Unlocking the $NaCl$-$AlCl_3$ Phase Diagram for Low-Cost, Long-Duration Energy Storage

J. Mark Weller, Kee Sung Han, Evgueni Polikarpov, David M. Reed, Vincent L. Sprenkle, and Guosheng Li*

Battery Materials & Systems Group, Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

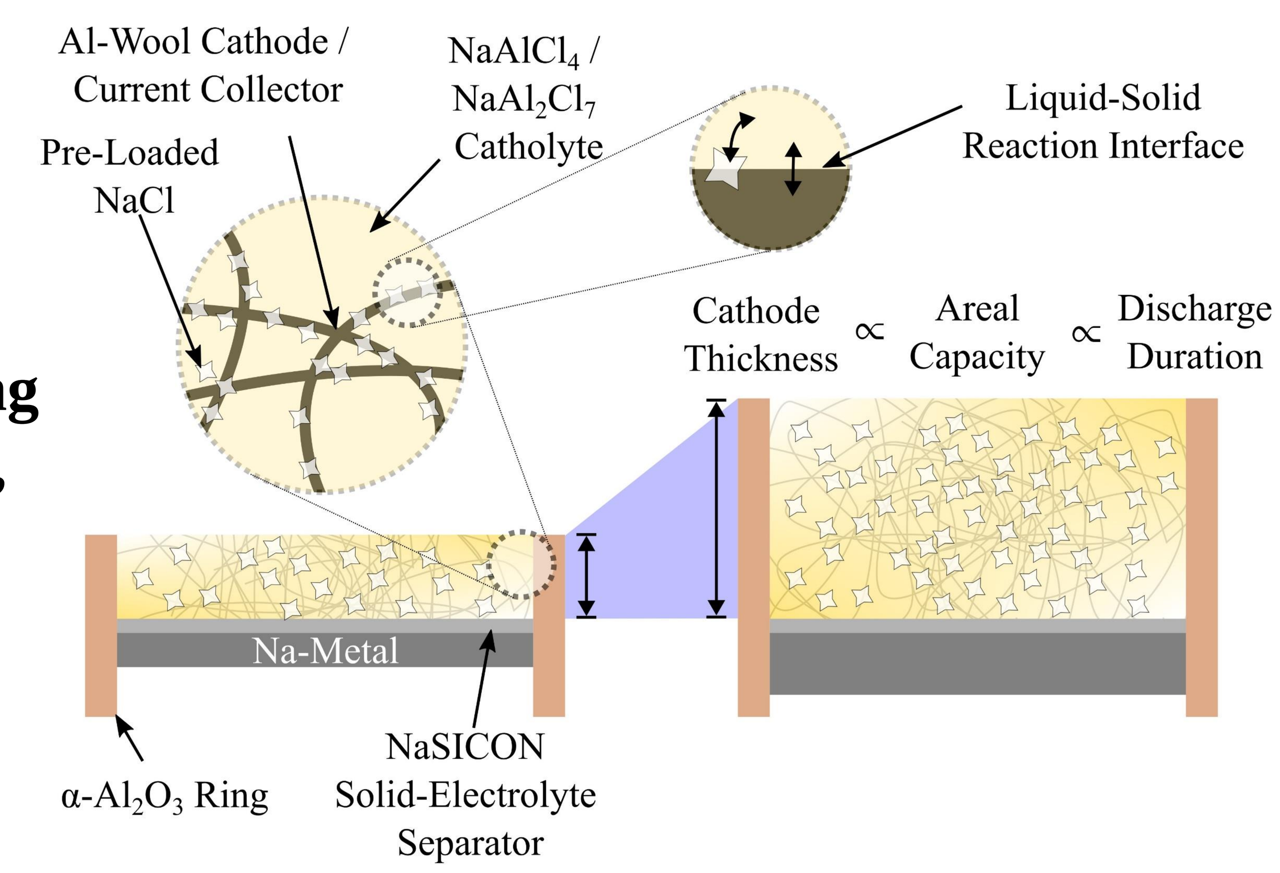
Background: Molten Na Battery Technologies

- Na-S: ~ 2V vs. Na/Na^+, 350 ° C, safety issues, corrosion
- Na-$NiCl_2$: ~ 2.58 V vs. Na/Na^+, 280 C, high cost of Ni
  - Significant PNNL innovation in Na-$NiCl_2$ and other Na-MH chemistries (lower operating T[1], low T Na-wetting[2,3,4], polymer seals[5])
- Na-Al: ~ 1.62 V vs. Na/Na^+, low-cost raw materials, fast kinetics

Challenge: low cost per kWh stored, long-duration

- Al: high specific capacity (2980 mAh g^{-1}), safe handling in air, Earth-abundant
- Na: abundant, low potential vs. SHE (-2.71 V), high specific capacity (1165 mAh g^{-1})

Objective: Unlock more capacity in the Na-Al battery, demonstrate long duration energy storage, move toward practical cathode compositions



Neutral[6,7] and Acidic[7] Chloroaluminate Chemistry

Reaction Mechanism:

Neutral[6] – highly reversible

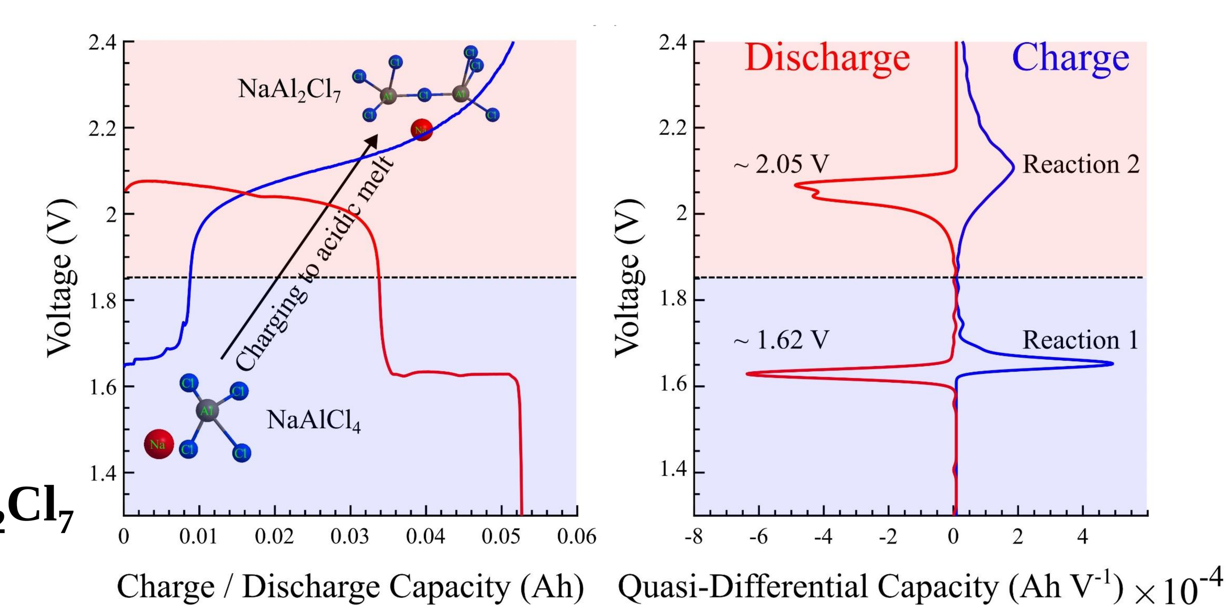
$Al + 4\ NaCl \rightarrow 3\ Na + NaAlCl_4$

E_o = 1.624 V at 180°C

Acidic[7] – also reversible!

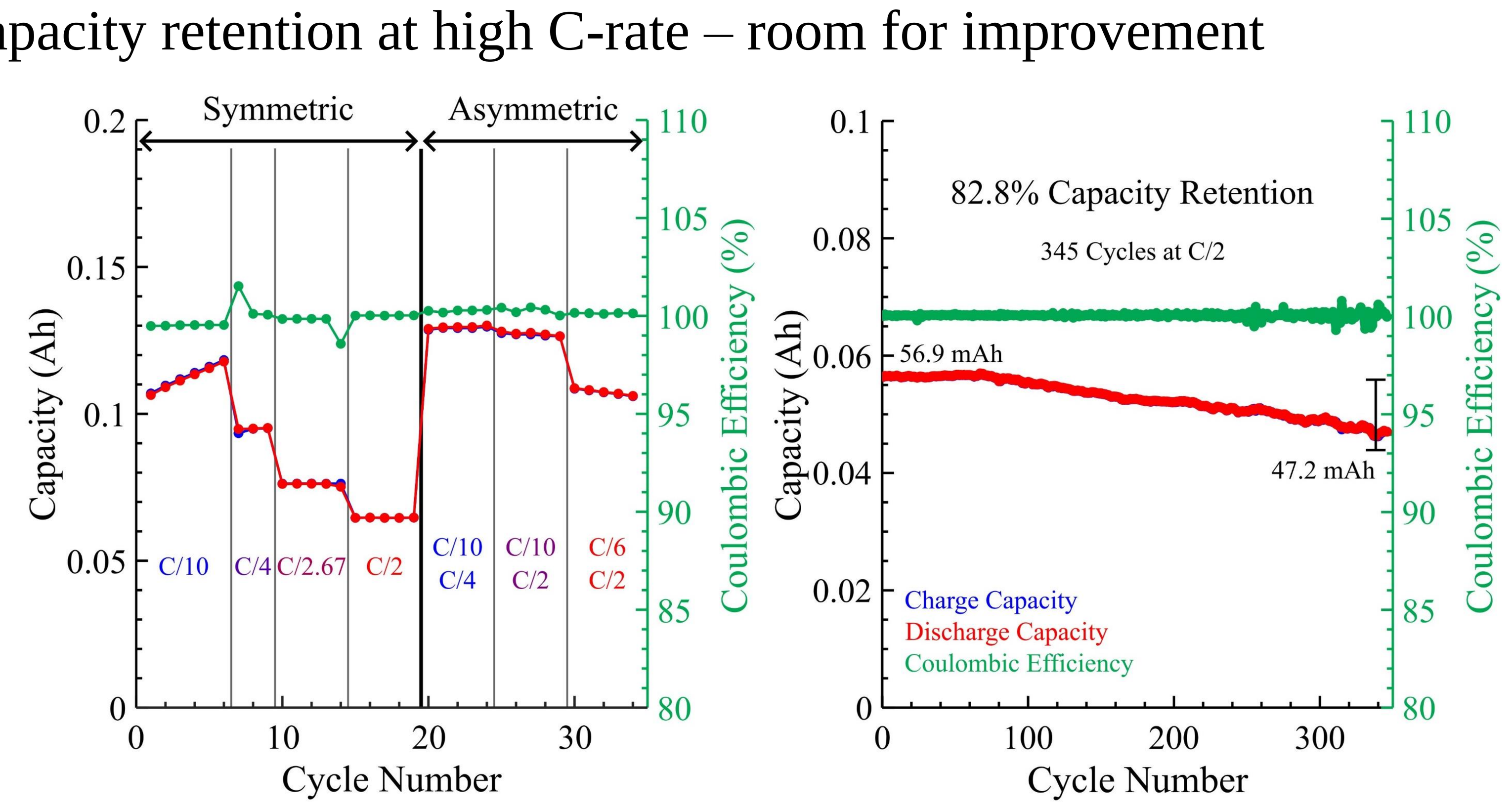
$Al + 7\ NaAlCl_4 \rightarrow 3\ Na + 4\ NaAl_2Cl_7$

E_o = 2-2.2 V at 180°C

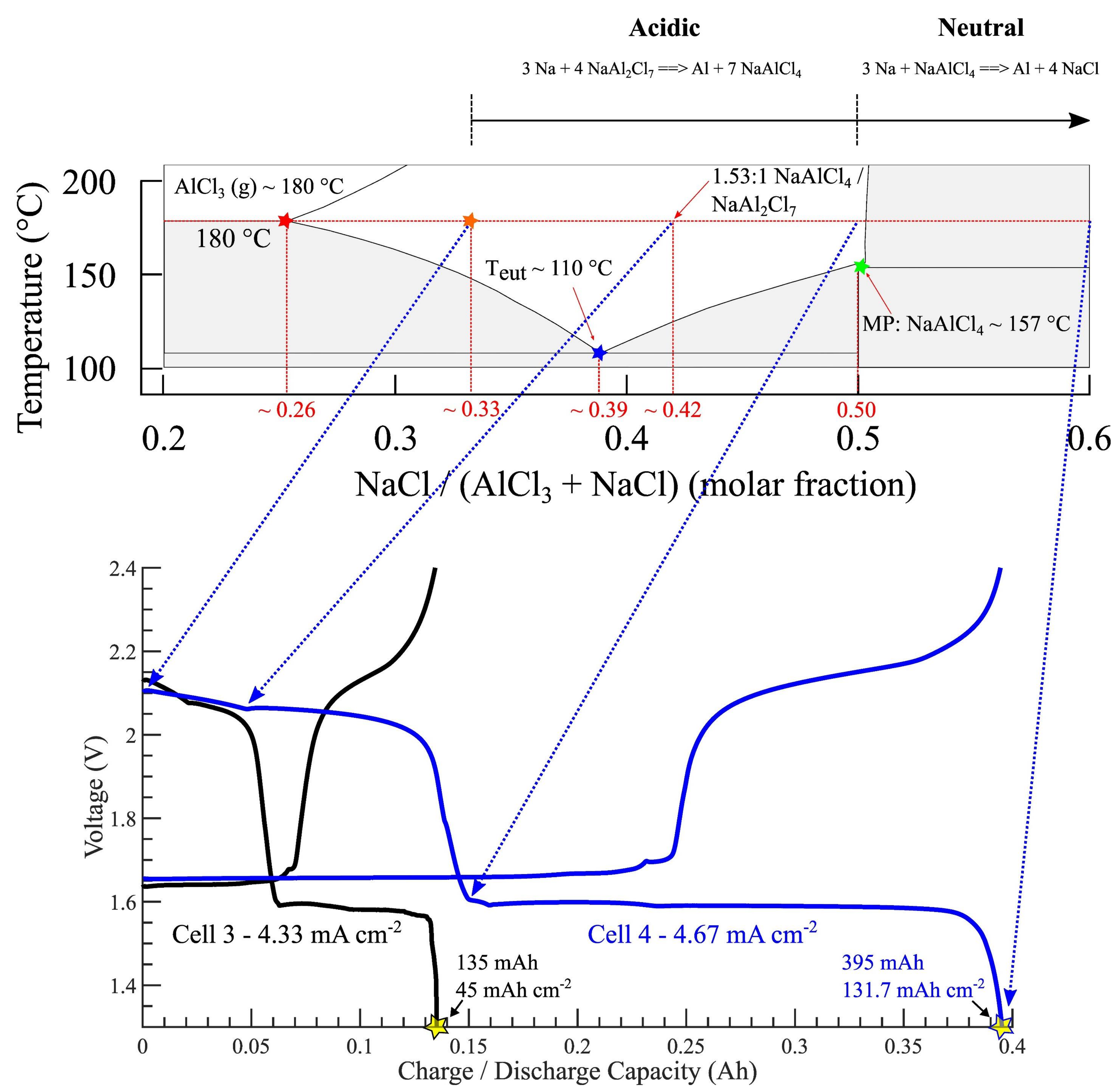


Acidic Chloroaluminate Chemistry:

- High coulombic efficiency
- C/10 charge (4 mA cm^{-2}) unlocks full capacity, fast discharge (20 mA cm^{-2}) possible with full utilization when asymmetric charge/discharge
- Good capacity retention at high C-rate – room for improvement



Extending the Chemistry: Acidic Chloroaluminate Melt

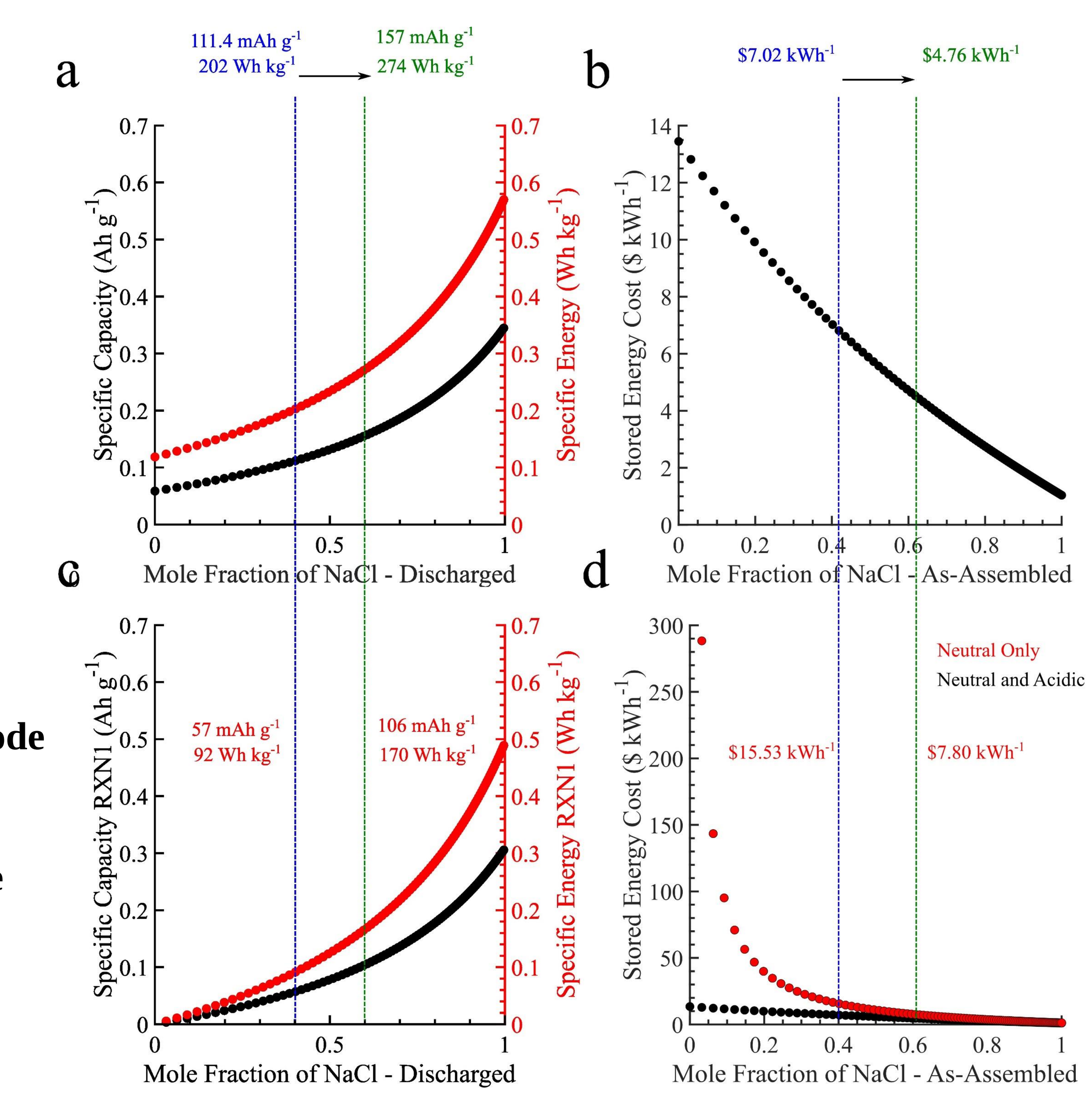


Unlocking More Capacity:

- **Same inexpensive materials (Al, NaCl, $NaAlCl_4$)**
- **Additional capacity and specific energy depending on pre-loading of NaCl and $NaAlCl_4$**
- **Utilization of more of $NaCl$-$AlCl_3$ phase diagram for reversible energy storage**
- **High areal loading (138.5 mAh cm^{-2}) and long discharge duration of 28.2 h at 4.67 mA cm^{-2}**
- **Enabled by fast mass transport and liquid-solid reaction mechanism (allows thicker cathode)**
- **Significant benefit to utilizing additional acidic reaction at practical cathode compositions**
- **Raw materials cost as low as \$7.02 kWh^{-1} possible –promising for cost-competitive storage**

Conclusions:

- **Demonstrated reversible $NaAl_2Cl_7$ chemistry**
- **28.2 h discharge duration - LDES**
- **Liquid-solid reaction, fast mass transfer enables thick cathode**
- **Demonstrated 111.4 mAh g^{-1} and 202 Wh kg^{-1} based on chemistry**



Future:

- **In Operando characterization of cathode chemistry**
- **Optimizing cathode composition to maximize energy density**
- **Mixed halide catholyte – lower temperature operation**
- **Improving charge kinetics**

Acknowledgments

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Contact: Guosheng Li, Ph.D.
Battery Materials & Systems Group
Pacific Northwest National Laboratory
Email: guosheng.li@pnnl.gov

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