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Inactive Materials Safety Issues in Lithium-ion Batteries

Christopher J. Orendorff, Ganesan Nagasubramanian, Timothy N. Lambert, and E. Peter Roth

Sandia National Laboratories
Power Sources Technology Group
PO Box 5800, MS-0614
Albuquerque, NM 87185-0614
corendo@sandia.gov

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Outstanding Materials Safety Issues

As energy and power densities increase for PHEVs and EVs, materials level safety issues remain a concern

- Cathodes (LiM_xO_2)
  - Energetic thermal runaway
  - Gas generation upon decomposition & cataylsis
  - Mitigated largely through new materials: $LiFePO_4$, $LiMn_2O_4$ spinel
- Anodes
  - Mitigated through new materials: $LiTi_5O_{12}$ (but sacrifice energy density)
- **Electrolytes**
  - Degradation to generate large volumes of CO_2
  - Reactivity and flammability of vented solvent
  - Flammability measurements are incomplete for possible failure modes
- **Separators**
  - Thermal/mechanical stability under abusive conditions
  - Susceptibility to internal short field failure

The objective is to develop and/or evaluate abuse tolerant inactive materials

Objective and Technical Approach

Safety and reliability issues are independent of any battery performance requirement and may prevent the widespread adoption of new chemistries and technologies

- ***Electrolyte development:***
  - Sulfonimide/hydrofluoroether (HFE) systems (non-$LiPF_6$, reduced carbonate fraction
  - Reduce the formation of gas degradation products, improve temperature stability, and reduce flammability
- ***Separator development:***
  - Higher thermally stable (>200 C) polymer and composite materials for lithium-ion cell separators
  - Demonstrate electrochemical performance and mechanical/thermal integrity

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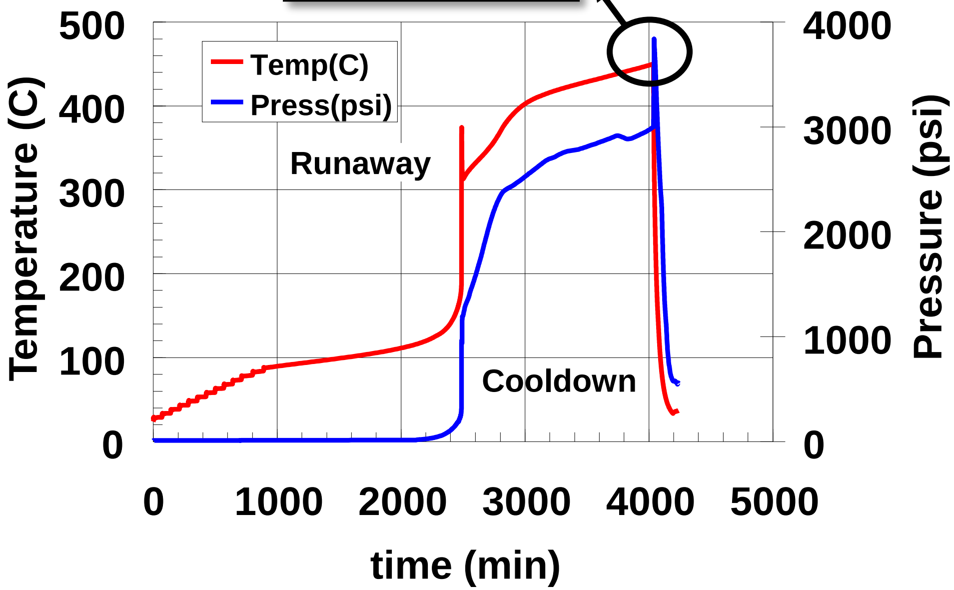
Electrolyte Breakdown → Gas Generation

Accelerating Rate Calorimetry (ARC)

1.2 Ah MCMB/$LiCoO_2$. in 1.2 M $LiPF_6$/EC:PC:DMC

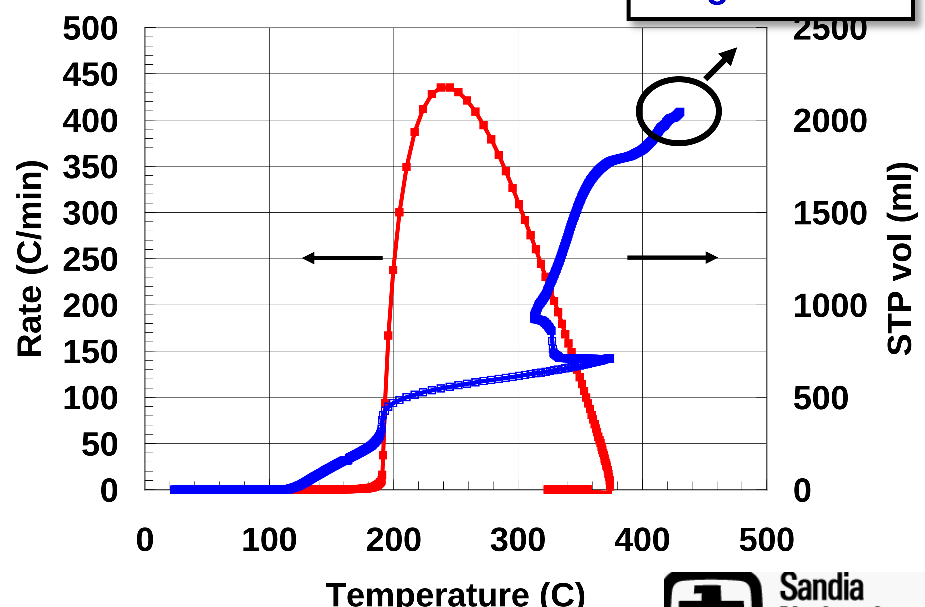
High pressure



Pressurizing an energetic closed system

Cell vent leads to a flammable solvent aerosol spray

Large volume



Limiting or slowing the rate of CO_2 generation will improve the safety performance of these cells

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Safety Issues with Conventional Electrolyte

Thermal ramp test of an 18650 Li^+ cell containing $LiPF_6$ electrolyte with a “flame retardant” additive

CO_2 build up vents electrolyte solvent aerosol, where even high flash-point, “non- flammable” additives readily burn

Reducing CO_2 generation and improving salt thermal stability will reduce the potential for a fire

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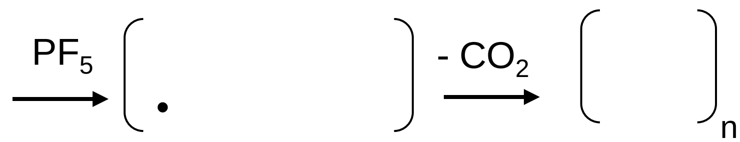
Sulfonimide/HFE electrolytes

- **$LiPF_6$ breaks down and catalyzes the degradation of carbonate electrolytes to give CO_2**
- **Examples of candidate electrolyte salts:**
  - **LiTFSI**
  - **LiBETI**
- **Other candidate electrolyte solvents:**
  - **Hydrofluoroethers (HFEs)**
    - **TMMP, TPTP**

Electrolyte breakdown:

$LiPF_6 \rightarrow \rightarrow PF_5 + POF_3$ …..



LiTFSI

TMMP

Avoid PF_6^- and minimize use of solvents with carbonate functionality

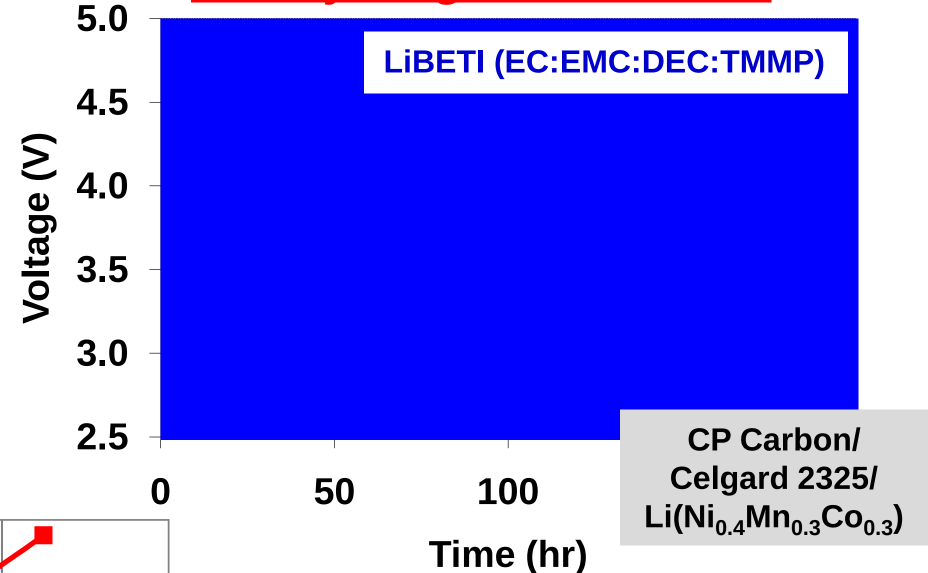
Data for 1 M LiX in either EC:EMC:DEC:TMMP (5:30:35:30) or EC:EMC:TPTP (5:45:50) (vol%)

Naoi, K. et al. J. Electrochem. Soc. 157, A190-A195, 2010;
Naoi, K. et al. J. Electrochem. Soc. 156, A272-A276, 2009

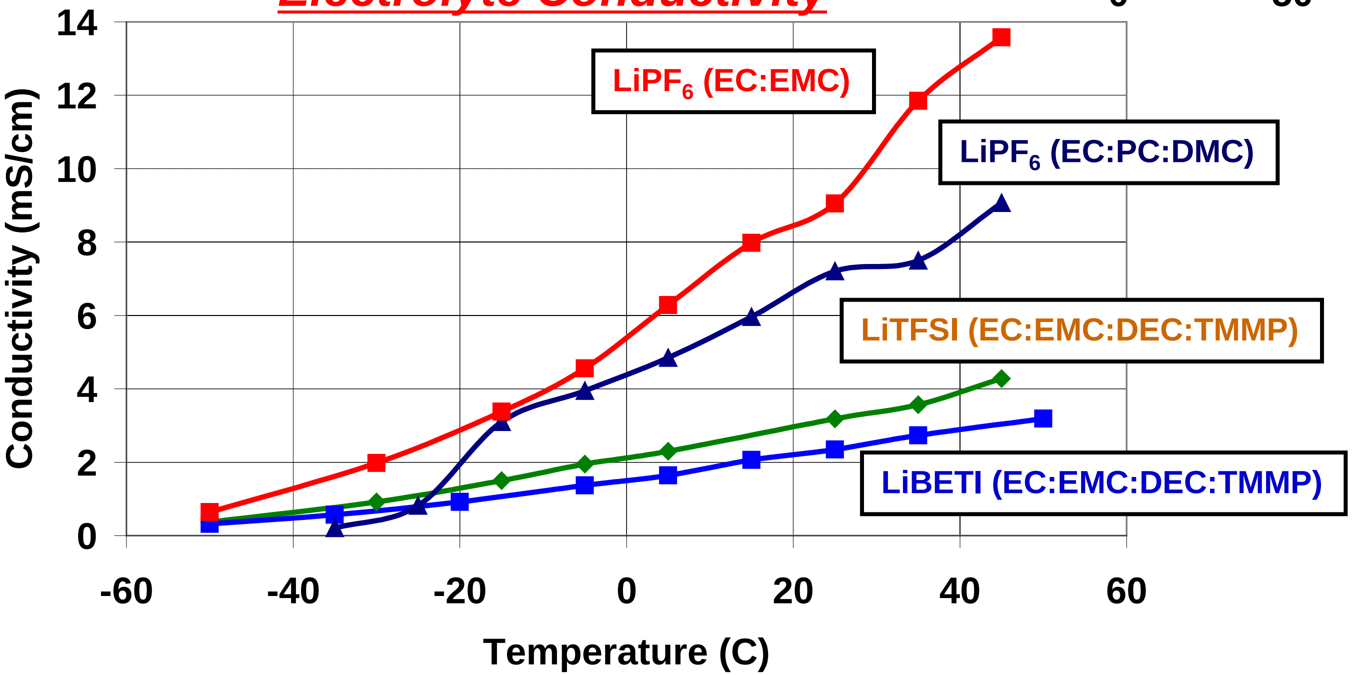
Sulfonimide/HFE Performance

- **Modest conductivity (better low temp.)**
- **RT cell cycling**
  - **18650 cells with TFSI/BETI – TMMP/TPTP electrolyte with 10-50 cycles**
- **High temperature cell cycling**
- **Degradation products/mechanism (normal use and abuse)**

Cell Cycling Performance



Electrolyte Conductivity



18650 Cell Capacities (1.1-1.2 Ah):
$LiPF_6$/EC:EMC > LiTFSI/TMMP > LiBETI/TPTP

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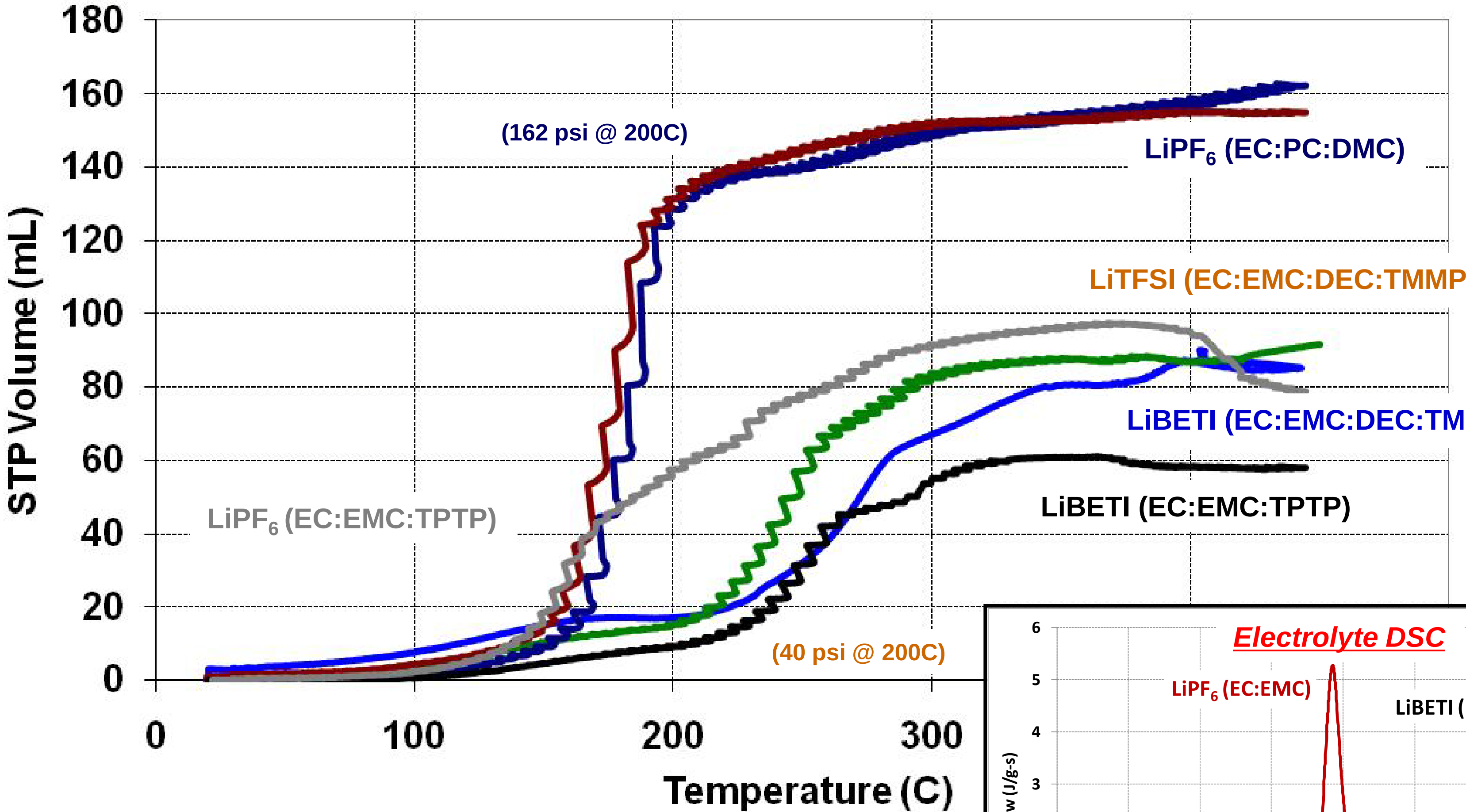
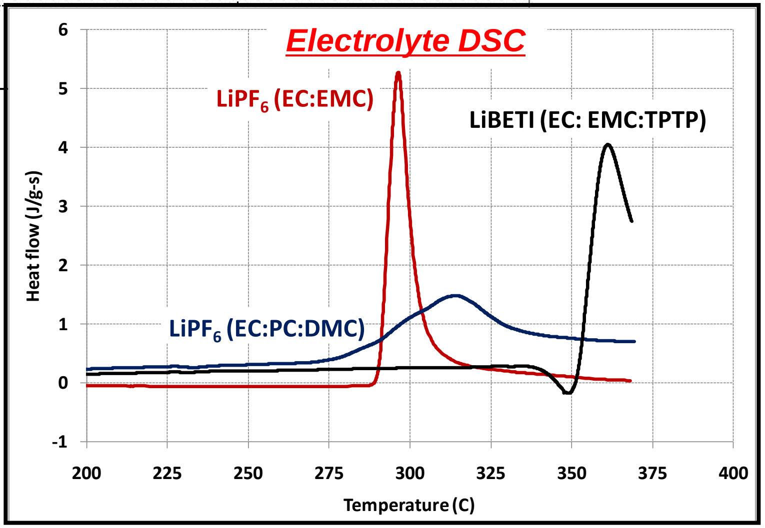
Reduced Gas Generation and Improved Thermal Stability

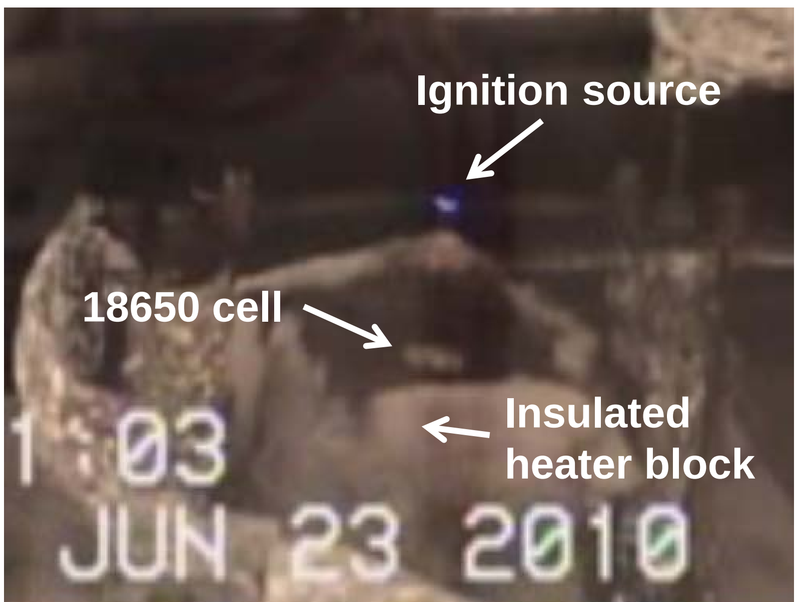




40-60% reduced gas generation (@ 300 °C)
Improved thermal stability

Electrolyte Flammability

- Traditional flammability experiments do not accurately capture the flammability hazard of a venting cell (pressure increase, solvent aerosol spray, etc.)
  - **Wick test/ignition test**
  - **Cotton ball fire**
- Flammability testing setup:



Reduced Flammability with HFE Solvents

Ignition of EC:EMC electrolyte

No ignition of the 50% TPTP HFE electrolyte

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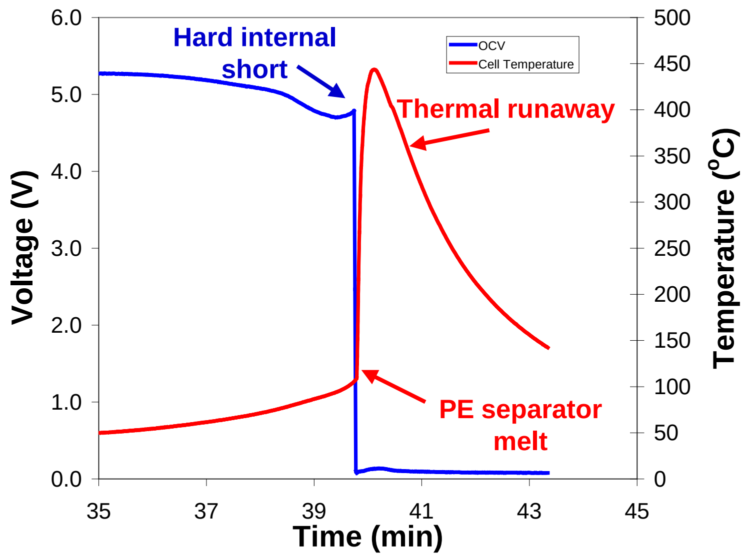
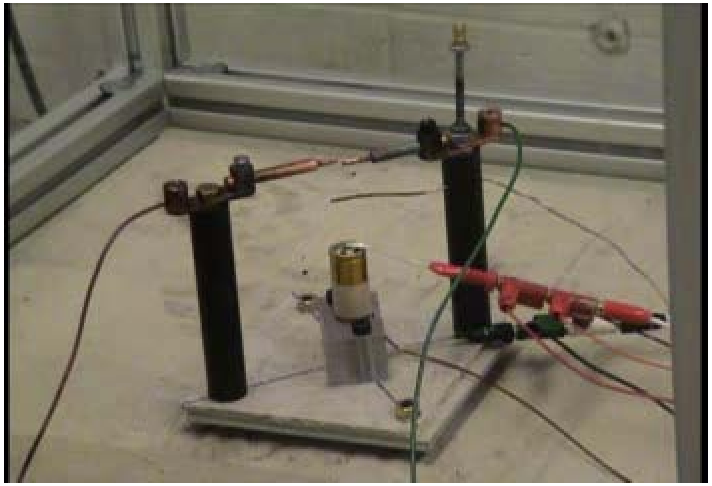
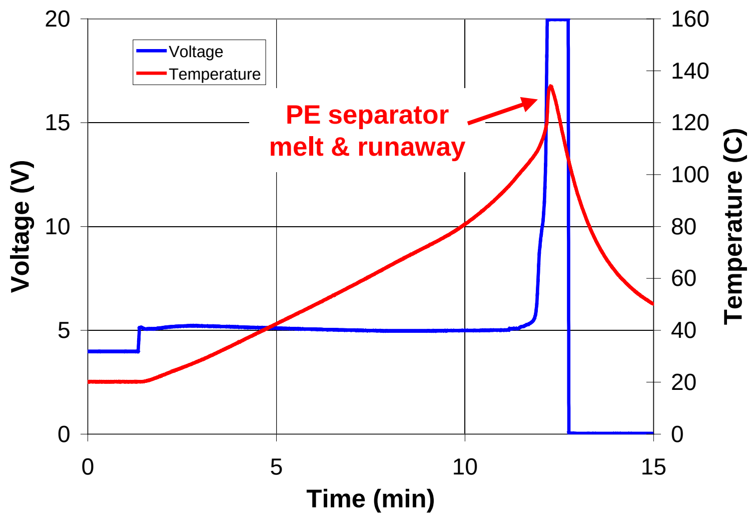
Safety Issues with Separator Failure Under Overcharge Abuse







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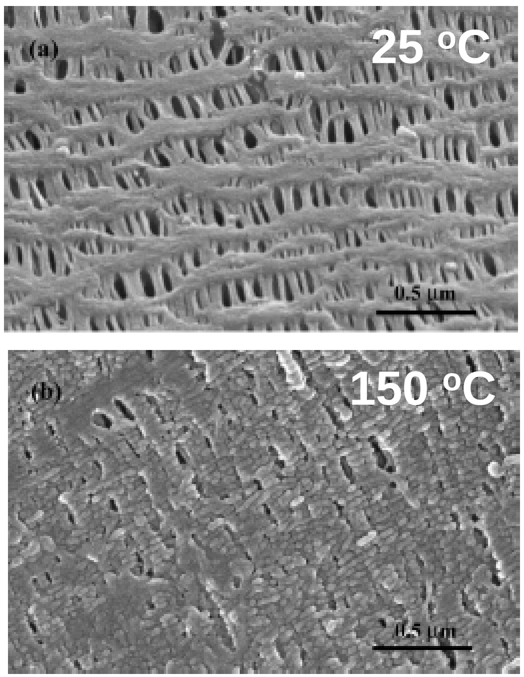
Abuse Tolerant Separators

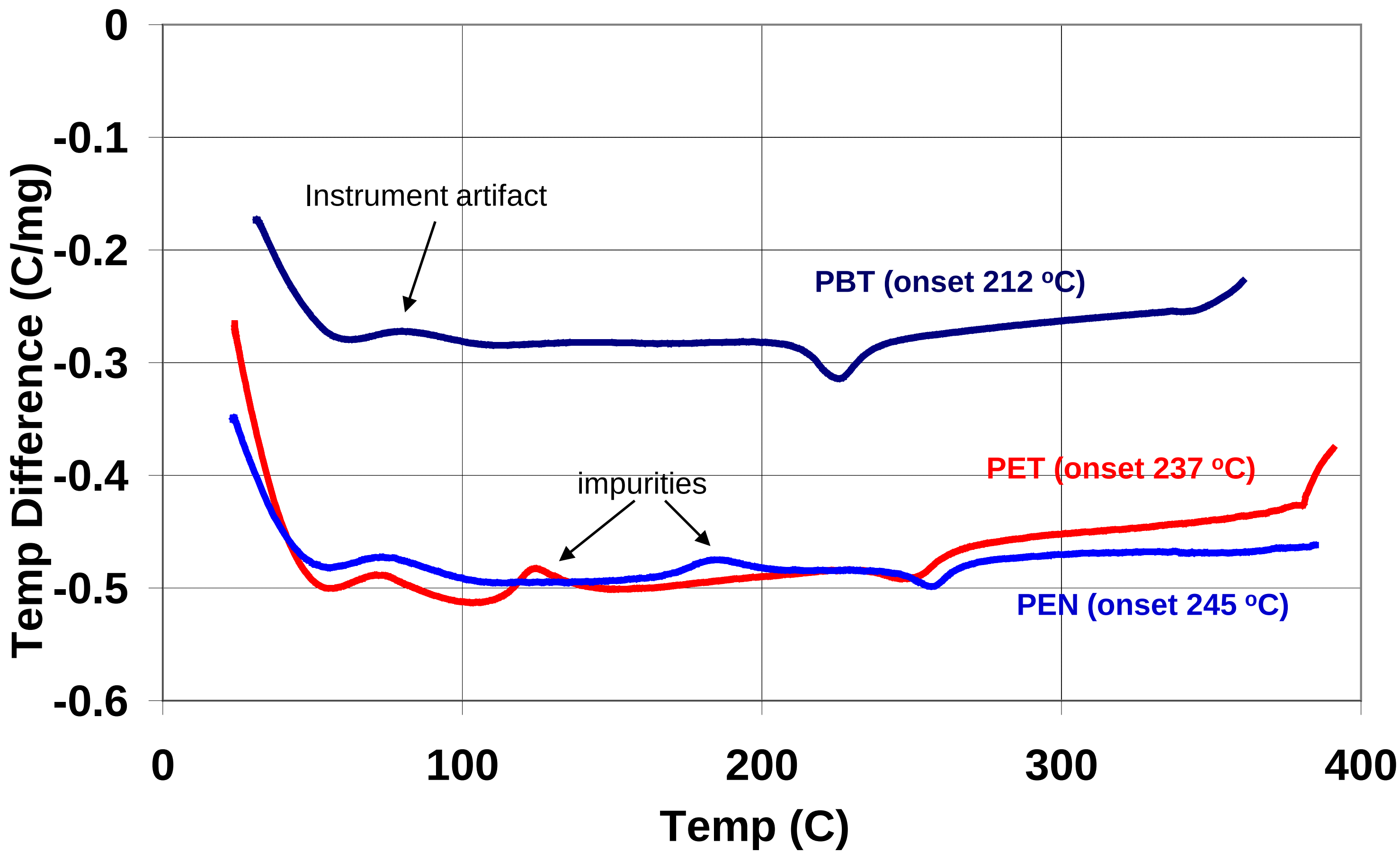
Incomplete separator shutdown



D. P. Abraham et al. *J. Power Sources*, 161 (2006), 648-657

- *Non-Shutdown Separator Characteristics*
  - Chemically inert (to Lithium)
    - No amides, no acrylates
  - Electrochemically inert (stable > 4.0 V)
  - Thermally stable (to > 200 ^{o}C)
- *Candidate polymers:*
  - Terephthalates (PBT, PET)
  - Napthalates (PEN)
  - Imides (PI)
- *Candidate ceramics:*
  - Alumina, silica, magnesia

DTA/TGA Analysis of SNL Separators



Thermal stability of SNL separators 210-240 ºC

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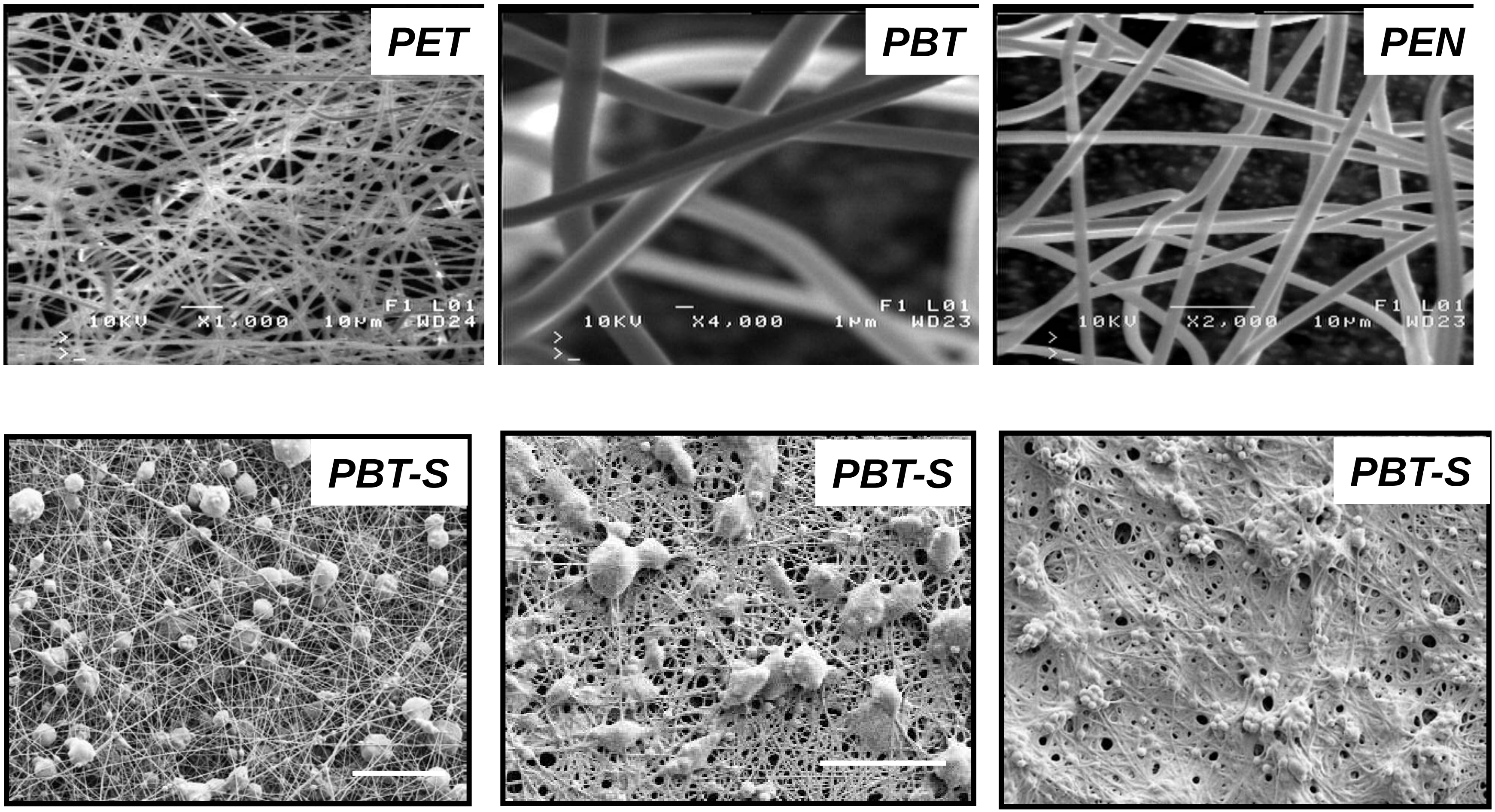
SEM Images of Prototype Separators

Electrospun Separators:



~25 cm^2 fiber mats, 20-50 µm thick (scale bar = 10 µm)

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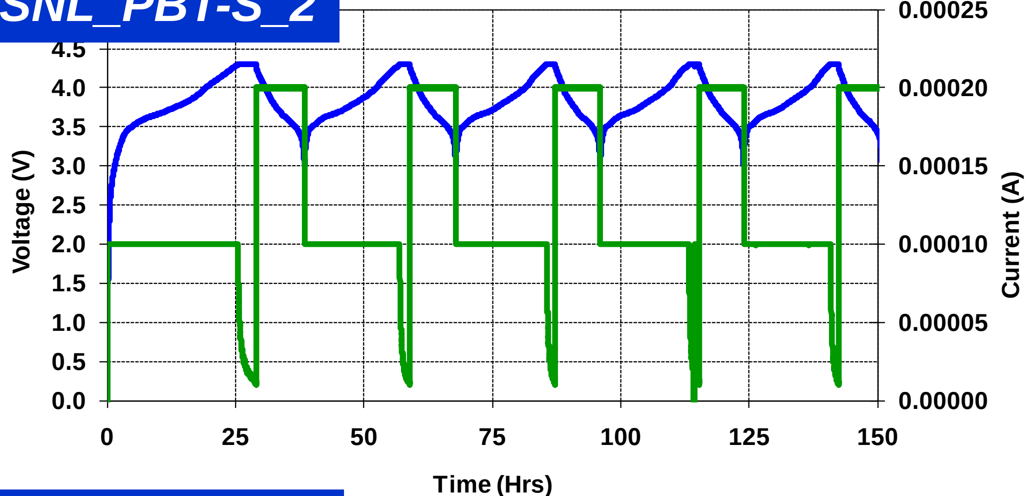
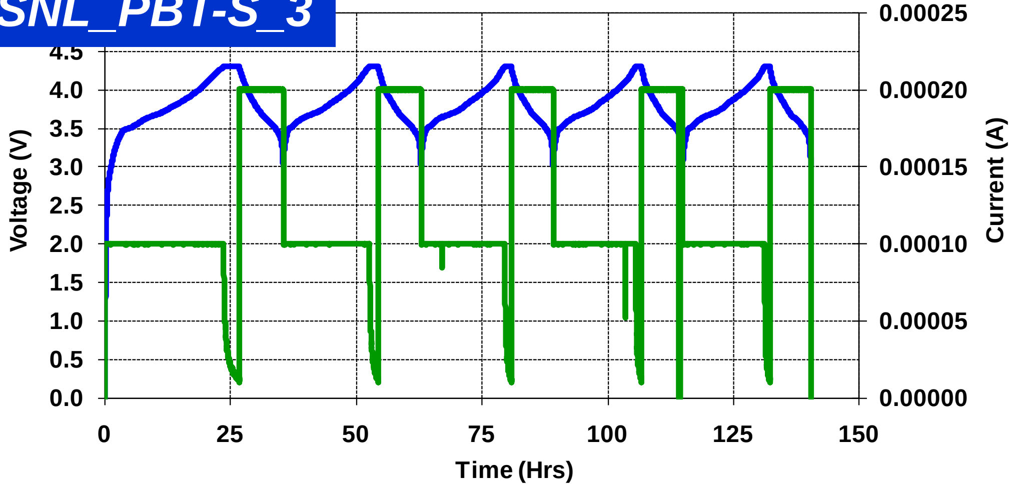
Performance of SNL Separators

SNL_PBT-S_2



SNL_PBT-S_3



Separator	(µm)	Gurley # (100 mL/s)
Celgard 2325	25	570± 4
Tonen 25MMS	25	637± 10
Tonen 20MMS	20	524 ± 9
Separion	20	23 ± 0.5
Porous Power HPX1	20	27 ± 4
SNL_SEV_1	15	137 ± 5
SNL_SEV_2	38	6027 ± 1562
SNL_PBT-S_2	12	298 ± 148
SNL_PBT-S_3	42	86 ± 16

Prototype performance comparable to commercially available separators

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Summary and Conclusions

- Demonstrated improved thermal stability of sulfonimide/HFE electrolytes to > 200 C compared to conventional $LiPF_6$/carbonate systems
- Demonstrated a 40-60% reduction in total gas volume generation using sulfonimide/HFE electrolytes compared to $LiPF_6$/carbonates
- Determined processing conditions and materials to prepare porous, high-melt integrity, separators for lithium-ion cells
- Preliminary indicators (porosity, film thickness, cell cycling) suggest comparable performance of prototype SNL separators to commercial materials
- Experiments to determine abuse response of cells built with HFE electrolytes and SNL separators are currently in progress

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