

# Tin via Four-Electron Conversion Chemistry for High-Performance Alkaline Batteries

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**Abstract:** To overcome the intrinsic limitation of low energy density associated with the conventional two-electron reaction of tin anodes, alkaline tin-based four-electron redox chemistry has emerged as a highly promising strategy. While the traditional two-electron  $\text{Sn}/\text{Sn}(\text{OH})_3^-$  redox couple delivers a limited theoretical specific capacity of  $451.6 \text{ mAh g}^{-1}$ , the four-electron  $\text{Sn}/\text{Sn}(\text{OH})_3^-/\text{Sn}(\text{OH})_6^{2-}$  pathway doubles the electron transfer number. This advancement not only elevates the application potential of tin-based batteries but also substantially boosts the theoretical capacity to  $903.2 \text{ mAh g}^{-1}$ , thereby markedly enhancing the overall energy density. This review systematically deconstructs the key challenges confronting alkaline tin-based four-electron reactions, pinpointing the formation of “dead Sn” induced by kinetic asymmetry and the shuttling of soluble  $\text{Sn}(\text{OH})_3^-$  intermediates as the core scientific bottlenecks. Subsequently, it provides a critical examination of the major regulatory strategies developed to achieve stable and reversible  $\text{Sn}/\text{Sn}(\text{OH})_3^-/\text{Sn}(\text{OH})_6^{2-}$  conversion, encompassing the implementation of ion-selective separators, electrolyte modulation, and current collector modification. Finally, forward-looking perspectives and actionable recommendations are proposed to steer the future development of high-performance four-electron tin-based batteries.

**Keywords:** alkaline tin-based batteries; four-electron tin chemistry; high-energy-density batteries

## 1. Introduction

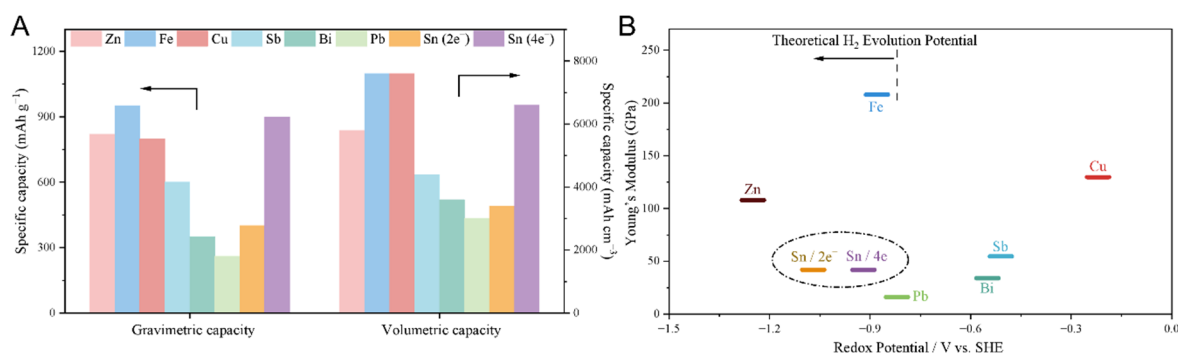
Amidst the global energy crisis and the push for sustainable transitions, advancing reliable and efficient energy storage systems is of paramount importance [1–8]. Lithium-ion batteries (LIBs) remain the dominant electrochemical technology, yet their expansive scalability is increasingly challenged by fundamental drawbacks [9–15]. These include the acute scarcity and uneven distribution of lithium resources, which exacerbates supply chain fragility, as well as the inherent safety risks tied to flammable organic electrolytes [16–21]. Additionally, the environmental burden posed by toxic materials and complex recycling processes cannot be overlooked [22–25]. Consequently, aqueous alkaline batteries are gaining traction as a viable next-generation platform. They offer intrinsic safety, abundant material reserves, facile manufacturability, and environmental sustainability, positioning them as a strategic response to the limitations of current LIB technologies [26–32].

To advance the practical deployment of alkaline aqueous batteries, critical performance bottlenecks associated with anode materials must be urgently addressed [33]. While state-of-the-art cathode materials, such as nickel-based (e.g.,  $\beta\text{-NiOOH}$ ) and cobalt-based (e.g.,  $\text{Co}_3\text{O}_4$ ) compounds, have demonstrated high reversible specific capacities and robust cycling stability ( $>200 \text{ mAh g}^{-1}$ ,  $>1000$  cycles) [16–18], the overall battery



performance remains insufficient to meet practical demands due to kinetic mismatches involving the anode. Solid-state phase-transition anodes, including Bi [34–39], Cd [40–42], and  $\text{FeO}_x$  [43–47], are fundamentally constrained by high phase-transition energy barriers, leading to inadequate rate capability [48–51]. In contrast, zinc metal anodes exhibit superior kinetic characteristics owing to their deposition/dissolution mechanism, which features a low reaction activation energy ( $<0.5$  eV) [26,52–55]. However, in alkaline electrolytes, Zn metal encounters more severe challenges than in neutral systems, including rampant dendrite growth, irreversible passivation primarily through the formation of a dense ZnO layer, and the competing hydrogen evolution reaction (HER) [56–58]. These issues result in generally short cycle life, significantly restricting the practical viability of Zn-based systems [59–66]. Consequently, the development of novel dendrite-free anodes operating via a deposition/dissolution mechanism has emerged as a critical research frontier aimed at overcoming the technical bottlenecks of alkaline aqueous batteries [67–71].

Among various transition metals, tin (Sn) has emerged as a prime candidate for anodes in alkaline aqueous batteries, owing to its low cost, high corrosion resistance, favorable biocompatibility, and exceptional theoretical capacities. These include  $451.6 \text{ mAh g}^{-1}$  and  $3281.3 \text{ mAh cm}^{-3}$  for the two-electron reaction pathway, and  $903.2 \text{ mAh g}^{-1}$ / $6562.6 \text{ mAh cm}^{-3}$  for the four-electron pathway, the latter being slightly higher than that of zinc (Figure 1A) [7,72–75]. In alkaline electrolytes, the redox potentials of most metal electrodes are concentrated in the range of  $-0.8$  to  $-0.4$  V vs. SHE. In contrast, Sn exhibits more negative redox potentials, specifically  $-0.909$  V vs. SHE for the  $\text{Sn}(\text{OH})_3^-/\text{Sn}$  couple and  $-0.935$  V vs. SHE for the  $\text{Sn}(\text{OH})_6^{2-}/\text{Sn}(\text{OH})_3^-$  couple, enabling it to deliver a higher operating voltage (Figure 1B) [76,77]. Moreover, unlike zinc, which crystallizes in a hexagonal close-packed (HCP) structure (space group  $P6_3/mmc$ ), Sn possesses a body-centered tetragonal structure (space group  $I4_1/amd$ ) [78–81]. The small surface energy difference among its crystal facets promotes the deposition of Sn in the form of polyhedral particles, effectively mitigating dendrite formation [72,82–86]. Additionally, the relatively low Young's modulus of Sn (42 GPa compared to 108 GPa for Zn) helps accommodate volume changes and relieves cyclic stress, thereby minimizing mechanical damage to the electrode/electrolyte interphase [87–92]. However, it is regrettable that existing studies have predominantly focused on the  $\text{Sn}^0 \leftrightarrow \text{Sn}^{2+}$  two-electron redox pathway, largely due to the shuttle effect of Sn intermediates and kinetic asymmetry. This limitation restricts capacity utilization to below 50%, severely hindering the full exploitation of Sn's potential and the achievable energy density of full cells [72,93–96]. Nevertheless, encouraging progress has been made in recent years. Pioneering works utilizing ion-selective separators, electrolyte regulation, and current collector modification have preliminarily validated the feasibility of reversible  $\text{Sn}^0 \leftrightarrow \text{Sn}^{4+}$  conversion. This breakthrough opens a valuable avenue for fully unleashing the theoretical capacity of Sn anodes and significantly boosting battery energy density. Consequently, a systematic investigation into promoting the four-electron reaction pathway of Sn is now a critical research direction to overcome current bottlenecks and unlock its full practical potential.



**Figure 1.** (A) Comparison of gravimetric and volumetric capacities for classical metal anodes in aqueous battery systems. (B) Benchmark of redox potentials and Young's moduli for Sn metal anodes against common metal anodes in aqueous alkaline electrolytes.

This review provides a systematic synthesis of recent advances toward enabling four-electron redox reactions in tin-based anodes, and outlines forward-looking perspectives on the future development trajectory of this emerging energy storage technology. We begin by revisiting the fundamental electrochemical principles, distinctive physicochemical attributes, and latest research progress underpinning four-electron tin anode chemistry (Figure 2). This is followed by a focused, systematic summary of core enabling pathways for achieving stable, reversible four-electron conversion (Table 1). The review concludes with an outlook on emerging trends and critical research priorities to accelerate the practical deployment of high-energy alkaline tin-based batteries.



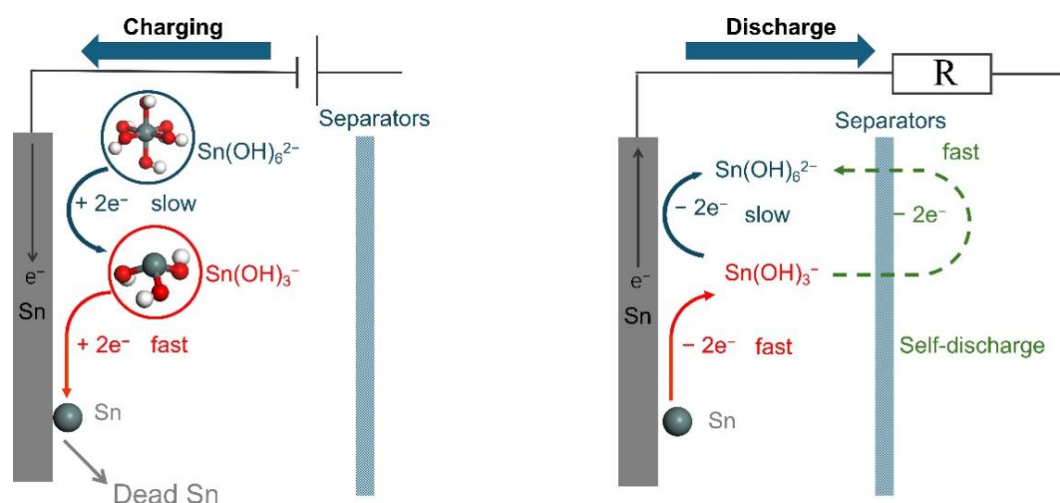
**Figure 2.** Schematic illustration of the four-electron transfer reaction at the aqueous tin anode.

**Table 1.** Summary of advanced performance of alkaline tin-based four-electron-reaction systems.

| Components        | Strategy                  | Battery System    | Electrolyte                                           | Full Cell Cycle Performance<br>(Cycles; $\text{mAcm}^{-2}$ ; Coulombic Efficiency) | Ref.  |
|-------------------|---------------------------|-------------------|-------------------------------------------------------|------------------------------------------------------------------------------------|-------|
| Separators        | Nafion membranes          | Sn-I Flow Battery | 2 M $\text{K}_2\text{Sn}(\text{OH})_6$ + 1 M KOH      | 500, 5, 97%                                                                        | [97]  |
|                   | Cation exchange membranes | Sn-Ni Static Cell | 1.7 M $\text{K}_2\text{Sn}(\text{OH})_6$ + 0.86 M KOH | 200, 1,99%                                                                         | [98]  |
| Electrolytes      | Urea Additive             | Sn-I Flow Battery | 1.5 M $\text{K}_2\text{Sn}(\text{OH})_6$ + 1 M KOH    | 200, 10, 92.4%                                                                     | [99]  |
| Current Collector | defect-modified TGF       | Sn-I Flow Battery | 1.5 M $\text{K}_2\text{Sn}(\text{OH})_6$ + 1 M KOH    | 110, 15, 94.8%                                                                     | [100] |
|                   | Cu foam                   | Sn-Ni Static Cell | 1.7 M $\text{K}_2\text{Sn}(\text{OH})_6$ + 0.86 M KOH | 200, 1, 98%                                                                        | [101] |

## 2. Key Challenges for Four-Electron Reactions of Alkaline Tin Anodes

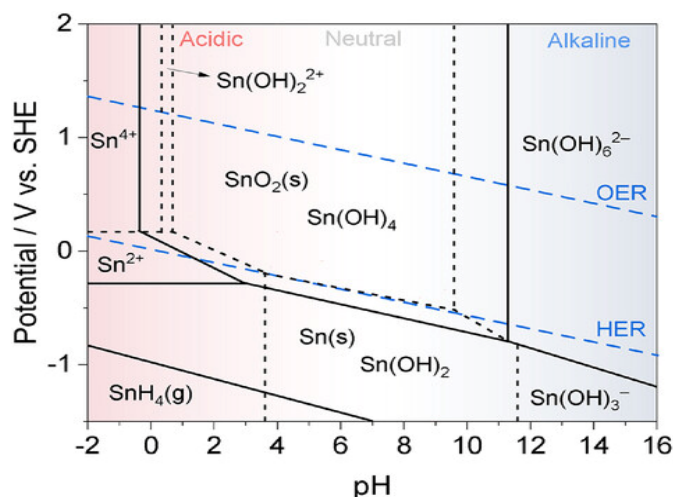
Compared to the two-electron reaction pathway, achieving four-electron energy storage reactions for Sn in alkaline media faces more severe bottlenecks, rooted in the inherent kinetic asymmetry throughout the charge–discharge process. This characteristic not only induces the formation of “dead Sn” but also exacerbates intermediate shuttle, which together constitute the core failure mechanisms of four-electron Sn anodes (Figure 3) [59].



**Figure 3.** Schematic diagram depicting the charge–discharge mechanism and soluble intermediate shuttle effect in a full alkaline tin-based aqueous battery.

As shown in Figure 4, the thermodynamic Pourbaix diagram of the Sn-H<sub>2</sub>O system demonstrates that Sn exists predominantly as soluble anionic complexes in alkaline media [59]. In alkaline electrolytes, Sn primarily exists as  $\text{Sn}(\text{OH})_3^-$  and  $\text{Sn}(\text{OH})_6^{2-}$ , a speciation highly dependent on OH concentration and ionic strength [98]. The charging process involves two sequential reduction steps. First,  $\text{Sn}(\text{OH})_6^{2-}$  is reduced to  $\text{Sn}(\text{OH})_3^-$  (Equation (1)), a

kinetically sluggish step ( $\Delta G = 0.85$  eV) requiring a substantial energy barrier to overcome. Subsequently, desolvated  $\text{Sn}(\text{OH})_3^-$  accepts electrons on the substrate surface to form metallic Sn (Equation (2)), a process characterized by rapid kinetics. This “slow-fast” kinetic disparity leads to the rapid depletion of  $\text{Sn}^{2+}$  within the Helmholtz layer without timely replenishment, triggering severe concentration polarization. Owing to the isotropic growth nature of Sn, polyhedral particles form initially [76,102,103]. However, as the deposition capacity increases, the adhesion between large-sized Sn particles and the substrate gradually weakens. This facilitates the detachment of electrochemically inert “dead Sn”, resulting in irreversible active material loss and increased internal resistance. Concurrently, the hydrogen evolution side reaction (HER, Equation (3)) induced by concentration polarization not only consumes active species but also generates bubble-induced scouring effects that further compromise the structural integrity of the deposition layer, accelerating the accumulation of “dead Sn” [104].



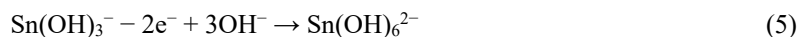
**Figure 4.** Pourbaix diagram of tin electrode in aqueous solution [59]. Copyright 2025, Wiley-VCH GmbH.

Significant kinetic asymmetry is likewise observed during discharge. Metallic Sn rapidly loses electrons to form  $\text{Sn}(\text{OH})_3^-$  (Equation (4)), whereas the subsequent oxidation of  $\text{Sn}(\text{OH})_3^-$  to  $\text{Sn}(\text{OH})_6^{2-}$  (Equation (5)) is relatively slow. This asymmetry allows the highly soluble  $\text{Sn}(\text{OH})_3^-$  intermediates to accumulate excessively at the anode interface and easily shuttle to the cathode for oxidation (Equation (6)), causing serious self-discharge and Coulombic efficiency decay [105].

Charge:



Discharge:



In summary, this alternating “fast-slow” kinetic mismatch simultaneously induces “dead Sn” formation and HER at the anode, while driving intermediate shuttle in the electrolyte. Therefore, a deep understanding and synergistic regulation of these critical steps through rational material design and precise interface engineering are imperative for constructing highly reversible four-electron Sn anode systems.

### 3. Strategies for Enabling Four-Electron Reactions in Alkaline Tin-Based Batteries

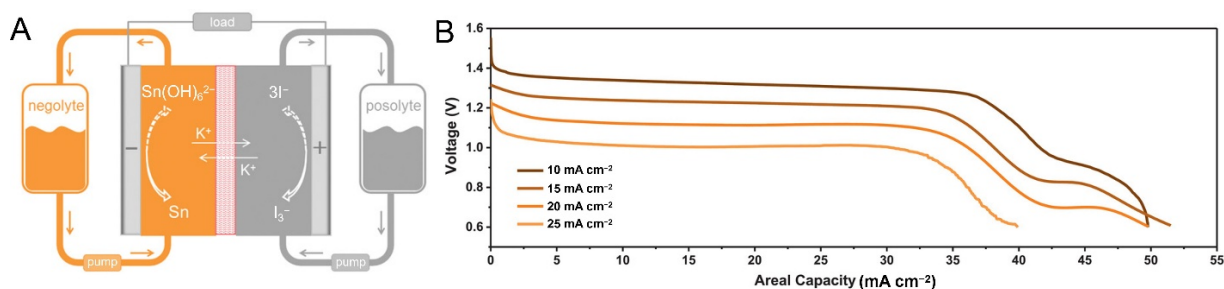
#### 3.1. Ion-Selective Separator Engineering

Separators play a pivotal role in batteries, serving to physically isolate the anode and cathode to prevent internal short circuits while permitting ion transport to establish ionic conduction pathways [61,106–115].



However, the kinetic asymmetry of Sn oxidation, wherein the  $\text{Sn} \rightarrow \text{Sn}(\text{OH})_3^-$  step is significantly faster than the  $\text{Sn}(\text{OH})_3^- \rightarrow \text{Sn}(\text{OH})_6^{2-}$  step, leads to substantial accumulation of  $\text{Sn}(\text{OH})_3^-$  intermediates at the anode. Conventional glass fiber or nonwoven separators lack ion-sieving capabilities, allowing these soluble intermediates to shuttle to the cathode and trigger severe self-discharge, which results in low Coulombic efficiency values of merely 50–80% [98]. Consequently, implementing ion-selective separators becomes imperative. Specifically, Yao et al. employed Nafion membranes to enhance Sn-based battery performance [97]. Their study demonstrated that Nafion effectively blocks  $\text{Sn}(\text{OH})_3^-$  shuttle while facilitating  $\text{K}^+$  transport (Figure 5A), thereby establishing a coherent ionic reaction pathway. Galvanostatic charge–discharge profiles exhibiting two distinct discharge voltage plateaus (Figure 5B) corroborated the characteristic kinetic asymmetry and stepwise oxidation of the four-electron Sn–I battery system.

Building on this, Wang et al. systematically evaluated the potential of cation exchange membranes (CEMs) and anion exchange membranes (AEMs,) [98]. While CEMs completely suppressed  $\text{Sn}(\text{OH})_3^-$  penetration via electrostatic repulsion, elevating CE to nearly 100%, they concurrently impeded  $\text{OH}^-$  conduction. This restriction limited charge transfer and constrained anode utilization to approximately 40%. In stark contrast, AEMs leveraged size-exclusion effects to achieve a significantly higher anode utilization of 64%, compared to 54% for nonwoven separators. This highlights the ability of AEMs to balance self-discharge suppression and ionic conductivity by blocking large  $\text{Sn}(\text{OH})_3^-$  species while allowing smaller  $\text{OH}^-$  ions to permeate freely, thus maintaining a coherent four-electron reaction pathway. Electrochemical assessments further confirmed that Sn–Ni cells with ion-exchange membranes delivered markedly superior CE compared to those with nonwoven separators (CEM: 97%, AEM: 93%, Nonwoven: 69–78%). Notably, operando X-ray diffraction (XRD) measurements revealed distinct behavior between the two separator types. In cells with nonwoven separators, the  $\text{Ni}(\text{OH})_2$  peak intensity recovered to its original value in half the charge duration. Conversely, cells with CEMs exhibited symmetric evolution of  $\text{Ni}(\text{OH})_2$  signals during cycling, providing direct evidence that  $\text{Sn}(\text{OH})_3^-$ -induced self-discharge at the cathode was effectively suppressed. As anticipated, the precise regulation of the four-electron reaction pathway enabled by ion-selective separators allowed the authors to maximize both efficiency and energy density in their assembled alkaline Sn–Ni batteries. The optimized cells achieved a balanced trade-off between efficiency and utilization, operated stably for over 800 h without significant capacity decay, and delivered a high energy density of  $143.1 \text{ Wh L}^{-1}$  alongside a cathode electrolyte capacity of  $170.5 \text{ Ah L}^{-1}$ . Despite the demonstrated efficacy of these ion-selective separators in suppressing self-discharge, future studies should prioritize evaluating membrane stability in alkaline media, time-dependent decay of ion-exchange capacity, and the economic viability of scaling up ion-selective separators for large-format cells.



**Figure 5.** (A) Schematic illustration of the working mechanism of a Sn–I flow battery employing a Nafion membrane. (B) Discharge curves at various current densities [97]. Copyright 2021, Wiley-VCH GmbH.

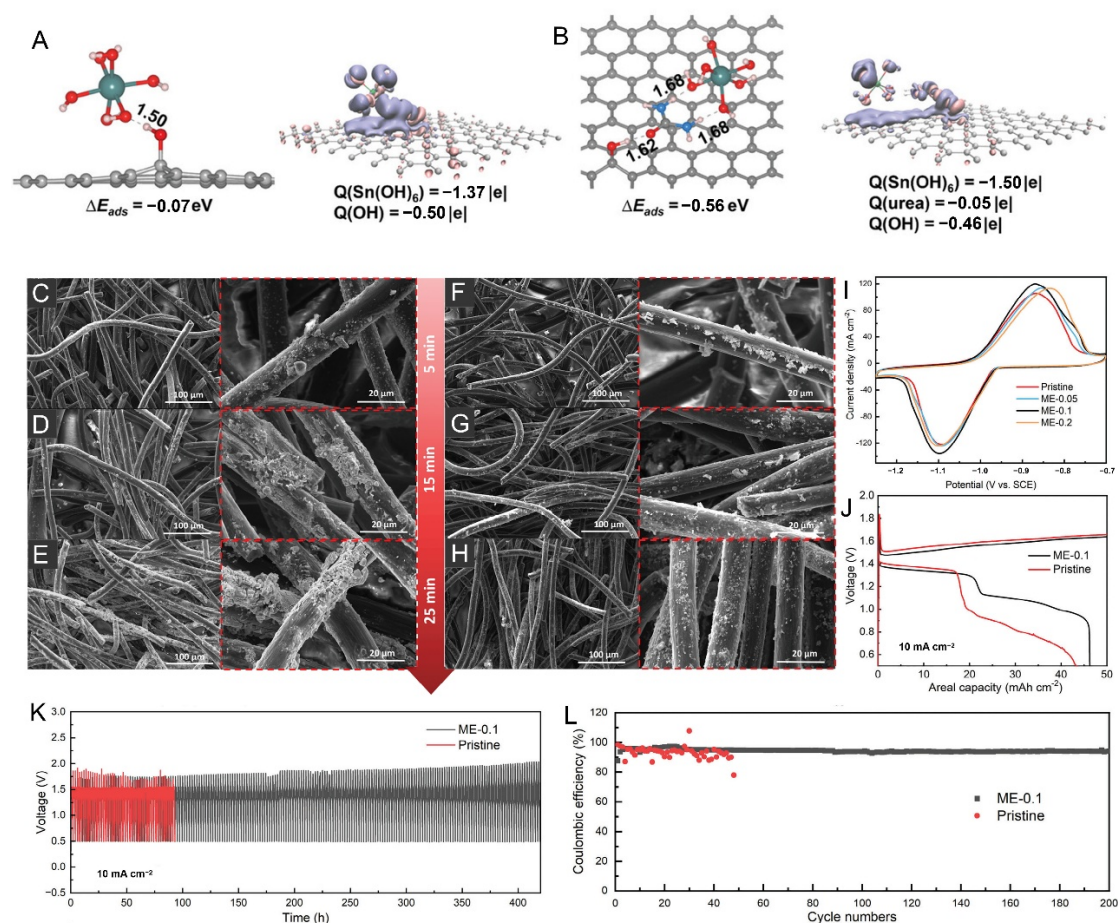
### 3.2. Electrolyte Additive Engineering

Another critical challenge in enabling four-electron reactions for alkaline tin-based batteries lies in addressing the uncontrolled morphological evolution of Sn deposits on the anode during plating. Sn deposition inherently favors the growth of bulky crystals, whose adhesion to the current collector progressively deteriorates over cycling. This eventually leads to the exfoliation of active Sn and the formation of electrochemically inert “dead Sn”, severely limiting battery cycle life [116]. Against this backdrop, developing effective deposition regulation mechanisms to suppress dead Sn formation is of paramount importance.

Among various modification strategies, electrolyte additive engineering stands out as a cost-effective, high-efficiency solution with considerable practical potential, as it directly modulates the electrode/electrolyte interface to steer uniform Sn deposition [117–120]. For instance, Yang et al. proposed a urea-based interfacial regulation strategy, and elucidated the pivotal role of hydrogen bonding in governing Sn deposition behavior [99]. Mechanistic investigations reveal that the amino ( $-\text{NH}_2$ ) and carbonyl ( $\text{C}=\text{O}$ ) groups in urea molecules act as

hydrogen bond donors and acceptors, respectively, forming an extensive hydrogen-bonding network with active  $\text{Sn}(\text{OH})_6^{2-}$  species and the thermal-treated graphite felt (TGF) substrate. This strong interaction substantially enhances the adsorption energy of  $\text{Sn}(\text{OH})_6^{2-}$  on the electrode surface, effectively lowering the nucleation barrier and overpotential for Sn deposition (Figure 6A,B).

More notably, SEM characterization demonstrates that urea induces preferential growth of Sn crystals along the (101) plane, while suppressing vertical expansion of the (200) plane. This steers two-dimensional lateral spreading of metallic Sn along the surface of graphite fibers. The resultant compact Sn deposit with strong interfacial adhesion effectively suppresses dead Sn formation (Figure 6C–H). Electrochemical measurements corroborate this mechanism. The notable increase in redox peak current densities in cyclic voltammetry (CV) curves, coupled with the extended initial discharge plateau in galvanostatic charge–discharge tests, confirm enhanced reaction kinetics and improved electrochemical activity (Figure 6I,J). Although the initial discharge voltage decreased slightly due to the reduced formation of bulky Sn aggregates, the battery delivered a significantly higher areal capacity of  $46.2 \text{ mAh cm}^{-2}$  at  $10 \text{ mA cm}^{-2}$ , prolonged cycling stability (200 cycles, 420 h), and superior capacity retention (Figure 6K,L). This work conclusively demonstrates that morphology regulation via electrolyte engineering provides a viable pathway to realize stable four-electron reactions in alkaline tin-based batteries. Notably, current implementations of alkaline tin-based four-electron reactions through electrolyte additive engineering are extremely scarce, with just one reported case. Future efforts should broaden the spectrum of additives to achieve a more comprehensive mechanistic understanding of interfacial regulation.



**Figure 6.** Optimized adsorption configurations of  $\text{Sn}(\text{OH})_6^{2-}$  on TGF surface in (A) pristine electrolyte and (B) urea-containing electrolyte. SEM images showing Sn deposition morphology on TGF in (C–E) pristine electrolyte and (F–H) urea-containing electrolyte. (I) Cyclic voltammograms of  $\text{Sn}(\text{OH})_6^{2-}/\text{Sn}$  redox reaction. (J) Galvanostatic charge–discharge profiles of the Sn–I full battery. (K) Galvanostatic voltage profiles. (L) Evolution of Coulombic efficiency for the Sn–I full battery during long-term cycling [99]. Copyright 2024, Wiley-VCH GmbH.

### 3.3. Current Collector Modification Engineering

Graphite felts, leveraging their excellent electrical conductivity and three-dimensional (3D) porous network structure, are widely employed as current collectors for Sn anodes in alkaline tin-based batteries. Consequently,

surface modification of the anode emerges as a pivotal strategy to regulate reaction kinetics and fully unlock the potential of the four-electron redox pathway [121–123]. Conventional thermal-treated graphite felt (TGF), however, suffers from high Sn nucleation barriers attributable to its surface inertness, which severely compromises Sn deposition efficiency [124–126]. To address this bottleneck, Faheem et al. constructed abundant intrinsic defects on the TGF surface via combined plasma pretreatment and cobalt nitrate etching, yielding defect-modified TGF (Dm-TGF) [100]. This modification strategy not only lowers the nucleation barrier but also homogenizes the interfacial electric field distribution by virtue of the uniform microscale surface curvature, effectively suppressing the tip effect at the source and ensuring the stability of the stepwise four-electron conversion process.

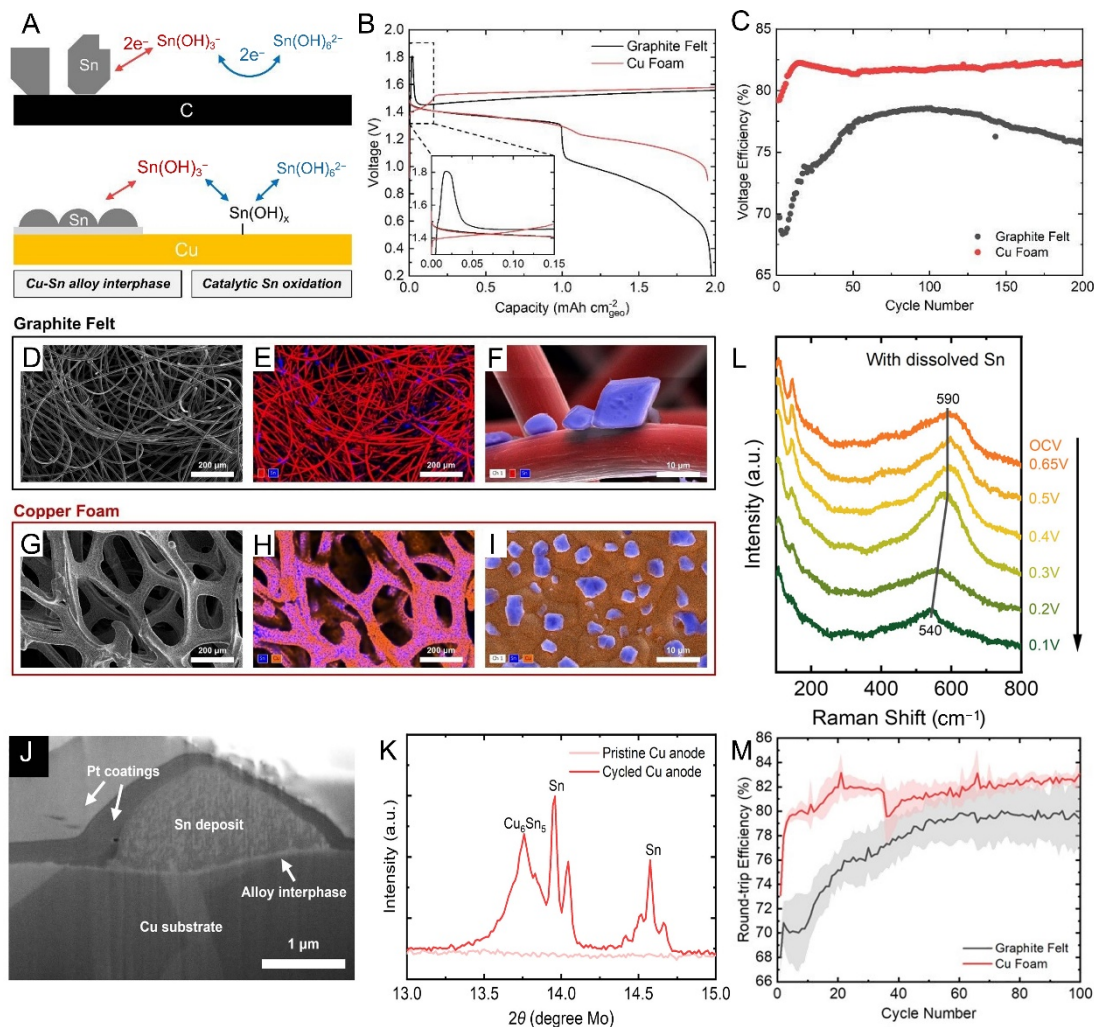
Furthermore, defect engineering induces preferential crystal orientation of Sn along the (211) plane, driving the lateral spreading of Sn atoms across the TGF surface to form a compact, layered deposition architecture. This structure effectively prevents sharp vertical protrusions, markedly enhances the structural integrity of the Sn deposit, and minimizes the formation of electrochemically inert “dead Sn”. A suite of complementary characterizations further substantiates this mechanism. Raman spectroscopy confirms the successful introduction of high-density defects, as evidenced by the increased intensity ratio of the D-band to G-band ( $I_D/I_G$ ) from 0.86 to 1.4. Building on this, XRD patterns reveal a significant shift in crystal growth orientation, where the peak intensity ratio of the Sn (211) to (200) planes rises from 1.19 to 1.6. Microstructural analysis via SEM demonstrates that this altered crystallography, coupled with increased surface nanopores on the modified TGF, promotes a uniform Sn deposition distribution. Theoretical simulations using the 2D finite element method (FEM) further elucidate the underlying cause, indicating that these defects effectively homogenize both the interfacial electric field and ionic concentration gradients. Benefiting from this dual optimization of structure and interface, the reversibility of the four-electron reaction in Sn-based anodes is significantly enhanced. Standby tests reveal a gradual voltage decay in both cell types over a 20 h resting period. The cell assembled with the Dm-TGF anode exhibits a voltage decay of only 124 mV, significantly lower than the 145 mV recorded for the pristine TGF-based cell. Collectively, these results demonstrate that the defect-rich anode surface effectively suppresses voltage decay and mitigates discharge capacity fade, owing to the uniform Sn deposition morphology. Ultimately, full Sn–I cells assembled with the Dm-TGF anode deliver exceptional energy storage performance, achieving an ultrahigh areal capacity of  $109.17 \text{ mAh cm}^{-2}$  at a current density of  $15 \text{ mA cm}^{-2}$ , and maintain stable, dead Sn-suppressed operation for over 300 h at  $10 \text{ mA cm}^{-2}$ . These findings unambiguously verify that defect engineering outperforms conventional electrodes and the majority of reported Zn-based systems, highlighting its considerable application potential in alkaline four-electron tin-based flow batteries. It is worth noting that future experimental studies should also prioritize the reproducibility and mechanical robustness of defect-engineered collectors under flow conditions, as these factors are decisive for practical deployment.

Conventional carbon-based anodes often suffer from inhomogeneous Sn deposition and sluggish kinetics of the  $\text{Sn(OH)}_6^{2-}/\text{Sn}$  redox couple, which severely constrains the efficiency of four-electron reactions in tin-based batteries. To address this challenge, Wang et al. employed Cu foam as a current collector and utilized Cu–Sn interfacial chemistry to achieve bidirectional kinetic enhancement, thereby ensuring uniform Sn deposition and smooth four-electron transfer pathways [101]. During the Sn deposition process, Sn *in situ* forms a  $\text{Cu}_6\text{Sn}_5$  alloy phase with Cu. This phase acts as a superior nucleation site, effectively lowering the nucleation barrier and overpotential for the four-electron reaction. During the Sn dissolution process, the Cu foam anode stabilizes  $\text{Sn(OH)}_x$  intermediates via strong chemisorption, inducing the reaction to follow a faster inner-sphere electron transfer pathway and significantly reducing the oxidation overpotential. In contrast, carbon substrates lack strong chemical interactions with Sn species, confining the reaction to a slow outer-sphere mechanism that fails to support efficient four-electron conversion (Figure 7A).

Electrochemical measurements corroborate this mechanism. Galvanostatic charge–discharge tests demonstrate that Cu foam not only eliminates the nucleation overpotential peak during Sn deposition but also significantly enhances cycling stability and energy efficiency while reducing overall polarization (Figure 7B,C). SEM images reveal that Sn deposits on the Cu substrate exhibit a more uniform morphology and higher nucleation density (Figure 7D–I). Cross-sectional SEM combined with XRD detection of the interfacial  $\text{Cu}_6\text{Sn}_5$  phase further confirms that alloying significantly enhances the interfacial adhesion of active species during four-electron cycling (Figure 7J,K). Crucially, *in situ* Raman spectroscopy provides direct evidence that  $\text{Sn(OH)}_x$  intermediate signals are stably captured on the Cu foam surface under both static and dynamic flow conditions, offering robust support for the inner-sphere reaction mechanism and the stable existence of intermediates (Figure 7L). Ultimately, benefiting from the introduction of Cu foam, the round-trip efficiency (RTE) of the cell at  $1 \text{ mA cm}^{-2}$  increases by 10% to reach 80%, with stable operation maintained for over 200 cycles (Figure 7M). This conclusively proves the effectiveness of anode interfacial chemistry regulation in optimizing the performance of four-electron reactions in alkaline tin-based batteries. Although Raman spectroscopy supports intermediate capture, systematic EIS and



Tafel analyses contrasting Cu with carbon, as well as explicit tracking of  $\text{Cu}_6\text{Sn}_5$  alloy reversibility or depletion, are still needed to consolidate the inner-sphere mechanism and assess practical durability. It is worth noting, however, that this modification strategy cannot fundamentally resolve the severe shuttle effect caused by highly soluble intermediates, and therefore remains highly dependent on the use of ion exchange membranes. Single-electrode modification alone struggles to simultaneously resolve all issues within the system. Future development of synergistic electrode–electrolyte regulation strategies is required to further break through performance limitations and reduce costs, thereby advancing the practical application of this system.



**Figure 7.** (A) Schematic illustration of the four-electron Sn conversion chemistry dually enhanced by Cu. Galvanostatic charge–discharge profiles (B) and voltage efficiency evolution (C) of Sn–Ni batteries with a CEM and different anodes. (D–I) SEM images and corresponding EDS elemental mappings of Sn deposits on (D–F) graphite felt and (G–I) Cu foam substrates. (J) Cross-sectional SEM image of Sn deposited on the Cu foam substrate after charging. (K) XRD patterns of the Cu electrode before and after cycling. (L) *In situ* EC-Raman spectra of the Cu electrode during discharge (gray lines: evolution of  $\text{Sn(OH)}_x$  species). (M) Comparison of RTE for different anode substrates [101]. Copyright 2025, The Royal Society of Chemistry.

#### 4. Conclusions and Perspectives

Tin-based batteries demonstrate substantial promise for next-generation high-performance energy storage devices, owing to their low cost, high safety, environmental benignity, and considerable theoretical capacities:  $451.6 \text{ mAh g}^{-1}$  ( $3281.3 \text{ mAh cm}^{-3}$ ) for the two-electron reaction pathway, and  $903.2 \text{ mAh g}^{-1}$  ( $6562.6 \text{ mAh cm}^{-3}$ ) for the four-electron reaction pathway. However, this technology remains in its nascent stage. Currently, the strategies capable of enabling tin-based four-electron reactions in alkaline media are rather limited, which means that realizing practical four-electron Sn redox reactions still faces formidable challenges including kinetic hysteresis, dead Sn formation, and soluble intermediate shuttle effects. This review systematically summarizes the key scientific bottlenecks hindering four-electron reactions in aqueous alkaline tin-based batteries, and categorizes

current optimization strategies into three core dimensions: current collector interface regulation, electrolyte additive engineering, and selective separator adoption.

To advance the development of this field, four critical research priorities warrant further attention:

- (1) Deepening the fundamental understanding of multi-electron reaction mechanisms. Most existing studies focus on two-electron Sn redox processes, leaving the four-electron conversion pathway underexplored, specifically regarding the shuttle mechanism of  $\text{Sn}(\text{OH})_3^-$  intermediates, the underlying interfacial electron transfer pathways, and the fractional capacity contributed by each redox step, all of which remain poorly understood. Future work should integrate advanced *in situ* characterization techniques with theoretical calculations to elucidate reaction laws in alkaline systems, deconvolute the fractional capacity of each redox step and extend the research scope to acidic and neutral electrolytes to lay a theoretical foundation for rational device design.
- (2) Mitigating cumulative effects induced by kinetic asymmetry. The vast kinetic disparity between the two sequential steps ( $\text{Sn} \rightarrow \text{Sn}(\text{OH})_3^-$  vs.  $\text{Sn}(\text{OH})_3^- \rightarrow \text{Sn}(\text{OH})_6^{2-}$ ) leads to enrichment of  $\text{Sn}(\text{OH})_3^-$  at the anode interface and subsequent shuttle behavior. Rational design of anode interface architectures or introduction of appropriate redox mediators (e.g., ferro-/ferricyanide and anthraquinone derivatives) to balance the reaction rates of the two steps represents a viable approach to resolve this issue. However, prior to practical implementation, their compatibility with alkaline electrolytes and their permeability through ion-selective membranes must be carefully evaluated.
- (3) Suppressing shuttle effects to reduce self-discharge. The high solubility of  $\text{Sn}(\text{OH})_3^-$  permits penetration of conventional separators and induces self-discharge. In addition to constructing high-performance ion-selective separators, future work may exploit nanomaterial-based separator modifications (e.g., MOFs) or anode interfacial functionalization to anchor intermediates, thereby achieving low-cost efficient ion sieving. Critically, to compare separator efficacy objectively, subsequent investigations must quantify the shuttle current density or crossover flux normalized by Sn loading and electrolyte volume, and establish explicit correlations with Coulombic efficiency decay.
- (4) Resolving capacity fading caused by “dead Sn”. As deposition capacity increases, large Sn particles detach from the substrate to form electrochemically inert dead Sn. Meanwhile, enriched  $\text{Sn}(\text{OH})_3^-$  intermediates in the electrolyte undergo spontaneous disproportionation to generate metallic Sn, which is also irreversibly lost from the electrode-electrolyte system. Future studies should establish quantitative measurements of the fraction of Sn that becomes inactive after cycling, so as to further clarify the internal mechanisms of dead Sn formation. Targeting this dual failure mechanism, developing redox couples capable of targeted oxidation to reactivate “dead Sn”, and converting detached Sn back into soluble active species, would be a transformative strategy to improve active material utilization and cycle life.

In summary, recent advances have demonstrated the feasibility of achieving efficient four-electron tin-based chemistry through the synergistic modulation of current collector architectures, electrolyte formulations, and membrane ion selectivity. These strategies underscore the remarkable chemical flexibility and tunability inherent in multielectron tin redox processes. Nevertheless, it is important to recognize that most tin-based batteries leveraging four-electron reactions remain confined to the laboratory scale as proof-of-concept demonstrations, and they remain heavily dependent on prohibitively costly ion-selective separators. This status quo implies significant challenges in fully translating the theoretical advantages of multielectron reactions into practical device-level energy density and long-term operational stability and cost-effectiveness. Moving forward, continuous integration of four-electron Sn redox chemistry with advanced electrolyte and interface engineering will be critical to bridging the gap between fundamental research and commercial applications. With deepening mechanistic understanding and maturing engineering technologies, high-energy tin-based batteries are expected to play a pivotal role in long-duration stationary energy storage and emerging hybrid energy systems.

## Author Contributions

Z.L.: writing—original draft, formal analysis; R.L.: writing—original draft; Y.Q.: Data curation; J.X.: visualization; Z.Y.: validation; X.L.: conceptualization, supervision, writing—review & editing, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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## Data Availability Statement

Data will be made available on request.

## Conflicts of Interest

The authors declare no conflict of interest.

## Use of AI and AI-Assisted Technologies

During the preparation of this work, the authors used Yuanbao (an AI-powered assistant developed by Tencent) to polish the language and refine the wording of the manuscript. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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