FY22 DOE OE Energy Storage Program Annual Peer Review Meeting

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Session 5: Medium and Long Duration Energy Storage

#503
Freeze-Thaw Battery Technology

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PNNL-SA-178002

PNNL is operated by Battelle for the U.S. Department of Energy

Long-duration/seasonal energy storage task

- **Project Team:**

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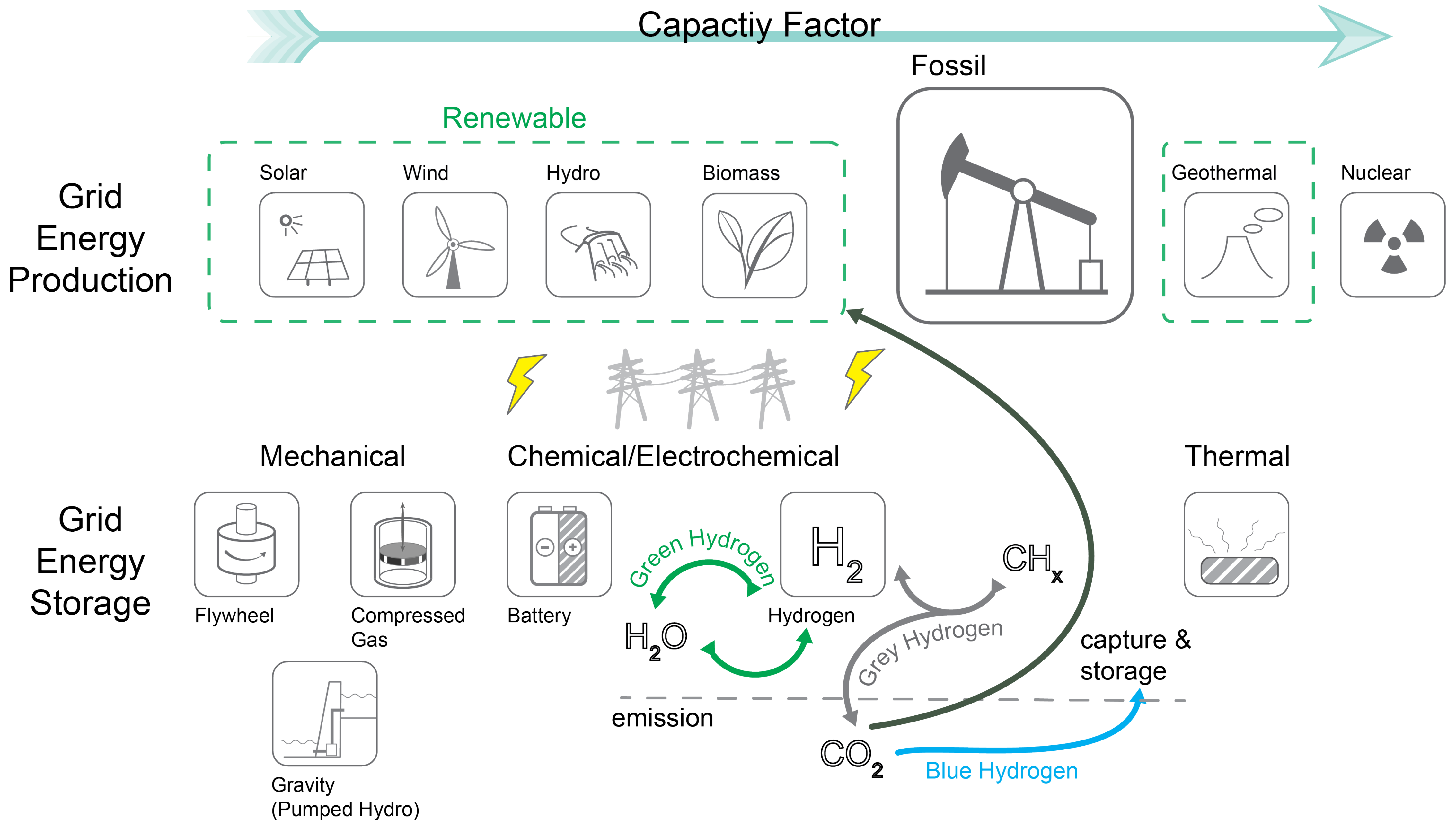
FY22	
Journal publications & Milestone	• "A freeze-thaw molten salt battery for seasonal storage" *Cell Rep. Phys. Sci* 3, 100821 (2022).
IP& Invention Reports	• Non-Provisional IP application filed (Freeze-thaw battery)
Collaboration	• DOE Energy I-Corps Program (>75 interviews) • Media & Industry Exposure (news releases and information inquiries)

Energy Production and Energy Storage Systems



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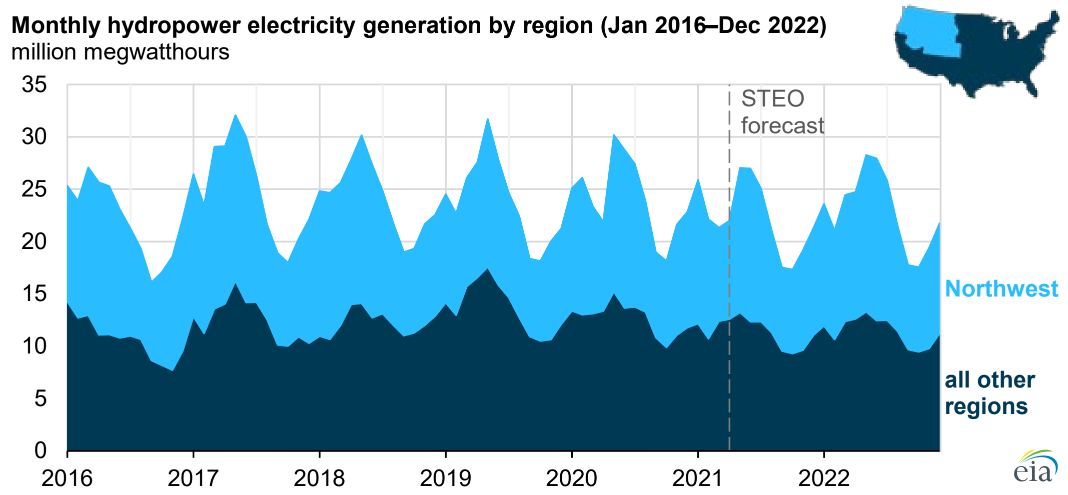
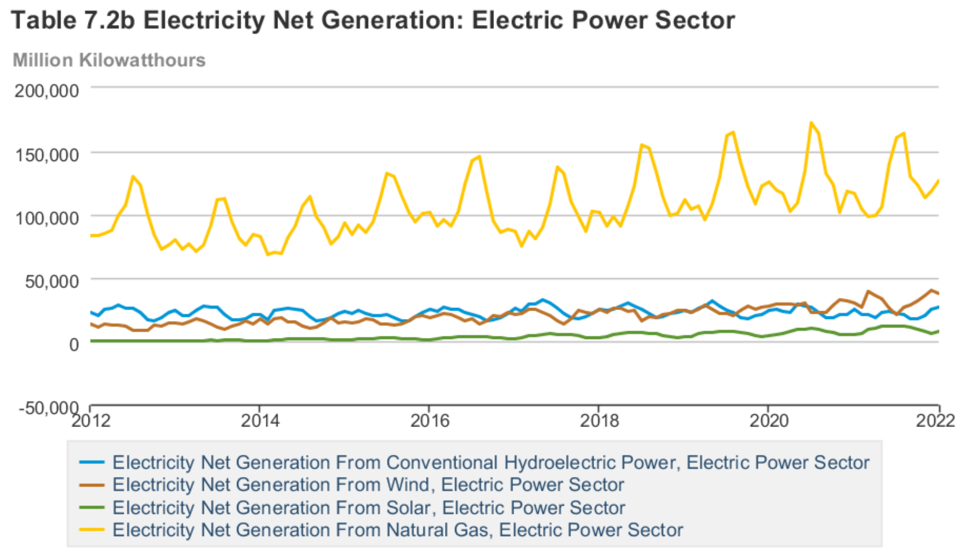
Energy storage is a necessity for renewables

- Renewable capacity fluctuates
- Fossil fuels stabilize demand response
- Decarbonization requires an energy bank
  - Likely a requirement for Net-Zero
  - More efficient production/distribution
  - Stability and emergency reserve
- Long-term capacity shift

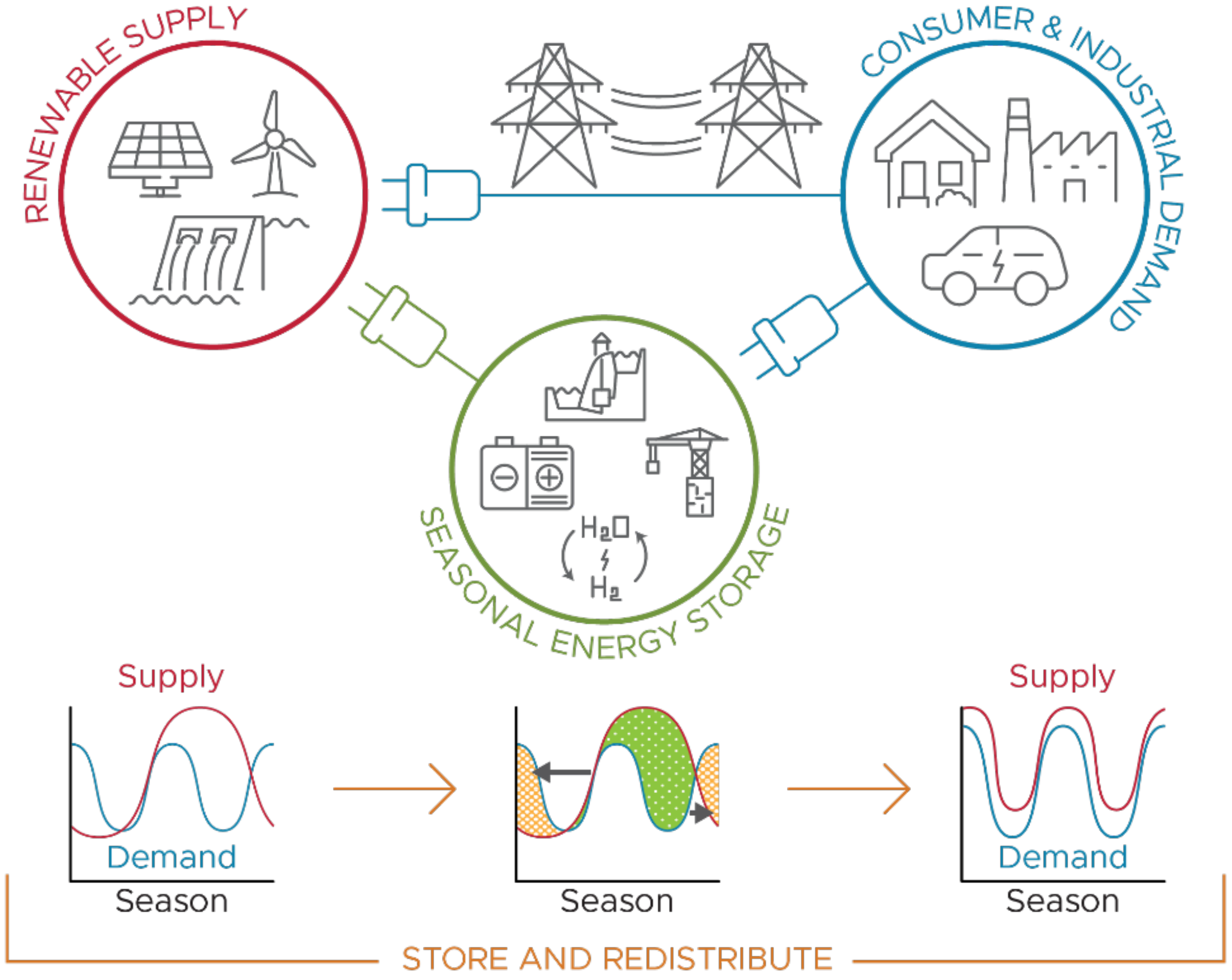




Data source: U.S. Energy Information Administration

Capacity shift by seasonal excess

- Require reliable strategies
  - Pumped hydro
  - Bio-fuels
  - Hydrogen
- Challenges
  - Infrastructure needs large investment
  - Take time to adapt new technologies
- Cheap battery for long shifts?
  - Find alternatives to lithium
  - Ways to stop self-discharge



Molten Salt: a page from history

- Thermal batteries provide reliable activation from dormancy
- Reliable performance from molten sodium batteries (e.g. ZEBRA)
  - M-MCl_2 surface conversion (M = Ni, Fe)
  - Ceramic β"-alumina key to stability, but problematic
- Taking the best from both
  - Using Al-Ni couple without a ceramic separator

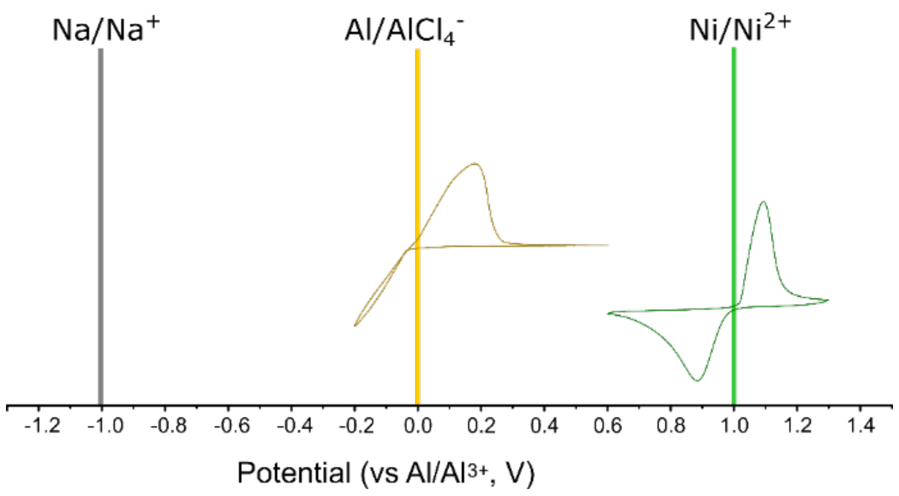
Anode:	$Al + NaCl + 3Cl^-$	→	$NaAlCl_4 + 3e^-$
Cathode:	$NiCl_2 + 2e^-$	→	$Ni + 2Cl^-$
Overall:	$2Al + 2NaCl + 3NiCl_2$	→	$2NaAlCl_4 + 3Ni$, E = 0.910V (180 °C)

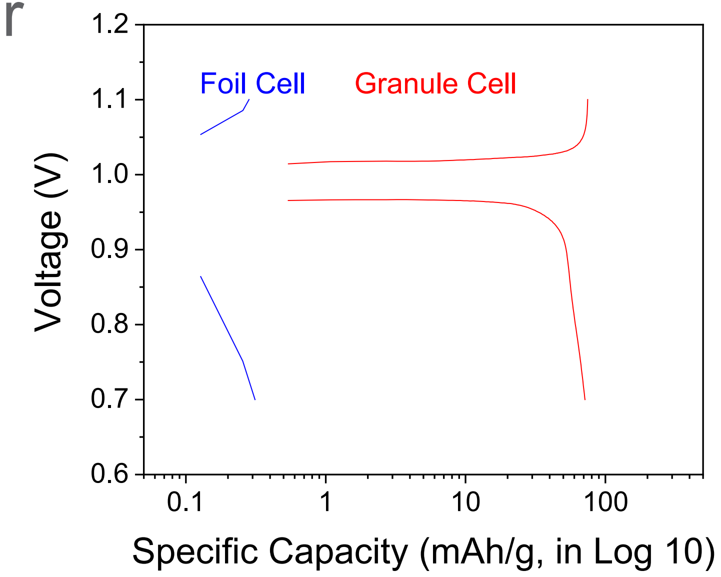
Specific capacity: 287.3 mAh/g

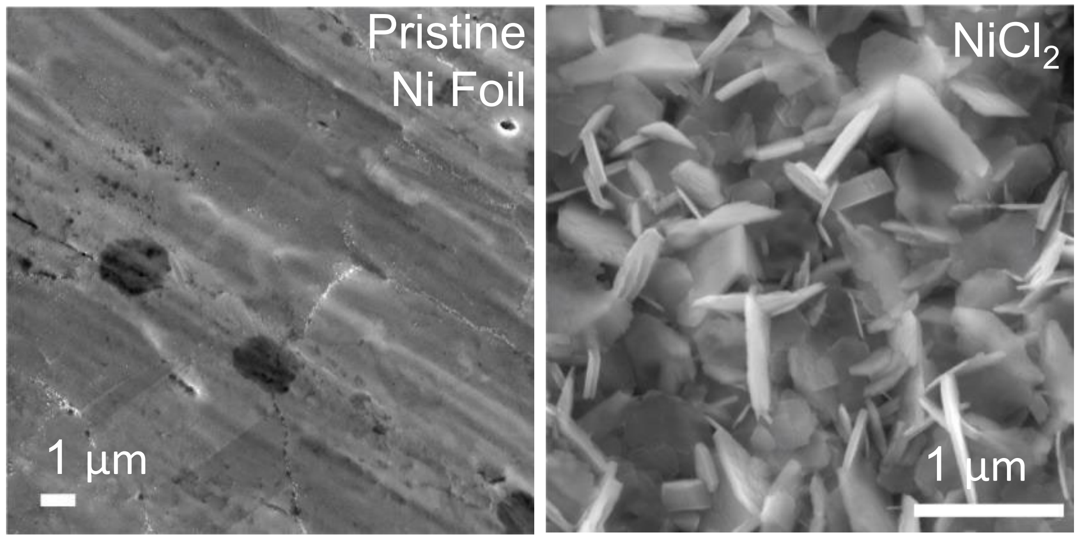
Li et al. *Cell Reports Physical Science* ***2022****, 3 (4), 100821.*

Electrode surface dictates performance

- Al-Ni couples have compatible chemistry
  - $Ni\text{-}NiCl_2$ surface conversion
- Increase performance by increasing surface area
  - Granulated metal powder







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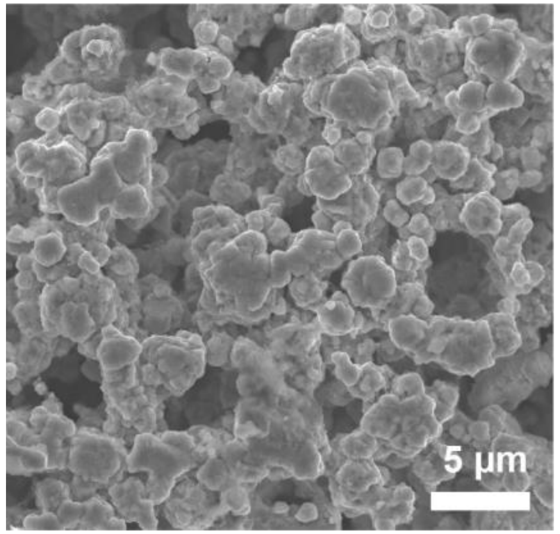
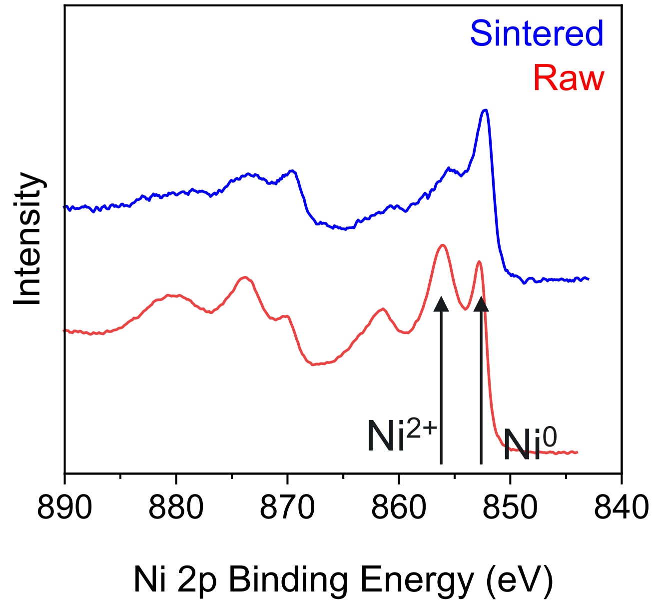
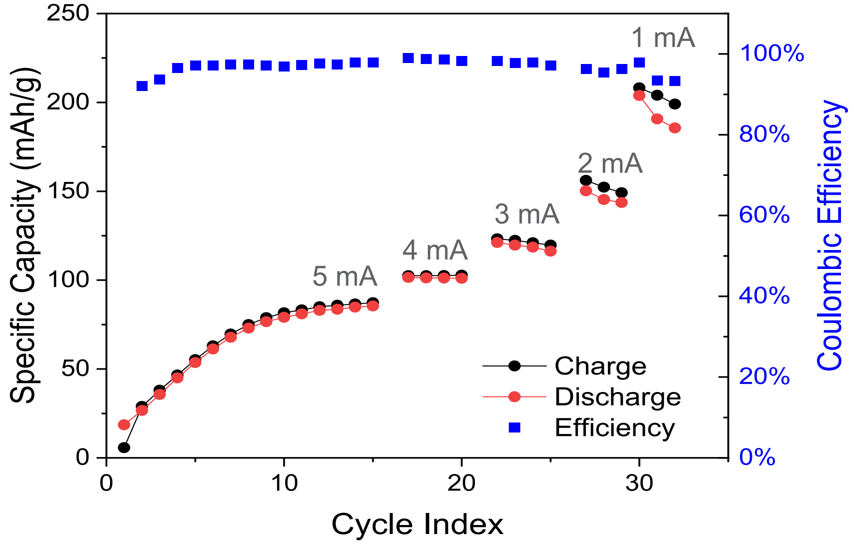
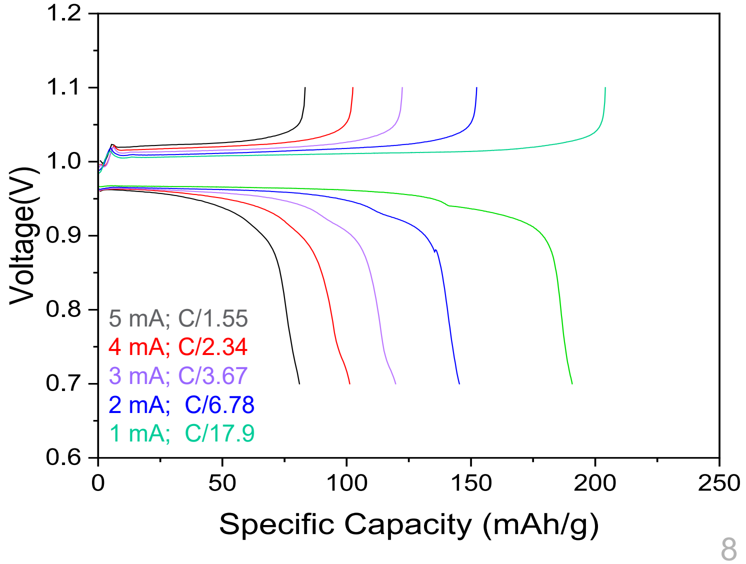
Improve cycling via reductive activation

- Increase performance by increasing surface activity
  - Remove oxide passivation
- Thermal treatment of Ni under H_2
  - Reduction of oxides
  - Create conductivity network



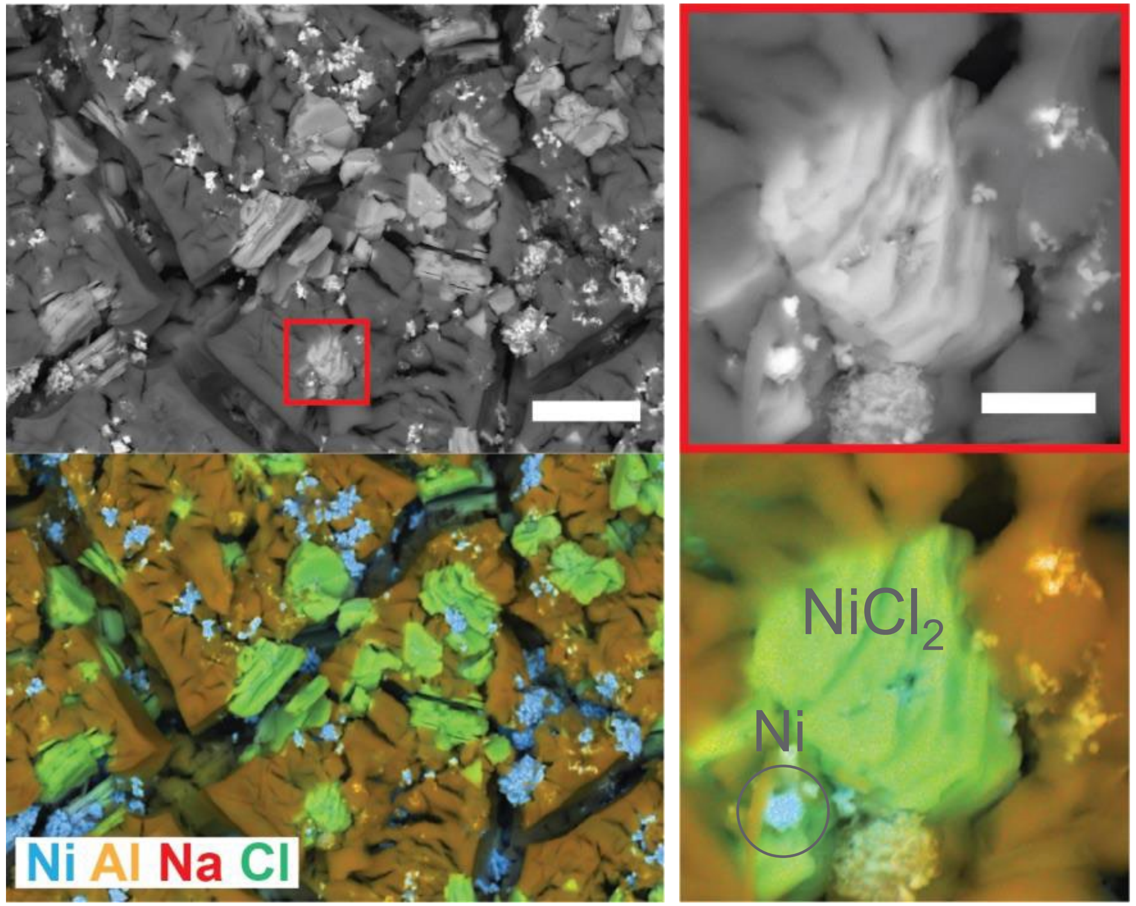


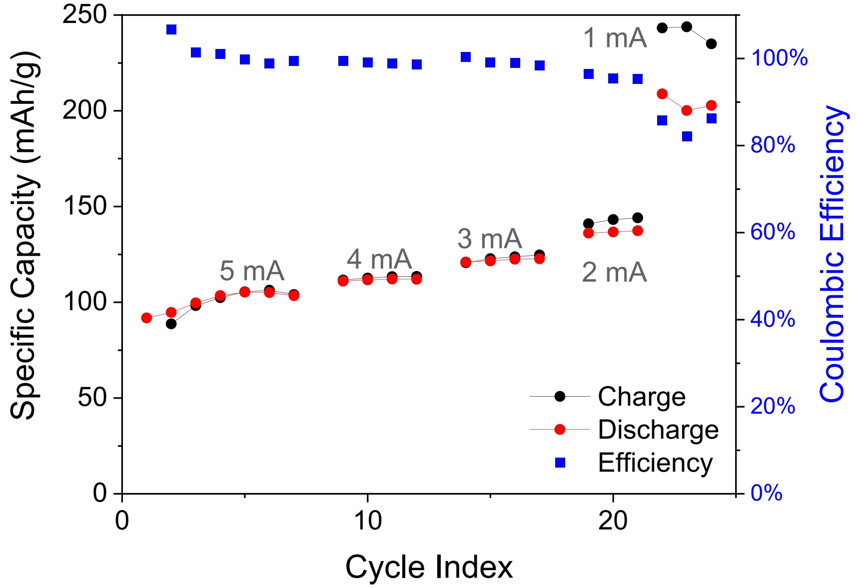


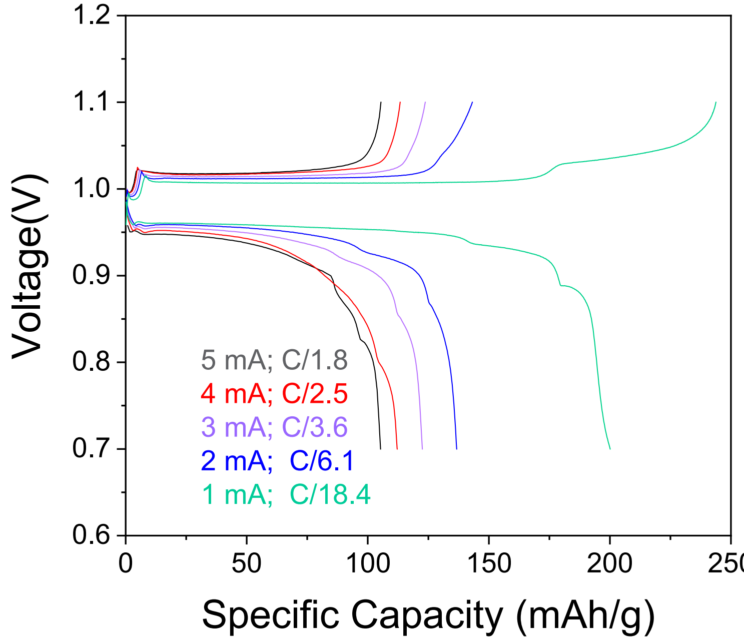


Conditioned cathode improves activation

- Cathodes from Na-$NiCl_2$ batteries can be transplanted
  - Existing stable Ni-$NiCl_2$ interfaces







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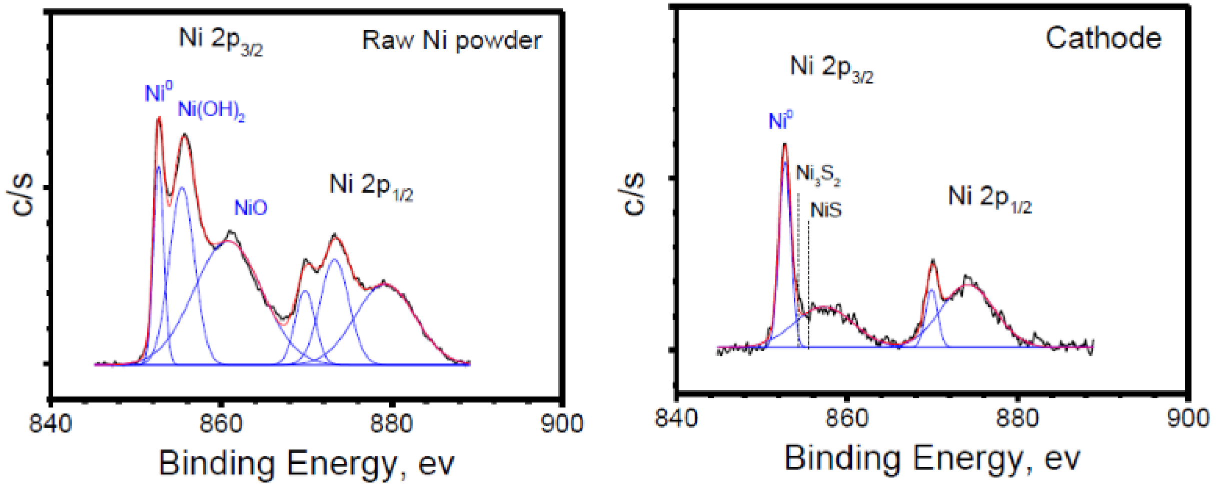
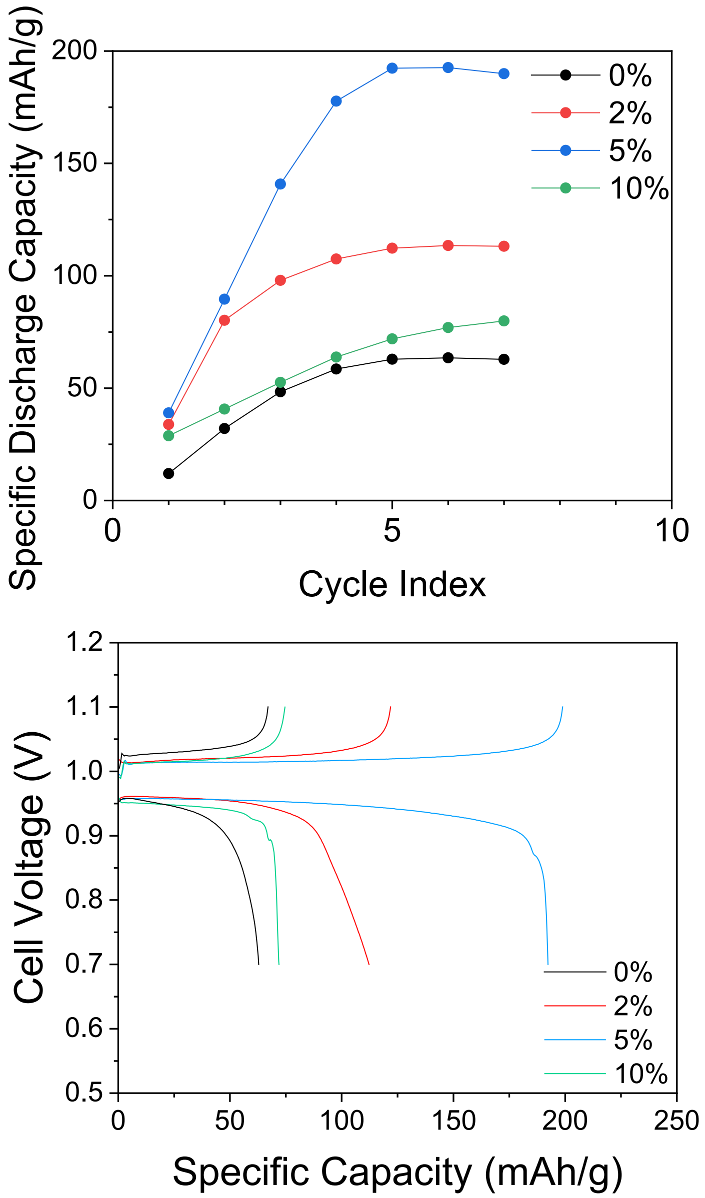
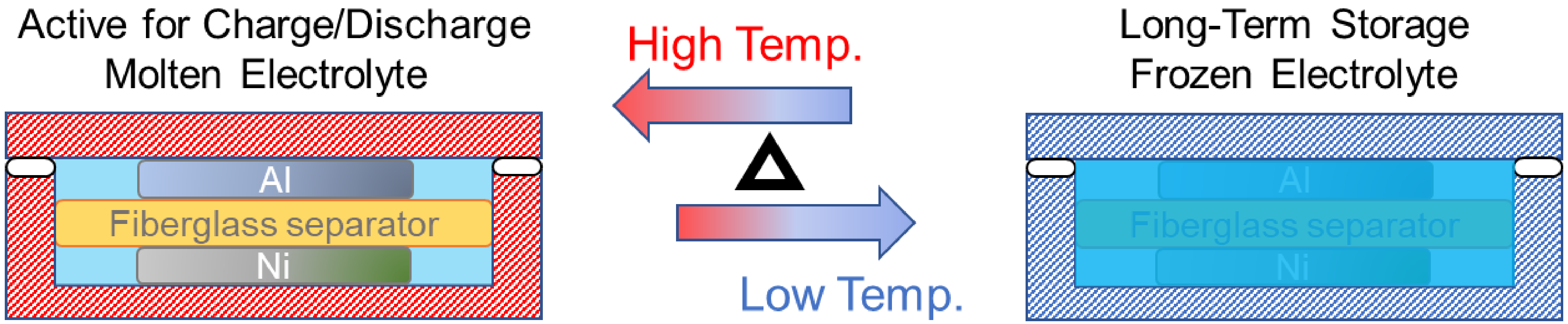
Cathode activation via sulfur doping

- Mixing sulfur powder directly into the electrolyte also removes oxidation
  - A simple procedure
  - Fewer cycles to full capacity

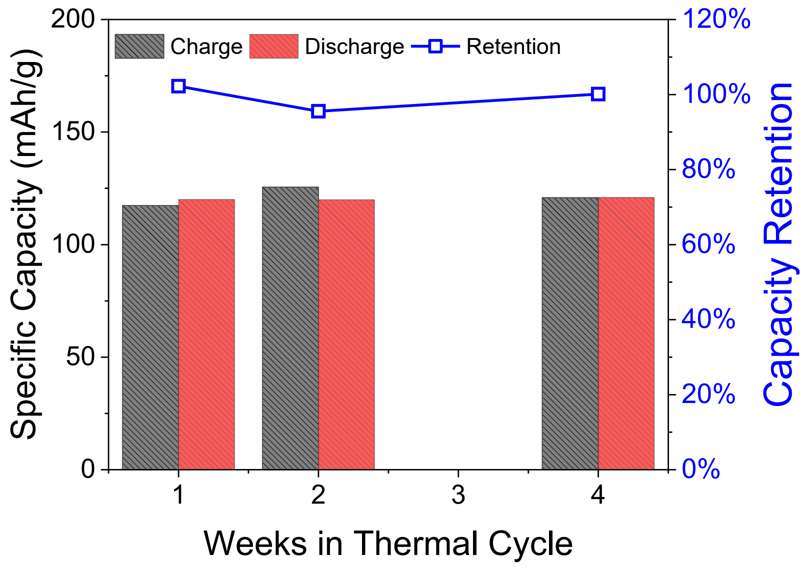


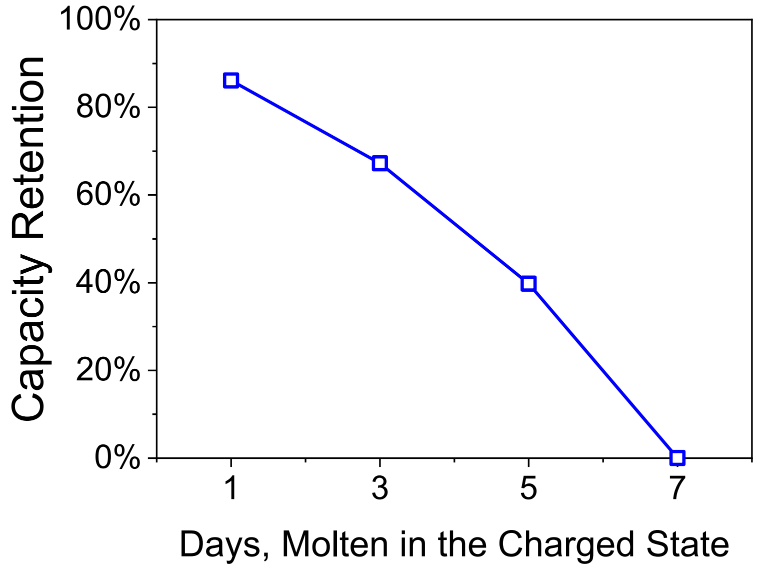


Freeze-then-thaw to shift capacity



- Battery activity or transport is temperature-controlled
  - High capacity retention after freezing
  - Otherwise, fast capacity fades in the molten state

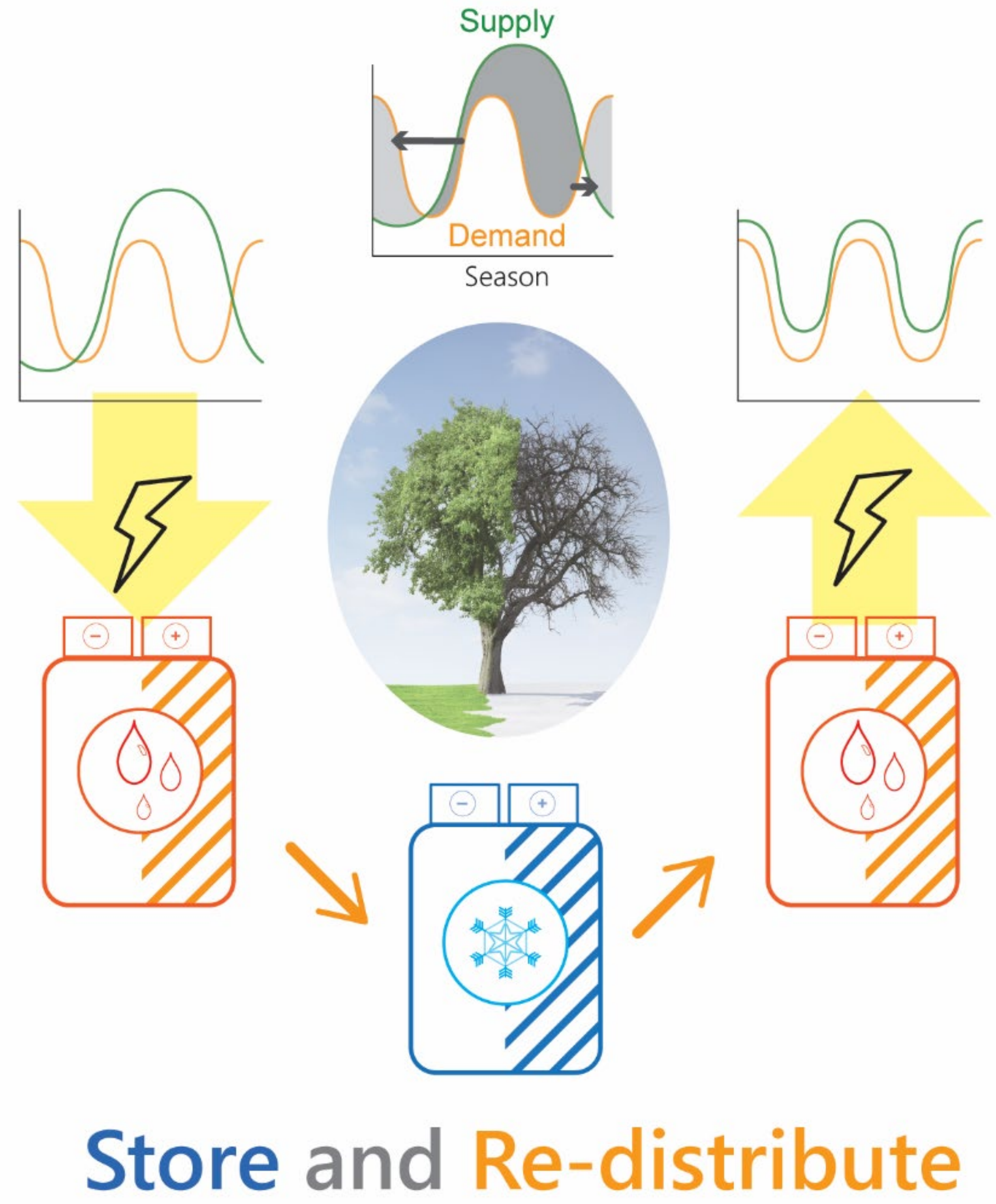




Energy in a time capsule

- Preliminary results show high retention close to half a year
  - 12 weeks: 92.3% (from charged-state granules)
  - 24 weeks: 85.7% (from 5% sulfur doping)

Week	Sintered (Discharged State)		Charged-State Granules		5% Sulfur Doping (Discharged State)	
	Capacity (mAh/g)	Retention	Capacity (mAh/g)	Retention	Capacity (mAh/g)	Retention
1	84.8	89.4%	120	> 99.5%	172	88.8%
2	72.5	89.6%	120	95.5%	180	95.1%
4	60.9	88.6%	121	> 99.5%	158	98.3%
8			93.6	98.5%	145.3	92.5%



Using Fe as an alternative cathode material

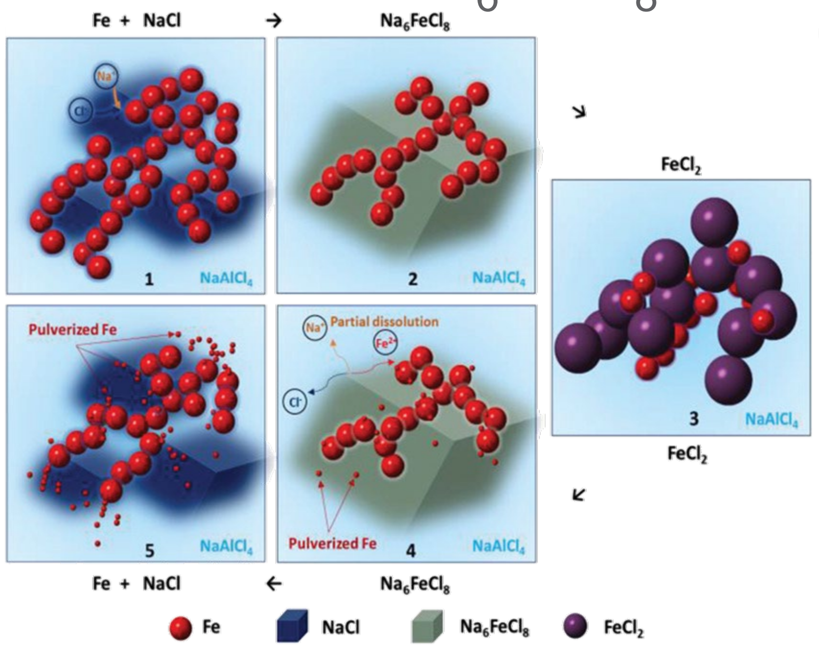
- Compatible electrochemistry on paper

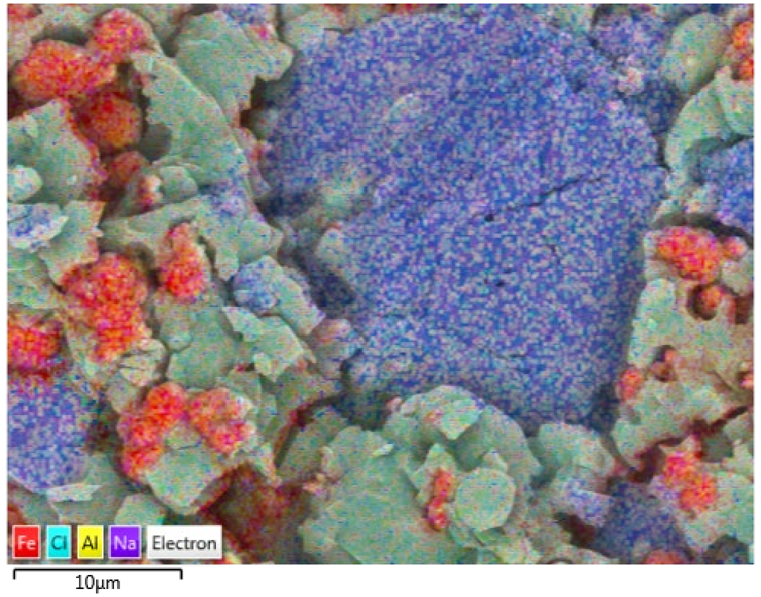
  Cathode: $FeCl_2 + 2e^-$ → $Fe + 2Cl^-$

  Overall: $2Al + 2NaCl + 3FeCl_2$ → $2NaAlCl_4 + 3Fe$, E = 0.67V (180 °C)

  Specific Capacity: 291.8 mAh/g

- Challenges
  - $FeCl_2$ has higher solubility than $NiCl_2$ in $NaAlCl_4$ (less stable charged species)
  - Formation of Na_6FeCl_8 intermediate





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Future Works and Acknowledgement

- Future works
  - Techno-economic analysis and commercial transition (DOE Energy I-Corps)
  - Expand feasibility of Fe-$FeCl_2$ chemistry
  - Explore systems with a phase transition between 60 and 80 °C

- Many thanks to my co-authors and collaborators
  - J. Mark Weller, Evgueni Polikarpov, Nathan L. Canfied, Mark H. Engelhard, David M. Reed, Vincent L. Sprenkle, and Guosheng Li

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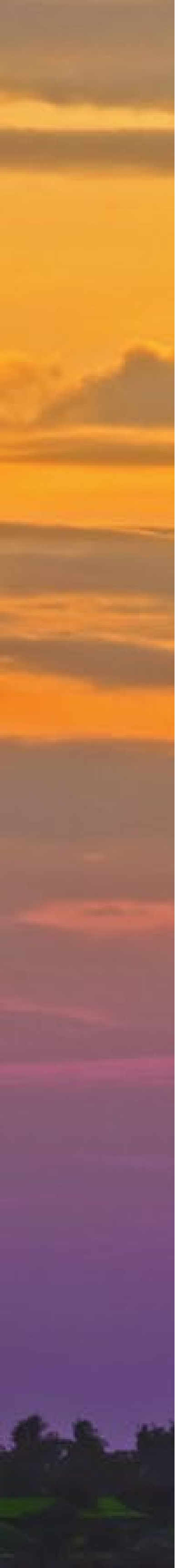

Thank you