LLM-Guided High-Throughput Discovery of Antifreeze Electrolytes Enabling −50 °C Stability and 99.5% Coulombic Efficiency

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1. Abstract

Problem: Zinc–bromine flow batteries (ZBFBs) experience significant performance degradation at low temperatures due to issues such as electrolyte freezing, slow Zn^{2+} diffusion, and dendrite formation. Dendrites contribute to poor cycling stability and low Coulombic efficiency (CE). While previous work[1] has focused on improving cycling stability and low CE, the effects of low temperatures on electrolyte stability and overall battery performance remain critical challenges. Furthermore, traditional electrolyte optimization methods are time-consuming and inefficient, given the vast compositional space that needs to be explored.

Solution: We employed a LLM-three-step Bayesian optimization (BO) framework to generate high-entropy electrolyte formulations with a mixture of five solvents. This was combined with high-throughput experimentation, using a robotic pipetting workstation to rapidly prepare and test candidate formulations. The BO model guides the selection of the most promising electrolyte compositions based on predicted performance.

Contribution: Our method significantly accelerates the discovery of antifreeze high-entropy electrolytes, identifying formulations that maintain liquid stability at −50 °C and exhibit high CE (99.46%). This work provides a data-driven pathway for the development of durable, low-temperature ZBFBs, establishing a new paradigm for intelligent electrolyte design, as well as discovering LogP and TPSA are key factors to anti-freeze electrolyte design with high CE.

2. Methods

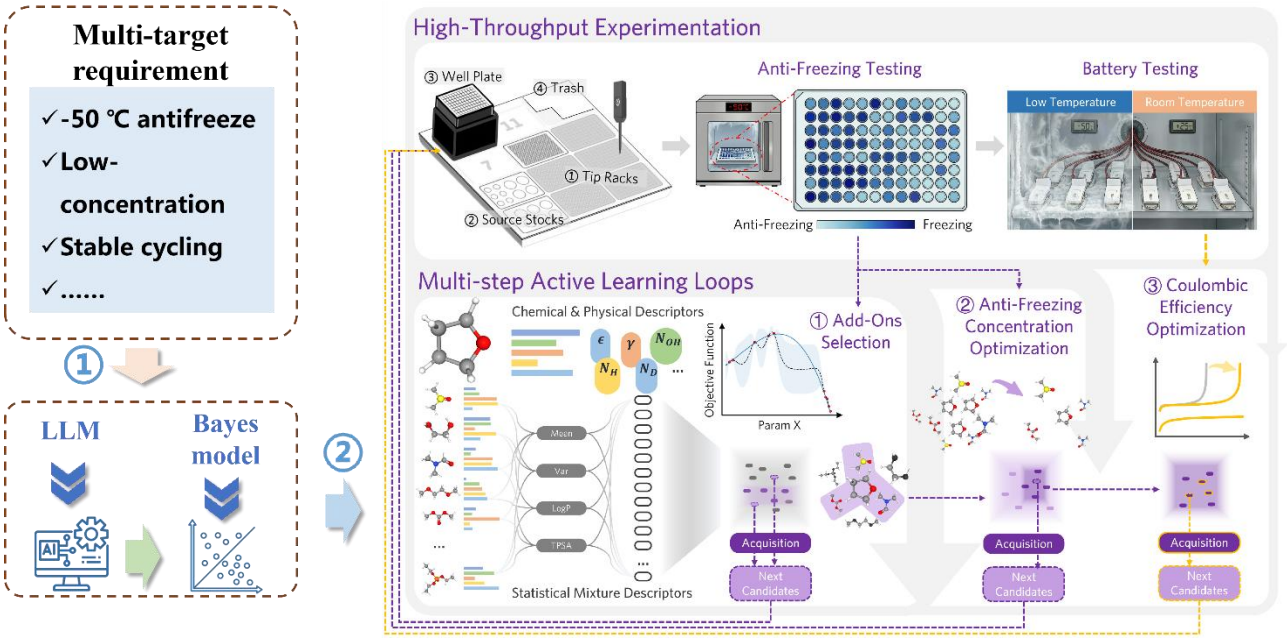

Figure 1. Schematic Illustration of the Robotic Experimentation Platform and the Hierarchical Active Learning Framework via Chemical Descriptors. (Left) Exploration space generated by LLM according to multi-target requirement. (Top-right) Automated liquid-handling robots perform combinatorial mixing of stock solutions into well plates, followed by solution mixing and property testing. (Bottom-right) The hierarchical active learning module leverages chemical and physical descriptors, as well as statistical mixture features, to construct predictive models of electrolyte performance.

3. Results

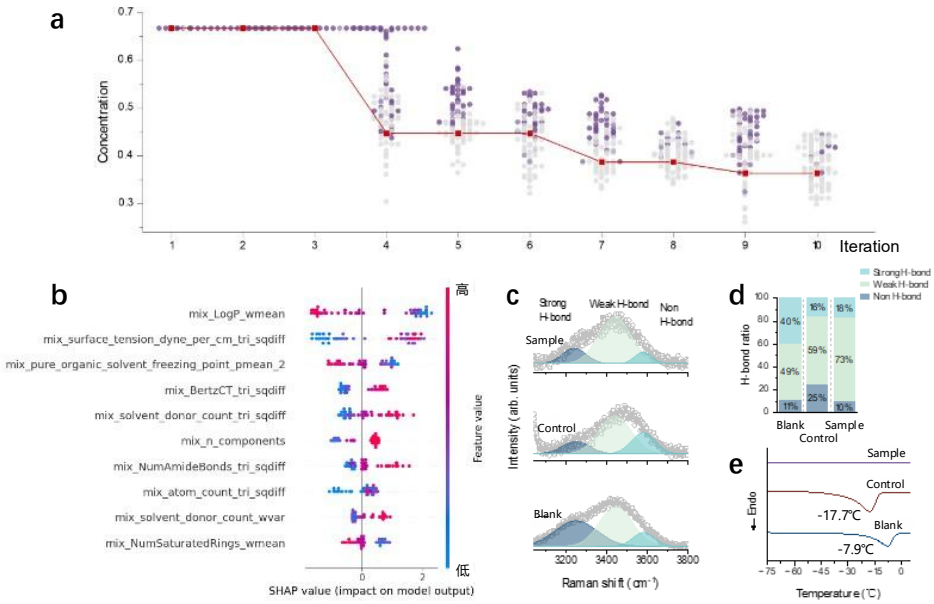

Figure 2. Optimization and mechanistic investigation of the antifreezing behavior of high-entropy electrolyte systems containing 20 organic cosolvents. (a) Bayesian optimization trajectory and candidate distribution, through which an optimized formulation capable of remaining unfrozen at −50 °C was identified from ~1,000 compositions after 10 iterations. (b) SHAP analysis of the antifreezing classification model, highlighting the importance of key descriptors, including the weighted-average logP of the mixed solvent system. (c) Deconvolution of the Raman spectra in the OH-stretching region for different formulations. (d) Relative proportions of different hydrogen-bonding types. (e) Comparative DSC curves.

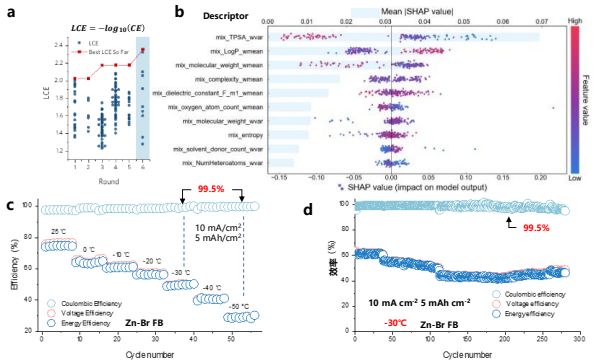

Figure 3. Attribution analysis of coulombic efficiency in antifreezing high-entropy electrolytes and device-level validation. (a) Optimization of low-temperature coulombic efficiency over six rounds of active learning; (b) SHAP feature-importance analysis showing that the weighted variance of TPSA in the mixed system is the key descriptor governing low-temperature coulombic efficiency; (c) Evolution of battery efficiency during stepwise cooling from 25 °C to −50 °C, demonstrating stable operation across the full temperature range; (d) Stable cycling of the Zn–Br battery for over 300 cycles at −30 °C with an average coulombic efficiency of 99.5%, validating the system's high low-temperature reversibility and engineering feasibility.

References

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