

Quantifying and mitigating gas generation in ether-based lithium metal batteries

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Suppressing uncontrolled gas evolution is essential to realizing the commercial potential of high-energy-density lithium metal batteries (LMBs), yet mechanistic studies of gas generation in ether-based electrolytes remain scarce ^[1]. In a recent study published in *Nature Chemistry*, Hung and co-workers quantify gas evolution in ether-based LMBs and elucidate the underlying degradation pathways across electrode interfaces. Oxidative decomposition at the cathode yields CO and CO₂, which undergo inter-electrode crosstalk and are subsequently consumed at the lithium anode to form passivating species such as Li₂CO₃. Conversely, anode-side degradation yields CH₄ as the dominant gaseous product, exhibiting a distinct delayed onset during cycling. They demonstrate that anode activation in high-concentration ether electrolytes refines lithium deposition morphology and mitigates interfacial side reactions. This approach extends the number of cycles to gas onset and cell failure by an order of magnitude without altering electrolyte chemistry, providing a practical strategy to improve the safety and longevity of high-capacity LMBs.

The central achievement of this study lies in its systematic deconvolution of gas generation pathways. Using differential electrochemical mass spectrometry (DEMS) and carefully designed half-cell configurations, the researchers traced the origin of gaseous products to their respective electrodes. They determined that CO₂ and CO are generated at the cathode through oxidative decomposition reactions, while CH₄ is produced at the anode via reductive processes involving the ether solvent. A particularly important finding is the fate of these gases within a full cell configuration. CO₂ and CO, though produced at the cathode, are not observed as net gas evolution in full

cells because they are consumed at the lithium metal anode, reacting to form solid lithium compounds such as Li₂CO₃. In contrast, CH₄ generated at the anode persists and accumulates, emerging as the dominant gaseous species in full-cell operation. Notably, CH₄ evolution is not immediate; it exhibits a distinct onset point after initial cycling, suggesting that gas generation is coupled to the evolution of the solid electrolyte interphase (SEI) and lithium deposition morphology ^[2]. This crosstalk between electrodes—where cathode-generated gases are scavenged by the anode while anode-generated gases persist—has profound implications for battery safety, as gas accumulation depletes electrolytes, disrupts SEI stability, and increases impedance. While the DEMS half-cell setups isolate individual electrode behaviors but fail to capture full-cell inter-electrode crosstalk, such as the anode consumption of cathode-derived CO and CO₂. Furthermore, titration-mass spectrometry (T-MS) quantification of crosstalk products like Li₂CO₃ is prone to errors from non-ideal baseline subtractions and interference from residual dissolved CO₂ reacting with lithium ^[3].

The study further establishes that gas evolution is strongly dependent on operational parameters. The total gas volume increases dramatically with increasing temperature and decreasing electrolyte concentration, underscoring the thermally activated nature of the decomposition reactions. These observations align with broader findings that high-concentration electrolytes can suppress solvent decomposition by altering the solvation structure and reducing free solvent availability ^[4]. Indeed, advances in localized high-concentration electrolytes (LHCEs) have demonstrated that tuning salt concentration and diluent polarity can

Received: September 14, 2026. **Revised:** September 19, 2026. **Accepted:** October 6, 2026. **Available online:** October 6, 2026

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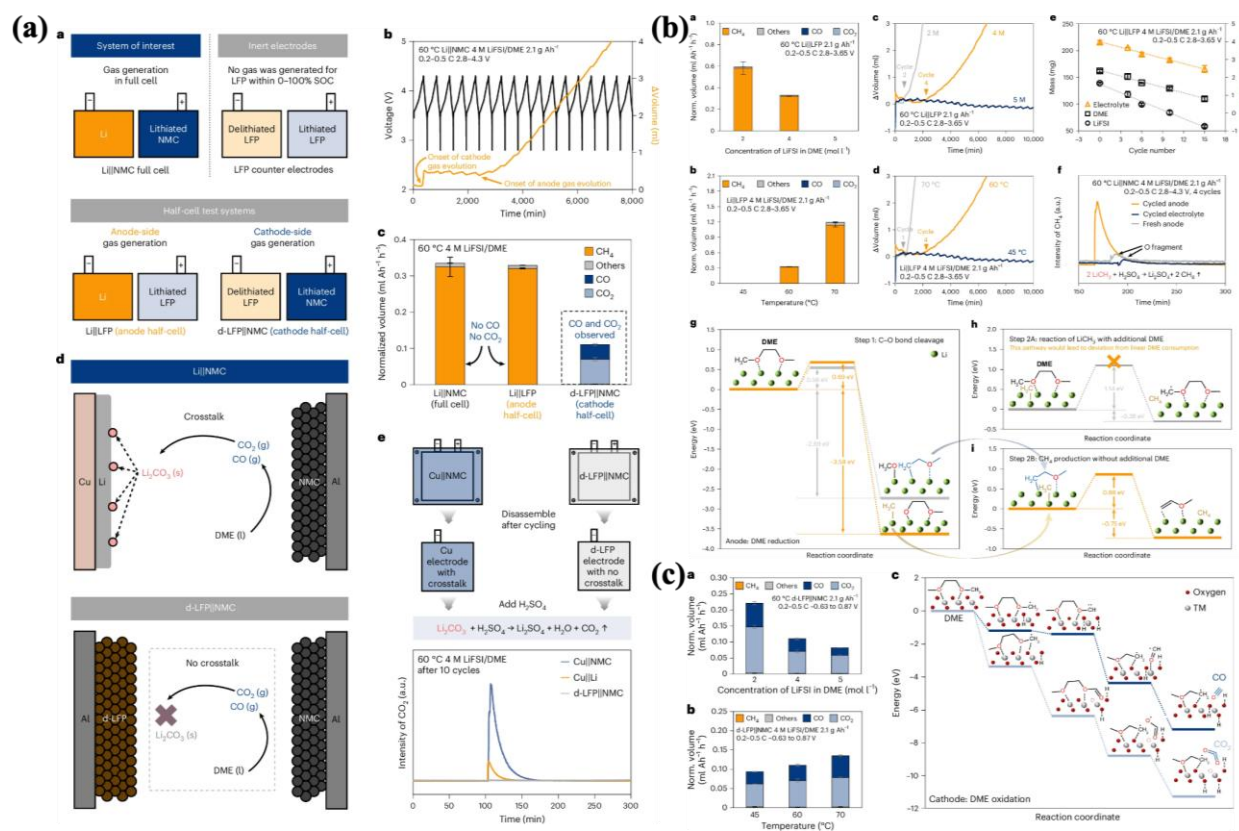


Figure 1. Mechanistic Understanding of Gas Evolution. (a) Systematic deconvolution of gas origins using full-cell/half-cell DEMS, crosstalk experiments, and acid titration. (b) CH₄ formation pathway via DME reduction at the lithium anode, including concentration/temperature dependence and DFT reaction coordinates. (c) CO/CO₂ generation from DME oxidation at the cathode, with reaction energy diagrams. (d, e) Crosstalk experiments demonstrating that CO₂ and CO are consumed at the lithium anode, whereas CH₄ persists. (f) Acid titration confirming the formation of Li₂CO₃ from cathode-derived CO₂ reacting with the lithium anode.

enhance SEI stability and mitigate dendrite growth. At the molecular level, the authors elucidated the reaction mechanism for CH₄ formation. Using density functional theory (DFT) calculations, they demonstrated that CH₄ originates from the reduction of 1, 2-dimethoxyethane (DME) at the lithium metal surface. C-O bond cleavage generates LiCH₃ and other surface-bound fragments; LiCH₃ subsequently reacts predominantly with DME-derived methoxyethyl species to form CH₄. Additionally, substituting terminal methyl groups with fluorinated moieties in a fluorinated ether electrolyte (FEE) successfully eliminates the LiCH₃ intermediate to suppress CH₄ generation. This mechanistic clarity is essential because it directly links gas evolution to electrolyte structure: the methyl groups on DME are the chemical source of CH₄, and therefore any strategy that modifies the solvent environment or interfacial reactivity can, in principle, suppress gas generation. However, the CH₄ accumulation lacks a quantitative gas volume-pressure-

safety threshold analysis linking gas evolution directly to pouch cell swelling, internal pressure buildup, and thermal runaway limits for commercial scaling.

These findings build upon earlier work showing that ether-based SEIs are layer-structured, with an outer organic/polymeric layer consisting of lithium oligoethoxides and an inner layer of simple inorganic oxides (Li₂O), and that DME and DOL follow distinct reduction pathways on lithium surfaces [5]. The observation that radical decomposition pathways in ether electrolytes can drive DOL polymerization and DME oxidation further contextualizes the complexity of ether electrolyte stability. Recent efforts to minimize solvent coordination in ether electrolytes through fluoroether and nitrile ether additives have shown promise for extending the electrochemical window beyond 4.5V, suggesting that molecular design of ether solvents can simultaneously address both oxidative stability and reductive gas suppression [6-7]. At the cathode, the oxidation of DME was shown to produce

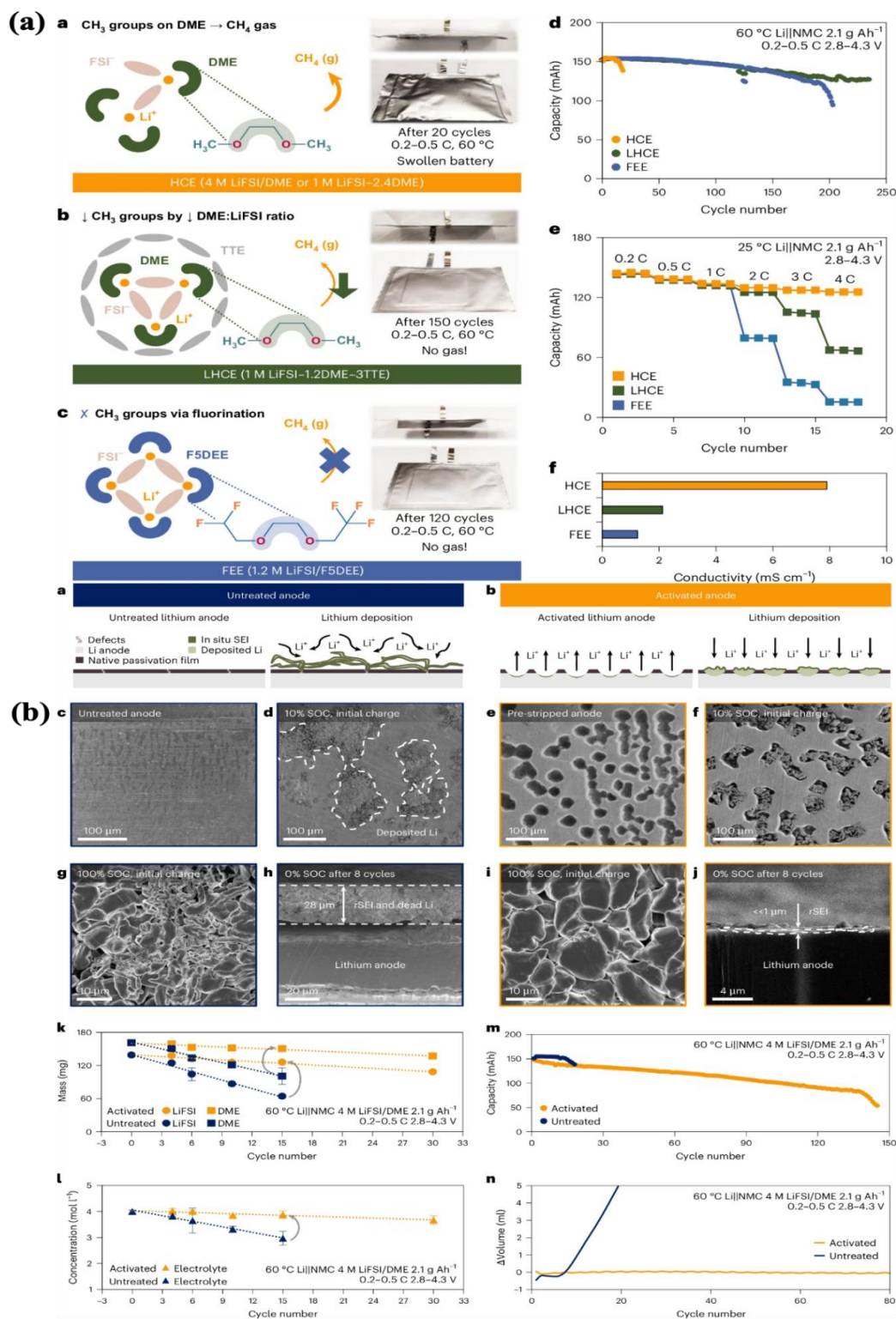


Figure 2. Strategies for Suppressing Gas Evolution. (a) Three electrolyte engineering approaches—high-concentration electrolyte (HCE), localized high-concentration electrolyte (LHCE), and fluorinated ether electrolyte (FEE)—with cycling performance and conductivity data. (b) Lithium anode surface activation strategy, comparing untreated vs. activated anodes via SEM morphology, cycling stability, mass loss, electrolyte consumption, and DEMS gas suppression.

CO and CO₂ through a multi-step reaction coordinate involving the formation of peroxy and formate intermediates. The authors detailed reaction energy diagrams reveal that these oxidative pathways are thermodynamically accessible under typical high-voltage operation, particularly at elevated temperatures [8].

Beyond mechanistic understanding, the study delivers a practical strategy for suppressing gas evolution: lithium anode surface activation. The researchers demonstrated that performing initial electrochemical activation protocols on the lithium metal anode creates a high density of uniform lithium nucleation sites—fundamentally alters the deposition morphology and interfacial chemistry. Scanning electron microscopy (SEM) revealed stark differences between untreated and activated anodes. Untreated lithium surfaces exhibit porous, mossy deposits with substantial "dead lithium" formation and interfacial cracking, creating fresh surfaces that continuously react with the electrolyte. Activated anodes, by contrast, display dense, columnar lithium deposits with a compact, stable SEI layer that minimizes ongoing electrolyte decomposition. This is consistent with the broader understanding that fabricating artificial interphases with controllable structures and desirable mechanical properties is a promising strategy for achieving stable cycles in LMBs. The electrochemical benefits are striking. Anode activation delayed the onset of critical LiCH₃ intermediate formation and CH₄ gas evolution by 800% and increased cell cycling life by 400%—all without altering the electrolyte formulation. This is a critical distinction because it demonstrates that interfacial engineering at the anode can decouple gas suppression from electrolyte design, offering broad applicability across various ether-based and potentially other electrolyte chemistries. While it also has limitations when considering condition dependence and scale-up feasibility under practical parameters like high-voltage cathodes, lean electrolyte ratios, and high areal capacities [9].

This work reframes gas evolution in LMBs not merely as a symptom of electrolyte instability but as a quantifiable, mechanistically understood process with distinct cathodic and anodic origins. By showing that CH₄ generated from the anode is the dominant persistent gas in full cells, while cathode-generated CO₂/CO are internally scavenged by the lithium anode, the authors provide a clear target for intervention on reducing exposed reactive surface area. The anode surface activation strategy is particularly compelling because it achieves dramatic performance gains through a surface-treatment approach that could be integrated into cell manufacturing without the formulation complexity of custom electrolyte design.

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