Overcharge Protection

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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

Partners

- ANL, BNL, INL, and SNL
- Berkeley program lead: John Newman

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 overcharge protection results with modified polymer composite separators and cell configuration.

Approach

- Optimize morphology and improve utilization of electroactive polymer composite.

- Investigate high-voltage polymers that are suitable for overcharge protection for PHEV batteries.

- Explore alternative cell configurations to achieve maximum protection.

Why Overcharge Protection

Overcharging Li-ion battery cells can cause:

- 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
- Current collector corrosion
- Explosion, fire, toxics released

Overcharging at low temperature:

- Cells are likely to be overcharged when it is cold (higher resistance)
- Lithium plating occurs at anode
- Redox shuttles are ***not*** effective (slower diffusion)

Overcharge Protection Requirements

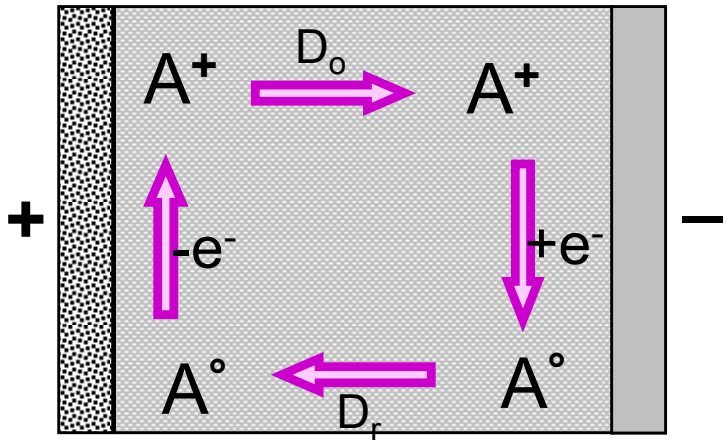
- Provide steady state potential at desired cell cut-off voltage (a current bypass route)
- No interference with the cell chemistry
- Minimum weight and volume
- Inexpensive
- Self discharge negligible
- Carrying a large amount of current density (2-3 mA/cm^2) or high rate capability (3C or above)
- Highly reversible with long cycle life (15 year life, 300,000 Cycles)
- Good temperature range (-30 to +52 ^oC)
- Efficient heat transfer out of the cell

Current Approaches Inadequate

- **External methods**
  - Inactivate the battery system when cells are overcharged (shutdown mechanism)
  - Examples: integrated control circuits (IC), pressure activated devices, and positive temperature coefficient (PTC) resistors
  - Adds cost, volume and weight to the cell pack

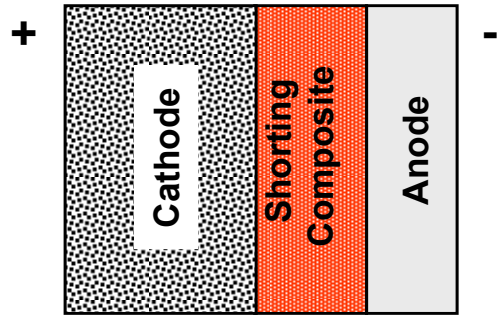
- **Internal methods**
  - Rely on the chemical reactions of an electrolyte additive
  - Examples: gassing agents, polymerizing monomers (conducting or non-conducting), and redox shuttles (current bypass mechanism)
  - Limited sustainable current density, solubility and volatility issues, interference with cell chemistry

Redox shuttle additive

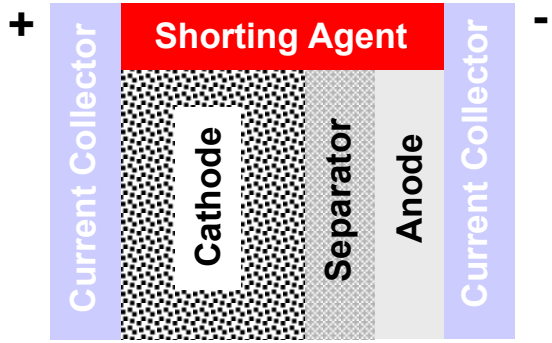


Our Approach – Reversible Soft-Shorting Activated by Cell Voltage

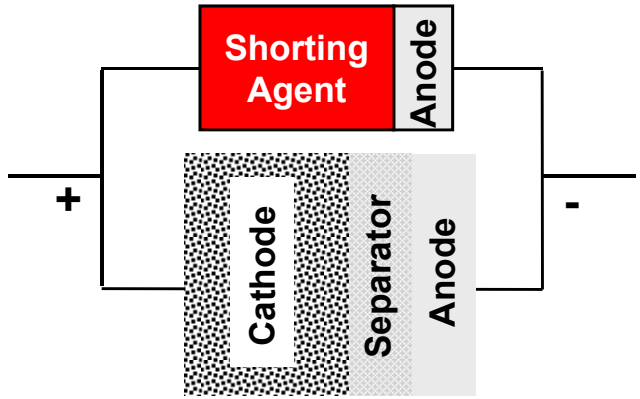
- Shorting agent impregnated in the separator between the battery electrodes



- Shorting agent placed between the current collectors

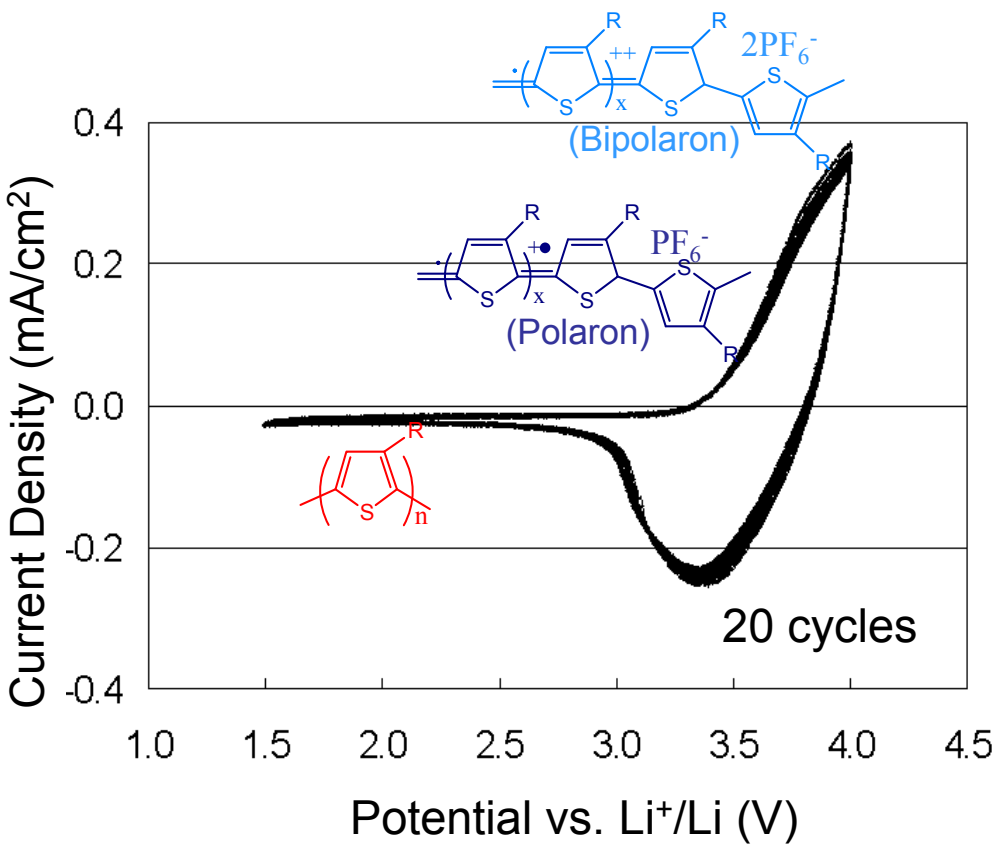


- Shorting agent used in an external component connected parallel to the battery cell

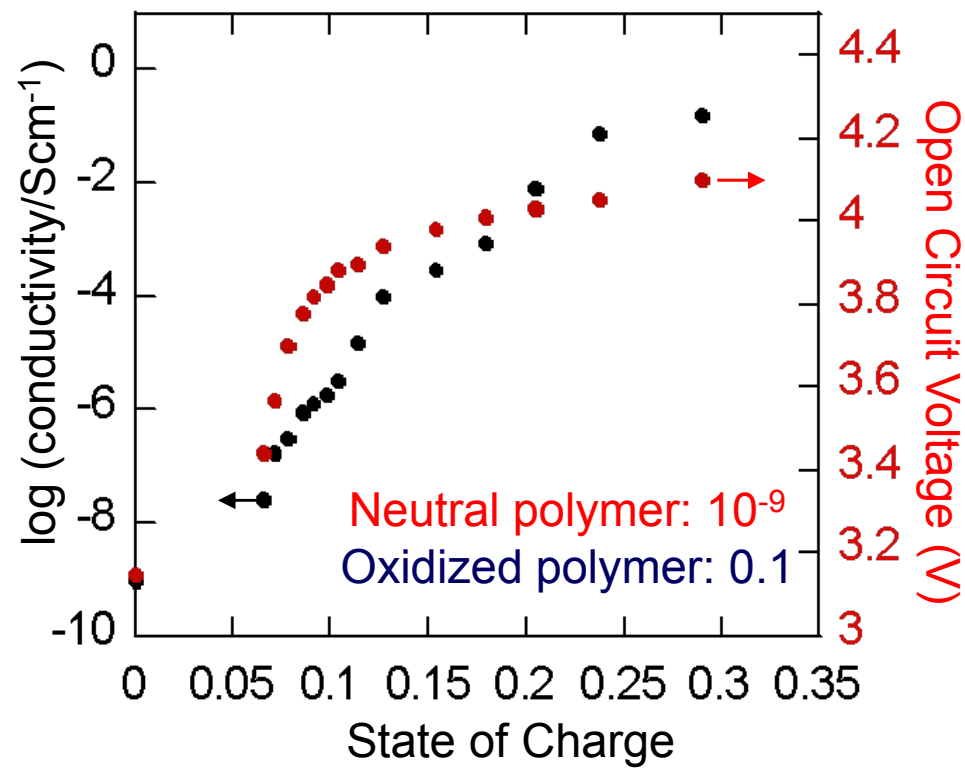


Shorting Agent
Electroactive Polymers

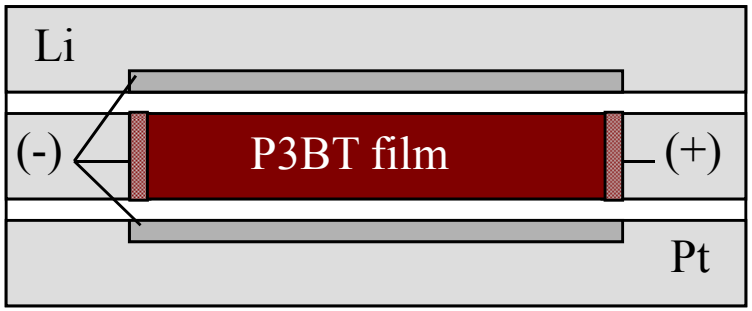
Redox couple highly reversible

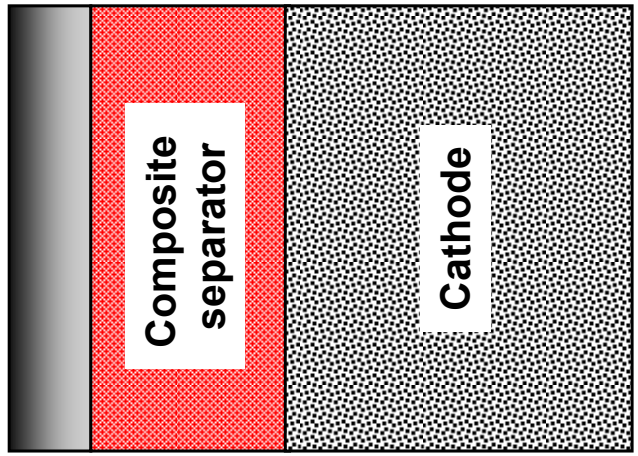


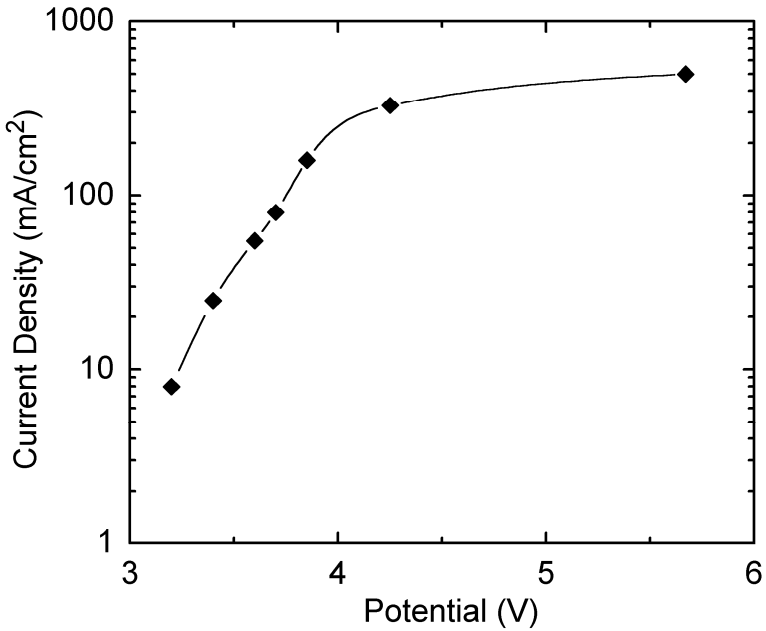
Conductivity varies with SOC

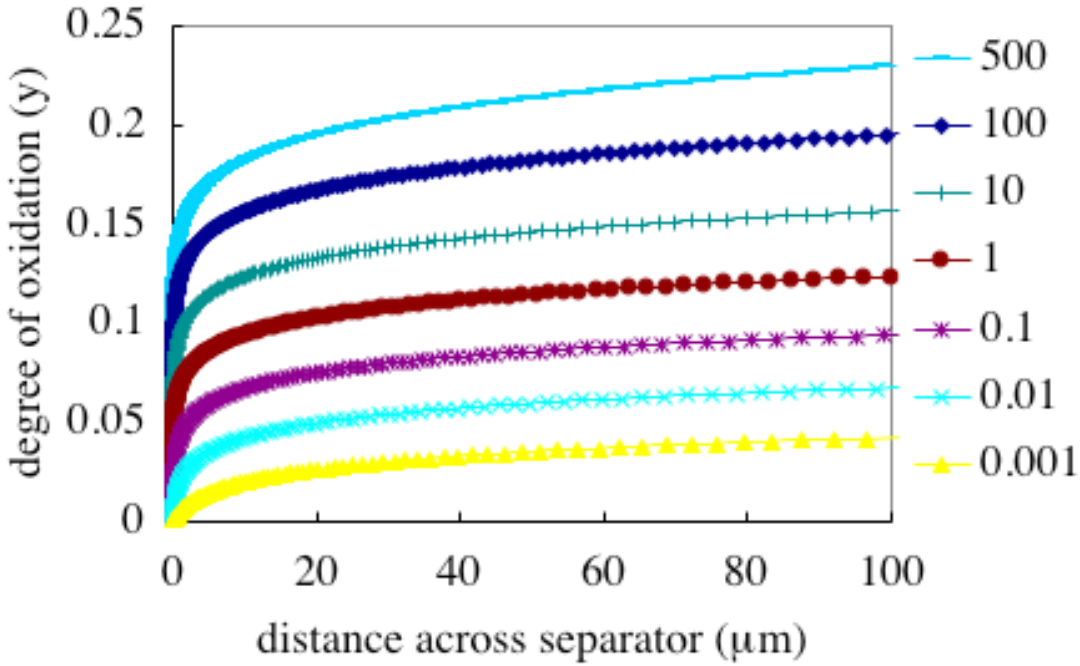


Electroactive Polymers – Large Sustainable Current Densities

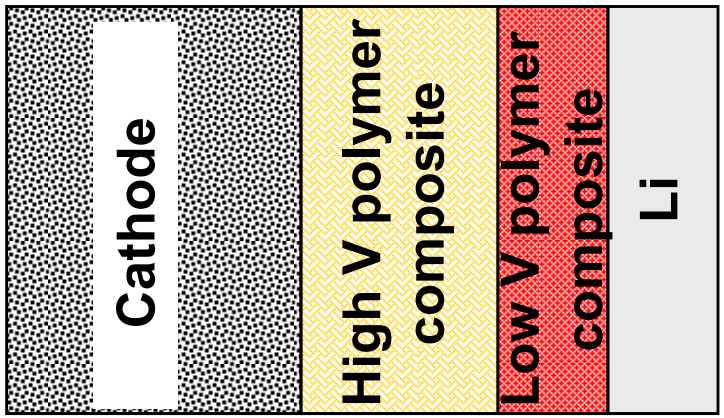


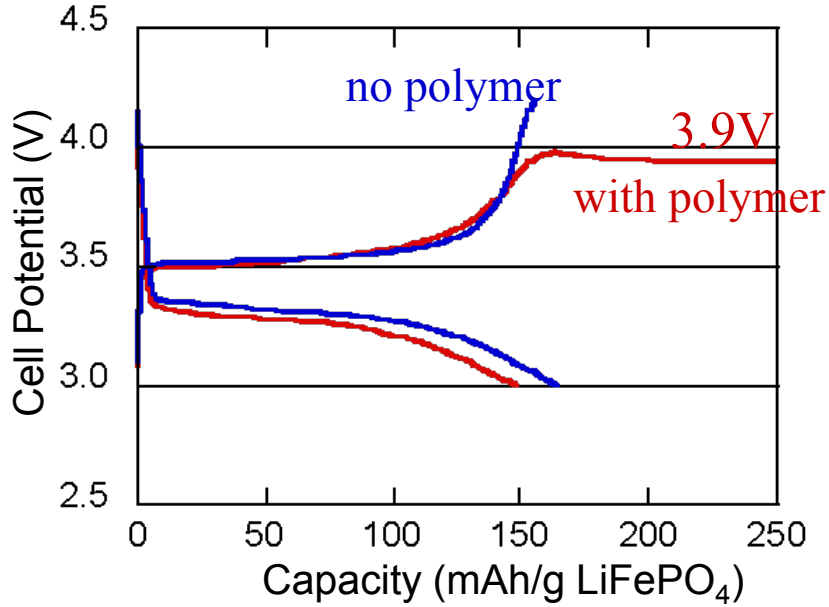


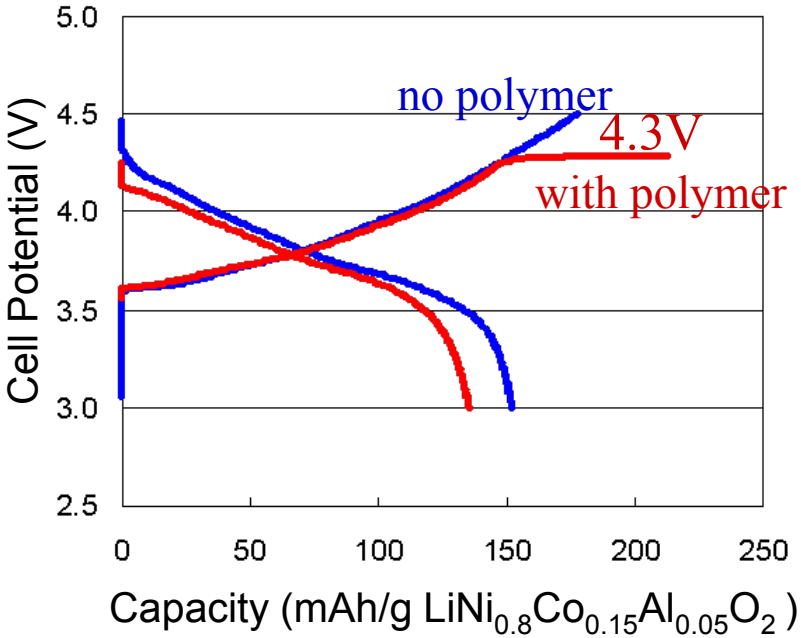


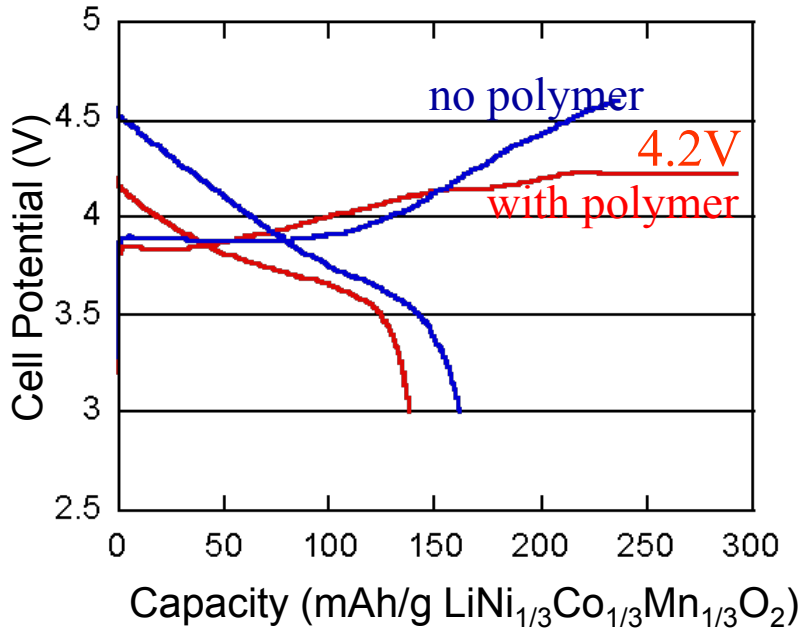


Overcharge Protection Achieved with Various Cathodes

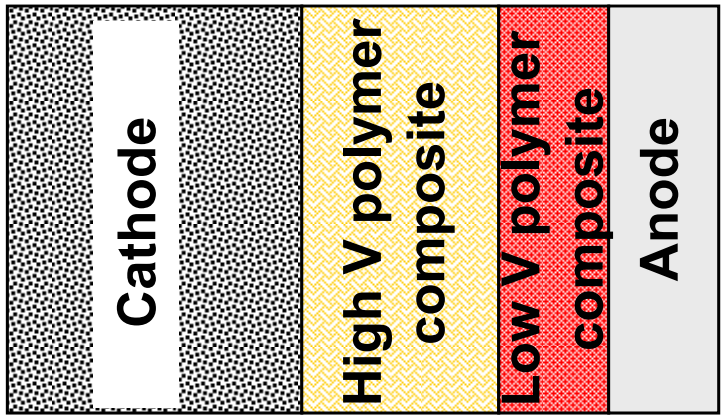


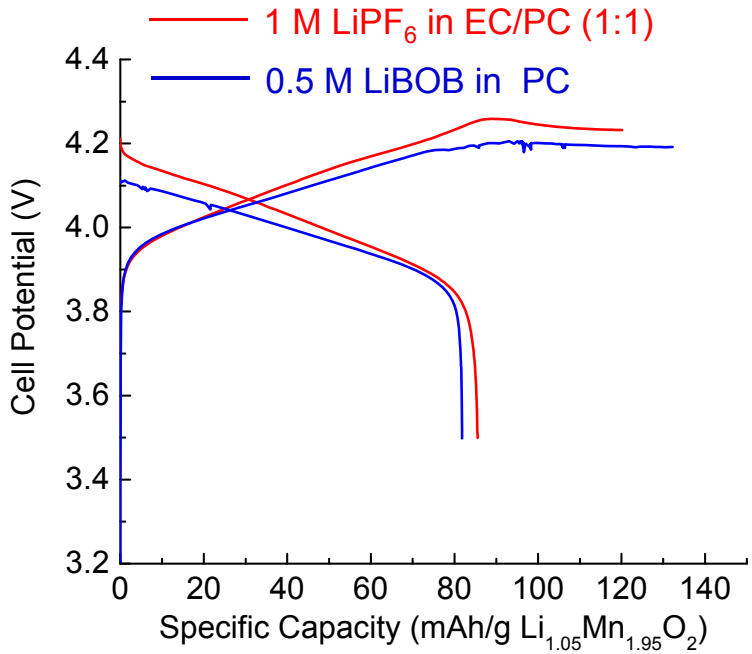




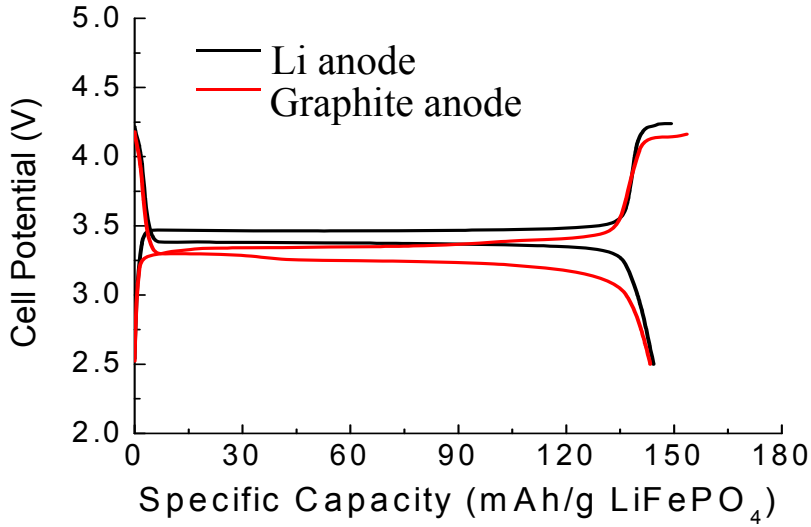


Overcharge Protection Achieved with Various Anodes and Electrolytes



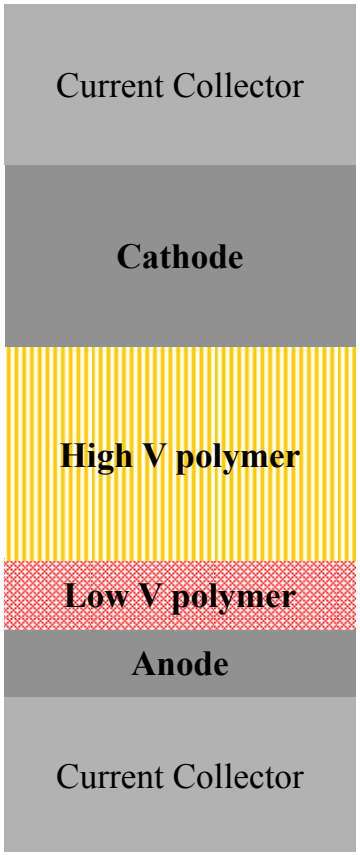


- Improvement in rate capability and cycle life needed.
- Cell configuration and polymer morphology need optimization.

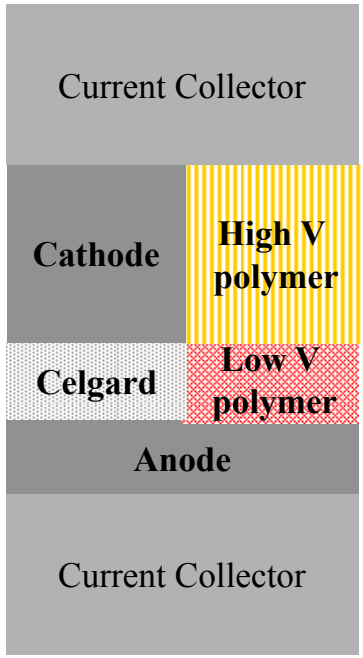


Effect of Cell Configuration

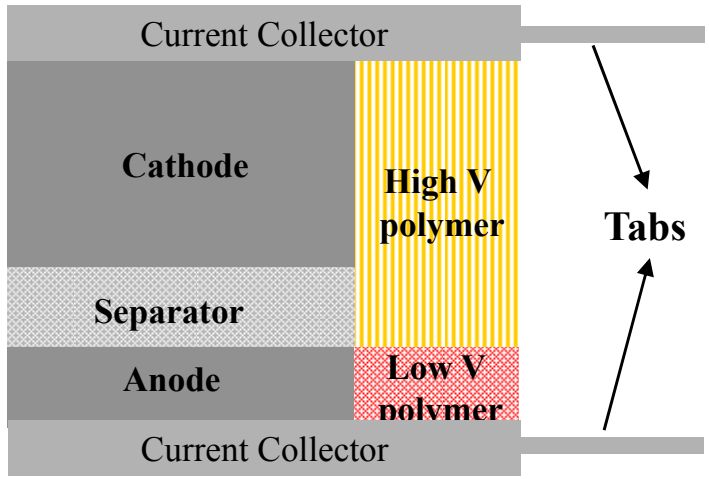
Previous configuration



New configuration (parallel internal)



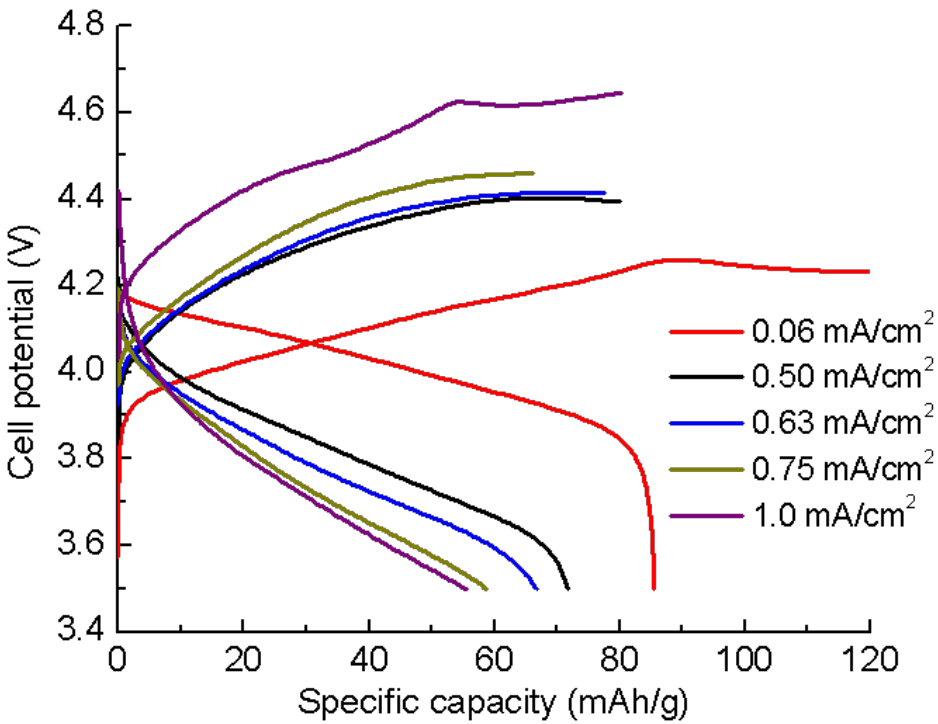
or

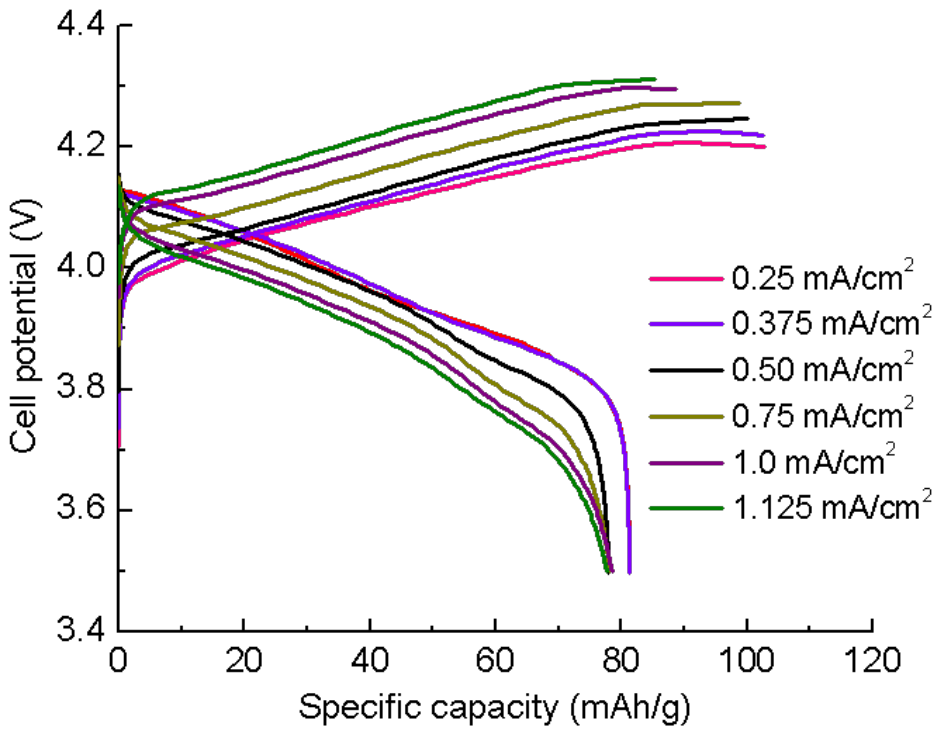


- Instead of placing it between the electrodes, the polymer protection is located outside the electrode assemble in the new configuration.

Effect of Cell Configuration

$Li_{1.05}Mn_{1.95}O_2$ - Li cell, PFO/P3BT, 1 M $LiPF_6$ in EC/DEC (1:1)

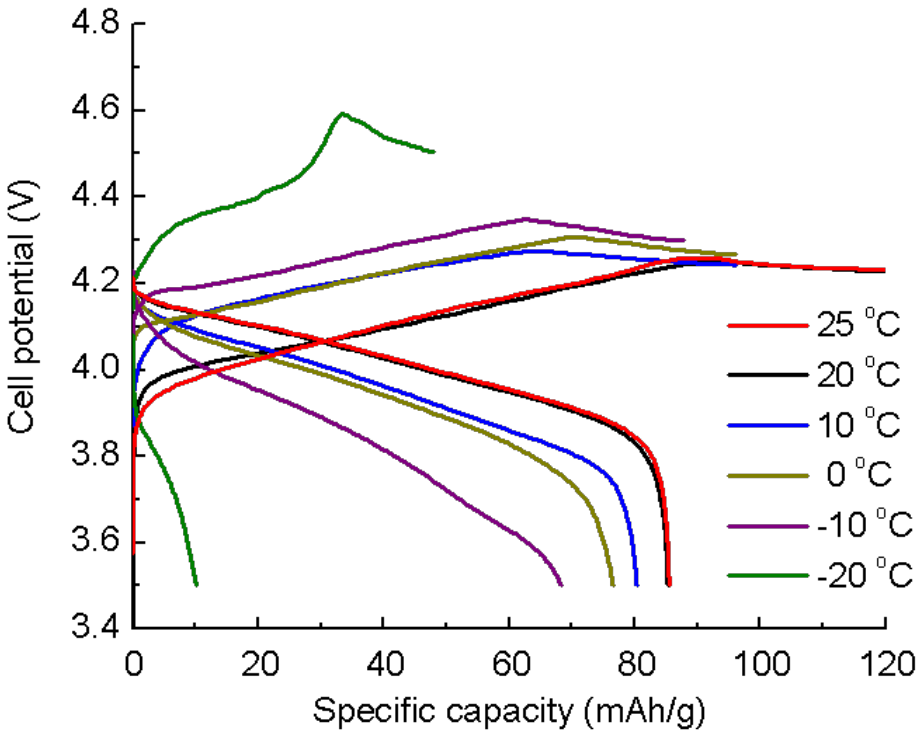


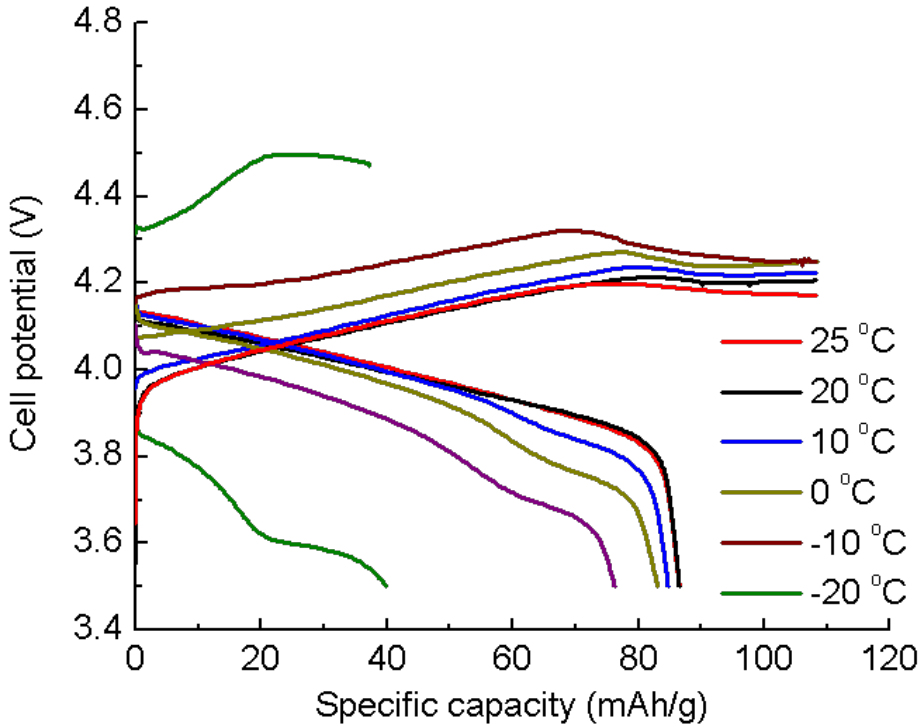


- Improved rate capability with the new cell configuration.

Effect of Cell Configuration

$Li_{1.05}Mn_{1.95}O_2$ - Li cell, PFO/P3BT, 1 M $LiPF_6$ in EC/DEC (1:1)

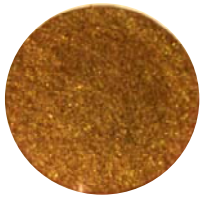




- Improved low temperature performance.

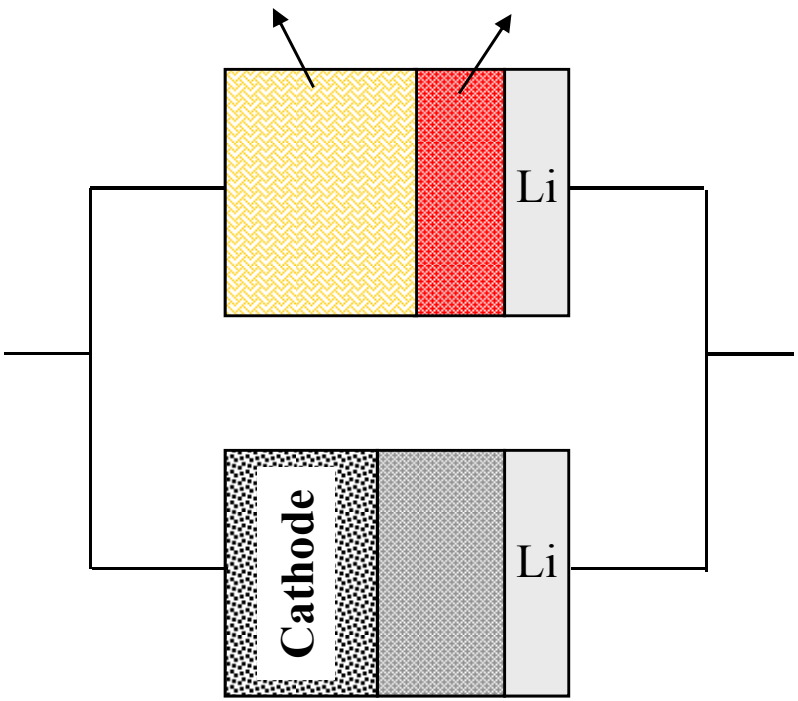
Effect of Cell Configuration

New configuration
(parallel external)

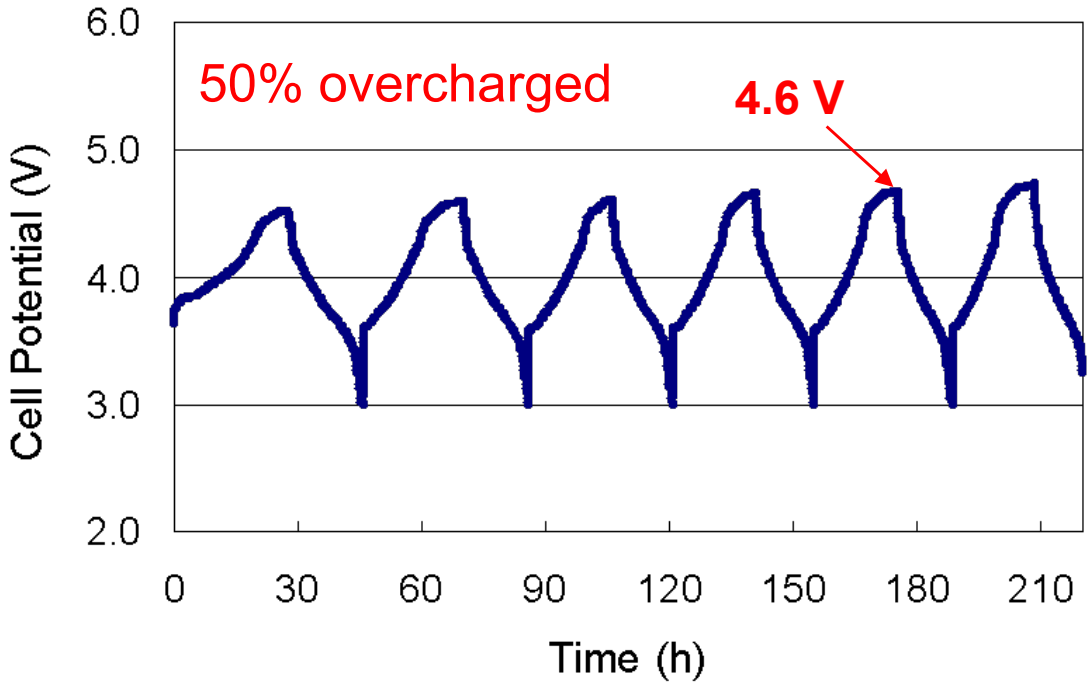


High V polymer
Viledon composite

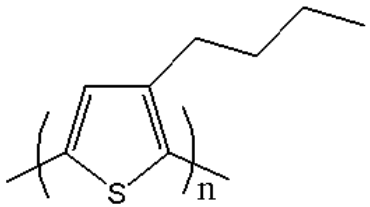
Low V polymer
Celgard composite



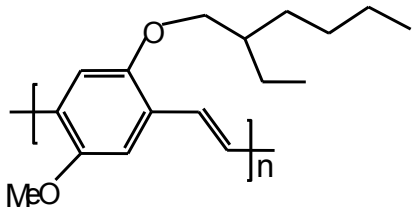
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ - Li cell,
PFO/P3BT, 1 M $LiPF_6$ in EC/DEC (1:1)



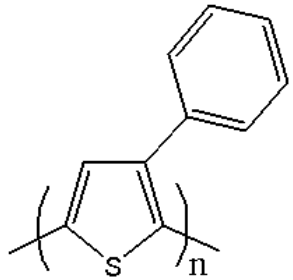
Electroactive Polymers – Tunable Redox Voltage Windows



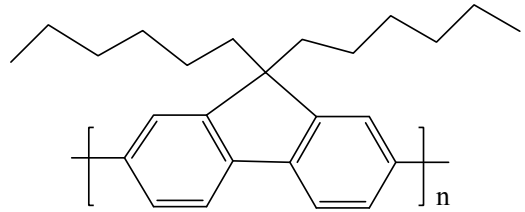
Poly(3-butylthiophene)
(P3BT, V_{onset} = 3.2 V)



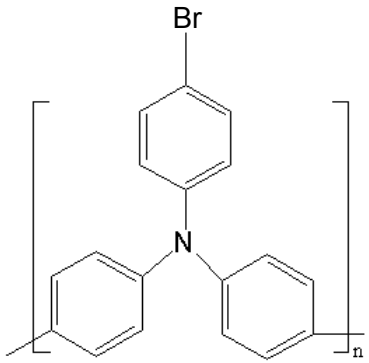
Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]
(MEH-PPV, V_{onset} = 3.6 V)



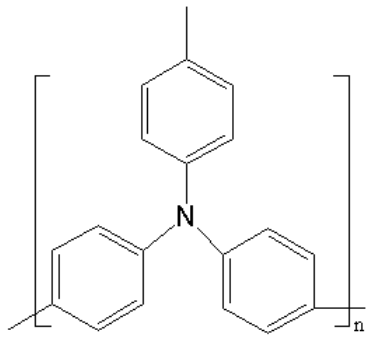
Poly(3-phenylthiophene)
(P3PT, V_{onset} = 3.9 V)



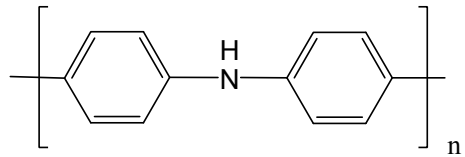
Poly(9,9-dioctylfluorene)
(PFO, V_{onset} = 4.1 V)



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



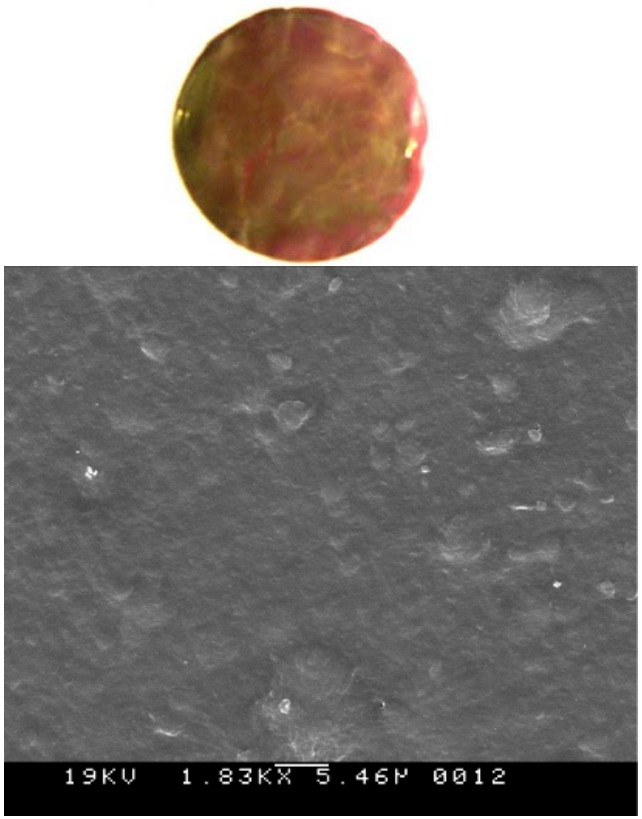
Polytriphenylamine
(PTPAn, V_{onset} = 3.8 V)



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

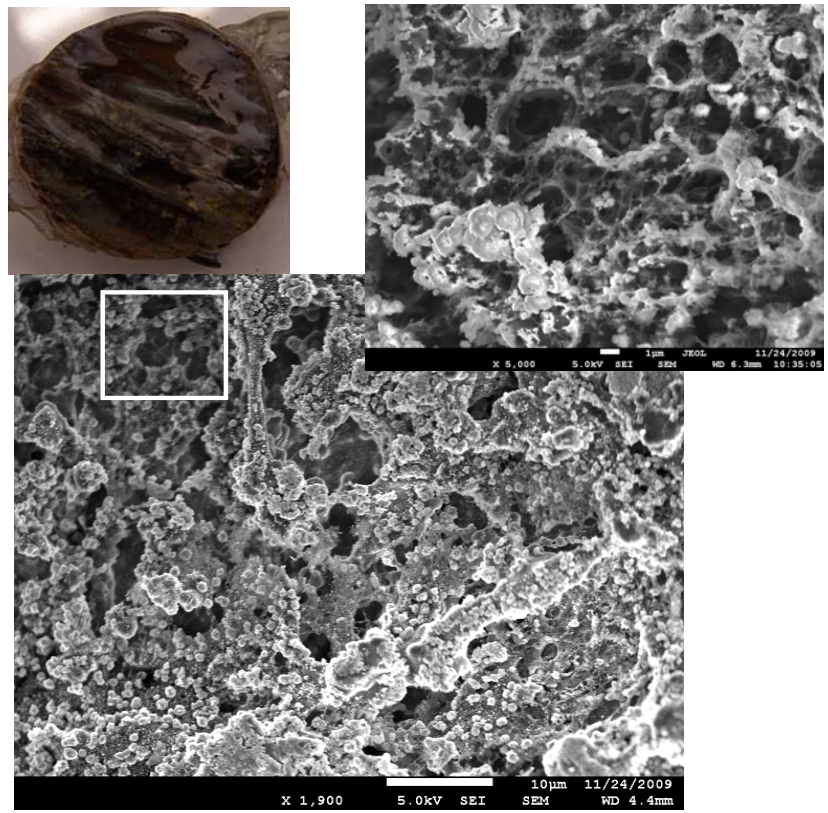
Polymer Morphology

Solution impregnation



- Large amount of polymer on membrane surface led to low utilization and rate capability.

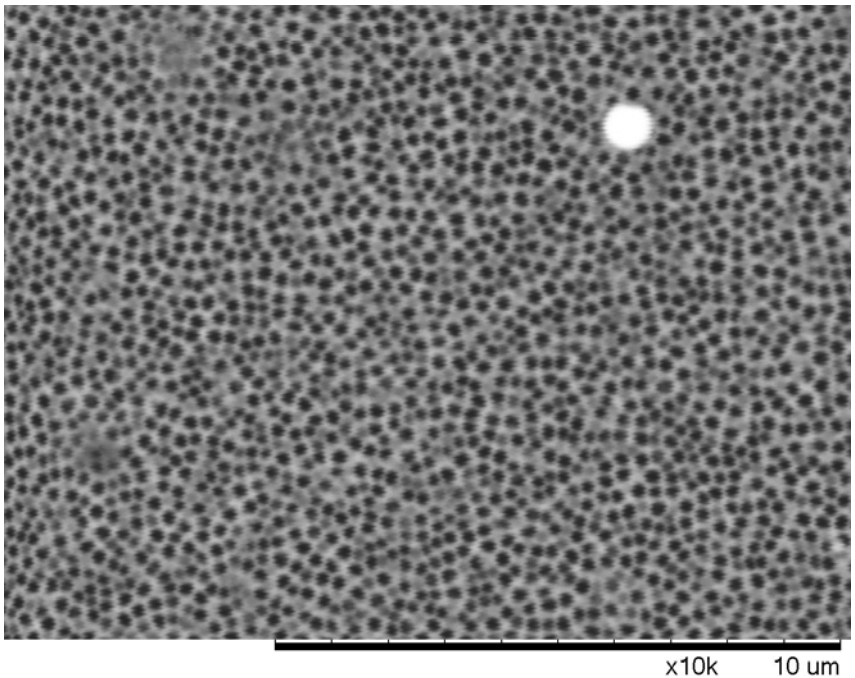
Electrochemical polymerization



- Highly interconnected polymer networks and more efficient conduction paths were created in the membrane pores.

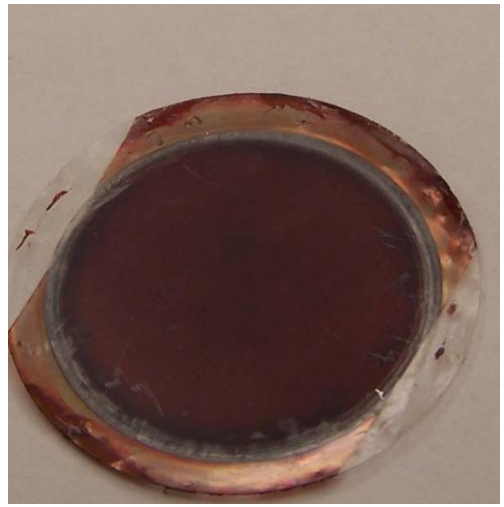
Polymer Morphology
Aligned Nanofibers

Alumina membrane template (AAO)
(25-50% porosity, 20nm pore size)



Electropolymerization →

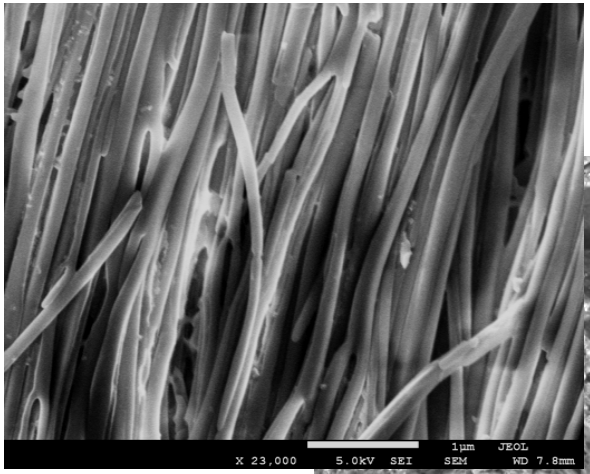
Polymer - AAO
composite

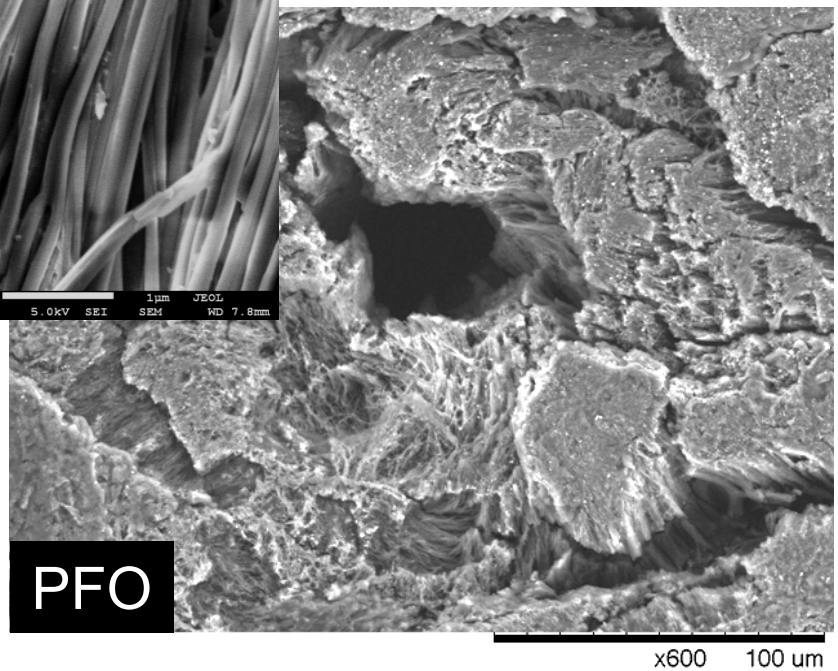


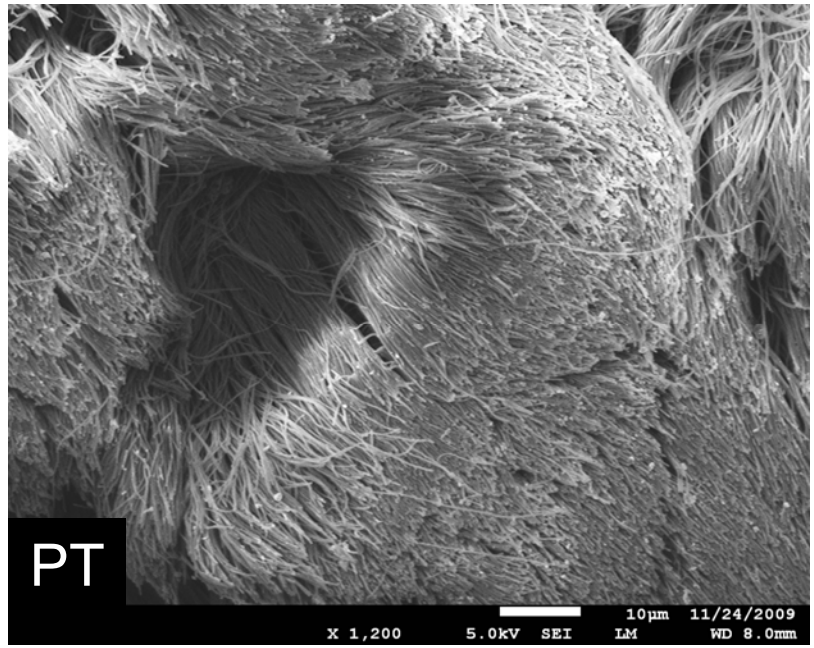
Template
removed ↓

Aligned
polymer nanofibers

Polymer Morphology
Aligned Nanofibers

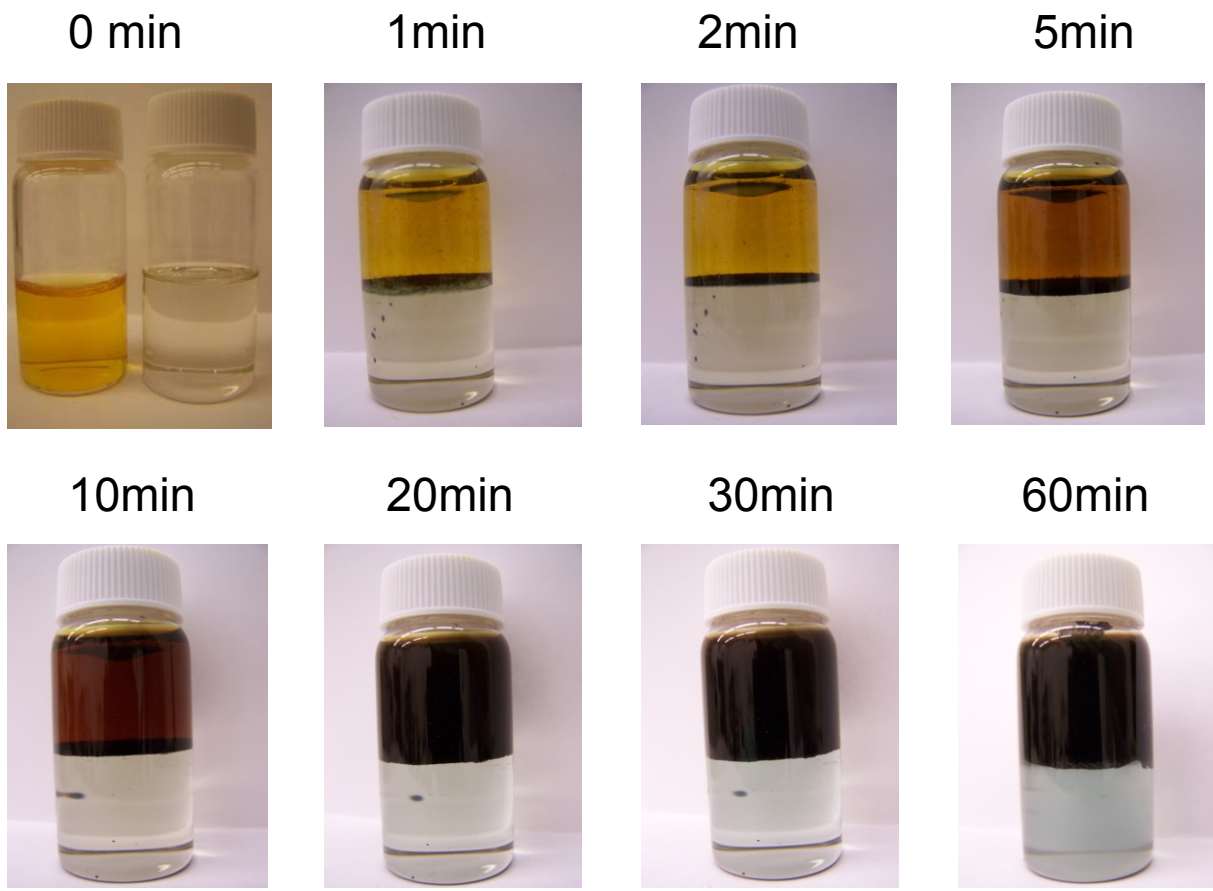






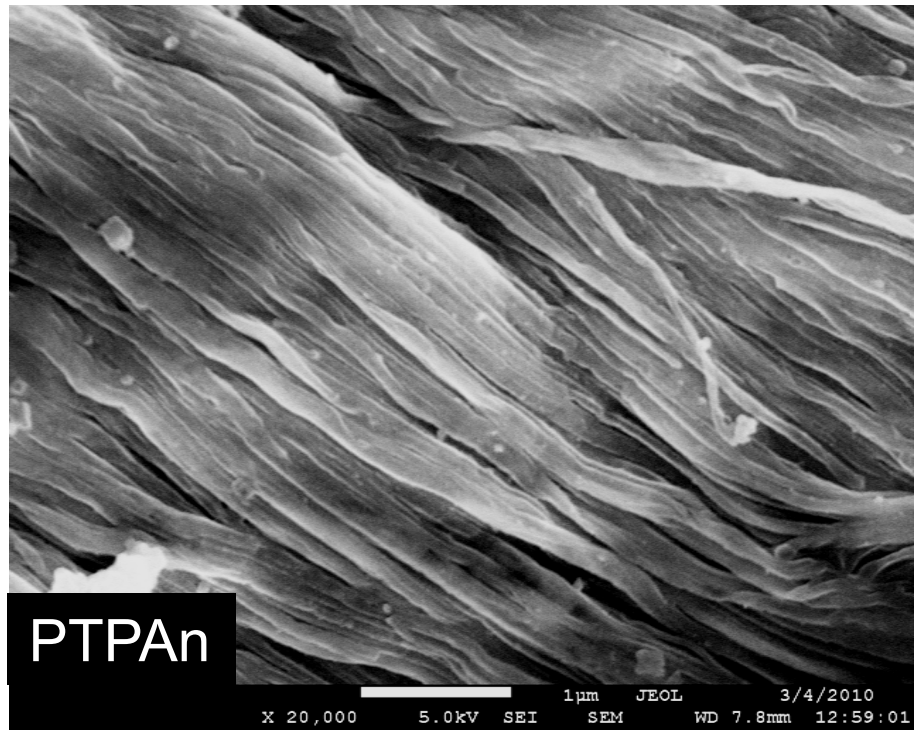
- Aligned nanorods extend the full thickness of the template.
- Each polymer nanorod may be used to provide a direct, high-current path between the electrodes.

Polymer Morphology
Aligned Nanofibers



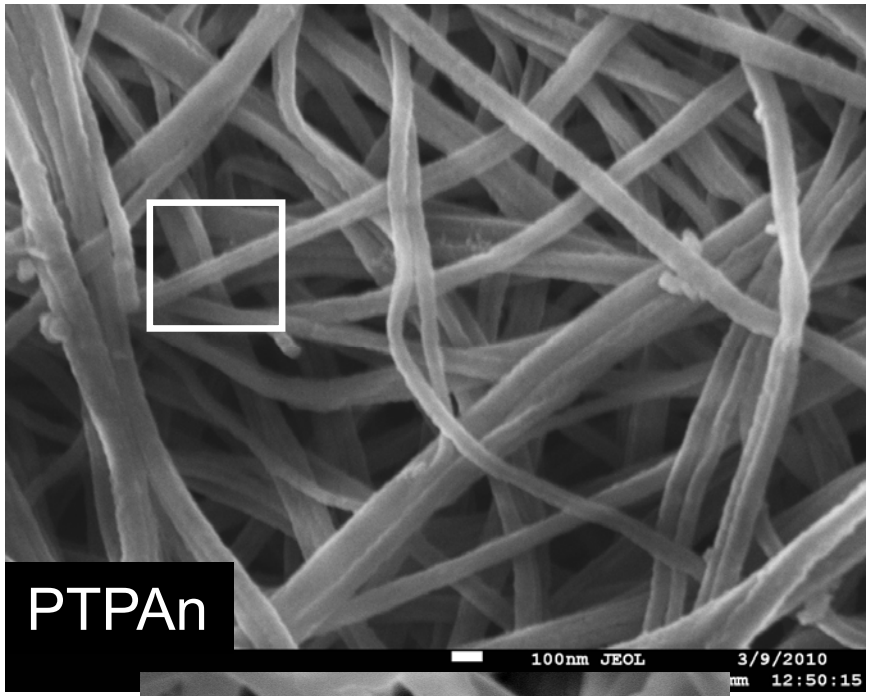
- Electroactive polymer synthesized in a simple one-pot reaction of a monomer, an oxidant and an initiator.
- Purification achieved by dialysis.

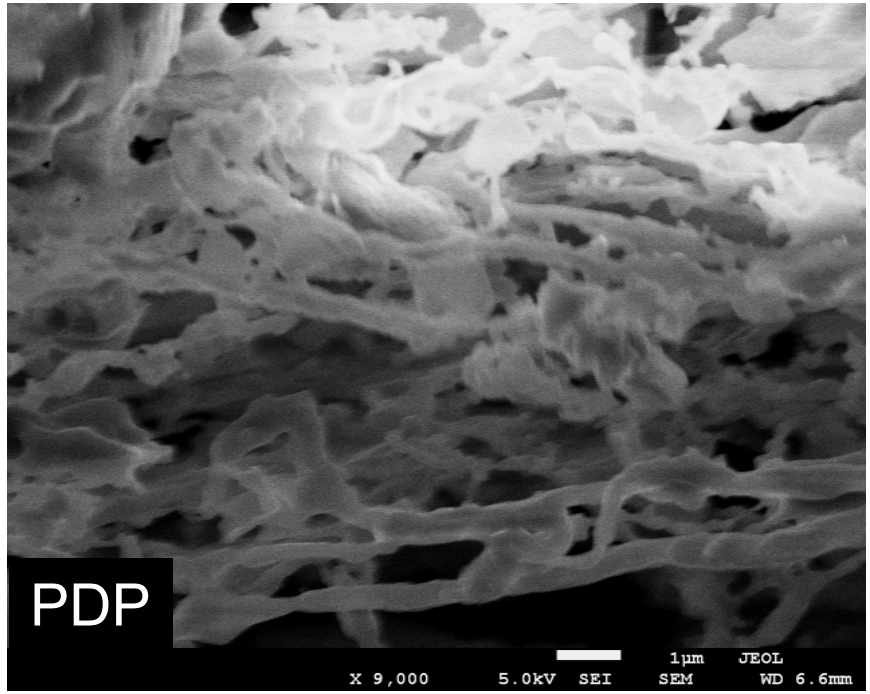
Polymer Morphology
Aligned Nanofibers

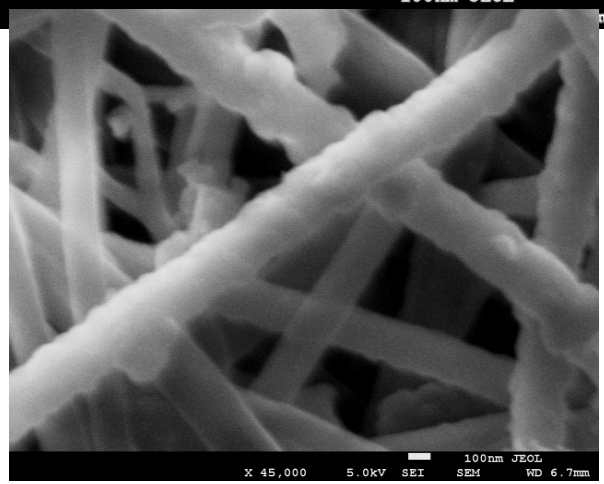


- Adding the initiator solution to the mixture of oxidant and monomer leads to the formation of aligned nanofibers.

Polymer Morphology
Unaligned Nanofibers



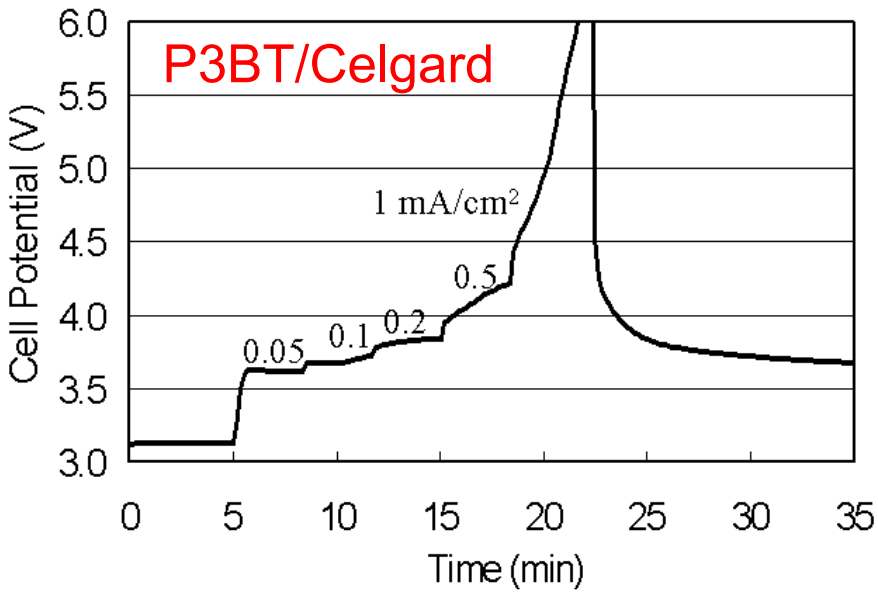


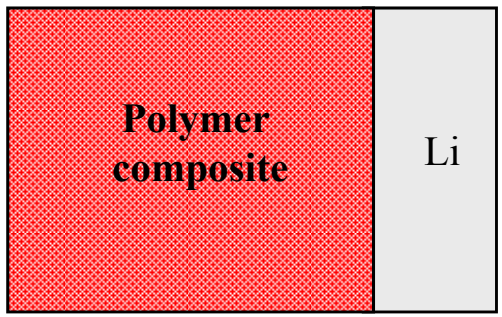


- Adding the oxidant solution to the mixture of initiator and monomer leads to the formation of unaligned nanofibers.

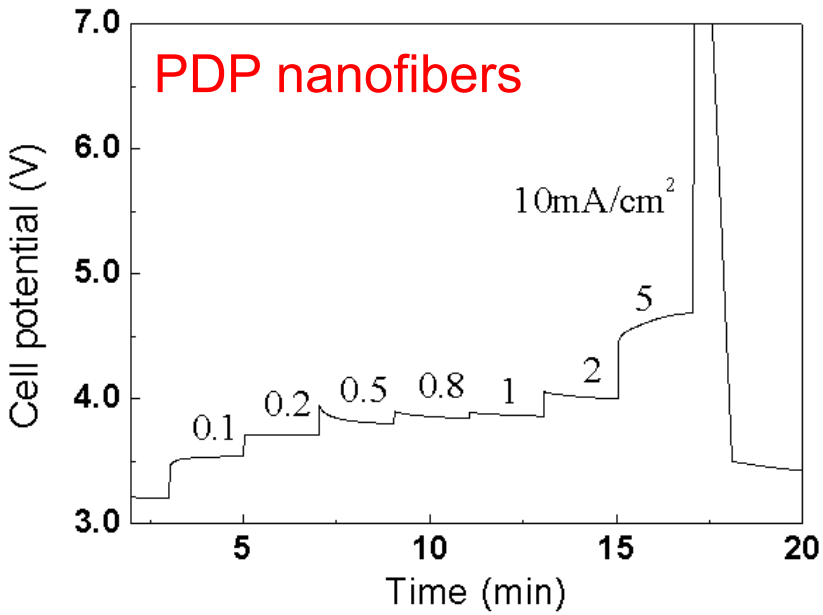
Rate Capability of the Composites

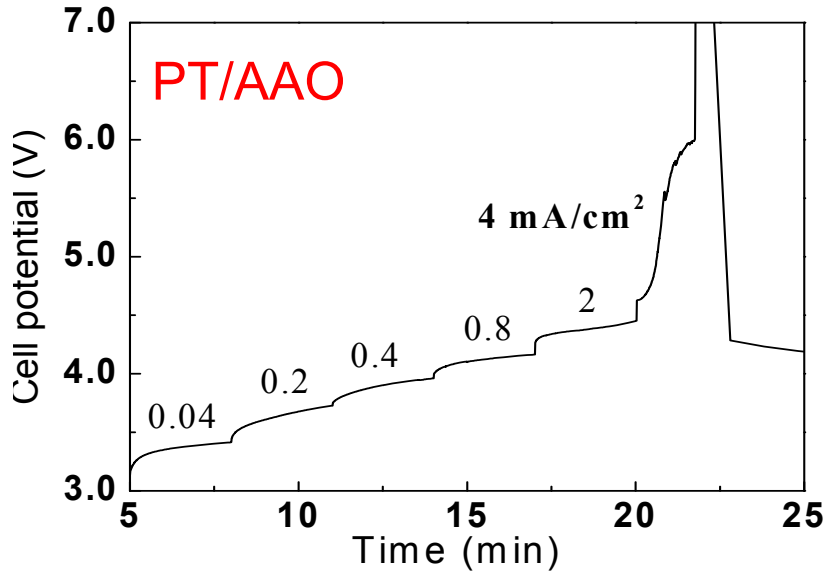
Previous morphology





Current morphology





- Up to 4x improvement in sustainable current density with the new polymer morphology.

Collaborations

- Robert Kostechi (LBNL) – Raman and FTIR Spectroscopy
- John Kerr (LBNL) – TGA and DSC
- Vince Battaglia, Marca Doeff, Gao Liu (LBNL) – Electrode Fabrication

Future Work

- Prepare composite separators with electroactive polymer nanofibers and evaluate their rate capability and cycle life.
- Investigate other high-voltage electroactive polymers that may be used for overcharge protection for PHEV. Optimize their morphology for maximum protection.
- Explore other cell configurations that may lead to improved protection and lower cost.

Summary

- New electroactive polymers were evaluated for their potential use as overcharge protection agents.
- Ways to produce various polymer morphologies have been explored. Aligned and unaligned polymer nanofibers were prepared.
- New polymer composites were found to have improved sustainable current densities.
- Alternative cell configurations have been investigated. Placing the polymer protection outside the electrode assemble improves the rate and low temperature performance.