A Physics-Aware ML-MD Framework for Electrolyte Screening

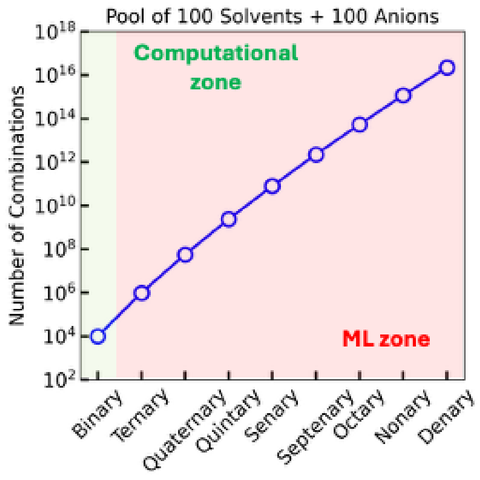
Nikhil Rampal[1], Marissa Wood[1], Tom Braun[1], Fredrick Omenya[2], Marcos Lucero[2], David Reed[2], Xiaolin Li[2], Jonathan Lee[1] and Liwen (Sabrina) Wan[1]

[1] Lawrence Livermore National Laboratory; [2] Pacific Northwest National Laboratory

Project profile:
Topic: Sodium Batteries | Vertical: Materials and Systems Innovation
Strategic Pathway: Grow
Project start and finish: FY25-FY26

PROBLEM

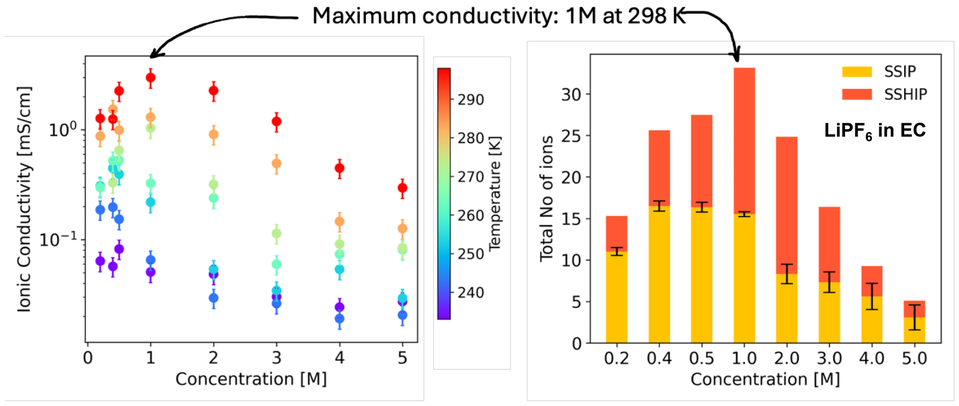
- **Why the electrolyte is crucial?** It strongly dictates system efficiency, safety/stability, cyclability and longevity of the electrochemical cell.
- **Electrochemical stability is a key metric.** SEI/CEI formation from rare solvated electrolyte species drives performance degradation, capacity fade and raise safety concerns.
- **Holistic design is a challenge due to the vast chemical space.** Solvent × salt × additive × concentration space is infeasible both experimentally and using transitional computational approach.
- **Data-driven approach is promising for large-scale, rapid screening.** It operates based on three integrated key elements that ultimately determines its predictive accuracy: training dataset, machine-learning (ML) architecture and feature encoding, property prediction.



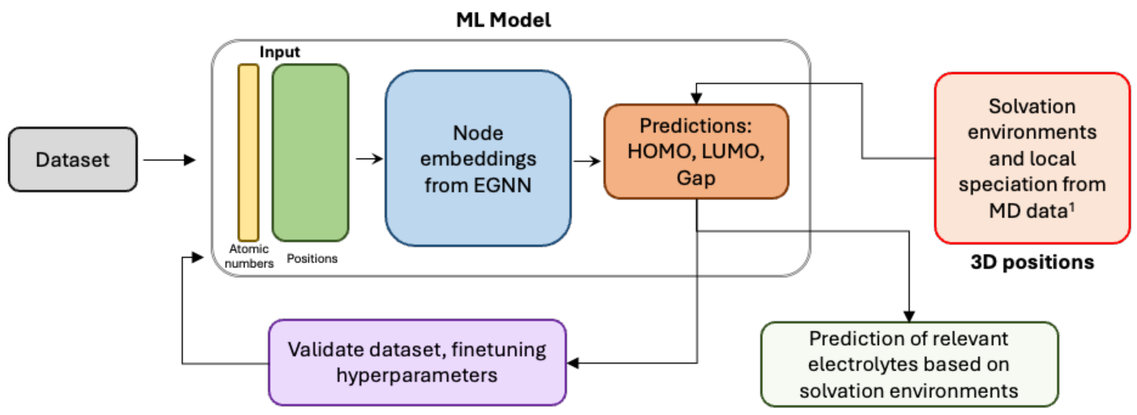
- **However, there is currently a lack of an established computational workflow that integrates physics-based modeling with ML for high-fidelity property prediction.**

APPROACH

- **Building on prior work:** Correlation mapping between speciation extracted from large-scale molecular dynamic simulations[1] with electrolyte properties is extended from ionic conductivity to electrochemical stability through ML.



- **Explicitly encoding 3D molecular structure in the ML model[2]:** Coordination geometry and chemistry, ion-pairing, and reduced (upon desolvation) and extended solvation structure (as a functional of local concentration fluctuation) determine structural, transport and electrochemical stability (frontier orbital levels).



- **Transferring chemistries:** The computational workflow is demonstrated for Li-ion electrolytes. Leveraging LLNL's unique capabilities in large-scale physics-based modeling, ML model development and implementation of agentic workflow, we are testing the effectiveness of current ML-MD framework to screen Na liquid electrolytes and further extending the functionality and property prediction capability, such the electrolyte decomposition products, which directly addresses the implication towards SEI/CEI formation at the electrolyte-electrode interfaces.
- **Need for experimental validation:** The ML-MD workflow needs to be rigorously benchmarked against well-controlled experiments, such as derivation of reductive/oxidative onset potentials, concentration profiles at interfaces, etc.

RESULTS

- **HOMO-LUMO gap sensitivity to solvation environment:** Taking NaTFSI in ethylene and propylene carbonate electrolyte as an example

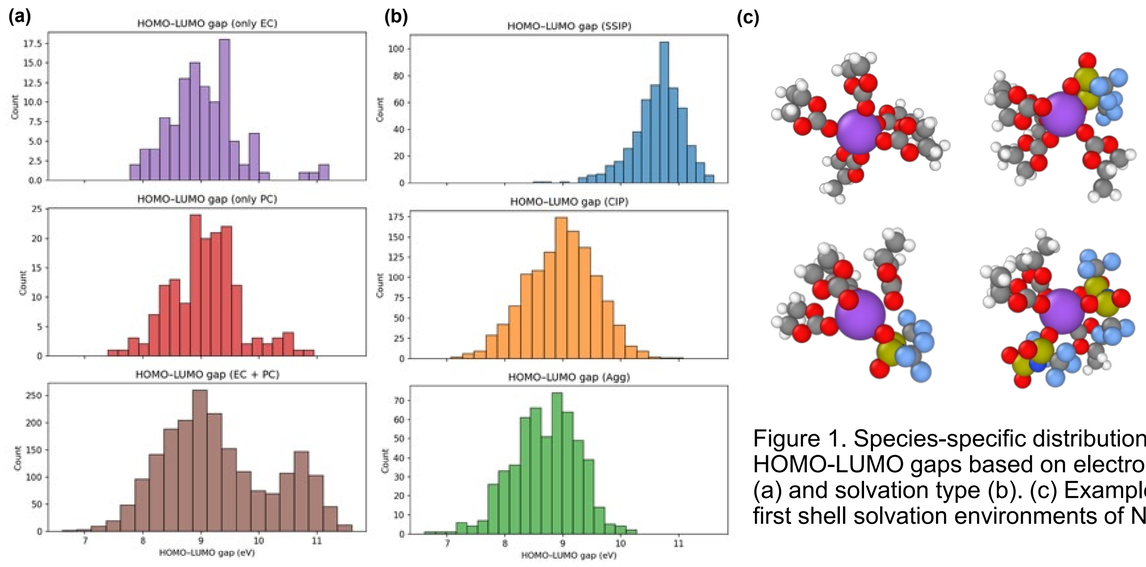


Figure 1. Species-specific distribution of HOMO-LUMO gaps based on electrolyte (a) and solvation type (b). (c) Example first shell solvation environments of Na.

- **Across diverse electrolyte systems:** Na + Anions (ClO4, PF6, FSI, TFSI and BFE) + solvents (linear carbonates, cyclic carbonates, fluorinated carbonates, linear ethers, cyclic ethers, glymes)

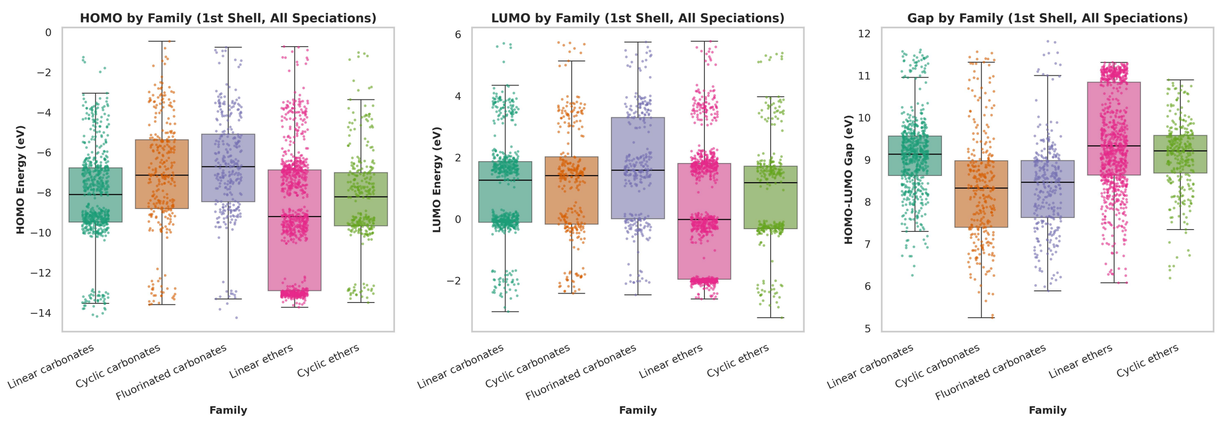


Figure 2. Predicted HOMO (left), LUMO (middle) and gaps (right) as a function of first shell environments of Na.

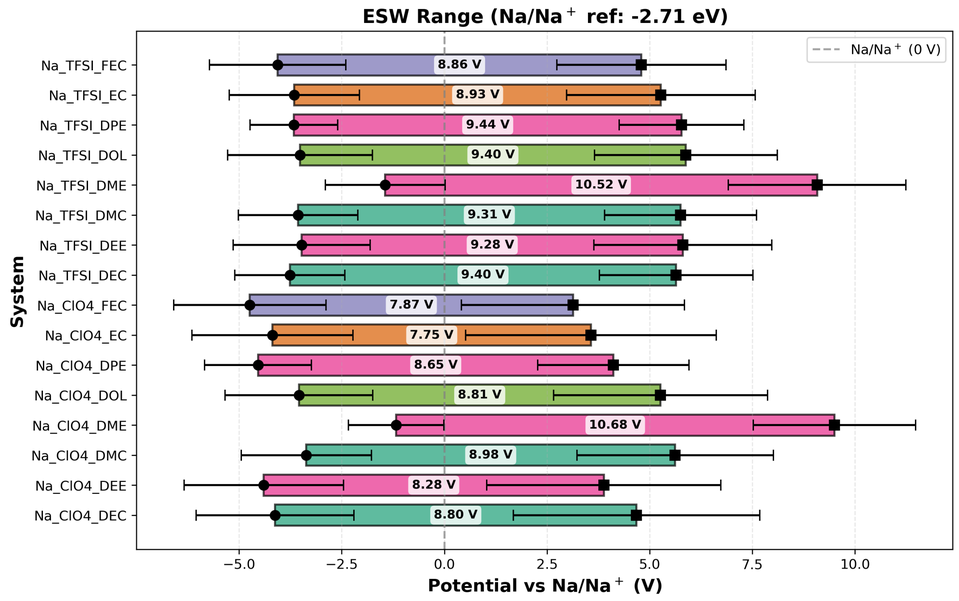


Figure 3. Electrochemical stability windows (ESW) for various Na-ion electrolytes.

CONCLUSIONS

- Established an interpretable, physics-grounded ML framework for rapid screening of Na electrolytes.
  - Electrochemical properties depend on both molecular structure and local chemistry, i.e. solvation environment, which is sensitive to concentration, electric double layer structure and cycling condition.
  - Incorporation of experimental benchmark data through reinforcement learning in a closed loop fashion to improve model fidelity and predictive accuracy.

FUTURE DIRECTIONS

- Validate a high-throughput, simulation-ready agentic workflow through incorporation of experimental data for high-fidelity property prediction and decision making to select the optimal electrolyte formulation for targeted performance metrics.
- **Address the key questions of** (1) which electrolyte environments are most prone to interfacial decomposition at various cycling condition? (2) what are the decomposed products that constitute major components of SEI/CEI.

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[1] Rampal, N., Weitzner, S. E., Cho, S., Orme, C. A., Worsley, M. A. and Wan, L. F. (2024) EES
[2] Sagireddy, S.*, Rampal, N.*, Weitzner, S. E. and Wan, L. F. (2026) EES Batteries.