Freeze-Thaw Molten Salt Batteries: Unlocking Low-Cost Energy Storage

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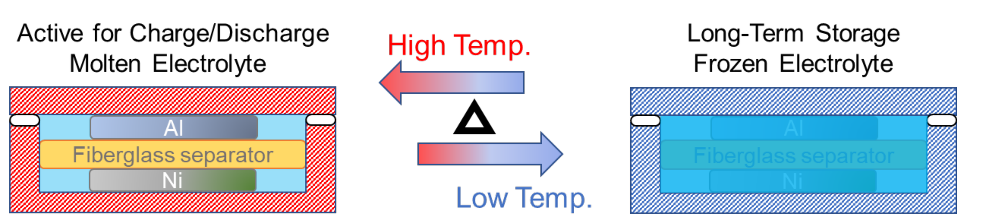
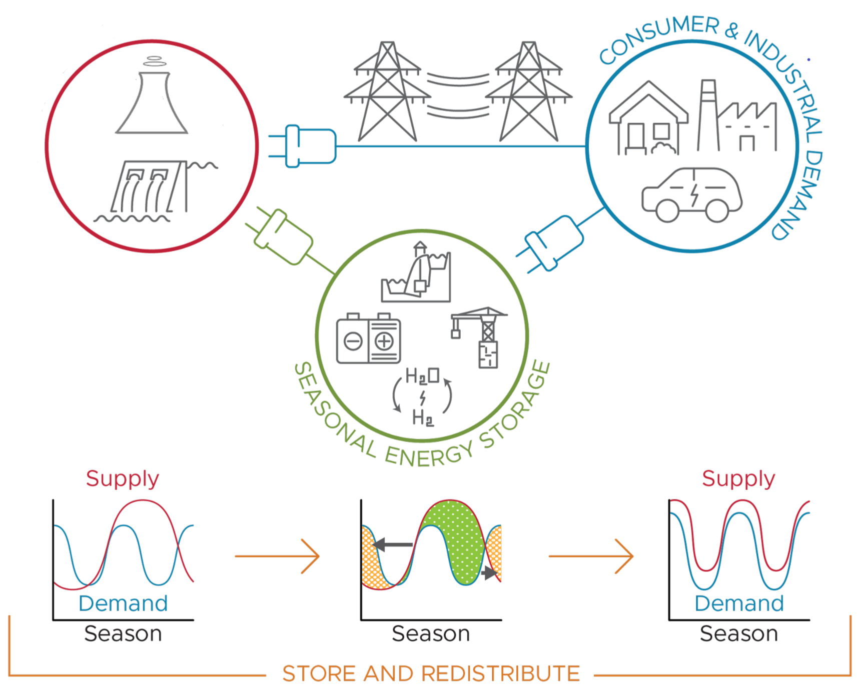
Background: Freeze-Thaw Al-Ni for Seasonal energy storage

Seasonal batteries, engineered to store energy across seasons, present a compelling solution for enhancing reliability, resilience, and cost-effectiveness in grid energy systems. Current technologies, such as conventional battery technologies and hydrogen-based systems, demand further system-level innovations to achieve economic viability. Pacific Northwest National Laboratory (PNNL) pioneered the development of a freeze-thaw molten salt battery specifically for low cost, long duration seasonal storage.



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

Theoretical Specific capacity: 287.3 mAh/g



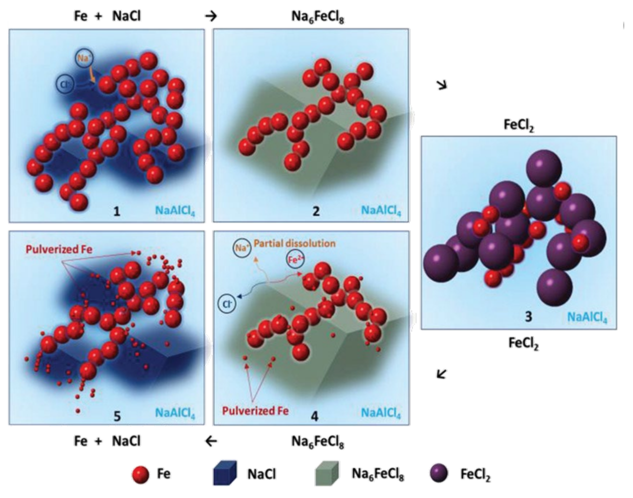
Li et al. *Cell Reports Physical Science 2022*

Possible cathodes and electrolytes alternatives for improved cost competitiveness

Al-Fe (as an alternative to Ni)

Adv. Energy Mater. ***2020, 10, 1903472-1903481.***

Cathode: $FeCl_2$ + 2e^- → Fe + 2Cl⁻
Overall: 2Al + 2NaCl + 3$FeCl_2$ → 2$NaAlCl_4$ + 3Fe, E = 0.67V (180 °C)
Specific Capacity: 291.8 mAh/g



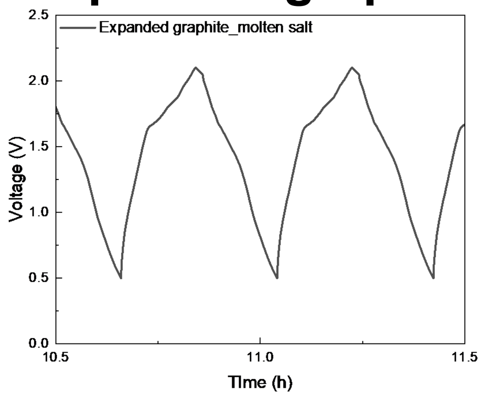
Challenges
- $FeCl_2$ has *much* higher solubility than $NiCl_2$ in $NaAlCl_4$ (less stable charged species)
- Formation of the intermediate Na_6FeCl_8 phase
- The self-discharge rate is high

Al-Graphite (as an alternative to Ni)

Anode: Al + 7[$AlCl_4^-$] → 4[$Al_2Cl_7^-$] + 3e^-
Cathode: C_n + [$AlCl_4^-$] → C_n[$AlCl_4^-$] + e^-

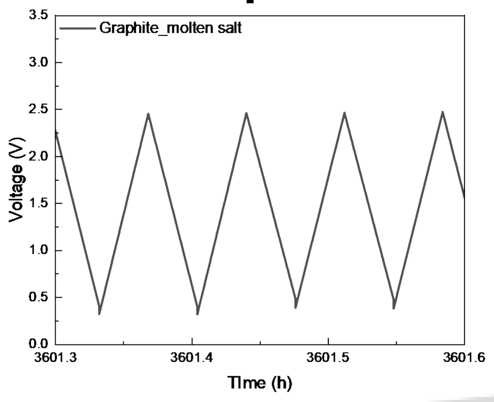
Challenges
- **Large Anion Size**: $AlCl_4$- is a bulky tetrahedral anion, making it difficult to fit between the narrow graphene
- **Steric Hinderance**: the spatial structure of $AlCl_4$- causes steric repulsion, which limits deep intercalation and layer expansion
- **Structure Degradation**: Repeated intercalation/deintercalation can lead to expansion, exfoliation, or cracking of graphite layer

Expanded graphite

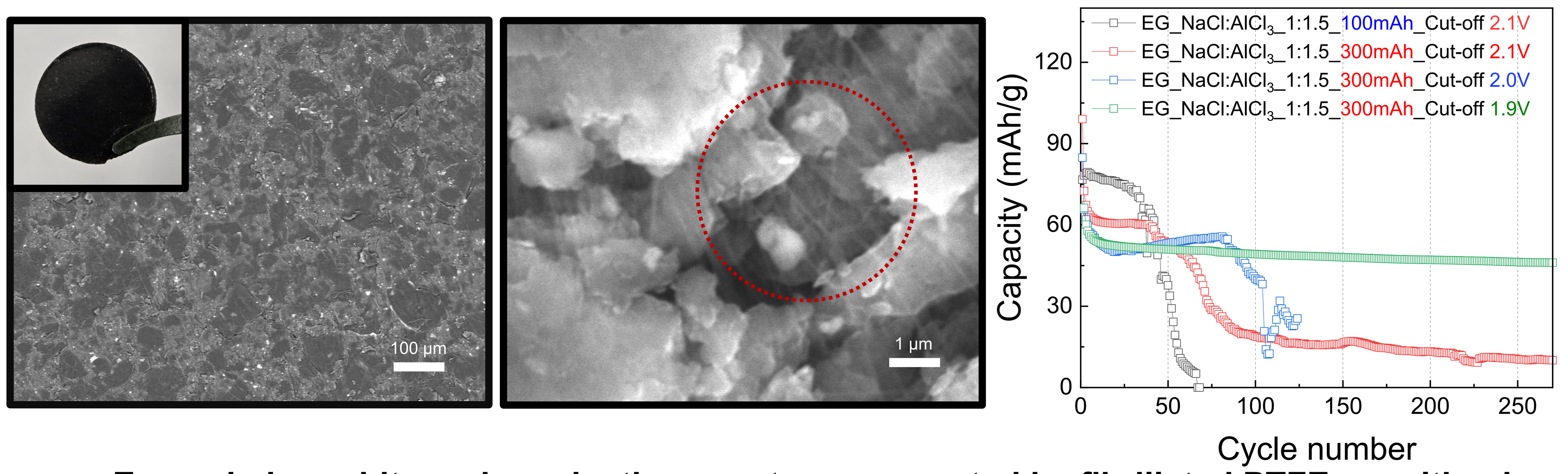


vs.

Graphite



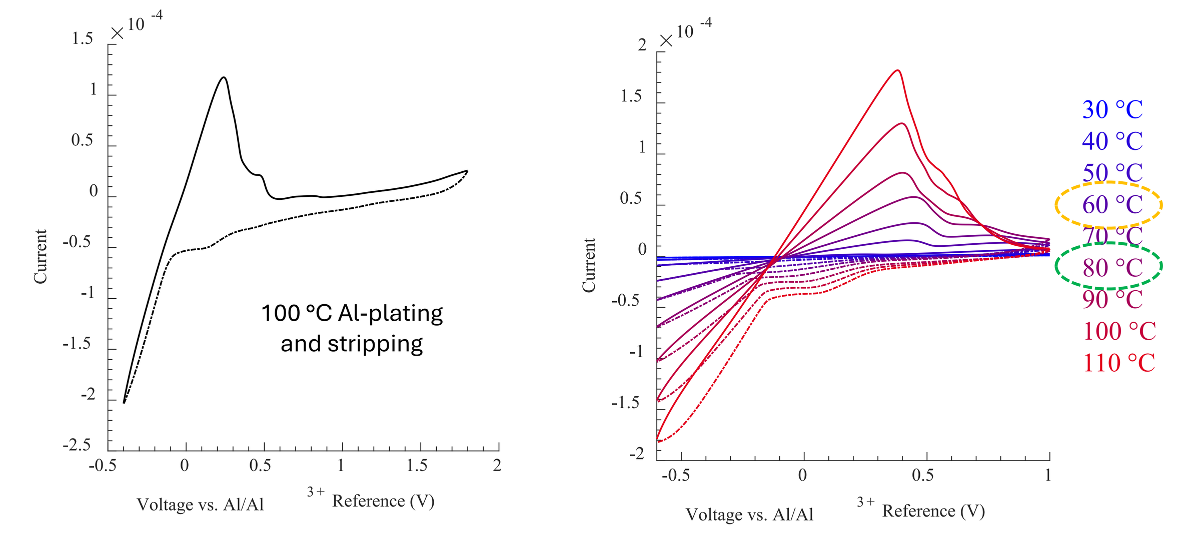
Expanded graphite (a solvent-free dry electrode) with molten salt electrolyte



- **Expanded graphite and conductive agent are connected by fibrillated PTFE, resulting in a self-standing electrode**
- **It shows stable cyclability over 250 cycles at a high C-rate (300 mA/g)**

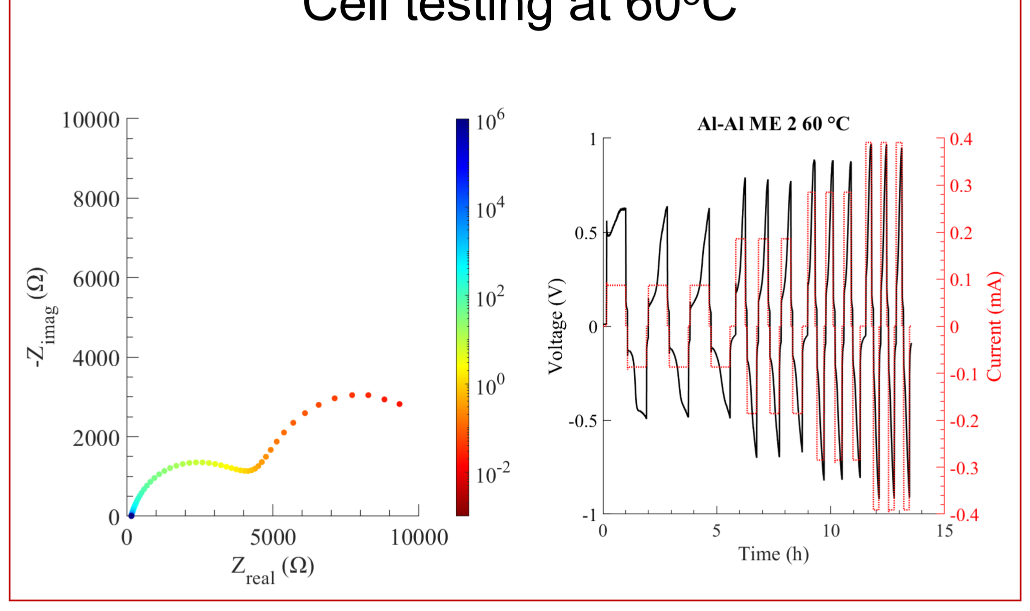
Lower melting point electrolyte

Exploring suitable electrolytes with intermediate melting temperatures
- Greater than RT and less than $NaAlCl_4$
- MP in the range of 40-100°C
- Thermal and electrochemical stability

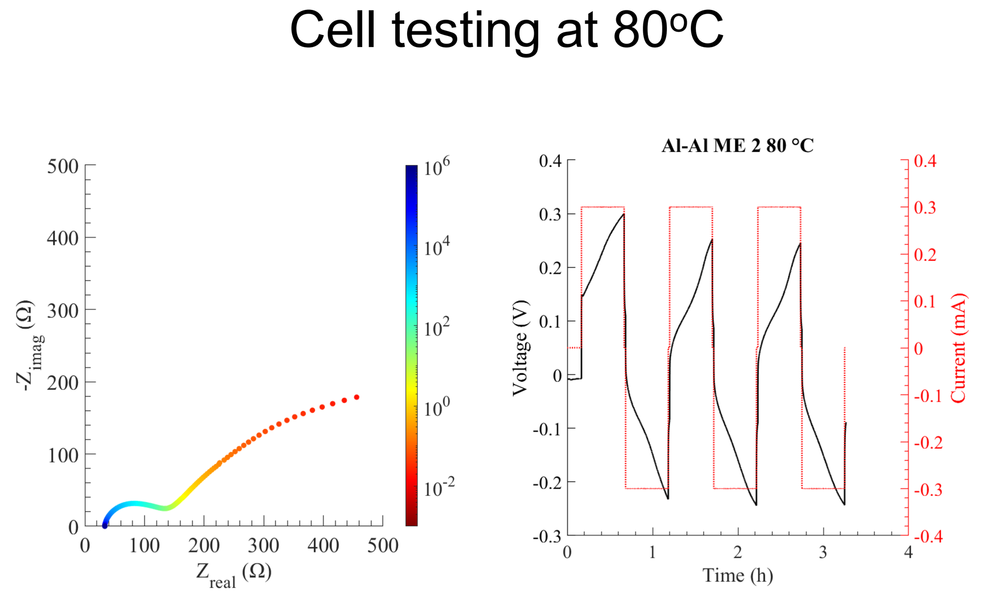


Lower Melting Point Cell Testing

Cell testing at 60°C



Cell testing at 80°C



- **Explanation about lower melting point cell testing**
- **Expanded graphite first and lower melting point electrolyte**

Conclusions and Future work

- **Expanded graphite exhibits superior performance for $AlCl_4^-$ intercalation when paired with a molten salt electrolyte, compared to conventional graphite**
- **The Al symmetric cell shows lower overpotential and impedance with the lower melting point electrolyte**
- **Plan to test expanded graphite with lower melting point electrolytes**

Acknowledgements

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This project is accelerating the development and testing of a new energy storage technology that is more cost-effective, safe, and durable, which is crucial to meeting the Administration's goal of providing reliable, affordable, secure, and resilient energy.

[1]Li et al., *Cell Rep Phys Sci.* 3 (4) (**2022**).
[2]Li et al. *Joule*, 7 (4) (**2023**).
[3]Weller et al. *Energy Storage Materials* 56, 108-120 (**2023**)
[4]Zhan et al. *Adv. Energy Mater.* 10, 1903472 (**2020**)

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