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Review

Beyond Half-Cells: Interfaces, Operando Chemistry, and Failure Pathways in Practical Lithium- and Sodium-Ion Batteries

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Abstract

Half-cell testing has long served as a convenient and informative platform for screening electrode materials in lithium-ion and sodium-ion batteries. However, the electrochemical performance obtained under such simplified conditions often fails to predict the behavior of practical full cells, where electrode balancing, mass loading, areal capacity, electrolyte amount, pressure, and interfacial instability impose much stricter constraints. In this review, we examine the limitations of half-cell-based assessment and discuss why moving beyond idealized configurations is essential for the realistic evaluation of advanced battery materials. Particular attention is given to the dynamic nature of interfacial chemistry, including the formation and evolution of the solid electrolyte interphase and cathode electrolyte interphase, as well as to the role of electrolyte decomposition, additives, binders, and electrode formulation in determining cell performance. We further analyze how operando and in situ characterization techniques, including X-ray-based methods, vibrational spectroscopies, microscopy, and electrochemical impedance analysis, are reshaping the understanding of structural evolution, interphase development, and degradation processes under realistic operating conditions. Major failure pathways in practical cells, such as capacity fade, impedance growth, mechanical degradation, electrolyte consumption, gas evolution, transition-metal dissolution, and surface reconstruction, are critically discussed for both lithium-ion and sodium-ion systems. Representative electrode chemistries are considered to illustrate how promising material-level properties do not always translate into practical-cell success. Finally, we address the metrics that matter for practical relevance, summarize current mitigation strategies, and highlight validation criteria and testing workflows that can better connect academic materials research with realistic battery development. By integrating interfacial chemistry, operando insight, and practical performance criteria, this review aims to provide a more translational framework for the design and assessment of next-generation lithium-ion and sodium-ion batteries.

Keywords: lithium-ion batteries; sodium-ion batteries; half-cell testing; full-cell validation; interfacial chemistry; operando characterization; degradation mechanisms; practical battery metrics

1. Introduction

Rechargeable lithium-ion and sodium-ion batteries continue to attract intense research interest because of their central role in portable electronics, electric mobility, and stationary energy storage. Over the past decade, major efforts have focused on developing electrode materials with improved capacity, rate capability, and cycling stability. However, despite these advances, the electrochemical

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evaluation of new materials is still dominated by half-cell configurations, which often provide an incomplete picture of practical battery behavior [1–4]. As the field moves toward more application-relevant metrics, increasing attention is being paid to the gap between half-cell results and full-cell performance, especially in relation to finite alkali inventory, electrode balancing, interfacial instability, and degradation under realistic operating conditions [2,3]. In this context, a more critical and translational assessment of advanced electrode materials is needed, particularly for lithium-ion and sodium-ion systems, where differences in interphase formation, irreversible losses, and practical cell constraints strongly influence real device performance [1–4].

1.1. Half-Cells and Practical Batteries

Half-cells have long served as the standard platform for the early evaluation of electrode materials in rechargeable batteries. In lithium-ion research, the active material is commonly tested against metallic lithium, whereas in sodium-ion studies an analogous configuration is frequently assembled using metallic sodium. This approach remains highly valuable because it simplifies electrochemical analysis, facilitates rapid materials screening, and enables the identification of intrinsic redox behavior, reaction mechanisms, and preliminary rate trends [2,3].

Nevertheless, the very features that make half-cells convenient also limit their predictive value for practical batteries. The use of an alkali-metal counter electrode provides an effectively unlimited ion reservoir and removes the need for realistic electrode balancing, thereby masking constraints that dominate full-cell performance, including finite cyclable ion inventory, irreversible capacity losses, N/P ratio, mass loading, areal capacity, and electrolyte availability [2]. As a result, materials that exhibit excellent specific capacity or cycling stability in half-cells often perform much less favorably when transferred to practical full-cell configurations. Recent analyses of full-cell design parameters have underscored that many academic studies still overlook factors that are decisive at the device level, such as electrode loading, electrolyte amount, and balanced cell design [2].

This discrepancy is further amplified by interfacial chemistry. In practical cells, the evolution of the solid electrolyte interphase and cathode electrolyte interphase, electrolyte decomposition, and electrode cross-talk occur in a dynamically coupled environment that is only partially reproduced in simplified half-cell architectures. For this reason, interfaces are increasingly recognized as central determinants of efficiency, degradation, and long-term stability, and recent perspectives have emphasized the need for operando characterization under realistic conditions rather than exclusive reliance on idealized model systems [3].

These considerations are especially relevant for sodium-ion batteries. Although lithium-ion and sodium-ion systems share common electrochemical principles, they differ in ion size, solvation, interphase chemistry, and initial coulombic efficiency, all of which influence their behavior in practical cells [1,4]. In particular, hard carbon has emerged as the leading anode candidate for sodium-ion batteries, but its practical implementation remains strongly affected by irreversible sodium consumption and the challenge of achieving high initial coulombic efficiency [1]. At the same time, sodium-ion batteries are attracting growing attention as a lower-cost and more resource-abundant complement to lithium-ion technology, which further strengthens the need for realistic and comparable evaluation criteria [4].

Accordingly, a central premise of this review is that the transition from half-cells to practical batteries is not merely a matter of scale, but a shift in the governing electrochemical framework. Parameters that may appear secondary in proof-of-concept studies become decisive in full cells, where interfacial instability, limited ion inventory, electrolyte depletion, and degradation pathways directly determine performance, durability, and safety [2,3]. A critical assessment of advanced battery materials must therefore move beyond half-cell data alone and incorporate practical metrics, realistic cell configurations, and operando insight [2,3].

1.2. Li-Ion and Na-Ion Systems

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Lithium-ion and sodium-ion batteries share the same broad conceptual foundation as rechargeable rocking-chair systems in which alkali ions shuttle reversibly between the positive and negative electrodes during charge and discharge [4,5]. In both cases, cell performance is governed by the coupled interplay among electrode chemistry, electrolyte formulation, interfacial stability, transport kinetics, and cell design. This common framework explains why many of the analytical tools, materials-design strategies, and failure-analysis approaches developed for lithium-ion batteries can also inform sodium-ion research. At the same time, direct extrapolation between both technologies is not always appropriate, because the physicochemical differences between Li^+ and Na^+ affect redox behavior, structural evolution, interphase formation, and practical cell engineering [1,4].

Among the most important distinctions is the larger ionic radius and higher atomic mass of sodium relative to lithium, which generally translate into less favorable gravimetric energy density and, in many host structures, slower diffusion kinetics or more pronounced structural strain [4,6]. These differences help explain why sodium-ion batteries, although highly attractive from the standpoint of elemental abundance and projected cost, are often considered more suitable for stationary storage and cost-sensitive applications than for high-energy mobile applications currently dominated by lithium-ion technology [5,6]. Recent techno-economic analyses have nevertheless shown that sodium-ion batteries may become competitive in selected application spaces, particularly if energy density continues to improve and supply-chain volatility for lithium-based systems remains significant [5].

Despite these differences, sodium-ion batteries are not simply lower-energy analogues of lithium-ion systems. Rather, they constitute a distinct technology family with their own materials landscape, interfacial chemistry, and practical constraints. In lithium-ion batteries, graphite remains the dominant commercial anode because of its low operating potential, high reversibility, and mature manufacturing base. In contrast, graphite is generally unsuitable for conventional sodium-ion storage under standard electrolyte conditions, and hard carbon has consequently emerged as the leading anode candidate for sodium-ion batteries [1]. This distinction alone has major implications for practical cell design, because the initial coulombic efficiency, interphase chemistry, and sodium inventory management of hard carbon-based cells differ substantially from those of graphite-based lithium-ion cells [1].

Differences are also evident on the cathode side. Lithium-ion technology has reached a high level of maturity through layered oxides, olivine phosphates, and related compounds, whereas sodium-ion systems currently rely more heavily on layered oxides, polyanionic frameworks, and Prussian blue analogs, each with its own trade-offs in voltage, structural stability, defect chemistry, and moisture sensitivity [4,6]. As a result, sodium-ion batteries must often be discussed not only in terms of lower raw-material cost and improved resource availability, but also in terms of different electrode-level limitations and degradation pathways that can alter the practical meaning of otherwise familiar metrics such as specific capacity, rate capability, or cycle retention [4,6].

Another major difference concerns interfacial chemistry. Because sodium ions exhibit distinct solvation behavior and interact differently with carbonaceous and inorganic host structures, the composition, structure, and mechanical stability of the interphases formed in sodium-ion cells may differ significantly from those found in lithium-ion batteries [4]. These differences are especially important in practical cells, where finite ion inventory and irreversible sodium consumption during early cycles can strongly penalize full-cell performance. For this reason, initial coulombic efficiency is often an even more critical descriptor in sodium-ion batteries than in conventional lithium-ion systems, particularly when hard carbon is used as the negative electrode [1].

A comparative discussion of lithium-ion and sodium-ion systems is therefore useful not because the two technologies are interchangeable, but because their similarities and differences sharpen the criteria for practical evaluation. Lithium-ion batteries provide the benchmark for mature rechargeable battery performance, manufacturing know-how, and practical testing protocols, whereas sodium-ion batteries offer an increasingly relevant platform for examining how cost, abundance, interphase chemistry, and realistic application targets reshape battery design priorities

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[5,6]. In this review, both systems are considered in parallel to highlight where established lithium-ion evaluation paradigms remain applicable and where sodium-ion batteries require distinct metrics, validation strategies, and mechanistic interpretation [1,2,4–6].

1.3. Interfaces, Operando Chemistry, and Scope of the Review

Among the factors that separate proof-of-concept battery studies from realistic cell evaluation, few are as decisive as interfacial chemistry. Electrode/electrolyte interfaces are dynamic regions where ion transport, electron leakage, electrolyte decomposition, mechanical stress, and chemical reconstruction occur simultaneously during cycling [3,7]. The properties of these buried interfaces strongly influence Coulombic efficiency, impedance growth, cyclable ion inventory, thermal stability, and long-term degradation, making them central to the practical behavior of both lithium-ion and sodium-ion batteries [3,7]. This interfacial perspective also explains why operando and in situ characterization have become increasingly important in battery research. Ex situ methods remain indispensable, but they often provide interrupted snapshots of systems that are dynamic, path-dependent, and sensitive to cell history. Techniques capable of probing structural, chemical, and morphological changes under representative electrochemical conditions are therefore essential for linking interphase evolution and degradation mechanisms to practical cell performance [3,7][8].

In this context, the aim of the present review is not to provide an exhaustive catalog of electrode materials, but to examine how battery assessment changes when the discussion moves beyond half-cells and toward practical lithium-ion and sodium-ion batteries. The review first analyzes why half-cell metrics frequently overestimate practical performance and then discusses the cell-level parameters that become decisive under realistic conditions, including electrode balancing, N/P ratio, areal capacity, electrode density, electrolyte amount, and pressure [2]. It then examines interfacial chemistry, operando and in situ characterization strategies, major failure pathways, representative electrode chemistries, practical metrics, mitigation approaches, and validation workflows that can better connect academic materials research with realistic battery development [1,2,4–6][3,7][8].

By integrating interfacial chemistry, operando insight, and practical performance criteria, this review seeks to provide a translational framework for the design and assessment of next-generation lithium-ion and sodium-ion batteries. In doing so, it aims to clarify which concepts can be meaningfully transferred from simplified half-cell studies and which require reinterpretation once the constraints of realistic cells are imposed [2][3,7].

This conceptual transition is summarized schematically in Figure 1. Half-cell testing remains valuable for rapid screening and mechanistic assessment, but it removes several constraints that dominate practical battery operation, including finite Li/Na inventory, realistic electrode balancing, practical areal capacity, high mass loading, lean electrolyte conditions, electrode compaction, stack pressure, and coupled SEI/CEI evolution. Practical full-cell evaluation therefore requires a shift from isolated electrode assessment to an inventory-limited, interface-sensitive, and mechanically constrained electrochemical system.

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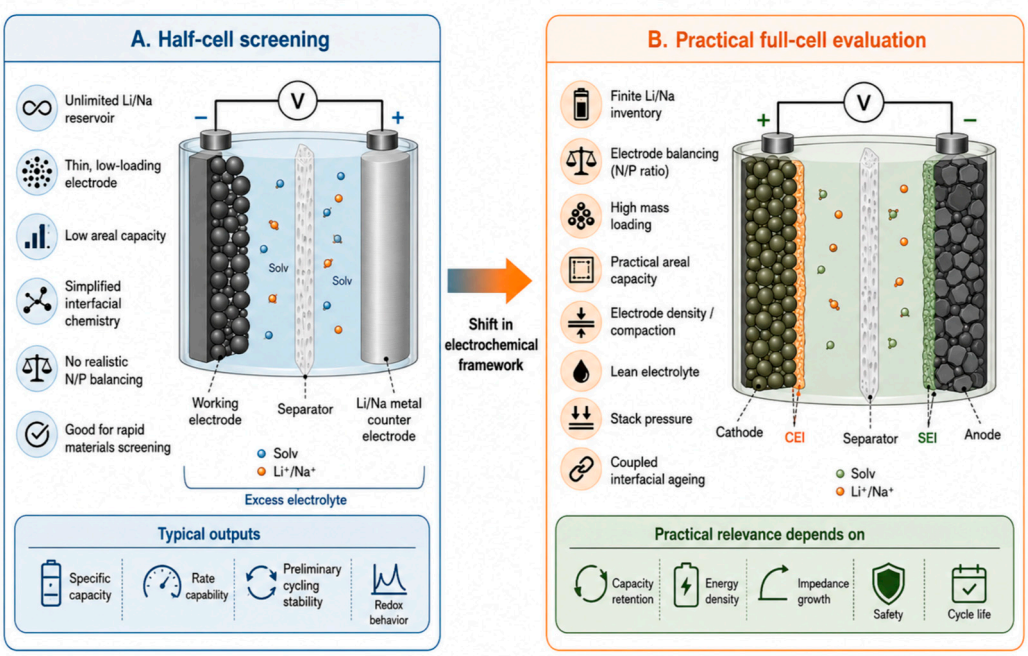

Figure 1. From half-cell screening to practical full-cell evaluation: key constraints lost in simplified testing. Half-cell configurations are useful for rapid materials screening and preliminary mechanistic assessment, but they remove several constraints that dominate realistic battery operation, including finite Li/Na inventory, electrode balancing, practical areal capacity, high mass loading, lean electrolyte conditions, electrode compaction, stack pressure, and coupled interfacial ageing. Practical full-cell evaluation requires a shift from isolated electrode assessment to an inventory-limited, interface-sensitive, and mechanically constrained electrochemical system.

2. Why Half-Cells Are Not Enough

Half-cell testing has played a foundational role in modern battery research and remains one of the most widely used experimental approaches for evaluating emerging electrode materials. Its popularity is understandable: half-cells simplify electrochemical interpretation, reduce experimental complexity, and allow rapid comparison among candidate materials under controlled laboratory conditions. For these reasons, they have become the default platform for screening new anodes and cathodes in both lithium-ion and sodium-ion batteries. However, the same simplifications that make half-cells experimentally attractive also limit their ability to predict practical battery behavior. Recent analyses have shown that many of the parameters governing realistic full-cell performance such as electrode balancing, areal capacity, electrolyte amount, initial coulombic efficiency, and finite alkali inventory are either absent or strongly distorted in half-cell configurations [1–3]. Against this background, the present section examines why half-cells remain useful, but also why they must be interpreted with caution. It first outlines the legitimate experimental role and major advantages of half-cell testing, and then discusses the main limitations that lead to overestimated performance and poor translation to practical cells. This perspective is especially important for sodium-ion batteries, where full-cell implementation remains more sensitive to irreversible alkali loss, hard-carbon behavior, and inventory management than is often apparent from half-cell data alone [1,2,5].

2.1. Role and Advantages of Half-Cell Testing

Half-cells remain indispensable in battery research because they provide a simplified and analytically tractable platform for probing the electrochemical behavior of individual electrode materials. In the most common configuration, the material under investigation is coupled with an alkali-metal counter/reference electrode, allowing the response of the working electrode to be examined without the additional complexity imposed by balancing a full positive–negative electrode pair. This design is especially useful during the early stages of materials development, when the

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primary objective is to determine whether a new compound, composite, or nanostructured architecture exhibits meaningful reversible alkali storage at all. Under these circumstances, half-cells provide a fast and practical route for identifying redox windows, preliminary reversible capacity, polarization trends, and basic cycling behavior [2,3].

A major strength of half-cell testing is that it facilitates mechanistic interpretation. Because the counter electrode is not intended to be the limiting component, electrochemical signals can be attributed more directly to the material of interest. This makes half-cells particularly valuable for studying lithiation or sodiation mechanisms, phase transitions, reaction reversibility, and structure–property relationships. Such configurations are also highly compatible with complementary characterization tools, including ex situ and operando diffraction, spectroscopy, microscopy, and impedance analysis, which are often easier to interpret when one electrode dominates the observable response. Recent perspectives on battery interphases have likewise noted that many operando strategies continue to rely on simplified or model configurations as an important first step toward understanding more complex realistic systems [3].

Half-cells also offer substantial practical advantages in terms of speed, reproducibility, and resource efficiency. They typically require less optimization than full cells, making them suitable for high-throughput screening of materials libraries, electrolyte formulations, surface coatings, or binder systems. This is particularly relevant in nanomaterials research, where a large number of compositions, morphologies, and synthetic variations may need to be compared before narrowing the field to the most promising candidates. In such contexts, half-cells serve as an efficient first filter, allowing researchers to identify broad electrochemical trends before committing to the more demanding process of full-cell design and balancing. Their continued use is therefore not only justified but necessary, provided their scope is clearly recognized [1,2].

Another advantage of half-cell testing is its utility in establishing comparative baselines across materials families. For both lithium-ion and sodium-ion systems, half-cells make it possible to compare different active materials under nominally similar conditions, thereby supporting the development of structure–performance relationships and the identification of promising design rules. In sodium-ion batteries, for instance, half-cell testing has been central to the development of hard carbon and other representative electrode families, even though subsequent full-cell translation remains challenging [1,5]. In this sense, half-cells should not be viewed as flawed by default, but rather as purpose-specific tools whose value lies in controlled screening and mechanistic insight rather than in direct prediction of practical-cell performance.

Accordingly, the problem with half-cells is not their use, but their overinterpretation. When employed as an early-stage research tool, they remain essential for isolating electrode behavior, accelerating discovery, and guiding materials optimization. Difficulties arise only when half-cell metrics are treated as if they were intrinsically transferable to realistic batteries without additional validation. For this reason, the advantages of half-cell testing should be understood as conditional strengths: they are highly effective for screening and mechanistic study, but insufficient on their own for establishing practical relevance [2,3].

2.2. Major Limitations of Half-Cells

Despite their value for early-stage screening and mechanistic analysis, half-cells have intrinsic limitations that restrict their usefulness as predictors of practical battery performance. The most fundamental issue is that they operate under an electrochemical framework that differs markedly from that of realistic full cells. In a conventional half-cell, the alkali-metal counter electrode acts as an effectively unlimited source and sink of Li^+ or Na^+, thereby removing the finite ion inventory constraint that governs practical batteries [2,3]. Under such conditions, irreversible losses during the first cycles may appear acceptable, whereas in a full cell they directly consume the limited cyclable alkali provided by the positive electrode and can substantially reduce usable capacity and energy density [2,9]. This issue is especially severe in sodium-ion systems based on hard carbon, where low initial coulombic efficiency remains one of the principal barriers to practical deployment [1,9].

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A second major limitation is the absence of realistic electrode balancing. In full cells, the electrochemical response depends not only on the intrinsic behavior of each electrode but also on their stoichiometric matching, areal-capacity ratio, electrode loading, and N/P ratio [2,10]. Half-cells largely bypass these constraints, which means that a material may display attractive specific capacity or rate performance without demonstrating whether it remains viable once coupled to a realistic counter electrode under practical conditions. Recent work on full-cell balancing has emphasized that these parameters are not secondary engineering details, but central determinants of accessible capacity, overpotential, degradation rate, and safety [2,10].

Half-cells also distort interfacial chemistry. Because the counter electrode is metallic lithium or sodium, the interphase evolution observed in a half-cell does not necessarily reproduce the coupled behavior of practical positive–negative electrode systems [3,7]. In realistic cells, the formation and evolution of the solid electrolyte interphase (SEI), cathode electrolyte interphase (CEI), and other buried interfaces are influenced by cross-talk between electrodes, finite electrolyte inventory, changing local current distribution, and ongoing interphase repair during cycling [3,7]. These coupled effects are only partially captured in simplified half-cell architectures, which can lead to an incomplete or even misleading picture of interfacial stability and degradation pathways [3].

Another important limitation is the widespread use of low mass loading and excess electrolyte in academic half-cell studies. These conditions are useful for obtaining reproducible proof-of-concept data, but they frequently exaggerate rate capability, suppress transport limitations, and mask electrolyte depletion or wetting-related problems that become important in realistic electrodes [2,10]. In practical cells, higher areal capacities and denser electrodes impose stronger ionic and electronic transport constraints, while lean-electrolyte conditions amplify the consequences of parasitic reactions and interfacial instability [2]. As a result, electrochemical trends established under low-loading half-cell conditions may not survive translation to full cells with application-relevant loadings or pouch-cell formats [2,10].

Half-cells may also overemphasize gravimetric capacity when considered in isolation. High specific capacity in a half-cell does not ensure practical relevance if it is accompanied by low initial coulombic efficiency, low electrode density, unstable interphases, or poor areal performance [1,2,9]. This is particularly relevant for nanostructured materials, which often benefit from short diffusion lengths and large active surface area in half-cell testing, yet suffer from excessive surface reactivity, greater electrolyte consumption, and weak volumetric performance under practical conditions [3]. In sodium-ion research, the consequences are even more pronounced because poor first-cycle efficiency directly penalizes sodium inventory and may require presodiation or modified cathode balancing strategies [1,9].

Finally, half-cells can encourage an overly material-centric interpretation of battery performance. Because they isolate one electrode and suppress many cell-level constraints, they may create the impression that electrochemical behavior is determined mainly by the intrinsic properties of the active material. In practice, however, realistic battery performance emerges from a coupled system involving electrode formulation, balancing, electrolyte quantity, pressure, current distribution, interphase evolution, and degradation of both electrodes simultaneously [2,3,7]. The main limitation of half-cells is therefore not that they are invalid experimental tools, but that they become conceptually misleading when their results are interpreted as direct indicators of full-cell viability without further validation [2,3].

2.3. Performance Overestimation and Translation Gaps

One of the most persistent consequences of half-cell testing is the systematic overestimation of practical battery performance. This overestimation does not usually arise from experimental error, but from the fact that half-cells are designed to isolate one electrode under favorable and highly simplified conditions. As a result, electrochemical outputs such as specific capacity, rate capability, and cycling stability are often interpreted outside the context in which they were obtained. Several studies have emphasized that performance metrics derived from thin electrodes, excess electrolyte,

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and metal-counter-electrode configurations cannot be assumed to translate directly to realistic full cells, where the governing constraints are fundamentally different [2,11,12].

A common source of overestimation is the disproportionate emphasis placed on gravimetric specific capacity. In half-cells, high-capacity values are frequently reported for materials tested at low mass loading and low areal capacity, conditions that minimize transport limitations and facilitate electrolyte access. However, these same materials may perform much less favorably when electrode thickness, tortuosity, ionic transport resistance, and electrolyte wetting become limiting under practical loading conditions. Work on electrode design and areal-capacity optimization has shown that the transition from thin laboratory electrodes to practically relevant electrodes is not a linear scale-up, but a change in the dominant transport and utilization regime [11,12].

Rate capability is also frequently overstated in half-cell studies. Fast charge–discharge behavior measured in low-loading electrodes can reflect short diffusion distances and favorable current distribution rather than intrinsically scalable kinetics. Once the same material is incorporated into thicker, denser, and better-balanced full cells, transport bottlenecks and polarization often become much more severe. This is one reason why apparently outstanding half-cell rate data do not always survive translation to realistic cell formats. The broader implication is that half-cell rate performance is often a useful screening indicator, but not a reliable predictor of practical power capability unless it is supported by more realistic electrode architectures and cell conditions [2,11,12].

Translation gaps are even more pronounced when first-cycle losses are considered. In lithium-ion systems, low initial coulombic efficiency reduces the usable lithium inventory of the full cell; in sodium-ion systems, the penalty can be even more severe because hard carbon anodes often suffer substantial irreversible sodium consumption during early cycling. In half-cells, these losses may be partially concealed using metallic sodium as an effectively unlimited sodium source. In practical sodium-ion cells, by contrast, poor initial coulombic efficiency directly reduces cell-level energy density and may necessitate presodiation, cathode oversizing, or other compensatory strategies [5,9]. This creates a clear example of how a material that appears acceptable in half-cells may still be poorly suited to realistic full-cell implementation [5,9].

Another important translation gap concerns the interpretation of interfacial stability. Long cycle life in half-cells is often taken as evidence of robust SEI or CEI formation, yet the interphase chemistry of practical cells is influenced by coupled electrode behavior, cross-talk, finite electrolyte inventory, and nonuniform local current distributions. Perspectives on buried interfaces and operando interphase characterization have emphasized that simplified half-cell configurations can miss exactly those interfacial processes that dominate long-term degradation in realistic cells [3]. In this sense, half-cell stability data may be directionally informative, but they are frequently insufficient to establish practical durability on their own [3].

Performance overestimation also contributes to broader misunderstandings about technology readiness. In sodium-ion research, for example, promising half-cell data are sometimes discussed as if they implied near-term competitiveness with lithium-ion batteries. However, techno-economic assessments have shown that competitiveness depends on much more than material-level electrochemistry: it also depends on full-cell energy density, manufacturability, cycle life, cost trajectories, and application-specific requirements [5]. This means that translation gaps are not only scientific or electrochemical; they are also technological and commercial. A material that performs impressively in a coin-cell half-cell may still fall short when judged against the demands of practical storage systems [5].

For these reasons, the main risk of half-cell overperformance is not simply that it produces optimistic numbers, but that it can distort research priorities. When materials are selected primarily on the basis of half-cell capacity, early-cycle reversibility, or short-term rate performance, the field may overvalue properties that are easy to measure under idealized conditions while undervaluing those that actually govern practical success, such as areal performance, electrode density, initial coulombic efficiency, realistic balancing, and interfacial durability [2,5,9,11,12]. A more translational

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evaluation framework therefore requires that half-cell results be treated as preliminary indicators rather than as stand-alone evidence of practical viability [2,3,5,9,11,12].

3. Key Parameters in Practical Cells

Moving from half-cells to practical batteries requires more than simply replacing a metal counter electrode with a second insertion electrode. It involves a shift toward a coupled electrochemical system in which cell performance is determined not only by the intrinsic properties of each active material, but also by the way both electrodes are configured, balanced, loaded, compacted, and operated together. In practical cells, parameters such as full-cell architecture, electrode balancing, areal capacity, electrode density, electrolyte quantity, and external pressure cease to be secondary experimental details and become central determinants of energy density, polarization, cycle life, and safety [2,10,12,13]. This is precisely why cell-level optimization often reveals limitations that remain invisible in half-cell studies.

The importance of these design variables has become increasingly evident in both lithium-ion and sodium-ion batteries. In lithium-ion systems, recent work has highlighted how high-loading electrodes, stoichiometric mismatch, and format-dependent polarization can strongly alter the apparent benefits of advanced materials once they are evaluated in full cells or pouch cells [2,10]. In sodium-ion batteries, the challenge is often even greater because practical cell design must account for lower energy density, harder constraints on sodium inventory, and greater sensitivity to first-cycle losses and interfacial instability [13]. Accordingly, a realistic assessment of battery materials requires that key cell-design parameters be treated as core scientific variables rather than as downstream engineering adjustments [2,10,12,13].

3.1. Full-Cell Configuration and Electrode Balancing

A full cell differs fundamentally from a half-cell because both electrodes are electrochemically active, finite, and mutually constraining. In this configuration, the accessible cell capacity is not governed by the best-performing electrode in isolation, but by the coupled balance between the positive and negative electrodes across the full operating window. This means that practical cell behavior depends on how the capacities, kinetics, voltage profiles, and irreversible losses of both electrodes interact during cycling [2,10]. As a result, full-cell configuration is not a mere assembly choice, but a primary determinant of whether a material can deliver meaningful performance under realistic conditions.

One of the central variables in full-cell design is electrode balancing. In practical terms, balancing refers to the relative sizing of the negative and positive electrodes so that neither side becomes prematurely limiting, unstable, or unsafe during operation. This balancing problem is commonly expressed through stoichiometric matching and, more specifically, through the negative-to-positive capacity ratio, although the true design problem is broader and also includes overpotential distribution, irreversible capacity loss, kinetic mismatch, and the selected application target [2,10]. Recent full-cell studies have shown that optimized N/P ratios do not simply maximize capacity; they also influence polarization, rate capability, aging behavior, and the likelihood of lithium plating or other side reactions under demanding conditions [10].

The importance of electrode balancing becomes especially clear at higher areal loading and in more practical cell formats. Williams et al. showed in high-loading Li-ion full cells and pouch cells that optimized N/P ratios minimized overpotentials at both low and high states of charge, while inappropriate balancing shifted the burden of polarization between the graphite anode and the cathode and negatively affected rate capability and cycling stability [10]. These results are important because they demonstrate that balancing is not only a matter of nominal capacity matching, but also of managing how electrochemical stress is distributed across the full cell during operation [10].

The same principle is reflected more broadly in the literature on practical electrode design. Gallagher et al. showed that increasing electrode thickness or areal capacity in lithium-ion electrodes does not automatically improve useful cell-level performance, because higher loadings also intensify

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ionic transport limitations and utilization gradients across the electrode thickness [12]. In a full cell, these effects interact with balancing choices, meaning that the optimal configuration cannot be defined by capacity values alone. Instead, it must reflect a compromise among areal capacity, transport resistance, utilization efficiency, and electrochemical stability [12].

A further point is that full-cell configuration can expose degradation behavior that remains hidden in half-cells. In the recent review on LMFP-based rechargeable batteries, it is explicitly noted that much academic work still relies on LMFP/Li half-cells, whereas practical deployment requires non-lithium counter electrodes such as graphite or LTO, where the coupled full-cell chemistry reveals additional limitations related to lithium loss, temperature sensitivity, and interfacial degradation [13]. The same review shows that capacity retention and thermal behavior in LMFP full cells may differ substantially from what is inferred from half-cell performance, underlining the importance of full-cell validation early in materials assessment [13].

These issues are equally relevant, and in some respects even more restrictive, in sodium-ion batteries. Recent sodium-ion reviews emphasize that hard carbon and leading cathode families may show encouraging half-cell behavior, yet practical sodium-ion full cells must contend with tighter sodium inventory management, lower cell-level energy density, and higher sensitivity to first-cycle inefficiencies and interfacial losses [14]. Consequently, full-cell balancing in sodium-ion systems is not simply an adaptation of lithium-ion practice, but a distinct design challenge that requires careful control of both electrode capacities and sodium inventory from the outset [14].

Overall, full-cell configuration and electrode balancing should be understood as part of the scientific evaluation of battery materials rather than as a final engineering correction. A material that performs well in a half-cell may still fail to deliver competitive full-cell behavior if its kinetic profile, first-cycle losses, voltage curve, or compatibility with the opposing electrode led to unfavorable balancing requirements. For this reason, realistic battery development increasingly depends on evaluating materials within properly balanced full-cell architectures that reflect the practical constraints of the targeted application [2,10,13,14].

3.2. N/P Ratio, Mass Loading, and Areal Capacity

Among the parameters that most strongly determine whether a battery material can function under realistic conditions, the negative-to-positive capacity ratio (N/P ratio), mass loading, and areal capacity are particularly important. These variables are closely interconnected: the selected N/P ratio influences lithium or sodium inventory management and overpotential distribution, while mass loading and areal capacity determine how much active material is actually incorporated per unit area and whether the electrode architecture approaches practical relevance [2,5,10,12]. In real cells, these factors do not act independently, but define a coupled design space in which energy density, transport limitations, fast-charging capability, and degradation must be balanced simultaneously [2,15].

The N/P ratio is often introduced as a simple measure of capacity balancing between the negative and positive electrodes, but in practice it has broader electrochemical implications. In lithium-ion full cells, adjusting the N/P ratio changes the state-of-charge window of each electrode, alters local polarization behavior, and affects the risk of undesirable side reactions such as lithium plating under demanding conditions [2,10,16]. Recent work on balanced high-loading Li-ion cells has shown that the optimum N/P ratio is not universal, but depends on the interplay between stoichiometry, kinetics, and cell format; values that appear acceptable in coin cells may behave differently in pouch cells, where polarization and transport heterogeneity become more pronounced [10]. Likewise, data-driven optimization studies have identified N/P ratio as one of the most influential cell-design variables when energy density, fast charging, discharge rate, and lifetime are considered simultaneously [15].

Mass loading is equally critical because it controls the transition from proof-of-concept electrodes to more realistic electrodes. Thin, low-loading electrodes are convenient for laboratory testing because they reduce ionic transport limitations, facilitate wetting, and often yield high

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apparent utilization. However, increasing mass loading inevitably leads to thicker electrodes, longer transport pathways, and greater sensitivity to pore structure, tortuosity, and electrolyte accessibility [12,17]. Gallagher et al. showed that optimizing areal capacity in lithium-ion electrodes requires understanding the trade-off between thicker electrodes for higher energy density and the resulting loss in rate capability and utilization [12]. More recent mechanistic studies on thick electrodes similarly indicate that increasing areal density can change pore microstructure and mass-transfer dynamics in ways that compromise redox homogeneity and high-rate performance [17].

Areal capacity is the practical metric that links electrode design to device-level relevance. While gravimetric specific capacity remains useful for comparing active materials, it is areal capacity that better reflects whether an electrode contributes meaningfully to the energy output of a real cell [2,12]. This is why very high specific capacities obtained with low-loading electrodes may have limited practical significance if the resulting areal capacity remains too small. Tutorial and perspective work on practical electrode design has stressed that areal-capacity targets must be considered together with thickness, porosity, utilization, and balancing, since simply increasing loading does not guarantee a better cell unless the electrode remains electrochemically accessible across its full thickness [2,12].

The interaction among N/P ratio, mass loading, and areal capacity becomes even more important under fast-charging or high-power conditions. Higher areal capacities can improve projected energy density, but they also raise diffusion resistance and current heterogeneity, making the cell more sensitive to balancing errors and kinetic mismatch [10,12,15]. This means that N/P optimization cannot be decoupled from loading optimization: an N/P ratio that performs well at low areal capacity may not remain optimal once electrode thickness and transport limitations increase [12,15]. The same principle has been observed in recent full-cell and pouch-cell studies, where balancing strategies that minimized polarization and improved performance at practical loading differed from those inferred from simpler small-cell conditions [12].

These considerations are also highly relevant to sodium-ion batteries. Because sodium-ion systems generally operate with lower cell-level energy density and are often more sensitive to first-cycle losses, the penalties associated with poor balancing or insufficient areal capacity can be particularly severe [2,5]. Recent assessments of sodium-ion roadmaps emphasize that competitiveness with lithium-ion technology will depend not only on abundant materials and cost advantages, but also on achieving practical full-cell metrics, including sufficient areal capacity and efficient sodium inventory management [5]. Accordingly, N/P ratio, mass loading, and areal capacity should be treated not as reporting details, but as core translational parameters that determine whether promising material-level results can become meaningful practical-cell performance [2,5].

3.3. Electrode Density, Electrolyte Conditions, and Pressure

Electrode density, electrolyte conditions, and external pressure are closely interconnected parameters in practical cells because all three influence how effectively a given electrode architecture can deliver usable energy under realistic constraints. In contrast to thin, loosely packed laboratory electrodes operated with abundant electrolyte and minimal mechanical confinement, practical batteries require denser electrodes, controlled electrolyte inventory, and mechanically stable stack conditions in order to approach competitive volumetric energy density and reproducible cycling behavior [2,18,19]. As a result, these parameters are not merely manufacturing details, but integral determinants of transport, interfacial stability, and degradation in full-cell operation.

Electrode density is particularly important because it mediates the trade-off between gravimetric accessibility and volumetric relevance. Calendering is routinely used to densify electrodes, decrease porosity, and improve particle–particle and particle–current-collector contact, thereby increasing volumetric energy density and often reducing electronic resistance. At the same time, excessive densification can compromise pore connectivity, hinder electrolyte infiltration, intensify concentration gradients, and promote mechanical damage in brittle or high-Ni electrode materials [18–20]. Recent work on calendering has shown that the relationship between compaction and performance is non-monotonic: optimal calendering can improve volumetric performance and

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cycling stability, whereas over-calendering may reduce rate capability or accelerate degradation through microstructural damage and transport limitations [18–20].

Electrolyte conditions are equally decisive. A large excess of electrolyte can mask interfacial instability, facilitate wetting, and improve apparent utilization, but it also distances laboratory testing from realistic cell design. Under lean-electrolyte conditions, parasitic reactions consume a larger fraction of the available liquid phase, wetting limitations become more consequential, and local transport heterogeneity becomes more difficult to ignore. For this reason, recent practical-cell studies have stressed that electrolyte amount must be treated as a core design variable rather than a secondary experimental convenience [2,21]. In nickel-rich lithium-ion cells, lean-electrolyte operation has been shown to impose a clear trade-off between electrochemical stability, safety, and material utilization, underscoring the fact that results obtained under electrolyte-rich conditions may significantly overestimate practical robustness [21].

Pressure adds a further layer of complexity because practical cell performance is not governed only by chemistry and transport, but also by evolving mechanical contact within the stack. In pouch cells and other mechanically compliant formats, external pressure influences interfacial contact, separator compression, local current distribution, and the ability of the cell to accommodate swelling and relaxation during cycling. Recent studies have shown that the method by which pressure is applied matters as much as the nominal pressure itself: constant-pressure fixtures and fixed-displacement fixtures do not produce equivalent pressure histories, and the resulting electrochemical behavior can differ substantially over time [22]. This means that “pressure” cannot be treated as a single scalar parameter in practical testing, since both its magnitude and temporal evolution affect cell behavior.

The importance of pressure becomes even more evident in systems that undergo substantial volume changes, such as silicon-containing anodes or lithium-metal-based pouch cells. In silicon-composite pouch cells, externally applied mechanical pressure has been shown to alter electrochemical performance and cycling behavior by changing the evolution of contact conditions and electrode expansion during operation [23]. Similarly, in pouch-type Li||$LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ (Li||NCM90) cells, stack pressure was found to significantly affect electrochemical behavior and the uniformity of Li plating, highlighting the broader principle that pressure can modulate degradation and reaction homogeneity in high-energy cells [24]. Although these examples are not identical to conventional graphite-based lithium-ion full cells, they illustrate a practical lesson that is widely relevant: pressure is an active electro-chemo-mechanical variable, not just a packaging condition.

These considerations are also relevant to sodium-ion batteries, although the specific optimal conditions may differ. Sodium-ion systems face their own constraints related to lower cell-level energy density, distinct electrolyte chemistry, and a stronger dependence on interfacial efficiency and sodium inventory management. Recent reviews have emphasized that electrolyte formulation is central to practical sodium-ion development, not only because of ionic conductivity and low-temperature behavior, but also because of its influence on SEI/CEI formation, oxidative stability, safety, and compatibility with hard carbon and leading cathode families [4,25]. This implies that, just as in lithium-ion batteries, electrolyte amount and electrode densification in sodium-ion cells cannot be optimized independently of interphase behavior and practical full-cell design.

As summary, electrode density, electrolyte conditions, and pressure should be viewed as coupled parameters that define the practical operating window of a cell. A dense electrode may improve volumetric energy density but become transport-limited under lean electrolyte; a favorable electrolyte formulation may still fail if the electrode is over-calendered or mechanically poorly constrained; and a well-balanced full cell may underperform if pressure evolution causes contact loss or local heterogeneity during cycling. For this reason, realistic battery evaluation requires these variables to be treated as fundamental elements of cell design rather than as secondary parameters to be fixed after material selection.

3.4. Practical Constraints in Li-Ion and Na-Ion Cells

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Although lithium-ion and sodium-ion batteries share the same general rocking-chair operating principle, the constraints that determine their practical implementation are not the same. Lithium-ion cells benefit from a far more mature manufacturing ecosystem, higher cell-level energy density, and a longer history of optimization in graphite-based full cells, layered-oxide cathodes, electrolyte formulations, and industrial processing routes [2,26]. Sodium-ion cells, in contrast, are developing under a different practical framework in which material abundance and lower projected cost are major advantages, but lower energy density, tighter alkali-inventory constraints, and stronger sensitivity to first-cycle losses remain significant challenges [1,4,26]. These differences mean that practical relevance cannot be assessed using a single chemistry-independent standard [4,26].

In lithium-ion batteries, one of the main practical constraints is the need to reconcile high energy density, long cycle life, fast charging, and safety within the same cell. These objectives are often in tension. Increasing Ni content in layered oxides can raise energy density, but also intensifies surface reactivity, thermal instability, and interfacial degradation. Likewise, pushing graphite-based cells toward faster charging increases the likelihood of lithium plating unless electrode balancing, local current distribution, temperature management, and electrolyte design are carefully controlled [2,27]. Practical Li-ion design is therefore constrained not only by the properties of the active materials themselves, but by the narrow operational space in which performance, durability, and safety remain simultaneously acceptable [2,27].

Sodium-ion batteries face a different set of dominant limitations. The larger ionic radius and higher mass of sodium reduce both theoretical and practical gravimetric energy density relative to lithium-ion systems, while hard carbon anodes introduce a stronger penalty associated with low initial coulombic efficiency and irreversible sodium consumption [1,4,26]. Because sodium-ion full cells operate with a finite sodium inventory, these early-cycle losses directly reduce usable capacity and energy density unless compensated by presodiation strategies, cathode oversizing, or improved interphase control [1,4]. Sodium inventory management therefore becomes a more explicit and central design variable than in conventional graphite-based lithium-ion cells [1,4].

Cathode-side constraints also differ appreciably between the two technologies. Lithium-ion batteries rely heavily on layered oxides and related cathode chemistries that already have established processing routes and relatively well-defined degradation mechanisms, even if high-voltage operation and Ni-rich compositions still pose serious challenges [2,27]. Sodium-ion batteries rely more strongly on layered oxides, polyanionic compounds, and Prussian blue analogs, each of which brings distinct practical limitations such as defect chemistry, water sensitivity, moderate working voltage, or restricted volumetric competitiveness [4,14,26]. For this reason, sodium-ion optimization often follows a different logic, one in which cost, robustness, and application-specific suitability may be more decisive than maximizing energy density alone [14,26].

Another important distinction lies in the intended application space. Lithium-ion cells remain the dominant choice for portable electronics and electric vehicles because of their superior energy density and manufacturing maturity. Sodium-ion cells are more frequently discussed in connection with stationary storage, grid support, and other cost-sensitive applications where abundance, affordability, and potentially improved safety can compensate for lower energy density [5,26]. Techno-economic analyses have accordingly emphasized that sodium-ion competitiveness should not be judged only by whether it matches lithium-ion performance across all metrics, but by whether it reaches sufficient practical performance within well-defined market niches [5]. This application dependence is itself a practical constraint, since it shapes which trade-offs between capacity, power, cycle life, safety, and cost are acceptable [5,26].

Early commercial and near-commercial sodium-ion cells are now beginning to make these issues more visible at the device level. Recent evaluations of early sodium-ion pouch or commercial-format cells indicate that practical voltage windows, control-relevant behavior, and cell-level performance may differ substantially from what would be inferred from materials-level half-cell studies alone [5,28]. This is particularly important because it confirms that many of the decisive constraints only

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emerge when both electrodes, the finite alkali inventory, the electrolyte system, and the real operating window are considered together [2,5,28].

These observations highlight that practical Li-ion and Na-ion cells are constrained by different combinations of chemistry, interfacial behavior, inventory management, manufacturability, and target application. In lithium-ion batteries, the main challenge is often how to push an already mature technology toward higher energy density and faster charging without compromising safety and lifetime. In sodium-ion batteries, the more pressing issue is how to manage lower energy density, first-cycle inefficiencies, and chemistry-specific design penalties while identifying the application domains where the technology can be genuinely competitive [1,4,5,26]. Recognizing these differences is essential if new materials and cell concepts are to be evaluated on realistic terms rather than against oversimplified expectations.

The processes discussed in the preceding subsections illustrate that electrode–electrolyte interfaces are dynamic, chemically active, and structurally evolving regions whose behavior governs much of the long-term performance of lithium- and sodium-ion batteries. Table 1 provides a concise comparative overview of these interfacial phenomena, highlighting their underlying mechanisms, commonly used characterization strategies, and implications for practical cell operation. By organizing these aspects side by side, the table helps clarify how apparently distinct degradation pathways are interconnected through coupled electrochemical, mechanical, and transport processes.

Table 1. Key practical-cell parameters that are commonly underrepresented in half-cell evaluation and their implications for translational relevance.

Parameter	Why it matters in practical cells	Typical distortion in half-cell testing	Practical consequence if neglected	References
Full-cell configuration	Real batteries are governed by coupled positive/negative electrode behavior rather than one isolated working electrode.	Metal-counter-electrode setups remove realistic counter-electrode constraints.	Overestimation of accessible capacity and cycling stability.	[2]
Finite alkali inventory	Practical cells have limited cyclable Li or Na.	Li or Na metal acts as an effectively unlimited ion reservoir.	Irreversible losses appear artificially tolerable.	[2,4]
N/P ratio	Governs stoichiometric balance, polarization distribution, and plating risk.	Often absent or not meaningful in half-cells.	Poor transferability to practical full-cell design.	[2]
Mass loading	Controls whether the electrode reflects realistic thickness and transport conditions.	Thin electrodes reduce diffusion limitations and exaggerate utilization.	Inflated rate capability and misleading cycling behavior.	[2]
Areal capacity	Better indicator of device-level relevance than gravimetric capacity alone.	Low-loading electrodes may show high specific capacity but poor areal relevance.	Misleading assessment of practical energy output.	[12]
Electrolyte amount	Lean electrolyte strongly affects transport, wetting, side reactions, and durability.	Excess electrolyte masks depletion and interfacial instability.	Overestimation of robustness and cycling tolerance.	[2]
Electrode density/ compaction	Determines volumetric relevance, transport tortuosity, and contact quality.	Looser electrodes may appear kinetically superior.	Translation failure when moving to compact practical electrodes.	[18]
Sodium inventory sensitivity	Particularly important in SIBs with hard carbon and low ICE.	Na-metal half-cells can conceal the full-cell penalty of Na loss.	Poor full-cell feasibility despite promising half-cell data.	[1]

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4. Interfacial Chemistry

Interfacial chemistry lies at the center of practical battery behavior because the electrode/electrolyte interface is the region where charge transfer, electrolyte decomposition, ion desolvation, passivation, and many degradation reactions converge. In real cells, performance is not dictated solely by the bulk structure of the active materials, but also by the chemistry, morphology, and stability of the interphases that form on their surfaces during operation. This is particularly important in lithium-ion and sodium-ion batteries, where the solid electrolyte interphase (SEI) at the negative electrode and the cathode electrolyte interphase (CEI) at the positive electrode strongly influence Coulombic efficiency, impedance growth, alkali inventory retention, and long-term cycling stability. Recent reviews emphasize that both SEI and CEI are dynamic, condition-dependent interphases rather than static passivation films, and that their formation and evolution must be understood under realistic electrochemical conditions.

From a practical standpoint, interfacial chemistry is where many of the translation gaps discussed in previous sections become most visible. Half-cell testing often masks the extent to which interphase behavior is shaped by finite alkali inventory, coupled electrode operation, electrolyte amount, local current distribution, and the evolving chemistry of both electrodes together. This is why recent literature increasingly treats interphases not as secondary by-products of cycling, but as functional components that control transport, selectivity, parasitic reactivity, and degradation pathways. In this section, the discussion therefore focuses first on the formation and evolution of SEI and CEI, and then on how electrolyte chemistry, additives, binders, conductive agents, and formulation variables modulate these buried interfaces in practical lithium-ion and sodium-ion cells.

The complexity of interfacial chemistry in practical batteries is summarized schematically in Figure 2. Rather than acting as static passivation layers, the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) evolve dynamically in response to electrolyte decomposition, local redox conditions, mechanical stress, and continued cycling. Their growth, repair, and reconstruction are closely coupled to cross-talk between both electrodes, so that interfacial instability at one side of the cell can propagate through the electrolyte and affect the behavior of the opposite electrode.

As illustrated in Figure 2, these coupled processes link local surface chemistry to whole-cell consequences, including cyclable Li/Na loss, transition-metal shuttling, gas evolution, and impedance growth. The figure also highlights that, although lithium-ion and sodium-ion batteries share the same broad interfacial framework, the relative importance of specific failure drivers differs between the two chemistries. In lithium-ion batteries, graphite interphases, Li plating risk, and cathode instability at high energy density are especially important, whereas in sodium-ion batteries hard-carbon interphases, stronger Na-inventory penalties, and distinct cathode/interphase chemistry become more central constraints.

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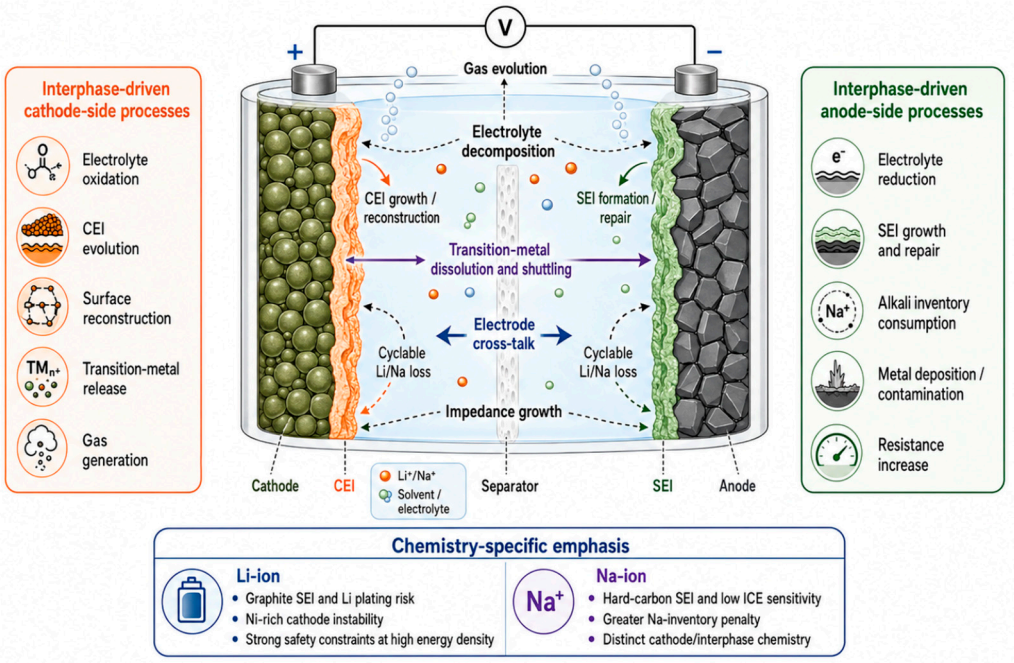

Figure 2. Dynamic interphase evolution and electrode cross-talk in practical Li-ion and Na-ion cells. In practical full cells, the cathode electrolyte interphase (CEI) and solid electrolyte interphase (SEI) are dynamic, coupled interphases whose evolution is governed by electrolyte decomposition, local redox conditions, and continuous electrochemical and mechanical perturbation. On the cathode side, interphase-driven processes include electrolyte oxidation, CEI evolution, surface reconstruction, transition-metal release, and gas generation. On the anode side, electrolyte reduction, SEI growth and repair, alkali inventory consumption, metal deposition or contamination, and resistance increase become dominant consequences of interfacial instability. Through electrode cross-talk and transition-metal shuttling, these local interfacial processes propagate into whole-cell ageing phenomena such as cyclable Li/Na loss and impedance growth. The figure also highlights chemistry-specific emphasis in Li-ion and Na-ion batteries, where the shared interfacial framework leads to distinct practical penalties depending on electrode chemistry and alkali inventory sensitivity.

Having established this coupled interfacial framework, the next step is to examine how the two principal interphases in rechargeable batteries, the SEI and the CEI, are formed and how they evolve during operation. Although they originate at opposite electrodes and under different electrochemical conditions, both interphases play analogous functional roles: they regulate ion transport, suppress or promote parasitic reactions, influence impedance growth, and determine how efficiently the cell preserves its finite Li or Na inventory. Their behavior is therefore not only a matter of local surface chemistry, but a central factor in the practical durability of full cells. The following subsection focuses on the formation and evolution of SEI and CEI layers, emphasizing their chemical heterogeneity, dynamic restructuring, mechanical vulnerability, and dependence on cell configuration. Particular attention is given to why interphases observed in half-cells may not fully represent those formed in practical full cells, especially in sodium-ion systems where hard-carbon SEI formation and irreversible Na consumption are strongly linked to full-cell feasibility.

4.1. SEI and CEI Formation and Evolution

The formation of the solid electrolyte interphase (SEI) and the cathode electrolyte interphase (CEI) is one of the earliest and most consequential events in battery operation. Although both interphases originate from electrolyte instability at electrified interfaces, they emerge under different thermodynamic and kinetic conditions and therefore develop distinct compositions, morphologies, and functional roles [3,29,30]. The SEI is generally produced by reductive decomposition of electrolyte components at the negative electrode, whereas the CEI forms through oxidative

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decomposition pathways at the positive electrode. In both cases, the resulting interphase must simultaneously suppress continued parasitic reactivity and allow efficient transport of Li^+ or Na^+, so its chemistry directly influences Coulombic efficiency, impedance evolution, and long-term cell stability [3,30].

At the anode side, SEI formation is typically initiated when the electrode potential falls below the electrochemical stability window of the electrolyte. The first-cycle interphase is therefore not a predesigned layer, but the kinetic outcome of competing decomposition pathways involving solvents, salts, impurities, and additives [1,30]. Rather than a uniform film, the SEI is now widely understood as a chemically heterogeneous interphase containing inorganic-rich and organic-rich domains whose spatial distribution depends on local solvation structure, current density, temperature, and substrate chemistry [1,30]. This point is important because the electrochemical quality of the SEI does not depend only on its thickness, but also on its continuity, mechanical compliance, ionic conductivity, and resistance to repeated rupture and repair during cycling [30].

The CEI forms through a different but equally important process. At high electrode potentials, electrolyte oxidation, surface oxygen activity, transition-metal surface chemistry, and residual surface species all contribute to the buildup of a cathode-side interphase [3,29]. In high-voltage or Ni-rich layered oxides, CEI formation is strongly coupled to surface reconstruction, gas evolution, and transition-metal dissolution, which means that the CEI is not merely a passive oxidation product but part of a broader interfacial degradation network [3,29,31]. As a result, CEI composition and stability influence not only cathode passivation, but also impedance rise, electrolyte consumption, and the extent of electrode cross-talk during long-term cycling [3,31].

A central point for practical batteries is that neither SEI nor CEI should be treated as a one-time formation event restricted to early cycles. Both continue to evolve as the cell is cycled, stored, heated, fast charged, or driven toward higher voltage limits [3,30]. Recent work on SEI evolution in lithium-ion batteries has emphasized that the interphase responds differently under standard cycling, fast charging, overcharge, overdischarge, and temperature excursions, with distinct consequences for growth rate, composition, and transport behavior [30]. Likewise, recent CEI studies have shown that cathode-side interphases may progressively shift in composition as electrolyte oxidation, fluoride enrichment, solvent fragmentation, and surface reconstruction accumulate over time [3,31,32]. These changes are particularly relevant because a CEI that appears stabilizing during early cycling may later become a source of resistance growth or surface instability under realistic operating conditions [3,32].

Mechanical effects are inseparable from this chemical evolution. Repeated expansion and contraction of the host structure can fracture the SEI, expose fresh active surface, and trigger renewed electrolyte decomposition, creating a self-reinforcing cycle of interphase repair and alkali loss [30,33]. This process is especially severe in alloy-type or conversion-type anodes, but it is not limited to them; even graphite and hard carbon can develop local heterogeneity, stress concentration, and SEI instability during prolonged cycling [1,30]. On the cathode side, surface reconstruction and local lattice strain can change the chemistry and integrity of the CEI, especially in layered oxides operated at high state of charge [3,31,33]. From this perspective, interphase evolution is not purely chemical but electro-chemo-mechanical, and this coupling is one reason why interfacial degradation remains difficult to predict from simplified tests alone [33].

The practical significance of SEI and CEI evolution becomes even clearer when finite alkali inventory is considered. In full cells, continued interphase growth consumes cyclable lithium or sodium and therefore reduces usable capacity even if the bulk active materials remain structurally intact [1,30]. This is particularly critical in sodium-ion batteries, where irreversible sodium losses are often more penalizing than analogous losses in conventional lithium-ion cells. Hard carbon anodes, while highly promising for sodium-ion technology, still face persistent challenges associated with low initial Coulombic efficiency and ongoing SEI-related sodium consumption [1,34]. In this context, interphase evolution is not simply a surface-science issue; it is a core determinant of full-cell energy retention and design feasibility [1,34].

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Another important point is that the interphases observed in half-cells may differ substantially from those formed in realistic full cells. Because metallic lithium or sodium counter electrodes alter the chemical environment, current distribution, and alkali reservoir, they can produce interphase signatures that are not fully representative of practical paired-electrode operation [3,34]. Recent sodium-ion work has explicitly demonstrated that the use of sodium metal as a counter electrode can significantly affect the observed SEI evolution and may lead to misleading conclusions about hard-carbon behavior in realistic full-cell conditions [34]. This has broad implications: SEI and CEI properties should not be regarded as fixed attributes of isolated materials, but as emergent outcomes of the full electrochemical environment in which the electrode is evaluated [3,34].

Recent advances in operando and near-operando characterization are beginning to clarify these issues. Techniques such as operando Raman spectroscopy, X-ray-based methods, liquid-phase electron microscopy, and multimodal interfacial analysis have shown that interphases are spatially and temporally heterogeneous, and that their evolution cannot be fully reconstructed from endpoint post-mortem analysis alone [3,32]. These methodological advances are especially valuable because they move the field away from static pictures of SEI and CEI and toward a more realistic view in which formation, repair, dissolution, and reorganization occur continuously during battery operation [3,32]. This change in perspective is essential for understanding why nominally similar materials can behave very differently once transferred from idealized half-cell tests to practical full-cell conditions.

What emerges from these studies is that SEI and CEI are better understood as dynamic functional interphases that mediate transport, passivation, and degradation simultaneously. Their early formation may enable reversible cycling, but their subsequent evolution often determines whether a battery maintains low impedance, high efficiency, and acceptable capacity retention over time[3,29,30]. For this reason, any realistic discussion of practical lithium-ion and sodium-ion cells must consider not only how interphases are formed, but also how they change with cycling conditions, electrode chemistry, and cell architecture. This naturally leads to the next subsection, where electrolyte decomposition and additive chemistry are addressed as direct drivers of interphase composition and stability.

4.2. Electrolyte Decomposition and Additive Effects

Electrolyte decomposition is not merely a parasitic side process in rechargeable batteries; it is one of the primary chemical routes through which SEI and CEI components are generated, consumed, and continuously restructured during operation. In practical cells, decomposition pathways depend on electrode potential, solvent environment, salt chemistry, local current distribution, temperature, impurity content, and the presence of functional additives. This means that interphase chemistry cannot be understood independently of electrolyte formulation: the electrolyte is not simply a transport medium, but a reactive precursor reservoir for the interphases that ultimately govern passivation, impedance, and long-term stability [25,35,36].

At the reductive side, electrolyte decomposition is strongly coupled to the lowest unoccupied molecular orbitals of solvents, salts, and additive molecules, as well as to the local solvation structure around Li^+ or Na^+. Molecules that are preferentially reduced at the negative electrode can produce inorganic-rich or organic-rich SEI components depending on their composition and reaction sequence. In lithium-ion batteries, this chemistry has long been exploited through film-forming additives such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), which are used to promote earlier, more selective reductive decomposition and thereby alter the composition and compactness of the interphase. Recent reviews emphasize, however, that additive action is not universal: the same additive can be beneficial, neutral, or detrimental depending on electrode chemistry, salt choice, voltage window, and operating conditions [35].

At the oxidative side, electrolyte decomposition is equally important because CEI formation is strongly influenced by the oxidation stability of the solvent–salt system and by the reactivity of the cathode surface. This is particularly relevant in high-voltage and Ni-rich lithium-ion cathodes, where the electrolyte must withstand not only high potentials but also reactive surface species, trace

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water/HF chemistry, transition-metal dissolution, and oxygen-related surface instability. Recent reviews on electrolyte engineering for Ni-rich cathodes show that additive selection, fluorination strategies, and solvation-structure regulation are increasingly being used to suppress harmful oxidation products and construct more robust cathode-electrolyte interphases rather than merely optimizing bulk ionic conductivity [36]. In this context, additives are not only SEI builders at the anode; they are also CEI regulators at the cathode [36].

A particularly important recent lesson is that additive effects can be electrode-specific and sometimes counterintuitive. FEC is a well-known example: it has traditionally been discussed mainly as an anode-side film-forming additive, especially in sodium-ion batteries. However, recent work on sodium vanadium phosphate systems showed that FEC can also exert a distinct cathode-side effect by promoting the formation of a NaF-rich CEI on the cathode surface, thereby reducing interfacial resistance and improving cycling and rate behavior [37]. This finding is important because it illustrates that additive action should not be assigned too narrowly to one electrode based only on conventional half-cell intuition; in practical cells, the same molecule may influence both interphases through different decomposition pathways [37].

In sodium-ion batteries, electrolyte decomposition and additive effects are particularly sensitive to solvent family and Na^+ solvation structure. Ether-based electrolytes have attracted renewed interest because they can provide faster desolvation, improved low-temperature kinetics, and favorable compatibility with hard carbon, but they also introduce challenges related to oxidative stability and safety. Recent reviews stress that the balance between kinetic benefits and oxidative robustness in sodium-ion electrolytes is largely determined by how solvents, salts, and additives reshape the Na^+ solvation sheath and, in turn, the chemistry of the SEI and CEI [25,38]. This is one reason why modern sodium-ion electrolyte engineering increasingly extends beyond single-additive screening toward broader control of solvation structure and electrolyte-derived interphase chemistry [25,38].

Additives can also be used more deliberately to address specific practical failure modes rather than only to improve initial cycling efficiency. Recent sodium-ion work using glutaric anhydride, for example, showed that additive design can be directed toward extending cycle life under more practical conditions by modifying interphase chemistry and suppressing continuous electrolyte degradation [39]. Likewise, electrolyte engineering for both Li-ion and Na-ion systems increasingly employs fluorinated solvents, borate/phosphate-containing additives, dual-salt formulations, and localized high-concentration design concepts to tune decomposition selectivity and favor more stable inorganic-rich interphases. The broader implication is that additives should not be viewed as minor formulation tweaks; they are increasingly central tools for steering decomposition chemistry toward desired transport and passivation outcomes [25,35,36,39].

From a practical perspective, the key issue is not whether electrolyte decomposition can be eliminated, but whether it can be redirected into chemically and mechanically useful interphase formation. Uncontrolled decomposition leads to alkali loss, gas generation, impedance rise, and cross-talk-driven degradation, whereas selective decomposition can generate thinner, denser, and more ion-conductive interphases that stabilize both electrodes [25,35–37]. A key implication is that electrolyte formulation and additive chemistry should be interpreted as interphase-engineering strategies rather than as isolated electrolyte variables. This provides the foundation for the next subsection, where binder chemistry, conductive additives, and overall electrode formulation are considered as additional factors that shape interfacial reactions beyond the liquid electrolyte alone [25,35–37].

4.3. Binder, Conductive Network, and Electrode Formulation Effects

Interfacial chemistry is not controlled exclusively by the liquid electrolyte. In practical electrodes, the binder, conductive additives, and overall formulation strongly influence the local chemical and mechanical environment in which interphases form and evolve. These components determine particle–particle contact, adhesion to the current collector, slurry rheology, coating

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homogeneity, pore accessibility, and the spatial distribution of electronically conductive domains. As a result, they directly affect how current is distributed across the electrode and how electrolyte-derived interphases develop during cycling [40–42]. Recent binder-focused reviews explicitly emphasize that binders are no longer regarded as inert mechanical glues, but as functional components capable of modulating interfacial stability, stress tolerance, ionic accessibility, and electrochemical durability.

The binder is especially important because it links electrochemical function to mechanical integrity. In conventional electrodes, poly(vinylidene fluoride) (PVDF) has been widely used because of its processability and chemical stability, but it often becomes insufficient when the electrode is subjected to high mass loading, high voltage, or large volume changes. More recent binder concepts therefore aim to introduce stronger adhesion, better elasticity, self-healing behavior, ionic functionality, or even partial electronic conductivity. Reviews from 2024–2026 show that modern binder design is increasingly framed in molecular terms, with attention to hydrogen bonding, supramolecular interactions, conjugation, and task-specific functionality rather than simple passive cohesion [40–42]. This shift is important because binder chemistry can influence not only electrode cracking and delamination, but also how fresh surface is exposed to the electrolyte and how continuously the SEI or CEI must be repaired during cycling.

At the cathode side, binder effects are particularly relevant in high-voltage and high-Ni systems, where interfacial instability is already severe. Recent work on advanced cathode binders highlights that binder selection can influence electrolyte uptake, oxidation tolerance, transition-metal surface stabilization, and the continuity of the conductive framework, thereby indirectly shaping CEI development and cathode degradation. In this sense, the binder contributes not only to mechanical cohesion but also to the chemical environment in which cathode–electrolyte reactions proceed [42]. This is especially relevant under practical conditions, where higher loading and denser calendered electrodes amplify the consequences of local heterogeneity and contact loss.

Conductive additives introduce a second layer of complexity. Carbon black, carbon nanotubes, graphene-derived additives, and related conductive agents are essential for establishing electronic percolation, but they also participate in interfacial reactivity. Their dispersion state, surface area, graphitic order, and interaction with the binder strongly affect slurry structure, coating microstructure, and the extent to which electronically connected pathways remain stable during cycling. Recent studies have shown that not all carbon blacks behave equivalently: differences in their structure and dispersion can significantly alter slurry rheology, electrical conduction, and cathode electrochemical response [43,44]. These findings matter because conductive additives are often treated as interchangeable percentages in electrode recipes, whereas in practice they shape both electron transport and local interfacial chemistry.

The conductive network can also affect electrolyte decomposition more directly. Modified carbon blacks in high-voltage lithium-ion batteries have been shown to influence oxidative electrolyte decomposition, indicating that conductive additives do not simply transmit electrons but can alter the chemical pathways occurring at the electrode/electrolyte interface [44]. Likewise, the amount of free carbon black in slurry-derived electrodes has been linked to drying-induced cracking, heterogeneous connectivity, and capacity fade in $LiFePO_4$ electrodes, illustrating how a formulation variable can propagate from slurry rheology to electrode microstructure and ultimately to long-term electrochemical performance [45]. These results reinforce a broader point: interfacial instability is often co-determined by the architecture of the conductive domain, not just by the active material and liquid electrolyte.

Formulation effects are especially visible during slurry preparation and coating, because the initial dispersion state of binder and carbon largely defines the final mesoscale organization of the electrode. Rheology studies show that slurry viscosity, storage modulus, and particle–binder interactions affect coating uniformity, pore formation, and phase segregation, all of which subsequently influence ion transport and interphase formation [46]. More recent work on binder–carbon black interactions has confirmed that the molecular conformation of binders such as

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carboxymethyl cellulose can strongly affect carbon-black dispersion in both solution and the dried electrode, thereby changing the quality of the conductive network and the microstructural environment in which electrochemical reactions occur [47]. What begins as a processing issue can therefore become an interfacial issue after cell assembly.

These considerations are highly relevant to sodium-ion batteries as well. In hard-carbon electrodes, binder choice can affect not only adhesion and coating quality, but also mass loading, low-voltage plateau utilization, and SEI behavior. Recent ACS Applied Materials & Interfaces work demonstrated that the type of Na-carboxymethyl cellulose binder significantly affects hard-carbon performance and SEI formation in sodium-ion batteries, confirming that even within one binder family, molecular-weight and substitution differences can translate into measurable interfacial consequences [48]. A 2025 study further showed that different binders in hard-carbon electrodes lead to meaningful differences in electrochemical, mechanical, and thermal stability, emphasizing that binder optimization in sodium-ion batteries should not be treated as a purely mechanical matter [49]. Together, these studies support the view that binder effects in sodium-ion systems are tightly linked to practical full-cell feasibility because they influence both processing and sodium inventory retention.

Taken together, these findings indicate that binder chemistry, conductive-network architecture, and electrode formulation should be viewed as active determinants of interfacial behavior rather than as secondary fabrication parameters. They influence where current flows, how stress is accommodated, how uniformly electrolyte penetrates the porous structure, and how readily parasitic reactions are initiated or suppressed. For this reason, realistic interphase engineering in lithium-ion and sodium-ion batteries cannot be achieved through electrolyte design alone; it must also incorporate the solid-state formulation of the electrode itself. That perspective also helps explain why nominally similar active materials can exhibit very different practical behavior once differences in binder system, carbon dispersion, or slurry processing are taken into account [41].

4.4. Li-Ion versus Na-Ion Interphases

Although lithium-ion and sodium-ion batteries share the same general requirement for electronically insulating yet ionically conductive interphases, the SEI and CEI formed in the two chemistries are not equivalent. The differences do not arise only from the larger ionic radius of Na^+, but from a broader change in solvation structure, reduction and oxidation pathways, interfacial kinetics, and the thermodynamic penalties associated with irreversible alkali consumption. Comparative reviews therefore increasingly argue that sodium-ion interphases should not be treated as simple sodium analogues of their lithium-ion counterparts, but as chemically and functionally distinct interphases with their own stability criteria and design challenges [26].

At the anode side, one of the clearest differences concerns the relationship between interphase formation and initial Coulombic efficiency. In conventional lithium-ion batteries based on graphite, SEI formation consumes cyclable lithium, but the maturity of graphite-based systems and the relative stability of their interphases make this penalty more manageable in practical full-cell design. In sodium-ion batteries, however, hard carbon remains the dominant practical anode, and its interphase behavior is more strongly coupled to irreversible sodium loss, low first-cycle efficiency, and sodium-inventory limitations. Recent reviews on hard-carbon electrolyte engineering and interface engineering both emphasize that SEI control is one of the main bottlenecks in sodium-ion commercialization because Na loss during early interphase formation is more difficult to absorb at the full-cell level than in established graphite-based lithium-ion systems [50,51].

This difference is closely linked to ion solvation. Sodium ions generally exhibit different solvent coordination and desolvation behavior from lithium ions, which affects which electrolyte components are preferentially reduced near the negative electrode and how compactly the resulting interphase can be organized. In sodium-ion batteries, especially those using hard carbon, electrolyte engineering is increasingly framed around reshaping the Na^+ solvation sheath to guide the chemistry of the SEI. This is one reason why ether-based electrolytes have attracted renewed attention in

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sodium-ion systems: they can promote favorable desolvation kinetics and interfacial behavior, but they also introduce their own trade-offs in oxidative stability and practical voltage window [25,51]. In contrast, Li-ion electrolyte design has historically evolved around a different balance of graphite compatibility, oxidative stability at the cathode, and long-term interphase robustness [25].

The cathode side also shows meaningful divergence. In lithium-ion batteries, CEI chemistry is strongly conditioned by high-voltage oxidation, lattice oxygen activity, surface reconstruction, and transition-metal dissolution, especially in Ni-rich layered oxides. Sodium-ion cathodes face analogous issues, but the interphase chemistry can differ significantly because the cathode families themselves differ more strongly from those used in mainstream lithium-ion technology. Layered sodium oxides, polyanionic compounds, and Prussian blue analogs introduce different surface chemistries, defect structures, and moisture sensitivities, so the CEI in sodium-ion batteries must often be discussed in relation to a different set of degradation drivers [26,31]. Recent sodium-ion CEI reviews specifically emphasize that CEI instability remains a major barrier for high-voltage sodium cathodes, particularly in dense-energy configurations [31].

Another important distinction is that Li-ion and Na-ion interphases may differ not only in composition but also in mechanical quality and persistence. In practical terms, a useful interphase must survive repeated cycling without excessive fracture, dissolution, or continuous regrowth. The literature on sodium-ion hard carbon suggests that Na-ion SEIs are often more difficult to stabilize over extended cycling because they are more strongly influenced by solvent choice, local structural heterogeneity in hard carbon, and the full-cell penalty associated with repeated sodium consumption [50,51]. By contrast, although Li-ion SEIs are far from ideal, the graphite/electrolyte combination in conventional lithium-ion cells benefits from a much longer history of optimization and a narrower practical design space [26,51]. This difference helps explain why interphase instability remains more explicitly visible as a commercialization bottleneck in sodium-ion systems [14,50,51].

The methodological consequences are also important. A growing body of sodium-ion work has pointed out that interphases studied against sodium metal counter electrodes may not accurately reflect the behavior of realistic sodium-ion full cells. In other words, the already significant gap between half-cell and full-cell interphase chemistry can be even more consequential in sodium-ion batteries because SEI composition and sodium inventory are so tightly coupled [14,50]. This reinforces the broader lesson of the present review: interphases are emergent properties of the full electrochemical environment, and the comparison between Li-ion and Na-ion systems is only meaningful when those interphases are interpreted in the context of realistic cell design [14,26,50].

From a practical standpoint, the comparison between Li-ion and Na-ion interphases highlights why direct transfer of electrolyte recipes, additive strategies, or evaluation criteria is often insufficient. Li-ion batteries provide a valuable benchmark for how stable interphases can support high efficiency and long cycle life, but Na-ion batteries demand more explicit control of interfacial sodium loss, hard-carbon surface chemistry, and cathode-side stability if they are to reach competitive full-cell performance in their intended application space [14,25,26,31,50,51]. The useful comparison is therefore not whether one chemistry "has an SEI and CEI like the other," but how each chemistry translates interphase formation into practical constraints on efficiency, voltage window, durability, and cell balancing [14,26].

5. Operando and In Situ Characterization

The growing emphasis on practical batteries has made it increasingly clear that ex situ characterization alone is often insufficient to capture the processes that govern real electrochemical behavior. Many of the key phenomena that determine battery performance—phase transitions, ion redistribution, interphase growth, electrolyte consumption, mechanical degradation, dendrite formation, and local reaction heterogeneity—are dynamic, path-dependent, and often strongly coupled to the instantaneous state of charge, current density, and cell architecture. As a result, the interpretation of battery materials has progressively shifted toward in situ and operando techniques

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capable of following structural, chemical, and morphological changes while the cell remains under electrochemical control [3,52–54].

Within this context, the distinction between in situ and operando characterization is not merely terminological. In situ measurements are generally performed while the system remains inside a functioning or function-mimicking electrochemical environment, whereas operando approaches seek to probe the material under dynamic working conditions that are more directly representative of real battery operation. This distinction matters because the more closely the experiment approaches realistic polarization, transport, and interface conditions, the more informative it becomes for understanding practical-cell behavior rather than only idealized or interrupted states [3,52–54].

For this reason, the present section examines why operando and in situ methods have become central to modern battery research, especially when the aim is to connect materials-level observations with full-cell performance and degradation. The discussion first considers the conceptual importance of operando approaches, and then moves to specific families of methods, including X-ray-based techniques, vibrational spectroscopies, microscopy correlation, electrochemical impedance analysis, and multimodal strategies. Particular emphasis is placed on how these techniques help resolve buried interfaces, reaction inhomogeneity, and degradation pathways that are difficult to infer from endpoint characterization alone [3,7,52,53].

The methodological framework required to study practical lithium- and sodium-ion batteries is summarized schematically in Figure 3. Because battery degradation involves coupled structural, chemical, morphological, transport, and kinetic processes, no single characterization technique can provide a complete description of cell behavior under operating conditions. Instead, operando and in situ approaches must be selected according to the specific mechanism under investigation and, when possible, combined in correlative or multimodal workflows. As shown in Figure 3, X-ray-based methods provide access to phase evolution, lattice changes, local coordination, oxidation states, and short-range disorder; vibrational spectroscopies are particularly useful for tracking electrolyte decomposition, solvation structure, and interphase chemistry; microscopy and imaging techniques help resolve spatial heterogeneity, cracking, swelling, and morphological evolution; and electrochemical impedance methods provide functional information on charge-transfer resistance, transport limitations, interfacial resistance, and impedance growth. Together, these approaches connect local physicochemical processes to cell-level performance loss, thereby enabling a more realistic diagnosis of degradation in practical Li-ion and Na-ion cells.

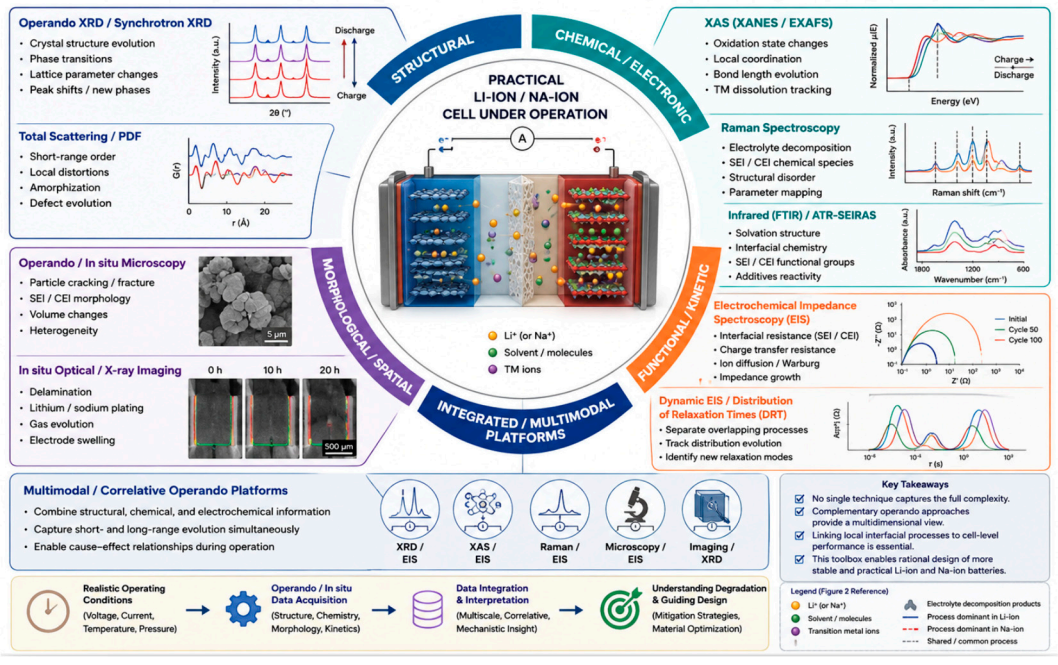

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Figure 3. Operando and in situ techniques provide complementary information on the dynamic processes that govern practical lithium- and sodium-ion battery performance. X-ray-based methods, including operando XRD, total scattering/PDF analysis, and XAS, probe crystallographic evolution, short-range disorder, local coordination, and redox-state changes during cycling. Vibrational spectroscopies such as Raman and infrared methods provide insight into electrolyte decomposition, solvation structure, SEI/CEI chemistry, and interfacial functional groups. Microscopy and optical or X-ray imaging approaches resolve morphological and spatially heterogeneous phenomena, including particle cracking, delamination, gas evolution, plating, and electrode swelling. Electrochemical impedance spectroscopy and dynamic EIS/DRT analysis provide process-sensitive information on interfacial resistance, charge transfer, ion diffusion, and impedance growth. When integrated into multimodal workflows, these techniques enable mechanistic diagnosis by linking structural, chemical, morphological, and kinetic changes to capacity fade, resistance increase, safety limitations, and practical cell design.

5.1. Why Operando Approaches Matter

Operando approaches matter because many of the most consequential processes in batteries do not occur in a static or equilibrium manner. Instead, they evolve continuously as the cell is charged, discharged, rested, heated, aged, or driven under aggressive conditions such as fast charging. Under these circumstances, the state of the electrode is not determined solely by composition, but also by the sequence of electrochemical events that produced it. Ex situ methods remain highly valuable, but they often provide only discontinuous snapshots of systems whose relevant chemistry and structure are transient, metastable, or highly sensitive to the measurement history [3,53,54].

One major reason operando methods are so important is that they preserve electrochemical context. Removing an electrode from the cell for post-mortem analysis can alter the very features one wishes to understand, especially when dealing with reactive interphases, solvated species, concentration gradients, or mechanically fragile microstructures. Reviews on operando interphase characterization have stressed that buried interfaces in batteries are particularly susceptible to misinterpretation when examined only after disassembly, because their composition and morphology may change once electrochemical control is removed or once the sample is exposed to air, vacuum, washing, or transfer procedures [3,7].

A second reason is that operando experiments can reveal coupling between processes that appear disconnected in ex situ analysis. Structural evolution, electrolyte depletion, SEI or CEI growth, particle cracking, and current redistribution often occur simultaneously and influence one another across multiple length scales. The 2025 review by Dorri et al. emphasizes that in situ and operando X-ray- and electron-based methods are especially powerful because they can directly follow reaction pathways, interfacial and side reactions, mechanical degradation, dendrite growth, and failure mechanisms in real time across Li-ion, Na-ion, and other battery chemistries [53]. This capability is essential when the objective is not merely to identify what phases are present after cycling, but to understand how and when they emerge, transform, or disappear during operation [53].

Operando methods are also crucial for identifying reaction inhomogeneity. Practical electrodes rarely react uniformly across their thickness, and this nonuniformity becomes more pronounced at high areal loading, high rate, lean-electrolyte conditions, or large pouch-cell formats. Techniques performed under operating conditions can reveal spatial gradients in lithiation or sodiation, local depletion of Li^+ or Na^+, interfacial bottlenecks, and the onset of degradation at specific regions of the electrode before these effects become visible as macroscopic performance loss [53,54]. This is one of the main reasons why operando methodologies are becoming increasingly important in the study of practical cells rather than only coin-cell proof-of-concept systems [53,54].

Another important advantage is that operando characterization provides stronger mechanistic discrimination. Different degradation routes can lead to similar endpoint signatures in ex situ analysis, but operando methods can help distinguish whether the dominant driver is, for example, progressive interphase thickening, kinetic bottlenecks, transport limitation, mechanical fracture, localized plating, or electrolyte starvation. Perspectives on recent advances in interface-sensitive

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operando characterization have therefore argued that these methods are central to establishing reliable composition–structure–property relationships at buried battery interfaces, particularly when attempting to move from descriptive to predictive understanding [7,52].

A further point is that operando approaches help bridge the gap between materials science and engineering relevance. In the past, many characterization studies were performed under highly simplified conditions because of instrumental limitations. While such studies remain useful, the field is increasingly moving toward experimental cells and measurement protocols that preserve more realistic electrode architectures, electrolyte compositions, and current–voltage conditions. This trend reflects a broader recognition that techniques capable of monitoring batteries under representative working conditions are more likely to generate insights that remain valid when materials are transferred from half-cells to realistic full-cell formats [3,52,53].

From a practical standpoint, the real value of operando characterization is that it improves the quality of causal inference. Rather than inferring degradation only from before-and-after comparison, operando methods allow researchers to observe when instability begins, how fast it propagates, which component triggers it, and under what operating conditions it becomes dominant. This does not make ex situ analysis obsolete, but it changes its role: ex situ methods become most powerful when used in combination with operando tracking, not as substitutes for it. That logic underpins the remainder of this section, where specific operando and in situ toolsets are examined in relation to the kinds of evidence they can provide for practical lithium-ion and sodium-ion batteries [3,7,52–54].

5.2. X-Ray-Based Techniques

X-ray-based operando and in situ methods are among the most powerful tools available for battery research because they can probe buried structures and chemical states without fully dismantling the electrochemical environment. Their main advantage is that they provide access to structural and electronic information across multiple length scales, from long-range crystallographic evolution to local coordination changes and mesoscale heterogeneity. This makes them particularly useful for practical lithium-ion and sodium-ion cells, where reaction pathways, phase transitions, interphase growth, and degradation often proceed inside opaque and dynamically evolving electrode architectures [55–57].

Operando X-ray diffraction (XRD) remains one of the most widely used approaches because it directly tracks crystallographic changes during cycling. In battery materials that undergo phase transitions, solid-solution behavior, or lattice breathing, operando XRD can reveal when structural transformations begin, whether they are reversible, and how they evolve with current rate, voltage window, and cycle number [56,57]. This is especially valuable in layered oxides, olivine phosphates, and many sodium-ion cathodes, where electrochemical behavior is strongly coupled to crystallographic evolution. Beyond simply identifying phases, modern operando XRD studies are increasingly used to detect reaction heterogeneity, metastable intermediates, and the structural signatures of degradation that would be difficult to infer reliably from endpoint measurements alone [56,57].

A particularly important development is the growing use of total X-ray scattering and pair distribution function-type analysis alongside conventional diffraction. While standard operando XRD is highly effective for following crystalline transformations, it is less sensitive to amorphous regions, short-range disorder, and nanoscale structural distortions. Recent 2026 review work has emphasized that combining operando XRD with total scattering expands the method from a purely crystallographic tool into a more complete probe of both ordered and disordered structural evolution in working batteries [57]. This is relevant for practical cells because structural degradation is often initiated not by a fully resolved bulk phase change, but by local disorder, strain accumulation, or surface-region reorganization that conventional diffraction alone may underrepresent [57].

Operando X-ray absorption spectroscopy (XAS) complements diffraction by probing local electronic structure and short-range coordination around selected elements. In practical terms, XAS is especially valuable when one needs to follow redox compensation, transition-metal oxidation

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states, changes in local symmetry, or coordination-environment evolution during cycling. This makes it a key technique for cathode materials in which charge compensation, oxygen activity, and transition-metal migration play major roles, including both lithium-ion and sodium-ion layered systems [55,58]. A major advantage of XAS is that it remains informative even when the material is poorly crystalline, multiphase, or structurally disordered, conditions under which diffraction can become less definitive [55,59].

Another reason XAS has gained importance is that it can now be implemented in more flexible experimental settings. Synchrotron-based operando XAS remains the benchmark for time resolution and sensitivity, but recent work has also demonstrated laboratory-based operando XAS on rechargeable battery electrodes using dedicated electrochemical cells and von Hámos spectrometer configurations [58]. This is an important methodological step because it reduces dependence on large-scale facility access and may broaden the use of operando local-structure analysis in more routine battery studies [58]. Even so, the interpretive power of XAS remains strongly dependent on experimental design, signal quality, and the ability to relate local spectroscopic changes to electrochemical state in a realistic cell geometry [55,58,59].

X-ray-based approaches are also valuable because they help bridge structural and interfacial understanding. Although diffraction and absorption techniques are often associated mainly with bulk materials analysis, recent perspectives on operando buried-interface diagnosis have argued that these methods are increasingly relevant to interphase-sensitive problems as well, especially when combined with tailored cell design and complementary analyses [59]. For example, operando XAS can indicate changes in the oxidation state or coordination environment associated with surface reconstruction and interphase formation, while diffraction and total scattering can reveal how those interfacial processes correlate with bulk structural response [55,57,59]. This kind of linkage is particularly important in practical cells, where bulk and interfacial degradation are rarely independent.

The reliability of X-ray-based operando experiments, however, depends strongly on experimental design. Cell windows, X-ray path length, absorption effects, stack architecture, and nonrepresentative current distribution can all distort the apparent electrochemical behavior of the system under study. Best-practice discussions have therefore stressed that the operando cell is not a neutral container but part of the measurement itself, and that poor cell design can lead to misleading structural conclusions even when the X-ray data appear technically sound [58,60]. This is especially relevant when moving from thin model electrodes to more realistic cells, where electrode thickness, electrolyte amount, and format-dependent heterogeneity become harder to control while preserving X-ray transparency [57,58,60].

From a practical standpoint, the strength of X-ray-based techniques lies in their ability to connect electrochemical response with structural and electronic evolution under working conditions. Diffraction is particularly powerful for following crystalline phase behavior, total scattering helps capture disorder and short-range changes, and XAS provides element-specific information on redox and coordination. Used together, these methods offer a much richer picture of practical-cell behavior than any one of them alone. They also provide a natural bridge to the next subsection, where vibrational spectroscopies and microscopy correlation will be considered as complementary approaches for resolving interphases, local heterogeneity, and reaction pathways that are less accessible to X-ray methods alone [55–60].

5.3. Vibrational Spectroscopies and Microscopy Correlation

Vibrational spectroscopies occupy a distinctive place in battery characterization because they are especially sensitive to local bonding environments, molecular fragments, solvation structure, and interphase chemistry. In contrast to many diffraction-based techniques, Raman and infrared methods are particularly well suited to probing electrolyte-derived species, surface films, and local structural distortions that may not produce a strong crystallographic signature. This makes them highly valuable for studying SEI and CEI evolution, electrolyte decomposition, ion solvation, and reaction

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heterogeneity in both lithium-ion and sodium-ion batteries [54,61,62]. Recent reviews emphasize that their real strength lies not only in chemical sensitivity, but in the possibility of following these changes under electrochemical control and, increasingly, with spatial resolution relevant to practical electrode heterogeneity [54,61–63].

Operando Raman spectroscopy has become one of the most informative approaches in this family because it can directly monitor structural fingerprints of active materials together with interfacial and electrolyte-related signatures. A key recent development is the growing recognition that experimental realism matters strongly in operando Raman battery studies. The 2026 Chemistry of Materials paper on designing realistic operando Raman experiments explicitly argues that measurement validity, spatial inhomogeneity, and cell geometry can strongly influence the apparent reaction behavior observed during cycling, particularly in graphite electrodes and other heterogeneous architectures [62]. This is important for practical-cell research because it shows that Raman spectroscopy is not only a tool for identifying species, but also a way to detect how reaction fronts, density gradients, and local transport limitations evolve across working electrodes [62].

Infrared spectroscopy provides complementary information because it is especially sensitive to polar bonds, solvent-derived species, salt decomposition products, and interfacial functional groups. The 2023 review by Amaral et al. shows that in situ and operando infrared spectroscopy has progressed from a relatively specialized technique to a broader platform for tracking electrolyte decomposition, ion coordination, and interphase-related chemistry across battery systems [54]. In practical terms, this makes infrared methods particularly useful when Raman signatures are weak, fluorescence is problematic, or species of interest are more IR-active than Raman-active. Raman and infrared spectroscopy should therefore be viewed as complementary rather than competing approaches for following chemical evolution in working batteries [54,62].

A major recent trend is the correlation of vibrational spectroscopy with microscopy. This is important because spectroscopic signatures alone do not always reveal where chemically distinct regions are located within a heterogeneous electrode. By combining vibrational methods with optical, electron, or fluorescence-based imaging, researchers can begin to map chemistry and morphology together rather than separately. A useful illustration is the 2025 Chemical Communications study by Quarrell et al., which used operando fluorescence lifetime imaging microscopy during Li^+ intercalation into graphitic electrodes to spatially resolve changes in emission behavior linked to electrolyte chemistry [61]. Although fluorescence lifetime imaging is not a vibrational technique itself, it demonstrates how optical imaging under operating conditions can complement spectroscopic information and reveal dynamic interfacial differences that would be difficult to infer from bulk electrochemistry alone [61].

This push toward spatially resolved correlation is becoming even more important at sub-particle and mesoscale levels. The 2026 review by Saqib et al. on in situ optical imaging of sub-particle heterogeneity highlights that electrochemical interfaces in batteries are often chemically and kinetically nonuniform even within single particles or local microdomains [63]. Correlating spectroscopic signatures with imaging-based heterogeneity therefore helps distinguish whether a spectral change is globally representative or localized to a specific region of the electrode. This is highly relevant for practical cells, where gradients in wetting, pressure, state of charge, and current distribution can produce local chemical environments that differ substantially across thickness and lateral position [62–64].

More broadly, the field is moving toward multimodal imaging frameworks in which vibrational spectroscopy is integrated with microscopy rather than used in isolation. The 2024 ACS Energy Letters review on in situ/operando imaging techniques for next-generation battery analysis reflects this trend by emphasizing that no single imaging modality fully captures the coupled structural, chemical, and morphological evolution of working batteries [64]. Within that broader toolbox, Raman and infrared methods contribute local chemical identity and interface sensitivity, while microscopy contributes spatial context, defect visualization, and mesoscale interpretation. The value of

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correlation is therefore not redundancy, but causal refinement: spectroscopy tells us what chemistry is occurring, whereas microscopy helps show where it occurs and how it propagates [63,64].

From a practical standpoint, vibrational spectroscopies and microscopy correlation are most useful when the research question involves interphases, electrolyte-derived species, or reaction heterogeneity that cannot be adequately resolved by diffraction-based approaches alone. Their main limitation is that they often require carefully engineered cells, transparent or optically accessible geometries, and cautious interpretation to avoid artifacts associated with fluorescence, laser penetration depth, or nonrepresentative optical pathways [54,61,62]. Even so, their ability to couple chemical sensitivity with spatial information makes them indispensable for understanding how local interfacial events develop into macroscopic degradation in realistic lithium-ion and sodium-ion electrodes [54,61–64].

5.4. Electrochemical Impedance and Multimodal Analysis

Electrochemical impedance spectroscopy (EIS) occupies a distinctive role in battery characterization because it probes the dynamic response of the cell rather than a single structural or chemical descriptor. In practical terms, impedance spectra integrate the contributions of charge transfer, ionic transport, interphase resistance, diffusion limitations, contact effects, and, in some cases, thermal and mechanical coupling. This makes EIS particularly valuable when the objective is not only to identify what species or phases are present, but to determine which processes are currently limiting battery performance and how those limitations evolve with state of charge, temperature, ageing, and operating conditions [65,66]. Unlike many structure-focused methods, EIS is inherently process-sensitive and therefore highly relevant to practical cells in which multiple degradation routes overlap [65,66].

One reason EIS is especially important in this review is that it provides a functional readout of the interphases discussed in Section 4. Changes in SEI or CEI composition do not matter only because they alter local chemistry, but because they modify resistance, capacitance, transport selectivity, and reaction kinetics at the electrode/electrolyte interface. EIS is one of the few techniques that can track these consequences continuously and non-destructively while the battery remains electrochemically active [65–67]. For this reason, recent reviews have emphasized that impedance analysis is not merely a diagnostic add-on, but a central bridge between interphase chemistry and practical battery behavior [65,66].

The value of operando impedance becomes even clearer when the cell is not at equilibrium. Traditional EIS is typically measured after rest, under near-stationary conditions, because the method assumes linearity and time invariance during the perturbation. Real batteries, however, rarely operate under such ideal conditions. During fast charging, plating/stripping, dynamic load changes, or continuous cycling, the system evolves while the measurement is being made. Recent work has therefore focused on dynamic and operando impedance strategies that retain the interpretive strengths of EIS while extending it to working conditions. A particularly relevant example is the study by Drvarič Talian et al., which combined operando impedance measurements with real-time overvoltage analysis in lithium-metal cells, enabling the identification of diffusion limitations, morphology changes, and dendritic growth under actual cycling conditions [67]. This kind of approach shows why operando impedance matters: it can reveal processes that are effectively invisible to conventional equilibrium-only measurements [67].

Another major advantage of EIS is its sensitivity to degradation before catastrophic failure becomes obvious in standard electrochemical metrics. Because impedance spectra respond strongly to interfacial resistance growth, diffusion bottlenecks, contact loss, and electrolyte depletion, they can serve as early indicators of safety-relevant or performance-limiting changes. This point has recently been emphasized in battery safety and management literature, where dynamic impedance methods are being explored not only for mechanistic research but also for state estimation, early warning, and health monitoring. Du et al. highlighted this transition clearly in their research on dynamic EIS, arguing that impedance-based monitoring can provide real-time insight into battery safety and

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internal electrochemical evolution in ways that traditional voltage- or temperature-only monitoring cannot [68]. This is highly relevant for practical cells, where the earliest signatures of degradation often appear as changes in interfacial or transport response before they become visible as capacity loss [68].

At the same time, EIS has well-known interpretive limitations when used alone. Similar spectral features may arise from different physical origins, and equivalent-circuit fitting can become ambiguous when multiple overlapping processes are present. This is particularly problematic in practical electrodes, where porous structure, inhomogeneous current distribution, temperature gradients, and evolving interfaces can all contribute to the measured response [65,66]. For this reason, recent literature increasingly emphasizes that impedance should be interpreted as part of a broader evidence framework rather than as a self-sufficient descriptor. In other words, EIS becomes most informative when correlated with structural, chemical, thermal, or imaging data that constrain the meaning of the spectral changes [65,66,69].

This is where multimodal analysis becomes especially powerful. A multimodal workflow does not simply accumulate measurements; it links complementary observables so that functional changes seen in EIS can be assigned to specific structural or chemical events. For example, an increase in interfacial resistance may be correlated with operando Raman evidence of electrolyte decomposition, X-ray evidence of phase heterogeneity, or microscopy evidence of cracking and contact loss. In this sense, multimodal analysis reduces the ambiguity of impedance interpretation while also increasing the causal value of the overall dataset [65,69]. The logic is not that EIS replaces other techniques, but that it provides a dynamic kinetic context into which those other measurements can be integrated [65,69].

Recent advances in multimodal operando platforms illustrate this trend clearly. The research by Zhang et al. introduced a multimodal operando characterization platform for lithium-ion pouch cells capable of nondestructive, real-time monitoring of cell evolution through coordinated measurements rather than single-technique snapshots [69]. Although such platforms remain experimentally demanding, they point toward a methodological future in which impedance, optical methods, X-ray tools, and thermal or mechanical sensing are combined to follow practical cells in a more holistic manner [69]. This kind of integration is particularly important for realistic battery systems, where performance loss typically emerges from coupled electro-chemo-mechanical processes rather than from a single isolated failure mode.

From a practical standpoint, the most important contribution of EIS is that it translates hidden internal changes into measurable system-level response. Structural and spectroscopic methods often reveal what is changing, whereas impedance reveals how strongly those changes affect transport and reaction kinetics. When combined with multimodal characterization, this makes EIS a particularly effective tool for distinguishing between chemically meaningful changes and changes that actually control battery function. That distinction is essential for practical lithium-ion and sodium-ion cells, where many local changes can be detected, but only some of them become dominant constraints on efficiency, safety, or cycle life [65–69].

5.5. Current Limitations and Practical Challenges

Despite the major advances in operando and in situ characterization, substantial limitations remain when these methods are applied to practical battery systems. One of the most persistent challenges is the trade-off between measurement quality and electrochemical realism. The more closely an experimental cell resembles a realistic battery in terms of electrode thickness, electrolyte quantity, mechanical confinement, and current distribution, the more difficult it becomes to preserve the optical, X-ray, or electron transparency required for advanced characterization. Conversely, the more a cell is simplified to accommodate the measurement, the greater the risk that the resulting observations no longer reflect realistic operation [53,60,62]. This tension is now widely recognized as one of the central methodological bottlenecks in operando battery science [53,60].

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A related issue is that the operando cell itself can influence the very processes being measured. Window materials, stack geometry, beam path, optical access, electrolyte volume, and fixture design may all alter wetting, pressure, local polarization, heat dissipation, and interfacial evolution. In X-ray experiments, for example, nonrepresentative electrode architecture or absorption path length can distort both electrochemical performance and data interpretation. Raman-based studies face analogous challenges when through-window geometries or localized probing generate sampling biases in heterogeneous electrodes [60,62]. The consequence is that not every operando measurement is automatically realistic simply because it is performed during cycling; realism must be demonstrated, not assumed [53,60,62].

Another major challenge is interpretation under multiphysics coupling. Practical batteries are not governed by isolated chemical or structural events, but by overlapping electrochemical, thermal, mechanical, and transport processes. A spectral change, an impedance feature, or an imaging contrast may therefore reflect several simultaneous causes rather than a single well-defined mechanism. This is especially problematic under fast charging, high loading, lean-electrolyte conditions, or large-format architectures, where reaction nonuniformity and local heterogeneity become more severe. Recent reviews on operando and advanced in situ techniques repeatedly stress that one of the field's main limitations is not a lack of data, but the difficulty of assigning causal meaning to increasingly complex datasets generated under nonideal working conditions [7,53].

Temporal and spatial resolution also remain difficult to optimize simultaneously. Some techniques provide rich chemical specificity but limited spatial mapping, whereas others offer high spatial resolution but poor time resolution or restricted chemical sensitivity. In practice, this means that many important degradation processes still fall between methodological scales: they may begin at buried interfaces or within local microdomains, propagate across electrode thickness, and only later become visible at the cell level. The literature increasingly points to this scale mismatch as a key obstacle in translating operando observations into predictive understanding of practical-cell ageing and failure [3,53].

Accessibility and reproducibility present an additional layer of difficulty. Many of the most powerful operando methods rely on synchrotron radiation, custom-built cells, advanced optics, or highly specialized data-processing pipelines. This can limit widespread adoption and complicate cross-comparison between studies. Even when the same nominal technique is used, differences in cell design, cycling protocol, beam damage, signal normalization, or data inversion can lead to substantially different conclusions. As a result, one of the practical challenges facing the field is the need for more standardized experimental design, reporting practice, and validation criteria so that datasets from different laboratories can be compared more meaningfully [7,53,62].

There is also a growing recognition that operando characterization must become less technique-centric and more question-driven. The most useful experiments are not those that apply the most sophisticated tool to every system, but those that match the method to the scale, chemistry, and failure process of interest. In this sense, the challenge is not only to improve instrumentation, but to develop better experimental logic: selecting measurement conditions that preserve battery relevance while still generating interpretable data. This is one reason multimodal approaches are increasingly valued—not because they are inherently superior, but because they can reduce ambiguity when carefully designed around a specific mechanistic question [3,7,53].

From a practical perspective, the field now seems to be moving from a phase of simple "operando visibility" toward one of quantitative diagnosis. That transition is critical. Observing that an interphase grows, a phase transition occurs, or heterogeneity emerges is no longer enough; the real challenge is to determine how strongly those phenomena affect capacity loss, impedance rise, plating risk, thermal instability, or failure onset in realistic cells [3,7]. Progress in this direction will likely depend on better cell platforms, improved correlative workflows, more robust data analysis, and stronger integration between operando characterization and practical-cell design. The long-term value of these techniques will therefore be judged not only by the richness of the data they generate,

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but by how effectively they improve causal understanding and guide the development of more durable and realistic lithium-ion and sodium-ion batteries [3,7,53,60,62].

The complexity of electrode–electrolyte interfaces and coupled degradation pathways requires characterization strategies capable of capturing chemical, structural, morphological, and transport-related changes under realistic operating conditions. In this context, Table 2 provides a comparative overview of key operando and advanced diagnostic techniques, emphasizing the information they deliver, their spatial and temporal sensitivity, and their main strengths and limitations. By placing these methods side by side, the table illustrates the need for complementary, multi-technique approaches to resolve the dynamic processes that govern performance decay, safety risks, and lifetime limitations in practical lithium- and sodium-ion batteries.

Table 2. Main operando/in situ characterization families discussed in this review, including their strongest contributions and key practical limitations.

Technique family	Primary information obtained	Best suited questions	Major strength	Main limitation in practical cells	References
Operando XRD	Crystallographic phase evolution, lattice changes, reversibility.	When do phase transitions start? Are they reversible?	Direct structural tracking during cycling.	Less sensitive to amorphous/disordered regions; cell design can distort realism.	[56]
Total X-ray scattering/ PDF	Short-range order, disorder, nanoscale distortions.	Is degradation initiated by local disorder rather than bulk phase change?	Captures ordered and disordered structural evolution.	Requires advanced analysis and often synchrotron access.	[57]
Operando XAS	Oxidation states, local coordination, redox compensation.	How do local electronic/coordination environments evolve?	Element-specific and informative in disordered systems.	Instrumentation and interpretation remain demanding.	[59]
Operando Raman	Structural fingerprints, local heterogeneity, electrolyte/interphase signatures.	Where do reaction fronts or inhomogeneities emerge?	Strong local chemical sensitivity.	Optical geometry and heterogeneity can bias results.	[62]
In situ operando IR	Solvation, salt/solvent decomposition, interfacial functional groups.	Which polar species form or disappear during cycling?	Complementary to Raman for electrolyte-derived species.	Cell engineering and signal complexity.	[54]
EIS/dynamic EIS	Charge-transfer, interphase, diffusion, contact and transport response.	Which process currently limits performance?	Functional, nondestructive, process-sensitive.	Ambiguous if used alone; equivalent-circuit overinterpretation.	[65,66]
Multimodal operando platforms	Correlated structural, chemical, electrochemical, thermal, and imaging evidence.	Which observed change is actually causally important?	Reduces ambiguity by linking observables.	High experimental complexity and limited standardization.	[64,69]

6. Failure Pathways in Practical Cells

Failure in practical batteries rarely results from a single isolated degradation event. In most cases, capacity loss, resistance increase, interfacial instability, mechanical damage, gas generation,

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thermal risk, and active-material degradation evolve in parallel and reinforce one another over time. This coupled nature of degradation is especially important in practical cells, where finite alkali inventory, realistic electrode loading, leaner electrolyte conditions, and nonuniform current distribution make the system more sensitive to interactions among degradation pathways than simplified half-cell studies would suggest [27,70–72]. Recent reviews on commercial lithium-ion ageing and on emerging battery technologies converge on this point: failure should be interpreted as a progressive systems-level process rather than as a sequence of independent material defects [27,71].

Within this framework, the most useful distinction is often not between “good” and “bad” materials, but between different dominant failure pathways and how they manifest under practical operating conditions. Some pathways primarily consume cyclable lithium or sodium; others isolate active material, increase impedance, destabilize interfaces, or compromise safety margins. In real cells, these processes are tightly linked, so that the same ageing trajectory may appear first as a modest impedance rise, later as measurable capacity fade, and finally as accelerated failure once structural or thermal instability becomes dominant [70,72,73]. For this reason, the present section focuses on the main observable failure modes in practical cells and on the underlying mechanisms that connect them.

6.1. Capacity Fade and Impedance Growth

Capacity fade and impedance growth are the two most widely observed electrochemical signatures of battery ageing, yet they should not be treated as independent or purely empirical descriptors. In practical cells, both arise from coupled degradation processes that alter the inventory of cyclable alkali, the accessibility of active material, and the kinetics of charge transfer and mass transport. This is why recent correlative analyses emphasize that capacity loss and resistance increase must be interpreted together if ageing is to be understood mechanistically rather than only quantified phenomenologically [71,72].

Capacity fade is most commonly associated with two broad categories of degradation: loss of lithium or sodium inventory and loss of active material. Loss of inventory occurs when alkali ions are irreversibly consumed in parasitic reactions, most notably through continued interphase growth, electrolyte decomposition, or plating-related side reactions. Loss of active material, by contrast, refers to the fraction of electrode material that remains physically present but becomes electrochemically inaccessible because of structural degradation, isolation from the conductive network, particle fracture, or changes in usable stoichiometric window [71,73]. In practical cells these two contributions frequently coexist, and their relative importance can shift with temperature, charge protocol, cell format, and chemistry [71,73].

Impedance growth reflects a related but not identical aspect of degradation. It arises when interfacial films thicken or become less conductive, when charge-transfer kinetics slow, when ionic transport through porous electrodes becomes more hindered, or when contact loss and inhomogeneity increase electronic resistance. In many cases, impedance rise precedes severe capacity loss because kinetic limitations can become significant while a substantial fraction of active material is still present. This makes impedance especially important in practical batteries, where power capability, fast-charging performance, low-temperature behavior, and internal heat generation are all strongly sensitive to growing resistance [8,27,72].

A critical point for practical cells is that capacity fade and impedance growth are often linked through the same root mechanisms. Continued SEI or CEI growth, for example, simultaneously consumes cyclable alkali and increases interfacial resistance. Lithium plating may initially appear as an inventory-loss pathway, but it can also promote local impedance rise, morphological instability, and secondary side reactions. Structural fatigue in cathode particles can isolate active regions and therefore reduce capacity, while also worsening transport heterogeneity and reaction polarization [71–73]. The consequence is that ageing cannot be adequately captured by a single scalar metric: a cell may retain relatively high nominal capacity while already suffering from severe resistance

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increase, or it may lose capacity with only modest bulk resistance change if inventory loss dominates early [71,72].

This coupling has been documented particularly clearly in recent correlative work on commercial lithium-ion batteries. Systematic analyses have shown that resistance and impedance metrics track ageing closely, but not always in a simple one-to-one manner with capacity loss. Instead, their joint evolution reflects the balance among interphase growth, transport degradation, and structural ageing within the specific operating window of the cell [72]. Such results are especially important for practical batteries because they show why degradation assessment based only on retained capacity can miss emerging failure risk, particularly under high-power or fast-charging conditions where impedance is often the first operational constraint [8,72].

In sodium-ion batteries, the same general logic applies, but the balance between the two failure signatures can differ. Recent studies on ampere-hour-scale sodium-ion cells indicate that loss of active sodium and interfacial resistance increase are both central drivers of capacity decay, with their relative contributions depending strongly on the ageing mode [70,74]. Under room-temperature cycling, sodium plating and inventory loss may dominate; under elevated-temperature storage or other stressful conditions, cathode degradation and continued sodium consumption by interphase growth can become more important [74]. This is a useful reminder that capacity fade in sodium-ion batteries cannot be understood solely by analogy with lithium-ion systems, because the practical penalty associated with irreversible sodium loss is often more severe and more immediately coupled to full-cell feasibility [70,74].

Another important implication is methodological. Capacity fade is relatively easy to measure, but it is not especially diagnostic on its own. Impedance growth is more mechanistically informative, yet it can still remain ambiguous unless interpreted alongside structural, chemical, or post-mortem evidence. This is why recent degradation-mode analyses increasingly argue that meaningful lifetime assessment requires separating observable ageing signatures from the underlying modes that generate them [8,73]. In other words, capacity loss and impedance rise should be regarded as system-level manifestations of deeper degradation pathways rather than as final explanations in themselves [8,73].

In practical cells, neither retained capacity nor resistance increase alone provides a complete picture of ageing. A battery may still preserve a substantial fraction of its nominal capacity while already suffering a level of impedance rise that limits power delivery, accelerates heat generation, or narrows the safe operating window. Conversely, significant capacity loss may occur before a dramatic increase in bulk resistance becomes evident if inventory loss dominates the ageing trajectory. For this reason, a meaningful assessment of degradation requires both metrics to be interpreted together and, whenever possible, linked to the underlying failure modes responsible for their evolution. This perspective is especially important in realistic batteries, where the operational consequences of ageing are determined not only by how much charge remains available, but also by how effectively and safely that charge can still be accessed.

6.2. Mechanical Degradation and Contact Loss

Mechanical degradation is one of the most pervasive yet sometimes underappreciated failure pathways in practical cells. During cycling, electrodes are repeatedly subjected to stresses generated by lithiation or sodiation, concentration gradients, phase transformations, particle anisotropy, and geometric confinement within the composite electrode. These stresses do not remain confined to the active particles themselves; they propagate across the binder matrix, conductive network, and current-collector interface, progressively altering the internal architecture of the electrode. Recent reviews therefore increasingly treat battery ageing as an electro-chemo-mechanical problem rather than a purely electrochemical one [33].

At the particle level, repeated insertion and extraction of alkali ions can induce cracking, pulverization, and local fracture. Even when catastrophic fragmentation does not occur, subcritical cracking can still create new reactive surface, redistribute stress, and locally isolate regions of active

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material. This is especially severe in high-volume-change materials, but it is not restricted to alloying or conversion electrodes; layered cathodes, hard carbon, and even more conventional intercalation hosts can develop structurally meaningful damage when cycling-induced strain is repeatedly accumulated [33]. The practical consequence is that mechanically degraded particles may remain present in the electrode while becoming electrochemically underutilized or increasingly heterogeneous in their reaction behavior [33].

Contact loss is the mesoscale manifestation of this damage. As particles crack, expand, shrink, or rearrange, the conductive pathways that initially connected them to carbon additives and to neighboring particles may be weakened or broken. At the same time, binder bridges can fail locally, promoting the formation of electronically isolated domains. The result is not necessarily the immediate disappearance of active material, but its progressive decoupling from the percolating electronic and ionic network needed for reversible operation [33,45]. This is one reason why mechanical degradation often appears electrochemically as both capacity loss and increased polarization rather than as a single abrupt failure event [33,45].

The current-collector interface constitutes another mechanically sensitive region. Cycling-induced stress, together with swelling, drying history, and interfacial weakness inherited from fabrication, can promote debonding of the active layer from the metal foil. Recent adhesion studies on battery electrodes show that interfacial delamination is not a minor fabrication artifact but a genuine ageing pathway that compromises electron transport, increases local resistance, and accelerates nonuniform current distribution [75]. T-peeling measurements on $LiFePO_4$ electrodes further demonstrate that fracture at the active-layer/current-collector interface can be quantified and related to interfacial durability, highlighting the importance of adhesion as a measurable design variable rather than a qualitative afterthought [75].

Processing history strongly modulates these failure routes. Calendering, for example, can improve density and interparticle contact, but excessive compaction can also intensify internal stress, reduce pore connectivity, and predispose the electrode to fracture or damage during cycling [76,77]. Recent work on hard carbon electrodes for sodium-ion batteries showed that calendering changes not only electrochemical behavior but also mechanical performance and sodium storage response, reinforcing the idea that electrochemical and mechanical optimization cannot be separated cleanly in practical electrodes [77]. Likewise, studies on slurry composition and drying-induced cracking have shown that free carbon black content and formulation heterogeneity can seed structural defects that later evolve into mechanically driven capacity loss [45].

Sodium-ion batteries offer a particularly instructive case because hard carbon, the leading practical anode, is often discussed mainly in terms of sodium storage mechanism and initial Coulombic efficiency, while its mechanical response can receive less attention. Real-time stress measurements in hard-carbon composite electrodes have shown that sodiation and desodiation generate measurable stress evolution during cycling, indicating that mechanical degradation is already relevant even in systems not typically classified as high-expansion anodes [78]. This matters because sodium-ion full cells operate under tighter inventory constraints, so any mechanically induced loss of reversibility, contact, or interphase stability can translate rapidly into practical performance penalties [77,78].

These observations underscore that mechanical degradation should not be viewed as a secondary consequence of other ageing mechanisms. In many practical cells, it is a co-driver of degradation that interacts directly with interphase growth, impedance rise, electrolyte consumption, and active-material isolation [33,45,77]. Cracking creates fresh surface for parasitic reactions; delamination alters local current distribution; contact loss worsens polarization; and rising polarization can in turn intensify nonuniform lithiation or sodiation, producing additional stress [33]. What appears macroscopically as ordinary ageing often reflects the accumulation of these coupled mechanical failures across several structural levels [33].

For practical-cell evaluation, the main implication is that mechanical robustness must be considered alongside electrochemical metrics from the outset. An electrode chemistry that appears

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promising in terms of capacity or voltage profile may still prove uncompetitive if it cannot preserve adhesion, conductive continuity, and structural integrity under realistic loading, compaction, and cycling conditions [33,75,77]. This is particularly relevant when translating materials from thin half-cell electrodes to thicker practical architectures, where the penalty associated with local fracture or loss of connectivity becomes much harder to absorb [33]. In that sense, mechanical degradation and contact loss are not just downstream consequences of ageing; they are part of the failure logic that determines whether a cell remains functionally usable over time [33].

6.3. Electrolyte Consumption, Gas Evolution, and Thermal Instability

Electrolyte consumption is one of the most consequential yet often underestimated degradation pathways in practical cells. Unlike isolated half-cell experiments performed with large electrolyte excess, realistic full cells operate with a finite electrolyte inventory that must simultaneously sustain ion transport, wet porous electrodes, and tolerate prolonged electrochemical and thermal stress. Once parasitic reactions consume a meaningful fraction of that liquid phase, the consequences propagate far beyond simple loss of solvent: wetting becomes less uniform, ionic transport becomes more resistive, interphase repair becomes more difficult to sustain, and local current heterogeneity becomes more pronounced [79–81]. In this sense, electrolyte depletion is not merely a chemical side effect of ageing, but a systems-level degradation route that progressively destabilizes the entire cell.

The chemical origins of electrolyte consumption are diverse. Continued SEI and CEI growth, trace water and HF-related reactions, oxidative decomposition at high-voltage cathodes, reductive side reactions at low-potential anodes, and alkali plating or stripping irregularities can all consume electrolyte components over time [80,82]. In practical cells, these processes become especially problematic under high state of charge, elevated temperature, fast charging, or prolonged storage, because the balance between passivation and continued decomposition shifts toward sustained parasitic reactivity [80,82]. A key point is that electrolyte consumption is self-reinforcing: once local depletion and transport resistance increase, fresh concentration gradients and interfacial instability may accelerate further decomposition.

Gas evolution is one of the clearest manifestations of this electrolyte-driven degradation. The gases generated during ageing or abuse are typically linked to solvent decomposition, salt breakdown, cathode-side oxygen activity, plating-related reactions, and thermally accelerated side chemistry. Reviews published in 2025 highlight that gas generation in lithium-ion batteries should not be viewed only as a late-stage thermal-runaway phenomenon; it is also a progressive degradation signature that can begin well before catastrophic failure and can already affect swelling, internal pressure, impedance, and safety margins during ordinary operation [81,83]. This is particularly relevant for practical cells because gas accumulation changes the mechanical and transport environment of the electrode stack even before venting or ignition occurs.

In lithium-ion batteries, the relationship between gas evolution and cell chemistry is especially pronounced in high-voltage and Ni-rich systems. Elevated nickel content, aggressive upper cutoff voltages, and temperature increase all intensify gas production and accelerate degradation, particularly in practical cylindrical or jelly-roll formats where the generated gases are not merely chemical products but contributors to internal stress and cell-level instability [84]. Gas-evolution studies in realistic full-cell formats further indicate that the type and amount of gas released depend strongly on cathode composition, temperature, and operating history, reinforcing the idea that gas generation is tightly linked to practical design choices rather than being a generic property of all lithium-ion cells [83,84].

The thermal implications of these processes are substantial. Electrolyte consumption and gas evolution both reduce the margin between normal ageing and hazardous failure by weakening thermal stability and amplifying heat-producing side reactions. Aged lithium-ion cells, for example, have been shown to exhibit altered thermal-runaway behavior and different gas-generation profiles at low temperature, with lithium plating, cathode fracture, and evolving gas composition all contributing to reduced safety robustness [85]. This is an important observation because it shows that

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thermal instability is not only a property of fresh high-energy cells under abuse, but also an outcome of ageing history. In other words, a cell that has already consumed electrolyte, accumulated interfacial damage, and developed internal heterogeneity may enter hazardous regimes more easily than its fresh counterpart under otherwise similar triggering conditions [85].

Sodium-ion batteries introduce a related but not identical picture. Their lower energy density does not automatically guarantee benign thermal behavior, and recent work has emphasized that sodium-ion thermal stability must be evaluated from material to cell level rather than inferred from chemistry labels alone [86,87]. Combined thermal–gas analyses published in 2025 show that the safety behavior of sodium-ion batteries depends strongly on the interplay between cathode chemistry, anode stability, electrolyte decomposition, and gas-release characteristics, much as in lithium-ion systems [87]. At the same time, perspectives on sodium-ion safety published in late 2025 argue that the current perception of inherently superior safety needs to be treated more carefully, especially as the technology moves toward larger cells, denser packaging, and commercial deployment [86]. This is highly relevant here because it means that electrolyte consumption and gas generation in sodium-ion cells should also be treated as practical-cell failure routes, not merely as isolated laboratory observations.

Gas evolution is important not only as a chemical symptom of electrolyte degradation, but also because it alters the physical state of the cell. Gas accumulation promotes swelling, changes internal pressure, weakens contact conditions, and intensifies local heterogeneity within the electrode stack. In this way, a process that begins as electrolyte decomposition can progressively affect transport pathways, current distribution, heat dissipation, and mechanical stability. The practical consequence is that gas generation should be understood as a coupled electro-chemo-mechanical degradation route rather than as an isolated by-product of side reactions [79].

Thermal instability emerges when these degradation products and stresses begin to interact faster than the cell can dissipate heat or maintain passivation. Once exothermic decomposition of electrolyte, lithiated anode, or delithiated cathode accelerates beyond control, the system can transition from progressive degradation to thermal runaway. Current reviews on lithium-ion thermal runaway and gas-release mechanisms emphasize that the fault-to-failure transition becomes faster as energy density rises and as the cell accumulates ageing-related weaknesses [81,88]. Accordingly, electrolyte consumption, gas generation, and thermal instability should not be treated as separate topics. They represent successive stages of a linked failure pathway in which chemical depletion, gas-producing side reactions, swelling, and heat release progressively erode the safe operating envelope of the cell [79,81,85,88].

6.4. Transition-Metal Dissolution and Surface Reconstruction

Transition-metal dissolution and surface reconstruction are among the most tightly coupled degradation pathways in practical cathodes. They rarely occur as isolated events. Instead, changes in near-surface structure, oxygen stability, electrolyte reactivity, and local metal–oxygen bonding progressively destabilize the cathode surface and promote the release of transition-metal species into the electrolyte [89–92]. This coupling is especially important in layered and spinel oxide cathodes, where the surface region often becomes chemically and structurally distinct from the bulk during cycling, storage, or high-voltage operation [89,90,92]. In practical cells, the consequence is not only the loss of cathode integrity, but also the onset of electrode cross-talk once dissolved metal species migrate through the electrolyte and interact with the negative electrode [90–92].

Surface reconstruction typically begins as a near-surface response to electrochemical and chemical instability. Under repeated delithiation or desodiation, the outermost region of the cathode may undergo cation migration, oxygen loss, local amorphization, phase transformation, or the formation of rock-salt-like or spinel-like surface layers [89,93]. These reconstructed regions are often less conductive for alkali transport, more resistive for charge transfer, and more reactive toward the electrolyte than the pristine cathode surface [89,93]. In Ni-rich lithium-ion cathodes, for example, surface degradation is frequently associated with oxygen instability, transition-metal migration into

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lithium layers, and the progressive development of poorly reversible surface phases that increase polarization and accelerate interfacial ageing [89,93]. Similar structural fragility is increasingly recognized in high-voltage sodium layered oxides, where surface instability and phase evolution can compromise cycle life and practical energy retention [94].

Transition-metal dissolution is often a direct consequence of this reconstructed and chemically weakened surface state. Manganese dissolution remains the classic example, especially in spinel and Mn-containing cathodes, but nickel and cobalt dissolution can also become significant under high-voltage or high-temperature conditions [90–92]. Zhan et al. established that dissolved transition-metal ions are generated at the positive electrode, migrate through the electrolyte, and then redeposit on both electrodes, particularly the negative one, where they destabilize the SEI and interfere with alkali intercalation [90]. That framework remains highly relevant, but more recent work has added temporal and mechanistic detail, showing that dissolution can vary strongly with operating voltage, electrolyte composition, and oxidation resistance [92].

The interaction between dissolution and cross-talk is particularly damaging in practical full cells. Once dissolved species leave the cathode, they no longer act only as markers of cathode degradation; they become active participants in further cell failure. Deposited transition metals at the anode can catalyze electrolyte reduction, perturb SEI composition, increase impedance, and accelerate inventory loss [90–92]. In other words, a degradation event that begins at the positive electrode can be converted into a whole-cell failure mechanism through migration and redeposition. Real-time operando sensing work on LNMO-based systems has recently made this process much more visible by directly tracking dissolution and shuttling behavior during operation, confirming that transition-metal release is dynamic, voltage-dependent, and strongly modulated by electrolyte stability [92].

This pathway is especially severe in cathodes already prone to near-surface instability. Reviews of Ni-rich layered oxides consistently identify surface reconstruction, microcracking, residual lithium chemistry, gas evolution, and transition-metal dissolution as mutually reinforcing degradation modes rather than separate problems [89,93]. Once the surface begins to reconstruct, fresh reactive area and structural disorder can intensify electrolyte decomposition; in turn, the chemically harsher interfacial environment further promotes dissolution and surface damage. This positive feedback loop helps explain why many high-energy cathodes exhibit relatively rapid deterioration once a threshold of interfacial degradation has been crossed [89,93].

Sodium-ion systems display related behavior, but the details are not identical. Layered sodium transition-metal oxides are particularly promising for practical sodium-ion cathodes, yet they also face challenges associated with structural collapse, oxygen loss, cracking, moisture sensitivity, and surface instability [94,95]. These features can make the surface more susceptible to degradation and can alter the way transition-metal dissolution contributes to cell ageing. Recent reviews on sodium layered oxides and high-voltage sodium cathodes indicate that practical stability depends strongly on controlling these coupled surface processes, especially when operating at higher voltage or aiming for dense-energy full-cell configurations [94,95]. The issue is therefore not simply whether sodium-ion cathodes “also” dissolve metals, but how their distinct structural chemistries translate that instability into practical failure.

A further difficulty is that surface reconstruction is not always easy to interpret correctly. Some reconstructed layers may be partially protective under selected conditions, while others become barriers to alkali transport or seeds for continued degradation. The practical distinction depends on thickness, composition, continuity, and whether the reconstructed region remains electrochemically compatible with the bulk cathode and the electrolyte [89,93]. This is one reason why recent cathode-focused literature increasingly treats surface reconstruction not only as a symptom of degradation, but as a critical design variable that can either be mitigated, redirected, or intentionally engineered depending on the material system [89,93–95].

What makes this pathway particularly important in practical cells is its asymmetry: a relatively localized surface process at the cathode can trigger a distributed cascade of consequences across the entire cell. Surface reconstruction increases resistance and chemical reactivity; dissolution removes

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redox-active species from the cathode; migrated ions destabilize the anode interphase; and the combined result is a coupled decline in capacity retention, impedance stability, and full-cell durability [89–92]. For this reason, transition-metal dissolution and surface reconstruction should be regarded as one of the clearest examples of how local cathode degradation becomes a whole-cell failure route under realistic operating conditions.

6.5. Distinct Failure Features in Li-Ion and Na-Ion Systems

Although lithium-ion and sodium-ion batteries share many broad degradation categories, the dominant balance among failure pathways is not the same in the two chemistries. In practical lithium-ion cells, ageing is often governed by the coupled effects of interphase growth, impedance rise, lithium inventory loss, cathode-side surface instability, and, under demanding conditions, lithium plating and thermal-risk escalation [27,71]. In sodium-ion batteries, by contrast, the practical penalty associated with irreversible sodium loss is often more immediate, and degradation is more strongly conditioned by hard-carbon interphase behavior, sodium inventory management, and the lower energetic margin available at the full-cell level [14,96,97]. For this reason, similar ageing signatures in Li-ion and Na-ion systems do not necessarily imply the same mechanistic priorities or the same practical consequences.

One of the clearest differences concerns inventory loss. In lithium-ion batteries, loss of cyclable lithium is a major ageing driver, but mature graphite-based full-cell design and extensive electrolyte optimization have made that penalty more manageable in many commercial systems. In sodium-ion batteries, irreversible sodium consumption is often less forgiving because the dominant hard-carbon/full-cell architecture remains more sensitive to first-cycle inefficiency and continued sodium loss during operation [14,96]. This means that degradation routes that consume alkali inventory may become practically limiting earlier in Na-ion cells than in established Li-ion systems, even when the nominal capacity retention appears superficially similar.

A second distinction lies in the relationship between ageing and safety. Lithium-ion batteries, especially high-energy systems based on Ni-rich layered oxides, are strongly constrained by the interaction between degradation, gas evolution, and thermal runaway hazard [71,98]. Sodium-ion batteries are often discussed as inherently safer, but recent safety-focused work suggests that this conclusion must be qualified. Their lower energy density can reduce some thermal-runaway hazards, yet safety behavior still depends strongly on cathode chemistry, gas release, state of charge, and cell format [98,99]. In other words, Na-ion systems may shift the safety landscape, but they do not eliminate the need to analyze degradation through a safety lens.

Cathode-side ageing also differs in emphasis. In lithium-ion batteries, particularly those based on layered oxides, degradation is often dominated by surface reconstruction, transition-metal dissolution, oxygen instability, crack formation, and progressive impedance rise [27,71]. Sodium-ion cathodes, especially layered transition-metal oxides, face analogous but not identical challenges: structural instability, air/moisture sensitivity, voltage-induced phase evolution, and practical voltage limitations can become particularly important [14,97]. As a result, the cathode failure logic in sodium-ion batteries is often shaped not only by interfacial deterioration, but also by chemistry-specific structural fragility and a narrower tolerance for parasitic sodium consumption at the full-cell level.

The anode side is likewise asymmetric. In practical lithium-ion batteries, graphite remains highly optimized, and although lithium plating remains a critical failure route under fast charging, low temperature, or poor balancing, its behavior is comparatively well studied and increasingly predictable in commercial formats [27,71]. In sodium-ion batteries, hard carbon is the leading anode, but its degradation behavior still presents a more open and chemistry-sensitive problem involving SEI stability, sodium trapping, rate-dependent reversibility, and strong dependence on electrolyte formulation [14,96]. This distinction matters because in Li-ion cells the dominant question is often how to prevent departure from a well-optimized graphite regime, whereas in Na-ion cells the challenge is more often how to stabilize a still-evolving hard-carbon regime under practical conditions.

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Another practical difference is the maturity of degradation diagnosis itself. Lithium-ion batteries benefit from a much larger accumulated body of ageing models, post-mortem protocols, and predictive degradation analysis across commercial cells. Sodium-ion batteries are now beginning to accumulate comparable cell-level evidence, including studies on ampere-hour and commercial-format cells, but the field is still in an earlier phase of establishing robust ageing baselines and chemistry-specific diagnostic logic [14,96,97]. This means that some degradation modes in sodium-ion batteries may currently appear less well defined not because they are intrinsically simpler, but because the experimental and commercial evidence base is still developing.

A further distinction concerns the practical meaning of ageing itself. In lithium-ion batteries, degradation is often judged against expectations shaped by demanding use cases such as electric mobility, fast charging, and high energy density. In sodium-ion batteries, the intended applications are more often stationary or cost-sensitive, so the same degree of impedance rise, thermal limitation, or capacity loss may carry a different practical significance depending on the operating context [14,99]. This does not make degradation less important in Na-ion systems; rather, it changes which failure routes become commercially decisive. Some ageing features that are unacceptable in a high-performance Li-ion application may be tolerable in a sodium-ion grid-storage context, while others—especially those tied to sodium inventory loss—may remain critical even at lower specific energy.

What emerges from the comparison is not that one chemistry fails "more" or "less" than the other in a general sense, but that the hierarchy of failure pathways differs. Lithium-ion batteries are more strongly constrained by the challenge of preserving safety and durability while pushing already mature systems toward higher energy and faster charging. Sodium-ion batteries are more strongly constrained by hard-carbon interphase stability, sodium inventory efficiency, cathode structural limitations, and the need to define realistic performance targets within their intended application space [14,96–99]. Recognizing these differences is essential if degradation in Li-ion and Na-ion cells is to be interpreted on chemistry-appropriate terms rather than through a single generic ageing framework.

The degradation phenomena discussed throughout this section reveal the highly interconnected nature of failure in lithium- and sodium-ion batteries. Chemical parasitic reactions, mechanical contact loss, electrolyte depletion, transition-metal dissolution, gas evolution, and thermal instabilities do not occur independently, but evolve through feedback mechanisms that progressively compromise cell performance and safety. Table 3 summarizes these coupled degradation pathways, emphasizing their mechanistic origins, experimental manifestations, and practical implications for advanced cell design. This comparative framework provides a useful basis for linking materials-level processes with cell-level aging behavior and for identifying the most relevant targets for mitigation strategies.

Table 3. Major failure pathways in practical Li-ion and Na-ion cells, their dominant manifestations, and chemistry-specific emphasis.

Failur pathway	Primary origin	Main cell-level manifestation	Particularly important Li-ion	Particularly inimportant in Na-ion	References
Loss of cyclable alkali inventory	Continued interphase growth, side reactions, plating	Capacity fade, poor energy retention	Yes	Yes, often more immediately penalizing in full cells	[4,71]
Impedance growth	Interphase thickening, transport limitation, contact loss	Lower power, poorer fast charging, more heat generation	Strong	Strong	[72]
Mechanical degradation/ contact loss	Cracking, delamination, conductive-network rupture	Active-material isolation, polarization increase	Strong in high-Ni, Si-rich, thick electrodes	Strong in hard-carbon and compact practical electrodes	[33]

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Electrolyte consumption	SEI/CEI growth, parasitic redox, high-voltage decomposition	Wetting loss, transport degradation, self-reinforcing ageing	Strong	Strong	[81,82]
Gas evolution	Solvent/salt decomposition, oxygen activity, thermal side chemistry	Swelling, pressure rise, safety-margin loss	Especially critical in high-energy Li-ion	Relevant; should not be assumed benign	[81,87]
Transition-metal dissolution/cross-talk	Surface instability and reconstructed cathode surface	Anode contamination, SEI destabilization, impedance rise	Strong in Mn-containing and Ni-rich oxides	Relevant in layered sodium oxides too	[90]
Surface reconstruction	Oxygen instability, cation migration, interfacial reactivity	Higher resistance, poorer transport, accelerated ageing	Strong in Ni-rich layered oxides	Strong in high-voltage layered sodium cathodes	[89,95]
Safety-linked ageing	Coupled gas evolution, heat generation, interphase breakdown	Thermal instability, narrower safe operating window	Major practical constraint	Also relevant; chemistry-specific	[99,100]

7. Representative Electrode Chemistries

The translation of promising electrode materials from half-cell demonstrations to practical lithium-ion and sodium-ion batteries requires a careful distinction between intrinsic material activity and cell-level feasibility. Representative electrode chemistries differ not only in theoretical capacity, redox mechanism, and voltage profile, but also in structural reversibility, interfacial stability, rate capability, volumetric strain, initial Coulombic efficiency, and compatibility with realistic electrode formulations [101–106]. In sodium-ion systems, these distinctions are especially important because the larger ionic radius of Na^+ imposes more severe constraints on ion diffusion, host structure stability, and electrode-electrolyte interfacial evolution than in lithium-ion systems.

To keep the comparison useful, the section uses a single synthesis table that groups chemistries by practical function rather than listing papers one by one. Table 4 highlights the central translation problem for each material family: the same property that makes a chemistry attractive can also create the failure mode that limits its use in practical cells.

Table 4. Representative electrode chemistries and the practical translation issue each chemistry raises.

Chemistry family	Electrode role	Main practical strength	Primary bottleneck	Practical validation focus
Carbon-based materials	Anodes	Low cost, structural stability, mature processing, and hard carbon relevance for SIBs.	Graphite is poorly suited for Na+ intercalation; hard carbon still faces ICE, rate, and cycling limitations.	Report ICE, areal capacity, electrode density, SEI behavior, and full-cell hard-carbon performance [102–105].
Alloying anodes	Anodes	Very high theoretical capacity, especially Sn, Sb, P, Ge, and related systems.	Severe volume expansion, pulverization, unstable SEI, and loss of electrical contact.	Validate mechanical integrity, binder/electrolyte compatibility, presodiation, and full-cell inventory retention [106,107].
Conversion and Mo-based materials	Anodes	High capacity and rich Na-reaction	Multiple phase transformations,	Track phase reversibility,

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		chemistry through intercalation and conversion reactions.	volume swelling, slow transport, and low surface activity.	impedance growth, particle fracture, and composite-electrode stability [101].
Layered transition-metal oxides	Cathodes	High energy potential and structural analogy to LIB layered cathodes.	Phase transitions, transition-metal migration, oxygen-related instability, and limited high-rate capacity.	Measure structural reversibility, air stability, surface reactions, rate capability, and long-term cycling [108].
Polyanionic cathodes	Cathodes	Framework stability, high operating voltage, safety, and limited volume change during Na^+ insertion and extraction.	Poor electronic conductivity, rate limitations, hygroscopicity, and thermal limitations in some chemistries.	Report conductivity enhancement, moisture tolerance, high-voltage stability, and practical electrode loading [109].
Prussian blue analogs	Cathodes	Open framework, low synthesis cost, favorable Na^+ diffusion, and promising rate/cycling behavior.	Vacancies, crystal water, lattice instability, and stress accumulation during cycling.	Quantify water/vacancy content, lattice reversibility, rate retention, and cycling stability in full cells [110].
Nanostructured materials	Cross-cutting design strategy	Shorter diffusion paths, higher active surface, volume buffering, and improved contact with conductive matrices.	Excess surface area can increase side reactions and irreversible electrolyte decomposition and may reduce tap density.	Evaluate mass loading, tap density, capacity, and whether nanoscale gains persist in practical electrodes [101–110].

7.1. Carbon-Based Anodes

Nikgoftar and co-workers [102] reviewed carbonaceous materials as anodes for both lithium-ion and sodium-ion batteries, emphasizing that carbon materials remain central to battery technology because of their relatively low cost, high electrical conductivity, structural stability, abundance, and environmental compatibility (see Figure 4). Their review classifies carbonaceous anodes into graphite, hard carbon, soft carbon, graphene, carbon nanotubes, and related carbon materials. Natural graphite is described as the dominant commercial anode for lithium-ion batteries because of its layered crystal structure, mechanical strength, long cycle life, and safety profile. However, the same graphite structure is not directly transferable to sodium-ion batteries because the larger size of Na^+ causes thermodynamic instability, limited electrochemical intercalation, and possible exfoliation. As a result, hard carbon has emerged as a more suitable carbonaceous anode for sodium-ion batteries [102].

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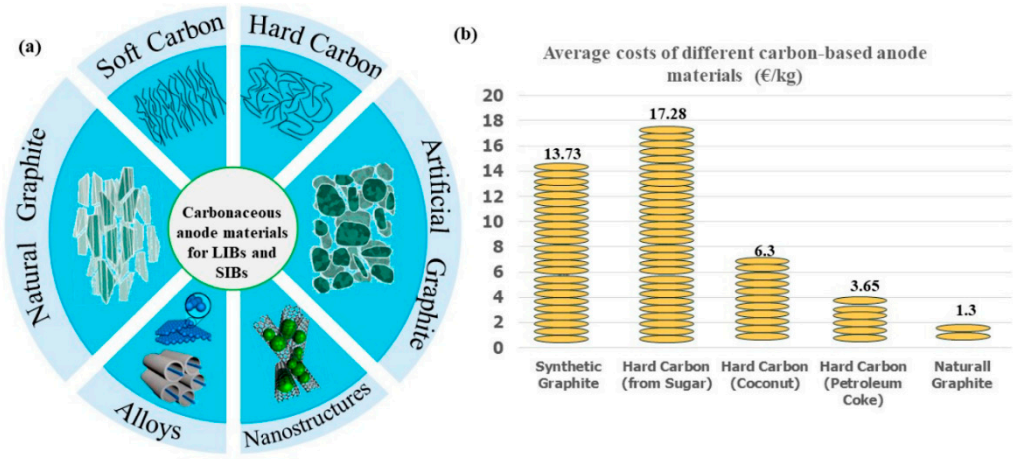

Figure 4. Representative carbonaceous anode materials for lithium-ion and sodium-ion batteries, including graphite, hard carbon, soft carbon, graphene, nanotubes, and related structures, with a comparative cost perspective. Adapted from Nikgoftar et al. [102].

Liu and co-workers [103] focused specifically on hard carbon anodes for sodium-ion batteries. They emphasized that hard carbon stands out among sodium-ion anode materials because of its favorable cost, resource availability, compatibility with industrial processing, and safety. However, unlike graphite in lithium-ion batteries, hard carbon is structurally disordered, and its sodium storage mechanism remains complex. They discusses several sodium storage models and highlights that performance depends strongly on the balance among defects, nanopores, graphitic domains, electrolyte chemistry, and surface area. The major unresolved issues for hard carbon include improving capacity, rate capability, cycling performance, and initial Coulombic efficiency [103].

Tan and co-workers [104] further clarified the sodium storage behavior of hard carbon by describing four models: the embedding-adsorption model, adsorption-embedding model, three-stage model, and adsorption-pore filling model. Their analysis highlights that Na^+ storage in hard carbon can involve adsorption at surface defects, insertion into graphitic-like layers, and filling of closed micropores. They also emphasized that morphology and structure regulation, heteroatom doping, and electrolyte optimization are the main strategies used to improve hard carbon performance. For practical application, the authors [104] identified low first-cycle Coulombic efficiency, poor rate performance, and insufficient cycling stability as key barriers that must be addressed before hard carbon can fully satisfy commercial sodium-ion battery requirements.

Jia and co-workers [105] expanded the discussion beyond hard carbon by studying hard carbon, soft carbon, graphite, graphene, carbon nanotubes, and porous carbon materials for sodium-ion batteries. They reported that hard carbon and soft carbon are important because of their cost-effectiveness and relatively stable electrochemical performance, while graphene and carbon nanotubes offer high surface area and favorable transport properties. However, graphene remains limited by complex preparation, relatively high cost, and lower initial Coulombic efficiency compared with optimized hard carbon. The authors [105] also noted that conventional graphite is not an optimal sodium-ion anode unless its interlayer spacing is expanded or a suitable electrolyte strategy is used. For example, expanded graphite containing MoSx pillars achieved an interlayer spacing of 5.38 Angstrom and delivered a second discharge capacity of 501 mAh g^{-1} when paired with ether-based electrolytes [105].

These studies show that carbon-based anodes offer the most mature pathway for sodium-ion battery commercialization, especially through hard carbon. However, they also demonstrate why half-cell capacity alone is insufficient for evaluating practical relevance. A carbon material with high sodium storage capacity may still fail under realistic conditions if it exhibits excessive surface reactivity, unstable SEI formation, low initial Coulombic efficiency, or insufficient areal capacity.

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7.2. Alloying and Conversion Anodes

Rehman and co-workers [106] studied alloying anodes for sodium-ion batteries, focusing on Sn, Sb, P, Ge, and Si. These materials are attractive because they can deliver higher theoretical capacities than intercalation-type carbon anodes. However, their practical implementation is hindered by severe volume expansion during alloying and dealloying, which links high capacity directly to mechanical and interfacial instability.

Among alloying anodes, Sn has received extensive attention because of its high theoretical capacity and electronic conductivity. The authors [106] reported that Sn-based anodes undergo multistep sodiation to form $Na_{15}Sn_4$, but their large volume expansion causes active material pulverization and unstable SEI formation. Strategies such as nanosizing, conductive carbon matrices, heteroatom doping, heterostructuring, electrolyte selection, additives, cross-linked binders, and presodiation have been used to improve Sn-based anodes. For example, ether-based electrolytes and cross-linked binders were reported to improve cycling behavior and initial Coulombic efficiency in Sn-based systems [106].

Jiang et al. [101] reported molybdenum-based materials as sodium-ion battery anodes, including molybdenum oxides, sulfides, selenides, and carbides. These materials are attractive because they can store sodium through intercalation and conversion reactions and provide higher capacities than many carbonaceous anodes. For example, MoO_3 has a theoretical capacity of 1117 mAh g^{-1}, which is substantially higher than TiO_2. However, molybdenum-based materials face several technical challenges, including multiple phase transformations, particle pulverization caused by volume swelling, slow electron and ion transport, and low surface reactivity during sodiation and desodiation [101]. The group [101] emphasized that materials engineering is required to address these limitations, especially through nanostructuring, conductive carbon integration, and composite architectures.

Phosphorus-based anodes are especially attractive because of their high theoretical capacity. Liu et al. [107] investigated phosphorus/carbon anode materials and reported that phosphorus offers a theoretical specific capacity of 2596 mAh g^{-1}. However, phosphorus has extremely low ionic and electronic conductivity, with conductivity below 10^{-14} S cm^{-1}, requiring combination with conductive carbon materials. The alloying reaction between phosphorus and sodium produces volume expansion exceeding 300%, which causes active material pulverization, detachment from the conductive network, and repeated SEI fracture and reformation [107]. Therefore, the most effective design strategies involve nanosizing phosphorus, embedding it within carbon matrices, strengthening P-C and P-O-C interfacial bonding, optimizing binders, and using electrolyte additives such as fluoroethylene carbonate to form a more stable NaF-rich SEI .

The combined evidence from alloying and conversion anodes demonstrates a recurring tradeoff. Materials with very high theoretical capacity frequently suffer from large volume changes and unstable interfaces. As a result, their practical viability depends less on theoretical capacity and more on whether electrode architecture, binder chemistry, electrolyte composition, and interfacial design can preserve mechanical and electrical continuity during long-term cycling.

7.3. Layered Oxide Cathodes

Ahangari et al. [108] researched layered transition metal oxide cathodes for sodium-ion batteries. These materials are among the most promising sodium-ion cathodes because they are structurally analogous to lithium-ion layered oxide cathodes and can potentially deliver high energy density at reduced cost. However, they also face significant limitations, including restricted capacity at high charge and discharge rates, structural instability during long-term cycling, phase transitions, and degradation associated with cationic and anionic redox processes [108]. A key issue in layered sodium transition metal oxides is structural evolution during Na^+ extraction and insertion. Ahangari [108] described layered oxide phases such as O_3, P_2, and P_3, where the sodium coordination environment and oxygen stacking sequence influence diffusion kinetics, phase stability, and electrochemical behavior. During cycling, extraction of sodium ions can create vacancies that

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promote transition metal migration into sodium layers. This transition metal migration can induce irreversible structural degradation and poor electrochemical performance [108]. Distortions in transition metal oxygen octahedra, especially those associated with transition metal oxidation or oxygen oxidation, can further drive structural instability. Ahangari [108] also discussed mitigation strategies for layered oxide cathodes, including elemental doping, transition metal combinations, surface modification, and structural design. For example, Fe substitution in $NaMn_{0.5}Ni_{0.5}O_2$ was reported to suppress capacity decay by improving structural stability and inhibiting MO_2 layer gliding and phase conversion. Surface coating with MoS_2 was also reported to improve electrical conductivity, air stability, and reduce electrolyte side reactions in $NaMn_{0.4}Ni_{0.4}Fe_{0.2}O_2$ [108]. These strategies highlight that layered oxide cathodes must be optimized not only for high capacity but also for structural reversibility and interfacial compatibility under extended cycling.

7.4. Polyanionic Cathodes and Prussian Blue Analogs

Zheng et al. [109] reviewed iron-based sulfate cathodes for sodium-ion batteries, focusing on sodium iron sulfate materials. They emphasized that cathode performance strongly controls the overall energy density, power density, cycling life, and safety of sodium-ion batteries. In the broader landscape of sodium-ion cathodes, they classified major cathode families into transition metal oxides, Prussian blue analogs, and polyanionic compounds [109]. Layered transition metal oxides offer high reversible capacity and energy density but suffer from structural degradation, moisture sensitivity, and limited cycle life. Prussian blue analogs offer low cost, favorable rate performance, and tunable voltage, but their lattice water and vacancies can compromise structural and chemical stability. Polyanionic compounds offer high operating voltage, good thermal stability, and three-dimensional frameworks with limited volume change during Na^+ insertion and extraction [109].

Within polyanionic cathodes, Zheng et al. [109] identified sodium iron sulfate as a promising high-voltage cathode because the strong inductive effect of the SO_4 group can regulate transition metal ions, stabilize the lattice, and limit oxygen release. Sodium iron sulfate materials possess a framework in which FeO_6 octahedra and SO_4 tetrahedra form channels for Na^+ migration. During discharge, Na^+ inserts into the cathode structure while Fe^{3+} is reduced to Fe^{2+}. During charge, Na^+ deintercalates while Fe^{2+} is oxidized to Fe^{3+} [109]. Despite these advantages, iron-based sulfate cathodes suffer from poor electronic conductivity, reduced rate capability, hygroscopicity, and limited thermal stability, which complicate synthesis, storage, and practical handling [109].

Song et al. [110] reported an iron-based Prussian blue cathode with an open-pore skeleton structure prepared using PVP and sodium citrate to control crystallization rate and morphology. This design addressed common problems in Prussian blue analogs, including defect vacancies, high crystal water content, lattice destabilization, and stress accumulation during Na^+ insertion and extraction. The optimized PB-3 electrode delivered strong rate performance, maintaining 92 mAh g^{-1} at 2000 mA g^{-1} in the abstract and 88.4 mAh g^{-1} at 2000 mA g^{-1} in the conclusions, with 90.2% capacity retention after 600 cycles at 500 mA g^{-1} [110]. Ex situ XRD showed highly reversible Na^+ insertion and extraction, supporting the conclusion that stabilized lattice behavior contributes to long-term cycling performance [110].

Together, polyanionic cathodes and Prussian blue analogs illustrate two different approaches to practical sodium-ion cathode design. Polyanionic compounds prioritize framework stability, safety, and high voltage through inductive effects. Prussian blue analogs prioritize open-framework Na^+ transport, low-cost synthesis, and tunable structures. Both chemistries require further optimization of conductivity, moisture tolerance, structural defects, and electrolyte compatibility before their practical-cell performance can fully match their half-cell promise.

7.5. Nanostructured Materials under Practical Conditions

Nanostructuring appears throughout the representative chemistries discussed above, but its practical significance is not uniform. In carbon-based anodes, defects, pores, expanded interlayers, graphene networks, and carbon nanotubes can improve sodium storage sites, ionic transport, and

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electronic conductivity [102–105]. In alloying anodes, nanosizing and carbon confinement can buffer volume expansion and preserve electrical contact [106,107]. In molybdenum-based conversion anodes, nanocomposites can mitigate pulverization, enhance surface activity, and improve electron and ion transport [6]. In cathodes, morphology control, coatings, doping, and open-pore structures can improve structural stability and electrochemical kinetics [108–110].

However, Rehman et al. [106] cautioned that nanostructuring can also create practical liabilities. Excessive surface area may increase side reactions, accelerate electrolyte decomposition, destabilize the SEI, and enhance mechanical cracking in materials that already experience large volume changes. Smaller particles may also lead to incomplete alloying and reduced overall capacity if equilibrium ion concentrations are limited [106]. Similarly, Liu and co-workers [107] noted that many phosphorus/carbon systems have been tested at laboratory-scale mass loadings below 2 mg cm^{-2} and area capacities of only 1 to 3 mAh cm^{-2}, which fall short of industrial expectations. They suggested that future work should target binder-free dry electrode processing, direct calendaring, mass loadings of 3 to 5 mg cm^{-2}, presodiation, and full-cell validation with compatible high-capacity cathodes [107]. Therefore, nanostructured electrode materials should not be judged only by high reversible capacity in half-cells. Their relevance to practical batteries depends on whether the nanostructure remains mechanically stable, limits irreversible interfacial reactions, supports high mass loading, maintains sufficient tap density, and performs in full-cell configurations. The most convincing future studies will combine nanostructural design with practical electrode metrics such as areal capacity, electrode density, initial Coulombic efficiency, lean electrolyte compatibility, cycling reproducibility, and full-cell validation.

8. Metrics for Practical Relevance

Practical relevance in lithium ion and sodium ion battery research is not established by a single high-capacity number. It is established when the reported performance survives a change in denominator, a change in cell architecture, a change in electrode loading, and a change in the length and reliability of the experiment. Specific capacity remains useful for screening active materials, but it cannot determine whether a chemistry is ready for practical cells unless it is interpreted together with areal capacity, volumetric energy, gravimetric energy, initial Coulombic efficiency, rate capability, cycling protocol, cell format, and reporting transparency [111–119].

8.1. Beyond Specific Capacity

Heubner et al. [112] warn against overinterpreting specific capacity. Their analysis distinguishes material level, electrode level, single cell element level, full cell level, and battery system level. In laboratory studies, capacity is often normalized to the mass of the active material, which is useful for assessing intrinsic utilization. However, the same value can become misleading when it is used to imply practical energy or power density. Thin electrodes can deliver high apparent rate capability because electrolyte diffusion limitations are minimized, but the full cell may perform poorly because the inactive mass and volume fractions become too large. The group [112] therefore proposed a Ragone calculator that translates electrode level electrochemical measurements into hypothetical full cell gravimetric and volumetric energy and power densities. This approach turns specific capacity from an isolated claim into an input for a more realistic cell level evaluation.

Xu [113] reached a similar conclusion from a reporting and interpretation perspective. The capacity of a whole battery is not the capacity of one electrode. It depends on the coupled capacities of the cathode and anode, as well as the voltage profile of the complete cell. Xu [113] emphasized that the energy output is determined by integrating cell voltage over capacity, which means that the basis used to calculate capacity or energy must be explicit. A high electrode specific capacity can be diluted by the counter electrode, by inactive components, or by a voltage profile that does not translate into high cell energy. In this sense, capacity values are not wrong by themselves, but they are incomplete when the denominator is unclear.

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Ghani et al. [114] extended this argument by reviewing the design parameters that govern full cell lithium-ion batteries. They identified form factor, material selection, component compatibility, electrochemical potential window, mass loading, N/P ratio, intrinsic conductivity, separator properties, electrolyte behavior, productivity, and cost as coupled design variables. Their research shows that practical relevance is a design problem, not only a materials problem. A material with promising capacity must be compatible with a safe voltage window, balanced electrode loading, stable interfaces, processable electrode formulations, and manufacturable cell geometry [114].

Scurtu et al. [115] sharpened the same concern at the level of cell format and scale. They argued that the format and geometric area of tested cells are often undervalued, even though these parameters provide essential information about electrode quality and data reliability. Their analysis notes that coin cells are useful for initial screening of specific capacity, initial Coulombic efficiency, and discharge rate capability, but they are inadequate predictors of cycling stability in studies that aim to move toward technology readiness levels of 4 or higher. They also highlighted that only about 28% of research articles reporting electrode composition specify electrode area, which directly limits comparability and reproducibility [115].

Taken together, these studies indicate that practical battery performance must be evaluated through a set of complementary metrics rather than through isolated capacity values. Each metric captures a different level of information, from intrinsic active material utilization to electrode loading, full cell energy output, transport limitations, and cycling reliability. Table 5 summarizes the main practical metrics discussed in this section, the specific information each metric provides, the limitations that may remain hidden when it is reported alone, and the minimum contextual information required for meaningful comparison across studies.

Table 5. Practical battery metrics, what each metric reveals, and the minimum information needed for meaningful reporting.

Metric	Question answered	What it can hide	Minimum reporting requirement	Sources
Specific capacity	How much charge the active material stores under a defined protocol.	Inactive mass, voltage profile, counter-electrode limitation, and full-cell balance.	State the denominator, voltage window, rate, electrode composition, and whether the value is electrode-level or full-cell-level.	[112,113,115]
Areal capacity and mass loading	Whether the electrode approaches practical loading and thickness.	Porosity, tortuosity, electrolyte excess, and transport limitations.	Report mAh cm^{-2}, mg cm^{-2}, electrode thickness, porosity, density, binder content, current collector, and electrolyte amount.	[112,114,116,117]
Gravimetric and volumetric energy	Whether material performance survives translation to cell mass and volume.	Heavy current collectors, separators, packaging, excess electrolyte, and low-density electrodes.	Calculate at single-cell or full-cell level and include inactive fractions and average voltage.	[112–115,118]

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Initial Coulombic efficiency and CE	How much lithium inventory is lost to irreversible reactions and interphase formation.	Half-cell excess sodium, precision limits, and time-dependent parasitic reactions.	Report first-cycle CE, high-precision CE when available, formation conditions, rate, voltage limits, and number of cells.	[111,113,114,118,119]
Rate performance	How capacity changes when current demand increases.	Thin-electrode artifacts, polarization losses, and early voltage cutoff rather than true active-material exhaustion.	Report rate protocol with practical areal capacity, thickness, transport analysis, and post-rate recovery.	[116,117]
Long-term cycling and reproducibility	Whether performance is durable and repeatable under transparent conditions.	Fast cycling can inflate cycle count while masking calendar and parasitic degradation.	Report cell format, area, number of cells, temperature, rest periods, cycle time, retention, impedance, and statistics.	[111,113–115,119]

A useful visual anchor for this discussion is the comparison between material level and full cell level metrics developed by Heubner and co-workers [112]. Figure 5 supports the transition from specific capacity to practical energy and power metrics because it shows that electrode thickness, porosity, and active-material fraction change full-cell performance even when the active material itself is unchanged.

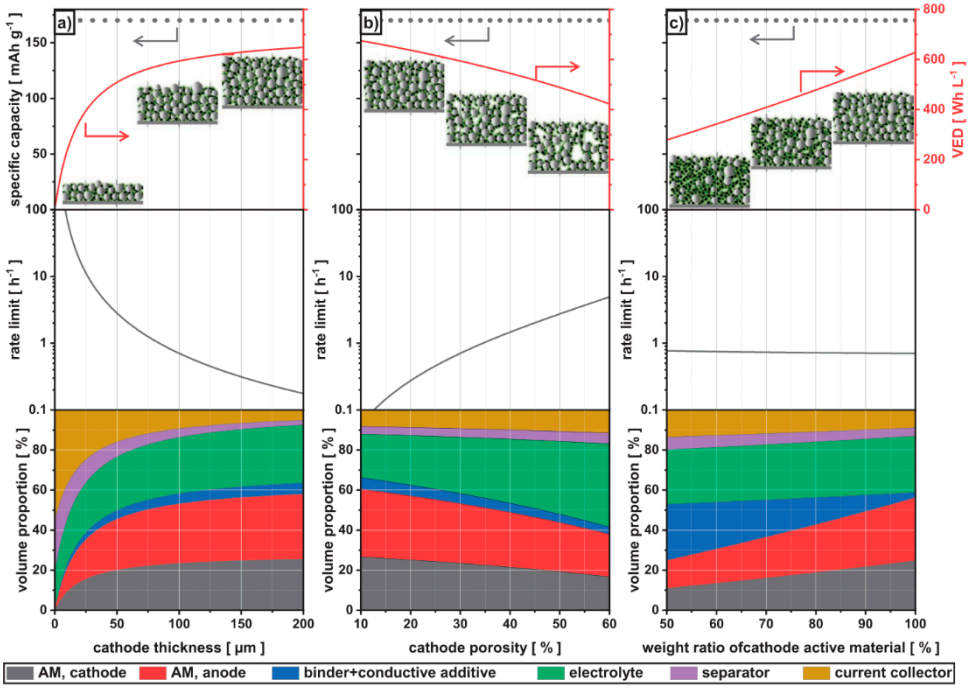

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Figure 5. Comparison of material-level and full-cell-level performance parameters, illustrating how cathode thickness, porosity, and active-material fraction alter volumetric energy density, rate limits, and component volume fractions. Adapted from Heubner et al. [112].

8.2. Areal, Volumetric, and Energy Metrics

Areal capacity is one of the simplest ways to move beyond idealized half-cell screening because it links electrochemical capacity to electrode loading. Heubner and co-workers [112] showed that low thickness electrodes, often below 20 micrometers and below 5 mg cm^{-2}, are common in laboratory studies because they are easy to fabricate and reduce diffusion limitations. However, when full cell metrics are calculated, increasing cathode thickness can improve volumetric and gravimetric energy density by reducing the relative share of inactive materials. The tradeoff is that thick electrodes often lose rate capability because transport through the porous electrode becomes more demanding [112].

Surace et al. [116] addressed this issue experimentally by focusing on high areal capacity NMC811 electrodes. Their study used electrodes with commercially relevant areal capacity near 4 mAh cm^{-2}, active material content above 90 wt.%, and low binder content of 3 wt.%. This design made their rate capability results more meaningful than low loading tests. The authors showed that water based NMC811 cathodes can approach or exceed NMP and PVDF electrode performance when binder chemistry and current collector design are optimized. With carbon coated aluminum current collectors, CMC:PAA based electrodes achieved about 172 mAh g^{-1} at 1C and about 88 mAh g^{-1} at 2C, with the 2C value exceeding PVDF based electrodes by about 30 mAh g^{-1}. The key lesson is that rate performance depends not only on active material chemistry but also on binder, current collector surface, electrode defects, and practical areal loading [116].

Dunne et al. [117] treated the same problem from a transport perspective. They noted that increasing the active material fraction by thickening electrodes can improve specific energy, but this often reduces high-rate performance. Their work proposed the mass transfer coefficient hm, derived from voltage and charge cycling measurements, as a quantitative indicator of electrode design quality. By comparing electrode thickness with and without corrugation, they showed how structured electrodes can reduce rate capacity retention losses. This is particularly relevant for practical batteries because thick electrodes are needed to reduce inactive fractions, but the associated transport penalty must be quantified rather than hidden by reporting only low-rate capacity [117].

Energy capacity also requires careful definition. Bašić et al. [118] proposed a method that defines battery energy capacity as the energy stored in the battery, while accounting for both charging and discharging losses. Their approach experimentally determines charging and discharging efficiencies under different power rates and ambient temperatures. The method outperformed baseline approaches for estimating energy capacity and state of energy because it included operational efficiency and temperature effects. At the end of one case study, where the real state of energy was 0%, their method estimated 2.7% at 0 °C and 1.8% at 25 °C, compared with baseline estimates ranging from 6.4% to 11.1% [118].

Liu et al. [119] further demonstrated that energy efficiency and Coulombic efficiency are dynamic quantities rather than fixed cell descriptors. Using lithium titanate batteries, they considered state of charge regions and discharge current rates as variables that affect efficiency. Their learning-based model used more than eight million empirical datasets to estimate continuous time energy efficiency and Coulombic efficiency, with a training error of 10^{-4}. This type of approach is important because practical batteries operate under changing current, state of charge, and environmental conditions, not only under a single constant current laboratory protocol [119].

8.3. Initial Coulombic Efficiency and Rate Performance

Initial Coulombic efficiency is a practical metric because it tracks the first cycle loss of cyclable inventory. In full cells, irreversible loss at either electrode cannot be ignored because there is no infinite lithium or sodium reservoir to compensate for side reactions. Scurtu et al. [115] noted that coin cells are commonly used to evaluate specific capacity, initial Coulombic efficiency, and discharge

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rate capability, but they warned that high current tests and lithium metal counter electrode effects must be interpreted critically, especially for working electrodes with high areal capacity. This is important because half-cell excess can disguise inventory loss that would reduce the available energy of a balanced full cell [115].

Madani et al. [111] focused directly on Coulombic efficiency under different current rates and prior cycling histories. Their experiments compared lithium-ion cells cycled at 0.4C and 0.8C, with an additional cell subjected to prior cycling at 0.2C, 0.4C, 0.6C, and 0.8C. They found that nearly all stored charge could be extracted even at higher currents, but capacity loss still appeared. At 0.8C, the average discharge and charge capacity loss rates were about 0.44% and 0.45% per cycle, respectively. The study also links Coulombic inefficiency to parasitic reactions that consume electrolyte ingredients or active lithium and reports higher parasitic reaction indicators at 0.8C than at 0.4C [111].

Xu [113] placed Coulombic efficiency in the broader context of reversibility. A high cycle number does not automatically mean long cycle life. Very high-rate cycling can accumulate many cycles quickly while masking parasitic reactions and self-discharge. For this reason, Xu [113] emphasized that high precision Coulombic efficiency and appropriately harsh low-rate testing can reveal reversibility problems that fast cycling may hide. This argument is central to practical relevance: a battery chemistry that survives many rapid shallow cycles may still fail under slower, high state of charge exposure because time dependent parasitic reactions are not captured.

Rate performance should therefore be interpreted as a coupled transport and design metric. Dunne and co-workers [117] explained that capacity recorded during constant current cycling decreases as C rate increases because voltage losses cause the cell to reach its lower voltage limit earlier. In other words, the active material may not be exhausted, but the usable capacity is cut off by transport and polarization losses. Their mass transfer coefficient approach provides a way to compare electrode designs through the physics of transport rather than through capacity retention alone [117].

Surace and co-workers [116] provided an applied example of this principle in high loading NMC811 electrodes. The best water-based electrodes depended on the interaction between binder mixture and current collector. On bare aluminum, the ternary CMC:PAA:SBR binder performed best, reaching 150 mAh g^{-1} at 1C. On carbon coated aluminum, CMC:PAA and sodium alginate formulations improved the performance, with CMC:PAA on carbon coated aluminum reaching about 170 mAh g^{-1} at 1C and 80 to 88 mAh g^{-1} at 2C. The recovery to 98% to 99% of initial capacity at C/10 after rate testing also helped separate reversible rate limitations from permanent degradation [116].

8.4. Long Term Cycling, Reproducibility, and Reporting Standards

The practical meaning of long cycling depends on how the experiment is designed and reported. Xu [113] warned that cycle number is often confused with cycle life, even though cycling rate, time at high state of charge, voltage limits, temperature, and Coulombic efficiency determine whether the result reflects durable reversibility. A cell cycled quickly can accumulate an impressive number of cycles while spending limited time under conditions that intensify parasitic reactions. Therefore, a cycling claim should report not only capacity retention and cycle count, but also current rate, voltage window, time per cycle, temperature, rest steps, cell format, electrode loading, and calculation basis [113].

Scurtu and co-workers [115] converted this reporting problem into a scale problem. They argued that the cell area and format must be specified because small formats can overrepresent edge effects, pressure effects, casing effects, and alignment artifacts. In their comparison, a 12 mm diameter coin cell electrode has a perimeter to geometric area ratio of 3.33 cm^{-1}, whereas a double side coated 21700 cylindrical cell electrodes has a ratio of 0.36 cm^{-1}, about ten times lower. Their experimental campaign with 34 cylindrical 21700 cells produced an average discharge capacity of 3.44 ± 0.03 Ah and a 1 kHz impedance of 12.6 ± 0.3 mOhm after formation, showing that large area wound formats can provide meaningful reproducibility data when the same materials, dimensions, design, and procedures are used [115].

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Ghani and group [114] similarly argued that test schemes must specify the working voltage window, C rate, electrode weight, and electrode thickness to determine lifespan accurately. They also emphasized the role of mass loading and the N/P ratio in balancing full cells. The recommended full cell N/P ratio commonly falls between 1 and 1.2, and changes in N/P ratio can affect initial Coulombic efficiency, lithium plating risk, specific capacity, and cycle life. Such information belongs in the main performance discussion rather than only in supporting information because it determines whether reported energy and cycling metrics are comparable [114].

Bašić and co-workers [118] added another reporting requirement: battery capacity should be periodically reestimated because the method describes the current state of the battery under a given temperature and aging condition. This is directly relevant to long-term studies because capacity and state of energy are not fixed properties. They change with aging, operating history, power rate, and ambient temperature. The same logic applies to the continuous time efficiency model of Liu and co-workers [119], which shows that efficiency changes with state of charge and current. Reporting a single efficiency value can therefore obscure dynamic performance during realistic operation.

9. Mitigation Strategies

The mitigation of failure in practical lithium ion and sodium ion batteries require more than selecting a high-capacity electrode. The papers analyzed in this section show that degradation is distributed across surfaces, interfaces, electrolytes, binders, morphology, and full cell coupling. A useful way to organize mitigation strategies is to treat each intervention as a response to a specific failure pathway. Surface coatings reduce direct electrolyte attack. Artificial interphases regulate ion flux and suppress dendrites. Electrolyte formulation determines which interphase species form and how stable they remain. Binders preserve mechanical and electronic integrity during volume fluctuation. Full cell design then tests whether the anode interphase and cathode interphase can operate compatibly in the same electrolyte [120–129].

For this reason, the section begins with a compact mitigation map. The table does not simply list strategies; it connects each intervention to a failure pathway, the mechanism by which the intervention works, and the practical tradeoff that must be checked before the strategy is considered successful.

Table 6 organizes the major mitigation strategies discussed in this section according to the failure pathway they are designed to address. Rather than presenting stabilization approaches as isolated solutions, the table links each strategy to its primary mechanism, its potential practical tradeoff, and the type of validation needed to support a meaningful stabilization claim. This organization is important because a mitigation strategy that improves one failure mode may introduce new limitations in impedance, manufacturability, volumetric energy density, or full cell compatibility.

Table 6. Failure pathways, mitigation levers, and practical tradeoffs that must be checked before claiming stabilization.

Failure pathway	Mitigation lever	Primary mechanism	Practical tradeoff	Validation focus
Repeated electrolyte decomposition at Si surfaces	Carbon, inorganic, polymer, nitride, oxide, or double-shell coatings.	Separates Si from the electrolyte, stabilizes SEI, buffers expansion, and can improve conductivity.	Coatings may add impedance or crack during repeated volume change.	Confirm ICE, impedance, morphology retention, and cycling at realistic loading [121,122].
Unstable Na metal SEI and dendrite growth	Artificial inorganic, organic, or hybrid SEI layers.	Regulates Na+ flux, improves mechanical robustness, and suppresses dendritic deposition.	Artificial SEI chemistry can evolve during cycling and may lose uniformity.	Track dendrite suppression, CE, interphase composition, and symmetric-to-full-

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				cell translation [123,129].
Dead Na, bare Na exposure, and uneven plating	Electrolyte optimization, deposition hosts, and protective layers.	Reduces side reactions, guides uniform deposition, and lowers local current density.	Hosts and protective architectures can reduce volumetric energy and complicate manufacturing.	Evaluate Na inventory loss, gas formation, separator safety, and full-cell compatibility [124,129].
SEI/CEI instability in SIB full cells	Electrolyte selection, additives, and paired interphase engineering.	Forms ion-conducting but electronically insulating passivation layers on both electrodes.	Half-cell stability may not predict paired SEI and CEI behavior.	Use full cells with finite sodium inventory and diagnose both electrodes after cycling [120,125].
Electrolyte degradation during storage or handling	Control salt quality, additives, temperature, container material, and Na exposure.	Reduces decomposition products before cycling and improves reproducibility.	Electrolyte degradation can occur without applied potential.	Report storage conditions and analyze degradation products when electrolyte instability is suspected [126,127].
Mechanical and electrical contact loss	Composite, conductive, self-healing, or binder-free electrode architectures.	Maintains adhesion, cohesion, and conductive pathways during volume change.	Binder chemistry must match the active material surface and processing solvent.	Measure adhesion, crack formation, impedance growth, and cycling under practical calendaring conditions [128].

Figure 6 provides a visual framework for the interface engineering strategies used to stabilize sodium metal anodes. The schematic summarizes three major intervention routes: electrolyte optimization, sodium deposition hosts, and protective interfacial layers. It also illustrates the failure pathways that these strategies are intended to suppress, including parasitic side reactions, uneven sodium deposition, dendrite growth, dead sodium formation, large volume fluctuation, and short circuit. This framework reinforces the need to evaluate mitigation strategies as coupled chemical, mechanical, and cell level interventions rather than as independent material modifications [124].

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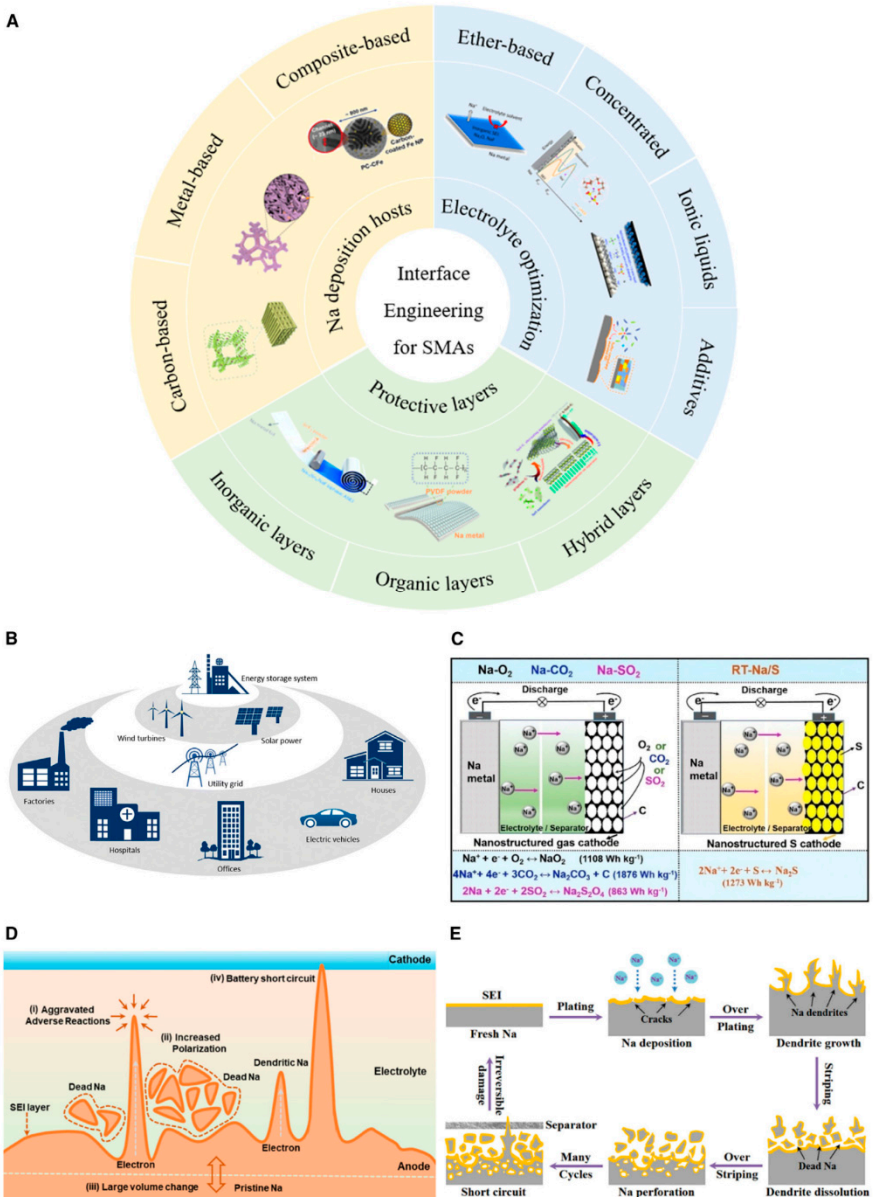

Figure 6. Interface engineering strategies for stabilizing sodium metal anodes, including electrolyte optimization, sodium-deposition hosts, and protective layers, together with major failure pathways such as side reactions, dendrite growth, dead sodium, and short circuit. Adapted from Liu et al. [124].

9.1. Surface Coatings and Artificial Interphases

Surface coating strategies for silicon negative electrodes represent one of the clearest examples of mitigation by spatial separation. Song and Chae [121] reviewed why silicon remains attractive for next generation lithium-ion batteries: it offers a theoretical specific capacity of approximately 4200 mAh g-1, a low operating potential below 0.4 V vs. Li/Li+, and abundant reserves. These advantages are counterbalanced by more than 300% volume change during lithiation and delithiation, unstable SEI formation, and intrinsically low electrical and ionic conductivity. Their central mitigation principle is direct and practical: the surface of silicon should not remain continuously exposed to the electrolyte. Surface coatings reduce electrolyte decomposition, help preserve electrical connectivity, stabilize SEI formation, and can be combined with nanostructure design to buffer expansion [121].

Nam and co-workers [122] developed the same coating argument from the perspective of coating materials. Their review classified coating materials for silicon-based anodes into carbon, inorganic materials, metal-based coatings, metal oxide coatings, nitride-based coatings, polymers, and double shell designs. Comparison is important because coating does not have a single function.

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Carbon coatings can improve conductivity and protect the surface. Inorganic or oxide coatings can improve chemical stability. Polymer coatings can provide elasticity and accommodate deformation. Double shell designs can combine complementary properties that a single layer cannot provide. In all cases, coating design must balance protection, ionic transport, electronic transport, and mechanical accommodation [122].

The same logic becomes more severe for sodium metal. Shi and co-workers [123] argued that the unstable and inhomogeneous SEI is a root cause of uncontrolled sodium dendrite formation and low Coulombic efficiency. They identified the ideal artificial SEI as chemically and electrochemically stable, ionically conductive, mechanically strong, flexible, robust, and able to distribute Na^+ flux and the electric field uniformly. Their review organized artificial interphase engineering into inorganic, organic, and hybrid inorganic or organic protective layers. This classification is useful because sodium metal anodes need simultaneous chemical passivation and mechanical control. A layer that is chemically stable, but brittle can crack during plating and stripping, while a flexible but poorly ion conducting layer may increase polarization [123].

Liu and co-workers [124] broadened artificial interphase design into a larger interface engineering framework for sodium metal anodes. They emphasized that sodium metal anodes offer high theoretical capacity of 1166 mAh g-1, low redox potential of -2.71 V vs. the standard hydrogen electrode, low cost, and sodium abundance. However, their practical use is restricted by unavoidable side reactions, unstable SEI, dendrite growth, large volume change, and safety concerns. The review grouped stabilization strategies into electrolyte optimization, construction of sodium deposition hosts, and artificial protective layers. This framing is valuable for practical cells because it separates three tasks that are often mixed: changing the chemistry of the interphase, changing the geometry of sodium deposition, and physically separating sodium metal from the bulk electrolyte [124].

Kulova and Skundin [125] provided the interphase foundation that explains why coatings and artificial SEI layers matter in sodium ion batteries. They reviewed SEI and CEI formation in sodium systems and emphasized that passive films on negative electrodes originate from electrolyte reduction, while passive films on positive electrodes originate from electrolyte oxidation. SEI formation consumes irreversible charge and therefore contributes directly to irreversible capacity. They also noted that SEI and CEI composition depends on the electrode material, electrolyte, additives, and electrode history. This reinforces why surface coatings and artificial interphases should not be evaluated only as external shells. They change the chemical environment in which the SEI or CEI forms [125].

9.2. Electrolyte and Additive Engineering

Electrolyte engineering is the chemical counterpart to surface engineering. Ji and co-workers [126] focused on sodium metal batteries and identified three major dilemmas of sodium metal anodes: sodium dendrite formation, dead sodium formation, and repeated exposure of bare sodium. The authors explained that electrolyte optimization can address these dilemmas through solvent chemistry, salt chemistry, additives, polymer electrolytes, and all solid-state electrolytes. Compared with deposition hosts or artificial SEI construction, changing electrolyte composition is often simpler because it changes the chemical environment without necessarily adding a new electrode architecture. However, the paper also makes clear that electrolyte optimization must regulate both sodium reactivity and sodium ion migration, not only bulk ionic conductivity [126].

Kulova and Skundin [125] showed why sodium electrolytes deserve special attention. Sodium metal forms natural SEI layers that are generally less protective than those in lithium systems. The review describes sodium dendrites as branched, bushy, or mossy, with a highly developed surface that accelerates electrolyte interaction. It also notes that SEI on sodium can be more soluble in electrolyte than SEI in lithium systems. These properties explain why electrolyte composition, additive choice, and artificial passivation are central mitigation strategies in sodium-based cells [125].

Hashimov and Hofmann [127] added a practical and often neglected dimension: electrolyte degradation can occur before electrochemical cycling and even without applied potential. Their GC-

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MS study investigated EC/PC electrolytes containing NaPF6 or NaTFSI, with FEC or NaDFOB additives, under different temperatures, vial materials, and sodium metal exposure. The study found that the conductive salt source significantly affected degradation, that FEC stability depended on storage temperature, vial material, and the presence of sodium metal, and that NaDFOB helped mitigate degradation. The presence of sodium metal accelerated degradation, particularly at elevated temperature, and aluminum vials performed better than PE vials. These findings are directly relevant to mitigation strategies because electrolyte handling and storage can change the apparent outcome of half-cell testing [127].

Zhang and co-workers [128] reviewed electrolyte additives for sodium ion batteries and emphasized that additives are among the simplest and most cost-effective approaches for improving the electrode electrolyte interface. Their review classified additives into carbonate, sulfur containing, silicon containing, phosphorus containing, inorganic, and other additives. They identified three major functions: participation in interfacial reactions to form SEI or CEI, modification of Na+ solvation structure, and improvement of safety or performance under extreme conditions. Although additive amounts are generally small, often below 5 wt%, their effect can be substantial. For example, VC and FEC can form protective interphase films, but excessive additive content can thicken SEI, increase internal resistance, increase polarization, and reduce cycling performance [128].

9.3. Morphology, Defect, and Binder Optimization

Morphology optimization has a dual role. It can reduce mechanical failure, but it can also create new interfacial areas for parasitic chemistry. For silicon negative electrodes, Song and Chae [121] described nanostructuring as a strategy to mitigate crack formation and provide space for volume change. However, they also warned that the enlarged surface area of nanostructured silicon can increase surface side reactions and reduce initial Coulombic efficiency. Their review therefore supports a combined approach: morphology should be engineered together with surface coatings, so that mechanical breathing space does not become an uncontrolled reaction surface [121].

Nam and co-workers [122] made this relationship explicit by emphasizing coating materials for nanosized or structured silicon. Their review shows that coating strategies can resolve the extra side reactions caused by high surface area nanostructures. This is particularly important for practical electrodes because a material can show impressive capacity at the particle level while losing cell relevance if its surface continuously consumes electrolyte and active lithium. In this sense, coating is not only an interfacial strategy. It is also a morphology management strategy because it controls how much reactive surface is chemically available during cycling [122].

Binders address a different but equally important failure mode: mechanical and electrical disconnection inside composite electrodes. Srivastava and co-workers [129] emphasized that binders account for less than 5% of battery weight but strongly influence electrode integrity. Binders provide homogeneous coating, adhesion of active material to the current collector, electrochemical compatibility, and pathways that support electron and ion movement. During lithiation and delithiation, volume changes can damage electrode structure, so binders require strength, elasticity, flexibility, and hardness. The review identifies mechanical interlocking, interfacial forces, and thermodynamic wetting as fundamental binder electrode interaction mechanisms, and it highlights failure modes such as contact interface destruction, rupture, and adherend breakage [129].

The binder strategies summarized by Srivastava and co-workers [129] align closely with the failure pathways described in the silicon and sodium metal literature. Composite binders combine the strengths of different binder components. Conductive binders can reduce the need for conductive additives and maintain electronic pathways. Self-healing binders can repair damage during cycling, which is especially relevant for alloying materials with large volume changes. Binder free electrodes are also discussed as a potential route to improve ionic and electrical conductivity and reduce inactive material, although such designs must still preserve mechanical stability during practical processing and cycling [129].

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For sodium metal anodes, morphology and defect control operate through deposition geometry. Liu and co-workers [124] described sodium deposition hosts as one of the main stabilization strategies. Hosts can reduce local current density, provide deposition sites, accommodate volume change, and promote more uniform sodium plating. However, deposition hosts can also increase fabrication complexity and occupy cell volume. This means that morphology-based mitigation must be evaluated against practical energy density, not only dendrite suppression in symmetric or half cells [124].

9.4. Cell-Level Design and Operando-Guided Strategies

The strongest argument for cell level mitigation comes from Zhang and co-workers [120], who reviewed electrode electrolyte interphases in sodium ion batteries from half cells to full cells. They emphasized that SIB operation depends on both SEI and CEI because one electrolyte must function at a reducing anode and an oxidizing cathode. Continuous loss of electrolyte and Na+ in full cells causes rapid capacity fade and a large drop in Coulombic efficiency. In addition, gas generation from electrolyte decomposition can increase interfacial impedance and polarization, intensify side reactions, and compromise safety. Their review therefore treats interphase compatibility as a full cell property, not simply the sum of two half-cell results [120].

This distinction is critical for the section. In half cells, sodium metal can provide an effectively unlimited sodium source and can mask the consequences of irreversible Na^+ consumption. In full cells, however, the cathode and anode must share a finite sodium inventory. Zhang and co-workers [120] noted that initial Coulombic efficiency is closely associated with SEI and CEI quality, and that excess electrolyte decomposition generates thick SEI and CEI along with gas. They further warned that half-cell interphase stability may not accurately predict full cell deterioration because full cells involve cross contamination, including transition metal dissolution products that migrate from the cathode and affect the anode interface [120].

Zhang and co-workers [120] proposed several directions that support operando guided mitigation. These include deeper studies of interphase formation, composition, thickness, and transport in different sodium storage electrodes; advanced in situ characterization of operating full cells; novel electrolytes such as ionic liquids; electrode surface optimization; artificial CEI and SEI construction; and multiscale simulations to predict interphase formation and dynamic evolution. The recommendation is not merely to add characterization after the fact. The goal is to use interphase evidence to guide electrolyte, coating, binder, and cell design decisions before long cycling failure occurs [120].

Taken together, the uploaded papers suggest that mitigation strategies should be validated through a progressive workflow. First, identify the dominant failure pathway: surface reaction, dendrite growth, electrolyte aging, interphase instability, particle fracture, or binder failure. Second, select the intervention that directly targets that pathway: coating, artificial SEI, electrolyte additive, host architecture, binder chemistry, or full cell electrolyte matching. Third, evaluate whether the intervention introduces a new penalty, such as increased impedance, lower initial Coulombic efficiency, reduced volumetric energy, manufacturing complexity, or poor storage stability. Finally, confirm the mitigation strategy in full cells using interphase aware diagnostics, because the SEI and CEI must remain compatible under the same electrolyte, voltage window, sodium inventory, and cycling protocol [120–129].

10. Toward Practical Batteries

The transition from promising electrode chemistry to a practical battery is not a single experimental step, but a validation sequence. At this stage, the central question is no longer whether sodium ions can be reversibly stored in a host material. The more relevant question is whether a reported chemistry can be balanced in a full cell, manufactured with realistic electrode loadings, operated under application-relevant constraints, and independently characterized without losing the performance advantages that justified the material in the first place.

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A useful way to organize the transition is to treat practical validation as a sequence of gates. Material-level capacity is only the first gate. Later gates require electrode architecture, interphase stability, sodium inventory management, full-cell balancing, diagnostic reproducibility, and realistic duty-cycle testing. Table 7 summarizes these gates and clarifies what each stage is meant to prove.

Table 7. Practical validation gates for moving sodium-ion battery materials toward application-relevant cells.

Validation gate	Required evidence	Failure mode revealed	Practical decision supported	Sources
Material plausibility	Reversible capacity, voltage profile, ICE, rate behavior, and early degradation signature.	False promise from isolated active material performance.	Whether the chemistry deserves electrode-level development.	[130–137]
Electrode realism	Mass loading, areal capacity, thickness, porosity, active material fraction, binder, conductive additive, and current collector.	Loss of performance when thin, low-loading electrodes are replaced by practical electrodes.	Whether the electrode architecture can support practical energy and power.	[131,135,137]
Balanced full cell	Cathode/anode pairing, N/P ratio, finite Na inventory, electrolyte amount, voltage window, and formation protocol.	Inventory loss, interphase incompatibility, and poor energy delivery.	Whether half-cell results survive full-cell constraints.	[131,135–137]
Prototype-format validation	Pouch or cylindrical format, cell capacity, EIS, rate capability, cycling, temperature response, and safety-device behavior.	Gas evolution, format effects, pressure effects, and failure modes not visible in coin cells.	Whether the design is manufacturable and diagnostically reproducible.	[130,137]
Application qualification	Duty cycle, operating temperature, storage protocol, thermal behavior, field demonstration, and use-case-specific acceptance criteria.	Mismatch between laboratory performance and field reliability.	Which application niche the SIB can realistically serve.	[130,132,134,135]

10.1. Minimum Validation Requirements

Minimum validation should begin with the recognition that a battery is not simply a container for an active material. A practical claim must specify the electrode, electrolyte, separator, current collectors, inactive fractions, cell format, and operating conditions. Barati and co-workers [131] make this point quantitatively by showing that SIB discharge capacity and reaction-zone stability are highly

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sensitive to electrode architecture. In their DFN-based framework, electrolyte diffusion coefficient and cation transference number remain fundamental constraints, but particle size, electrode thickness, porosity, and active material volume fraction become decisive for capacity delivery and spatially uniform reaction at moderate-to-high C-rates. Their optimization improved SIB capacity by up to 70% and reached a calculated specific energy of 244.5 Wh kg^{-1} at 0.5C, illustrating that cell-level engineering can substantially narrow the gap between sodium-ion and lithium-ion performance [131].

The minimum validation package therefore needs both electrochemical and structural descriptors. At the electrochemical level, it should include initial Coulombic efficiency, average discharge voltage, areal capacity, rate performance, energy efficiency, long-term cycling, voltage hysteresis, and impedance growth. At the electrode level, it should include electrode loading, coating thickness, porosity, calendering state, particle size distribution, binder and conductive-carbon content, electrolyte amount, current collector identity, and formation protocol. This level of reporting is particularly important for SIBs because their attractive cost and sustainability profile can be undermined if low-energy, low-loading, or electrolyte-rich laboratory cells are used as the basis for commercial claims.

The industrial and application reviews reinforce this point. Zhao and co-workers [132] emphasize that SIBs are promising for large-scale electrical energy storage because of sodium availability and cost, but they frame commercialization around engineering constraints, not only electrode chemistry. Chayambuka and co-workers [133] similarly argue that SIBs should be assessed through a balance of power, cyclability, safety, cost, and cell design. Bača and co-workers [134] place this assessment in the context of applications, noting that stationary storage prioritizes safety and cost, whereas portable or mobility applications impose stronger size and weight constraints. Another group [135] synthesize these perspectives into a commercialization roadmap in which durability, safety, manufacturability, interphase control, and reproducibility are the decisive requirements.

Laufen and co-workers [136] provide one of the clearest examples of minimum validation applied to a commercial SIB. They investigated a 1.2 Ah 18650 sodium-ion cell using teardown, half-cell measurements, GC-MS, ICP-OES, Hg-porosimetry, XRD, SEM, EDX, EIS, C-rate tests, float current tests, micro-CT, and ultrasonic measurements. This workflow demonstrated that methods established for lithium-ion cells can be transferred to sodium-ion cells, while also revealing sodium-specific questions such as electrolyte behavior, gas evolution, and balancing uncertainty. The investigated commercial cell had moderate specific energy of 97 Wh kg-1 and high specific power of 810 W kg-1, making it more relevant for high-power applications than for maximum-energy applications [136].

Figure 10.1 presents the conceptual basis for linking electrode architecture, ion transport, and reaction zone distribution in rechargeable metal ion batteries. The schematic illustrates the coupled movement of ions through the electrolyte and electrons through the external circuit during charge and discharge, while the DFN framework resolves transport and reaction processes across the positive electrode, separator, negative electrode, electrolyte phase, and active material particles. This type of representation highlights why practical cell validation requires simultaneous consideration of particle size, electrode thickness, porosity, electrolyte transport properties, and active material utilization, rather than evaluation based solely on active material capacity [131].

The relationship between electrode architecture, ionic transport, and spatial reaction distribution is illustrated schematically in Figure 7. The upper panel represents the coupled movement of ions through the electrolyte and electrons through the external circuit during charge and discharge, while the lower panel shows how the DFN model resolves transport and reaction processes across the positive electrode, separator, negative electrode, electrolyte phase, and active material particles. This framework supports the need to evaluate practical batteries through coupled structural and electrochemical parameters, including particle size, electrode thickness, porosity, electrolyte transport properties, and active material utilization [131].

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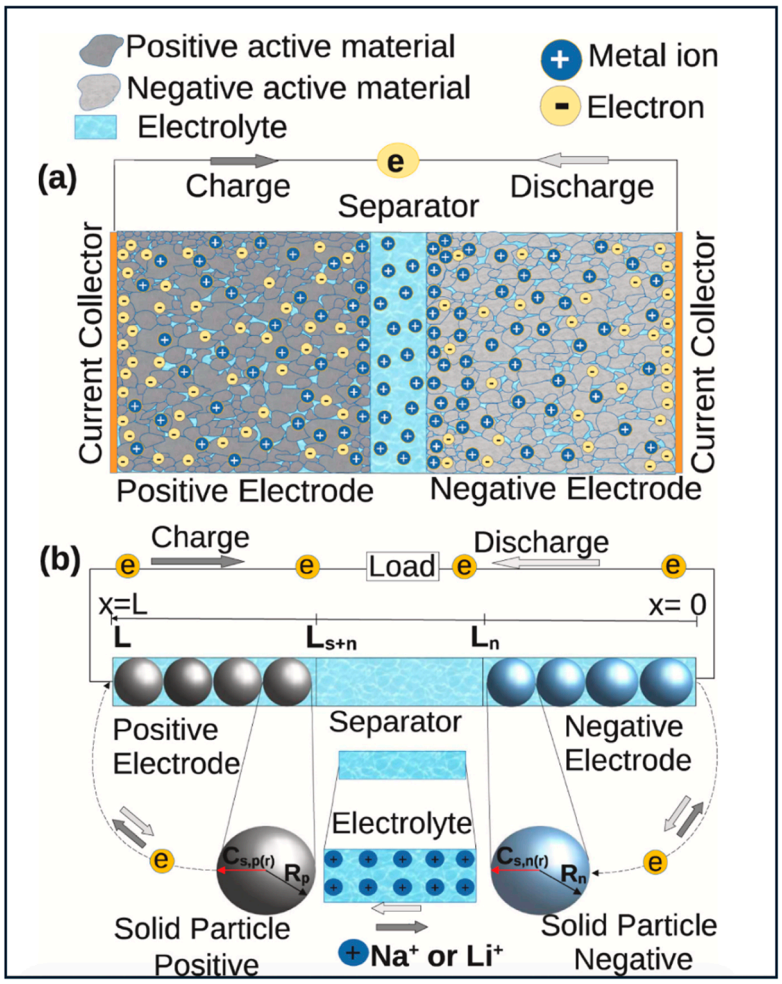

Figure 7. Schematic representation of metal-ion battery components and the DFN-based modeling framework used to connect electrode architecture, electrolyte transport, and reaction-zone design. Adapted from Barati et al. [131].

10.2. From Half-Cells to Full Cells

Half-cells remain valuable for isolating a cathode or anode reaction, but they are not a reliable final predictor of practical performance. The main reason is that half-cells often use sodium or lithium metal counter electrodes, excess electrolyte, thin electrodes, relaxed pressure conditions, and simplified balancing. These conditions can hide sodium-inventory loss, interphase incompatibility, electrolyte depletion, gas formation, and impedance accumulation. A full cell forces all of these constraints into the same finite system.

The gap between half-cells and full cells is especially important for sodium-ion batteries because sodium inventory is finite, hard-carbon anodes often exhibit first-cycle irreversible loss, and cathodes can be sensitive to structural water, vacancies, phase transitions, or high-voltage interfacial reactions. Yadav and co-workers [137] identify high first-cycle capacity loss, unsuitable electrolytes, air and moisture instability of cathodes, and limited energy density as major obstacles for sodium-based batteries. They also point to Na-compensation methods, cathode and electrolyte additives, mixed-metal cathodes, alloying anodes, and solid-state electrolytes as routes toward more robust sodium-based battery technology [137].

The commercial-cell studies show why this translation must be tested directly. Laufen et al. [136] found that half-cell fitting of data from a commercial 1.2 Ah SIB could not fully resolve the balancing state of the fresh cell, and they could neither confirm nor dismiss presodiation or sacrificial-salt use from the available fitting results. That uncertainty matters because sodium inventory management directly influences full-cell capacity retention. Their study also found that excessive electrolyte

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decomposition triggered the cell current interrupt device, preventing a deeper lifetime analysis. This is a practical reminder that full-cell validation must include safety-relevant cell behavior, not only capacity retention [136].

Shelke et al. [130] move the validation target further toward application by testing sodium-ion pouch cells under laboratory and field-like extreme conditions. Their pouch cells delivered approximately 96 Wh kg-1 at room temperature, 74 Wh kg-1 at -25 °C, and 46 Wh kg-1 at -50 °C. They also demonstrated operation under windy and snowy environments and reported solar charging at -100 °C, with about 70 Wh kg-1 under that extreme condition. This work is important because it shows that full-cell validation can be designed around an intended use case, in this case renewable energy storage and emergency backup in cold environments [130].

The broader commercialization reviews support the same conclusion. Hu et al. [138] describe Na-ion batteries as a rising technology for grid electrical energy storage because of similar operating principles to lithium-ion batteries, abundant sodium resources, and mature fabrication technologies. However, they also emphasize that cathodes, anodes, and electrolytes must continue to be optimized together. Other researchers [135] argue that SIBs have moved beyond academic plausibility, but that their realistic near-term role is in stationary storage and power-oriented markets where lower energy density can be offset by supply-chain resilience, safety, and cost advantages.

10.3. Realistic Testing Workflows

A realistic testing workflow should move from controlled materials screening toward progressively less forgiving cell formats. The goal is not to abandon half-cells, but to prevent them from carrying conclusions they cannot support. The first stage can use half-cells to identify reversible redox behavior and degradation signatures. The second stage should use practical electrodes to confirm that the material still works at realistic loading, thickness, porosity, and binder content. The third stage should use full cells to evaluate balancing, sodium inventory, electrolyte compatibility, initial Coulombic efficiency, impedance growth, and voltage profile. The fourth stage should use pouch or cylindrical formats to evaluate thermal behavior, pressure, safety features, manufacturability, and reproducibility. The final stage should test the cell under duty cycles that resemble the intended application.

The strongest workflow among the uploaded papers is the commercial-cell analysis by Laufen et al. [136]. Their study combines destructive and non-destructive methods, electrochemical testing, electrolyte analysis, active-material characterization, and aging diagnostics. This type of workflow is essential because a commercial sodium-ion cell is a complex object. A single cycling curve cannot reveal whether capacity fade arises from electrolyte decomposition, gas generation, cathode degradation, anode imbalance, pore-structure changes, or safety-device activation. The same study also shows that established lithium-ion diagnostic methods can be used for SIBs, but sodium-specific interpretation is still necessary [136].

Model-informed testing is another essential part of the workflow. Barati et al. [131] demonstrate that DFN modeling, sensitivity analysis, and multi-objective optimization can identify which parameters control capacity and reaction-zone stability. In their simulations, large particle sizes and thick electrodes in SIBs intensified solid-state diffusion limitations and electrolyte concentration polarization, especially above 1 C. This gives a practical role to modeling: it can guide which electrode parameters should be experimentally prioritized before expensive prototype testing begins [131].

Field-relevant testing should be added when the target application demands it. Shelke et al. [130] are useful here because they tested pouch cells not only in controlled laboratory conditions, but also in cold, windy, and snowy environments. Their work shows that a realistic workflow can include environmental stress conditions, batch reproducibility through EIS, equivalent-circuit fitting, and direct demonstration of the intended energy-source pairing, such as wind or solar. This type of test is more informative for renewable energy storage than a room-temperature coin-cell rate test alone [130].

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10.4. Opportunities and Bottlenecks for Na-Ion Batteries

The opportunity space for sodium-ion batteries is strongest where the application rewards cost, safety, power capability, resource availability, and manufacturability more than maximum gravimetric energy density. Zhao et al. [132] position SIBs as promising for large-scale electrical energy storage because they can support renewable energy integration and grid functions. Chayambuka et al. [133] also identify SIBs as one of the most promising beyond-lithium technologies because lithium and cobalt supply chains face cost and availability pressure, whereas sodium is more abundant and more widely distributed. Bača et al. [134] sharpen the application logic by noting that stationary storage prioritizes safety and cost, while portable and mobility applications place heavier emphasis on weight and volume.

Several technical advantages support this position. SIB manufacturing can draw from lithium-ion infrastructure [133,136]. Sodium does not alloy with aluminum under the same practical constraint as lithium, which creates the possibility of lower-cost aluminum current collectors on the negative side [134,137]. PBA-based and polyanionic systems can offer strong power, stability, or safety advantages depending on the chemistry [132,134,136]. Commercial and near-commercial companies have already moved the field beyond laboratory curiosity, with Yadav et al. [137] listing companies such as Novasis Energies, Faradion, Natron Energy, Rechargion Energy, HiNa, Altris, Tiamat, AGM, and CATL as active in sodium-based battery development.

The bottlenecks are equally clear. SIBs generally deliver lower energy density than lithium-ion batteries because sodium has a higher atomic mass, larger ionic radius, and a less negative standard potential. Bača et al. [134] explain that the larger Na^+ radius limits direct transfer of graphite-based lithium-ion anodes and contributes to lower cell voltage and specific energy. Yadav et al. [137] further identify first-cycle capacity loss, unsuitable electrolytes, and cathode air or moisture instability as major practical challenges. Chayambuka et al. [133] describe the commercialization path as promising, especially because of power, safety, and cycling results, but they do not frame SIBs as a universal replacement for LIBs. Other team [135] similarly conclude that the most realistic route to mass commercialization is not a single breakthrough material, but integrated maturation of cell design, electrolyte and interphase packages, scalable processing, and application-focused qualification.

A second bottleneck is that commercial data remain limited. Laufen et al. [136] show the value of independent analysis of commercial cells, but their study also reveals that lifetime assessment can be interrupted by gas-related safety-device activation. This highlights the need for standardized third-party testing, postmortem analysis, electrolyte diagnostics, and aging protocols. A third bottleneck is environmental robustness. Shelke et al. [130] show that pouch-cell SIBs can operate at very low temperatures when designed with low-temperature-compatible components, but their study also underscores that most prior low-temperature work has been conducted in coin-cell or half-cell formats rather than practical prototypes. Therefore, more application-specific pouch and cylindrical testing is needed before broad deployment claims can be made.

In practical terms, sodium-ion batteries should be positioned as a complementary technology. Their strongest near-term opportunities are stationary storage, uninterruptible power supply, peak shaving, renewable integration, cold-region emergency backup, high-power applications, and selective light mobility or short-range uses. Their most important bottlenecks are energy density, interphase stability, full-cell sodium inventory, low-temperature and high-temperature reliability, gas evolution, reproducible manufacturing, and long-term field data. The development pathway should therefore be organized around application-specific qualification rather than direct comparison with the highest-energy lithium-ion cells.

Overall, the movement toward practical batteries requires a change in evidence. A material that performs well in a half-cell should be treated as a candidate, not as a technology. A technology claim should require practical electrodes, balanced full cells, transparent reporting of inactive components, diagnostic evidence, realistic temperature and C-rate testing, and reproducible prototype formats. The strongest papers in this section provide complementary pieces of that pathway: Barati et al. [131]

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supply the modeling framework for rational reaction-zone design; Laufen et al. [136] show the value of independent commercial-cell characterization; Shelke et al. [130] demonstrate application-facing pouch-cell validation; and Zhao, Chayambuka, Bača, Yadav, and Hu [132–136] establish the commercialization logic, opportunities, and constraints that should guide sodium-ion battery development.

11. Conclusions

11.1. Main Lessons

The development of advanced lithium ion and sodium ion batteries requires a fundamental shift from material centered evaluation toward cell level validation. Half-cell testing remains essential for early screening because it enables rapid assessment of electrochemical activity, reaction mechanisms, and comparative material behavior. However, half-cell performance alone cannot establish practical relevance. Once promising materials are translated into full cells, their behavior becomes governed by electrode balancing, finite ion inventory, areal loading, electrode density, electrolyte amount, pressure, interfacial stability, and the interaction between active and inactive components. Therefore, the central lesson of this review is that practical battery performance is not defined by isolated specific capacity, but by the ability of a material, electrode, electrolyte, and interphase system to operate together under realistic constraints.

Interfacial chemistry is one of the most decisive factors controlling this translation. The formation, evolution, and instability of the solid electrolyte interphase and cathode electrolyte interphase determine irreversible capacity loss, impedance growth, electrolyte consumption, gas evolution, and long-term cycling behavior. These processes are especially important in sodium ion batteries, where larger ionic size, different solvation behavior, and distinct interphase chemistry create challenges that cannot be solved by direct transfer of lithium-ion battery design rules. Likewise, alloying, conversion, layered oxide, polyanionic, Prussian blue analog, carbon based, and nanostructured electrodes each present different combinations of opportunity and limitation. A chemistry that appears promising at the material level may become impractical if it cannot sustain structural reversibility, interfacial stability, sufficient electrode loading, and reproducible full cell performance. Operando and in situ characterization methods provide an essential bridge between electrochemical data and mechanistic understanding. X ray-based techniques, vibrational spectroscopy, microscopy, impedance analysis, and multimodal approaches help reveal structural evolution, interphase formation, reaction heterogeneity, gas generation, and degradation pathways while the cell is operating. These tools are not only diagnostic. They should increasingly guide materials selection, electrolyte formulation, electrode engineering, and full cell design.

11.2. Key Challenges

The major remaining challenge is the gap between impressive laboratory results and realistic battery operation. Many reported advances still rely on thin electrodes, excess electrolyte, low mass loading, metal counter electrodes, limited cell formats, and incomplete reporting of inactive components. Such conditions can overestimate rate capability, mask inventory loss, reduce the apparent severity of interfacial degradation, and limit reproducibility across laboratories. For this reason, practical evaluation must include areal capacity, volumetric and gravimetric energy, initial Coulombic efficiency, rate performance, electrolyte amount, electrode thickness, porosity, density, cell format, number of tested cells, and long-term reproducibility. Failure in practical cells is rarely caused by a single process. Capacity fade, impedance rise, mechanical cracking, contact loss, electrolyte depletion, gas generation, transition metal dissolution, surface reconstruction, and interphase instability often reinforce one another. Mitigation strategies must therefore be designed as integrated systems rather than isolated modifications. Surface coatings, artificial interphases, electrolyte additives, binder optimization, morphology control, and cell level engineering can each improve specific failure modes, but each can also introduce new tradeoffs such as increased

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impedance, reduced volumetric energy density, processing complexity, or incomplete compatibility between the anode and cathode interphases. For sodium ion batteries, the opportunity is substantial but application dependent. Sodium ion systems offer attractive advantages for cost sensitive, resource constrained, and stationary energy storage applications. They also benefit from similarities to lithium-ion manufacturing infrastructure. Nevertheless, lower energy density, first cycle sodium inventory loss, cathode moisture sensitivity, electrolyte instability, gas evolution, and limited long term commercial cell data remain important bottlenecks. These limitations do not diminish the relevance of sodium ion batteries, but they clarify that their near-term success will depend on targeted applications rather than direct replacement of the highest energy lithium-ion systems.

11.3. Future Directions

Future research should adopt validation workflows that progressively move from material screening to practical electrodes, balanced full cells, prototype formats, and application specific testing. Early half-cell studies should be followed by high loading electrode measurements, lean electrolyte conditions, realistic voltage windows, controlled pressure or stack conditions, and clear reporting of electrode and cell architecture. Full cell studies should explicitly address electrode balancing, finite lithium or sodium inventory, formation protocol, interphase compatibility, and post cycling diagnostics. Prototype level studies should include pouch, cylindrical, or other scalable formats whenever the goal is practical translation. The field would benefit from stronger standardization in reporting and from closer alignment between academic testing and industrially relevant performance metrics. Capacity, energy, power, cycling stability, and Coulombic efficiency should be reported with clear denominators and sufficient experimental context. Reproducibility should be treated as a core performance metric, not as a secondary detail. Similarly, operando and postmortem characterization should become routine tools for connecting observed electrochemical behavior with physical and chemical degradation mechanisms. Overall, the path beyond half cells requires an integrated framework that combines interfacial chemistry, realistic metrics, advanced characterization, and practical validation. Next generation lithium ion and sodium ion batteries will not emerge only from higher capacity materials. They will require electrode chemistries that remain stable under practical loading, interphases that regulate transport while suppressing parasitic reactions, electrolytes that maintain compatibility across both electrodes, and testing workflows that reveal rather than hide failure pathways. By moving from idealized material assessment toward translational cell design, battery research can more effectively identify which chemistries are not only electrochemically promising, but also practically viable.

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Abbreviations

The following abbreviations are used in this manuscript:

CEI	Cathode–Electrolyte Interphase
DFN	Doyle–Fuller–Newman
DRT	Distribution of relaxation times
EDX	Energy-dispersive X-ray spectroscopy
FEC	Fluoroethylene carbonate
GC-MS	Gas chromatography–mass spectrometry
ICE	Initial Coulombic efficiency
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LMFP	Lithium manganese iron phosphate
LNMO	Lithium nickel manganese oxide
LTO	Lithium titanate oxide
N/P ratio	Negative-to-positive capacity ratio
NaDFOB	Sodium difluoro(oxalato)borate
$NaPF_6$	Sodium hexafluorophosphate
NaTFSI	Sodium bis(trifluoromethanesulfonyl)imide
NCM	Lithium nickel cobalt manganese oxide
NCM90	$LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$
NMC	Lithium nickel manganese cobalt oxide
NMC811	$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$
NMP	N-Methyl-2-pyrrolidone
PAA	Poly(acrylic acid)
PBA	Prussian blue analog
PDF	Pair distribution function
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
SBR	Styrene-butadiene rubber
SEI	Solid–Electrolyte Interphase
SHE	Standard hydrogen electrode
VC	Vinylene carbonate
XAS	X-ray absorption spectroscopy

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