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Biochar-Based Materials for Electrochemical Energy Storage

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ABSTRACT

The global transition toward sustainable energy technologies is reshaping the design principles of electrochemical energy storage systems. Biochar, a tunable, carbon-rich material derived from biomass, has emerged as a promising platform for next-generation electrodes due to its abundant feedstock, cheapness, tailored porosity, intrinsic heteroatom content, and renewable origin. In this review, we critically examine recent advances in engineering the physicochemical properties of biochar to enhance its electrochemical performance in batteries. We highlight how microstructural control, surface functionality, and graphitization influence charge storage, ion diffusion, and cycling stability. Emphasis is placed on the interplay between synthesis conditions and electrochemical function, offering insights into structure–property relationships. Finally, we discuss the challenges of standardization, scale-up, and environmental trade-offs, and outline strategies for integrating biochar into scalable, low-carbon energy storage technologies aligned with circular economy principles.

1 | Introduction

Carbon is fundamental to life on Earth. Although it ranks only 15th in abundance in the Earth's crust, its origin from stellar nucleosynthesis and unparalleled bonding versatility give rise to extraordinary chemical diversity, with more known compounds than any other element [1–3]. On our planet, carbon primarily cycles through natural processes; yet modern society increasingly depends on synthetic carbon-based materials [4], including plastics [5, 6], textiles [7], paper [8], wood products [9], and fuels [10]. The extraction, processing, and large-scale deployment of these materials are progressively disrupting environmental equilibria [11].

The historical “take–make–waste” economic model has left a lasting legacy, presenting profound societal and technological challenges, particularly in the context of climate instability

and resource insecurity [12]. In response, the European Union (EU) has placed circularity, renewable feedstocks, and sustainable secondary raw materials as central pillars of its long-term strategy, targeting climate neutrality by 2050 [13, 14]. Within this framework, decarbonizing energy systems extends beyond renewable electricity generation: large-scale deployment of intermittent sources such as solar and wind critically depends on scalable, sustainable, and geopolitically secure energy-storage technologies capable of grid stabilization, energy buffering, and electrified mobility [15, 16].

Alkali-metal intercalation batteries, most notably lithium-ion batteries (LIBs), currently dominate electrochemical energy storage (EES) [17–20]. However, their rapid global adoption is increasingly constrained by dependence on critical raw materials (CRMs), including lithium (Li), cobalt (Co), nickel (Ni), and

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graphite-based anodes [21–23]. Natural graphite is predominantly fossil-derived, energy-intensive to process, and subject to pronounced supply-chain concentration [24–27]. Recognizing these vulnerabilities, graphite has been formally designated as a CRM in the EU, highlighting the urgency of diversifying carbon architectures for energy storage [28, 29].

In parallel, substantial efforts are being directed toward alternative battery chemistries based on more abundant and geographically distributed elements, particularly sodium and potassium. Sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) retain the intercalation–deintercalation mechanisms of LIBs while relying on earth-abundant resources, rendering them intrinsically more sustainable and geopolitically resilient [30, 31]. While significant progress has been achieved for cathode materials, the anode remains a critical bottleneck, limiting rate capability, cycling stability, and overall coulombic efficiency.

Among candidate anode materials, carbonaceous structures dominate due to their abundance, chemical stability, and relatively low volume expansion during cycling [32, 33]. Yet, the continued reliance on mined graphite, now strategically at risk, underscores the need for renewable, structurally distinct carbon frameworks capable of supporting next-generation EES systems [34, 35]. In Figure 1, current trends in the anode market and the applications of carbon materials in battery technologies are shown.

Within this context, biochar has emerged as a highly promising alternative. Biochar is a renewable, carbon-rich material produced through the thermochemical conversion of biomass, with its structure readily tunable through pyrolysis temperature (PT) and processing conditions [36, 37]. Low-temperature pyrolysis (<900°C) yields highly functionalized, amorphous carbons rich in oxygen-containing groups, whereas higher temperature treatment (typically >900°C) produces hard carbons (HCs), a nongraphitizable yet structurally robust phase characterized by turbostratic short-range order, enlarged interlayer spacing, and closed nanopores [38–41].

Unlike petroleum-derived carbons, which can undergo graphitization at extreme temperatures, biomass-derived carbons remain intrinsically nongraphitizable due to their molecular

heterogeneity and cross-linked aromatic structure [42–45]. This intrinsic disorder is advantageous for alkali-ion storage, particularly in NIBs, where enlarged interlayer spacing and disordered pore networks enable ion-storage mechanisms inaccessible to crystalline graphite [46, 47].

Beyond structural tunability, biochar can be produced from a wide range of renewable feedstocks [48], including agricultural residues, forestry by-products, food-processing waste, and marine biomass. Scalable synthesis routes such as slow pyrolysis, hydrothermal carbonization, molten-salt processing, and physical or chemical activation [49–53] allow precise control over porosity, surface chemistry, defect density, interlayer spacing, and heteroatom incorporation, within the limits of nongraphitizable carbon frameworks [48]. As a result, biochar-based carbons have emerged as environmentally friendly and functionally competitive alternatives to commercial graphite across multiple electrochemical systems [54, 55].

In EES, biomass-derived HCs have demonstrated significant potential not only for LIBs and NIBs but also for emerging technologies such as KIB, lithium–sulfur batteries (Li–S), dual-ion capacitors, and metal–air systems [56–58]. Their disordered microstructure supports a combination of surface adsorption, interlayer intercalation, and low-voltage pore-filling mechanisms, while heteroatom doping and defects engineering further enhance electronic conductivity and interfacial kinetics [59–61]. Increasingly, well-engineered biochar-based electrodes achieve high reversible capacity, strong rate performance, and long cycle life while enabling decentralized, low-carbon production pathways consistent with circular-economy principles [56, 59].

Despite this progress, substantial challenges remain. Biomass feedstocks are intrinsically heterogeneous, with variations in ash content, lignocellulosic composition, and metal impurities, all of which influence carbon yield, microtexture, and electrochemical behavior [62]. Even under controlled synthesis conditions, batch-to-batch reproducibility remains a major barrier to industrial deployment [63]. Moreover, aggressive activation strategies and high-temperature treatments, while effective in boosting performance, can compromise environmental sustainability, scalability, and safety, necessitating careful life-cycle and techno-economic evaluations [64, 65].

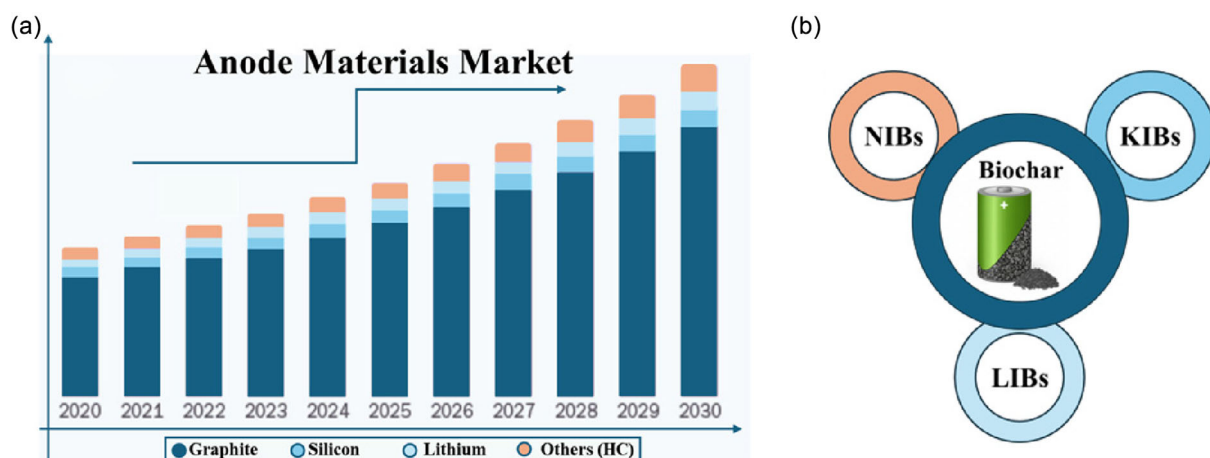


FIGURE 1 | Current trends and applications of carbon materials in battery technologies. (a) Global anode materials market landscape. (b) Main applications of nongraphitic carbons in intercalation-type batteries, including LIBs, NIBs, and KIBs.

In the last 2 years, several recent reviews published in the literature have comprehensively examined biomass-derived carbons for electrochemical applications, with particular emphasis on sodium-ion storage mechanisms, heteroatom-doping strategies, and high-surface-area architectures for enhanced capacity [66–69]. These studies have significantly advanced understanding of defect-mediated sodium storage and pore-filling mechanisms in HCs, frequently highlighting record capacities achieved through microstructural engineering and surface functionalization [33, 70–72]. Complementary analyses have addressed sustainability metrics and life-cycle considerations of biomass-derived electrodes, underscoring the role of feedstock circularity and environmental impact in carbon-material development.

Notwithstanding these advances, a unifying comparative framework across LIBs, NIBs, and KIBs remains insufficiently articulated. Existing reviews commonly treat these chemistries independently and rarely establish systematic correlations between ionic radius, carbon microstructure, defect chemistry, and the governing ion-storage mechanisms. Likewise, the interplay between graphite-substitution strategies in LIBs, HC optimization for NIBs, and defect-rich architectures for KIBs has not been critically synthesized within a single integrative perspective. As a result, materials design principles are often presented in isolation rather than positioned along an ion-dependent structural continuum.

The present review addresses this gap by establishing cross-system correlations and defining ion-specific materials-design gradients for biochar-derived carbons. Moving beyond capacity-driven reporting, we adopt a mechanism-informed framework that links pyrolysis chemistry, microstructural evolution, heteroatom functionality, and pore architecture to alkali-ion storage behavior. Specifically, we critically analyze how synthesis strategies, activation pathways, and feedstock variability shape structure–property relationships; examine approaches to mitigate batch-to-batch heterogeneity; and outline scalable routes for integrating biochar-based carbons into low-carbon, geopolitically resilient energy-storage architectures aligned with circular-economy objectives.

2 | Classification of Carbon Materials: From Soft to HC

Carbon materials are commonly classified according to their degree of structural order and their ability to undergo graphitization upon high-temperature treatment [73]. Ordered carbons, exemplified by graphite, exhibit long-range stacking of sp^2 graphene layers with well-defined crystallographic coherence and an interlayer spacing (d_{002}) of ≈ 0.335 nm [74–77]. In contrast, disordered carbons consist of turbostratic, misaligned graphene domains characterized by limited stacking order, rotational disorder, and enlarged interlayer spacing. Beyond structural order, a more fundamental distinction is provided by graphitizability. Graphitizable carbons, often referred to as soft carbons, can reorganize into crystalline graphite above $\sim 2500^\circ\text{C}$ – 2800°C through thermally activated layer realignment. Nongraphitizable carbons, by contrast, retain a rigid, cross-linked aromatic framework even under extreme heat treatment, as their microstructure kinetically inhibits graphitic ordering [74, 75, 78].

Within this framework, biowaste-derived carbons occupy a distinctive and nonoverlapping domain. Their heteroatom-rich composition, molecular irregularity, and intrinsically cross-linked aromatic architecture inhibit true graphitization, even at temperatures exceeding those required for petroleum-derived precursors [79]. Unlike pitch, coke, or carbon black, classified as graphitizable soft carbons, biomass-derived carbons are inherently nongraphitizable [43, 80]. Their thermal evolution therefore proceeds along a continuous pathway from low-temperature biochar to high-temperature HCs, both residing within Kinoshita's nongraphitizing carbon framework (see Figure 2) [75]. This distinction underpins their unique morphological, electronic, and electrochemical behavior in energy-storage systems.

At low PTs (typically 300°C – 500°C), biomass decomposition is incomplete, yielding a material commonly referred to as Low-T biochar [81, 82]. This early-stage carbon is structurally heterogeneous and chemically rich, containing abundant oxygenated surface groups (e.g., carboxyl, hydroxyl, carbonyl functionalities), residual lignocellulosic motifs, small aromatic clusters, and low fixed-carbon content [75, 83]. Although sometimes described as

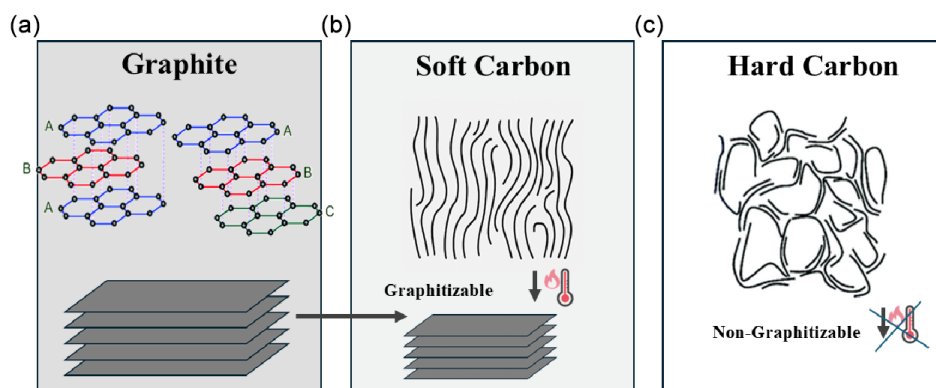


FIGURE 2 | Structural hierarchy and graphitizability of carbon materials. Schematic comparison of (a) graphite, (b) graphitizable soft carbons, and (c) nongraphitizable HC, illustrating the progressive loss of stacking order and increasing topological constraint from ordered graphite to disordered biomass-derived carbons. Graphite exhibits long-range AB-stacked graphene layers with well-defined interlayer spacing. Soft carbons consist of turbostratic graphene domains that retain sufficient structural mobility to reorganize into crystalline graphite upon high-temperature treatment ($>2500^\circ\text{C}$ – 2800°C). In contrast, HCs are composed of highly curved, cross-linked aromatic fragments forming rigid three-dimensional networks with closed porosity, which kinetically inhibit graphitic ordering even under extreme thermal conditions. Adapted from [75].

“soft-carbon-like” in terms of disorder, such materials are not graphitizable soft carbons in the strict structural sense, as they lack the mesophase-forming intermediates required for graphitic reorganization. Their high polarity, wettability, and surface reactivity may be advantageous for catalysis, capacitive storage, or sensing applications, but they severely limit battery performance [36, 83, 84]. In this regime, biochar exhibits low electronic conductivity, high irreversible capacity loss, unstable solid-electrolyte interphase (SEI) formation, and sluggish charge-transfer kinetics, precluding efficient and reversible alkali-ion intercalation [38, 85].

Increasing the PT to intermediate values (~600–900°C) drives dehydration, deoxygenation, aromatization, and polycondensation reactions, progressively transforming biochar into a more carbon-rich and structurally coherent material [86]. Turbostratic nanodomains emerge, heteroatom content decreases, and hierarchical porosity develops as cellulose- and hemicellulose-derived microstructures collapse. These transformations are typically accompanied by a decrease in interlayer spacing toward ~0.36–0.38 nm, a reduction in Raman I_D/I_G ratio dispersion, and a marked increase in electronic conductivity [60, 87]. In this transitional regime, the material begins to exhibit characteristics associated with HC precursors, including improved SEI stability and the onset of Na⁺ insertion. However, electrochemical performance remains strongly dependent on precursor chemistry and residual surface functionality.

True HC is obtained only after high-temperature pyrolysis, typically above 1000°C [88]. In this regime, biomass-derived carbons undergo extensive aromatization and microtexture reorganization, forming highly disordered turbostratic layers composed of curved, misaligned graphene fragments with enlarged interlayer spacing (~0.36 nm) [89]. Crucially, despite this increased short-range ordering, biogenic carbons remain nongraphitizable and do not develop three-dimensional graphitic stacking (AB stacking) [90, 91]. Instead, their structure stabilizes into the characteristic house-of-cards architecture of HC, featuring slit-shaped voids, closed nanopores, and sp^2 -rich domains interconnected by topological defects (Figure 2) [92, 93]. These structural motifs

enable the three canonical storage mechanisms observed in high-performance NIB anodes: surface adsorption, interlayer intercalation, and low-voltage pore filling. Concurrently, the reduction of surface oxygen groups enhances SEI stability and suppresses parasitic reactions, while increased conductivity supports high-rate operation [94]. In Table 1, a summary and interplay of PT and structural properties is reported.

Electrochemical performance across the pyrolysis spectrum arises from the coupled evolution of carbon microstructure, heteroatom chemistry, and surface energetics [80]. While PT is the primary driver of structural ordering and aromatic condensation, feedstock chemistry establishes the initial boundary conditions for carbon evolution [95]. Lignin-rich precursors (e.g., hardwoods, softwoods, nutshells) yield a higher fixed-carbon content and more condensed aromatic domains upon pyrolysis, producing biochars with lower surface area, reduced oxygen content, and enhanced electronic conductivity [96]. These characteristics favor improved initial Coulombic efficiency (ICE) and enhanced charge transport in LIB systems, where excessive surface functionality promotes irreversible lithium consumption and unstable SEI formation.

In contrast, cellulose- and hemicellulose-rich herbaceous residues undergo rapid devolatilization, generating greater microporosity and higher densities of oxygen-containing functional groups [97]. The resulting defect-rich carbons exhibit lower intrinsic conductivity but possess abundant adsorption sites and enlarged interlayer spacing [98]. While such architectures are less suited for graphite-mimetic LIB performance, they become advantageous in NIB and KIB systems, where defect-mediated adsorption and pore filling dominate the storage mechanism. Mineral constituents naturally present in agricultural biomass (e.g., K, Ca, and Mg) may further catalyze pore development or induce local structural rearrangements during pyrolysis, thereby modulating ion transport pathways and electron transport.

Structural ordering governs conductivity and ion diffusion; high-temperature treatment modulates heteroatom content, electronic structure, redox activity, surface area, defect density, and pore

TABLE 1 | Pyrolysis-temperature-driven structural evolution of biomass and fossil-derived carbons. Typical ranges of PT, feedstock origin, Raman disorder ratio (I_D/I_G), and interlayer spacing (d_{002}) for biochar, HC, soft carbon, and graphite, highlighting the transition from nongraphitizable biomass-derived carbons to graphitizable fossil-based carbon frameworks.

Carbon class	Pyrolysis temperature, °C	Typical feedstock	Raman (I_D/I_G)	$d(002)$, nm	Structural features
Low-T biochar	300–500	Lignocellulosic biomass (straw, shells)	0.7–1.0	0.38–0.42	Amorphous carbon, High O-content Low aromatic clusters
Transitional biochar	600–800	Agricultural waste, lignin-rich residues	0.9–1.2	0.36–0.39	Emerging turbostratic domains, hierarchical porosity
HC	>900	Hardwood, nutshells, biomass chars	1.0–1.4	0.36–0.38	Turbostratic graphene, closed nanopores, nongraphitizable
Soft carbon	>1000 (graphitization >2500)	Pitch, coke, carbon black	0.8–1.1	0.335 after HTT	Graphitizable turbostratic layers
Graphite	>2800 (or natural)	Synthetic, fossil-derived / natural	<0.3	0.335	Long-range AB stacking

Abbreviation: HTT, high-temperature treatment.

architecture, which control interfacial charge-transfer kinetics [99]. Accordingly, low-temperature biochars exhibit high surface reactivity, but limited reversibility, transitional carbons balance conductivity and accessibility, and high-temperature HC optimize ion storage through their turbostratic framework and stabilized surface chemistry [100, 101]. Crucially, regardless of treatment temperature, biomass-derived carbons remain nongraphitizable. This intrinsic topological constraint preserves enlarged interlayer spacing and closed porosity, features essential for efficient Na^+ and K^+ storage [102, 103].

From a materials-design perspective, PT represents the dominant control parameter governing morphology and electrochemical behavior. In contrast, feedstock composition and activation chemistry define the inherent conductivity–functionality–porosity trade-off that thermal treatment subsequently refines. Lignin-rich precursors (e.g., woody biomass) typically yield more condensed aromatic frameworks with lower oxygen content and improved electronic conductivity, thereby favoring higher ICE and stable cycling in LIBs. Conversely, cellulose- and hemicellulose-rich residues generate more disordered carbons with higher microporosity and surface functionality. While such defect-rich structures can enhance Na^+ and K^+ storage through adsorption-dominated mechanisms, they often increase irreversible capacity and reduce ICE due to amplified surface reactivity (cation caging effect). In addition, mineral species (e.g., K, Ca, and Mg) further influence carbon evolution by catalyzing pore formation or local graphitization; however, residual ash may destabilize the SEI and promote parasitic reactions. As a result, applying identical pyrolysis conditions to chemically distinct biomasses can produce markedly different microstructures and electrochemical behaviors, complicating reproducibility and scale-up. Systematic precursor classification, targeted pre-treatments (e.g., demineralization), and predictive process–structure–performance models are therefore essential to achieve

scalable biochar-based anodes. Resolving this multidimensional optimization remains the central challenge for translating biomass-derived HC into reliable next-generation energy-storage technologies [104, 105].

3 | Biochar-Based Carbons in Alkali Metal-Ion Batteries

Alkali metal-ion batteries, including lithium-, sodium-, and potassium-ion systems, share a common electrochemical foundation: the intercalation-based “rocking-chair” mechanism, first articulated by Scrosati and co-workers, in which alkali ions reversibly shuttle between two host structures during charge and discharge. In Figure 3, a schematic representation of an LIB intercalation battery is reported.

Within this paradigm, the anode plays a central role in governing energy density, rate capability, efficiency, and cycle life, as it must accommodate repeated ion insertion and extraction while maintaining structural and interfacial stability. Carbonaceous materials have therefore emerged as the universal anode platform across alkali-ion chemistries (Li^+ / Na^+ / K^+), owing to their chemical robustness, low volumetric strain, and compatibility with intercalation-based storage.

The rapid scale-up of alkali metal-ion batteries is, however, increasingly constrained by the reliance on graphite and fossil-derived carbons, which are inherently unsustainable. These challenges are amplified as battery technologies expand beyond lithium to sodium and potassium, where the larger ionic radii of Na^+ and K^+ fundamentally limit the applicability of crystalline graphite. This convergence of electrochemical and geopolitical pressures has stimulated intense interest in biomass-derived carbons, particularly biochar and biochar-derived

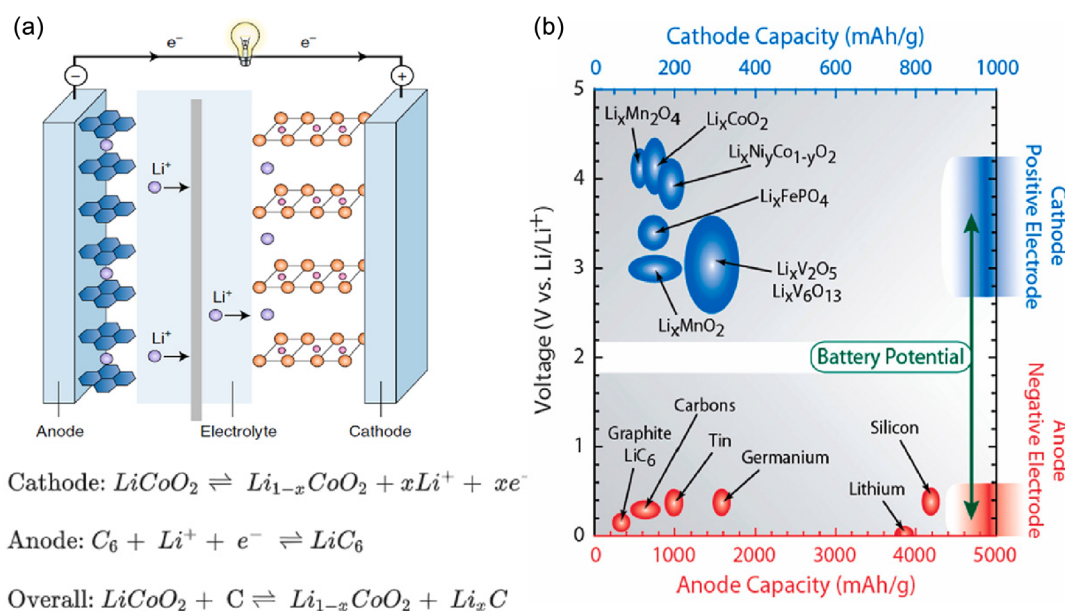


FIGURE 3 | Intercalation-based alkali metal-ion batteries and the central role of carbon anodes. (a) Schematic of a rocking-chair intercalation battery, illustrating reversible alkali-ion shuttling between host electrodes during cycling. (b) Typical specific capacity of carbon anodes in LIBs, highlighting the intrinsic capacity limitation of crystalline graphite and motivating the development of structurally distinct carbon architectures, including biochar-derived HC, for Li-, Na-, and K-ion systems.

HC, as renewable and structurally adaptable alternatives for negative electrodes.

From a materials perspective, most biowaste-derived carbons fall within the HC family already depicted. By tuning synthesis parameters, these materials can access a continuum of storage behaviors, ranging from predominantly intercalation-driven mechanisms to defect-mediated adsorption and pore-filling processes. Although the development of HC has historically been driven by NIBs, the same structural toolbox is increasingly being applied across lithium- and potassium-ion systems, positioning biochar-based carbons as a chemistry-agnostic anode platform.

Beyond electrochemical performance, biowaste-derived carbons offer intrinsic advantages over petroleum cokes and mined graphite. The diversity and abundance of biomass feedstocks enable decentralized production and texture tailoring, while inherent heteroatom content often enables in situ N/O/S doping without additional synthetic steps. When locally sourced and integrated into existing thermal or biorefinery infrastructures, biochar production can achieve competitive life-cycle metrics in terms of energy demand and carbon footprint. At the same time, persistent challenges—most notably low ICE, feedstock variability, and the environmental cost of aggressive activation or graphitization treatments, must be critically addressed to enable industrial deployment.

Against this backdrop, LIBs provide a stringent yet strategically important benchmark for assessing the viability of biochar-based carbons. In Section 3.1, we examine their role in LIBs, both as active anode materials and as conductive or structural components. Sections 3.2 and 3.3 then extend the discussion to NIBs and KIBs, respectively, where HC is already approaching commercial relevance and where the intrinsic structural features of biochar-derived carbons are often better matched to ion size and voltage window than in conventional LIB chemistries.

3.1 | LIBs

In LIBs, biowaste-derived carbons have been deployed in three main roles: (i) as direct alternatives to graphite in the form of biochar or bio-HC anodes; (ii) as engineered “bio-graphites” obtained through catalytic graphitization of biomass-derived precursors; and (iii) as functional additives partially replacing carbon black or other conductive carbons in conventional composite electrodes. Over the past 3 years, the field has evolved from predominantly phenomenological half-cell demonstrations toward more deliberate microstructural design, increasingly coupled with explicit considerations of sustainability, feedstock origin, and circular-economy metrics. A comparative summary of synthesis conditions (including PT), reversible capacity, ICE, and rate performance in recent LIB studies is provided in Table 2 to enable direct comparison across systems.

Attention has been devoted to engineering biochar and bio-HCs as structural alternatives to graphite, aiming to replicate intercalation-dominated lithium storage while maintaining sustainability advantages [125]. In contrast to highly porous carbons that rely predominantly on surface-driven mechanisms, graphite-replacement strategies typically employ controlled pyrolysis (800°C–1200°C) to reduce surface area, suppress excessive defect density, and promote turbostratic microdomains capable of hosting lithium through quasi-intercalation processes [126, 127].

These materials generally deliver reversible capacities in the range of 250–380 mAh g⁻¹, approaching that of graphite, with improved cycling stability but still lower initial coulombic efficiencies due to residual surface functionality and irreversible lithium trapping [128]. Efforts to enhance practical viability have therefore focused on heteroatom regulation, pore closure strategies, prelithiation approaches, and densification treatments to improve volumetric energy density [129]. While complete parity with commercial graphite remains challenging, particularly in terms of ICE and tap density, the literature demonstrates that appropriately engineered bio-HCs can operate within the performance window required for graphite substitution in half-cell configurations [130].

Biomass-derived biochars have attracted significant attention as LIB anode materials owing to their tunable porosity, surface chemistry, and intrinsic heteroatom content. A recurring observation across studies is the strong dependence of electrochemical performance on the biomass precursor and processing conditions. For example, Wang et al. [106] reported nitrogen-doped porous carbons derived from chlorella and oyster shell that exhibited pseudographitic features and delivered a reversible capacity of 1384.9 mAh g⁻¹ over 150 cycles at 0.1 A g⁻¹, retaining 737.6 mAh g⁻¹ after 1000 cycles at 1.0 A g⁻¹. In a different approach, Ge et al. [107] demonstrated that pine-needle-derived biochar with a hierarchical porous architecture could function both as a conductive additive and as a high-rate anode, providing a stable capacity of 192.3 mAh g⁻¹ at 0.5 C. Similarly, Shi et al. [108] showed that biochar obtained from *Poria cocos* waste achieved an exceptionally high surface area (2290.6 m² g⁻¹), enabling an initial capacity of 1139.6 mAh g⁻¹ at 0.1 A g⁻¹ and retaining 806.6 mAh g⁻¹ after 300 cycles.

These results illustrate the considerable versatility of biomass-derived carbons in LIBs, but they also highlight a critical limitation: exceptionally high capacities are often dominated by surface-driven storage processes, including adsorption, pseudocapacitive contributions, and extensive SEI formation. Consequently, low ICE and limited volumetric energy density remain persistent challenges for the direct replacement of graphite in practical LIB anodes.

The role of PT in governing lithium storage behavior is well illustrated by bamboo-derived biochars produced via slow pyrolysis. Barbosa et al. [109] reported that biochar synthesized at 800°C delivered a reversible capacity of approximately 230 mAh g⁻¹ at a C/5 rate (corresponding to a full charge/discharge in 5 h), whereas increasing the PT to 1000°C resulted in superior high-rate performance, maintaining ~95 mAh g⁻¹ at 10 C.

This behavior was attributed to enhanced electronic conductivity and a more open pore network in the high-temperature sample, facilitating faster lithium-ion (Li⁺) transport. Electrochemical signatures, including sloping voltage profiles and cyclic voltammetry responses, indicate a hybrid storage mechanism combining surface adsorption with limited intercalation into turbostratic domains, rather than classical graphite-like staging. Notably, both materials exhibited excellent cycling stability, retaining nearly their full capacity after 450 cycles at C/5 (C-rate; see Figure 4).

Beyond their use as standalone anodes, biomass-derived carbons have shown increasing promise as functional additives in LIB. Belmesov et al. [124] reported that prelithiated yellow-pine biochar containing 3 wt% LiF formed microporous soft-carbon-like

TABLE 2 | Summary of the most relevant biochar-derived carbon used as LIB electrode material (2023–2025).

Feedstock	Treatment	Pyrolysis temp., °C	Role in cell	Reversible capacity, mAh g⁻¹	ICE, %	Cycling / Rate performance	Ref.
Chlorella + oyster shell	Ball milling, high-temperature carbonization	n.d.	LIB anode	1385 (@0.1 A/g, 150 cycles); 738 (@1 A/g, 1000 cycles)	n.d.	Stable over 1000 cycles	[106]
Pine needles	Activation (KCl) + thermal treatment + N-doping	n.d.	Conductive additive	192.3 (@0.5 C)	n.d.	Excellent retention	[107]
Portia cocos waste	Chemical–thermal treatment	n.d.	LIB anode	1139.6 (@0.1 A/g); 806.6 (@300 cycles); 227.85 (@1 A/g)	n.d.	Good rate performance	[108]
Bamboo	Slow pyrolysis (B800/B1000)	800 / 1000	LIB anode	250 (@C/5)	n.d.	Stable 450 cycles	[109]
Yellow pine biochar	Carbonization + 3 wt% LiF	1000–1400	LIB anode	256→235	n.d.	$R = 6.6 \Omega$, $b = 0.75$	[110]
Tannin	CO ₂ activation	900	LIB anode	n.d.	n.d.	High SSA 1370 m ² /g; hierarchical porosity	[111]
Antibiotic bacteria residues	Carbonization + incorporation of N and O elements	n.d.	LIB anode	n.d.	n.d.	Layered porous; N-doped; good cycling	[112]
Rice straw	Pyrolysis + activation	n.d.	LIB anode	n.d.	n.d.	Low-cost; good rate	[113]
Market biochar + catalytic treatment	Hybrid catalyst + catalytic Graphitization	n.d.	LIB anode	n.d.	n.d.	Scalable graphitization; improved anode performance	[114]
Discarded bamboo chopsticks	Carbonization + SnO ₂ nanosheets	n.d.	LIB anode	1182.5 (initial); 570.5 (500 cycles)	n.d.	500 cycles	[115]
Jack wood	NaOH activation	800	Anode/activated carbon	n.d.	n.d.	High SSA; promotes Li ⁺ transport	[116]
Olive pomace	H ₃ PO ₄ activation	500	LIB anode	n.d.	n.d.	Eco-friendly precursor; low SSA 10.6 m ² /g	[117]
Cu/MnO-biochar	Metal-oxide functionalization	n.d.	LIB anode	1070 (@0.1 A/g)	100	200 cycles	[118, 119]
Seaweed-derived biochar (Si@N-Gam-5)	N-doping + Si integration	n.d.	LIB anode	1483 (@0.1 A/g)	63.3	n.d.	[120]
Bio-graphite	Biochar graphitization	n.d.	LIB anode	293 (@0.02 A/g)	75.6	n.d.	[114]
Biochar (Rice straw) + spent LIBs	Oxalic acid + microwave activation	n.d.	Microwave catalyst	n.d.	n.d.	Max heating 720°C/min; H ₂ -rich syngas 50.2 vol%	[121]
Rice husk	Fast pyrolysis	700–800	SiOx/C anode	1366/800/275 (@1st/5th/200th cycles)	n.d.	Conductive pathways; buffers expansion	[122]
Corn stalk	NaOH activation	800	LIB anode	n.d.	n.d.	Improved Li storage; SSA 255 m ² /g	[123]
Red seaweed and seagrass	Stepwise pyrolysis	500–700	LIB anode	391→300	n.d.	70 % C, >5 % N	[124]

Abbreviations: B800/B1000, bamboo pyrolyzed at 800°C or 1000°C; C, C-rate; ICE, initial Coulombic efficiency; LiF, lithium fluoride; n.d. not determined; SSA, specific surface area; SiOx/C, silicon oxide/carbon composite.

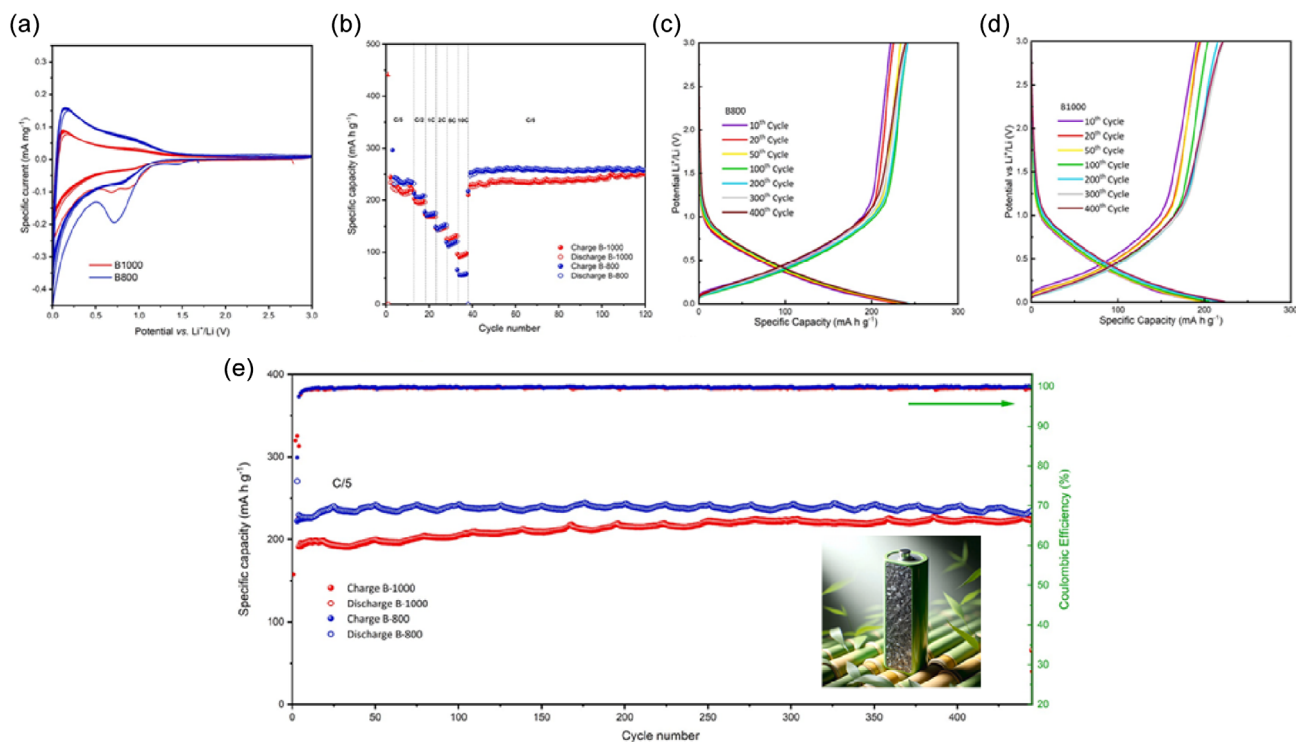


FIGURE 4 | Electrochemical performance of bamboo-derived biochar anodes in LIBs: (a) CV curves at a scan rate of 0.05 mV s^{-1} ; (b) rate capability from C/5 to 10 C and back to C/5; (c,d) galvanostatic charge–discharge profiles at C/5; and (e) long-term cycling performance over 450 cycles at C/5. Reproduced from ref. [109]. Creative Commons CC-BY license.

structures that facilitated Li^+ transport, achieving a reversible capacity of $235.25 \text{ mAh g}^{-1}$ at 20 mA g^{-1} with low series resistance. Detailed electrochemical analysis, including galvanostatic charge–discharge profiles, Coulombic efficiency (CE), and rate-capability measurements, demonstrated stable performance across a range of operating conditions, underscoring the value of biochar-based carbons as multifunctional components rather than simple conductive fillers (see Figure 5).

Taken together, these examples demonstrate that the electrochemical performance of biochar-based materials in LIBs, including specific capacity, rate capability, and cycling stability, is strongly governed by feedstock selection, PT, and surface functionalization. Controlled processing enables the development of cost-effective and environmentally benign carbons with competitive performance in LIB half-cells. Nevertheless, LIBs remain a stringent benchmark for biomass-derived carbons: the small ionic radius of Li^+ , narrow operating voltage window, and strict requirements on ICE strongly favor crystalline graphite. Consequently, while biochar-derived carbons are unlikely to fully displace graphite as LIB anodes in the near term, they represent a compelling platform for conductive additives, hybrid electrode architectures, and mechanistic insight. These findings directly inform their more natural and technologically impactful deployment in NIBs and KIBs, as discussed in Sections 3.2 and 3.3.

3.2 | NIBs

NIBs are emerging as a compelling complement to lithium-ion technology, particularly for stationary storage and cost-sensitive markets, driven by the abundance and broad geographic

distribution of sodium (Na) resources, as well as the potential to leverage existing battery manufacturing infrastructure. From an anode perspective, however, NIBs face fundamental limitations with conventional graphite: unlike Li^+ , Na^+ does not form a thermodynamically stable intercalation compound in pristine graphitic lattices, rendering graphite largely inactive [131, 132]. Consequently, the anode design space in NIBs is dominated by nongraphitizable disordered carbons (i.e., HC), which enable Na storage through multiple mechanisms, including adsorption at defects/edges, insertion between turbostratic graphene layers, and clustering within porosity and defects of HC [93, 133–136].

The sodium-storage signature of HC is typically decomposed into two voltage regimes: a slope region ($>0.1 \text{ V}$) governed primarily by adsorption at defects/edges and shallow insertion into disordered domains, and a low-voltage plateau ($<0.1 \text{ V}$), associated with interlayer insertion and pore filling (often described as Na clustering in closed micropores). This mechanistic framework places biochar-derived HC in a privileged position: their microtexture naturally combines turbostratic graphene domains (expanded d_{002}), abundant defect chemistry, and controllable open/closed porosity. Importantly, more interlayer spacing is not always better. Once d_{002} exceeds the minimum required to accommodate Na^+ insertion (often discussed around $\sim 0.37 \text{ nm}$), further expansion does not guarantee higher capacity and may instead correlate with excessive disorder, high surface area, and parasitic reactions [137, 138]. Similarly, oxygen and other heteroatom functionalities are a double-edged sword: carbonyl-rich motifs (e.g., quinone/anhydride-like $\text{C}=\text{O}$ environments) can provide reversible Na-binding sites and enhance electrolyte wettability, whereas highly labile $\text{C}=\text{O}$ species increase irreversible capacity via extensive SEI formation. Therefore, NIB anode

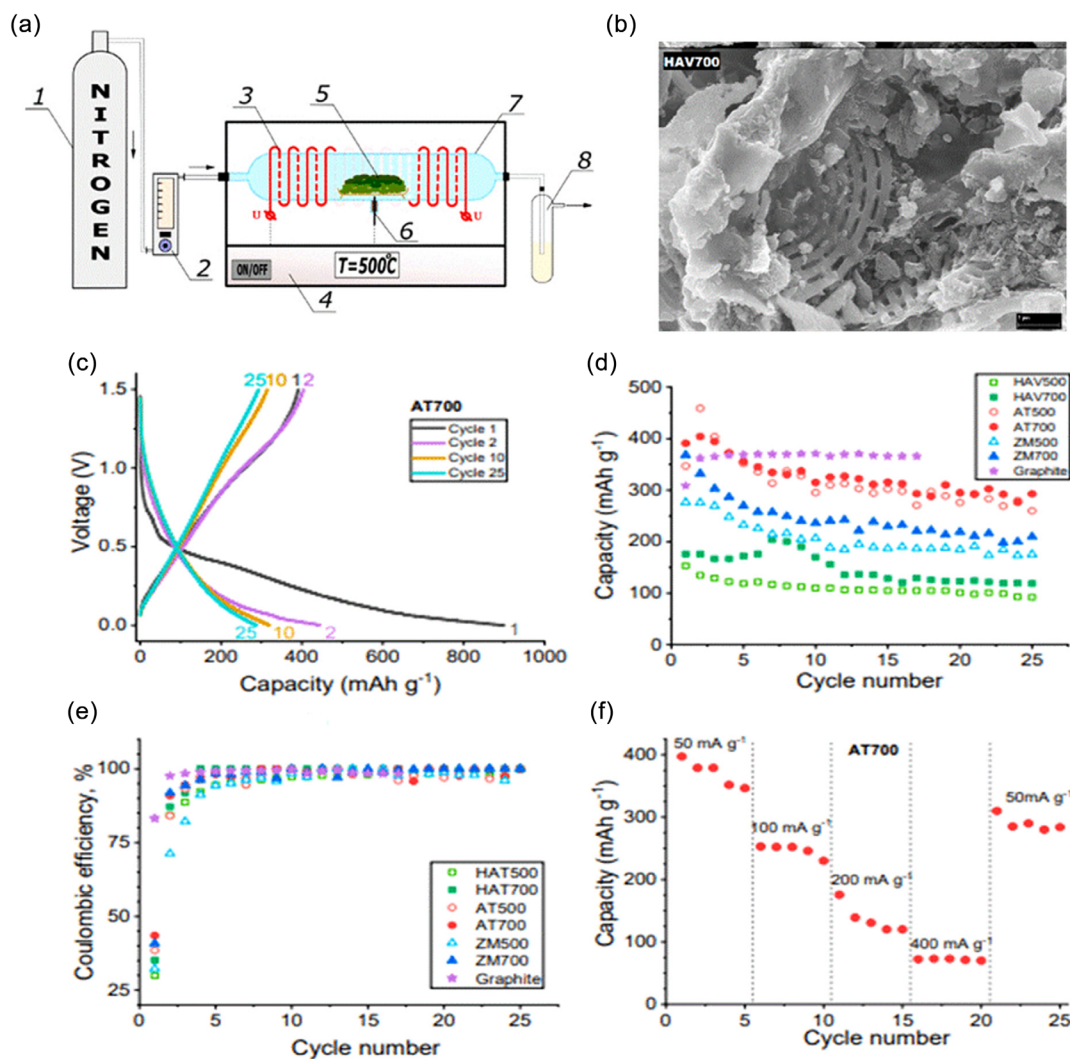


FIGURE 5 | (a) Schematic illustration of biochar synthesis through pyrolysis; (b) representative SEM micrographs of the resulting biochar; (c) galvanostatic charge–discharge profiles of the AT700-based cell; (d) cycling stability of cells employing the investigated biochars; (e) CE measured at a current density of 36 mA g⁻¹; and (f) rate-dependent cycling performance of the AT700 electrode under various charge–discharge conditions. Reproduced from ref. [124], Creative Commons CC-BY license.

optimization is best treated as a multiparameter problem, where capacity, plateau fraction, ICE, and rate capability are jointly dictated by a coupled set of descriptors: d_{002} , closed-pore fraction, active surface area, defect density, and functional-group speciation [139]. Figure 6 summarizes the main understood pathways and mechanisms for Na⁺ intercalation in HC.

Across biomass-derived systems, PT remains the first-order tuning of Na-storage behavior because it controls graphitization degree, interlayer spacing, defect density, and pore structure. From the reviewed literature, specific structure–property trends can be highlighted. For low temperatures pyrolysis (700–900°C), the precursors undergo an incomplete carbonization, retaining original biomass features with many defects and oxygen groups. Low PTs are also predominantly associated with a large surface area and modest graphitic ordering. Such features favor high surface capacity but low ICE, corresponding to poorer cycling capabilities due to excessive SEI formation and unstable surface [57, 142–144]. Increasing the PT to the range 1000–1300°C is often considered an optimal window for biomass-derived NIB anodes. At this

temperature, the carbonization modifies the microstructure, leading to an appropriate balance between disorder and graphitization, defect content, and expanded interlayer spacing (typically 0.36–0.39 nm). In addition, the formation of useful micro/mesopores is observed. For example, Wu et al. [142] increased the PT from 900°C to 1100°C to prepare pomegranate peel-derived HC (PPHC-1100), obtaining an interlayer spacing ~0.38 nm, a suitable oxygen content, and low surface area (1.7 m² g⁻¹), delivering 330 and 175 mAh g⁻¹ after 200 cycles. Also, olive-pomace HC shows strong enhancement when increasing PT from 750 to 1250°C, increasing the specific capacity from 94 to 248 mAh g⁻¹ and ICE from 47%–48% to 67%–68% [145]. Increasing the PT above 1300°C is not always beneficial for bio-HC. At this temperature, the C structure is characterized by an increased graphitic order and a corresponding reduced d-spacing. Moreover, the volume of closed and open pores can decrease, directly impacting the Na⁺ insertion/adsorption [57, 144, 146, 147]. Pomegranate-peel HC shows a trend to graphitization and loss of beneficial surface structure at 1200°C–1300°C, with graphite-like smooth sheets and poorer Na

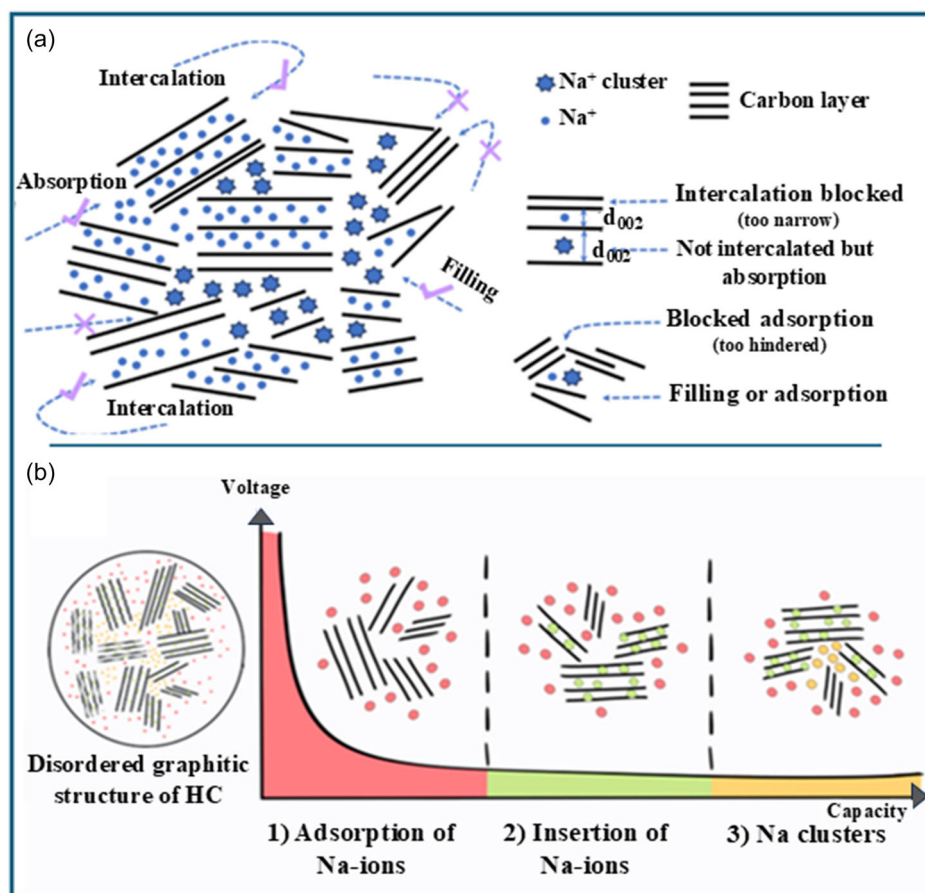


FIGURE 6 | Sodium-ion intercalation mechanisms. In (a) interaction of Na⁺ ions within the complex structure of HC anodes. Adapted from [140], permission requested. In (b) the electrochemical correlation of Na⁺ ions storage mechanism: adsorption on pores, edges, and defects, insertion into turbostratic domains, and clustering of ions in micropores. Adapted from [141], Creative Commons CC-BY license.

performance [142]. Overall, when d -spacing falls below ~ 0.36 nm, Na⁺ intercalation is strongly hindered with concomitant plateau capacity drop [57].

This behavior is illustrated in banana-peel-derived carbons, where increasing carbonization temperature markedly improves reversible capacity and kinetics (e.g., high-temperature HC achieving ~ 357 mAh g⁻¹ versus ~ 142 mAh g⁻¹ at lower temperature), consistent with reduced charge-transfer resistance and removal of electrochemically inactive moieties [148]. Similar optimization windows are observed for wheat-straw-derived HC (≈ 280 mAh g⁻¹ over 200 cycles at 0.1 A g⁻¹), where the best performance reflects a balance between pore development and conductivity rather than maximization of any single structural metric [45].

Among reported biochar-derived anodes, one of the highest sodium-storage capacities was achieved by Sun et al., who developed a lotus stem-derived porous carbon featuring a nanowire framework decorated with graphene quantum dots (GQDs) [149]. Synthesized at 700°C via a self-templating strategy, the material exhibited an exceptionally high surface area (~ 1574 m² g⁻¹) and delivered a reversible capacity of ~ 460 mAh g⁻¹ at 0.2 C after 300 cycles, albeit with a relatively low ICE ($\sim 50\%$). The outstanding performance was attributed to dominant capacitive-controlled storage, fast Na⁺ diffusion pathways, and effective accommodation of volume changes during cycling.

Comparable high-capacity behavior was reported by Zhang et al. for a nitrogen-doped HC (N-ZAHC) derived from kapok fibers. This material was engineered via a pre-crosslinking and precarbonization strategy to retain pyridinic-N species during high-temperature pyrolysis [140]. The optimized N-ZAHC anode delivered a reversible capacity of 401.7 mAh g⁻¹ at 0.05 A g⁻¹ with an ICE of 75.9%, benefiting from enlarged interlayer spacing (~ 0.387 nm), moderate SSA (~ 319 m² g⁻¹), controlled mesoporosity, and carbonyl-rich surface chemistry. These features collectively stabilized the SEI and enhanced Na⁺ storage.

From the reviewed literature, practical guidelines can be derived for the optimization of biochar for NIB anodes. The primary objective is to achieve expanded but not collapsed carbon layers, abundant but controlled closed pores, and moderate defect/heteroatom levels, thereby enabling high capacity, improved ICE, and long-term cycling stability. Generally, the intermediate temperature range (1000°C–1300°C) is the most suitable but requires an empirical tuning of the exact temperature for each specific precursor. For example, corncob and pinenut-derived carbons benefit from pyrolysis around 1300°C–1400°C, whereas pomegranate peel and many nut/wood precursors perform optimally at 1100°C–1200°C [57, 142, 144, 145, 147]. The interlayer spacing and graphitization must be controlled, aiming for $d_{002} \sim 0.36$ – 0.39 nm to balance Na⁺ intercalation plateau capacity and structural stability while avoiding overgraphitization ($d_{002} < 0.36$ nm), which sharply reduces plateau capacity. In addition, the closed

pore structure is important for high plateau capacity via the adsorption-filling mechanism. At the same time, open microporosity must be controlled since directly related to SSA, low ICE, and thicker SEI growth.

Pretreatments and activations processes can remove impurities, tune volatile content, and favor the formation of disordered matrices that later develop optimal *d*-spacing and porosity under high temperature pyrolysis [57, 145, 150–153]. Lastly, two-step or staged pyrolysis (low-T precarbonization followed by higher-T treatment) is important to optimize interlayer spacing, lattice ordering, and pore development while retaining structural robustness [57]. A summary of the influence of carbonization temperature on structure/Na-storage behavior is reported in Table 3.

Beyond temperature control, pretreatment strategies such as acid washing and hydrothermal carbonization (HTC) are increasingly employed to improve reproducibility and ICE by moderating surface area and removing ash or metal impurities that destabilize the SEI. Hydrothermal pretreatment prior to high-temperature pyrolysis has been shown to increase carbon yield, tailor microporosity, and deliver ICE values of ~70%–76% with stable cycling over hundreds of cycles [154, 155]. Recent advances further demonstrate that targeted microtexture engineering, particularly closed-pore design, can simultaneously enhance capacity and ICE. Deliberate conversion of open pores into closed micropores reduces electrolyte accessibility, mitigates irreversible reactions, and promotes Na⁺ clustering within confined domains, yielding reversible capacities approaching ~385 mAh g⁻¹ with ICE up to ~88% [156]. In parallel, scalable activation strategies are evolving beyond conventional KOH-based protocols. Milder chemical activators, such as K₂CO₃, or templating can produce interconnected microporosity while retaining a modest fraction of closed pores, balancing high capacity and electrochemical stability.

For instance, hemp-hurd-derived HC activated with K₂CO₃ and carbonized at ~800°C exhibits a favorable combination of electrochemical properties: an ICE of ~73%, a reversible capacity of ~267 mAh g⁻¹ at low current, high-rate performance of ~79 mAh g⁻¹ at high current, and strong capacity retention (~96% after 300 cycles at 2 A g⁻¹) [157]. Similarly, morphology-controlled HC from the same precursor, tubular, sheet, or spherical, demonstrate that microstructure, rather than feedstock alone, governs ICE and cycling stability. Tubular architectures with enlarged *d*₀₀₂ (~0.37 nm) and moderated surface area can achieve reversible capacities of ~265 mAh g⁻¹ with ICE ~76%–77% and long-term stability over hundreds of cycles (Figure 7) [154]. A key criticism of field maturation is the increasing frequency of full-cell demonstrations and electrolyte-aware

designs. Honeycomb-like, salt-templated biochars with controlled heteroatom content and optimized electrolyte chemistry have achieved high ICE (~86%) and excellent high-rate stability, sustaining thousands of cycles with >95% capacity retention, while full cells reaching energy densities on the order of ~180 Wh kg⁻¹ with sodium vanadium phosphate (Na₃V₂(PO₄)₃)-based cathodes [158]. Complementary approaches, such as acid washing and temperature optimization (e.g., pomegranate-peel HC carbonized at ~1100°C), reinforce a central design principle: an optimal carbonization window exists, in which *d*₀₀₂, oxygen speciation, and surface area collectively maximize reversible capacity without sacrificing ICE [142]. Exceeding this window can reduce slope-region capacity by removing functional sites and decreasing interlayer spacing.

Beyond pure HC, biochar-derived composites are being explored to provide faradaic contributions or improve kinetics. For instance, SnO₂/carbon hybrids and porous biochars have been used as selenium hosts in lithium–selenium (Li–Se) and sodium–selenium (Na–Se) systems, where hierarchical porosity and high surface area enable high Se loading and long-cycle stability [159]. Likewise, lotus-stem-derived porous carbons with embedded graphene quantum dots (GQDs) achieve high capacities in both LIBs and NIBs, although the frequently observed low ICE (~50% for high-surface-area architectures) reinforces the need for practicality-aware benchmarking (see Table 4).

Despite rapid progress, three limitations continue to define the translation gap for biomass-derived HCs in NIBs: (i) ICE and electrolyte consumption remain the dominant barrier, particularly for high-surface-area carbons where SEI formation dominates early cycling [159]. Closed-pore engineering and surface-area control are therefore non-negotiable for practical deployment. (ii) Feedstock variability and ash chemistry translate into batch-to-batch dispersion in microtexture and SEI behavior. Pretreatment, demineralization and standardized pyrolysis protocols are essential to industrial relevance. (iii) Practical cell validation is still uneven. Many reports remain half-cell, low-loading demonstrations; broader adoption requires systematic testing at areal loadings ≥2 mg cm⁻², realistic N/P ratios, lean electrolyte, and full-cell configurations [141, 154, 160]

Overall, biochar-derived HC are uniquely aligned with the mechanistic requirements of sodium storage. Their nongraphitizable turbostratic framework, enlarged interlayer spacing, and engineerable porosity enable adsorption–insertion–pore-filling behavior inaccessible to graphite. The most credible pathway forward is co-optimization rather than maximizing a single metric (surface area, *d*₀₀₂₁, or doping level): closed-pore fraction, oxygen/nitrogen speciation, and active surface area must be

TABLE 3 | Effects of carbonization temperature on biomass structure and Na⁺ storage behavior.

Temperature range	Structural changes	Electrochemical impact	Ref.
700°C–900°C	Disordered, high defects/O, high SSA, incomplete carbonization	Higher surface capacity, low ICE, poorer long-term stability	[57, 142, 143, 146]
1000°C–1300°C	Expanded <i>d</i> -spacing (~0.36–0.39 nm), moderate defects, controlled porosity	High reversible capacity, improved ICE, good rate and cycling	[57, 142, 144, 145, 147]
>1300°C	More graphitic, reduced <i>d</i> -spacing, loss of useful porosity	Lower Na ⁺ intercalation/adsorption, capacity decline despite higher ICE	[57, 142, 144–147]

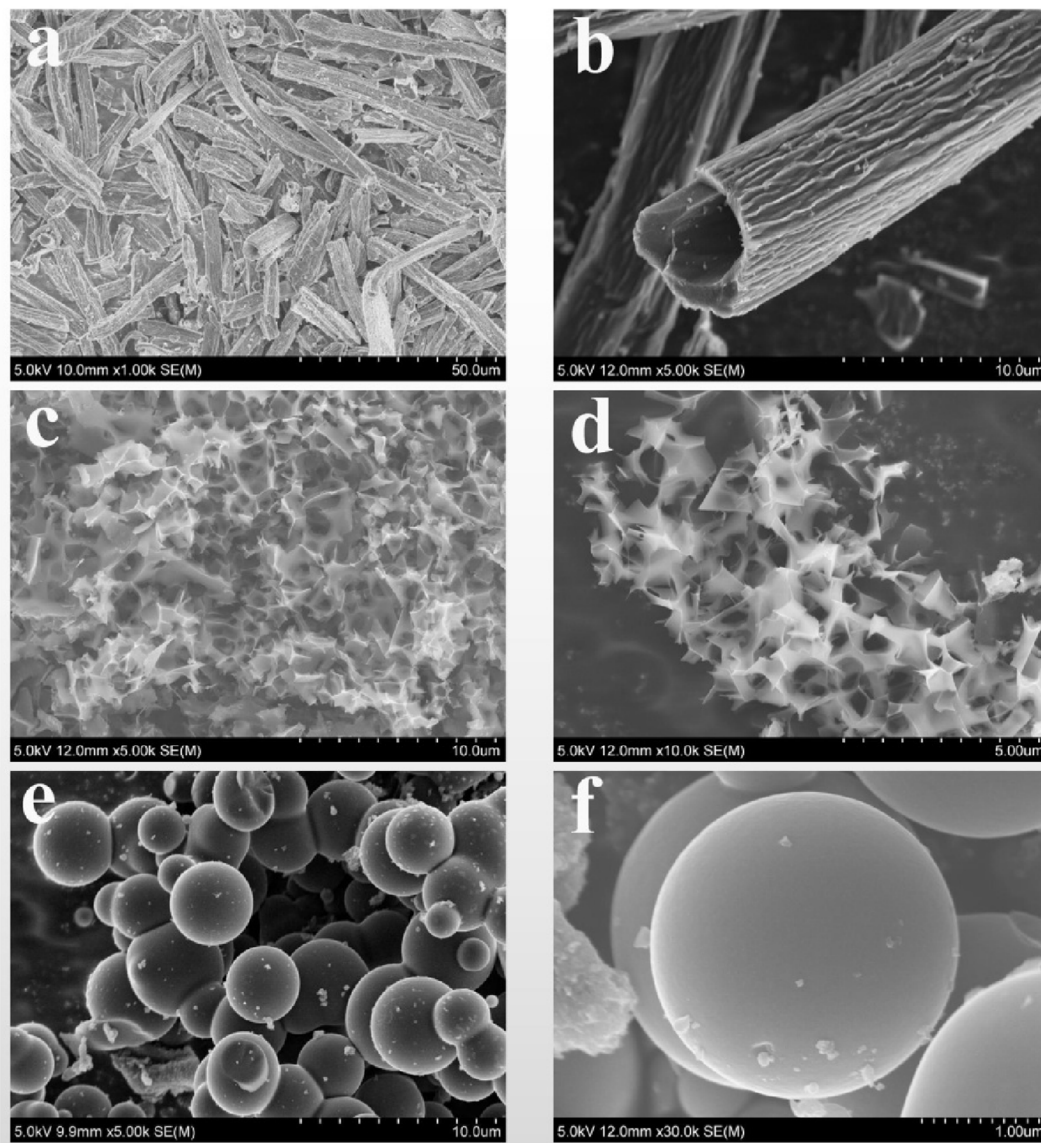


FIGURE 7 | Different morphologies of the same precursor (sisal fiber) but different pretreatment before pyrolysis at 900°C, 1 h in N₂ atmosphere. (a,b) Tubular (TSFC) prepared with HTC treatment in KOH, 160°C, 14h; (c,d) sheet (SSFC) where the HTC in KOH was followed by heating and stirring (80°C) the sample with 2.5 mol L⁻¹ KOH solution before pyrolysis; (e,f) spherical (GSFC) prepared with HTC in HCl solution at 180°C for 12 h. Reproduced from [154], Creative Commons CC-BY license.

balanced under realistic electrochemical protocols. In this context, NIBs represent a natural technological landing zone for biochar-based anodes and a proving ground for scalable, circular carbon manufacturing.

3.3 | KIBs

Following the first demonstrations of reversible potassium intercalation in graphite in 2015 [169–171], KIBs have rapidly emerged as a promising alternative to lithium-ion systems for large-scale and cost-sensitive energy-storage applications. Although potassium shares key electrochemical similarities with lithium and sodium, its significantly higher natural abundance in the Earth's crust (~1.5 wt%) makes it more appealing from the perspectives of both sustainability and resource security. Figure 8 illustrates the publication growth in KIB research over the past decade.

Several intrinsic characteristics distinguish KIBs from both LIBs and NIBs. First, potassium does not form stable Al–K intermetallic compounds, enabling the use of aluminum current collectors on the anode side instead of copper, with clear benefits in terms of cost and weight reduction [172]. Second, the standard redox potential of the K/K⁺ couple (–2.94 V vs. SHE) lies between Li/Li⁺ and Na/Na⁺, allowing KIBs to achieve higher operating voltages and, in principle, higher energy densities than sodium-based systems. Third, although K⁺ possesses a larger bare ionic radius than Li⁺ and Na⁺, its weaker solvation leads to a smaller effective Stokes radius in common electrolytes, which translates into faster ionic transport and improved interfacial kinetics [173, 174].

Carbon-based materials dominate anode development for KIBs, including graphite, graphene, and disordered carbons (soft and HC) [173, 174]. Similar to lithium intercalation, potassium can form graphite intercalation compounds (GICs) such as

TABLE 4 | Most relevant biochar-derived carbon used as NIBs electrode material (2023–2025).

Feedstock/ precursor	Processing / Post-treatment	Pyrolysis temperature, °C	Reversible capacity, mAhg⁻¹	ICE	Rate capability	Ref.
Pine sawdust	Molten salt pyrolysis (ZnCl ₂ -KCl-NaCl, 1:10 ratio) + HCl washing	500°C, 30min	389 (@2.5C) (Na/Se cathode)	n.d.	300 cycles (@1C), 98% (Na/Se)	[159]
Lotus stem	HTC (water) 180°C, 24h + chemical activation in KOH	700, 2 h	460 (@ 0.2C)	50%	300 cycles (@0.2C), 93%	[149]
Hemp hurd (Cannabis sativa L.)	Prepyrolysis at 500°C + chemical activation with K ₂ CO ₃	800, 1 h	267 (@ 0.03 Ag ⁻¹)	73%	300 cycles (@2 Ag ⁻¹), 96%	[157]
Birch tree waste and SnO₂ composite	HTC (H ₃ PO ₄) 150°C, 16h	800, 1 h	373 (@ 0.1C)	52%	162 cycles (@0.1 Ag ⁻¹), --	[160]
Waste cotton	HTC (KOH) 250°C, 4 h	800, 2 h (char/KOH mixtures)	330 (@ 0.1 Ag ⁻¹)	79%	400 cycles (@1 Ag ⁻¹), 96%	[141]
Sisal fiber	HTC (KOH)160°C, 14 h	900, 1 h	265.2 (@ 0.1 A g ⁻¹)	76.70%	400 cycles (@ 0.05 Ag ⁻¹), 99%	[154]
Aegle marmelos shell	HTC (H ₂ SO ₄) RT, 2 h, 200°C, 48 h	900, 1000	223 (900°C), 212 (1000°C) (@ 0.01 Ag ⁻¹)	99%	2500 cycles (@1 Ag ⁻¹), 68% (900°C), 86% (1000°C)	[161]
Poplar tree biomass tar (N-doped)	N-doping with urea	1000, 1.5 h	257.5 (@ 0.025 Ag ⁻¹)	59.30%	200 cycles (@1 Ag ⁻¹), 70.3%	[162]
Xanthium sibiricum fruit (honeycomb biochar)	NaCl template, prepyrolysis at 600°C	1000, 2 h	161 (@ 4.0 Ag ⁻¹)	86.50%	3000 cycles (@2.0 Ag ⁻¹), 97%	[158]
Pomegranate peel	Acid washing with HCl and HF	1100, 2 h	330 (@ 0.1C)	45%	200 cycles (@0.5C), 68%	[142]
Vine shoots	Precarbonization at 500°C + HCl washing	1200, 2 h	259 (@ 0.03 Ag ⁻¹)	71%	315 cycles (@0.1 Ag ⁻¹), 97%	[45]
Sunflower seed shell	HTC (water) 250°C, 24 h	1200, 2 h	280 (@ C/15)	76%	500 cycles (@1C = 372 mAhg ⁻¹), 86%	[155]
Spent coffee grounds	HTC (water) 250°C, 24 h	1200, 2 h	240 (@ C/15)	40%	500 cycles (@1C = 372 mAhg ⁻¹), 85%	[155]
Rose stems	HTC (water) 250°C, 24 h	1200, 2 h	210 (@ C/15)	35%	500 cycles (@1C = 372 mAhg ⁻¹), 74.5%	[155]
Kapok fiber (N-doped)	ZnCl ₂ -assisted pre-cross-linking, precarbonization with C ₇ H ₅ NO ₄ at 220°C	1200, 2 h	401.7 (@ 0.05 A/g)	76%	500 cycles (@0.4Ag ⁻¹), 98%	[140]
Walnut shell + polystyrene	Two prepyrolysis at 1000°C and 700°C adding polystyrene	1200, 2 h	385 (@ 0.05 Ag ⁻¹)	88%	300 cycles (@1Ag ⁻¹), 99.9%	[156]

(Continues)

TABLE 4 | (Continued)

Feedstock/ precursor	Processing / Post-treatment	Pyrolysis temperature, °C	Reversible capacity, mAhg ⁻¹	ICE	Rate capability	Ref.
Sorghum husk	N-doped with HTC (HNO ₃) post treatment, 180°C, 6 h	1200, --	322 (@ 0.05 Ag ⁻¹ , -20°C)	91%	600 cycles (@1 Ag ⁻¹), --	[163]
Basswood	Bacterial/enzymatic tailoring	300, 2 h + 1300 for other 5h	366.4 (@ 0.02 Ag ⁻¹)	88.20%	200 cycles (@0.1 Ag ⁻¹), 98.8%	[164]
wasted Sulfuric acid paper	H ₂ SO ₄ washing + preoxidation at 300°C, 4 h in air	1400, 2 h	350.1 (@ 0.03 Ag ⁻¹)	77.30%	100 cycles (@ 0.3 Ag ⁻¹), 80.7%	[165]
Metaplexis japonica seed hair fibers	Prepyrolysis at 500°C in N ₂ + HCl washing	1400, 2 h	331.7 (@ 0.03 Ag ⁻¹), 229 (@ 3 Ag ⁻¹)	94.8% (@0.03 Ag ⁻¹)	2000 cycles (@2 Ag ⁻¹), 84.1%	[166]
Cellulose	None	1500, 1 h	308 (@ 0.0372 Ag ⁻¹)	87%	50 cycles (@0.0372 Ag ⁻¹), 95%	[167]
Lignin	None	1500, 1 h	273 (@ 0.0372 Ag ⁻¹)	80%	50 cycles (@0.0372 Ag ⁻¹), 95%	[167]
Chitosan	None	1500, 1 h	256 (@ 0.0372 Ag ⁻¹)	86%	50 cycles (@0.0372 Ag ⁻¹), 96%	[167]
Potato starch	Stabilization in air, 200°C, 3 days	1500, 1 h	291 (@ 0.0372 Ag ⁻¹)	89%	50 cycles (@0.0372 Ag ⁻¹), 92%	[167]
Rice starch	Stabilization in air, 200°C, 3 days	1500, 1 h	39 (@ 0.0372 Ag ⁻¹)	85.80%	50 cycles (@0.0372 Ag ⁻¹), 92%	[167]
Pine nut shells	Oxygen functionalization via O ₂ pyrolysis at 400°C + carbonization via N ₂ pyrolysis at 400°C	1500, 2 h (char/ KOH mixture)	378.1 (@ 0.1C)	88%	200 cycles (@1.5 Ag ⁻¹ , (5C)), 85.2%	[139]
Black locust wood	6M HCl pretreatment	500, 2 h + 1500 for other 2 h	382 (@ 0.1C)	67%	100 cycles (@ 0.3C), 90%	[168]

Abbreviations: X₂CO₃, potassium carbonate; KOH, potassium hydroxide; NaCl, sodium chloride; ZnCl₂, zinc chloride.

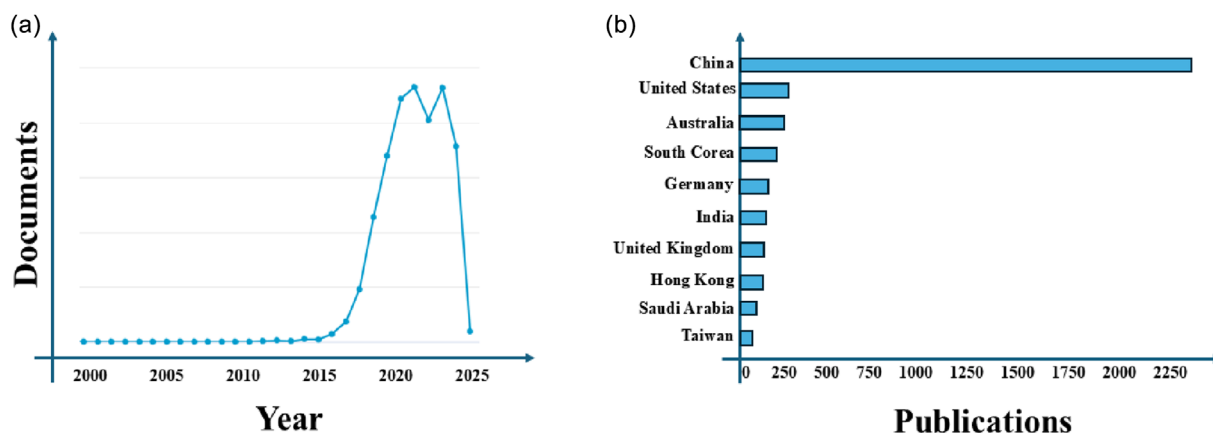


FIGURE 8 | Publication trends in potassium-ion battery research from 2015 to 2024. Data retrieved from the Scopus database (Elsevier) using the query “potassium-ion battery” and “carbon anode.” Figure adapted and reprocessed by the authors. In (a) the annual number of published documents. In (b) the distribution of publication output by country, highlighting the relative contribution of major producing nations.

KC₃₆, KC₂₄, and KC₈, yielding a theoretical capacity of 279 mAh g⁻¹ [172]. However, graphite suffers from severe structural instability during K⁺ intercalation. The graphite interlayer spacing expands from 0.335 to ~0.530 nm, corresponding to a ~63% volumetric expansion. This drastic lattice dilation promotes exfoliation, structural collapse, and rapid capacity fading upon repeated cycling. Consequently, strategies including interlayer spacing modification, heteroatom doping, surface engineering, and morphology optimization have been extensively explored to mitigate these intrinsic limitations [175, 176]. Achieving high performance while maintaining mechanical integrity remains a central challenge in KIB anode design.

In this context, biochar-derived and biomass-based HC represent a structurally superior platform for potassium storage [177]. Their turbostratic, nongraphitizable frameworks possess intrinsically enlarged interlayer spacing and disordered pore networks capable of accommodating large K⁺ ions. Closed nanopores further function as mechanical buffers, alleviating stress during repeated insertion–extraction cycles.

Compared to LIBs and NIBs, biochar-derived HCs face more pronounced limitations in KIBs. The larger ionic radius and higher mass of K⁺ slow diffusion and promote steric hindrance within disordered carbon frameworks, leading to channel blockage and faster capacity decay [178–180]. Additionally, the typically higher ash content and heteroatom-rich surface of biochar intensify side reactions. Due to the higher reactivity of K⁺, this results in thicker and less stable SEI layers, increased polarization, and progressive interfacial degradation [150, 178–180]. While microporosity enhances capacity in LIBs and NIBs, in KIBs it promotes irreversible K⁺ trapping and electrolyte confinement, lowering ICE and accelerating capacity fading [178, 179].

Electrochemically, potassium storage in HC mirrors the behavior observed in sodium-ion systems. Galvanostatic profiles typically display two distinct regions: a higher potential sloping region associated with K⁺ adsorption on surface defects, edges, and heteroatom sites, followed by a lower potential plateau attributed to interlayer insertion and pore-filling processes. This multimechanism storage enables higher reversible capacity and improved cycling stability compared to crystalline graphite.

To optimize these properties, a variety of synthetic strategies have been explored, largely paralleling those developed for SIBs. These include single- and multistep pyrolysis, hydrothermal carbonization (HTC), salt-templating, chemical activation, and heteroatom doping (notably N, O, P, and S). Such approaches enable precise control over interlayer spacing, defect density, electronic conductivity, and pore architecture, all critical parameters for efficient K⁺ storage.

Among reported studies, outstanding cycling stability was achieved by Wang et al. [181], who synthesized an N-doped HC derived from lignin using Zn-assisted multistep pyrolysis under Ar/H₂ at 1100°C, followed by ammonia activation at 800°C. The resulting material (denoted on-CZL) demonstrated exceptional durability, sustaining 10,000 charge–discharge cycles at a high current density of 5 A g⁻¹. This performance was attributed to a synergistic combination of factors: (i) a large interlayer spacing of ~0.44 nm dictated by the lignin precursor; (ii) Zn vapor-induced expansion and restructuring of graphitic domains; (iii) Zn-catalyzed cross-linking effects that promote curvature and turbostratic disorder; and (iv) nitrogen doping, which further modulates interlayer spacing and electronic structure.

An alternative morphological strategy was proposed by Wang et al. [182], who prepared MnO₄ as a sacrificial template to construct a nanotube-like carbon architecture. This material delivered a reversible capacity as high as 407 mAh g⁻¹ at 0.1 A g⁻¹, representing one of the highest values reported for carbonaceous KIB anodes to date. The enhanced performance was attributed to the combination of high accessible surface area, shortened diffusion pathways, and structural resilience against volume expansion.

Overall, these studies demonstrate that biochar-derived and HC offer decisive advantages over graphite for potassium-ion storage, provided that their microstructure, chemistry, and morphology are rationally engineered. A comprehensive overview of biochar- and biomass-derived HC anodes for KIBs, including synthesis routes, structural parameters, and electrochemical performance metrics, is provided in Table 5.

3.4 | Correlations Across Alkali-Ion Systems

A systematic correlation emerges across alkali-ion battery systems as the ionic radius increases (Li⁺, 0.76 Å < Na⁺,

TABLE 5 | Summary of the most relevant biochar-derived carbon used as KIBs electrode material (2023–2025). HTC, hydrothermal carbonization.

Biowaste precursor	Processing/Modification	Pyrolysis temperature, °C	Reversible capacity, mAhg⁻¹	ICE	Performance	Ref.
Cellulose nanofiber and coal tar pitch	Solution mixing of cellulose and coal tar pitch	1200	366 (@ 0.03Ag ⁻¹)	n.d.	1000 cycles (@1 Ag ⁻¹), 74.2%	[183]
Pinus massoniana bark	Ore-oxidation at 250°C, 4 h + HTC (water) 180°C, 12 h + ball milling post pyrolysis	600, 3 h	256.1 (@ 0.1Ag ⁻¹)	46%	3000 cycles (@1 Ag ⁻¹), 80%	[184]
Calophyllum inophyllum L. (N-doped)	Ball milling + wet impregnation urea + HCl washing after pyrolysis	1200, 3 h	208.9 (@ 0.05 Ag ⁻¹)	59%	1000 cycles (@0.5 Ag ⁻¹), --	[185]
Lignite + Starch	Ball milling + preoxidation at 260°C, 2 h in air	1300, 1 h	284.9 (@ 0.1C)	74%	500 cycles (@1C), 92.2%	[186]
Coffee waste + Graphene	Mixture freeze-dried for 3 days, ball milling after pyrolysis	950, 1 h	175 (@ 0.1C)	n.d.	300 cycles (@1C), >80%	[187]
Sorghum biomass (N-S-doped)	Delignification with NaOH, coprolysis with thiourea for doping	600, 1 h	268 (@ 0.1 A g ⁻¹)	60%	2400 cycles (@ 1 Ag ⁻¹), high	[188]
Kigelia africana fruit	HCl washing after pyrolysis	1100, 2 h	230 (@ 0.02 Ag ⁻¹)	42%	200 cycles (@0.2 Ag ⁻¹), 83.7%	[189]
Black liquor + Deinking sludge (paper mill waste)	HCl pretreatment + ball milling with pore enlarging agent	800, 3 h	303.5 (@ 0.05 Ag ⁻¹)	n.d.	500 cycles (@2 Ag ⁻¹)	[190]
Poplar fallen leaves	HTC (water) 200°C, 10 h + HCl washing + KOH washing + ball milling after pyrolysis	1300, 3 h	283.3 (@ 0.02 Ag ⁻¹)	84.2%	550 cycles (@0.1 Ag ⁻¹), 76%	[191]
Organic carbon	MnO ₂ template + citric acid final washing	900, 2 h	407 (@0.1 Ag ⁻¹)	48%	200 cycles (@0.1 Ag ⁻¹), 94.8%	[182]
Boron-doped glucose	HTC (boric acid) 200°C, 12 h	1200, 2 h	361 (@0.03 Ag ⁻¹)	n.d.	800 cycles (@1 Ag ⁻¹), 70.5%	[192]
Coconut shell	HTC (water) 200°C, 12 h + ball milling + HCl washing	1300, 3 h	280 (@0.05 Ag ⁻¹)	87%	100 cycles (@ 0.05 Ag ⁻¹), 92.8%	[193]
Wedelia chinensis	Ethanol soaking, 12 h	800, 2 h	350 (@0.1 Ag ⁻¹)	50%	500 cycles (@0.1 Ag ⁻¹), low	[194]
Tender coconut peels + reduced Graphene Oxide	Prepyrolysis at 500°C, 5 h + HCl washing post pyrolysis	1100, 5 h	321.7 (@0.03 Ag ⁻¹)	84%	600 cycles (@0.2Ag ⁻¹), 15.6%	[195]
Pinecone (N-doped)	Fe ₂ O ₃ composite, nitric acid activation 70°C, 5 h	HTC 150°C, 30 h	178.7 (@0.05 A/g)	76%	500 cycles (@0.5Ag ⁻¹), 83.4%	[196]

(Continues)

TABLE 5 | (Continued)

Biomass precursor	Processing/ Modification	Pyrolysis temperature, °C	Reversible capacity, mAhg ⁻¹	ICE	Performance	Ref.
Lignin (N-doped)	Zn powder assisted multistep pyrolysis: Ar/H ₂ ; NH ₃	1100, 2 h; 800, 30 min	303 (@1 Ag ⁻¹)	26%	10 000 cycles (@5 Ag ⁻¹)	[181]
Sisal hemp	HTC(HCl) 160°C, 12 h + hydrazine hydrate 120°C, 12 h	1300, 2 h	310 (@0.1C)	n.d.	1000 cycles (@1C), 64.2%	[197]
D-Xylose (inedible lignocellulosic biomass)	FeCl ₃ + KOH solution, multistep pyrolysis + HCl washing	120, 2 h; 600, 2 h; 1000, 4 h	301 (@0.1 Ag ⁻¹)	n.d.	1700 cycles (@0.5 Ag ⁻¹), 79.2%	[198]
Platanus occidentalis L. fruit	Pre-treatment at 400°C, 2 h in Ar + HCl washing after pyrolysis	800, 2 h	234.2 (@0.1 Ag ⁻¹)	63.7%	300 cycles (@ 0.3 Ag ⁻¹)	[199]
Camphor leaf residue (P-doped)	Sodium phytate mixture, HTC (water) 180°C, 12 h, pressed before pyrolysis, HCl washing after pyrolysis	1400, 2 h	275.4 (@0.1 Ag ⁻¹)	33%	500 cycles (@0.1 Ag ⁻¹)	[200]
Corn stalks, corn cobs and corn leaves	HCl washing after pyrolysis	800, 2 h	110 (@ 0.05 Ag ⁻¹)	n.d.	800 cycles (@0.2 Ag ⁻¹)	[201]
Corn stalks, corn cobs and corn leaves	KOH washing after pyrolysis	800, 2 h	151 (@ 0.05 Ag ⁻¹)	n.d.	800 cycles (@0.2 Ag ⁻¹)	[201]
Corn stalks, corn cobs and corn leaves (N-P-S-doped)	KOH washing + urea/thiourea/phosphoric acid activation	800, 2 h	225 (@ 0.05 Ag ⁻¹)	n.d.	1000 cycles (@0.2 Ag ⁻¹)	[201]
sugarcane bagasse	HCl washing	1200, 8 h	235 (@ 0.1 Ag ⁻¹)	n.d.	2000 cycles (@0.5 Ag ⁻¹), --	[202]
Rhus typhina wood	Ethanol soaking, 12 h + HTC (water) 180°C, 10 h; KOH second pyrolysis	500, 1 h	108.4 (@ 0.2C)	n.d.	1000 cycles (@0.2C), --	[203]

1.02 Å < K⁺, 1.38 Å): the dominant storage mechanism progressively shifts from intercalation-controlled behavior toward defect-mediated adsorption and pore filling [204]. This transition fundamentally alters the structural requirements of carbon anodes and explains why graphite remains optimal for LIBs but fails for NIBs and performs only marginally in KIBs [205].

In LIBs, lithium readily intercalates into the well-ordered graphene layers of graphite via a staged mechanism (LiC₆), delivering a theoretical capacity of 372 mAh g⁻¹ with high ICE (>90% in commercial systems) [206]. Consequently, high structural ordering, low surface area, and minimal defect density are essential to suppress irreversible lithium trapping and excessive SEI formation. Hard carbons and biochars with large surface areas often exhibit high apparent capacities (>400 mAh g⁻¹), but these are frequently dominated by surface adsorption and pseudocapacitive contributions, which compromise ICE and volumetric energy density [125]. Thus, for LIB applications, biochar must approach a graphite-mimetic architecture, moderate turbostratic stacking, reduced heteroatom content, and controlled porosity to achieve competitive practical performance.

In contrast, sodium ions do not form stable graphite intercalation compounds under standard conditions due to thermodynamic and kinetic limitations associated with their larger ionic radius and weaker binding to graphene layers [126]. Instead, sodium storage in HC proceeds through a hybrid mechanism, as already described in Section 3.2; in this case, controlled disorder becomes advantageous rather than detrimental. Moderate defect density, expanded interlayer spacing (>0.37 nm), and hierarchical porosity enhance sodium uptake while maintaining cycling stability [207]. Heteroatom doping (e.g., N or O) can further improve Na⁺ adsorption energetics and electronic conductivity, often increasing reversible capacity without the severe ICE penalties observed in LIB systems [208]. Consequently, biochar-derived HC materials are particularly well suited to NIB systems, where their intrinsic turbostratic structure aligns with the required storage mechanism. The trend becomes even more pronounced in potassium-ion batteries.

The larger ionic radius of K⁺ and its lower Lewis acidity favor surface-controlled storage and capacitive contributions over classical intercalation [171]. While graphite can reversibly host potassium via KC₈ formation, the associated volume expansion and sluggish diffusion limit long-term stability [169]. In disordered carbons, potassium storage is strongly influenced by defect density, pore accessibility, and surface chemistry [209]. Larger mesopores facilitate ion transport, while oxygen- and nitrogen-containing functional groups enhance adsorption kinetics and capacitive contributions [210]. As a result, highly porous biochars that would be suboptimal for LIBs may exhibit competitive performance in KIBs, particularly at high rates.

Across the three systems, therefore, a clear materials-design gradient can be identified:

- LIBs favor structural order, low surface area, and graphite-like staging behavior.
- NIBs benefit from turbostratic HC with controlled microporosity and moderate defect density.
- KIBs increasingly favor defect-rich, hierarchical porous carbons enabling surface-dominated storage.

Importantly, heteroatom functionalities exhibit opposite effects depending on the ion: in LIBs, they often reduce ICE due to irreversible lithium consumption during SEI formation, whereas in NIBs and KIBs, they can enhance adsorption energy and capacitive charge storage [208, 210]. This inversion underscores that biochar optimization cannot be universally graphite-mimetic but must be tailored to the specific ionic species and its associated thermodynamic and transport constraints.

Taken together, these correlations demonstrate that the intrinsic structural plasticity of biochar, tunable interlayer spacing, defect density, and surface chemistry via pyrolysis engineering provide a versatile platform adaptable across alkali systems. However, the optimal carbon architecture shifts systematically with ionic radius, necessitating ion-specific design strategies rather than a single universal carbon blueprint.

3.5 | Role of Heteroatom Doping in Modulating Alkali-Ion Storage Mechanisms

Heteroatom doping represents one of the most effective strategies for tailoring the electrochemical behavior of biochar-derived HCs, yet its impact is intrinsically ion-dependent. The incorporation of heteroatoms such as N, P, S, or B modifies the electronic structure, local bonding configuration, and defect topology of the carbon matrix, thereby altering both bulk transport properties and interfacial reactivity. Importantly, doping does not simply increase capacity; it reshapes the dominant storage mechanism by tuning adsorption energetics, interlayer spacing, and surface chemistry. The standard doping procedure relies on heteroatom incorporation during high-temperature pyrolysis. However, an appropriate synthesis strategy can be implemented to select specific functional groups [211].

From an electronic standpoint, substitutional or edge-site heteroatoms perturb the π -conjugated carbon network by donating or withdrawing electron density, increasing carrier concentration and reducing charge-transfer resistance [57, 212–214]. These effects are particularly relevant for rate performance and high-power operation. Structurally, heteroatom incorporation can expand interlayer spacing, distort graphitic domains, and promote the formation of micro- and mesopores, facilitating the accommodation of larger alkali ions and increasing the density of redox-active sites [213]. Simultaneously, polar functional groups enhance electrolyte wettability and promote surface-dominated, pseudocapacitive contributions [212, 215].

However, the role of heteroatoms is not universally beneficial and must be interpreted within the ion-specific context. In LIBs, excessive defect density and surface functionality can amplify irreversible lithium consumption during SEI formation, reducing ICE. While moderate N-doping may enhance conductivity and kinetics, overly reactive surfaces are detrimental in systems where intercalation-dominated storage is already highly efficient. Thus, for lithium chemistry, doping must be restrained and carefully controlled.

In contrast, NIBs benefit more directly from heteroatom incorporation. Because sodium storage relies on a hybrid mechanism combining interlayer insertion and adsorption within nanopores, controlled expansion of d-spacing and enhanced surface polarity can significantly increase reversible capacity. This behavior is reflected in several representative studies. For example, N-doping

of pinecone-derived HC increased reversible capacity from 197 to 273 mAh g⁻¹ with ~80% capacity retention after 250 cycles, attributed to improved electronic conductivity and additional adsorption sites [146]. Phosphorus incorporation into spherical HC expanded interlayer spacing and enhanced the low-voltage plateau contribution, delivering 343 mAh g⁻¹ with 92% ICE [216]. Likewise, N/P codoping has demonstrated the possibility of simultaneously enlarging *d*-spacing and stabilizing defect structures, achieving 336 mAh g⁻¹ with 99.8% capacity retention over 2000 cycles [217]. These examples illustrate that heteroatom engineering in NIBs functions not merely as defect introduction, but as controlled modulation of turbostratic order and sodium adsorption energetics.

For KIBs, the impact of heteroatom doping becomes even more nuanced. The large ionic radius and lower charge density of K⁺ favor surface-controlled storage and adsorption processes, suggesting that polar heteroatom sites could enhance ion affinity and capacitive contributions. At the same time, the higher chemical reactivity of potassium exacerbates interfacial instability, meaning that excessive functionalization may intensify continuous SEI growth and accelerate degradation. Systematic studies specifically addressing doped biochar in KIBs remain limited [214], and a mechanistic understanding of how heteroatom chemistry influences SEI composition and stability in potassium systems is still emerging.

Codoping strategies (e.g., N/S or N/P) introduce additional complexity by generating synergistic electronic and structural effects. While such approaches can create hierarchical defect networks and improved ion diffusion pathways, they may also compromise mechanical integrity or electronic continuity if the defect density becomes excessive. Consequently, the optimization variable is not the absolute heteroatom content but rather its bonding configuration, spatial distribution, and interaction with the carbon backbone.

Overall, heteroatom doping should not be viewed as a universal performance enhancer, but as a precision tool for modulating storage mechanisms in an ion-specific manner. The central challenge moving forward is to identify optimal doping levels and configurations that balance electronic conductivity, defect-mediated capacity, ICE, and long-term interfacial stability. Achieving this balance will require advanced characterization techniques capable of resolving dopant bonding states and local environments, coupled with predictive models that relate dopant chemistry to electrochemical response across different alkali-ion systems.

4 | Current Limitations and Future Perspectives

The correlations outlined in Section 3.4 make one point clear: biochar cannot be optimized using a single structural paradigm across LIBs, NIBs, and KIBs. As the ionic radius increases from Li⁺ to K⁺, the dominant storage mechanism progressively shifts away from classical intercalation toward adsorption and pore-mediated processes. The practical implication is that the performance ceiling of biochar-derived HC is not intrinsic, but ion-dependent [218].

In LIBs, the limitation is largely thermodynamic and interfacial. Lithium intercalation favors highly ordered graphitic domains

with minimal surface reactivity. Biochars, by contrast, inherently possess turbostratic disorder, residual heteroatoms, and significant surface area. While these features can inflate specific capacity through adsorption contributions, they simultaneously intensify SEI formation and depress ICE [219]. For lithium systems, where ICE, volumetric density, and long-term stability are already optimized in commercial graphite [220], the tolerance for surface-driven storage is low. Thus, biochar must approach graphite-like behavior to be competitive, which paradoxically reduces the very structural complexity that makes it attractive.

For NIBs, the situation is more favorable but not unconstrained. Sodium does not intercalate efficiently into graphite under standard conditions, making turbostratic HCs intrinsically suitable. However, performance is highly sensitive to interlayer spacing and pore topology. If spacing is insufficient, plateau capacity collapses; if microporosity is excessive, irreversible Na⁺ trapping increases and ICE deteriorates [221]. The challenge is therefore not simply introducing disorder but controlling it with precision.

In KIBs, the constraints become more severe and more interfacial in nature. The large ionic radius and high reactivity of K⁺ amplify steric limitations and electrolyte decomposition. Even when structural diffusion pathways are adequate, interfacial instability dominates cycling behavior. Thick, continuously evolving SEI layers and increased polarization accelerate degradation [222]. Highly porous carbons may show attractive rate capability, yet excessive defect density intensifies irreversible trapping and side reactions. Here, interfacial engineering, not merely pore optimization, becomes decisive.

Across all systems, several structural trade-offs persist. Increasing surface area enhances ion accessibility but proportionally increases irreversible alkali consumption. Raising PT improves conductivity and structural stability yet narrows interlayer spacing and suppresses defect-mediated storage [223]. No single metric, whether Raman *I_D/I_G*, *d*₀₀₂ spacing, or BET surface area, adequately predicts performance. What is required is coordinated control of spacing, pore hierarchy, defect chemistry, and surface passivation.

A central manifestation of these trade-offs is the limited ICE and long-term cycling stability often observed in biochar-derived carbons. Low ICE primarily arises from extensive SEI formation on high-surface-area, defect-rich structures, irreversible ion trapping within ultramicropores, and side reactions associated with residual functional groups or mineral impurities. Strategies to mitigate these effects include controlled high-temperature pyrolysis to reduce surface reactivity, pore-size optimization to limit ion confinement, surface passivation or artificial SEI layers, and precursor demineralization [67]. Long-term stability challenges, particularly pronounced in KIBs, are instead governed by continuous SEI growth, interfacial instability, and structural degradation under repeated insertion/extraction. Mitigation, therefore, requires balanced defect engineering, hierarchical porosity design, and electrolyte/interphase optimization rather than simply increasing disorder [224].

Beyond materials design, translational barriers remain significant. Benchmarking inconsistency, differences in electrode loading, electrolyte excess, formation protocols, and half-cell configurations continue to obscure meaningful comparison across studies. Without standardized evaluation under practical

conditions (high areal loading, lean electrolyte, full-cell validation), laboratory-scale gains risk being overstated.

Feedstock variability further complicates reproducibility. Differences in lignin content, mineral residues, and inherent heteroatom distribution alter carbonization pathways even under identical thermal profiles, producing divergent microtextures and electrochemical responses [225]. Rational precursor classification and predictive process–structure–performance frameworks are therefore not optional but necessary for scale-up.

Closely related to feedstock variability is the challenge of batch-to-batch reproducibility. Even when precursor type is nominally constant, fluctuations in biomass provenance, seasonal composition, moisture content, and inorganic impurities can subtly modify carbonization kinetics. Additional variability may arise from reactor-scale effects such as thermal gradients, heating-rate fluctuations, residence-time dispersion, or inconsistencies in post-treatment and washing steps [226]. These factors translate into measurable differences in interlayer spacing, defect density, porosity distribution, and residual ash content, ultimately affecting ICE, rate capability, and cycling stability. Achieving industrial relevance, therefore, requires tighter control of precursor conditioning, programmable and monitored pyrolysis protocols, standardized postprocessing, and the development of predictive models capable of reducing empirical variability. Activation strategy further determines both electrochemical performance and scalability. Chemical activation (e.g., KOH, ZnCl₂, H₃PO₄) typically generates very high surface area and microporosity, enhancing adsorption-driven capacity, particularly in NIBs and KIBs [227]. However, excessive surface area lowers ICE due to intensified SEI formation and introduces environmental concerns associated with chemical consumption and wastewater treatment. In contrast, physical activation (e.g., CO₂ or steam) enables more moderate porosity development, improved structural stability, and better compatibility with continuous, low-impact thermal processing. From a translational perspective, controlled activation combined with precursor engineering appears more promising than aggressive chemical etching, particularly when integration into waste-valorization or biorefinery infrastructure is considered.

Finally, sustainability must be critically assessed. Some high-capacity carbons rely on aggressive chemical activation or templating routes that are energy-intensive and environmentally burdensome. If the processing footprint outweighs the renewable origin of the precursor, the circular-economy argument weakens. Scalable thermal routes, mild activation strategies, and integration with biorefinery infrastructure represent more credible paths forward.

Biochar should not be framed as a universal graphite replacement. Its value lies in structural adaptability. For LIBs, this adaptability must be restrained; for NIBs, it must be tuned; for KIBs, it must be coupled with interfacial stabilization. Progress will depend less on maximizing surface area and more on understanding how ion size, thermodynamics, and interfacial chemistry redefine the optimal carbon architecture in each system.

5 | Conclusions

Biochar-derived carbons occupy a distinctive position within the carbon materials landscape for EES, combining renewable origin

with a level of structural tunability that is difficult to achieve using fossil-derived carbons. While their intrinsic disorder, high surface area, and feedstock-dependent heterogeneity impose clear limitations in LIBs, particularly in terms of ICE and volumetric energy density, these same features become enabling in systems based on larger alkali ions. When rationally engineered, biochar-derived HCs provide the enlarged interlayer spacing, defect chemistry, and pore architecture required for efficient sodium and potassium storage, positioning them as a natural alternative to graphite in next-generation intercalation batteries. The transition from laboratory demonstrations to industrial relevance will depend on the convergence of standardized benchmarking, scalable and low-impact manufacturing, and data-driven optimization of structure–property relationships. Achieving this convergence would allow biochar to evolve from a promising material into a cornerstone of circular, resilient energy-storage technologies.

Author Contributions

Valerio C. A. Ficca: writing – original draft (equal). **Afef Dhaffouli:** writing – original draft (supporting). **Rocco Cancelliere:** conceptualization (lead), visualization (lead), writing – original draft (equal), writing – review and editing (lead).

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Conflicts of Interest

The authors declare no conflicts of interest.

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