

Solvation-Controlled Accessibility and Irreversible Finalization of Aminoxy Intermediates in TEMPO/Benzothiadiazole Nonaqueous Redox Flow Batteries

Hermias J. Venter, Ole Nickel, Robert H. Meißner, Markus Ostermann, Markus Valtiner, and Christian M. Pichler*



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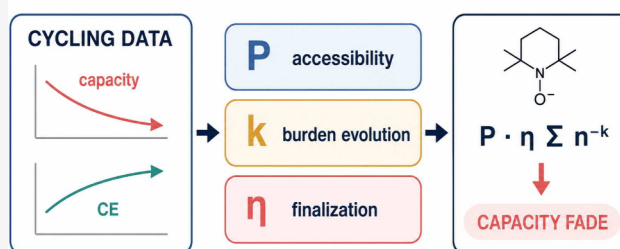


Supporting Information

ABSTRACT: Understanding how reactive intermediates form and evolve during electrochemical operation is essential for improving the stability of molecular energy-storage systems. Here, we investigate the degradation chemistry of an all-organic nonaqueous redox flow battery based on a nitroxide catholyte and a benzothiadiazole anolyte. By combining electrochemical analysis, full-cell cycling experiments, and molecular dynamics simulations, we reveal how the solvation environment governs both the electrochemical accessibility and the chemical fate of transient reduced intermediates. To rationalize these effects, we introduce a chemically informed framework that decouples electrochemical exposure of parasitic pathways from the probability that such events culminate in irreversible product formation. This minimal model quantitatively captures the relationship between coulombic efficiency and capacity loss across a range of ionic liquid electrolytes, providing a unified description of degradation behavior under realistic operating conditions. Molecular-level analysis further shows that electrolyte-dependent solvation and local coordination environments modulate the stabilization and reactivity of key intermediates, thereby controlling the balance between reversible redox processes and permanent inventory loss. These findings establish a direct link between electrolyte solvation structure and electrochemical degradation pathways, offering a general strategy to diagnose and mitigate failure mechanisms in molecular electrochemical systems. More broadly, the approach provides a conceptual framework for connecting reactive intermediate chemistry with macroscopic device performance in organic energy-storage technologies.

KEYWORDS: nonaqueous redox flow battery, TEMPO, benzothiadiazole, ionic liquids, electrolyte engineering

DECONSTRUCTING CAPACITY FADE



1. INTRODUCTION

Organic redox flow batteries (RFBs) are a promising approach for large-scale energy storage, balancing the fluctuating nature of renewable electricity generation. Compared to the state-of-the-art vanadium-based systems, organic redox-active molecules can be synthesized from abundant elements and tailored through molecular design. Nonaqueous RFBs (NARFBs) use organic solvents to expand the electrochemical operating window, providing an additional benefit.^{1–3}

Utilizing these advantages in practice, however, has proven difficult due to factors such as chemical instability and decomposition or crossover of the redox-active species, resulting in relatively low coulombic efficiencies and capacity fade.⁴ Within this landscape, the nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is a widely studied catholyte because the TEMPO/TEMPO⁺ couple exhibits fast kinetics and good intrinsic electrochemical reversibility.^{5,6} On the anode side, benzothiadiazole (BTD) derivatives have emerged as promising low-potential candidates, undergoing reductions near –2 V vs.

ferrocene and offering functionalization strategies to improve solubility and reduce permeability.^{7–9}

This pairing is therefore an appealing high-voltage, all-organic NARFB concept. Nevertheless, full TEMPO/BTD cells frequently underperform in long-term cycling, indicating that cell-level degradation is controlled by processes that are not captured by considering only the stability of the positive TEMPO/TEMPO⁺ couple. Very often, degradation and capacity loss are described empirically.^{5,6} For example, capacity loss in TEMPO/BTD systems is attributed to crossover-driven parasitic redox cycling (shuttling) and self-discharge. To better and

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more accurately describe RFB systems, model systems are urgently needed that efficiently describe degradation and aging phenomena. However, this requires a deeper understanding of the underlying processes during degradation.

In terms of TEMPO and BTM, both components (and their charged forms) can contribute to parasitic current and coulombic inefficiency. However, the parasitic current does not automatically imply permanent inventory loss. Exposure of a crossed-over species to the opposing electrode can be largely reversible (a redox shuttle) or it can trigger irreversible chemical conversion to electrochemically inactive products. Distinguishing these outcomes matters, if the degradation of RFBs is to be efficiently modeled.^{10–13}

Especially for nitroxide-related catholytes, this distinction is mechanistically well motivated. When TEMPO reaches sufficiently negative potentials, it can be reduced to an aminoxy anion. This intermediate can be chemically labile, leading to degradation products such as hydroxylamine that are not recovered under normal cycling.¹⁴ Ionic liquids (ILs) provide a practical platform to examine these coupled effects because they can strongly influence solvation structure, ion pairing, and redox energetics.^{15,16} This can change the character of TEMPO reduction and alter the chemical lifetime of aminoxy once formed. At the same time, IL composition can modify transport properties and therefore influence crossover propensity. A chemistry-aware interpretation of cycling behavior therefore must consider electrochemical accessibility, transport burden, and chemical finalization together.¹⁰

In this work, we introduce a chemically informed model approach to quantitatively describe the degradation of RFB systems. We demonstrate the validity of this model in a series of TEMPO/BTD nonaqueous flow cells employing ionic liquid-based supporting electrolytes using matched cyclic voltammetry, full-cell cycling, and molecular dynamics simulations. The model includes several specifically defined parameters, such as the effective half-wave potential $E_{1/2}$ of the quasireversible TEMPO/TEMPO[−] couple, which locates the aminoxy-forming reduction relative to the anolyte operating window and thereby quantifies the electrochemical accessibility of this parasitic pathway. The next element of the model describes the effective crossover burden through an empirical rate parameter k that captures how parasitic behavior evolves during cycling under a fixed cell configuration. Finally, we introduce an irreversible finalization fraction η to quantify the extent to which parasitic charge is converted into permanent inventory loss. By combining those parameters, the resulting model quantitatively captures the degradation performance in TEMPO/BTD NARFBs and resolves the influence of different ILs on the cell behavior, demonstrating a significant advancement in understanding RFB degradation. Besides fundamental insight, the model can also serve as a diagnostic tool for RFB systems and inspire the development of improved electrolyte compounds.

2. RESULTS AND DISCUSSION

2.1. Theoretical Framework

To connect electrolyte-dependent half-cell electrochemistry to full-cell cycling outcomes, we employ a compact three-parameter framework that separates (i) electrochemical accessibility of the TEMPO-to-aminoxy pathway within the BTM

operating window, (ii) the effective crossover burden and its cycle-dependent evolution, and (iii) the irreversible finalization probability of parasitic events. Full derivations, numerical procedures, and experimental details are provided in the SI.

2.1.1. Electrochemical Exposure: The Effective Half-Wave Potential $E_{1/2}$. Matched cyclic voltammograms (CVs) of TEMPO and BTM, recorded under identical conditions (same electrolyte, same scan rate, and fifth scan), are used to locate the TEMPO-to-aminoxy reduction relative to the potential region in which the anolyte operates. From the cathodic and anodic peak potentials E_{pc} and E_{pa} of the quasireversible TEMPO/TEMPO[−] wave, the effective half-wave potential is obtained as

$$E_{1/2}^{\text{am}} = (E_{pc} + E_{pa})/2 \quad (1)$$

which includes contributions from both the thermodynamics and the kinetics of the electron transfer. The half-wave potential of the BTM/BTD^{•−} couple, $E_{1/2}^{\text{BTD}}$, is obtained analogously and is found to be essentially electrolyte-independent in the present series (-1.79 ± 0.01 V vs. Ag/AgNO₃). The signed separation

$$\Delta E_{\text{acc}} = E_{1/2}^{\text{am}} - E_{1/2}^{\text{BTD}} \quad (2)$$

then locates the aminoxy-forming reduction relative to the anolyte wave: $\Delta E_{\text{acc}} > 0$ places the TEMPO reduction anodic of the BTM couple, meaning that any electrode polarized far enough to cycle BTM necessarily drives aminoxy formation, and less negative values indicate increasingly facile parasitic reduction. Because $E_{1/2}^{\text{am}}$ and ΔE_{acc} are signed quantities, cathodic and anodic shifts of the TEMPO wave move them in opposite directions, so the direction of an electrolyte-induced shift is always unambiguous. $E_{1/2}^{\text{am}}$ is strictly a CV-derived accessibility metric; it does not incorporate any flow-cell information (crossover rates, reservoir concentrations, or cycling capacity).

2.1.2. Three-Parameter Model for Cycling Observables. Flow-cell degradation is described through an effective parasitic loss fraction per cycle,

$$\epsilon_n = P n^{-k} \quad (3)$$

where P is a dimensionless parasitic demand parameter capturing the effective magnitude of parasitic side reactions under full-cell polarization, and $k > 0$ is a burden-relaxation exponent describing how the crossover burden diminishes with cycle number (e.g., due to separator conditioning or progressive wetting). The coulombic efficiency at cycle n is then

$$\text{CE}_n \approx 1 - P n^{-k} \quad (4)$$

and the normalized discharge capacity after N cycles is

$$\frac{Q_N}{Q_1} \approx \exp \left[-\eta P \sum_{n=2}^N n^{-k} \right] \quad (5)$$

where $\eta \in [0, 1]$ is the irreversible finalization fraction, representing the per-event probability that a crossed-over, parasitically reduced TEMPO-derived species is chemically converted

into an electrochemically inactive sink (e.g., via protonation to hydroxylamine) before re-oxidation. Parameters (P , k , η) are extracted by a robust two-step procedure that follows the physical roles of the parameters: P and k are obtained from the CE trajectory ($CE_n = 1 - P n^{-k}$) using a robust loss, and η is then obtained from the capacity decay given (P , k) (see SI Section S1.1). We note that the model is formulated at a phenomenological level, where the aggregated parameters capture the net effect of all operative degradation processes, including crossover-induced reactions, solvent interactions, and chemical degradation pathways, without explicitly assuming a single, defined mechanistic pathway. The empirical fit alone does not prove a specific degradation mechanism, and the framework should be understood as a diagnostic tool rather than a mechanistic proof. The relationship between the CV-derived $E_{1/2}^{\text{am}}$ and the full-cell parameter P is discussed in the SI.

The power-law form of the per-cycle burden (eq 3) is a deliberate choice rather than an arbitrary one. Physically, it encodes a diminishing parasitic burden: a steep early loss that relaxes into a slow, quasi-steady tail, which is the behavior expected when several conditioning processes (progressive wetting, separator equilibration, and interfacial adsorption) relax over a distribution of timescales rather than a single one. A single-exponential decay, by contrast, imposes one privileged characteristic cycle number and therefore under-fits the long tail. To put this on a quantitative footing, we refitted all four cycled electrolytes with competing cycle-dependent forms (a constant burden, a single exponential, a stretched exponential, and an exponential relaxing to a finite plateau) using the same robust two-step fitting procedure (and the identical data, cycle window, and objective), and compared them by RMSE and the small-sample-corrected Akaike information criterion (AICc). The power law is decisively preferred over the constant, single-exponential, and stretched-exponential forms in every electrolyte, and approaches the more flexible exponential-plus-offset form while using one fewer parameter and without invoking a privileged cycle scale. The full comparison, including the goodness-of-fit table and overlaid fits, is provided in Figures S1, S2 and Table S3 (SI Section S1.2).

2.2. Electrochemical Accessibility Analysis

This subsection establishes the electrochemical-accessibility evidence: matched half-cell voltammetry constrains the effective half-wave potential $E_{1/2}^{\text{am}}$ (eq 1) and, through it, the accessibility parameter P . The analysis in this section is structured around the quantities defined in the Theoretical Framework: the effective half-wave potential $E_{1/2}^{\text{am}}$ of the TEMPO/TEMPO[−] couple and its separation ΔE_{acc} from the BTd wave (eq 2), the crossover-evolution parameter k , and the irreversible finalization fraction η . Extended derivations and full experimental protocols are provided in the SI.

Figure 1 compares representative CVs of TEMPO and BTd in acetonitrile with different ionic liquids as electrolyte additives. While these examples illustrate the key shifts in reduction behavior, the complete set of matched cyclic voltammograms for all investigated electrolytes (used to determine the half-wave potentials) is provided in Supplementary Figures S6–S12. The BTd reduction appears as a single quasireversible wave with a cathodic peak near -1.86 V vs. Ag/AgNO₃ and shows only modest sensitivity to electrolyte identity under the present conditions.¹⁷ By contrast, TEMPO exhibits two distinct regimes: the TEMPO/TEMPO⁺ couple (around 0.3 V vs. Ag/AgNO₃) is largely unchanged across ionic liquids, consistent

with its established robustness in nonaqueous media,^{6,8} whereas the negative-potential reduction of TEMPO toward the aminoxy anion shifts in onset potential and wave shape (in Figure 1 from -1.6 to -1.9 V). This electrolyte dependence indicates that the electrochemical accessibility of the aminoxy pathway is strongly modulated by the supporting-electrolyte identity.¹⁸

To quantify how readily the TEMPO-to-aminoxy reduction is driven within the region where the anolyte operates, we determine the effective half-wave potential $E_{1/2}^{\text{am}}$ defined in eq 1 from the matched half-cell voltammograms. Here, $E_{1/2}^{\text{am}}$ is strictly a CV-derived accessibility metric. It is calculated solely from the peak potentials of the current–potential data and does not incorporate any flow-cell information such as crossover rates, reservoir concentrations, or cycling capacity.

Figure 2A illustrates the determination procedure using representative fifth-scan CV data (TBA[ClO₄] electrolyte). The cathodic peak potential E_{pc} of the TEMPO/TEMPO[−] wave and the anodic peak potential E_{pa} of its return wave are located by a prominence-based peak search on the smoothed voltammogram and $E_{1/2}^{\text{am}}$ is taken as their average; the same construction applied to the BTd voltammogram yields $E_{1/2}^{\text{BTd}}$.

Figure 2B summarizes the resulting half-wave potentials across the electrolyte series. The imidazolium-based electrolytes place the aminoxy reduction at the least negative potentials (BMIM[FSI]: -1.25 V; BMIM[BF₄]: -1.28 V vs. Ag/AgNO₃), whereas the ammonium- and pyrrolidinium-based electrolytes cluster substantially deeper (TEA[ClO₄]: -1.54 V; TBA[ClO₄]: -1.57 V; BMPyr[TFPI]: -1.58 V; TEA[*p*-TSO]: -1.58 V; TBA[PF₆]: -1.63 V). Referenced to the BTd couple, the separation ΔE_{acc} spans $+0.16$ to $+0.54$ V and is positive in every electrolyte: the aminoxy-forming reduction always lies anodic of the BTd wave; this means in all cases, sufficient driving force for parasitic TEMPO reduction is provided. What distinguishes the electrolytes is how far the parasitic wave sits inside the operating region. Importantly, these values quantify only electrochemical accessibility. They do not imply differences in crossover rates between electrolytes, but describe how readily a crossed TEMPO molecule is electrochemically converted into the aminoxy species if it reaches the negative electrode.¹⁹

It is important to be explicit about what $E_{1/2}^{\text{am}}$ does and does not represent. The TEMPO/TEMPO[−] wave is strongly quasireversible in the present media, with peak separations of 0.59 – 0.91 V at 10 mV s^{−1}, so the effective $E_{1/2}^{\text{am}}$ deliberately convolutes thermodynamic and kinetic (Butler–Volmer) contributions to the electron transfer and is not a formal potential. This is intentional: both contributions co-determine how much parasitic reduction occurs during operation. All voltammograms entering the comparison are matched (same electrolyte, same scan rate, and fifth scan), so the cross-electrolyte comparison is internally consistent; in case a clean, scan-rate-independent formal potential of the TEMPO/aminoxy couple is required, differential pulse voltammetry (DPV) could provide a complementary route by suppressing capacitive and kinetic broadening. For the comparative scope of this work, the effective $E_{1/2}^{\text{am}}$ is the appropriate quantity, and its chemical reading is direct and single-valued: a less negative $E_{1/2}^{\text{am}}$ means the aminoxy state is more stabilized and the parasitic reduction is easily accessible, resulting in increased formation of aminoxy species during operation, followed by more degradation. This reading is fully aligned with thermodynamic intuition.

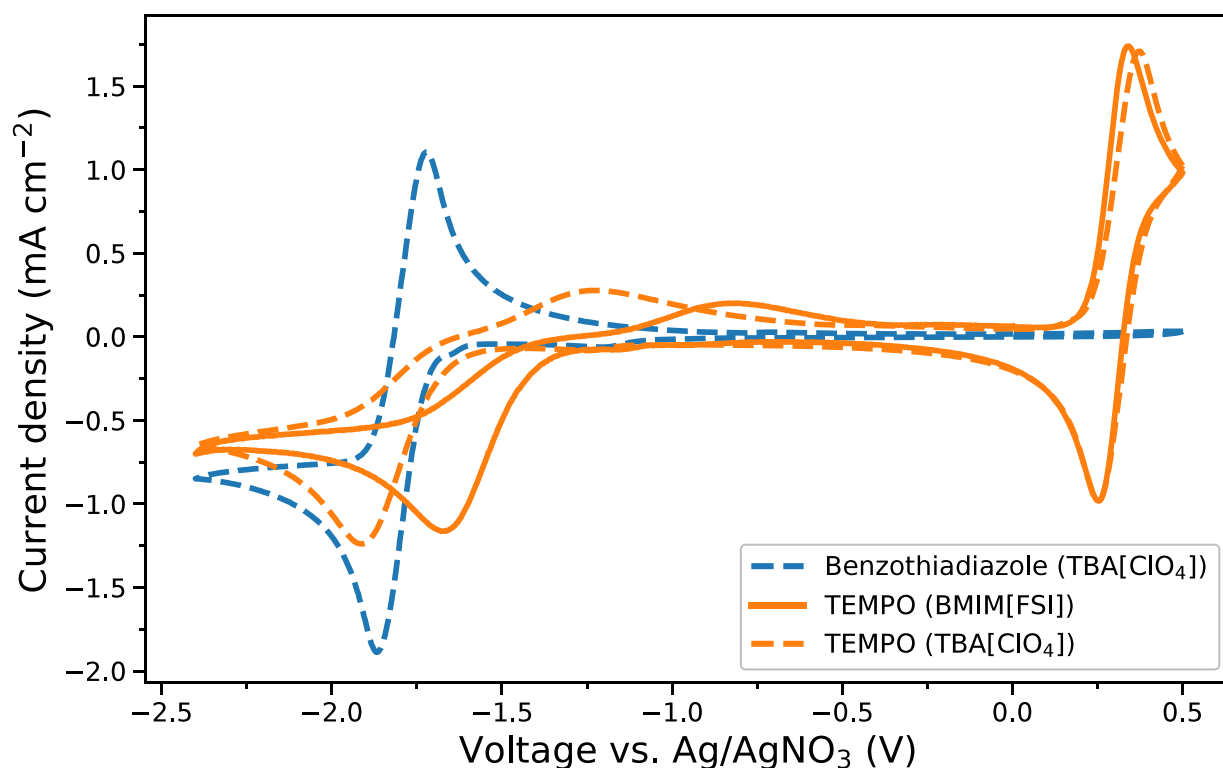


Figure 1. Fifth-cycle CVs of BTD (blue) and TEMPO (orange) in acetonitrile with BMIM[FSI] (solid) and TBA[ClO₄] (dashed) supporting electrolyte. The TEMPO/TEMPO⁺ couple near 0.3 V is electrolyte-insensitive, whereas the TEMPO-to-aminoxy reduction (−1.6 to −1.9 V) shifts with electrolyte identity. Potentials vs. Ag/AgNO₃.

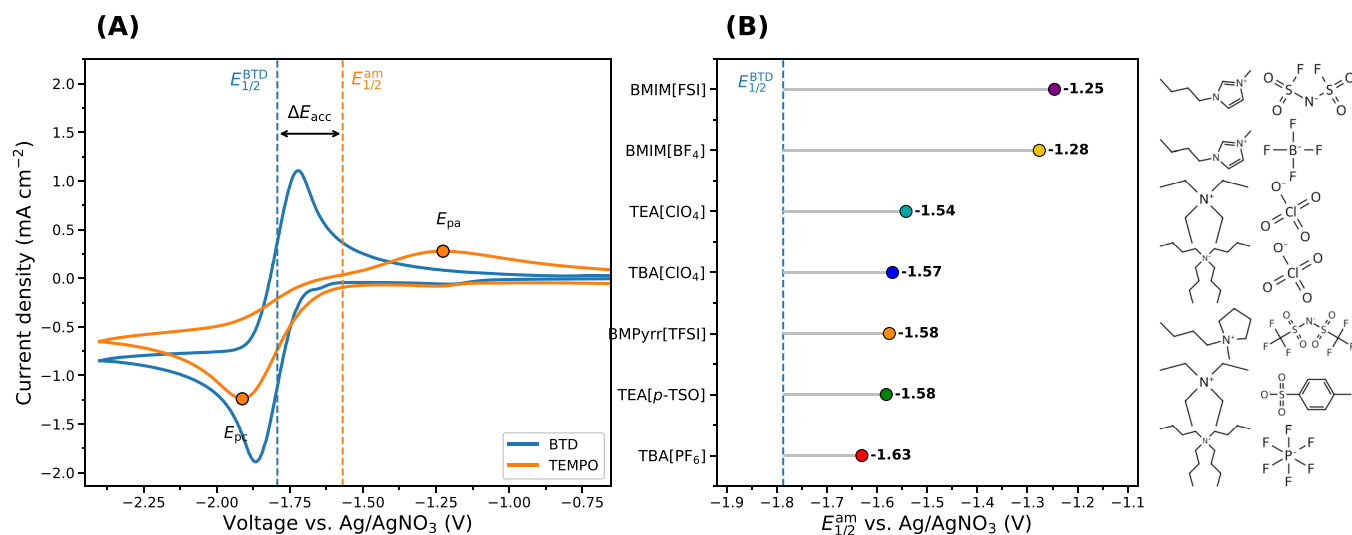


Figure 2. Effective half-wave potential of the TEMPO/TEMPO[−] couple. (A) Matched fifth-scan CVs (TBA[ClO₄]); circles mark E_{pc} and E_{pa} , dashed lines mark the resulting half-wave potentials (eq 1), and the arrow marks the accessibility separation (eq 2). (B) $E_{1/2}^{\text{am}}$ across the electrolyte series; stems start at the electrolyte-insensitive BTD half-wave potential (−1.79 V).

The ranking is also robust to the choice of descriptor: ordering the electrolytes by the cathodic peak potential alone reproduces the $E_{1/2}^{\text{am}}$ ranking (Spearman $\rho = 0.86$), with an identical order for the four flow-cell electrolytes (SI Table S1), confirming that the comparison is not an artifact of the weak anodic return wave.

Having established a CV-based ranking of electrochemical accessibility, we next assess whether the accessible range of $E_{1/2}^{\text{am}}$ values is large enough to influence full-cell capacity

retention. Figure 3 addresses this question through an illustrative one-factor sensitivity analysis within the reduced three-parameter framework (eqs 4 and 5). The curves shown are not experimental flow-cell data. Rather, we generate forward projections by varying only the model accessibility parameter P , with P values indexed to the CV-derived $E_{1/2}^{\text{am}}$ through the empirical linear calibration obtained from the four cycled electrolytes (the relationship between $E_{1/2}^{\text{am}}$ and P is discussed

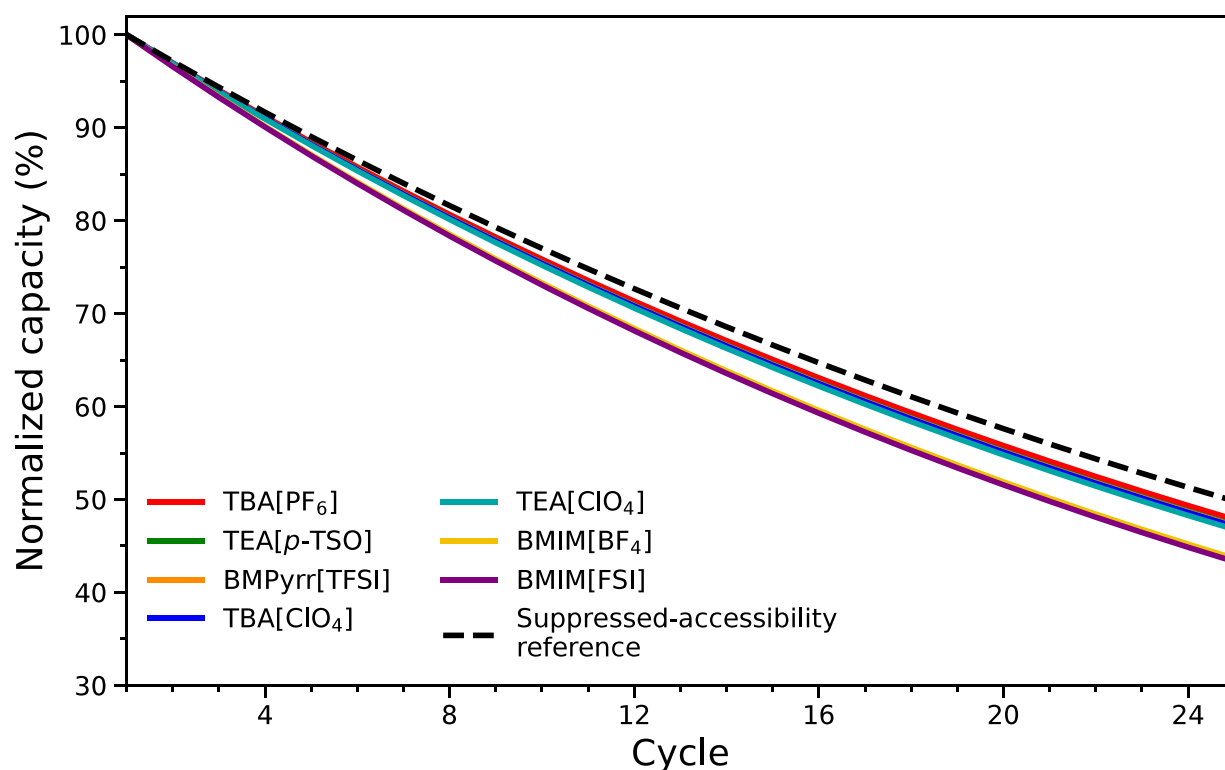


Figure 3. Projected capacity retention when only the accessibility term P varies, indexed to $E_{1/2}^{\text{am}}$ through the empirical calibration of SI Section S1.1, with k and η held fixed. Curves are model projections, not measurements; the dashed reference corresponds to $\Delta E_{\text{acc}} = 0$.

in detail in SI Section S1.1), while all other model parameters are held fixed. This isolates the impact of solvation-controlled electrochemical accessibility by holding other influences, such as crossover flux, constant across the series.

A systematic dependence is observed in these projections: electrolytes with more negative $E_{1/2}^{\text{am}}$ yield higher predicted retention, while the imidazolium electrolytes, whose aminoxy wave sits closest to the operating window, show the most rapid decay; over 25 cycles the projected end-of-window capacity differs by about five percentage points (roughly 10% in relative terms) between the extremes of the measured accessibility range. For context, a suppressed-accessibility reference trajectory ($\Delta E_{\text{acc}} = 0$, i.e. the aminoxy wave centered on the BTd couple) is included. Notably, this reference does not approach perfect retention: extrapolating the empirical P - $E_{1/2}^{\text{am}}$ calibration to $\Delta E_{\text{acc}} = 0$ leaves a residual parasitic demand ($P \approx 0.29$), which quantifies the portion of the parasitic burden that is not attributable to aminoxy accessibility (for example, bidirectional shuttling of BTd- and TEMPO-derived species). Within the present framework, solvation tuning of the aminoxy accessibility thus modulates a substantial, but bounded, fraction of the total parasitic demand.

Taken together, Figure 3 motivates two points that guide the remainder of the analysis. First, $E_{1/2}^{\text{am}}$ is a meaningful accessibility descriptor: shifting the aminoxy wave cathodically, away from the operating window, is predicted to improve capacity retention, consistent with the exposure term in eq 3. Second, accessibility alone is unlikely to uniquely determine degradation severity in practice, because electrolytes with comparable electrochemical accessibility can still diverge if the chemical fate of the reduced state differs. We therefore analyze the coulombic

efficiency and capacity jointly using the three-parameter framework (P , k , η) introduced in eqs 4 and 5.

2.3. Cycling Analysis and Model Fitting

This subsection turns to the full-cell cycling evidence, which constrains all three model parameters: coulombic efficiency fixes the parasitic-demand parameter P and its cycle-dependent evolution k , while capacity retention fixes the irreversible finalization fraction η .

Figure 4 juxtaposes the two experimental cycling observables that most directly describe parasitic behavior in TEMPO/BTD cells: normalized discharge capacity (which encodes net inventory loss) and coulombic efficiency (CE) (which encodes the fraction of charge that returns as discharge under the applied protocol). Across electrolytes, capacity fade is front-loaded, with a steep early decline followed by a slower tail, indicating that the dominant loss processes are most active during the initial cycles and then relax toward a quasi-steady burden.²⁰ In the same experiments, CE rapidly approaches an electrolyte-dependent plateau, below unity, after the initial cycles. While the observed CE values (70–86%) are lower than the 99.99% target for practical NARFBs, this nonideal regime is deliberately studied here to validate the model under conditions where degradation processes are experimentally resolvable. This plateau behavior is consistent with a persistent parasitic redox channel that remains active after an initial transient, but whose net magnitude stabilizes under fixed current density and voltage limits. Representative galvanostatic charge/discharge voltage profiles for each electrolyte are provided in SI Figure S13–S16.

Importantly, CE alone does not specify whether parasitic charge corresponds primarily to reversible shuttling or to

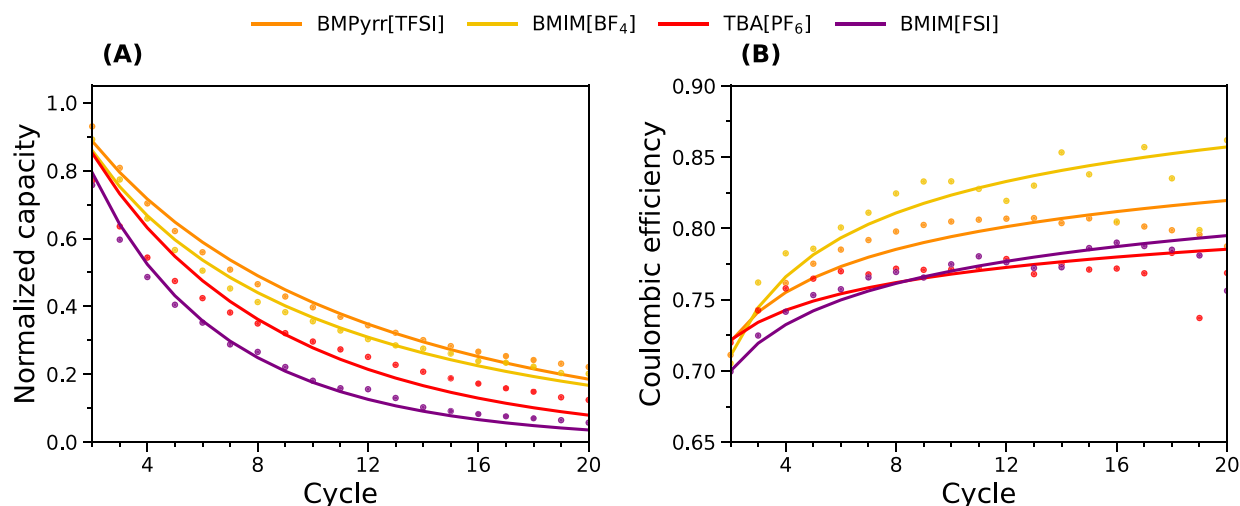


Figure 4. Normalized discharge capacity (A) and coulombic efficiency (B) for the four cycled electrolytes. Symbols: experimental data; lines: simultaneous fits to eqs 4 and 5 (parameters in Table 1).

permanent loss. Under porous-separator operation, both TEMPO- and BTD-derived species can contribute to bidirectional shuttling and cross-contamination, which can depress CE while remaining at least partially reversible on the timescale of a cycle.^{21,22} Net capacity loss, by contrast, requires that a nonzero fraction of parasitic events terminate in electrochemically inactive sinks (e.g. irreversible formation of side products from redox active species). Interpreting the cycling data, therefore, requires a model that uses CE to constrain the magnitude of parasitic charge flow while using capacity decay to constrain how much of that parasitic flow is irreversibly finalized.²³ To separate these effects without introducing a detailed mechanistic scheme, we fit CE and normalized discharge capacity simultaneously using the three-parameter framework in eqs 4 and 5. In this framework, P is a dimensionless parasitic-demand parameter capturing the early-cycle magnitude of parasitic charge diversion under full-cell polarization (folding in both electrochemical accessibility and transport/protocol contributions), k captures how the effective parasitic burden evolves with cycling, and η is an effective finalization fraction for parasitic events. Of the seven ionic liquid electrolytes initially screened by cyclic voltammetry, four were selected for full-cell cycling based on their favorable electrochemical characteristics and practical viability; the remaining candidates were excluded due to insufficient electrochemical performance or prohibitive cost that rendered extended cycling impractical. Representative fits for BMPyrr[TFSI], BMIM[BF₄], TBA[PF₆], and BMIM[FSI] are shown in Figure 4; the extracted parameters and fit metrics are summarized in Table 1.

Several robust trends emerge from Table 1. First, the fitted parasitic-demand parameter P spans a meaningful range, with the lowest values obtained for TBA[PF₆] (0.301) and BMPyrr[TFSI] (0.319), and the largest for the imidazolium electrolytes BMIM[BF₄] (0.358) and BMIM[FSI] (0.336). Notably, P increases with the CV-derived $E_{1/2}^{\text{am}}$ across the four cycled electrolytes (Table 1): the two imidazolium electrolytes, whose aminoxy waves have the most positive values, exhibit the largest parasitic demand, and the electrolyte with the most cathodic aminoxy wave (TBA[PF₆]) exhibits the smallest. The correspondence is monotone within the fit uncertainties: the

only inversion occurs between BMIM[BF₄] and BMIM[FSI], whose half-wave potentials differ by only 30 mV and whose P values differ by 0.02, within the bootstrap uncertainties (± 0.01 – 0.03 ; SI Section S1.3). A linear relation captures the correspondence with $R^2 = 0.78$ (SI Section S1.1), supporting the interpretation of P as an accessibility-dominated demand parameter. Cell resistances and energy efficiencies for each electrolyte system are reported in SI Table S2; these vary with electrolyte viscosity and conductivity as expected but do not correlate directly with capacity retention, further supporting the dominance of chemical finalization effects. Because transport properties (e.g., viscosity and conductivity) can also influence the crossover flux, such effects primarily change the amount and evolution of parasitic charge flow and are therefore absorbed into P and k through the CE constraint; in contrast, η is conditioned on the parasitic charge and quantifies the probability of irreversible inventory loss per unit parasitic charge, so systematic variation in η indicates electrolyte-dependent chemical finalization beyond flux alone within the present framework. Importantly, the lowest P (TBA[PF₆]) does not coincide with the highest capacity retention. This highlights that reducing the early-cycle parasitic burden captured by P is helpful but not sufficient for durability, if the chemical fate of crossed species remains destructive. Deviations from a perfect one-to-one correspondence with the CV-derived metric are expected because P also reflects full-cell polarization and transport contributions.

Second, k is positive in all fitted cases. Within our power-law framework ($\epsilon \propto n^{-k}$), a positive exponent describes a burden that diminishes with cycling, whereas a negative k would imply a parasitic process that accelerates over time. The observed positive values therefore capture a system where the dominant parasitic contribution is strongest early and becomes less severe as the system conditions. The exponent is the smallest for TBA[PF₆] ($k \approx 0.113$), indicating a burden that barely relaxes and instead persists at a near-constant level, and the largest for BMIM[BF₄] ($k \approx 0.3$). This behavior is compatible with several time-dependent effects; for example, progressive wetting and equilibration in porous components, changes in interfacial adsorption, or separator conditioning that reduces the effective

Table 1. Fitted Parameters (P , k , η), Composite Irreversible Burden ($P\eta$), and CV-Derived $E_{1/2}^{\text{am}}$ for the Cycled Electrolytes^a

electrolyte	$E_{1/2}^{\text{am}}$ (V)	P	k	η	$P\eta$	RMSE (CE/Cap.)
BMPyrr[TFSI]	−1.58	0.319	0.190	0.403	0.129	0.0128/0.0225
BMIM[BF ₄]	−1.28	0.358	0.307	0.486	0.174	0.0192/0.0227
TBA[PF ₆]	−1.63	0.301	0.113	0.531	0.160	0.0143/0.0514
BMIM[FSI]	−1.25	0.336	0.165	0.685	0.230	0.0112/0.0230

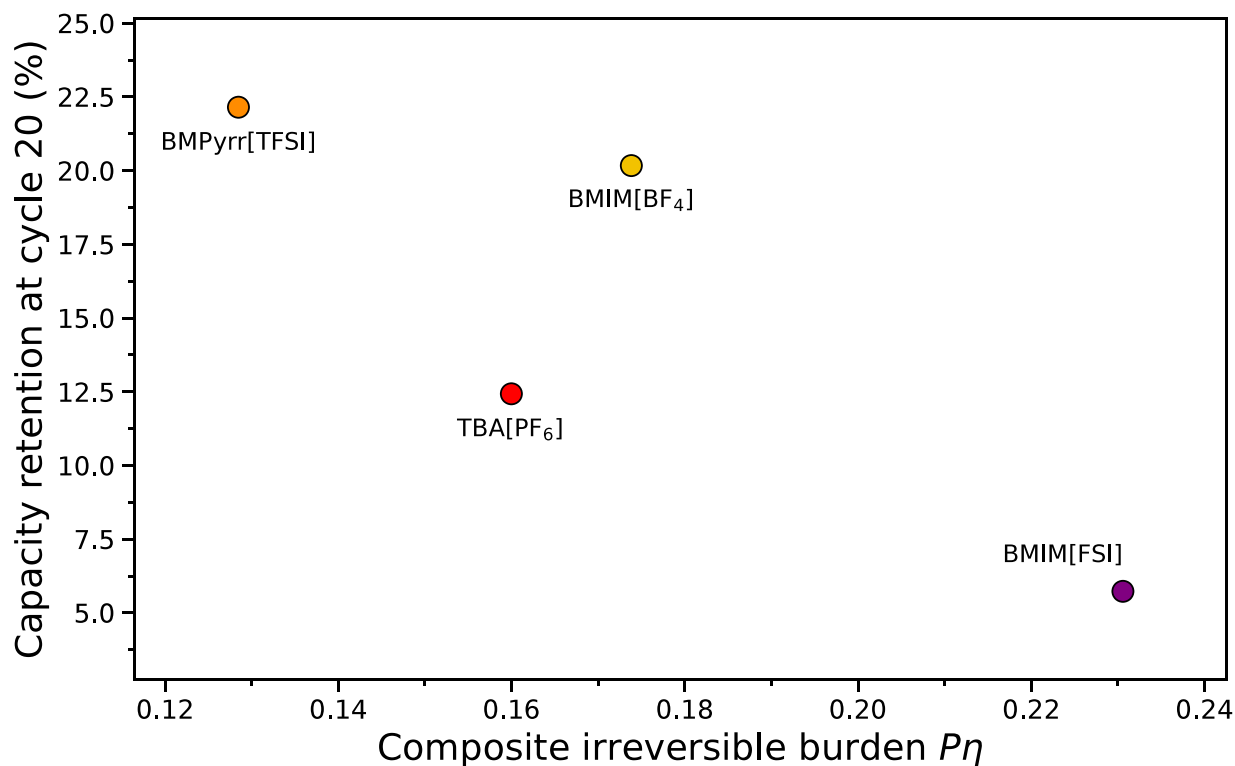
^aCE constrains P and k ; capacity retention constrains η (SI Section S1.1). RMSE refers to the CE/capacity reconstructions. Fits use cycles 2–20.

parasitic burden (for instance, via reduced net crossover flux) with time. Additionally, electrolyte-dependent transport properties such as viscosity and solvated-species size may influence how rapidly the crossover flux equilibrates across the separator, potentially contributing to differences in k across the electrolyte series. Disentangling these individual contributions to k would require dedicated, time-resolved crossover measurements under controlled conditions and remains a target for future investigation.

Third, the irreversible finalization fraction η varies substantially across electrolytes (0.403–0.685) and serves as the decisive discriminator. For instance, TBA[PF₆] has the lowest parasitic demand of the series (low P), yet exhibits a high finalization probability ($\eta \approx 0.531$), implying that the parasitic events it does generate are chemically punishing. In contrast, BMPyrr[TFSI] combines a similar P with the lowest finalization fraction in the set ($\eta \approx 0.403$). As a result, the composite irreversible burden $P\eta$ which, in the model, governs the rate of inventory loss is lower for BMPyrr[TFSI] (0.129) than for TBA[PF₆] (0.160). This explains why the pyrrolidinium system

outperforms the ammonium system despite the latter's lower P . Overall, $P\eta$ differs by nearly a factor of two between the best (BMPyrr[TFSI], 0.129) and worst (BMIM[FSI], 0.230) cases, consistent with performance differences being dominated by the coupling of accessibility-related demand (P) and chemical finalization (η).

To close the cycling analysis with a compact, model-consistent comparison across electrolytes, we consider the composite irreversible burden $P\eta$, which captures how strongly parasitic accessibility under full-cell polarization (P) is coupled to net inventory loss (η) within the present minimal framework. Figure 5 plots the observed capacity retention at cycle 20 (the last cycle included in the fits) against $P\eta$ for the representative subset in Table 1. Within this subset, higher $P\eta$ is associated with lower capacity retention, with the extremes set cleanly by the lowest- $P\eta$ electrolyte (BMPyrr[TFSI], best retention) and the highest- $P\eta$ electrolyte (BMIM[FSI], worst), consistent with the interpretation that the most detrimental conditions combine both substantial electrochemical access to the parasitic manifold and a high

**Figure 5.** Observed capacity retention at cycle 20 (the last fitted cycle) versus the composite irreversible burden $P\eta$ (Table 1).

probability that parasitic events terminate in irreversible loss.²⁴ TBA[PF₆] falls somewhat below this trend: despite a moderate $P\eta$, its very small k means the parasitic burden barely relaxes and the loss continues to accumulate over cycling, which illustrates that the burden-evolution exponent k modulates the $P\eta$ -retention relationship as a secondary factor. This comparison is intentionally descriptive rather than universal: it uses a small number of electrolytes and a deliberately reduced model, and it does not identify the underlying chemical sinks. Nonetheless, it provides a useful summary of what the cycling data do resolve in a defensible way, namely that electrolyte choice modulates both the effective accessibility of parasitic reduction and the effective irreversible fraction, and that their product largely accounts for the observed separation in capacity trajectories under identical hardware and operating limits. The application of the model allows the identification of shortcomings in the battery system, by quantifying the influence of the individual parameters. As each parameter is connected to a set of phenomena (electrochemical accessibility, chemical termination, or time-dependent aspects), this can provide a first indication of optimization potentials in the overall systems. In its current form, the model is diagnostic rather than strictly predictive: the parameters P , k , and η are extracted from cycling data and their physical interpretability enables rapid identification of performance-limiting factors across electrolyte formulations, thereby guiding targeted system optimization without requiring detailed mechanistic resolution of each degradation pathway.

To establish which parameters actually dominate capacity decay and whether they are uniquely determined, we carried out a sensitivity and identifiability analysis of the fit (SI Section S1.3). A normalized one-at-a-time sensitivity shows that capacity retention is by far the most responsive to P and η , which carry equal and the largest local elasticities, while the burden-relaxation exponent k has a smaller local elasticity (although its wide spread across electrolytes still contributes to the cross-electrolyte differences in retention, as seen for the small- k TBA[PF₆] in Figure 5); because P and η enter the capacity expression only through their product, the composite $P\eta$ is the single quantity to which retention is locally most sensitive. The identifiability analysis (parameter correlations and a residual bootstrap) shows that η and the composite $P\eta$ are the best-determined quantities, that P and k are positively correlated and trade off against each other, and that k is the least constrained parameter (most uncertain for TBA[PF₆], whose burden barely relaxes), though it remains identifiable in all four systems. This is itself informative: capacity retention alone cannot separate P from η , so it is the independent coulombic-efficiency constraint (which depends on P but not η) that makes the decomposition identifiable. The three parameters also map onto measurable quantities: P is anchored to the CV-derived half-wave potential $E_{1/2}^{\text{am}}$ and to the coulombic efficiency, k is, in principle, accessible from time-resolved cross-over measurements, and η is linked to the local chemical environment probed by the molecular dynamics simulations below.

These results motivate a microscopic question: what electrolyte-level features control the relative stabilization and local structure of the aminoxy state in a way that can shift electrochemical accessibility and plausibly influence irreversible finalization. We address this using molecular dynamics simulations.

2.4. Molecular Dynamics Simulations

Molecular dynamics simulations provide a physically grounded interpretation of how electrolyte composition modulates electrochemical accessibility of the aminoxy pathway and, indirectly, the irreversible consequences of parasitic reduction. Rather than attempting to resolve specific reaction mechanisms, the simulations are used here to probe how the local solvation environment of the aminoxy anion varies across electrolytes in ways that are consistent with the experimentally extracted trends in the half-wave potential $E_{1/2}^{\text{am}}$ and effective irreversible burden. While density functional theory (DFT) calculations with implicit solvation models could, in principle, capture qualitative trends in solvation-dependent redox potentials, they do not resolve the explicit ion coordination and local structuring effects that are central to the present analysis;^{25,26} MD simulations provide these structural details at moderate computational cost and enable direct comparison across the full electrolyte series.

Figure 6 shows that the differential solvation free energy of the aminoxy state relative to acetonitrile varies systematically with electrolyte identity and correlates with the experimentally observed shifts in the TEMPO reduction potential. Electrolytes that preferentially stabilize the aminoxy anion reduce the energetic penalty for accessing this reduced state, shifting the reduction toward less negative potentials. This trend is directly consistent with the half-wave-potential analysis: enhanced stabilization of the reduced state shifts $E_{1/2}^{\text{am}}$ anodically, toward and into the anolyte operating window, whereas weaker stabilization shifts the reduction cathodically, away from the window.²⁷ In this sense, the simulations provide a thermodynamic rationale for why electrolyte choice acts as a control knob for electrochemical exposure, as captured by the CV-derived $E_{1/2}^{\text{am}}$ and the fitted parasitic-demand parameter P .

The structural origin of these energetic differences is reflected in the local coordination environment of the aminoxy oxygen. As shown by the cumulative-ion-count analysis in Figure 6, ionic liquids based on imidazolium and pyrrolidinium cations exhibit more pronounced first-shell structuring (higher cumulative ion count) around the aminoxy oxygen than tetraalkylammonium-based electrolytes. We note that the cumulative ion count is reported as a continuous function of distance; the conventional coordination number corresponds to its value at the first minimum of the ion density (see SI Section S1.6). Representative simulation snapshots illustrating the cation arrangement around the aminoxy oxygen, including the simultaneous adsorption of two BMIM cations versus a single TBA cation, are provided in SI Figure S17. This tighter and more persistent coordination is consistent with stronger electrostatic and hydrogen-bond-like interactions in the immediate solvation shell. In contrast, the anion cumulative-ion-count profiles (Figure 7) confirm that anions are effectively excluded from the immediate vicinity of the aminoxy center due to coulombic repulsion. This structural separation indicates that the observed electrolyte-dependent stabilization is primarily driven by the cation environment. Consistently, an analysis of the cation–anion pair structure of the ionic liquids themselves (SI Figures S18 and S19) shows that larger anions increase the average cation–anion distance, while the anion identity only has a minor influence on the solvation environment of the aminoxy anion, the cation provides the dominant influence. Such differences in the local structure offer a plausible microscopic

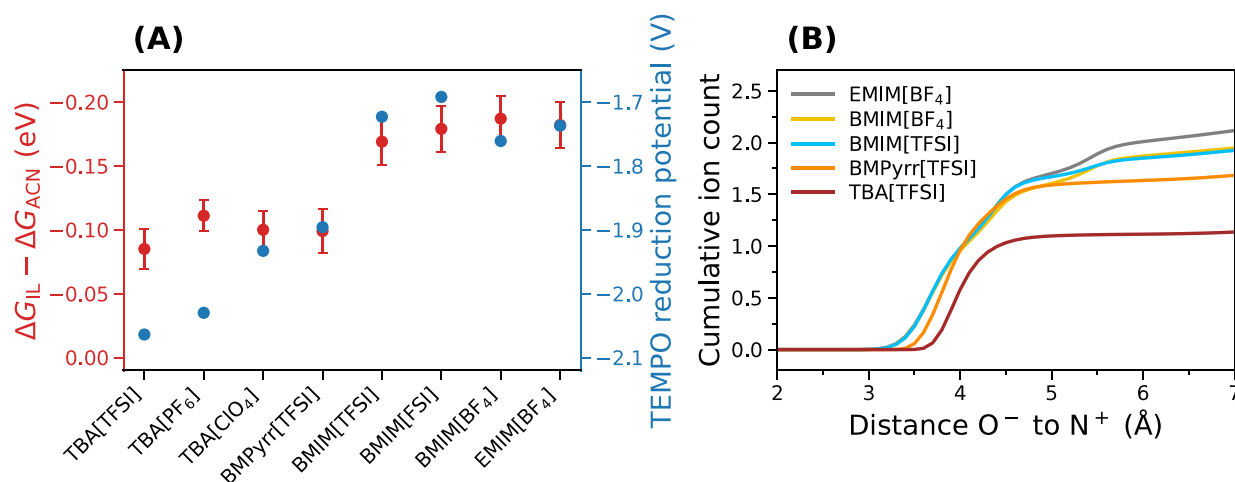


Figure 6. Molecular descriptors of aminoxy energetics. (A) Differential solvation free energy of the aminoxy anion (red, MD; error bars: SD over eight TI replicas) and experimental TEMPO reduction potential (blue). (B) Cumulative cation count around the aminoxy oxygen (three-replica average).

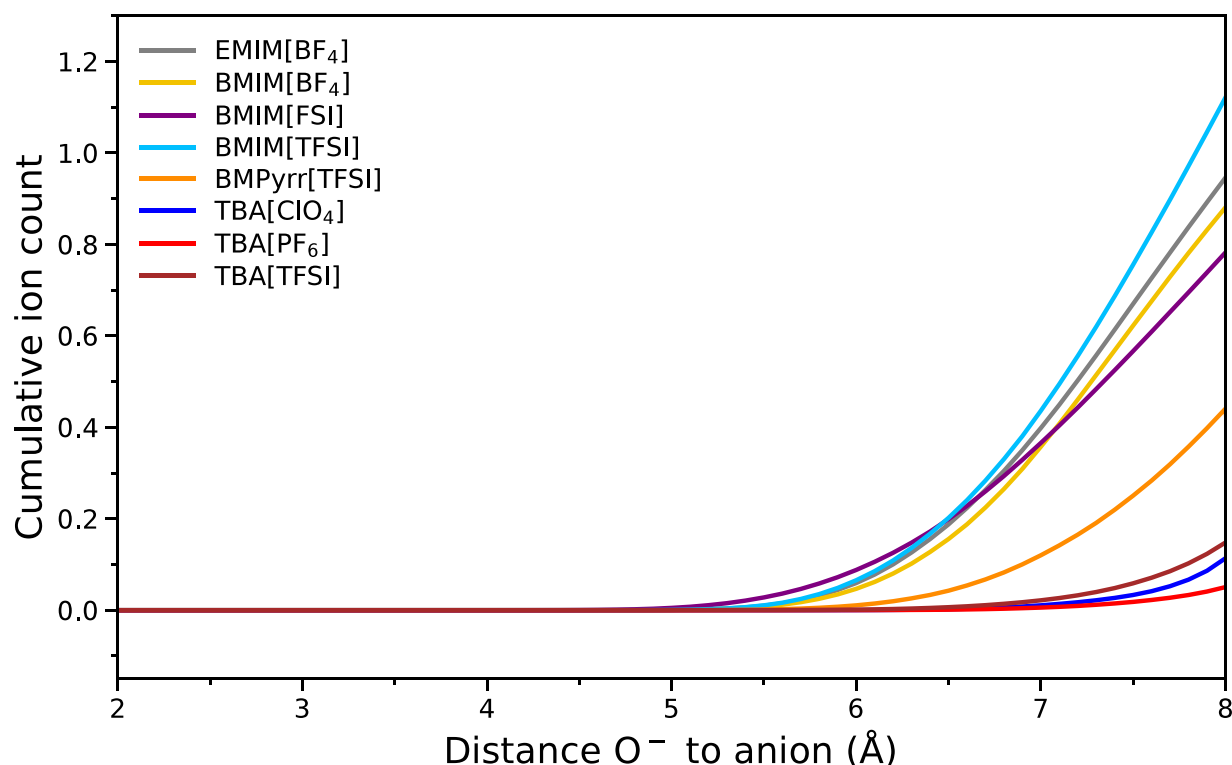


Figure 7. Cumulative anion count around the aminoxy oxygen of TEMPO[−] for the investigated ionic liquids.

explanation for the observed electrolyte dependence of aminoxy stabilization, without invoking changes in the intrinsic redox chemistry of TEMPO itself.

Beyond redox energetics, differences in local solvation structure also provide a qualitative link to the electrolyte dependence of irreversible finalization inferred from cycling.²⁸ A more structured solvation environment around the aminoxy oxygen can influence the lifetime and reactivity of the reduced state by modulating access of trace proton donors, electrophiles, or

other reactive species present at low concentrations. While the present simulations do not identify specific chemical sinks, the electrolyte-dependent differences in aminoxy coordination and stabilization are consistent with the observation that η varies substantially across electrolytes, even when electrochemical accessibility is comparable. In this interpretation, η reflects an aggregate outcome of how the reduced state is chemically processed within its local environment, rather than a single dominant reaction pathway.

A natural mechanistic hypothesis for the irreversible termination pathway is the protonation of the aminoxy anion to form hydroxylamine, which requires a proton source within the local solvation environment. This is consistent with the known chemistry of nitroxide reduction.²⁹ In this context, the acidity of the electrolyte cation is potentially relevant. Imidazolium cations carry a moderately acidic proton at the C2 position ($pK_a \approx 21$ –24 in DMSO), which has been extensively characterized in the ionic liquid literature.^{30,31} Notably, BMIM[FSI] exhibits the highest η in the present data set (0.685) and employs an imidazolium cation, consistent with a scenario in which C2–H proton donation contributes to aminoxy finalization. However, TBA[PF₆] also exhibits a relatively high η (0.527) despite the tetrabutylammonium cation lacking conventionally acidic protons and the two imidazolium-based electrolytes themselves differ in η (0.486 for BMIM[BF₄] vs. 0.685 for BMIM[FSI]), indicating that the anion identity and the broader solvation environment also modulate the finalization outcome. These observations suggest that η reflects contributions from multiple proton-source pathways, including cation acidity, trace water, and possibly electrolyte decomposition products, rather than a single dominant mechanism. Disentangling these individual contributions would require targeted spectroscopic studies (e.g., operando infrared (IR) or nuclear magnetic resonance (NMR)) capable of identifying specific protonation products under cycling conditions, and represents a valuable direction for future work.

Taken together, the molecular dynamics results support a unified picture in which electrolyte composition influences degradation through two coupled but distinct effects. First, solvation thermodynamics determine how readily the aminoxy state is accessed electrochemically, governing the half-wave potential $E_{1/2}^{am}$ and the effective accessibility parameter P . Second, local solvation structure influences the chemical fate of the aminoxy state once formed, contributing to electrolyte-dependent differences in the effective irreversible finalization fraction η . Importantly, the simulations do not replace the experimental analysis, but rather provide microscopic context that is consistent with the separation of exposure and fate established from full-cell cycling. This reinforces the central conclusion of the Results and Discussion: electrolyte engineering can simultaneously bias electrochemical accessibility and irreversible finalization, but durable operation in TEMPO/BTD systems will require controlling both effects in concert with transport and separator design.^{18,32} This separation also makes the framework actionable for electrolyte design, because each parameter maps onto a distinct, tunable physicochemical descriptor. The accessibility term P (and the CV-derived $E_{1/2}^{am}$ to which it is anchored) is governed by the solvation thermodynamics of the aminoxy anion, that is, by its differential solvation free energy and by the strength of cation coordination in its first shell, both of which are resolved by the present MD analysis. The finalization fraction η is instead governed by the availability of proton donors in the local environment, principally, cation acidity (for example, imidazolium C2–H) and trace water. The resulting rule of thumb for durable formulations is therefore twofold and must be satisfied jointly: favor weak stabilization and loose cation coordination of the aminoxy anion, so that parasitic reduction is rarely accessed (low P), and simultaneously favor a low proton-donor activity, so that any aminoxy that does form is unlikely to be irreversibly finalized (low η). Further studies are necessary to disentangle the individual

microscopic contributions for parameter k (involving time-dependent membrane and wetting behaviour) and η (to determine the exact nature of chemical sinks and proton sources); in particular, interfacial characterization by electrochemical impedance spectroscopy and Tafel analysis would provide a complementary, kinetics-resolved view of the parasitic channel and is a natural direction for future work.

The scope of this framework should be stated clearly. It is designed for degradation that can be written as a parasitic charge channel (an accessibility term that evolves with cycling) coupled to a probabilistic irreversible finalization step, which describes crossover-driven parasitic cycling of labile reduced or oxidized intermediates such as the aminoxy anion studied here. It is not expected to map cleanly onto strongly nonstationary failure modes whose rate is not a smoothly relaxing function of the cycle number, such as membrane failure, gas evolution, electrode passivation, or autocatalytic decomposition; these would require different, possibly nonmonotonic, burden formulations. Within its scope, the functional form is transferable across chemistries, but the parameter values are not universal constants: P , k , and η retain their physical meaning (accessibility, burden relaxation, and finalization) but must be re-extracted for each system, because they fold in chemistry-specific solvation, transport, and proton-donor environments.

3. CONCLUSIONS

The central new understanding from this work is that two effects usually conflated in redox-flow-battery degradation can, and should, be separated: the electrochemical accessibility of the parasitic intermediate, that is, whether the aminoxy state is reached at all, and the chemical fate of that intermediate once formed, that is, whether it is irreversibly finalized into an inactive product. Using the TEMPO/benzothiadiazole system as a testbed, our combined electrochemical and molecular dynamics analysis shows that these two effects are controlled by different molecular features: accessibility is set by the solvation thermodynamics and cation coordination of the aminoxy anion, whereas finalization is set by the availability of local proton donors. Because the two are governed independently, an electrolyte can be favorable on one axis while unfavorable on the other; TBA[PF₆], for instance, restricts accessibility (low P), yet finalizes a large fraction of the events it does generate (high η). The practical consequence is a concrete design principle rather than a descriptive observation: minimizing electrochemical accessibility is necessary but not sufficient for durability, and a durable electrolyte must simultaneously suppress both axes, by combining weak aminoxy stabilization and loose cation coordination (to keep P low) with low proton-donor activity such as low cation acidity and low trace-water content (to keep η low).

This understanding is operationalized by the three-parameter model, which decomposes measured coulombic efficiency and capacity retention into the accessibility demand P , its cycle-dependent relaxation k , and the irreversible finalization fraction η , with the composite $P\eta$ governing the rate of permanent inventory loss. Because each parameter is tied to a measurable, physically interpretable descriptor, in particular, the effective half-wave potential $E_{1/2}^{am}$ of the TEMPO/TEMPO^{•−} couple for the accessibility axis, the framework anticipates degradation behavior in new systems: a candidate electrolyte can be ranked from half-cell half-wave potentials and proton-donor descriptors before extended cycling, and the model then diagnoses which

axis limits a given formulation. The functional form transfers to other parasitic-charge-plus-finalization chemistries, while the parameter values remain system-specific and must be re-extracted. More broadly, the approach provides a route to connect reactive-intermediate chemistry with macroscopic device performance and to guide the rational design of more durable nonaqueous redox flow battery electrolytes.

4. METHODS

4.1. Electrochemical Measurements (Half-Cell CV)

CV was performed in a three-electrode configuration (glassy carbon working electrode, Pt counter, and organic Ag/AgNO₃ reference) under argon in acetonitrile. Supporting electrolytes were screened at 0.1 M; TEMPO and BTD were measured in separate solutions to obtain matched voltammograms under identical electrolyte identity. CVs were recorded at scan rates of 10–100 mV s^{−1} over −2.4 to +0.5 V vs. Ag/AgNO₃; fifth-scan data were used for the half-wave-potential analysis to reduce first-scan conditioning artefacts. Peak potentials were located with a prominence-based peak search on Savitzky–Golay-smoothed voltammograms, and the electrolyte-insensitive TEMPO/TEMPO⁺ couple served as an internal potential standard to detect and correct reference-electrode drift (applied to one dataset, BMIM[BF₄]; see SI Section S1.1). Full experimental details are provided in SI Section S1.4.

4.2. Flow-Cell Experiments (TEMPO/BTD Full Cells)

Full TEMPO/BTD cells (9 cm² active area, carbon felt electrodes, porous PVC–silica separator) were cycled galvanostatically at 1C (5 mA cm^{−2}) between voltage limits of 1.5 and 2.5 V. Both reservoirs contained 37 mM redox-active species (TEMPO catholyte, BTD anolyte) and 0.36 M supporting electrolyte in acetonitrile. This concentration was chosen consistent with prior studies of TEMPO and BTD systems in nonaqueous electrolytes, which typically operate in the range of 10–50 mM for fundamental investigations.^{6,13,33} The porous separator was chosen intentionally to permit measurable crossover, enabling quantification of electrolyte-dependent accessibility and finalization. A comparison experiment with the FAPQ-330 anion-exchange membrane showed comparable capacity fade rates, confirming that degradation under these conditions is dominated by chemical processes rather than membrane-dependent crossover (see SI Figures S20 and S21). Full experimental details are provided in SI Section S1.5.

4.3. Molecular Dynamics Simulations

MD simulations were performed in LAMMPS using OPLS-based force fields. Each system comprised one TEMPO molecule, 9 ion pairs, and 500 acetonitrile molecules (≈0.3 M), spanning imidazolium, pyrrolidinium, and tetraalkylammonium cation families.^{34,35} Differential solvation free energies of TEMPO vs. TEMPO[−] were computed via thermodynamic integration (19 coupling steps, 8 independent replicas per electrolyte). Radial distribution functions and cumulative ion counts around the aminoxy oxygen were extracted from 10 ns production trajectories, averaged over three independent replicas with different initial configurations; the small replica-to-replica variation confirms that these structural observables are converged

within the simulated timescale (SI Section S1.6). Full simulation details are provided in SI Section S1.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acselectrochem.6c00171>.

Extended derivations of the three-parameter degradation model and of the half-wave-potential accessibility analysis, comparison of alternative burden model forms, sensitivity and identifiability analysis, full experimental protocols for electrochemistry and flow-cell cycling, molecular dynamics simulation details, the complete set of matched cyclic voltammograms for all investigated electrolytes with annotated half-wave potentials, galvanostatic voltage profiles, supplementary molecular dynamics data (representative snapshots and cation–anion pair structure), and membrane comparison experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Christian M. Pichler – CEST GmbH, Centre for Electrochemical Surface Technology, Viktor-Kaplan-Straße 2, Wiener Neustadt 2700, Austria; Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10, Vienna 1040, Austria; Email: christian.pichler@tuwien.ac.at

Authors

Hermias J. Venter – CEST GmbH, Centre for Electrochemical Surface Technology, Viktor-Kaplan-Straße 2, Wiener Neustadt 2700, Austria; Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10, Vienna 1040, Austria

Ole Nickel – Institute of Surface Science, Helmholtz-Zentrum Hereon, Max-Planck-Straße 1, Geesthacht 21502, Germany

Robert H. Meißner – Institute of Surface Science, Helmholtz-Zentrum Hereon, Max-Planck-Straße 1, Geesthacht 21502, Germany; Institute for Interface Physics and Engineering, Hamburg University of Technology, Am Schwarzenberg-Campus 1, Hamburg 21073, Germany

Markus Ostermann – CEST GmbH, Centre for Electrochemical Surface Technology, Viktor-Kaplan-Straße 2, Wiener Neustadt 2700, Austria; Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10, Vienna 1040, Austria

Markus Valtiner – CEST GmbH, Centre for Electrochemical Surface Technology, Viktor-Kaplan-Straße 2, Wiener Neustadt 2700, Austria; Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10, Vienna 1040, Austria;  orcid.org/0000-0001-5410-1067

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acselectrochem.6c00171>

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Notes

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