Sodium based Solid Electrolytes and Na-Metal

David Mitlin *et al.*

Materials Science Program and Texas Materials Institute
The University of Texas at Austin, Austin, Texas 78712-1591

COVER. Energy & Environmental Science, 2017, 10, 153.

Supported by Energy Storage Program, Office of Electricity (Grant Numbers: DE-AC05 00OR22725). CINT User proposal 2019AC0016 and IMS

TEXAS
The University of Texas at Austin

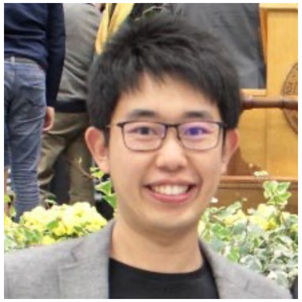
Project Team

PI: David Mitlin
UT-Austin

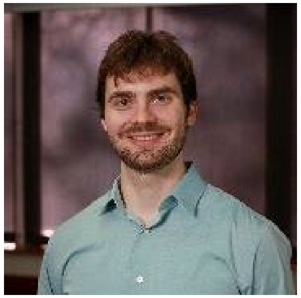
Jagjit Nanda
SLAC National Lab
Stanford University

John Watt
LANL - CINT

Hongchang Hao
UT-Austin



Yixian Wang
UT-Austin



Ethan Self
ORNL

Guang Yang
ORNL

Thrust Area : Cost Competitive Materials and Systems for Enabling Long Duration Energy Storage (LDES)

(i) Development and demonstration of high-performance electrochemical systems and components utilizing earth abundant materials

(ii) Research on novel materials and system components to resolve key cost and performance challenges for electrochemical energy storage systems meeting demands for grid-scale energy storage

Potential Use Case – Long Duration Energy Storage (10-100 Hrs. at rated power)

Long Term Goals and Requirements

- Reduce the cost of energy storage systems by 90% by the decade for 10+ hours of storage as per the DOE's Long Duration Storage Earth Shot
- Levelized cost of electricity (LCOS) at 5 cents/KWhr for long duration storage.
- Energy round trip efficiency (RTE) > 50%
- Provide multiple value streams : Enable several applications with a single, long operating-life asset

Key Accomplishments

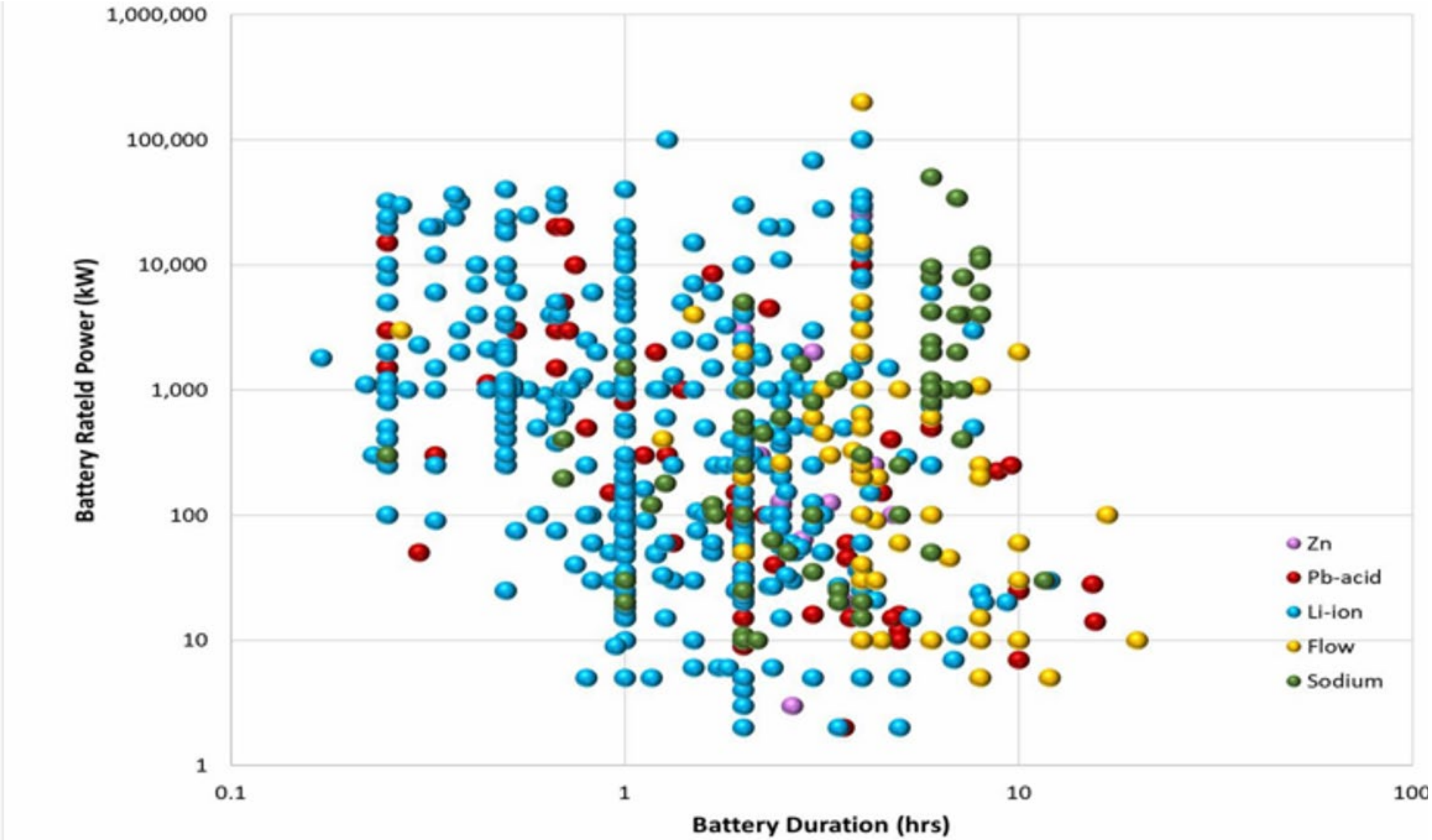
- **New Na solid-state electrolytes (SSEs), $Na_{2.895}W_{0.3}Sb_{0.7}S_4$ and $Na_{2.7}W_{0.3}Sb_{0.7}S_4$.** Both exhibit record low activation energy for Na^+ diffusion and enhanced low (-20° C) and RT ionic conductivity; 0.09 eV, 24.2 mS/cm and 0.12 eV, 14.5 mS/cm. All-solid-state battery (ASSB) using $Na_{2.895}W_{0.3}Sb_{0.7}S_4$ and a sodium sulfide (Na_2S) cathode obtains reversible capacity of 400 mAh/g.

- **New molybdenum carbide-based electrocatalyst for Sulfur-based SMBs.** MoC/Mo_2C@PCNT-S cathodes delivered exceptional charge/discharge performance, 987 mAh g^{-1} at 1 A g^{-1}, 818 mAh g^{-1} at 3 A g^{-1}, and 621 mAh g^{-1} at 5 A g^{-1}. The SMBs retain 650 mAh g^{-1} after 1000 cycles at 1.5 A g^{-1}, corresponding to 0.028% capacity decay per cycle.

- **New multifunctional separator for potassium-metal batteries (KMBs) and (SMBs)**. Industry-compatible tape-cast AlF_3 coating on polypropylene (AlF3@PP) enhances cycling and rate capability. Symmetric cells are stable after 1,000 cycles (2000 hours) at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2}, with 0.042 V overpotential. Stability is maintained at 5.0 mA cm^{-2} for 600 cycles (14,400 minutes), with 0.138 V overpotential. Post-cycled plated surface is dendrite-free, while stripped surface contains a smooth SEI.

- **All three innovations may be low cost and ultimately industrially scalable.**

New Materials for Low-Cost Sodium – Based Energy Storage

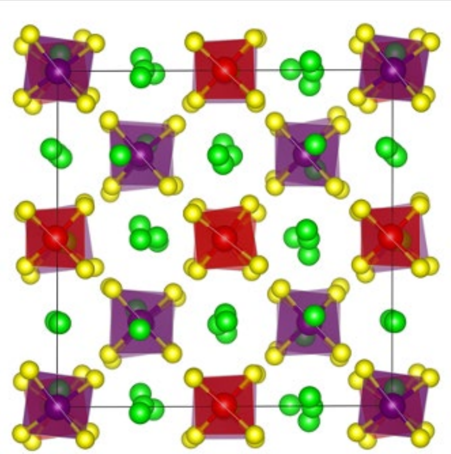


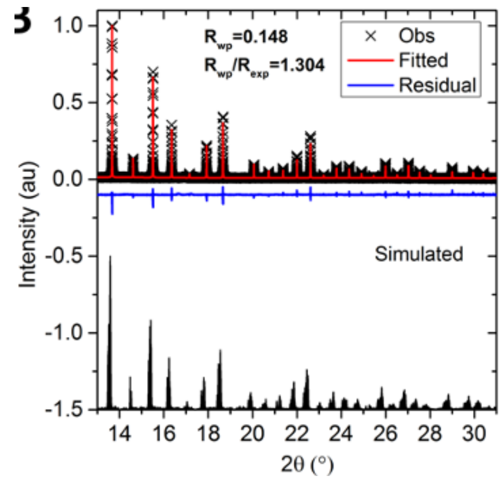
Source: US DoE Energy Storage Database, March 2019, https://www.energystorageexchange.org/
Based on Shell International Exploration & Production (US) Inc.; analysis presented by Shell 11 March 2019, ARPA-e DAYS

Sodium-ion batteries (SIBs) can dominate Long Duration applications. Far ahead of LIBs due to Lower Cost. Potassium and Zinc can be competitive too.

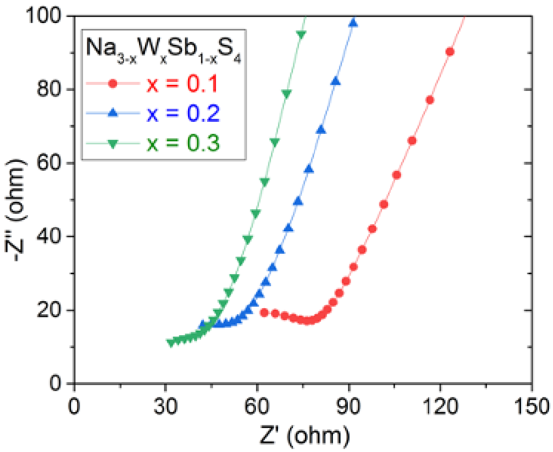
Metal batteries (MBs) with thin (< 20 micron) metal anode have up to 1.5X higher energy vs. state-of-the-art ion anode batteries (LIBs).

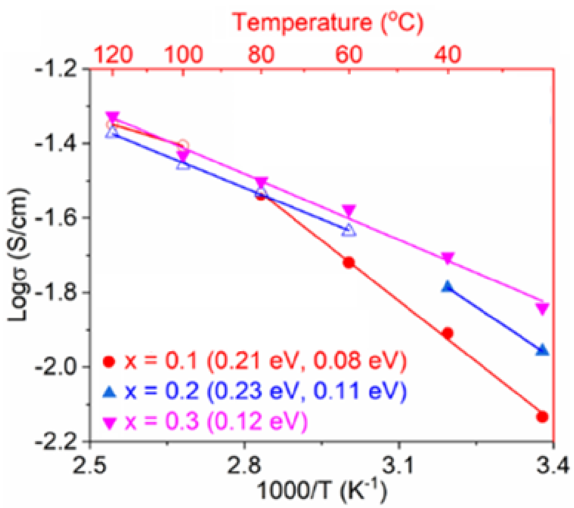
Heavily Tungsten Doped Sodium Thioantimonate Solid-State Electrolytes

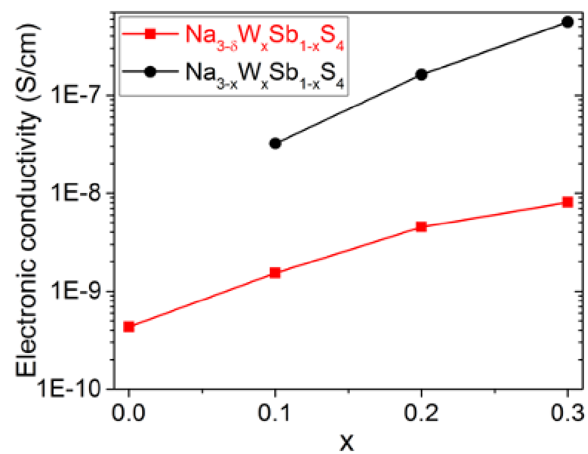




Theory predicted high-ionic conductivity structure of $Na_{3-x}W_xSb_{1-x}S_4$ (shown $Na_{2.7}W_{0.3}Sb_{0.7}S_4$, with SbS_4^{3-} units purple, WS_4^{2-} units red and Na green) with synchrotron confirming the results.







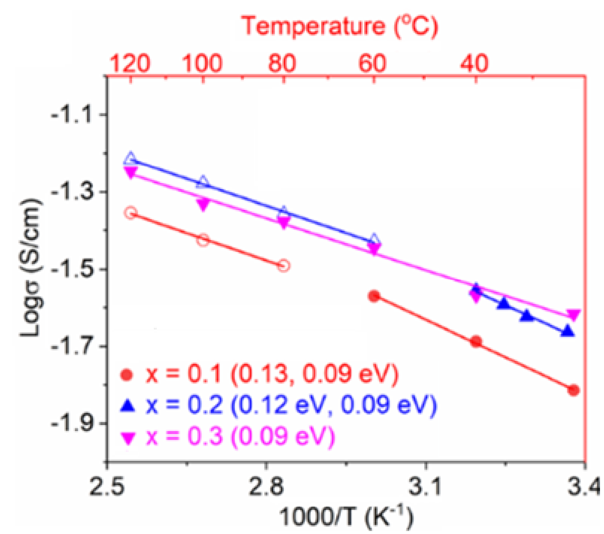
$Na_{2.7}W_{0.3}Sb_{0.7}S_4$ High ionic conductivity down to -15° C, electrical insulator
Theory: ionic conductivity is due to extra vacancies, weak Na-W bonds and strong Na-Na repulsions

Heavily Tungsten-Doped Sodium Thioantimonate Solid-State Electrolytes with Exceptionally Low Activation Energy for Ionic Diffusion. **Angewandte Chemie International Edition**. 2021 Dec 6;60(50):26158-66.

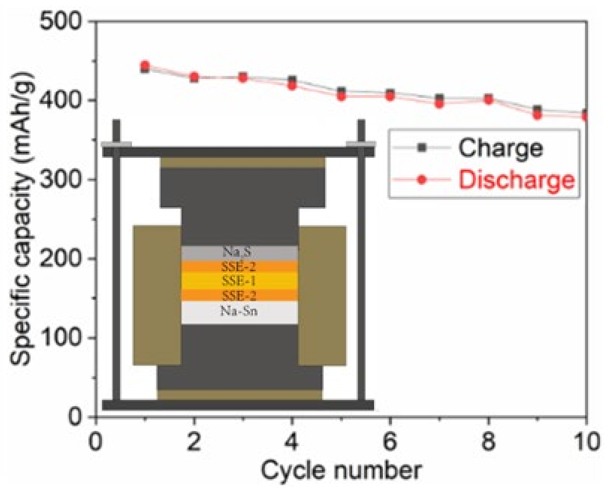
Heavily Tungsten Doped Sodium Thioantimonate Solid-State Electrolytes

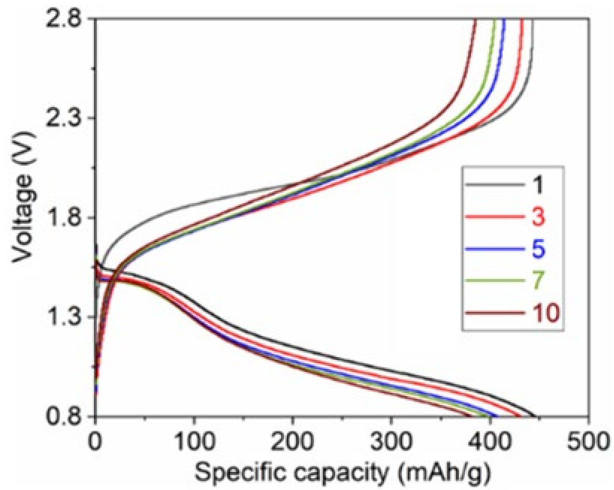
Table 1. Comparison of key properties of the known sulfide sodium solid electrolytes, showing that the heavily W-doped systems in this study exhibit the highest RT ionic conductivities and the lowest activation energies.

Solid state electrolyte	SSE preparation	Crystal system	σ at RT (mS/cm)	E_a (eV)	Ref.
$Na_{2.7}W_{0.3}Sb_{0.7}S_4$	Cold pressed with 350 MPa	Orthorhombic	14.5	0.12	This work
$Na_{2.895}W_{0.3}Sb_{0.7}S_4$	Cold pressed with 350 MPa	Cubic	24.2	0.09	This work
Na_3PS_4	Cold pressed and heated at 270 °C	Cubic	0.2	0.28	[52]
$Na_{2.9375}PS_{3.9375}Cl_{0.0625}$	Spark plasma sintering, 100 MPa, 300 °C for 5 min	Tetragonal	1.14	0.25	[54]
$Na_{3.8}PS_{3.8}Cl_{0.2}$	Cold pressed, heated at 420 °C and then natural cooling to RT	Tetragonal	2	0.19	[42]



$Na_{2.895}W_{0.3}Sb_{0.7}S_4$ High ionic conductivity down to -15° C (bulk 23 mS/cm total 5.5 mS/cm)

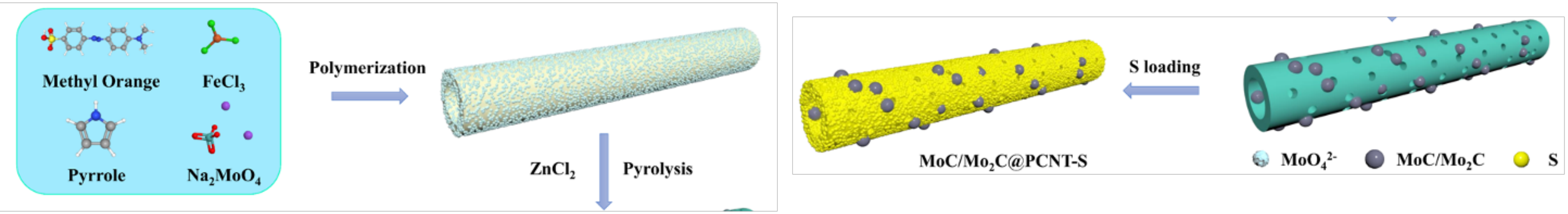




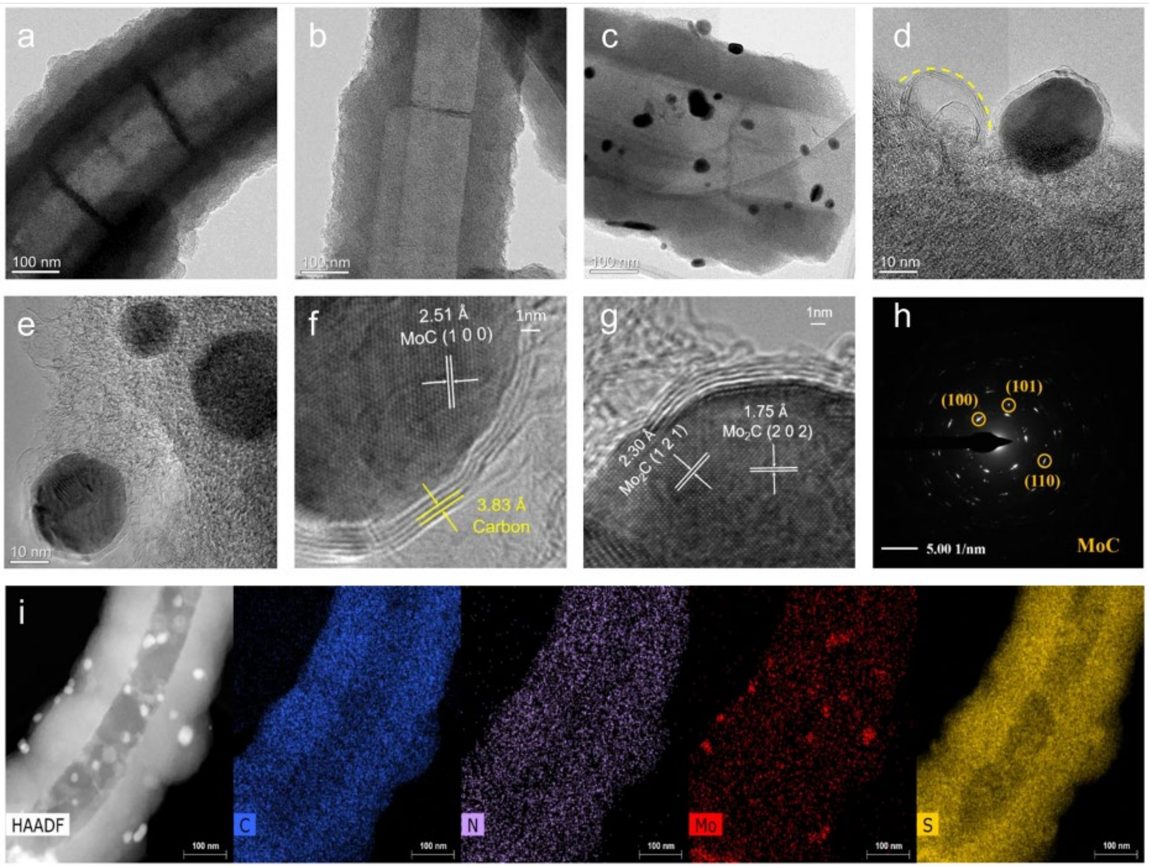
BUT The cyclability needs much improvement, requires stable Ion Conducting Interphases (ICI) between metal or ion anode, SSE and S or Ceramic Cathode. Tuned Interlayers should help.

Heavily Tungsten-Doped Sodium Thioantimonate Solid-State Electrolytes with Exceptionally Low Activation Energy for Ionic Diffusion. **Angewandte Chemie International Edition**. 2021 Dec 6;60(50):26158-66.

MoC/Mo_2C Electrocatalyst Promotes Rapid Kinetics in Na-S Batteries



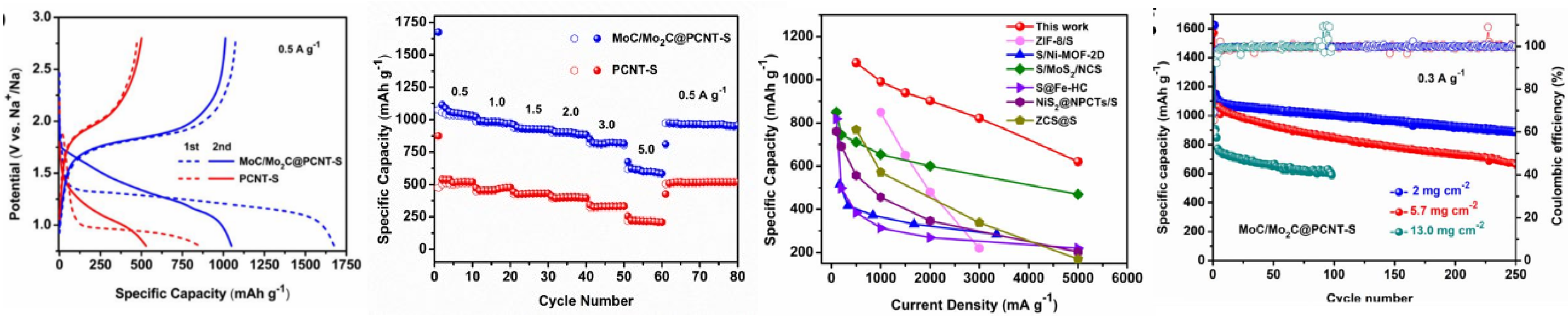
Schematic fabrication process and structure of MoC/Mo_2C@PCNT-S composite.



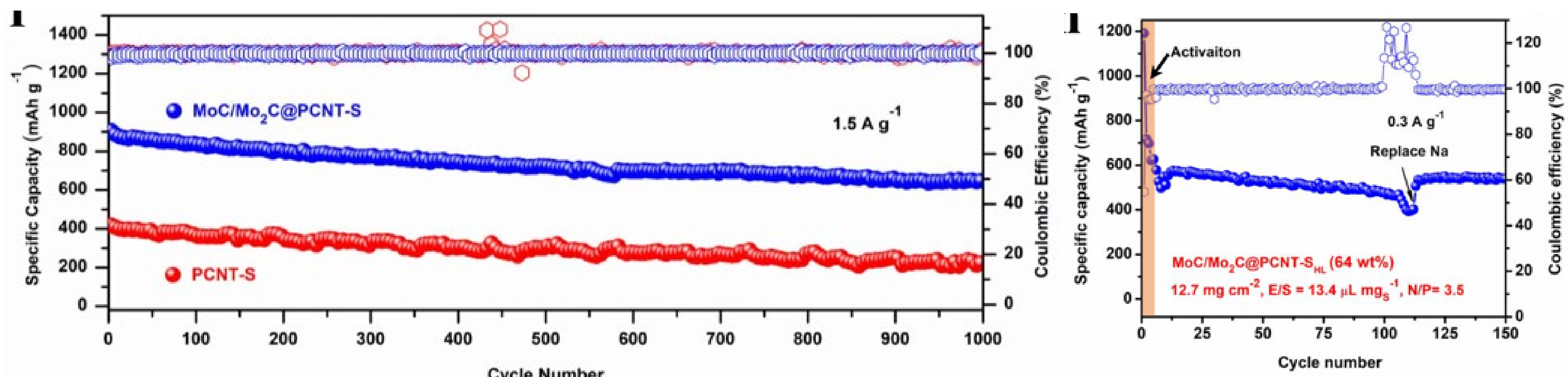
- New molybdenum carbide-based electrocatalyst for sulfur-based sodium metal batteries (SMBs/NMBs).
- MoC/Mo_2C is *in-situ* grown on nitrogen-doped carbon nanotubes in parallel with formation of extensive nanoporosity.
- Sulfur impregnation (50wt.% S) results in unique triphasic architecture termed MoC/Mo_2C@PCNT-S.

Molybdenum Carbide Electrocatalyst In Situ Embedded in Porous Nitrogen-Rich Carbon Nanotubes Promotes Rapid Kinetics in Sodium-Metal–Sulfur Batteries. **Advanced Materials**. 2022 Apr 21:2106572.

MoC/Mo_2C Electrocatalyst Promotes Rapid Kinetics in Na-S Batteries



- Quasi-solid-state phase transformation to Na_2S is promoted in carbonate electrolyte, with *in-situ* Raman, XPS and optical analysis demonstrating minimal soluble polysulfides.
- Among the most promising rate performance characteristics: 987 mAh g^{-1} at 1 A g^{-1}, 818 mAh g^{-1} at 3 A g^{-1}, and 621 mAh g^{-1} at 5 A g^{-1}.



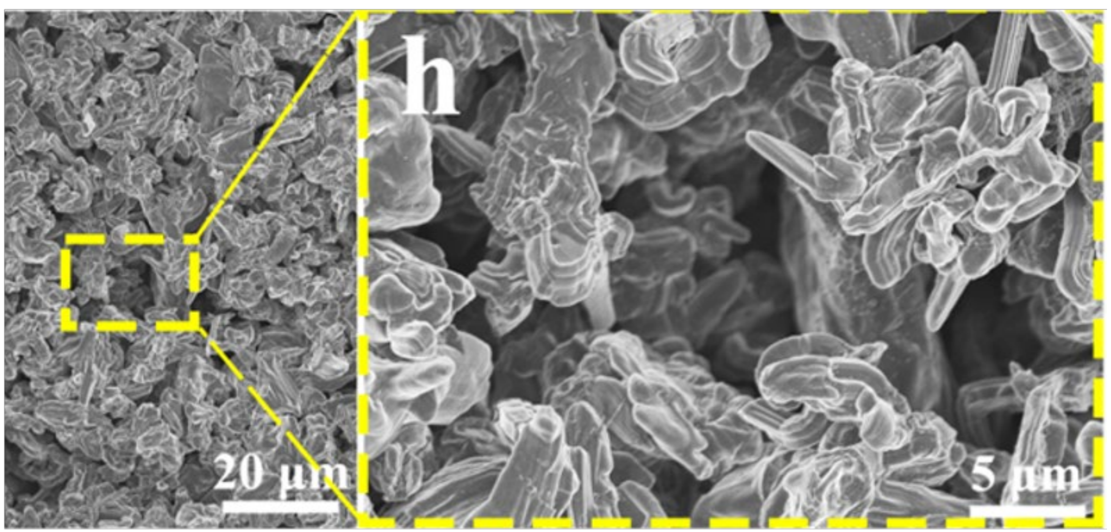
- Superior cycling stability, retaining 650 mAh g^{-1} after 1000 cycles at 1.5 A g^{-1}, = 0.028% capacity decay per cycle.
- High mass loading cathodes (64wt.% S, 12.7 mg cm-2) have cycling stability, with anode degradation due to deep plating/stripping driving capacity decay.

All LIB and Beyond-Lithium Batteries Have “Issues”

Tesla ‘big battery’ fire fuels concerns over lithium risks
Latest incident comes as utilities around the world increasingly rely on lithium-ion to store renewable energy
https://www.ft.com/content/8c9c3d50-98a3-4cdf-907f-901f8c328b90

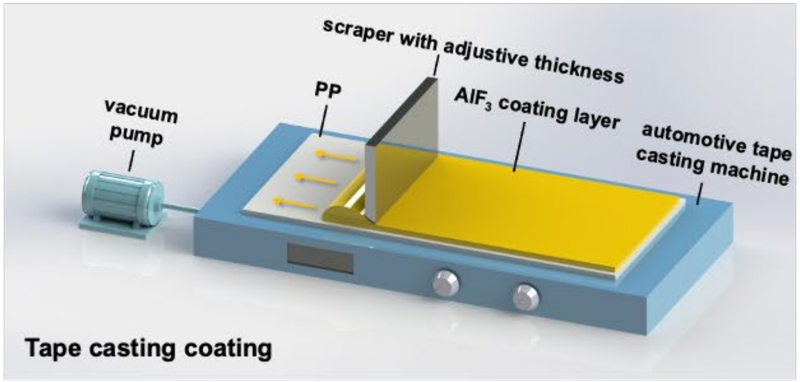
Uncontrolled Oxygen Release from Cathode due to Overcharging, leading to self-sustaining fires.

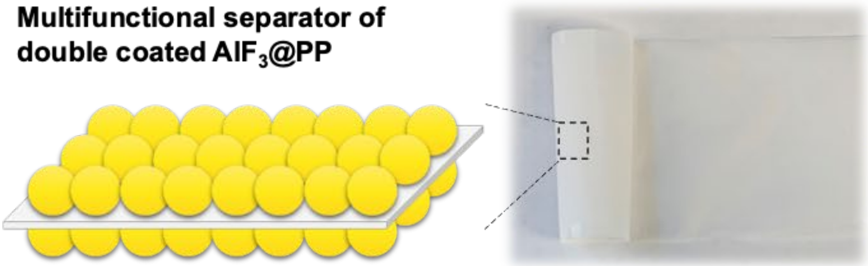
Metal Dendrites (Li, Na, K, Zn), forming even in commercial LIBs at low T and at fast charge, leading to potentially catastrophic failures.



- **Dendrites (sharp metal filaments) form and grow at the anode.**
- **Dendrites increase cell impedance, consuming electrolyte, and potentially shorting the two electrodes.**
- **Fires have been reported to be caused by such shorts.**

Industrially Scalable Multifunctional Separator Allows Stable Cycling of Potassium Metal Anodes and of Potassium Metal Batteries

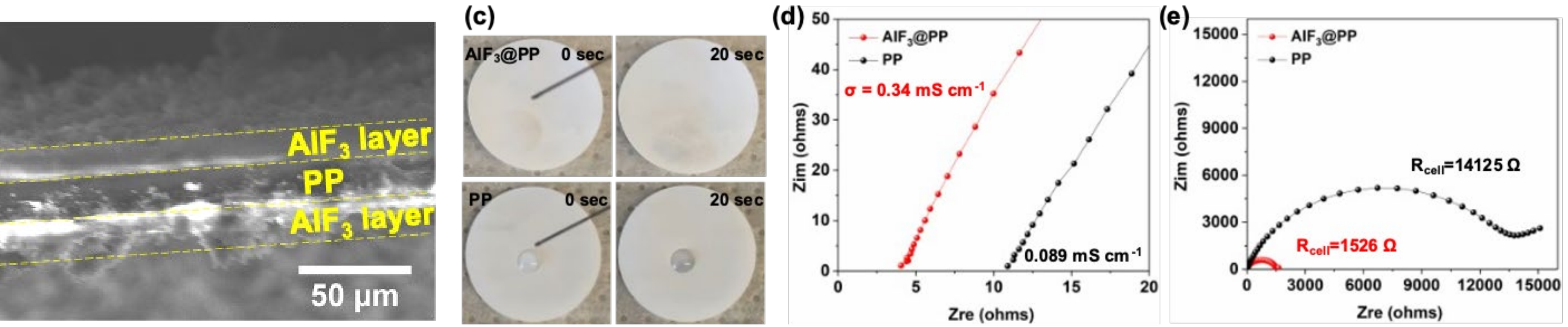




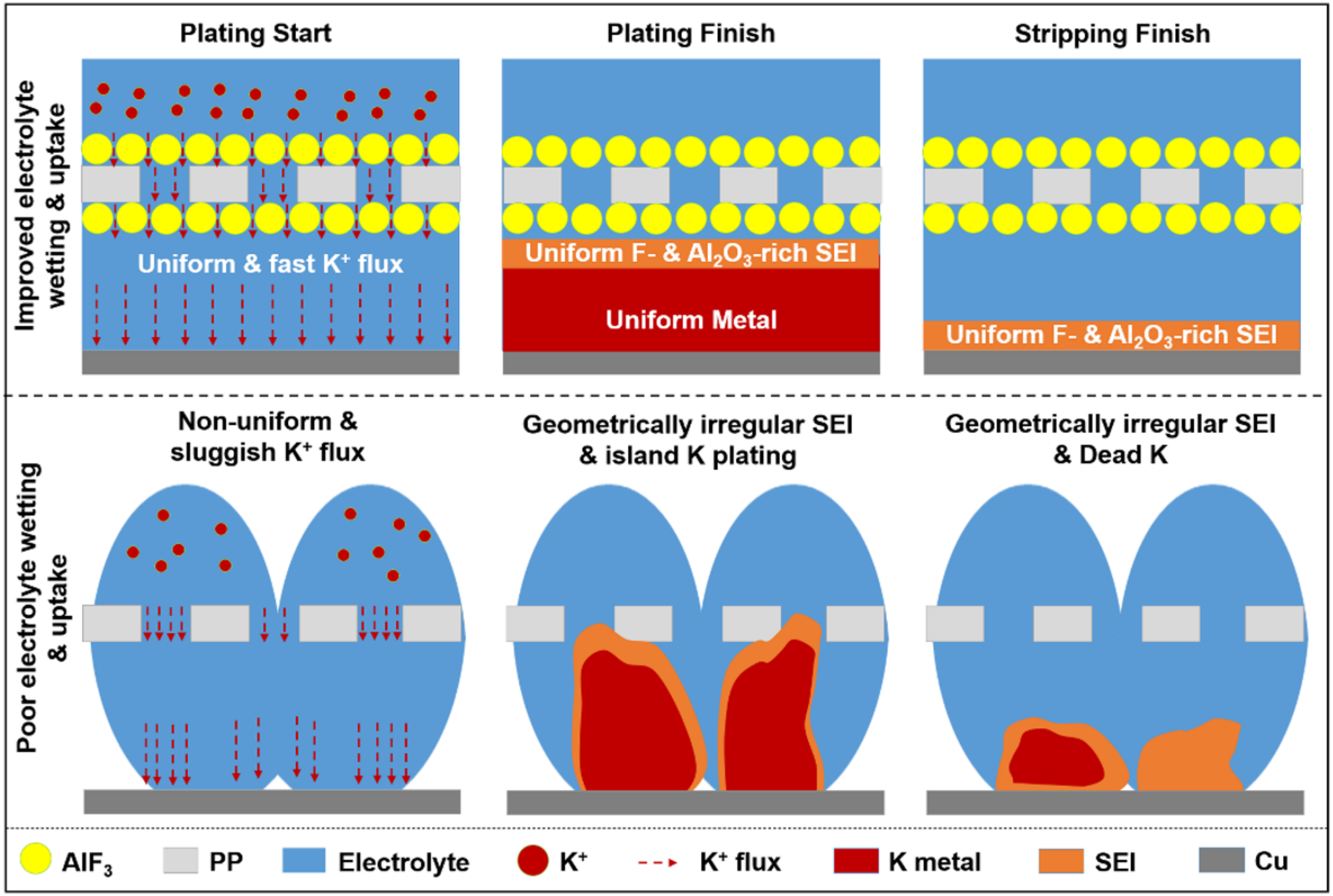
Multifunctional separator - polypropylene (PP) double coated with a reactive micro-scale AlF_3 layer: AlF_3@PP.

- **AlF_3@PP promotes complete electrolyte wetting and enhances uptake, improves ion conductivity, and increases ion transference number.**

- **The ability of AlF_3 to enhance electrolyte wetting and battery performance is general, demonstrated with ester- and ether-based solvents, with K-, Na- or Li- salts, and with different commercial separators as substrates.**

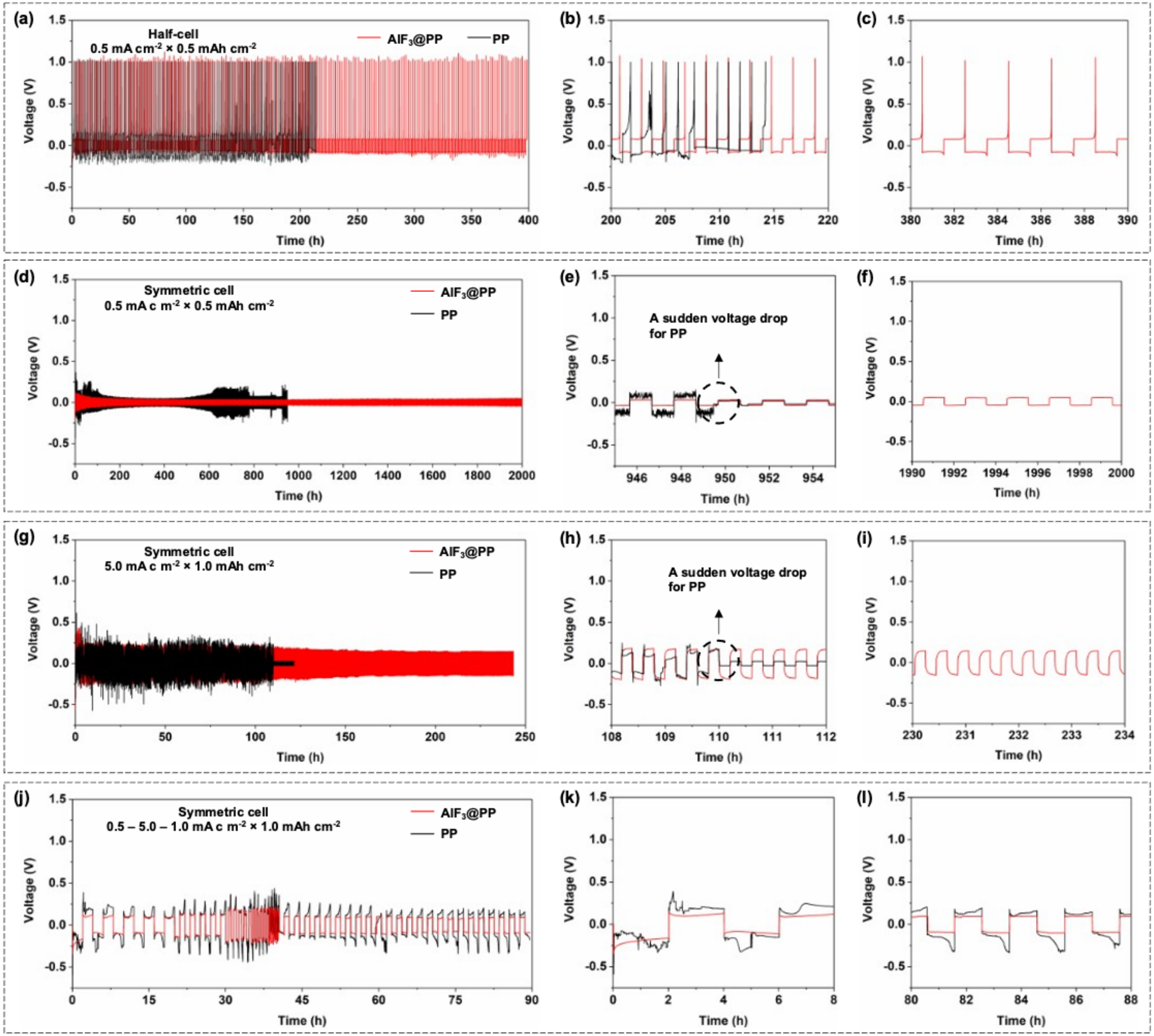


Multifunctional Separator Allows Stable Cycling of Potassium Metal Batteries

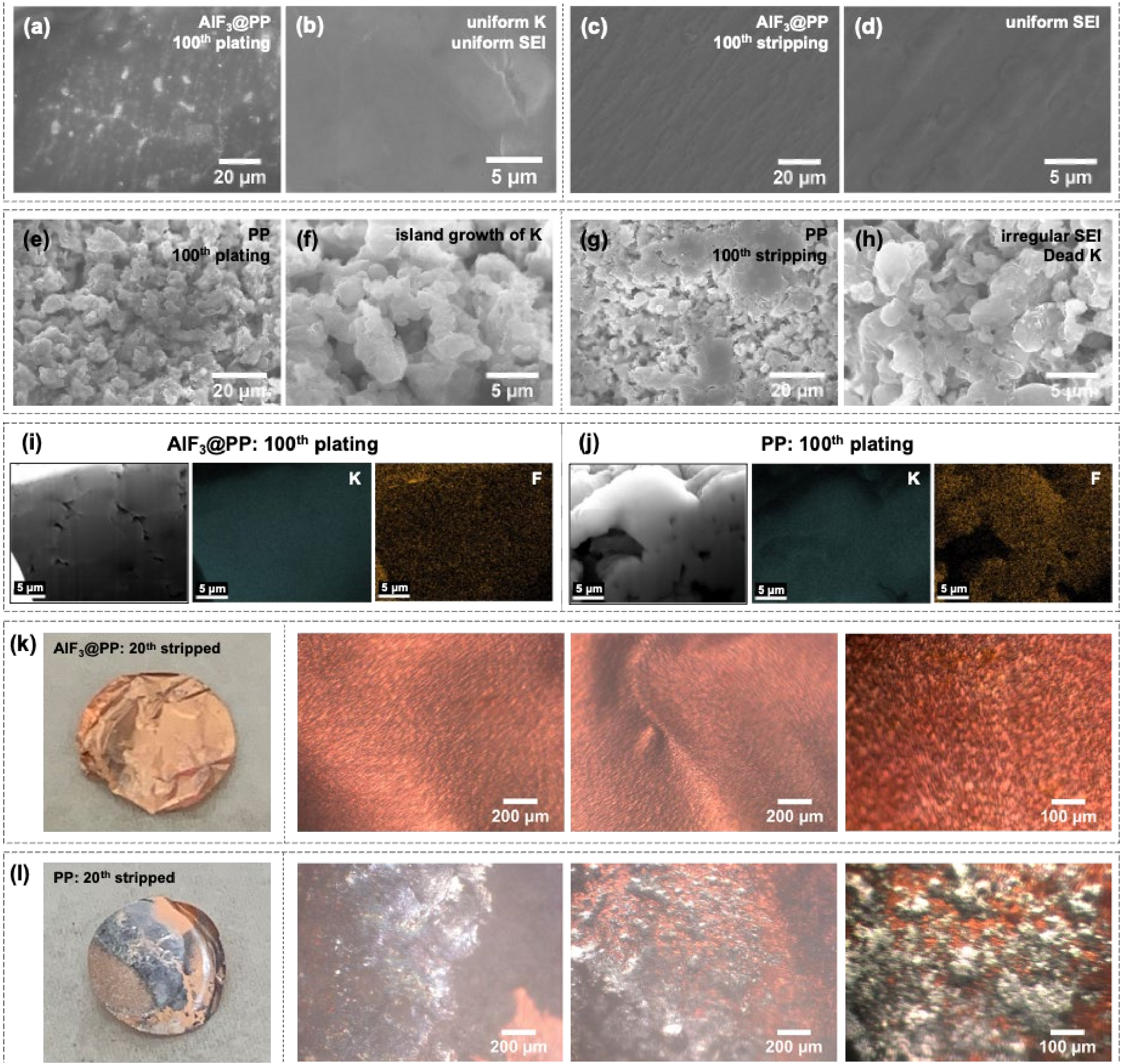


Role of AlF_3@PP in stabilizing the plating and stripping reactions, preventing dendrite growth and dead metal. The AlF_3@PP possesses improved electrolyte wetting and uptake, improved ion conductivity, and increased ion transference numbers. It also partially reacts to form an artificial SEI. Top and bottom, AlF_3@PP versus baseline PP.

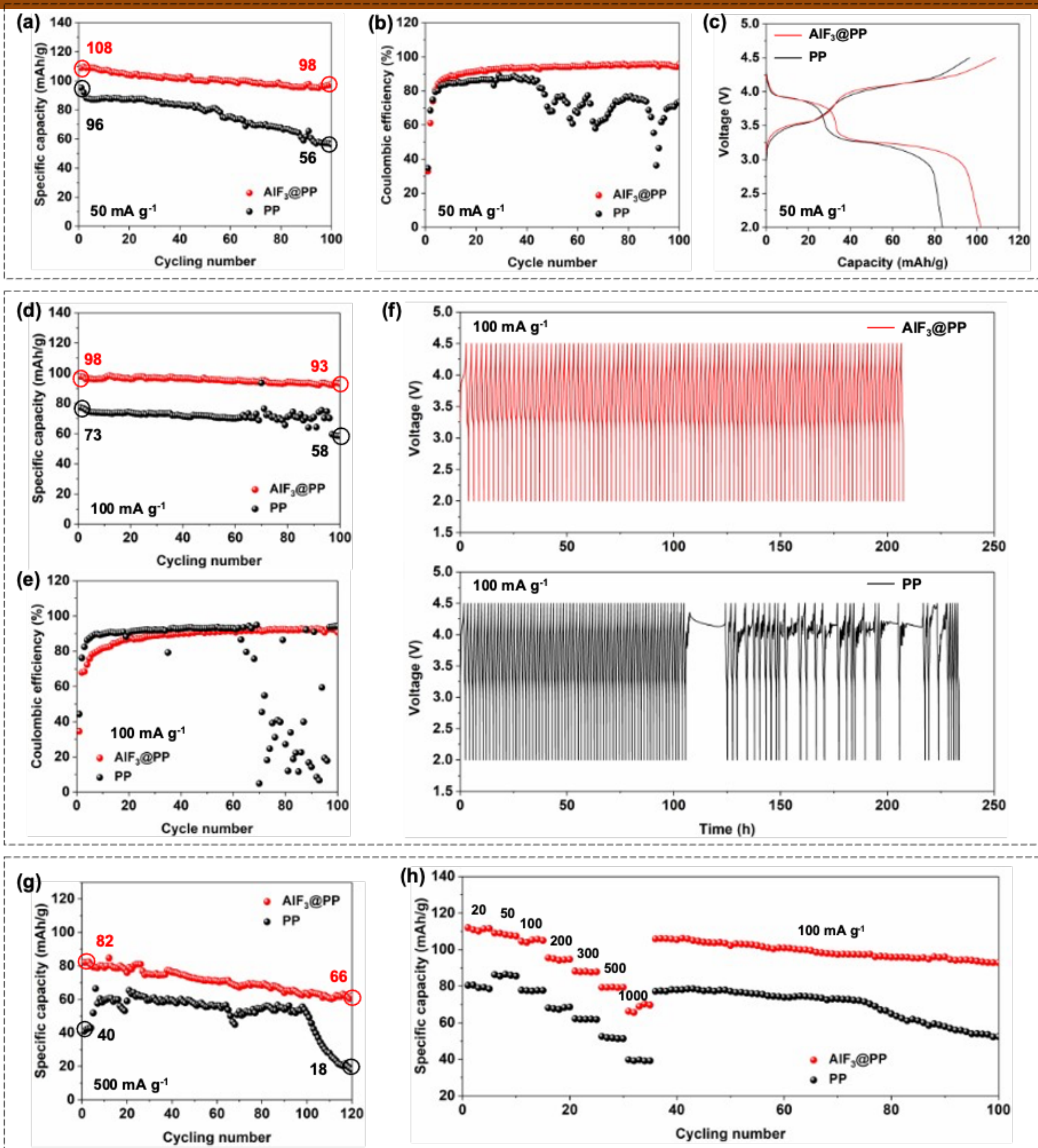
Multifunctional Separator Allows State-of-the-Art Cycling of Metal Anodes



Multifunctional Separator Allows Stable Cycling of Potassium Metal Anodes



Separator Allows State-of-the-Art Cycling of Potassium Metal Batteries (KIBs)



Full cells with $KFe^{II}Fe^{III}(CN)_6$ cathode using AlF_3@PP vs. baseline PP separator. Comparison at the current density of 50 mA/g.

(a) cycling performance, **(b)** CE, and **(c)** charging-discharging curve of 40th cycle. Comparison at the current density of 100 mA/g: **(d)** cycling performance, **(e)** CE, **(f)** comparison of whole charging-discharging profiles of AlF_3@PP vs. baseline PP. **(g)** Comparison of cycling performance at a large current density of 500 mA/g. **(h)** Comparison of rate performance.

Ongoing and Future Work (FY23)

Stable sodium-based solid-state electrolytes (SSEs)

Benchmark the performance of various full SSE batteries with interlayers to enhance cycling stability.

  - **Targets**: Achieve over 100 cycles at intermediate current density.
- Investigate the role of interlayer structure and chemistry on cycling performance
- Perform limited scaleup studies for target SSEs, focusing on producing gram-scale quantities

Economical Carbide electrocatalyzed sodium – sulfur batteries

- Develop economical high-performance carbide formulations that may be scaled
  - **Target**: Produce sulfur with carbide electrocatalysts architectures in gram quantities
- Investigate cycling of high-mass loading cathodes and high DOD metal anodes
- Inhibit Na dendrite growth and polysulfide dissolution

Functional separators for sodium ion, sodium sulfur, and sodium metal batteries

  - **Targets**: Tunable solvent wetting and uptake, total thickness $< 60\ \mu m$, dendrite prevention.
- Investigate transport properties and cross-over using analytical methods
- Perform basic scaleup studies and technoeconimic analysis