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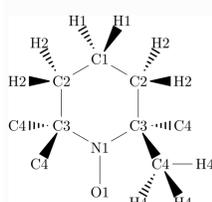
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Introduction

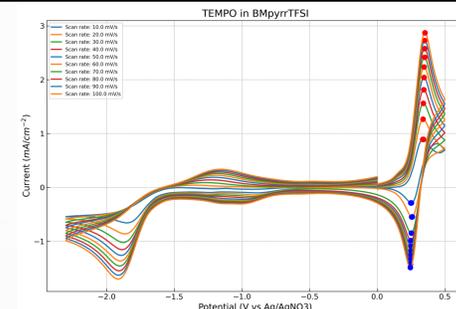
The rapid increase in renewable energy demands efficient, high-capacity energy storage solutions. Nonaqueous redox flow batteries (NARFBs) offer greater electrochemical stability and energy density compared to aqueous systems. TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) and benzothiadiazole (BTD) are attractive redox-active materials for NARFBs but face significant stability challenges, particularly the irreversible reduction of TEMPO to aminoxy anion that overlaps with BTD reduction potentials. This study investigates electrolyte engineering using ionic liquids (ILs) in acetonitrile to shift TEMPO's degradation potential negatively. By selecting ILs with sterically hindered cations and suitable anions, electrochemical stability and battery performance can be enhanced. Experimental cyclic voltammetry and molecular dynamics simulations are combined to clarify how IL composition influences solvation environments, providing critical insights for optimizing electrolyte designs in advanced NARFB systems.

CHEMICALS AND METHODS

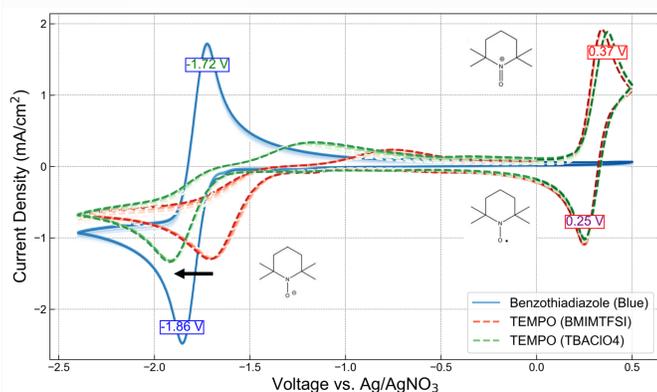
type	TEMPO charge / e	TEMPO ⁻ charge / e
O1	-0.412728	-0.716389
N1	0.041709	-0.576976
C1	-0.058971	0.076207
C2	-0.155537	-0.205289
C3	0.527298	0.785782
C4	-0.473958	-0.429986
H1	0.034946	-0.028664
H2	0.0354	0.000122
H4	0.114234	0.069413



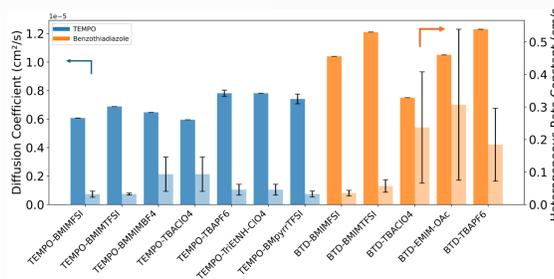
- Cyclic voltammetry (CV): Characterized electrochemical behaviour of TEMPO and BTD in various ionic-liquid-based acetonitrile electrolytes.
- Molecular dynamics (MD) simulations: Analysed solvation environments and ion coordination around TEMPO species.
- Flow cell cycling tests: Evaluated electrolyte performance and long-term stability under realistic operating conditions.



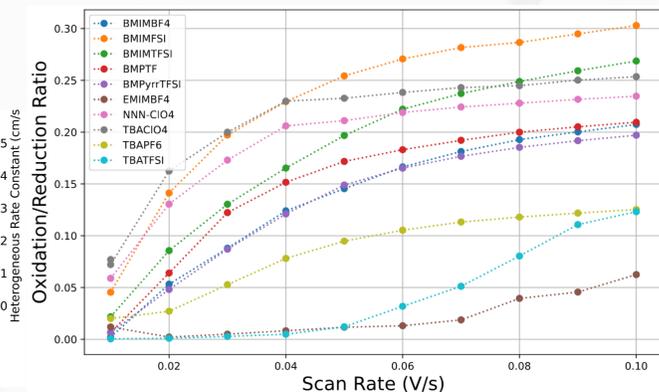
RESULTS AND DISCUSSION



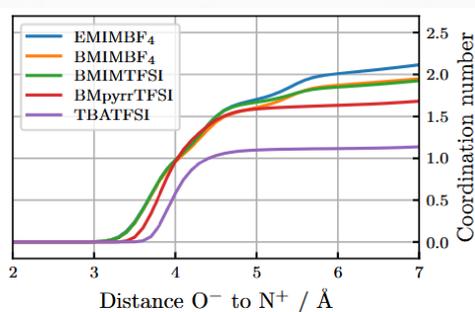
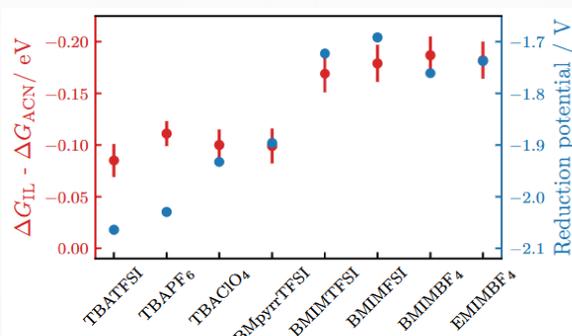
Voltage window alignment (Fig. 1). Overlay CVs show the destructive TEMPO → TEMPO⁻ peak normally coincides with the BTD reduction. Introducing bulky tetra-alkyl-ammonium ILs (e.g., TBACIO₄) shifts that peak to more-negative potentials.



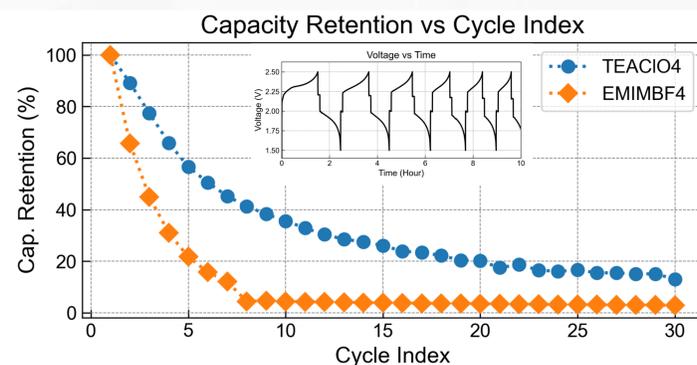
Redox kinetics & transport (Fig. 3). Across all electrolytes the redox couples remain fast: TEMPO exhibits $k^0 \approx 0.03\text{--}0.09 \text{ cm s}^{-1}$ and $D \approx 6\text{--}8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, while BTD is even quicker (k^0 up to 0.3 cm s^{-1} , D up to $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).



Suppressing chemical follow-up (Fig. 2). The re-ox/red current ratio for the aminoxy anion rises with scan rate but remains ≤ 0.1 in ILs containing large, hydrophobic cations (TBA⁺, TEA⁺) paired with weakly coordinating anions (TFSI⁻, BF₄⁻). Smaller, more polar cations (BMIM⁺, EMIM⁺) allow ratios ≈ 0.3 , evidencing slower protonation and rate of irreversible loss.



Solvation-controlled shift (Fig. 3). MD and electrochemical data track one another: the TEMPO → TEMPO⁻ reduction potential moves with the IL-derived solvation energy. Small, strongly coordinating imidazolium cations (BMIM⁺, EMIM⁺) crowd two ions around TEMPO⁻, add large stabilising energies, and shift the peak $\approx 0.1 \text{ V}$ positive, overlapping BTD; bulky tetra-alkyl cations (TBA⁺, TEA⁺) coordinate only once at longer range, give weaker stabilisation, and push the peak $\approx 0.1 \text{ V}$ negative, widening the safe voltage window.



Cycling stability (Fig. 4). Flow-cell curves echo the half-cell trends: an electrolyte with a bulky, sterically hindered cation (e.g., TEA⁺ in TEACIO₄) still retains $\approx 36\%$ of its initial charge after ten cycles, whereas one built on a small imidazolium cation (EMIM⁺ in EMIMBF₄) falls to $\approx 4\%$. The better retention arises because large cations push the TEMPO → TEMPO⁻ peak more negative and sterically limit proton access, slowing irreversible aminoxy chemistry, while small, tightly coordinating cations both stabilise TEMPO⁻ thermodynamically and leave protons free to quench it, driving rapid capacity fade.

CONCLUSIONS

Our work underscores the pivotal influence of solvation chemistry on suppressing the destructive TEMPO → TEMPO⁻ process in TEMPO/BTD non-aqueous redox-flow batteries. Comprehensive electrochemical tests and molecular simulations reveal that electrolytes formulated with bulky, sterically demanding cations and suitably non-coordinating anions drive TEMPO's reduction peak to lower (more negative) potentials, diminishing its overlap with the BTD couple. While this approach does not entirely eliminate capacity fade, it clearly shows that electrolyte tailoring can unlock valuable voltage headroom for high-energy organic flow systems. Moving forward, expanding the solvent-ionic-liquid design space and conducting extended flow-cell cycling will be essential to translate these gains into long-term, practical performance.