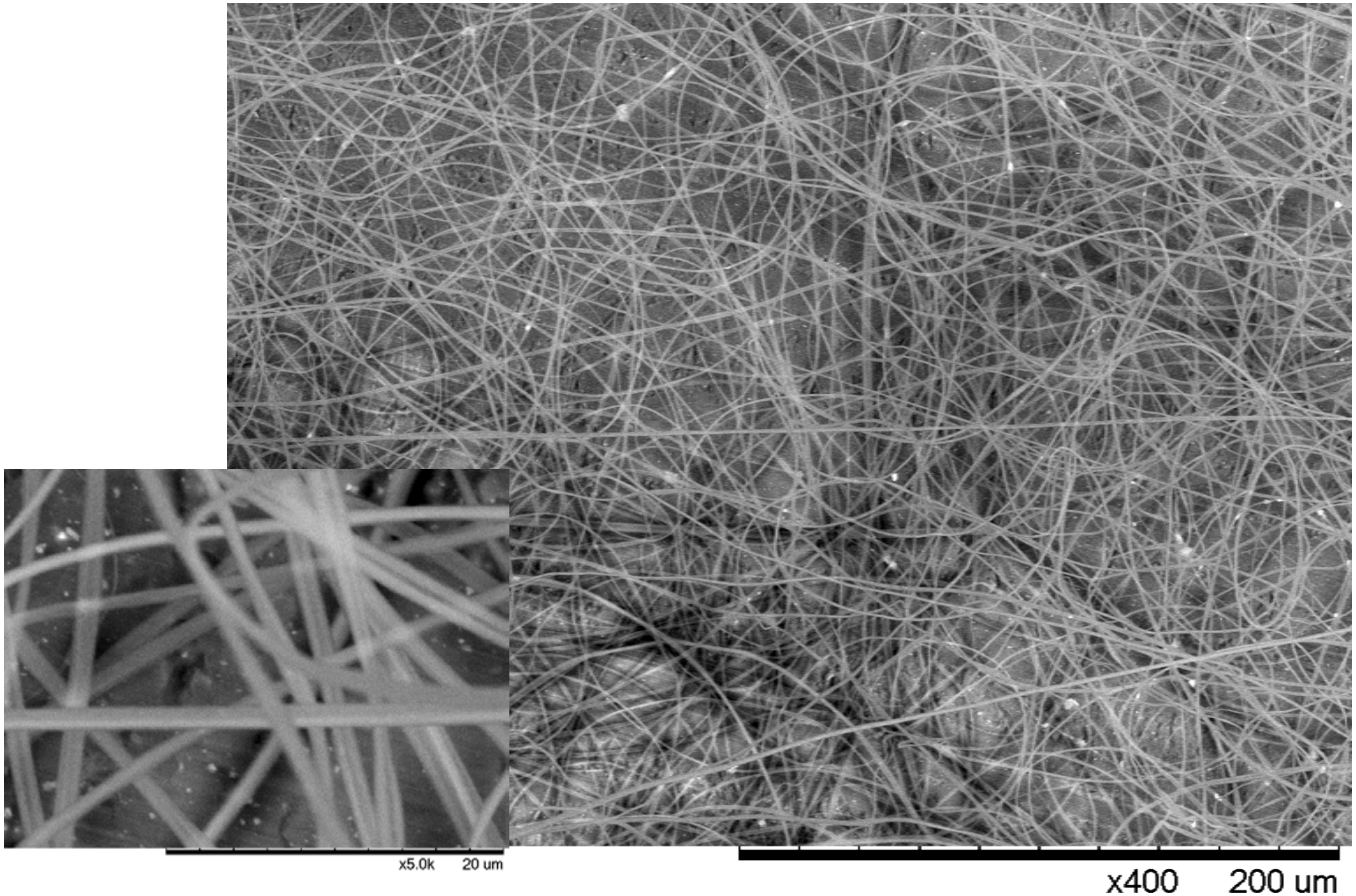
- Polymer impregnated into the separator by solution casting.
- Simple process but non-uniform distribution and poor utilization of the polymer.

Morphology and Rate Capability



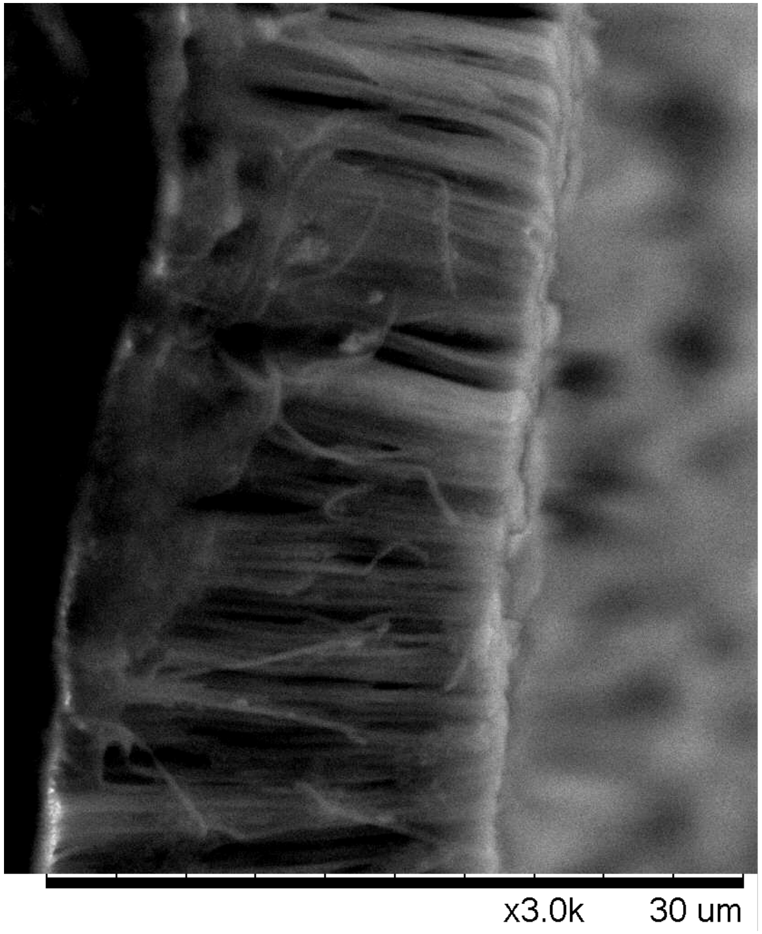
- Aligned nanorods extend the full thickness of the AAO template prepared by electrochemical deposition.
- Each polymer nanorod is capable of providing a direct, high-current path between the electrodes.

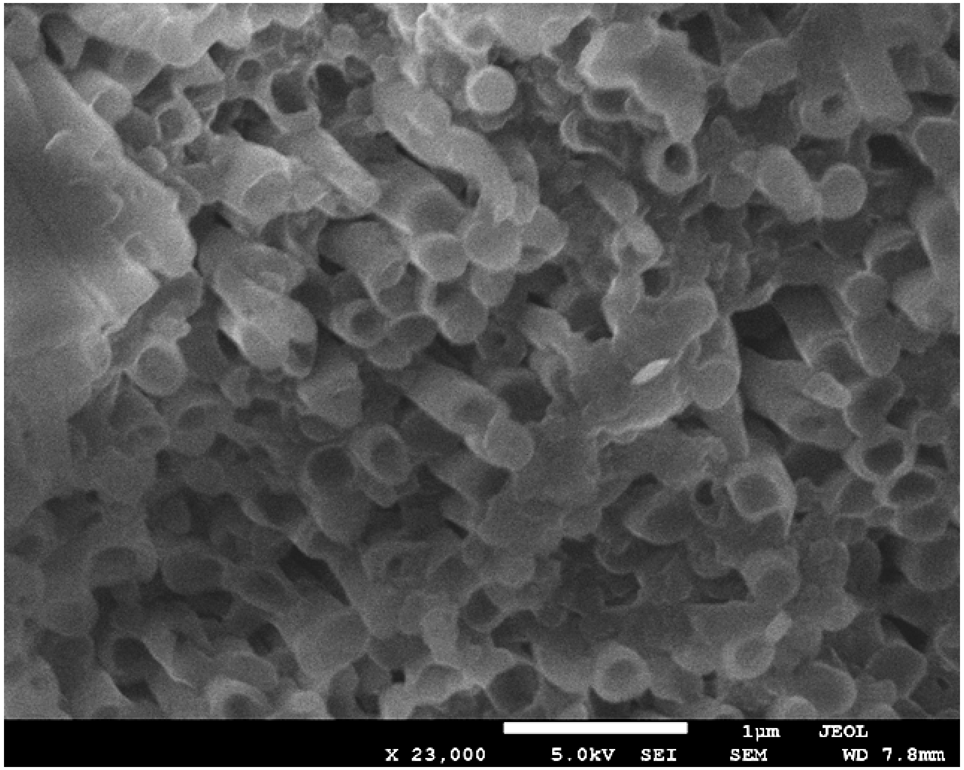
Morphology and Rate Capability



- Polymer fibers prepared on Al substrate by electrospinning.
- Aspect ratio of the fibers are easily adjusted by synthesis conditions.
- Process is easy to scale up.

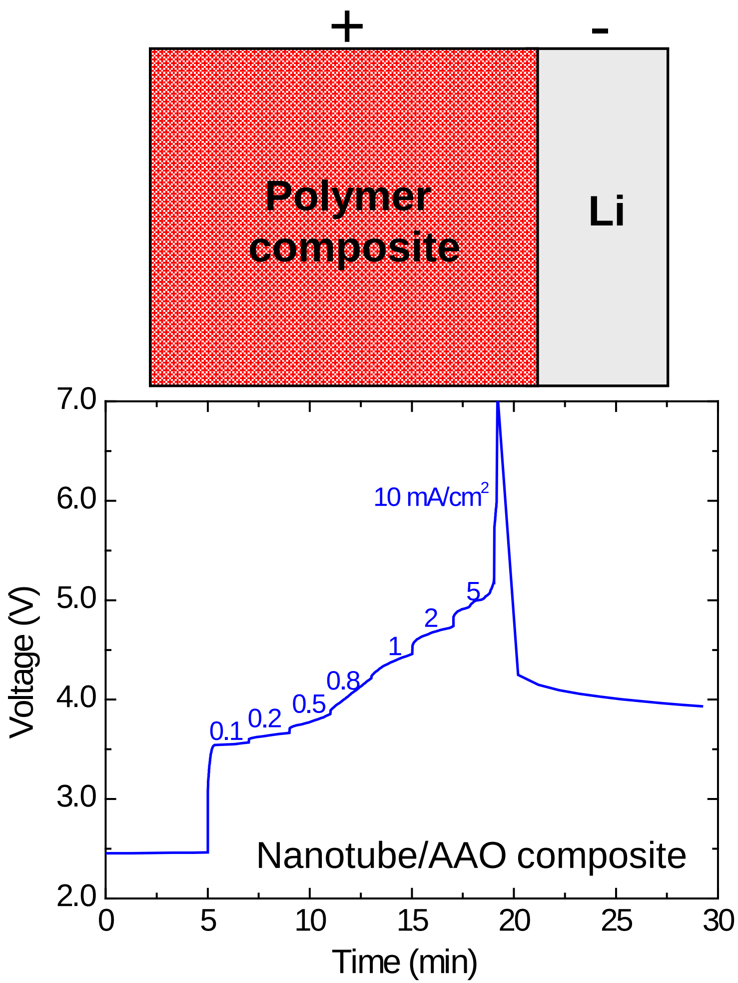
Morphology and Rate Capability

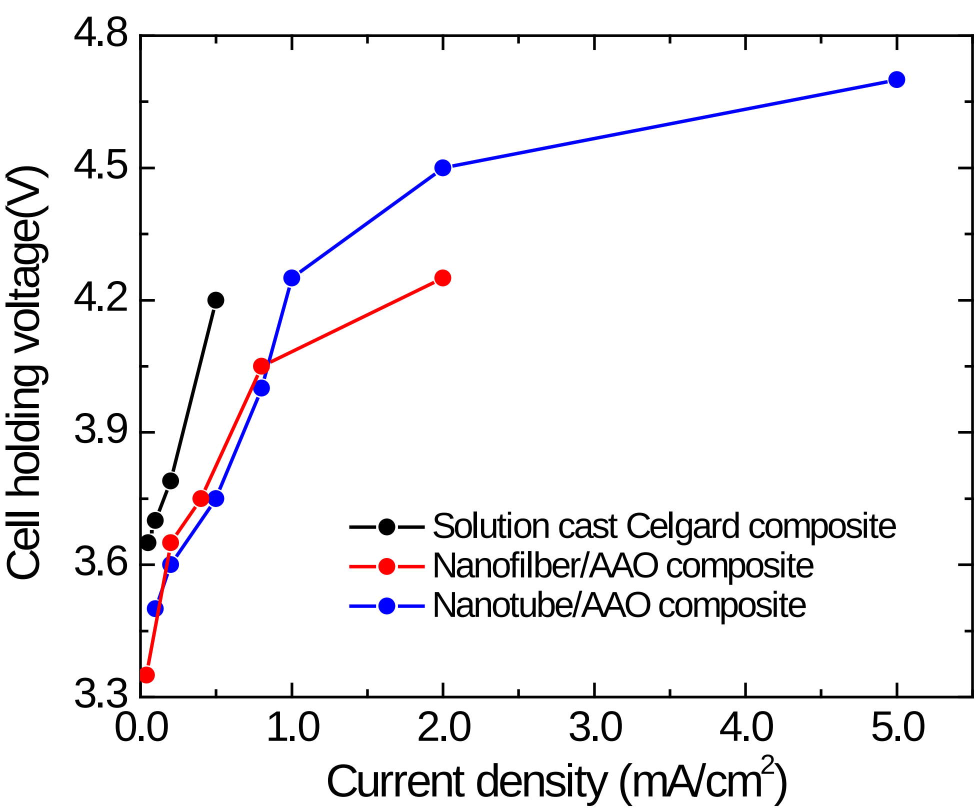




- Polymer nanotubes electrochemically deposited in AAO template.
- Pore size and length of the nanotubes tunable.

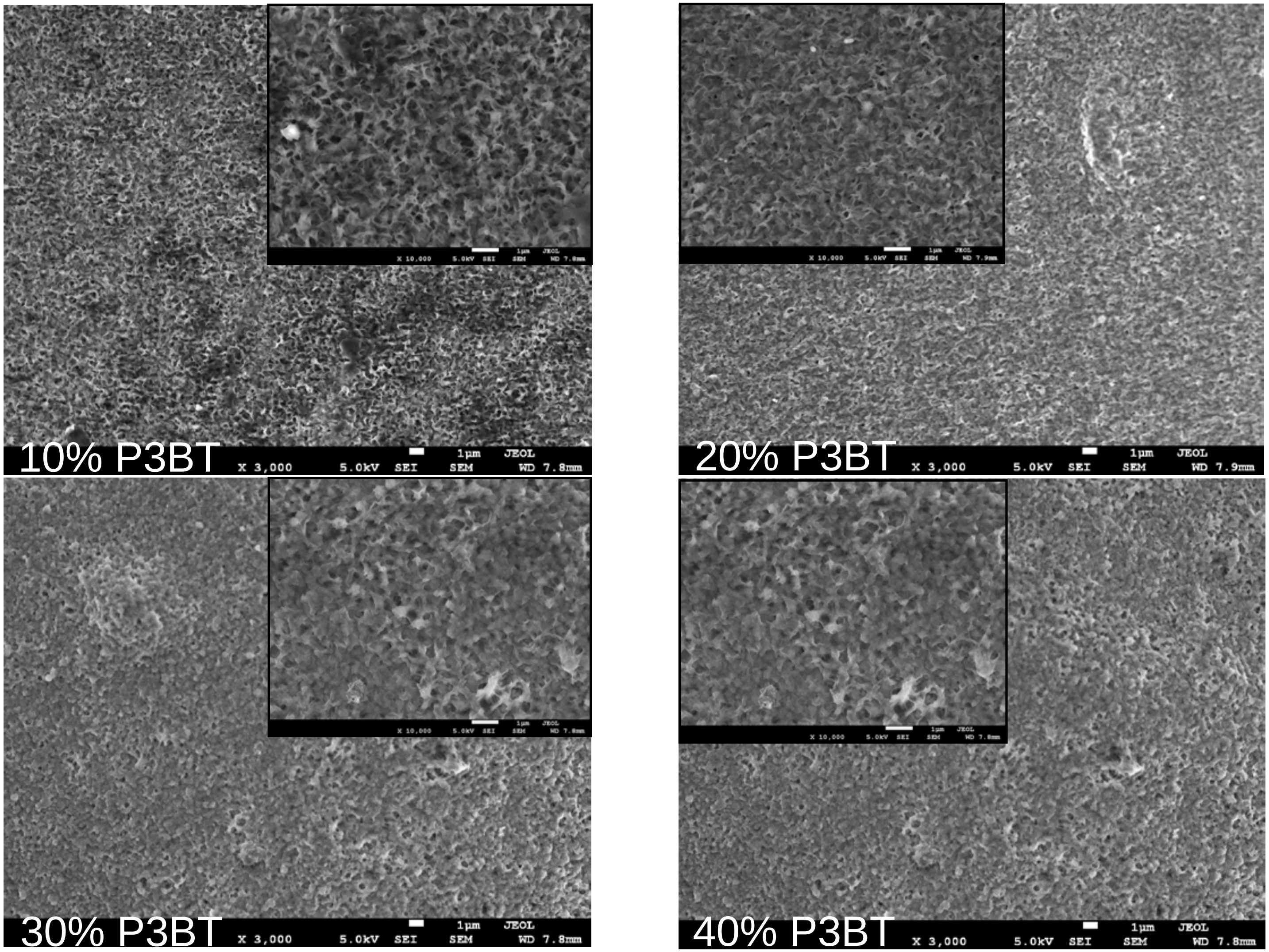
Morphology and Rate Capability





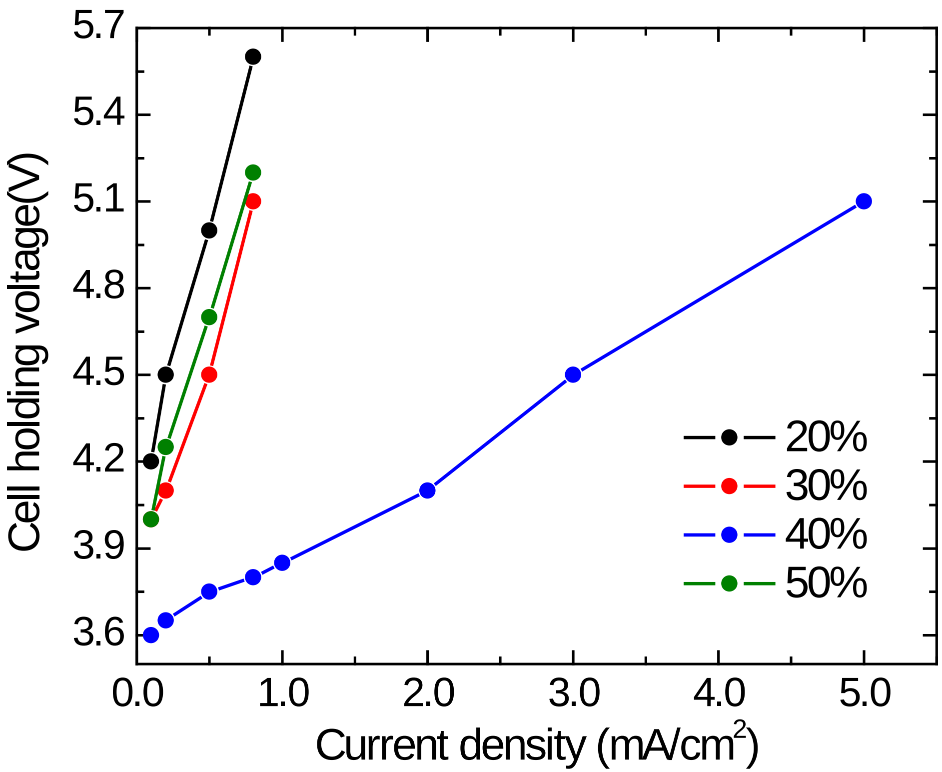
- Rate capability improved with new polymer morphologies.
- Highest sustainable current density achieved in the nanotube composite.
- Ten times improvement compared to the previous morphology.

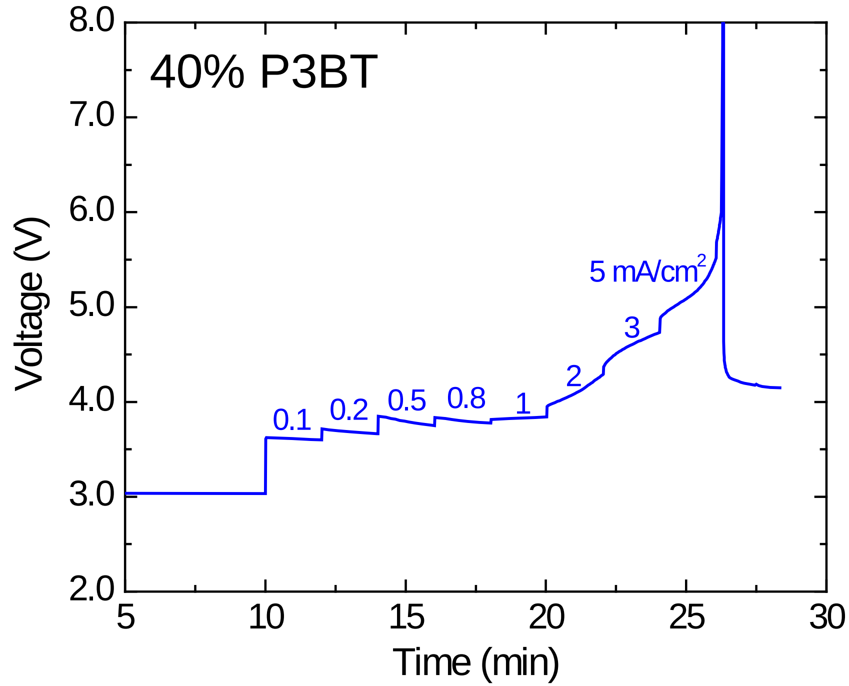
Polymer Composite Membranes



- P3BT/P(VDF-HFP) composite membranes prepared by solution casting.
- Polymer ratio has minimal impact on separator morphology.
- Need to increase density for use as separators.

Polymer Composite Membranes

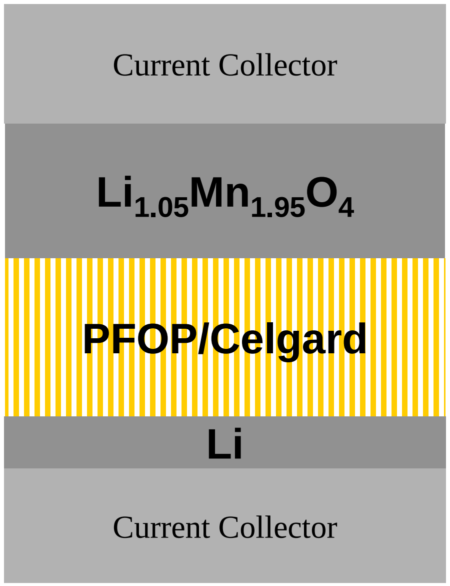


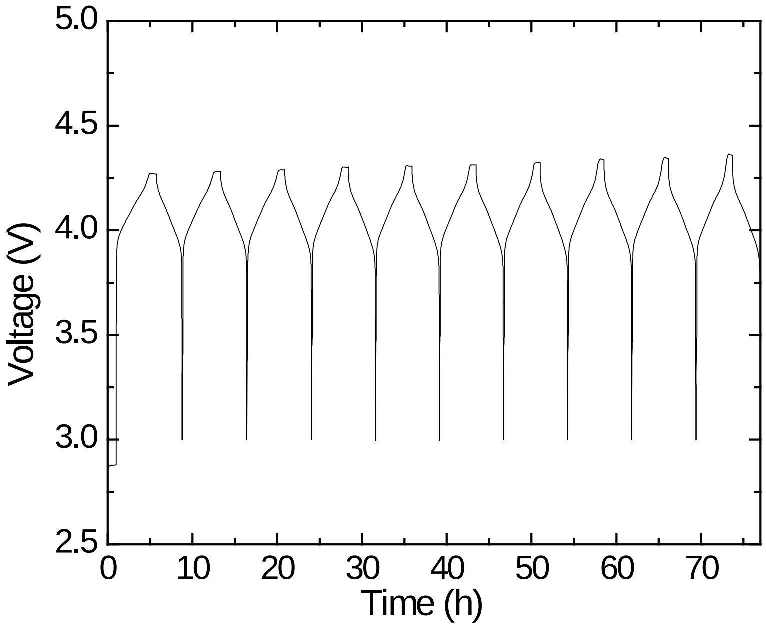


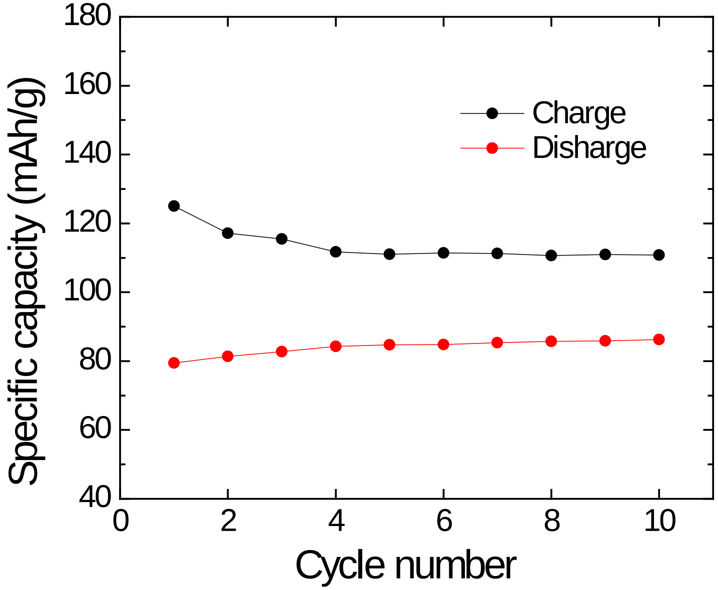
- Best rate capability achieved with 40% of electroactive polymer.
- Further optimization is planned.
- The process will be applied to make composite membranes incorporating fibers and nanotubes of the electroactive polymers.

Overcharge Protection – Spinel

"Swagelok-type" Cell

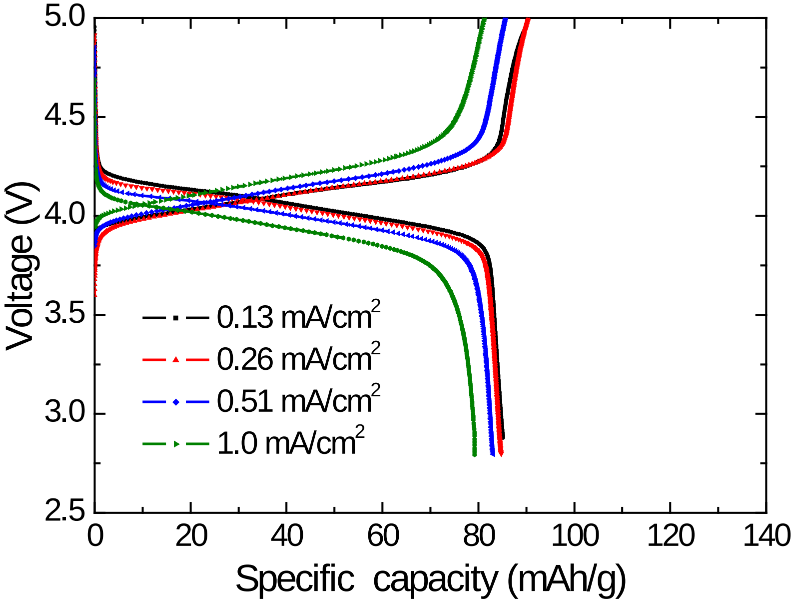


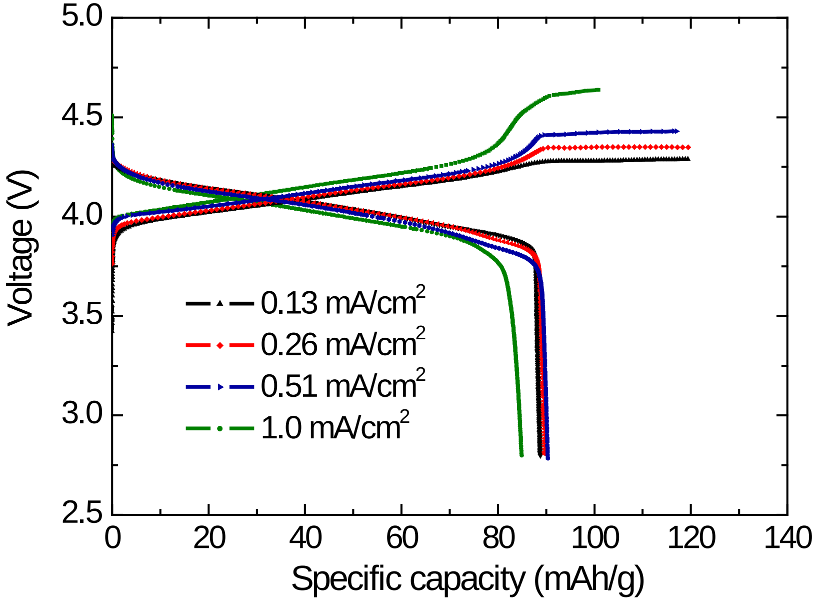




- Overcharge protection with single electroactive polymer.
- C/4 rate, 20% overcharged at a holding voltage of 4.3 V.
- Long term stability is under further evaluation.

Overcharge Protection – Spinel

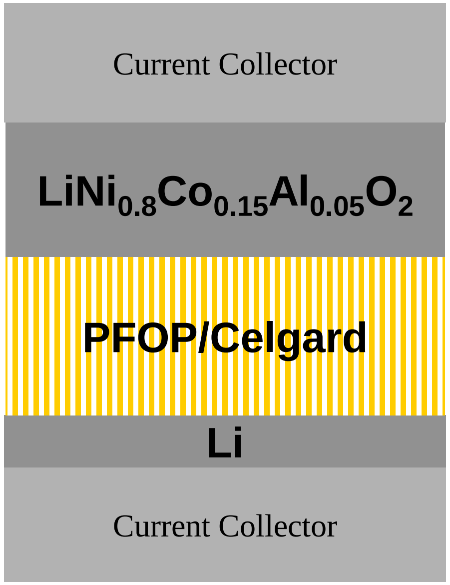


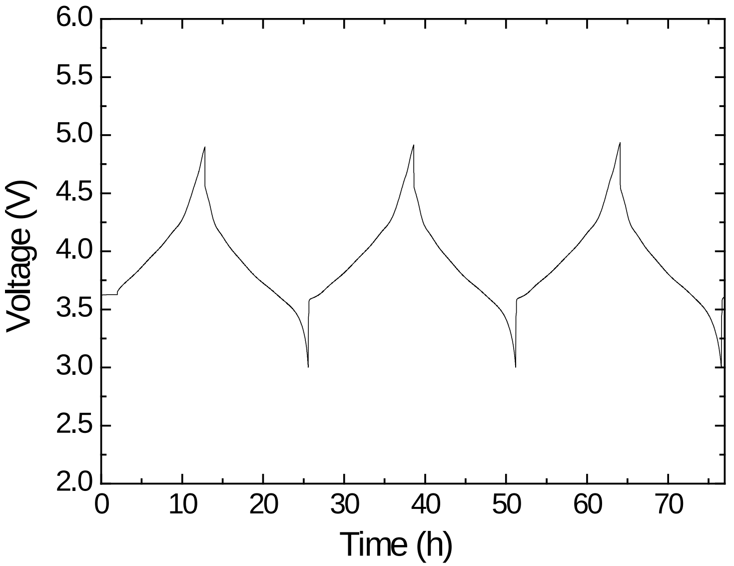


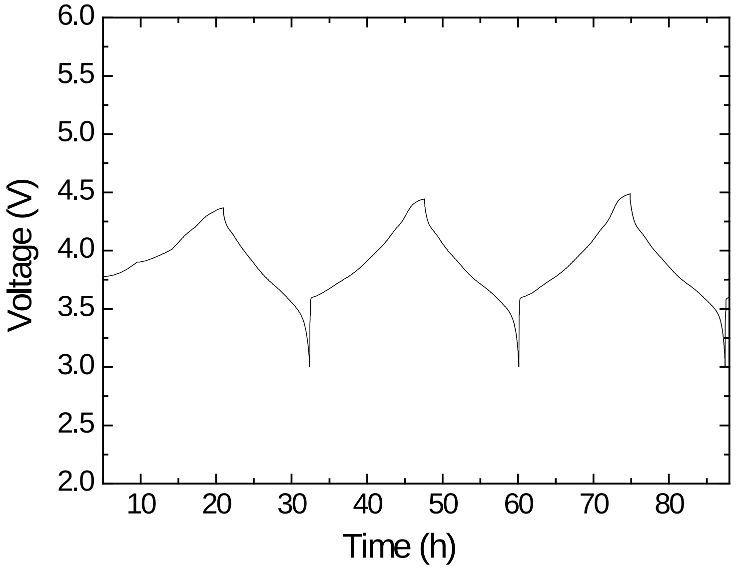
- Slightly higher discharge capacity in the protected cell.
- No self-discharge observed.
- Rate capability up to 1 mA/cm^2 (2C).

Overcharge Protection – Gen 2

"Swagelok-type" Cell



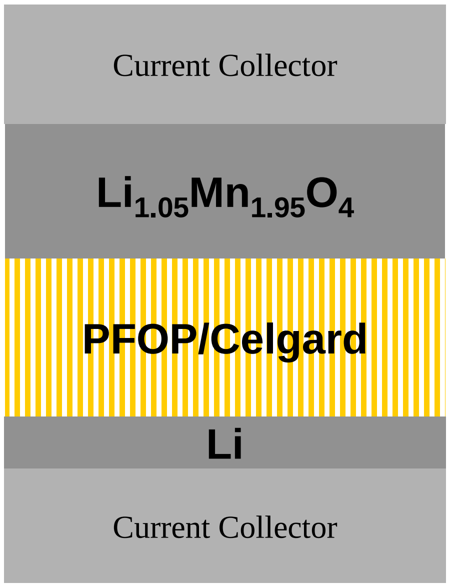


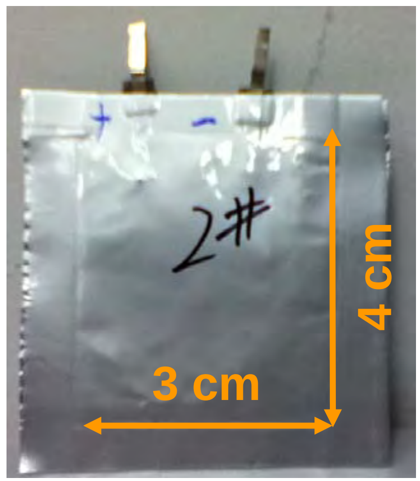


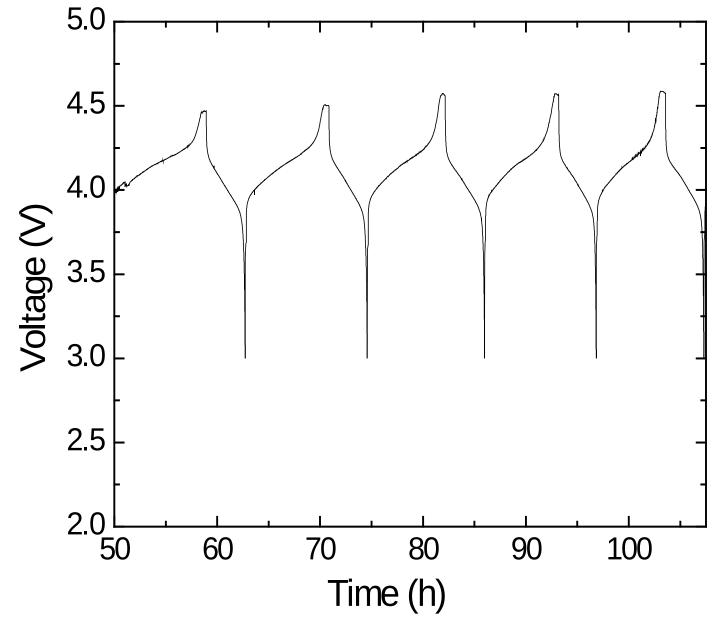
- C/12 rate, 20% overcharged at a holding voltage of 4.4 V.

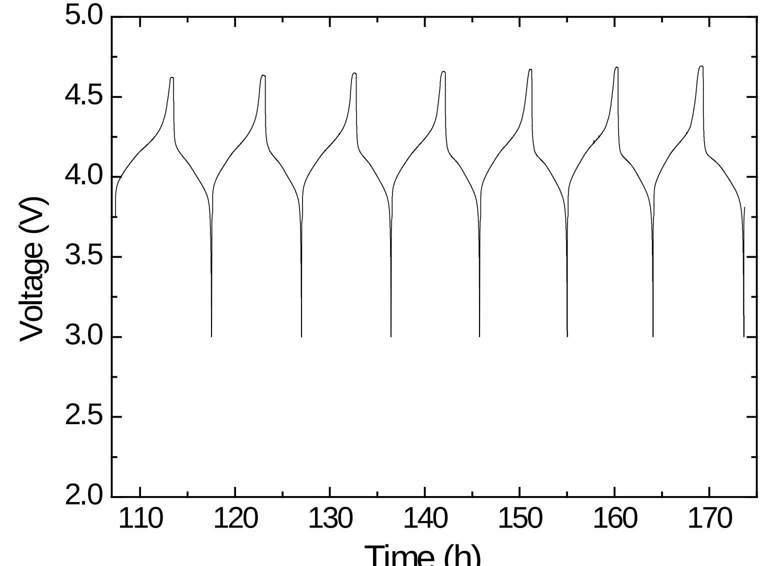
Overcharge Protection – Pouch Cell

Pouch Cell
"sandwich-type" configuration





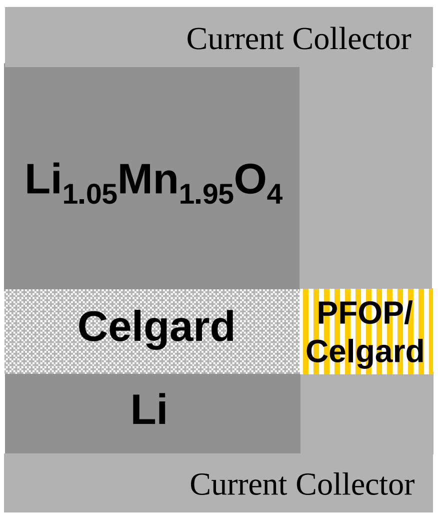


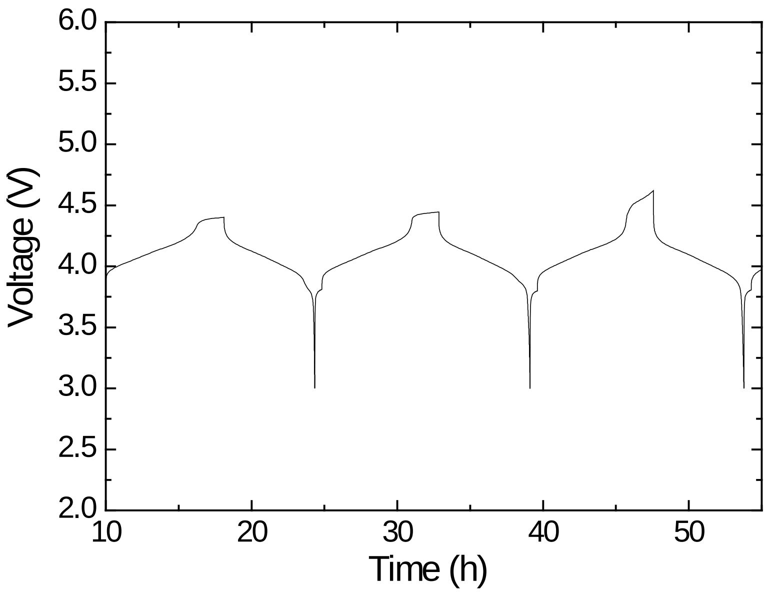


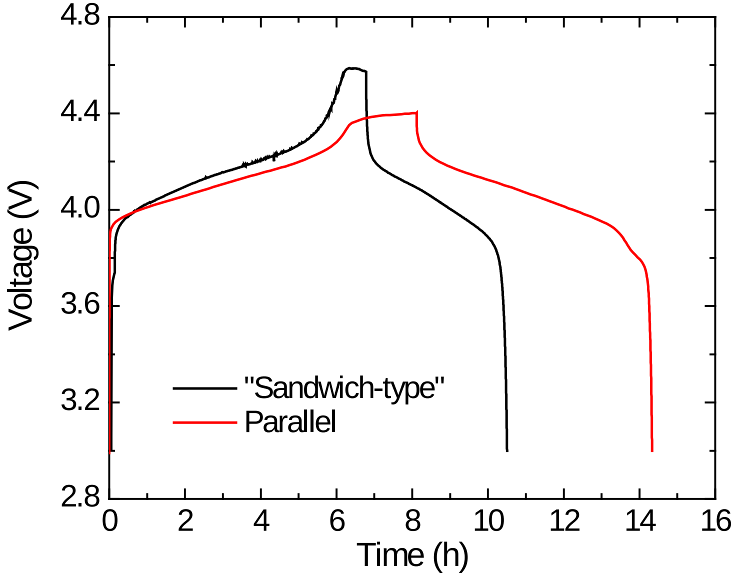
- C/7 rate, 20% overcharged at a holding voltage of 4.6 V.
- Initial test showed overcharge protection for over ten cycles.

Overcharge Protection – Pouch Cell

Pouch Cell
parallel configuration







- Area ratio between the polymer and the electrode is 40:60.
- C/6 rate, 20% overcharged at a holding voltage of 4.4 V.
- Lower internal resistance in the parallel configuration.

Collaborations

- Robert Kostechi (LBNL) – Raman and FTIR Spectroscopy
- John Kerr (LBNL) – TGA and DSC
- Vince Battaglia, Marca Doeff (LBNL) – Electrode fabrication
- Gao Liu (LBNL) – Polymer synthesis
- Yueguang Zhang (Molecular Foundry) - Electrospining

Future Work

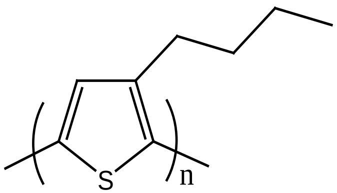
- Prepare composite separators with electroactive polymer fibers and nanotubes, and evaluate their rate capability and cycle life.
- Investigate other high-voltage electroactive polymers that may be suitable for overcharge protection for PHEV batteries. Optimize their morphology for maximum protection.
- Explore other cell configurations that may lead to improved protection and lowered cost.
- Investigate practical issues in “scaling-up” the concept.

Summary

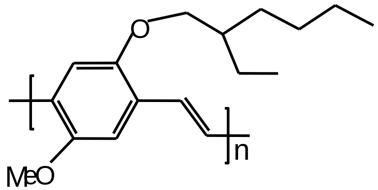
- A high-voltage polymer was found to have improved stability at low voltage. It provided overcharge protection for various battery chemistries.
- Polymer nanotubes were found to carry higher current densities compared to other morphologies.
- Ways to cast composite separators incorporating electroactive polymer were explored.
- Overcharge protection was achieved in pouch cells in both “sandwich-type” and parallel configurations. The latter was found to have lowered holding potential due to reduced internal resistance.

Technical Back-Up Slide

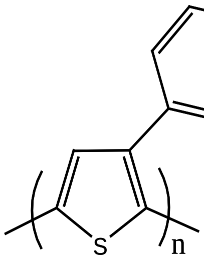
Oxidation Potentials of Studied Polymers



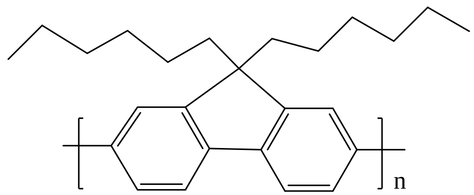
Poly(3-butylthiophene)
(P3BT, V_{onset} = 3.2 V)



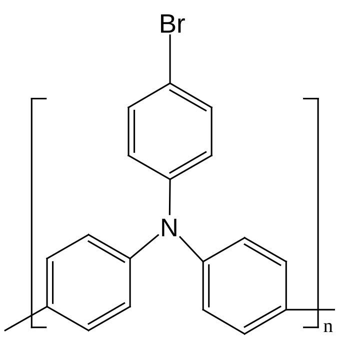
Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]
(MEH-PPV, V_{onset} = 3.6 V)



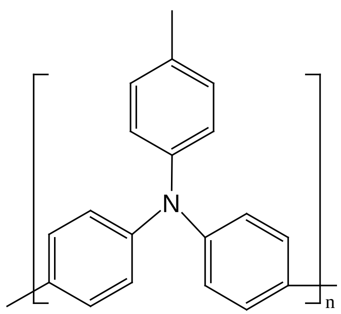
Poly(3-phenylthiophene)
(P3PT, V_{onset} = 3.9 V)



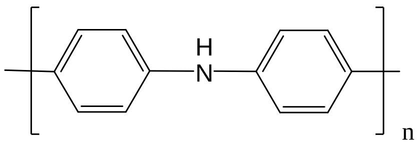
Poly(9,9-dioctylfluorene)
(PFO, V_{onset} = 4.1 V)



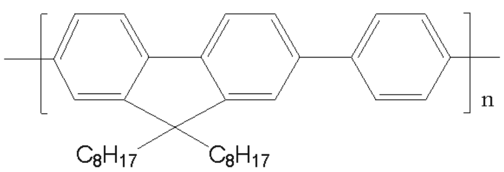
Poly(4-bromo triphenylamine)
(PBTPAn, V_{onset} = 3.7 V)



Polytriphenylamine
(PTPAn, V_{onset} = 3.8 V)



Polydiphenylamine
(PDP, V_{onset} = 3.7 V)



Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)]
(PFOP, V_{onset}= 4.25 V)