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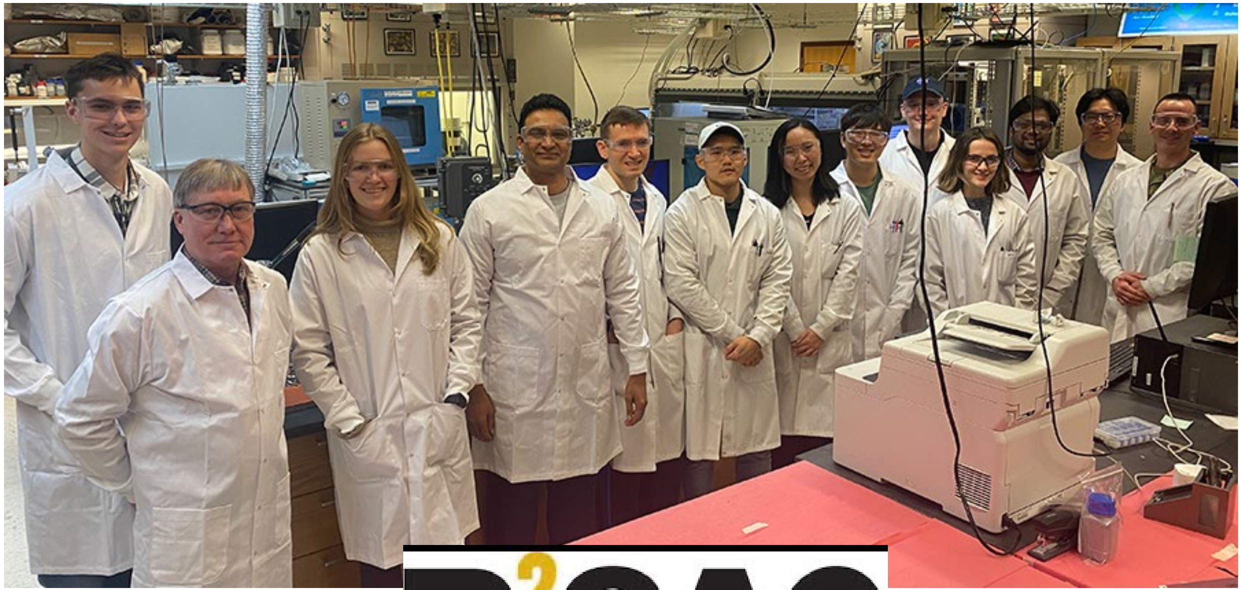
ViPER
Vilas Pol Energy Research

Mastering the Science and Engineering of Lithium-ion Battery Safety

Vilas G. Pol

Professor of Chemical Engineering



P2SAC
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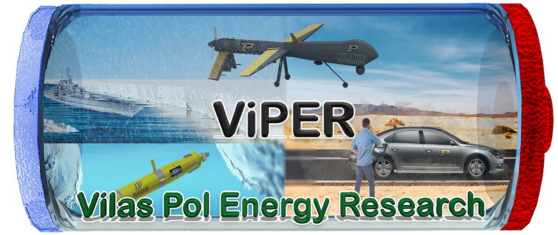
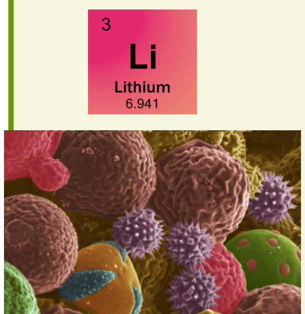
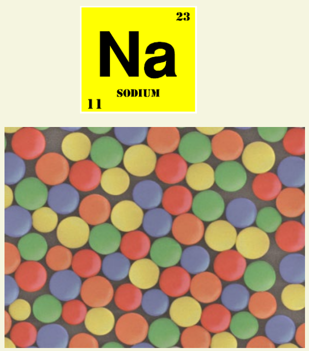
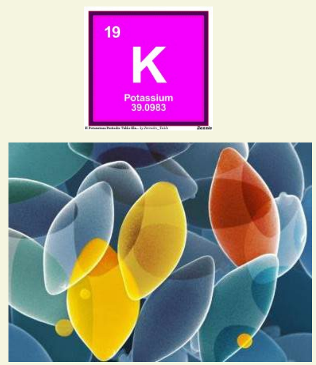


Research Areas

Lithium-ion	Sodium ion	Potassium ion	Li-S/Solid state	Flow
				

300+ Publications; 64 H index, 200+ invited talks
27 issued US patents (10+ pending), 40+ awards

Li-ionBattery Research Challenges

New

- **Cost**

  Current projected cost (25 kW battery) ~ $1000

  - Target cost (25 kW battery) ~ $500

Battery 2012 Safety

- **Safety**

  Inherently safe batteries needed

  - Overcharge protection circuitry expensive

- **Life**

  Current technology ~ 5 to 10 years

  - Target ~ 15 years

- **Low Temperature Performance**

  Current technology ~ Sluggish < 0 ºC

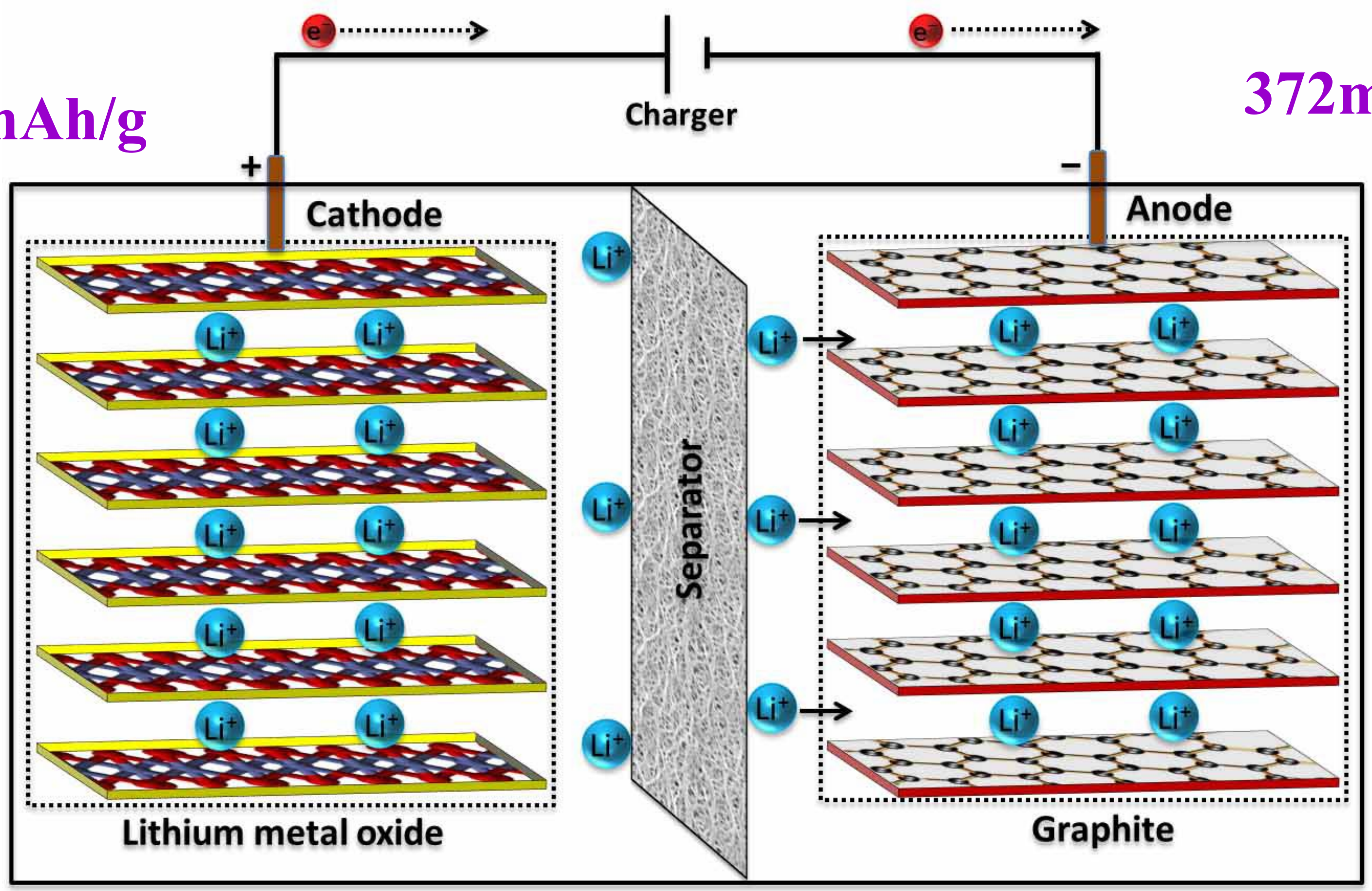
  - Target ~ -30 ºC (cold cranking)

John B. Goodenough *et al.*, *Chemistry of Materials* **(2010)** *22*, 587

How Li-ion Batteries Work?

200 mAh/g

372mAh/g

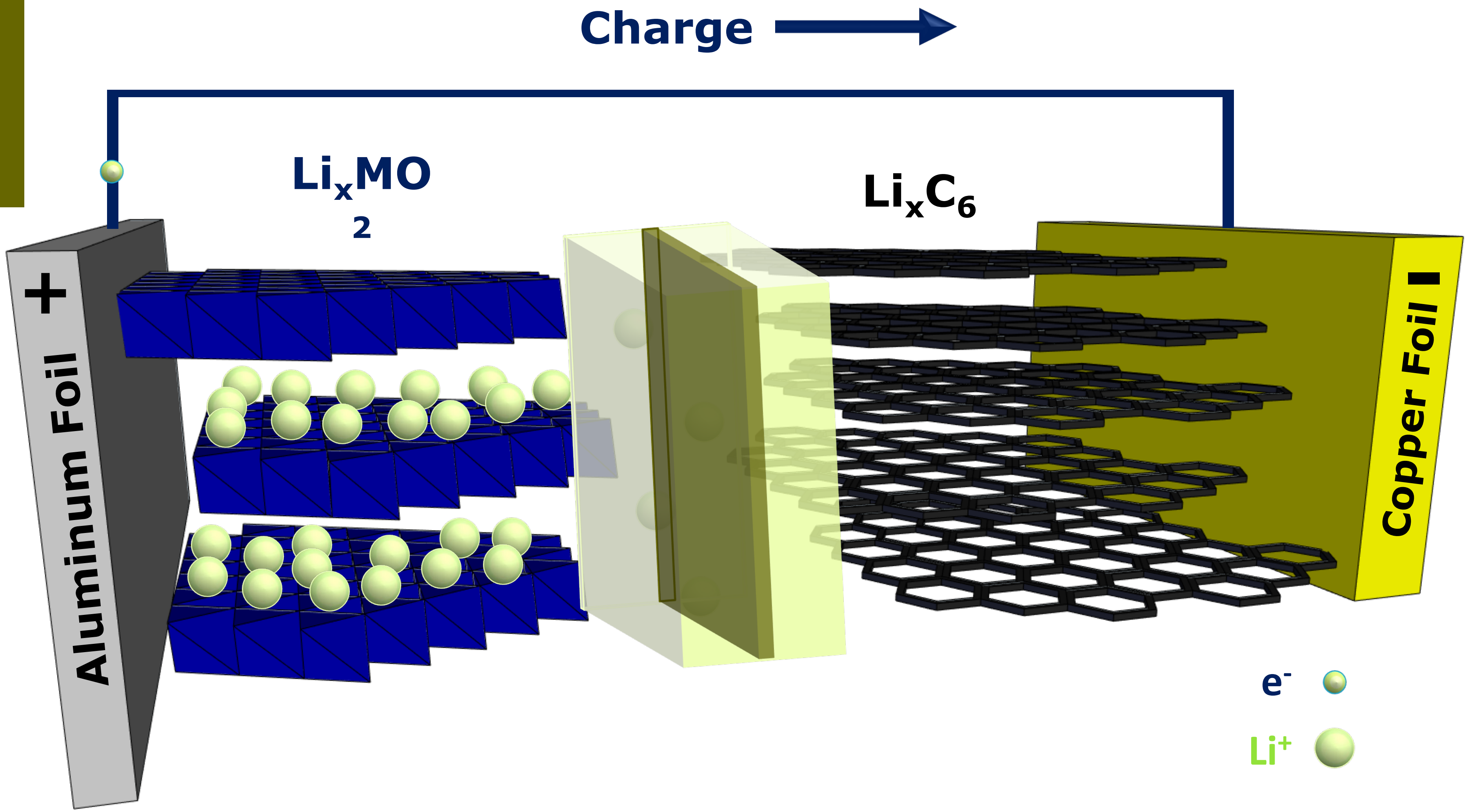


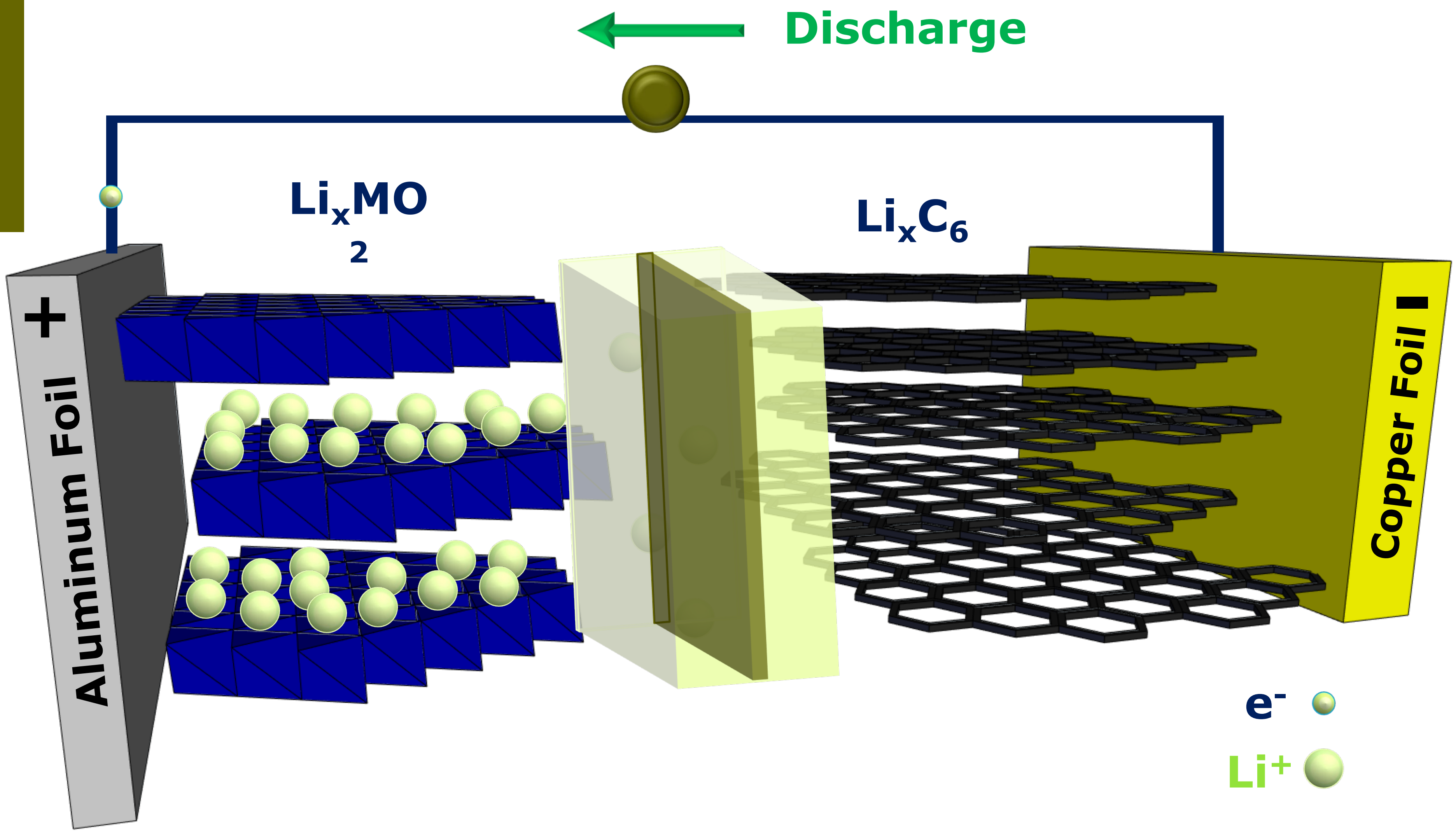
LiC_6

✓ **Process reversibility should be 100% to have longer cycle life**

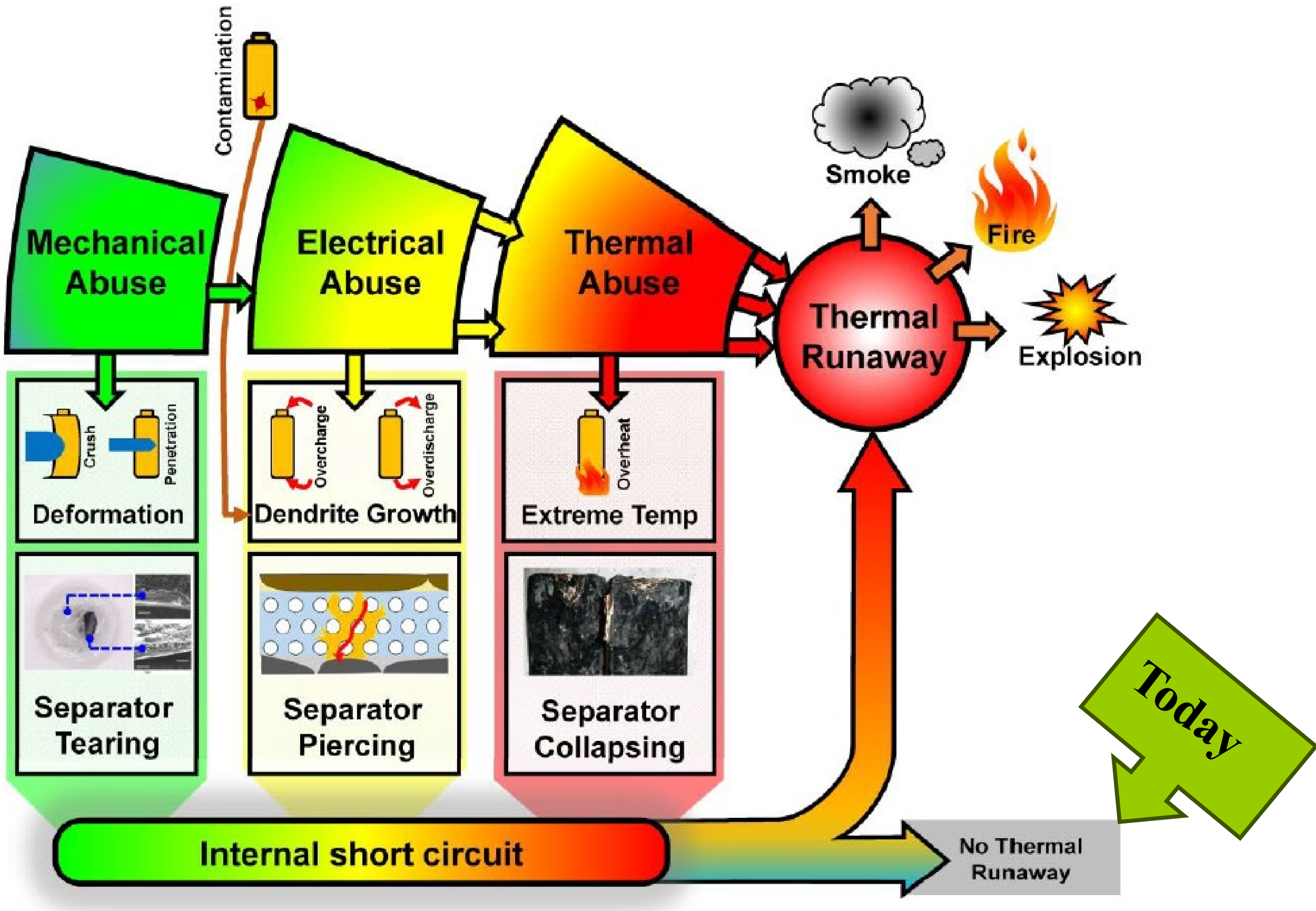
✓ **Requires high capacity electrode materials**

How Does Lithium-ion Battery Works?



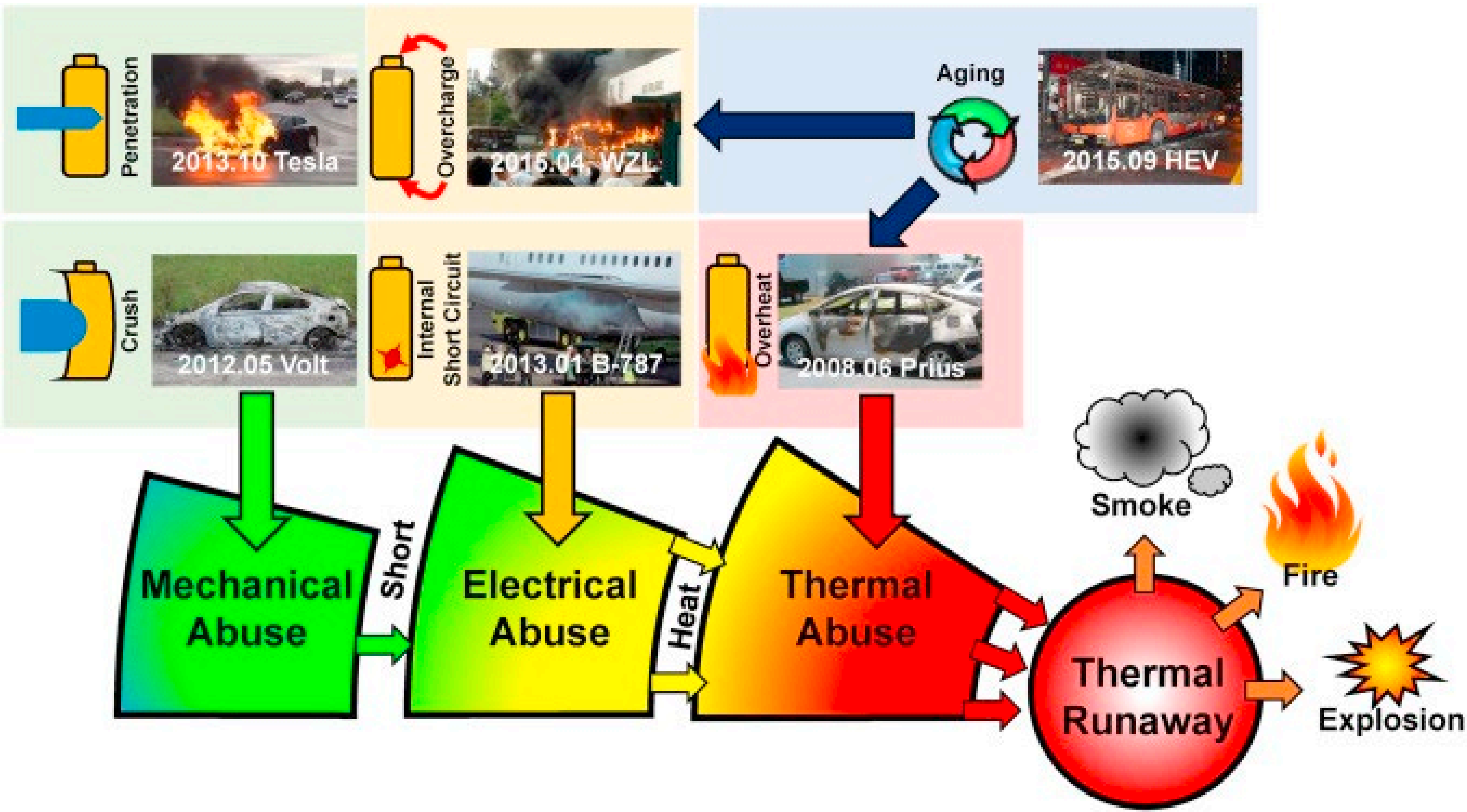

Discharge
Li$_x$MO
2
Li$_x$C$_6$
+
Aluminum Foil
Copper Foil
e$^-$
Li$^+$

Thermal runaway mechanism of lithium-ion battery



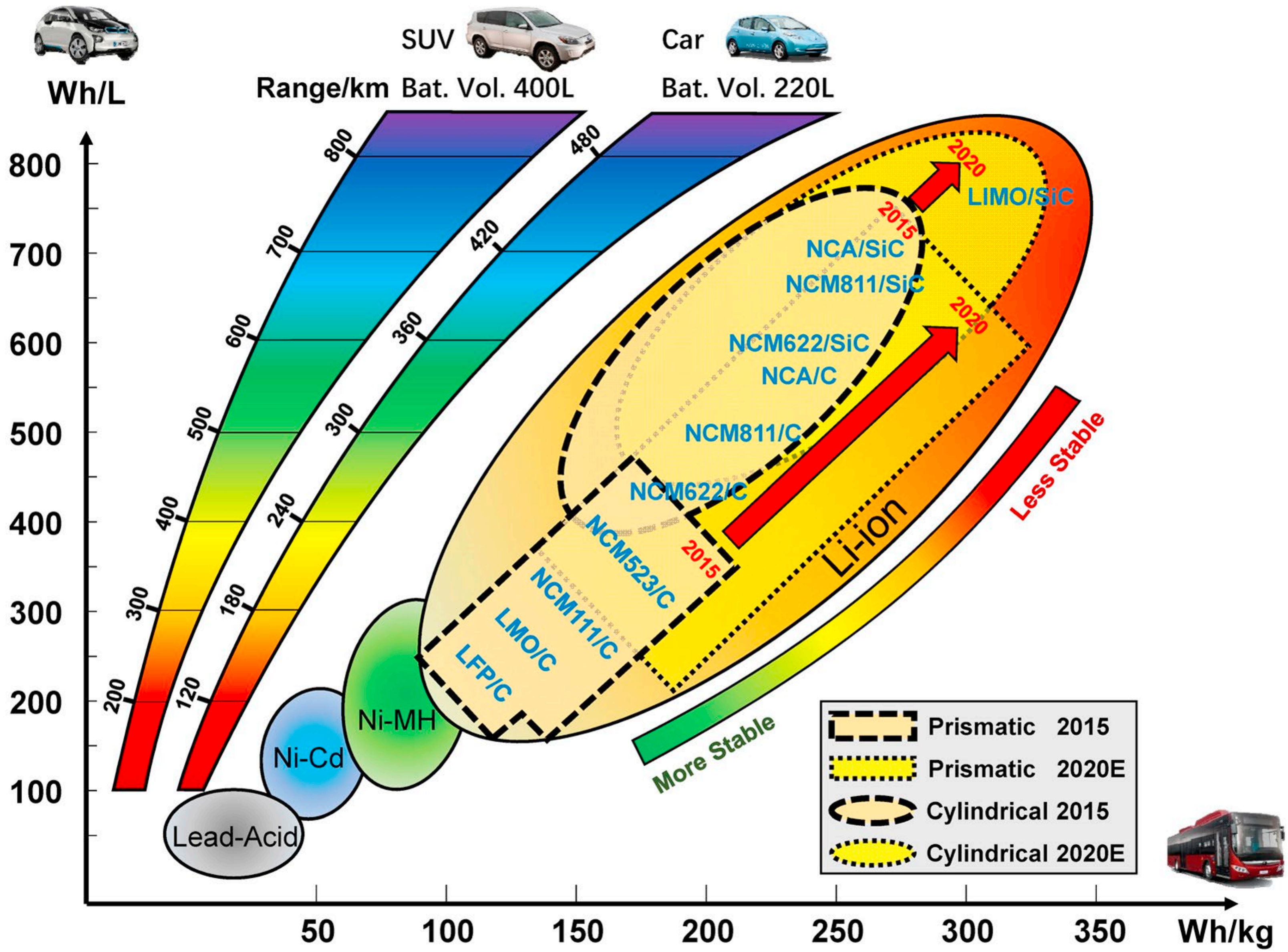
Feng et al. *Energy Storage Materials,* 2018, 10, 246.

Accidents related with lithium-ion battery failure



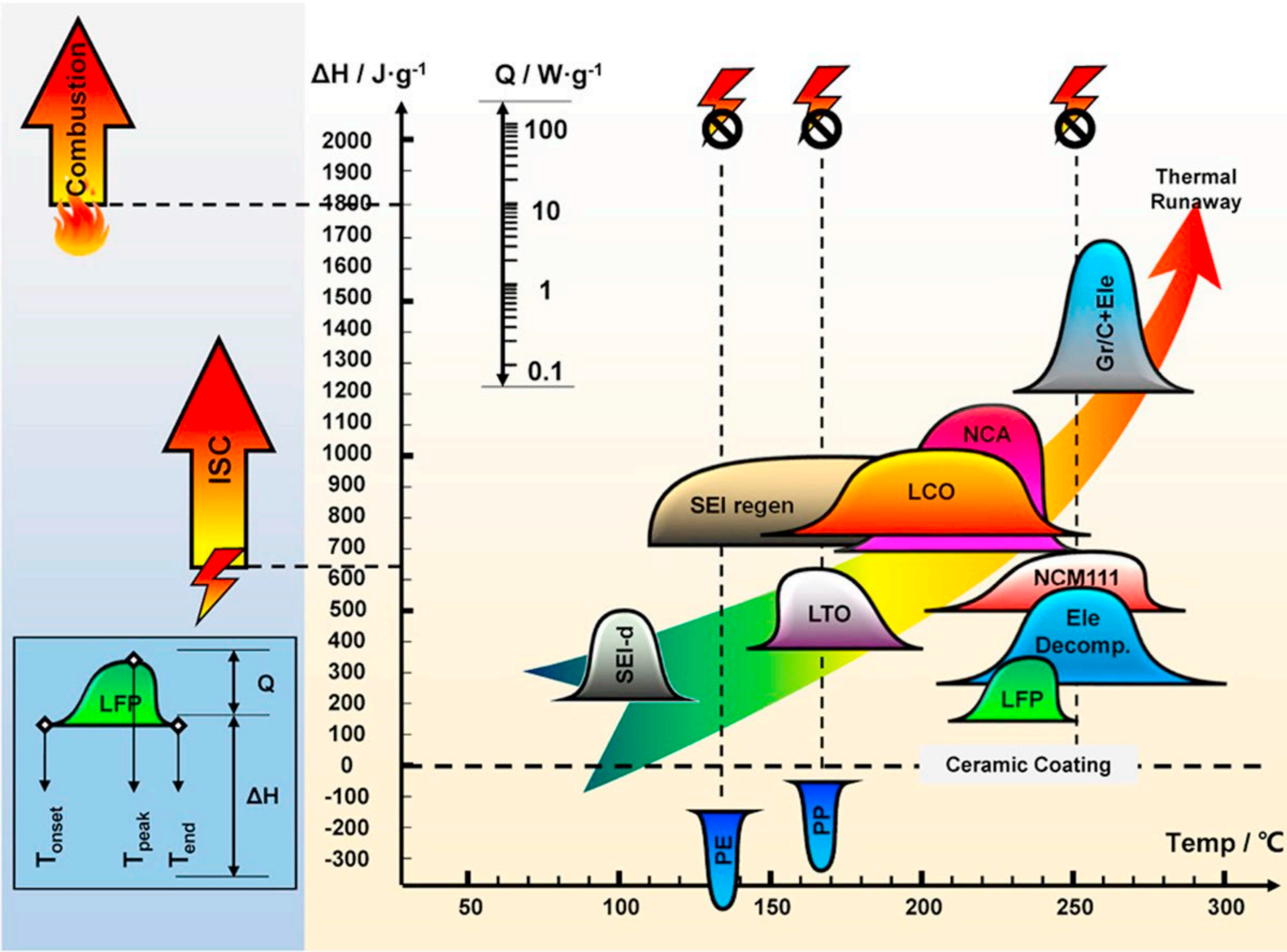
Feng et al. *Energy Storage Materials,* 2018, 10, 246.

The roadmap of the lithium-ion battery



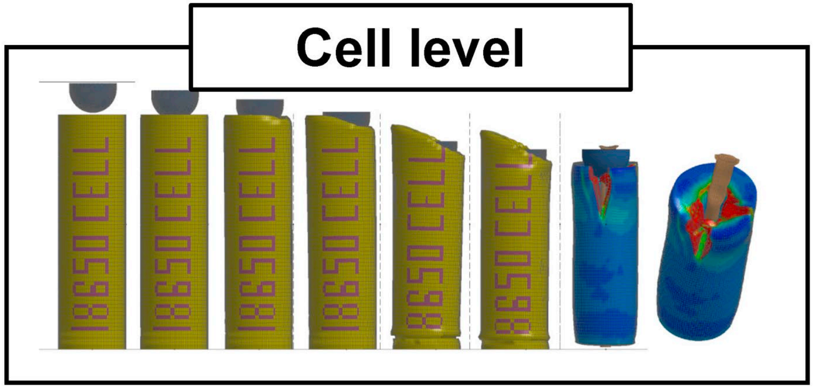
Feng et al. *Energy Storage Materials,* 2018, 10, 246.

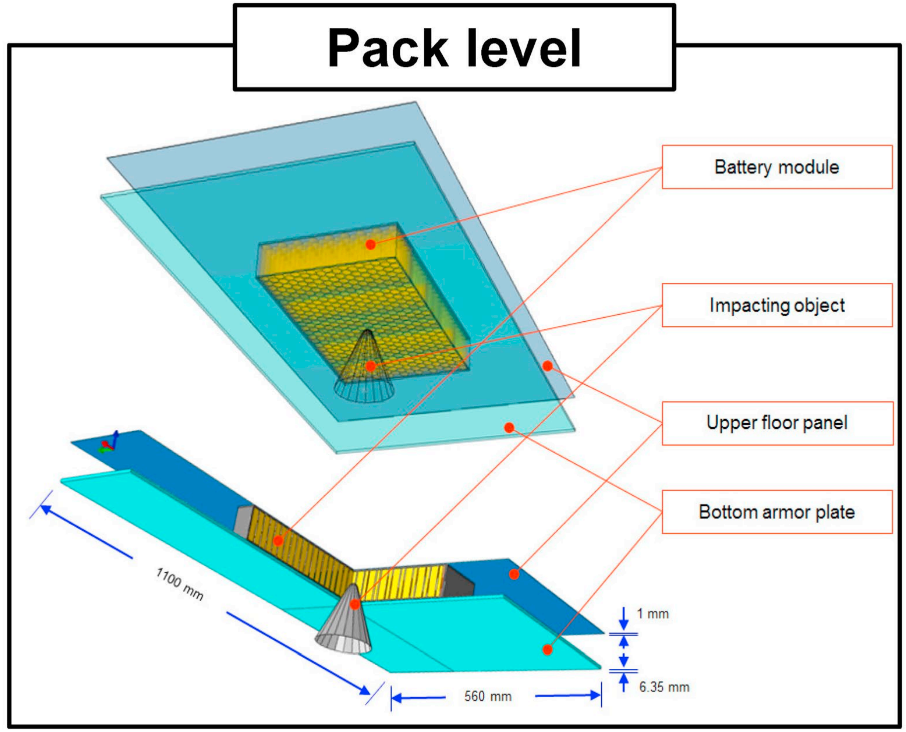
Components contribution in heat generation

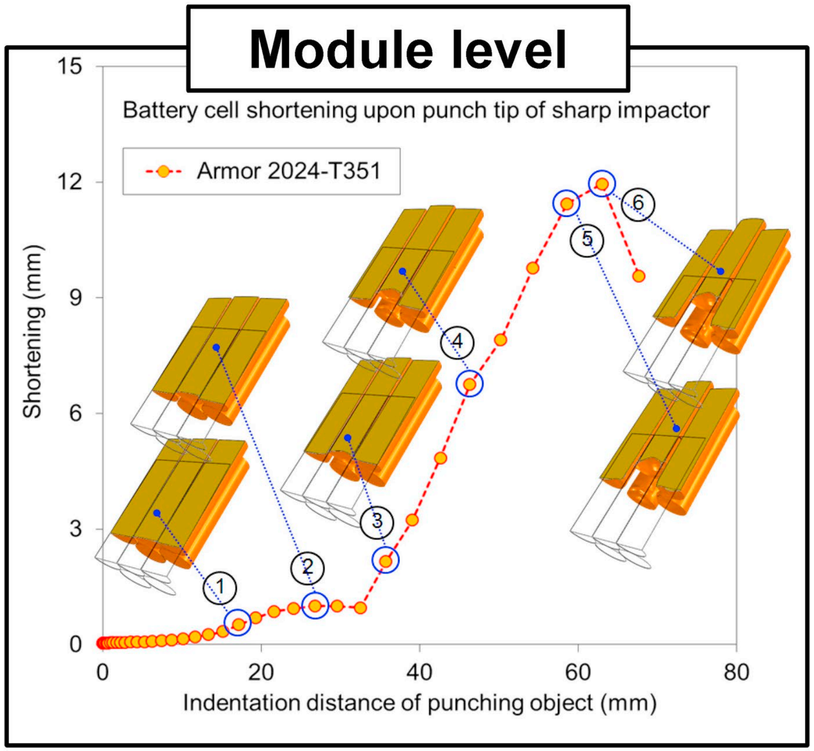


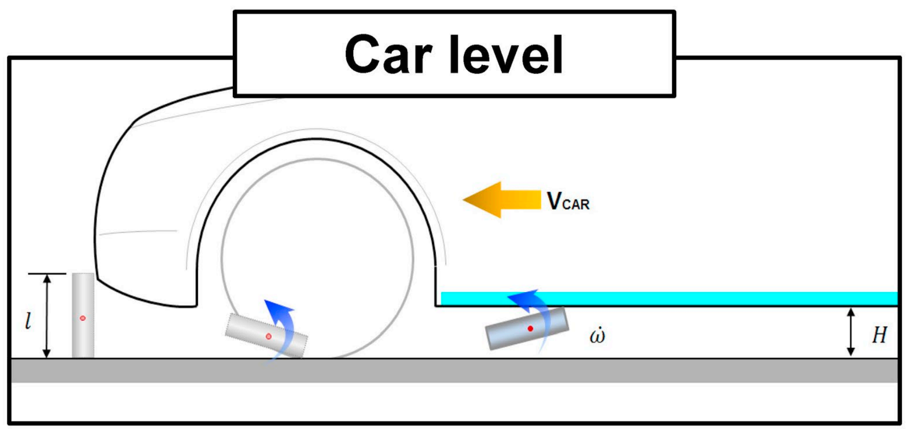
Feng et al. *Energy Storage Materials,* 2018, 10, 246.

Simulation of possible crush conditions



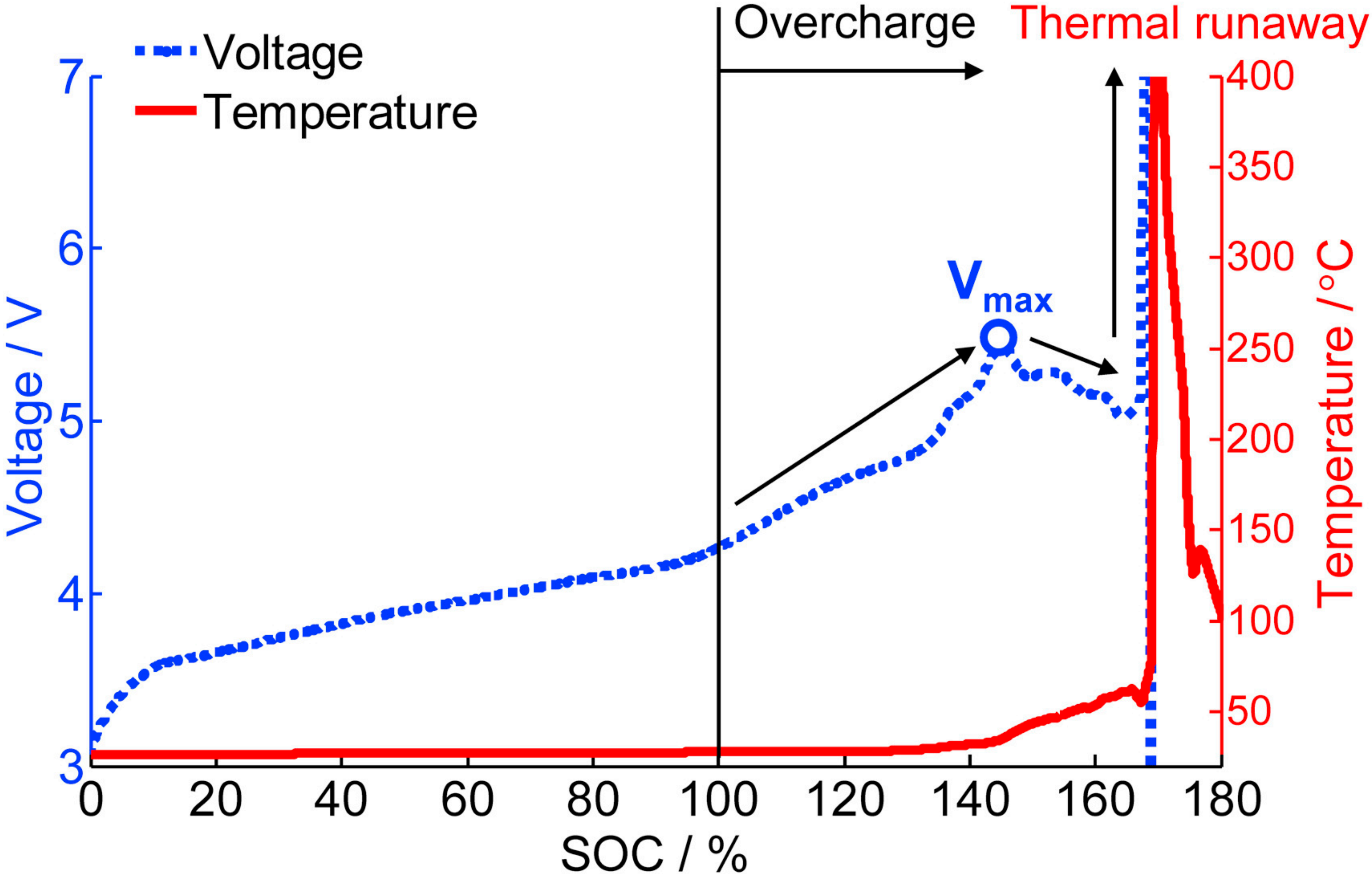






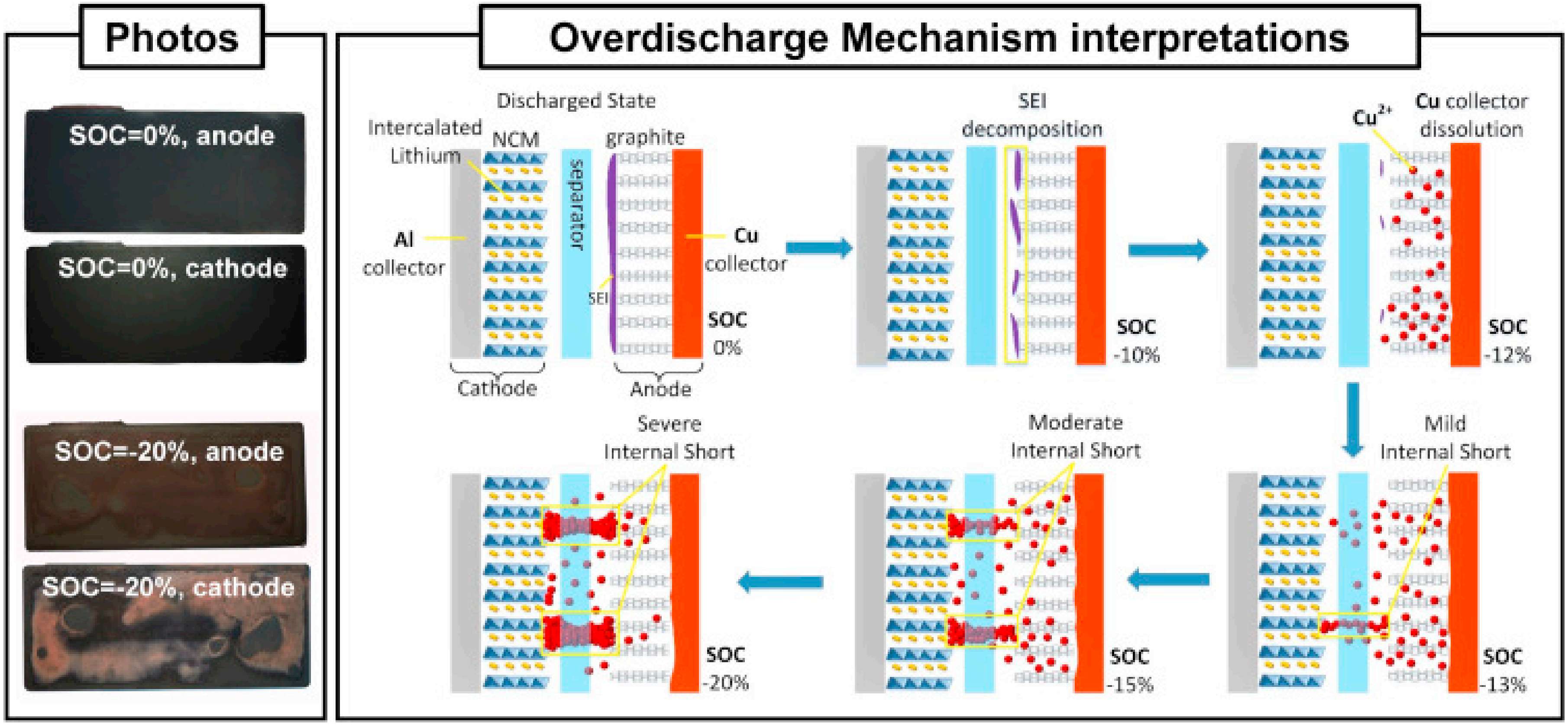
Feng et al. *Energy Storage Materials,* 2018, 10, 246.

The results of overcharge induced TR for a commercial lithium-ion battery



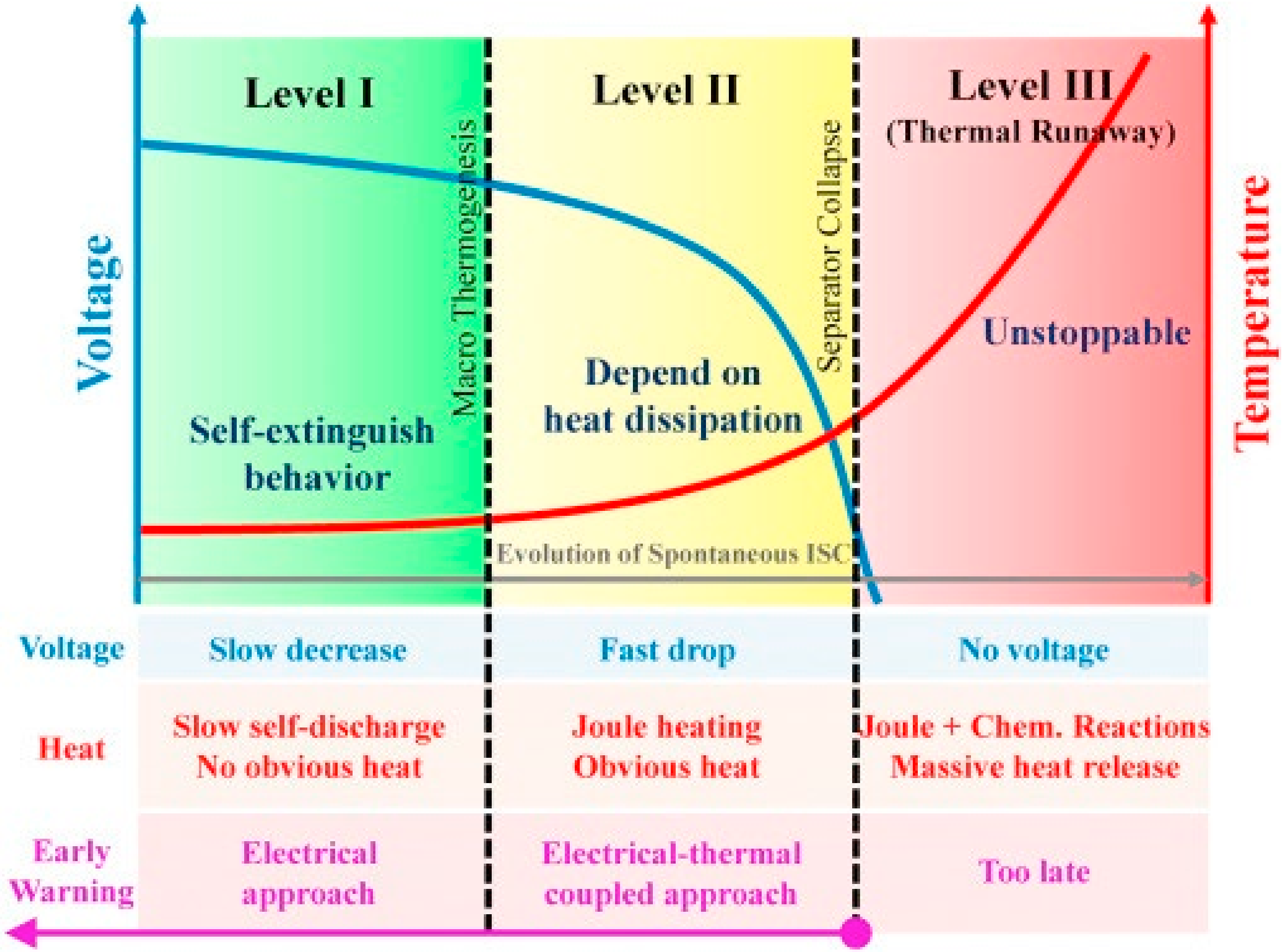
Feng et al. *Energy Storage Materials,* 2018, 10, 246.

The mechanism of the internal short circuit caused by overdischarge due to copper dissolution and deposition



Feng et al. *Energy Storage Materials,* 2018, 10, 246.

The three level of the internal short circuit



Feng et al. *Energy Storage Materials,* 2018, 10, 246.

What happens to solvents and salt in batteries during thermal runaway?

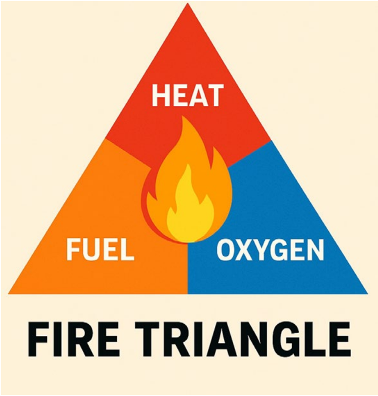
$C_3H_4O_3$ (EC) + $(C_2H_5O)_2CO$ (DEC) + $LiFF_6$ salt

	$2CH_2OCO_2Li_2 \rightarrow Li_2CO_3 + C_2H_4\uparrow + CO_2\uparrow + \frac{1}{2}O_2$	(1)	
	$2Li + CH_2OCOOCH_2 \rightarrow Li_2CO_3 + C_2H_4\uparrow$	(2)	70-120 °C
	$2Li + C_2H_5OCOOC_2H_5 \rightarrow Li_2CO_3 + C_2H_4\uparrow + C_2H_6\uparrow$	(3)	

$LiPF_6 + H_2O \rightarrow LiF + HF\uparrow + POF_3$	(4)	
$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOOPF_4 + HF\uparrow + C_2H_4\uparrow$	(5)	
$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOOPF_4 + C_2H_5F\uparrow$	(6)	>120 °C
$C_2H_5OCOOPF_4 \rightarrow HF\uparrow + C_2H_4\uparrow + CO_2\uparrow + POF_3$	(7)	
$C_2H_5OCOOPF_4 + HF \rightarrow PF_4OH + CO_2\uparrow + C_2H_5F\uparrow$	(8)	

Cathode decomposes

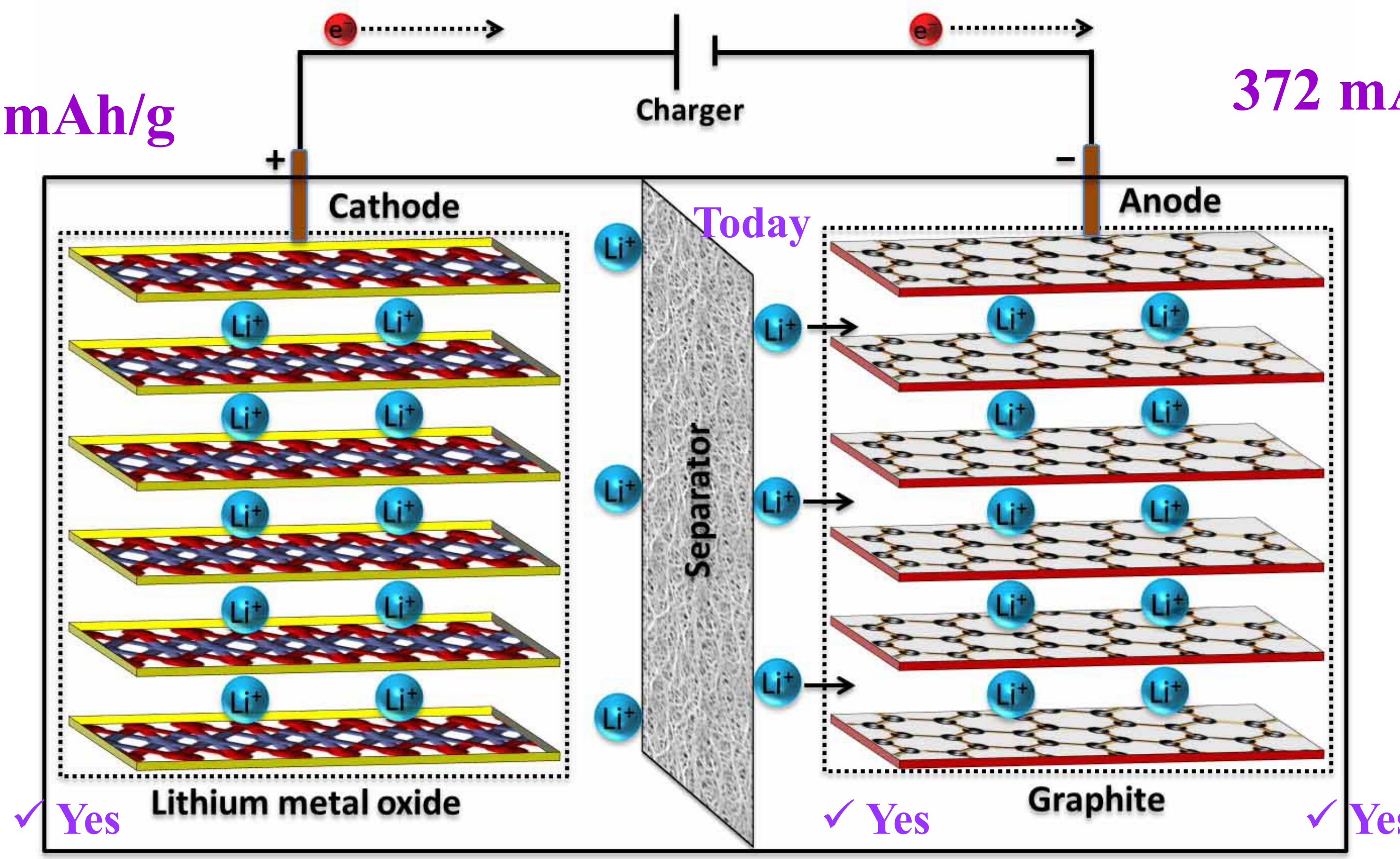
e.g., $LiCoO_2$ at 150 °C, $LiNi_xCo_yMn_zO_2$ at 210°C, $LiMn_2O_4$ at 265 °C, and $LiFePO_4$ at 310°C.



Can we make separator better to enhance safety ?

200 mAh/g

372 mAh/g



LiC_6

- ✓ Process reversibility should be 100% to have longer cycle life
- ✓ Requires high capacity electrode materials

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Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/electacta

Freestanding polyimide fiber network as thermally safer separator for high-performance Li metal batteries

Jassiel R. Rodriguez[a,*], Deep Jokhakar[a], Harsha Rao[a], Keng-Wei Lin[b], Chieh-Tsung Lo[b], Sandra B. Aguirre[c], Vilas G. Pol[a]

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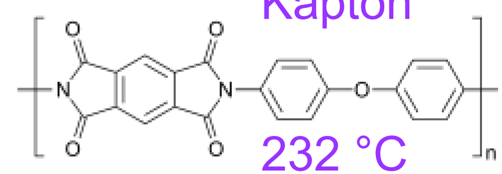
[c] Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada 22860, Mexico

Kapton



232 °C

resistant to flame

ARTICLE INFO

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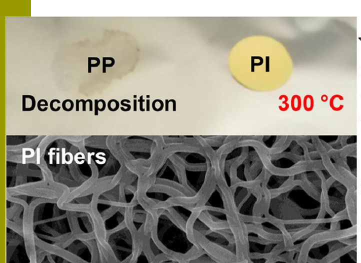
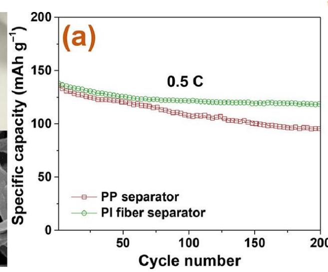
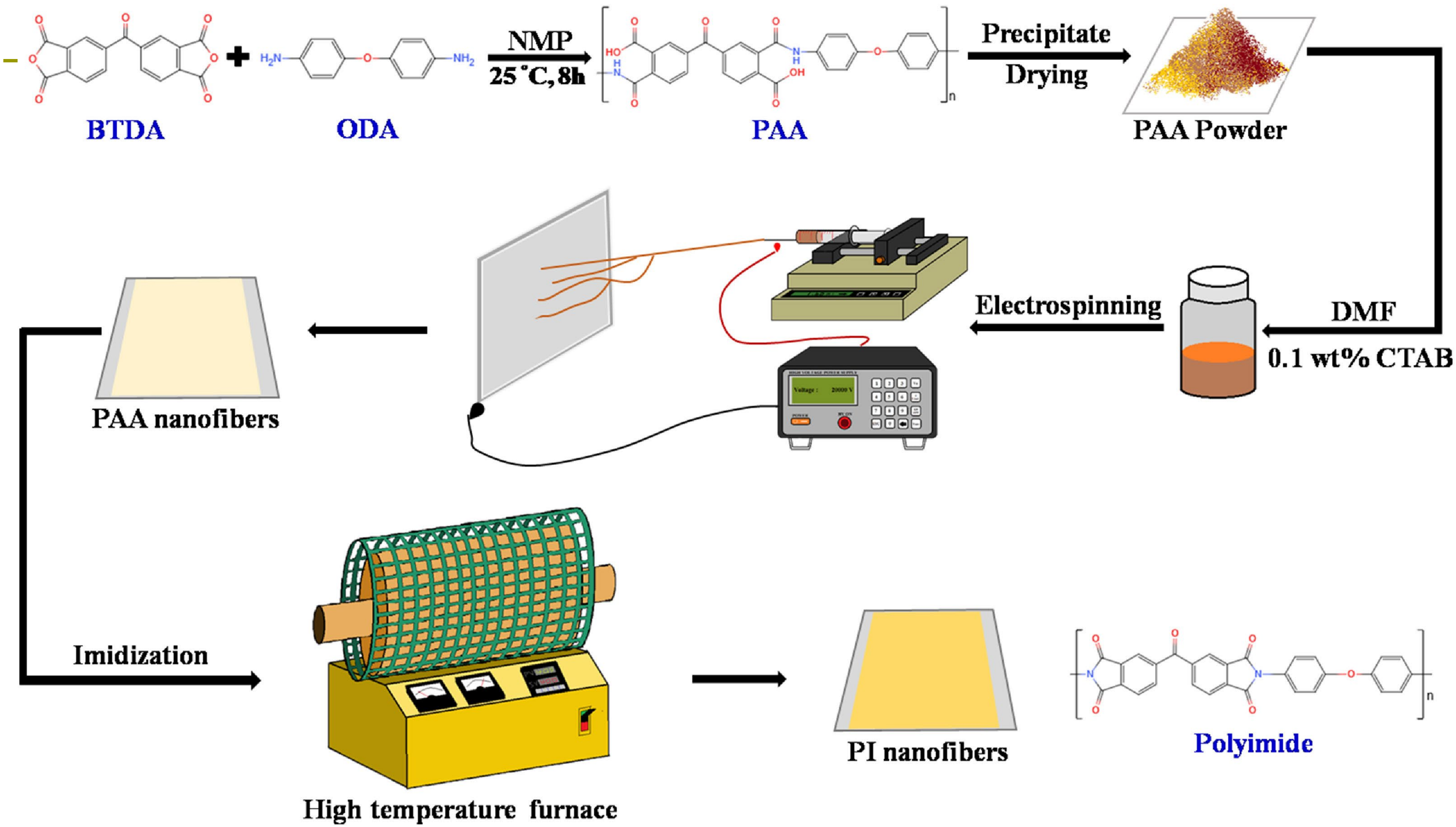
ABSTRACT

A stable and high-performance polyimide (PI) fiber mat was prepared via a facile two-step procedure, electrospinning deposition followed by an imidization process. The PI fiber separator presents higher thermal stability (>300 °C) than the commercial polypropylene (PP) separator (<160 °C). In Li/Cu half-cell configuration, PI fiber separator shows long cycle life performance with a coulombic efficiency of 82% at 0.5 mA cm^{-2} after 100 cycles and an impedance of 29 Ω. It also showed suppression of sharp Li dendrite growth. While the commercial PP separator delivers a poor coulombic efficiency of 24% after 100 cycles and an impedance of 99 Ω because of the formation of dendritic Li. Moreover, the Li/$LiFePO_4$ full cell with a PI fiber separator exhibits a lower polarization and charge transfer impedance than the commercial PP separator. The PI fibers enhanced the electrochemical cycle performance and stability of the full cells that deliver a charge capacity of 118 mAh g^{-1} at a C-rate of 0.5 C with a capacity retention of 86% and a coulombic efficiency of > 99% after 200 cycles. Additionally, the multimode calorimetry (MMC) studies under *in-situ* mode revealed that the freestanding PI fiber separator presents high thermal stability in Li/$LiFePO_4$ full cells.



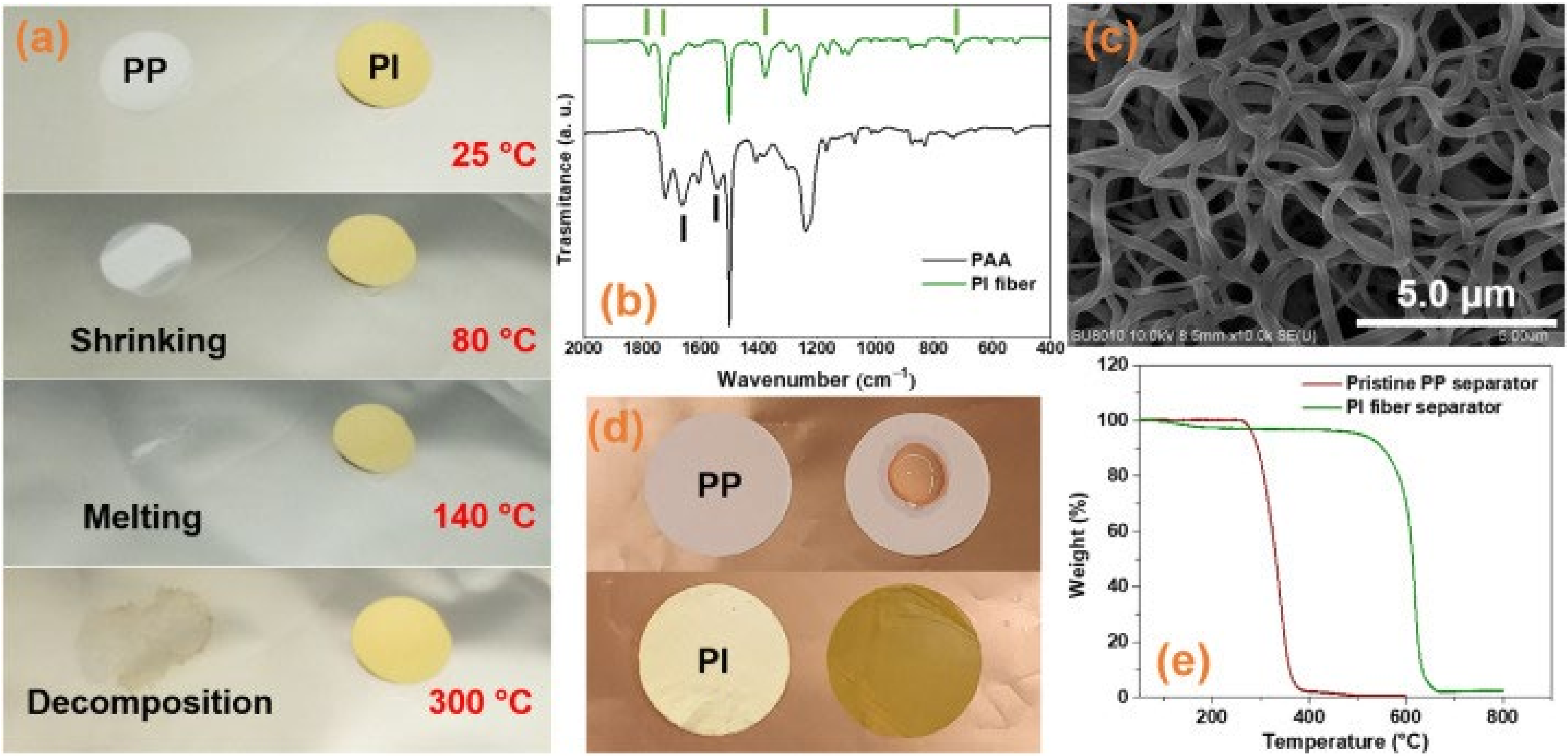


Electrospinning of PI fibers

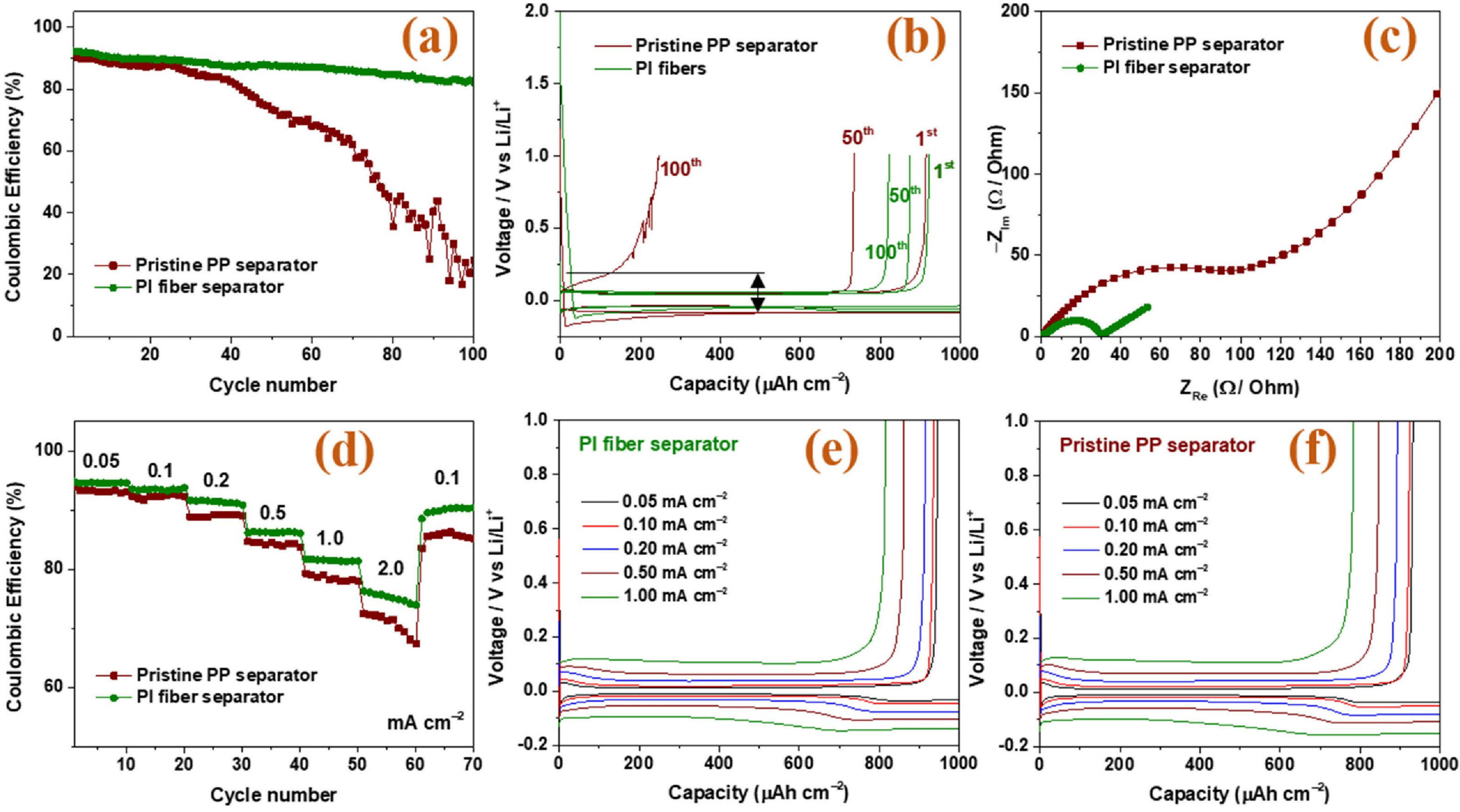


BTDA: 3,3,4,4-benzophenonetetracarboxylic acid dianhydride
ODA: 4,4-oxydianiline
PAA: polyamic acid

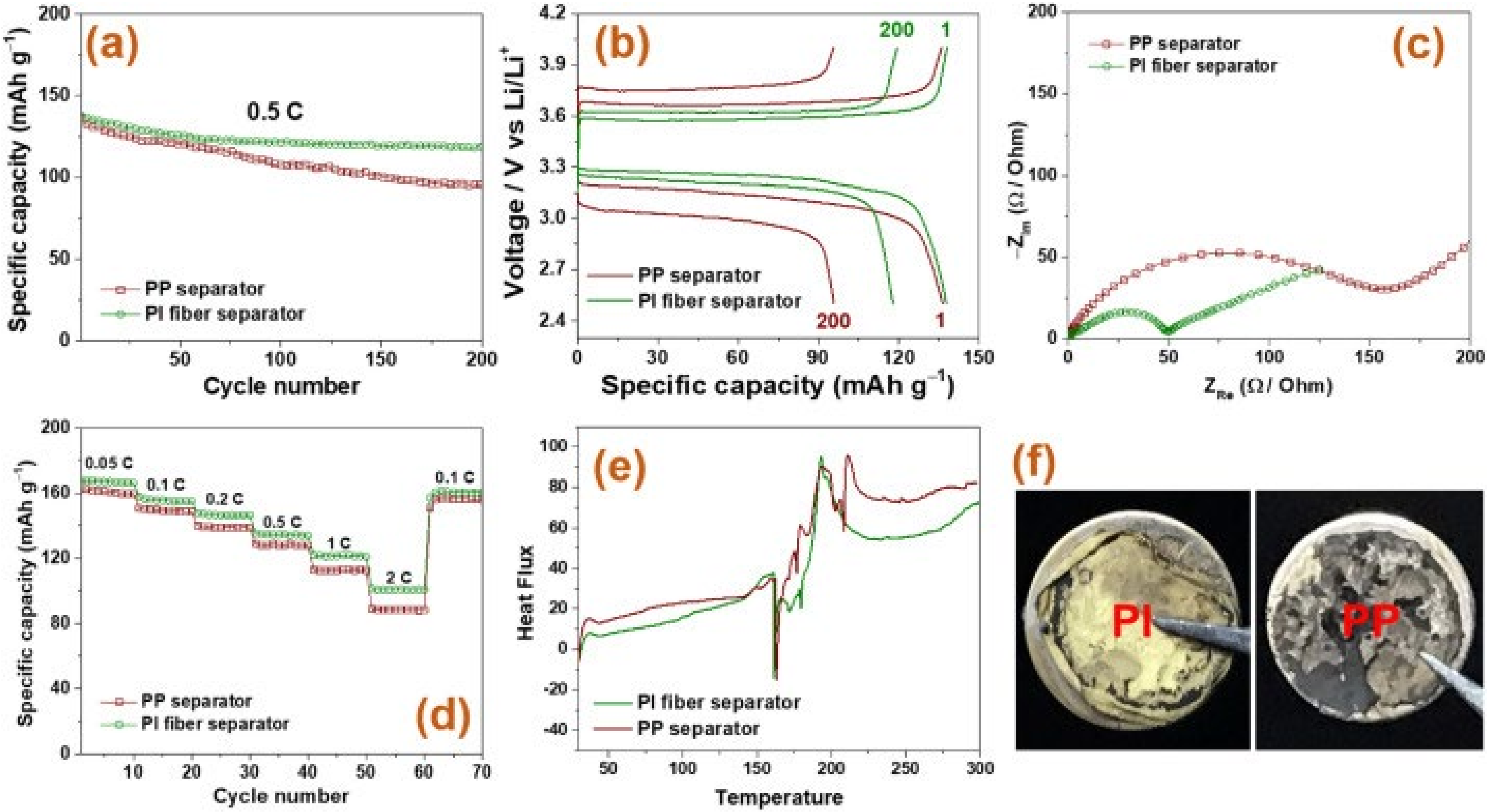
Thermal, spectroscopic, topographical and wettability



Comparative plating/stripping evaluation of the PI and PP separators



Electrochemical performance and safety studies of the Li/LFP full cells with PI fibers and PP membrane



✓Multimodule calorimetry

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Research Article

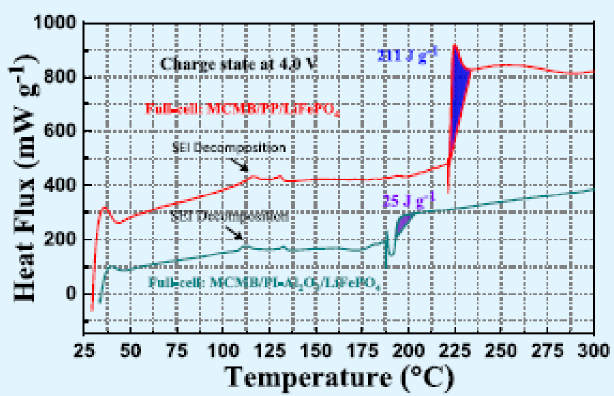
In Situ Thermal Safety Aspect of the Electrospun Polyimide-Al_2O_3 Separator Reveals Less Exothermic Heat Energies Than Polypropylene at the Thermal Runaway Event of Lithium-Ion Batteries

Manikandan Palanisamy,* Keng-Wei Lin, Chieh-Tsung Lo, and Vilas G. Pol*

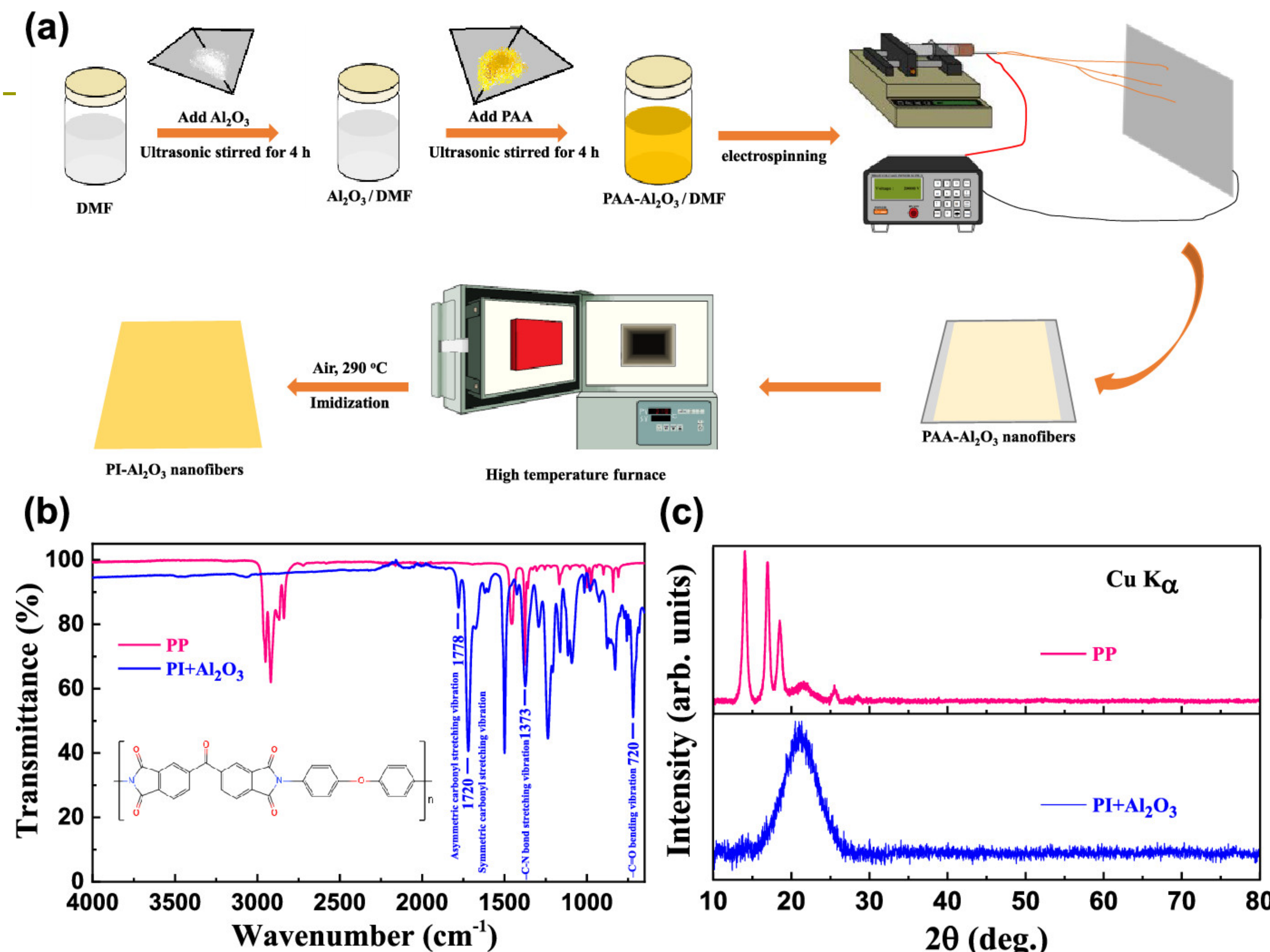
Cite This: *ACS Appl. Mater. Interfaces* 2022, 14, 28310−28320

Read Online

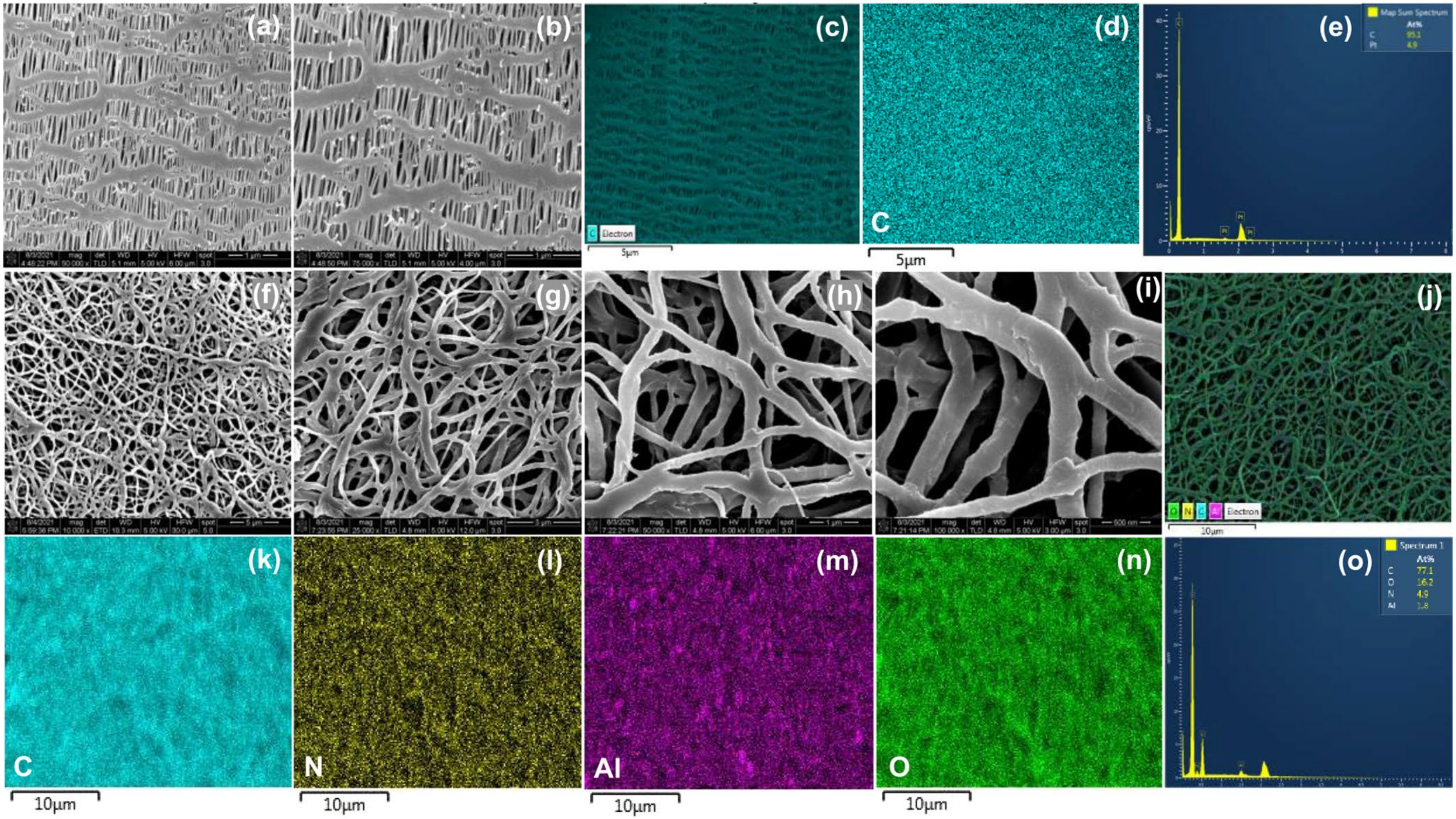
ABSTRACT: Polyimide-Al_2O_3 membranes are developed as a direct alternative to current polyolefin separators by the electrospinning technique and their chemical structures confirm the carbonyl group with the presence of asymmetric and symmetric stretching and bending vibrations at 1778, 1720, and 720 cm^{-1} and stretching vibration at 1373 cm^{-1} for the imide group. Porous nanofiber architecture morphology is realized with a nanofiber thickness of ~200 nm and shows an ultrasmooth surface and >1 μm pore size in the architecture, built with the chemical constituents of carbon, nitrogen, aluminum, and oxygen elements. The galvanostatic cycling study of the Li/PI-Al_2O_3/$LiFePO_4$ lithium cell delivers stable charge−discharge capacities of 144/143 mAh g^{-1} at 0.2 C and 110/100 mAh g^{-1} at 1 C for 1−100 cycles. The fabricated MCMB/PI-Al_2O_3/$LiFePO_4$ lithium-ion full-cell reveals less charge transfer resistance of R_{ct} ~ 25 Ω and yields stable charge−discharge capacities of 125/119 mAh g^{-1}. The thermogravimetric curve for the PI-Al_2O_3 separator discloses thermal stability up to 525 °C, and the differential scanning calorimetric curve shows a straight line until 300 °C and depicts high thermal stability than the PP separator. In situ multimode calorimetry analysis of the MCMB/PP/$LiFePO_4$ full-cell showed a pronounced exothermic peak at 225 °C with a higher released heat energy of 211 J g^{-1} at the thermal runaway event, while the MCMB/PI-Al_2O_3/$LiFePO_4$ full-cell revealed an almost 8-fold less exothermic released heat energy of 25 J g^{-1} than the Celgard polypropylene separator, which was because the MCMB anode and $LiFePO_4$ cathode can be mechanically isolated without any additional separator's melting and burning reactions, as a fire-suppressant separator for lithium-ion batteries.



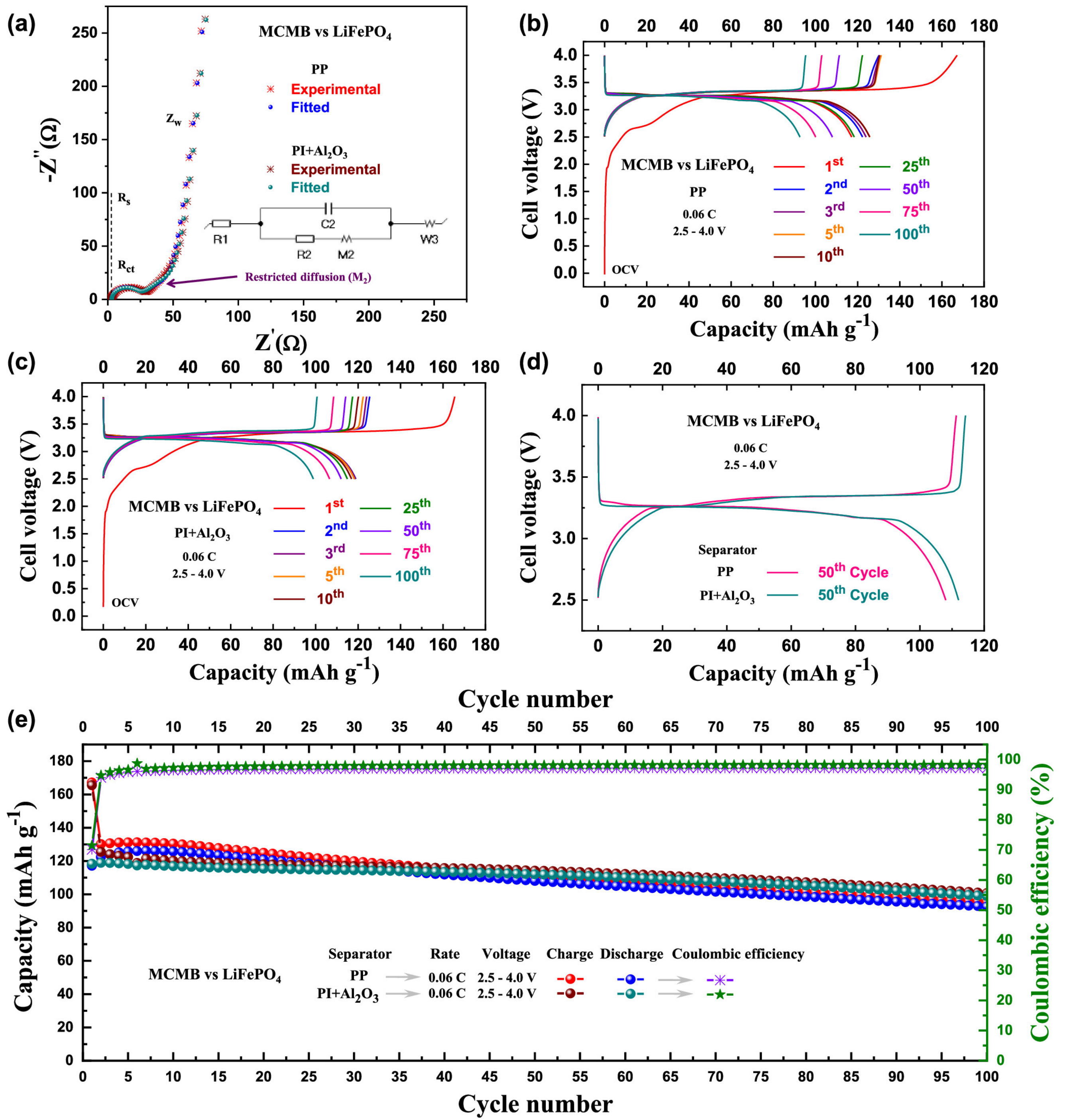
Synthesis of the electrospun PI-Al_2O_3 membrane and its chemical structure



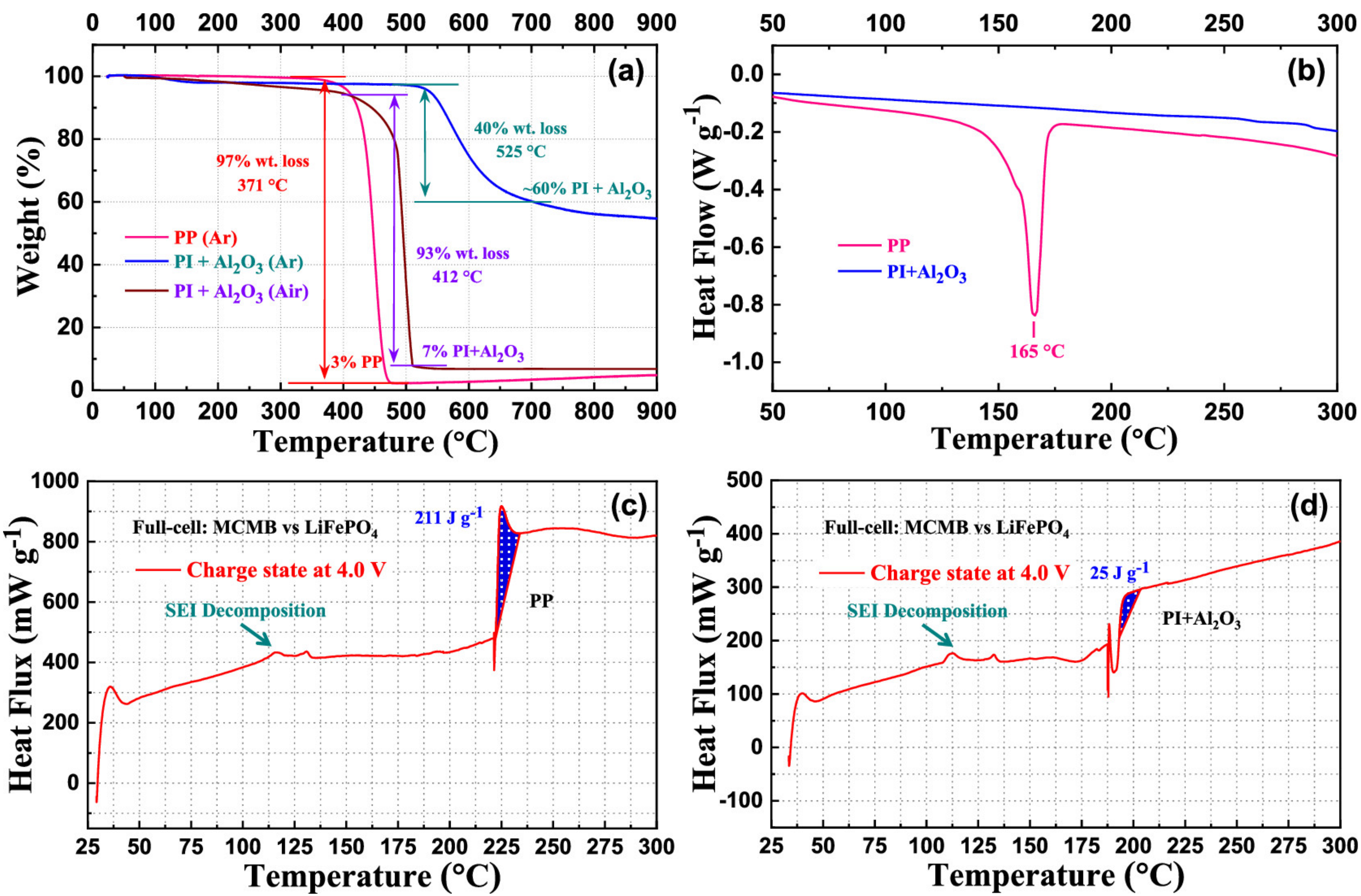
Morphological investigation of the electrospun PI-Al_2O_3 membrane



Electrospun PI-Al_2O_3 membrane for lithium-ion full-cells



Ex-situ and *in-situ* thermal safety aspects of the electrospun PI-Al_2O_3 separator



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The Role of Separator Thermal Stability in Safety Characteristics of Lithium-ion Batteries

Hanwei Zhou,[1] Conner Fear,[1,*] Mihit Parekh,[2] Frederick Gray,[3] James Fleetwood,[3] Thomas Adams,[4] Vikas Tomar,[5] Vilas G. Pol,[2] and Partha P. Mukherjee[1,*,z]

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[3]*Battery Innovation Center, Newberry, Indiana 47449, United States of America*
[4]*Naval Surface Warfare Center Crane Division, Crane, Indiana 47522, United States of America*
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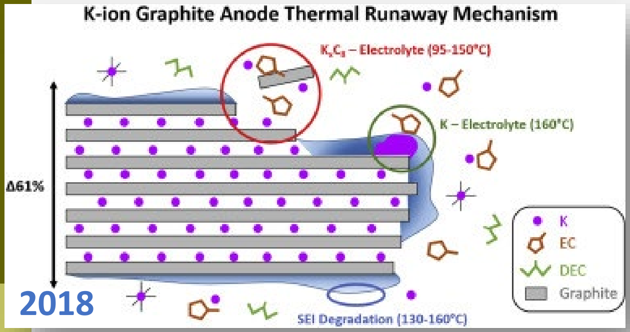
The thermal instability of polymer separators severely threatens the safety characteristics of lithium-ion (Li-ion) batteries. Separators will melt, shrink, vaporize, and collapse under high temperatures, leading to internal short circuits and thermal runaway catastrophes of the cell. Therefore, the amelioration of battery safety challenges benefits from a fundamental understanding of separator behaviors under thermally abusive scenarios. This work investigates the role of separator thermal stability in modulating Li-ion cell safety performance. Three types of separators made of commercially available cellulose, trilayer polypropylene/polyethylene/polypropylene, standard polypropylene, and an in-house modified graphene-polydopamine coated separator are fabricated in custom single layer pouch cells and subjected to accelerating rate calorimeter (ARC) tests to investigate dynamic thermo-electrochemical interactions. The safety hazards of 18650 cylindrical cells asso ed with different types of separators are predicted using a verified ARC computational model to con the effects of sep or heat resistance on cell-level thermal runaway risks. This study reveals the thermally robust mecha ns of diverse separ microstructures, indicating how the in-house modified graphene-polydopamine coated separator sign antly enhances the ty limits of Li-ion batteries.
 [DOI: 10.1149/1945-7111/

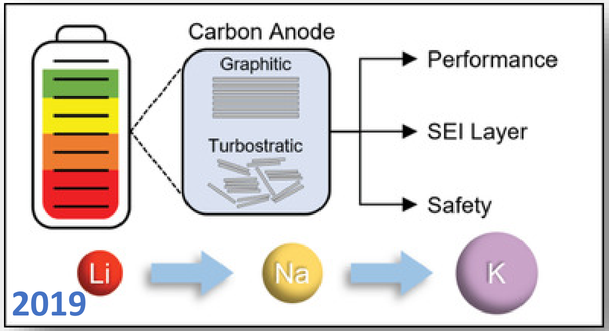
Mechanistic Elucidation of Thermal Runaway in Potassium-Ion Batteries

NSF CBET-1804300

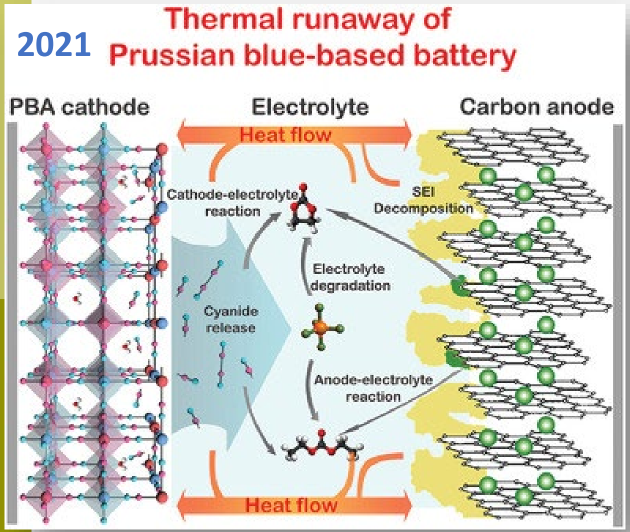
Highlighted works:



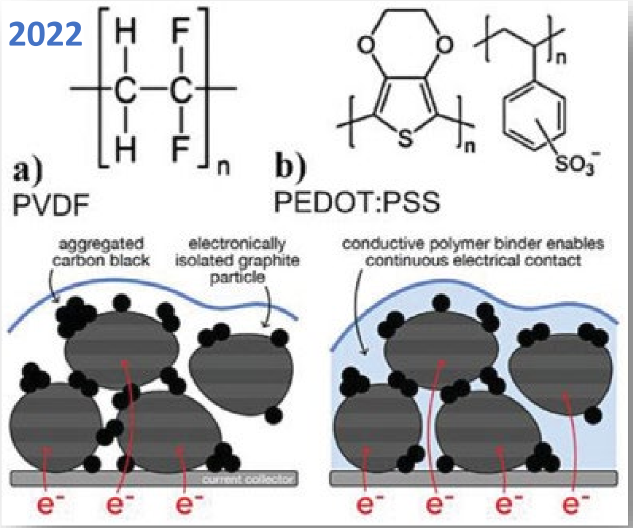
Thermal runaway mechanism of graphite anode



Overview of carbonaceous materials safety



Thermal runaway mechanism of PIB full cells



Improving the PIB safety with an electron-conducting binder

Full publication list:

(2018). **Mechanistic elucidation of thermal runaway in potassium-ion batteries.** Journal of Power Sources, 375, 131-137.

(2019). **Temperature dependent electrochemical performance of graphite anodes for K-ion and Li-ion batteries.** Journal of Power Sources, 410, 124-131.

(2019). **Carbon anodes for nonaqueous alkali metal-ion batteries and their thermal safety aspects**. *Advanced Energy Materials*, *9*(35), 1900550.

(2021). **Revealing the Thermal Safety of Prussian Blue Cathode for Safer Nonaqueous Batteries.** *Advanced Energy Materials*, *11*(42), 2101764.

(2022). **Mechanistic Elucidation of Electronically Conductive PEDOT: PSS Tailored Binder for a Potassium-Ion Battery Graphite Anode: Electrochemical, Mechanical, and Thermal Safety Aspects.** Advanced Energy Materials, 12(14), 2103439.

This project successfully interpreted the thermal runaway mechanism of PIBs. In-depth scientific insights and guidelines were developed for building safer next-generation PIBs.

Summary

1. Polyimide based separators are safer, Al_2O_3 nanoparticles further enhanced the safety

2. Potassium ion batteries could be safer than conventional Lithium-ion batteries after multiple modifications.

3. Graphite exfoliates, initial SEI breakdown at lower temperatures.

4. Prussian blue based cathode releases trapped moisture and could form CN toxic gases

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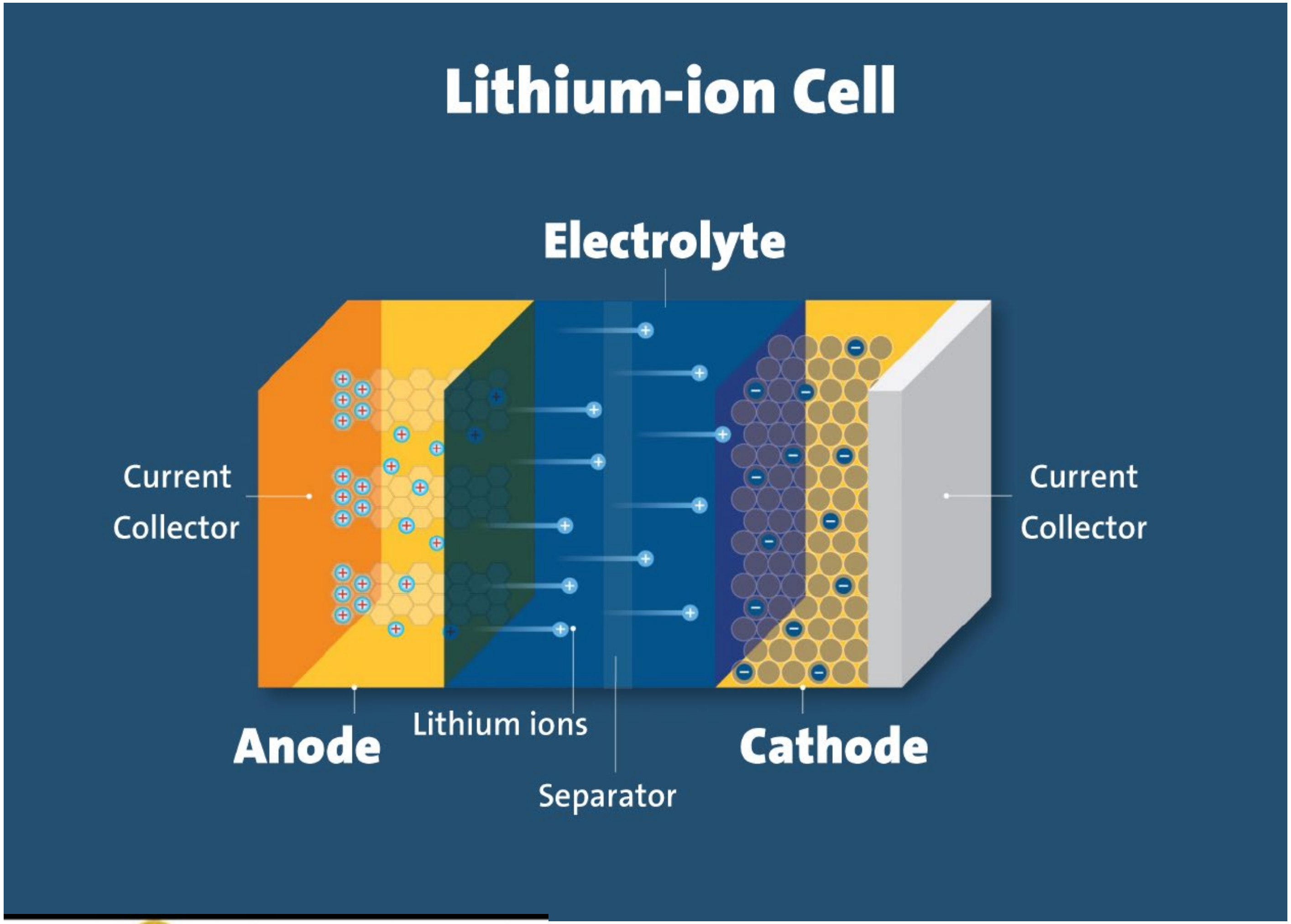
Summary



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Thank You!