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From Palm Kernel Shell to Dual-Pathway Energy-Storage Carbon: Engineering Porous Carbon for Supercapacitors and Hard Carbon for Sodium-Ion Batteries through Feedstock–Processing–Microstructure–Performance Relationships

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Abstract

Oil-palm processing generates lignocellulosic residues that are commonly used for low-value combustion, mulching, or other bulk applications but increasingly represent promising precursors for advanced carbon electrodes. This critical qualitative literature review examines the conversion of palm kernel shell, empty fruit bunch, mesocarp fibre, oil-palm frond, and related residues into porous carbon for supercapacitors and hard carbon for sodium-ion batteries. Rather than treating biomass-derived carbon as a single material class, the review develops a feedstock–processing–microstructure–performance framework showing that the optimum carbon architecture depends fundamentally on the intended charge-storage mechanism. Supercapacitors generally benefit from accessible hierarchical porosity, electrolyte wettability, heteroatom functionality, conductivity, and short ion-transport pathways. Sodium-ion battery anodes require a different balance involving suitable turbostratic interlayer spacing, controlled defects, limited reactive external surface, stable solid-electrolyte interphase formation, and appropriately developed closed pores. Aggressive activation therefore creates a central engineering paradox: it can increase capacitance while simultaneously worsening irreversible sodium consumption and initial Coulombic efficiency. Recent palm-derived materials demonstrate that oil-palm residues can support both technological pathways when processing is application-specific. However, translation requires standardized characterisation, realistic mass loading, full-cell testing, carbon-yield reporting, chemical recovery, life-cycle assessment, and integration with palm-oil mills. A technology-selection framework is proposed to match feedstock characteristics and processing intensity with the most appropriate electrochemical application.

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Introduction

The expansion of renewable electricity, distributed energy systems, electrified transport and digital infrastructure has intensified demand for electrochemical storage technologies that can deliver energy, power, durability and acceptable cost while reducing dependence on critical raw materials. Carbon remains one of the most versatile electrode families because its properties can be adjusted over a wide structural range extending from highly porous amorphous materials to turbostratic hard carbons and partially graphitic structures. Biomass-derived carbons add another dimension to this flexibility because their precursors are renewable, chemically heterogeneous and often already available as agricultural or industrial residues [1-4].

The oil-palm industry is particularly relevant to this transition because processing generates several solid lignocellulosic streams, including palm kernel shell (PKS), empty fruit bunch (EFB), mesocarp fibre, oil-palm fronds and trunks. These materials differ in lignin, cellulose, hemicellulose, ash, silica, extractives and mineral composition, meaning that they cannot be expected to produce identical carbon structures under identical thermal conditions. Pretreatment studies of oil-palm biomass similarly show that removing hemicellulose, disrupting lignocellulosic structure and modifying mineral content can substantially alter downstream conversion behaviour [5]. Transforming these residues into value-added materials therefore represents more than a waste-management strategy; it creates the possibility of integrating the palm-oil sector with advanced material manufacturing.

PKS has become especially attractive because of its comparatively dense structure, high carbon-forming potential and established availability at palm-oil mills. Recent work has demonstrated hierarchical PKS-derived carbon with specific surface areas exceeding 2,500 $m^2 g^{-1}$ and specific capacitance of approximately 360 F g^{-1}, showing that the residue can be converted into an electrode material rather than being restricted to boiler fuel or conventional activated-carbon applications [6]. Alternative PKS pathways include phosphoric-acid activation, lignin extraction followed by carbon-fibre formation, polymer–carbon composites and naturally heteroatom-containing carbon structures [7-9].

The scientific opportunity is wider than supercapacitors. Sodium-ion batteries (SIBs) have become increasingly important as an alternative or complement to lithium-ion batteries, particularly where resource availability, material cost and stationary storage are important considerations. Hard carbon is widely regarded as the leading practical anode family for SIBs because graphite does not accommodate sodium under conventional carbonate-electrolyte conditions as effectively as it accommodates lithium. Hard carbon provides disordered graphene-like domains, defects, enlarged interlayer spacing and nanometre-scale pores that collectively offer several Na-storage mechanisms [10-13].

Palm-derived carbon has now entered this SIB research frontier. Recent PKS-based work has moved beyond simple carbonisation toward elemental regulation, ultramicropore engineering and development of closed-pore-rich hard carbon. An optimised PKS-derived material reported an initial Coulombic efficiency (ICE) of 94.6%, a reversible capacity of 410.2 mAh g^{-1} and a low-potential plateau capacity of 315.5 mAh g^{-1}, illustrating the importance of differentiating hard-carbon design from conventional high-surface-area activated carbon design [14]. Palm-oil-shell-derived SiO_2/hard-carbon-like nanocomposites have also demonstrated that inherited inorganic phases and pyrolysis-dependent defect ordering can influence Na-storage kinetics [15].

This distinction motivates the central argument of the present review. There is no universally optimum "palm-derived carbon". A material designed for rapid electrostatic ion adsorption in a supercapacitor requires a different combination of pore accessibility, surface chemistry and conductivity from a hard-carbon anode intended to minimise irreversible Na loss while providing low-voltage storage sites. Maximizing Brunauer–Emmett–Teller (BET) surface area can therefore be a successful supercapacitor strategy but a poor sodium-ion strategy when the additional open surface promotes electrolyte decomposition and excessive solid-electrolyte-interphase (SEI) formation [16-18].

The objectives of this review are consequently fivefold. First, it examines how compositional differences among

oil-palm residues affect carbon formation. Second, it evaluates how carbonisation, activation, purification, heteroatom engineering and thermal treatment control electrochemically relevant microstructures. Third, it differentiates the structural requirements of supercapacitor porous carbon from those of SIB hard carbon. Fourth, it critically examines the trade-offs between laboratory performance and industrial manufacturability. Finally, it proposes a technology-selection framework linking oil-palm feedstocks, processing routes, carbon structures and intended electrochemical applications.

Literature Review: Conceptual Foundations

Lignocellulosic Feedstocks as Programmable Carbon Precursors

Biomass carbon formation is governed by the thermal behaviour of cellulose, hemicellulose, lignin and inorganic constituents. Hemicellulose generally decomposes at relatively low temperatures, cellulose undergoes rapid depolymerisation and volatilisation over a comparatively narrow temperature region, whereas lignin decomposes across a broader thermal range and can contribute substantially to aromatic char formation. Consequently, lignin-rich feedstocks may show favourable carbon yield, whereas highly cellulosic structures may create distinctive inherited morphologies after pyrolysis. Oil-palm biomass therefore behaves as a family of feedstocks rather than a chemically uniform residue stream [5].

Minerals add further complexity. Potassium, calcium, magnesium, phosphorus, silicon and transition-metal traces can catalyse carbon reactions, alter graphitisation, generate pores or remain as electrochemically active/inactive phases. Their role can be beneficial in one application and undesirable in another. For porous supercapacitor carbons, certain minerals may function as endogenous pore-forming agents or contribute to wettability. In hard carbon, however, catalytic impurities may change carbon-layer ordering and pore evolution in ways that suppress the disordered structures needed for effective Na storage. This explains why washing and acid purification are not merely cleaning operations but microstructure-engineering steps [12,14,19].

EFB illustrates how inherited inorganic chemistry can become functional rather than simply contaminating. Yulianti et al., reported SiO_2-containing EFB-derived activated carbon in which suitable micropore/mesopore distribution, surface functionalities and enhanced wettability contributed to strong capacitive behaviour [20]. Subsequent SiO_2–N/S co-doping research showed that heteroatoms and hierarchical meso/macroporosity can work synergistically in flexible solid-state supercapacitors [21]. The implication is that "purity" cannot be treated as an absolute objective; the correct question is whether each inherited component improves or disrupts the targeted charge-storage mechanism.

Carbonisation, Activation and Structural Evolution

Carbonisation converts an organic precursor into a carbon-rich solid through dehydration, devolatilisation, bond rearrangement and progressive aromatic condensation. Temperature is particularly important because it simultaneously affects heteroatom removal, conductivity, defect concentration, interlayer ordering and pore evolution. Raising temperature can improve electronic conductivity but may reduce surface functional groups, collapse accessible micropores or create excessively ordered domains. The optimum temperature is therefore application dependent [2,22, 23].

Activation extends the structural tunability of carbon. Chemical agents such as KOH, NaOH and H_3PO_4 can generate large accessible pore volumes through redox reactions, dehydration, intercalation and etching. Physical activation with CO_2 or steam generally produces porosity without requiring large quantities of corrosive activation chemicals, although it may demand longer processing or higher thermal inputs. Hybrid approaches combine carbonisation and activation to control hierarchical porosity [24-26].

The relationship between activation severity and performance is not linear. In supercapacitors, insufficient activation can leave inaccessible surfaces and slow ion diffusion, while excessive activation can weaken the carbon framework, reduce packing density and increase process cost. The best-performing electrode therefore does not necessarily correspond to the highest BET surface area. Pore width must be compatible with solvated or partially desolvated electrolyte ions, mesopores must support transport, and electrical conductivity must remain sufficient to minimise equivalent series resistance [2,27-29].

For SIB hard carbon, the distinction is more profound. Hard carbon is non-graphitisable carbon composed of curved and defective graphenic fragments, disordered regions and pores. Pyrolysis severity determines the evolution of interlayer spacing, graphenic domain size, defects, functional groups and closed pores. Unlike a supercapacitor, a sodium-ion anode does not necessarily benefit from a highly accessible external pore network because the electrolyte can react across that surface during the first cycle [10,11,30].

Supercapacitor Charge Storage

Electric double-layer capacitors store charge predominantly through electrostatic ion accumulation at the electrode–electrolyte interface. Their performance is therefore related to accessible area rather than geometric surface alone. Micropores provide substantial adsorption area, mesopores shorten ion-transport resistance, and macropores can act as reservoirs that improve electrolyte distribution. A hierarchical network can integrate these functions, particularly at high charge–discharge rates [22, 24,26].

Surface heteroatoms can contribute through several mechanisms. Oxygen-containing groups may enhance hydrophilicity but can also increase resistance if present excessively. Nitrogen, phosphorus and sulfur can alter electronic structure, add redox-active sites and improve electrolyte interactions. Biomass-derived carbons are especially interesting because some heteroatoms are naturally inherited while others can be introduced during activation or post-treatment [21,29].

Performance is generally described through specific capacitance, energy density, power density, rate capability, ESR and capacitance retention. However, direct comparison across studies requires caution. Three-electrode configurations frequently report higher apparent specific capacitance than realistic two-electrode devices, while electrolyte composition and calculation conventions influence energy density. Active-mass loading also matters: extremely low loadings can mask transport limitations that become important in practical electrodes [22,23]. Recent work on high-mass-loading biomass electrodes further shows that practical areal capacitance and ion transport through thicker electrodes should be considered alongside favourable gravimetric capacitance [31].

Sodium Storage in Hard Carbon

Hard-carbon sodium storage remains an active mechanistic field. Proposed descriptions include adsorption on defects and surfaces, insertion between expanded graphenic layers and filling of nanopores at low potentials. These processes generate a characteristic voltage profile containing a sloping region and a low-potential plateau. Their relative contributions vary with precursor, pyrolysis, defect concentration, surface chemistry, interlayer spacing and pore structure [10,11,32].

The role of closed pores is particularly important. Unlike open pores that are readily wetted by the electrolyte, closed nanopores can provide internal Na-storage volume while limiting direct electrolyte contact. Research has increasingly connected appropriately developed closed pores with enhanced low-potential plateau capacity. Zhou et al, for example, demonstrated that regulating closed pores substantially improved Na storage even at relatively modest carbonisation temperatures [33]. Later studies strengthened the connection between closed-pore volume, interlayer spacing and plateau capacity [14,33,34]. Recent closed-pore engineering studies reinforce this interpretation by directly linking engineered closed-pore populations with low-voltage plateau capacity and by separating the roles of closed pores and carbonyl groups in storage and interphase chemistry [35,36].

ICE is another decisive variable. During the first sodiation, sodium is irreversibly consumed by SEI formation, trapping at high-energy defects and reactions with surface functionalities. High external area can therefore decrease ICE, creating a direct penalty for full-cell energy density because the cathode contains a finite Na inventory. Strategies include reducing reactive surface area, controlling oxygen functionalities, modifying electrolytes, adjusting microstructure and using presodiation [12,16-18].

Method

This study employed a critical qualitative literature review (QLR) rather than a systematic literature review. The objective was interpretive synthesis of engineering relationships, technological contradictions and translational barriers rather than exhaustive enumeration of every publication or quantitative meta-analysis. Accordingly, PRISMA procedures, formal

meta-analytic pooling and systematic-review claims were not applied.

The primary literature window covered 2020–2026, with emphasis on peer-reviewed journal papers indexed by major academic databases and published by established scientific publishers. Literature was identified using combinations of terms including palm kernel shell, oil palm biomass, empty fruit bunch, oil palm frond, porous carbon, activated carbon, hierarchical carbon, hard carbon, sodium-ion battery, supercapacitor, closed pore, initial Coulombic efficiency, heteroatom doping, carbonisation, activation, sodium storage mechanism, and biomass-derived electrode.

The analytical procedure used five coding domains. The first was feedstock chemistry, including lignocellulosic composition, ash, mineral content and natural morphology. The second was processing, including pretreatment, acid washing, carbonisation temperature, atmosphere, residence time, physical/chemical activation and heteroatom modification. The third domain was microstructure, including specific surface area, pore-size distribution, defects, interlayer spacing, graphitic ordering, closed pores and surface functional groups. The fourth domain was electrochemical outcome, covering capacitance, resistance, energy/power density and cycling for supercapacitors, and reversible capacity, ICE, slope/plateau capacity, rate performance and cycling for SIBs. The fifth domain was translation, including carbon yield, chemical consumption, washing, thermal energy, electrode loading, full-cell validation, reproducibility and prospective mill integration.

Palm-specific studies were prioritized for feedstock and application evidence, while broader biomass-carbon research was used where the underlying electrochemical mechanisms were more developed than in the palm-specific literature. This structure allows evidence from non-palm hard carbon or porous carbon to illuminate mechanisms without assuming that performance can be transferred directly between feedstocks [19,37,38].

Results: Feedstock–Processing–Microstructure Relationships

Palm Kernel Shell: a Dual-Purpose Precursor

PKS is the most compelling candidate for a dual-pathway platform because it has been successfully converted into both strongly porous activated carbon and increasingly sophisticated hard carbon. For supercapacitors, carbonisation followed by KOH activation can generate extensive micro/mesoporosity. Li et al., reported hierarchical PKS-derived porous carbon with a surface area of approximately 2,521 $m^2 g^{-1}$ and capacitance of 360 F g^{-1} [6]. This performance demonstrates that shell structure can withstand sufficiently aggressive processing to produce a large ion-accessible surface while retaining useful conductivity.

PKS can also support alternative electrode architectures. Thongsai et al., extracted PKS lignin and combined it with polyacrylonitrile to produce free-standing carbon-fibre mats, demonstrating that fractionation before carbonisation can create a different value pathway from bulk activated carbon [7]. Pam et al., showed that phosphoric-acid impregnation allows substantial control over PKS porosity and yield [8]. Wibowo et al., integrated PKS porous carbon with polyaniline, illustrating how biomass carbon can serve as a conductive framework in hybrid pseudocapacitive systems [9].

The hard-carbon pathway requires almost the opposite logic. Ren et al., demonstrated that mineral regulation and ultramicropore-defect engineering could convert PKS into closed-pore-rich hard carbon with high ICE and plateau-dominated Na storage [14]. Instead of maximising electrolyte-accessible surface, the strategy controlled impurities and transformed ultramicropore defects into internal storage structures. This is a strong demonstration that a single agricultural precursor can lead to fundamentally different electrode products depending on the processing objective.

Figure 1 summarises how identical oil-palm residues can enter two distinct processing and electrochemical pathways. The diagram should be read from feedstock through processing to two application-specific carbon architectures rather than as a single linear optimisation route.

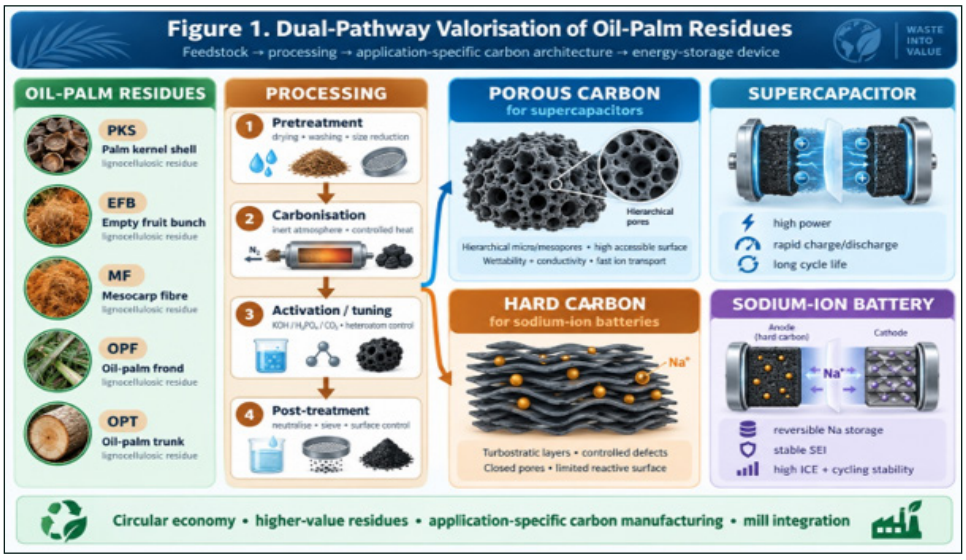

Figure 1: Dual-Pathway Valorisation of Oil-Palm Residues

Figure 1 emphasizes that feedstock identity does not predetermine final application. Instead, preprocessing and thermal history redirect the same biomass toward different microstructures. The porous-carbon route attempts to expose electrolyte-accessible area and shorten ion pathways, whereas the hard-carbon route seeks an appropriate combination of disordered carbon layers, limited external reactivity and internal closed-pore storage. The value of PKS is therefore its processing flexibility rather than one inherent "ideal" electrochemical structure.

Empty Fruit Bunches: Hierarchical Architecture and Inorganic Functionality

EFB is compositionally and morphologically different from PKS. Its fibrous architecture provides opportunities for preserving transport pathways, while naturally occurring inorganic components—particularly silica—can influence carbon chemistry and wettability. Rustamaji et al., demonstrated nitrogen-modified mesoporous activated carbon from EFB, showing that post- or co-processing chemistry can substantially improve electrochemical behaviour beyond that of untreated biomass carbon [39].

Yulianti et al., developed EFB-derived hierarchical activated carbon containing naturally inherited SiO_2 [20]. An optimised sample exhibited approximately 459 F g^{-1} specific capacitance, with performance attributed not only to surface area but also to balanced micro/mesoporosity, structural defects, functionality and wettability. The work is particularly relevant because the best material did not simply correspond to unconstrained surface-area maximization; rather, activation temperature controlled several interdependent properties simultaneously.

Later work introducing N/S alongside SiO_2 created hierarchical meso/macroporous EFB carbon for flexible solid-state devices with 93% capacitance retention after 10,000 cycles [21]. These results suggest that EFB may be particularly attractive for supercapacitors when natural morphology and inorganic chemistry are intentionally retained rather than completely removed.

Oil-Palm Fronds: Activation-Free Graphitic Carbon

Oil-palm fronds illustrate a different pathway. Ullah et al., produced graphitic carbon as a function of thermal treatment duration and reported approximately 269 F g^{-1} in sulfuric-acid electrolyte for a five-hour treatment, with enhanced device-level performance when a redox-active electrolyte was used [40]. The study is significant because high capacitance was obtained without relying exclusively on extremely high surface area. Conductivity, graphitic development and electrolyte chemistry instead became important parts of the performance equation.

Subsequent work using pre-pelleted frond biomass and one-step carbonisation provides an additional scale-up

perspective because pelletisation can simplify material handling and may reduce dependence on multiple chemical activation and washing stages [41]. Although an activation-free route may sacrifice some maximum surface area, its potential advantages include reduced chemical input, less wastewater, easier solid handling and more straightforward furnace integration. These trade-offs matter when laboratory electrode performance is evaluated against manufacturing feasibility.

Feedstock Identity Versus Processing Intensity

Cross-biomass evidence supports the conclusion that electrochemical performance is not determined by precursor taxonomy alone. Yan et al., directly compared several biomass-derived hard carbons and observed substantial variation in ICE, reversible capacity and retention, which they associated with carbon-layer spacing, functional groups and lamellar structure [38]. Jin et al., similarly examined relationships between biomass-processing variables and hard-carbon performance, reinforcing the idea that predictive design requires coupled precursor and processing descriptors rather than labels such as "shell-derived" or "wood-derived. [19]"

This distinction is essential for oil-palm research. A comparative study in which PKS, EFB, mesocarp fibre and frond are processed under identical conditions may reveal differences attributable to feedstock, but it does not establish that identical processing is optimal for each feedstock. Industrially useful research should instead identify each feedstock's processing window: the range of temperatures, washing conditions and activation severities that produce acceptable structure at reasonable yield and energy use.

Palm-Derived Porous Carbon for Supercapacitors Why Hierarchical Porosity Matters

The classical intuition for carbon supercapacitors is that larger surface area enables more double-layer charge storage. Contemporary biomass-carbon research refines this concept by emphasizing accessible rather than total area. Micropores contribute high surface density, but pores that are too narrow for electrolyte ions contribute less effectively. Mesopores facilitate diffusion into microporous domains, while macropores improve electrolyte buffering and transport at larger length scales [2, 22,26].

Hierarchical structures therefore provide a plausible route to combine capacitance and rate performance. Similar conclusions have emerged from pepper-, coconut-shell-, bio-oil- and other biomass-derived carbon systems, in which activation conditions simultaneously alter pore size, heteroatom content and conductivity [27-29,42]. The broader literature is valuable for palm applications because it demonstrates that optimizing pore networks is a multivariable design problem rather than a race toward the highest BET area.

Heteroatom chemistry adds another performance layer. O, N, P and S can modify surface polarity, electronic states and redox behaviour. Dong et al., demonstrated O/P co-doped hierarchical carbon nanosheets with high capacitance and strong long-term retention. Palm-shell-derived carbon may naturally contain P and S after processing, while EFB can retain SiO_2 and be modified with N/S, indicating that naturally available chemistry may reduce the need for expensive synthetic dopants when appropriately controlled [29].

Electrolyte Accessibility and Wettability

Electrolyte wetting is critical because nominal pore volume has limited value if ions cannot rapidly reach the internal carbon surface. Surface oxygen can enhance aqueous-electrolyte wettability, but excessive oxygen may decrease electronic conductivity or increase side reactions. EFB-derived SiO_2 provides an interesting example in which improved hydrophilicity was linked with reduced contact angle and enhanced interfacial accessibility [20].

Electrolyte identity also changes the interpretation of pore size. A pore distribution that is effective in aqueous KOH may not deliver the same performance with larger organic ions or ionic liquids. Consequently, pore optimisation should be performed together with electrolyte selection rather than independently. This also affects the voltage window and thus device energy density, which scales with the square of operating voltage.

The Danger of Comparing Isolated Capacitance Numbers

Biomass-supercapacitor literature often highlights very high gravimetric capacitance under optimised laboratory conditions. Examples outside palm biomass have reported several hundred F g^{-1}, demonstrating

what carefully activated carbon can achieve [27,28]. However, such values should not be interpreted without electrode configuration, current density, electrolyte, voltage window and mass loading.

Three-electrode measurements evaluate a working electrode against an idealized reference/counter configuration and are useful for material screening, but practical symmetric or asymmetric devices require two active electrodes and exhibit different energy and capacitance relationships. Likewise, a few milligrams of loosely packed porous carbon may exhibit excellent gravimetric properties while delivering inadequate volumetric capacitance. High activation severity can remove substantial carbon mass and produce low-density structures, creating a hidden trade-off between F g^{-1} and F cm^{-3}.

The processing–Structure Map

Figure 2 shows why carbonisation and activation cannot be discussed separately from electrochemical performance. It also highlights that each processing lever can create simultaneous structural benefits and penalties depending on the target device.

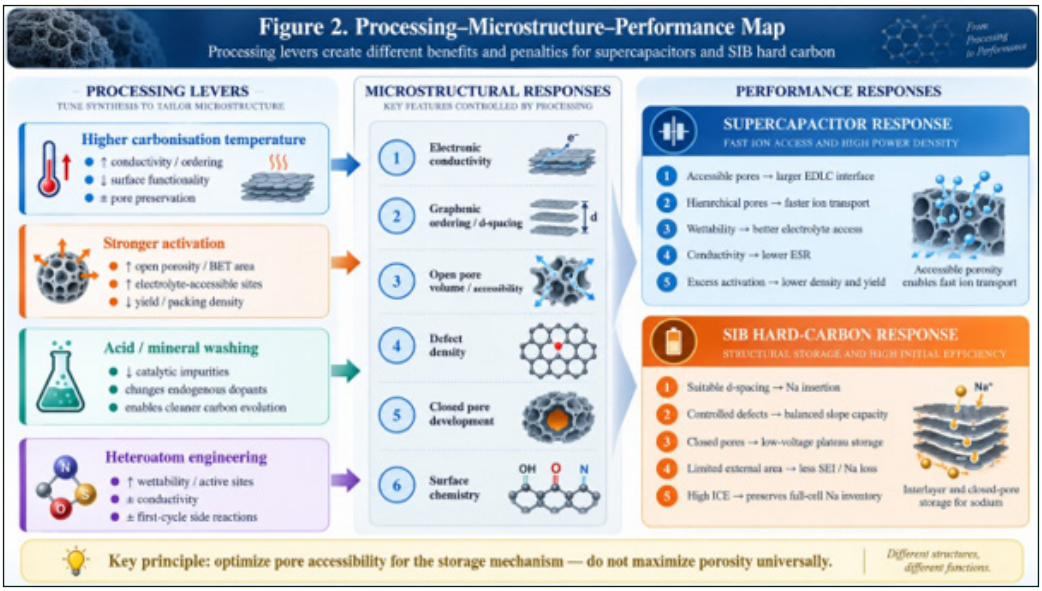

Figure 2: Processing–Microstructure–Performance Map for Palm-Derived Carbon

Figure 2 explains that no processing variable is universally beneficial. Increasing carbonisation temperature may improve conductivity but reduce useful functionality. Strong activation can improve supercapacitor ion accessibility while simultaneously reducing yield and density. Mineral washing may stabilise hard-carbon formation but remove potentially beneficial inorganic species for a supercapacitor. The figure therefore represents processing as a multi-objective optimisation problem.

Palm-Derived Hard Carbon for Sodium-Ion Batteries

Why Hard Carbon Rather than Activated Carbon?

The difference between activated carbon and hard carbon is not semantic. Activated carbons are usually designed around extensive electrolyte-accessible surface. Hard carbon is designed around a disordered bulk structure with interlayer gaps, defective graphene fragments and internal pores capable of storing sodium while limiting excessive interfacial reactivity. Reviews since 2020 consistently identify hard carbon as the most commercially credible carbon-anode family for SIBs [10-13,37].

Hard-carbon voltage curves often show two distinguishable regions. The sloping region at higher potentials is commonly associated with adsorption at defects, functional groups and other heterogeneous sites, although contributions from interlayer insertion may overlap. The plateau near low voltage has increasingly been

linked with filling of internal nanopores and sodium clustering within appropriately developed closed-pore structures. Mechanistic details remain debated, and no single simplistic model explains every precursor and pyrolysis history [10,30,43].

Interlayer Spacing and Microcrystalline Structure

Graphite has highly ordered layers and an interlayer spacing that is poorly suited to conventional Na intercalation. Hard carbon provides wider and less uniform spacing. Biomass pyrolysis gradually transforms polymeric precursor structures into short-range graphenic domains, while complete graphitisation is prevented by cross-linking and structural disorder. The resulting architecture contains curved, defective and misaligned carbon sheets.

Microcrystalline evolution is sensitive to lignin/cellulose chemistry and heat treatment. Increasing temperature tends to enlarge and reorder graphenic domains while reducing heteroatoms and some defects. Excessive ordering can decrease accessible Na-storage sites or shrink spacing, whereas insufficient heat treatment can leave too much reactive surface chemistry. The optimum material therefore occupies a structural middle ground [11,12].

Closed Pores and Low-Potential Sodium Storage

Closed pores have emerged as a defining hard-carbon design variable. Zhou et al., showed that controlling biomass composition before pyrolysis could increase closed-pore formation and significantly improve Na storage [33]. More recent work has strengthened this relationship by deliberately regulating biomass-derived closed pores through thermal treatment or pore conversion strategies [14, 34].

PKS appears especially promising in this context because its dense lignocellulosic framework can evolve toward internal nanovoids when mineral chemistry and thermal treatment are carefully controlled. Ren et al., linked elemental regulation and ultramicropore-defect engineering to a strong low-potential plateau and high ICE [14]. The reported 94.6% ICE is especially significant because many biomass hard carbons suffer from substantial irreversible first-cycle losses. The result suggests that high capacity need not require a highly reactive external surface.

Initial Coulombic Efficiency as a System-Level Metric

ICE is sometimes treated as a material property, but its importance is ultimately cell-level. In a Na-metal half-cell, sodium supply is effectively unlimited; low ICE can therefore appear tolerable during laboratory testing. In a full cell paired with a finite-sodium cathode, every sodium ion irreversibly consumed by SEI formation or trapping reduces accessible cell capacity. ICE consequently influences full-cell energy density much more strongly than a half-cell capacity plot alone suggests [17,18].

Defects illustrate the problem clearly. They can provide adsorption sites and improve rate capability, particularly in the slope region, but excessive defects also create chemically reactive sites and can worsen irreversible capacity. Heteroatom doping presents a similar trade-off. Jin et al., demonstrated surface-dominated storage using heteroatom-doped hard carbon, while Aristote et al., showed that S/N/P doping could improve Na-ion kinetics [44,45]. However, industrial optimisation must balance extra active sites against ICE, side reactions and synthesis complexity.

Electrolytes also influence ICE and cycling. Hirsh et al., demonstrated strong electrolyte dependence of hard-carbon stability and long-cycle behaviour, highlighting the interaction between carbon surface and SEI chemistry [16]. Consequently, a palm-derived hard carbon should not be described as intrinsically "high ICE" without specifying electrolyte, formation procedure and cutoff voltage.

Palm-Shell SiO_2/Hard-Carbon-Like Composites

Mas'udah et al., demonstrated a distinct route based on palm-oil shell converted into SiO_2/hard-carbon-like nanocomposites through one-step pyrolysis [15]. Pyrolysis temperature altered the balance between defects and graphitic domains, with impedance behaviour indicating changes in charge-transfer resistance and Na diffusion. This approach is noteworthy because silica, often regarded as ash to be removed, becomes part of the engineered composite architecture.

However, composite strategies introduce additional interpretive challenges. Long-term cycling may depend on structural stability of the inorganic phase, and practical electrode density can differ from pure hard

carbon. The contribution of silica to reversible Na storage, irreversible reactions, and mechanical stability should therefore be separated experimentally from that of the carbon matrix.

Contrasting Storage Mechanisms

Figure 3 provides the mechanistic bridge required to understand why a carbon structure optimised for one technology should not automatically be transferred to the other. Its side-by-side design contrasts electrolyte-accessible open porosity in EDLCs with controlled interlayer and closed-pore storage in hard carbon.

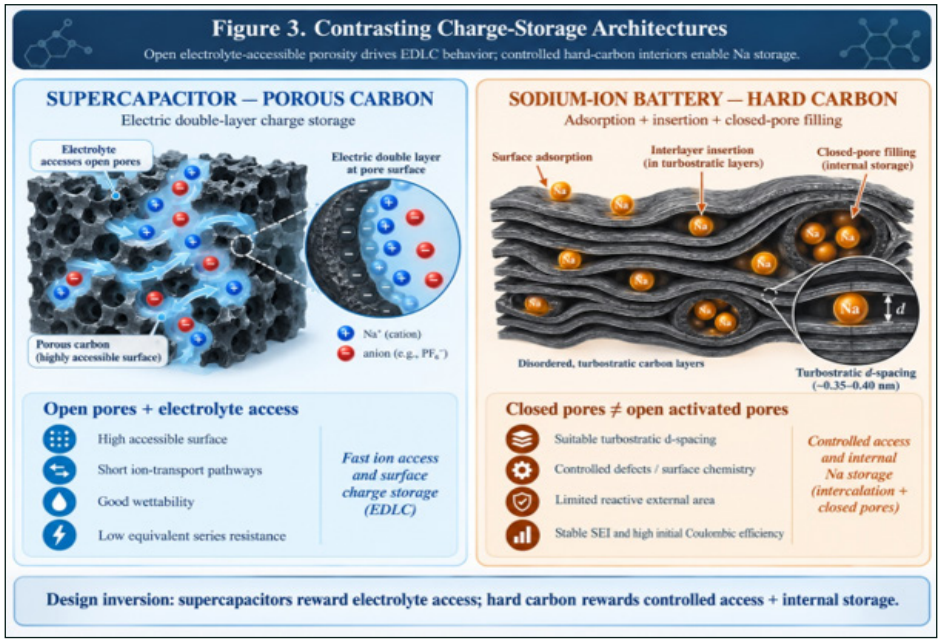

Figure 3: Contrasting Charge-Storage Architectures

Figure 3 explains that in an EDLC, electrolyte access to internal carbon surfaces is essential. In a hard-carbon SIB anode, some of the most valuable low-potential storage volume can instead be located behind carbon walls in closed pores, reducing direct exposure to electrolyte. This inversion of the preferred pore architecture is the mechanistic basis of the porosity paradox.

Discussion and Critical Analysis

The Porosity Paradox

The most important insight emerging from this literature is that “more porosity” is not a universal electrode-design rule. For supercapacitors, increasing suitably sized accessible porosity can create more double-layer interface and improve ionic transport. This is why KOH activation and hierarchical pore design remain dominant approaches in biomass-derived supercapacitors [2,24-26].

For SIB hard carbon, however, exposing additional surface can increase electrolyte decomposition and enlarge the SEI. Highly activated carbon may offer many Na-adsorption sites yet consume an unacceptable fraction of available sodium during the first cycle. Closed pore volume, appropriate carbon-layer spacing and defect control can be more valuable than maximum nitrogen-accessible BET area [10,12,14,33].

This produces a technological divergence within a common feedstock platform. The same PKS precursor that benefits from high-KOH-ratio activation for supercapacitors may require purification and controlled thermal reconstruction for SIB hard carbon. From a biorefinery perspective, this is advantageous: feedstock streams need not compete for one single product specification. They can be directed toward differentiated higher-value markets.

The Porosity Paradox

Figure 4 is a central conceptual figure because it visually represents the article's most original synthesis. The schematic makes explicit that the practical optimum shifts toward lower open-surface exposure for SIB hard carbon than for supercapacitor porous carbon.

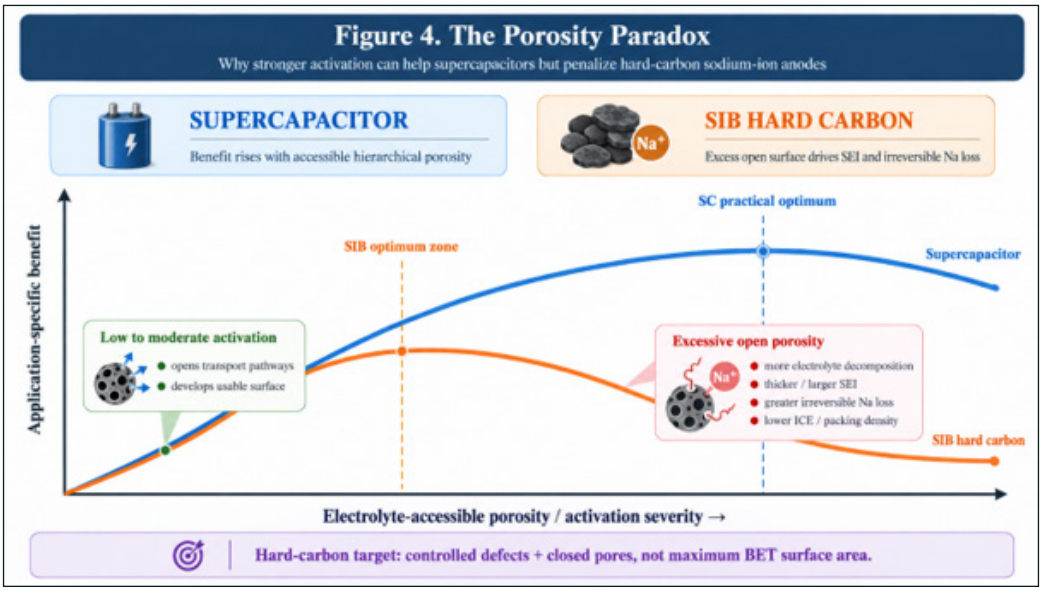

Figure 4: The Porosity Paradox: Why Activation has Opposite Implications

Figure 4 does not imply a universal quantitative curve; it is an engineering hypothesis synthesized from the literature. Supercapacitor performance often rises as accessible hierarchical porosity develops until density, resistance or mechanical penalties become important. Hard-carbon performance is different because excessive electrolyte-accessible surface can reduce ICE. The hard-carbon target should therefore shift from maximising porosity to controlling its location and accessibility.

Beyond BET Surface Area

BET surface area remains useful for porous-carbon characterisation, but it should not be elevated to a universal predictor. Nitrogen adsorption at cryogenic temperature may not fully represent electrolyte accessibility, and it is particularly inadequate for quantifying closed pores relevant to hard carbon. Pore-size modelling, small-angle scattering, gas adsorption with different probe molecules, electron microscopy, Raman spectroscopy, X-ray diffraction and advanced operando characterisation should therefore be combined.

Supercapacitor research similarly requires more sophisticated descriptors. A carbon with 2,500 $m^2 g^{-1}$ is not necessarily superior to one with 1,200 $m^2 g^{-1}$ if a large fraction of the additional area is inaccessible to electrolyte ions or accompanied by poor packing density. Yulianti et al., provide a useful palm-specific illustration because high capacitance was obtained from a moderate surface area through the interaction of pore distribution, defects, SiO_2 chemistry and wettability [20].

Heteroatoms: Functional Sites Versus Uncontrolled Chemistry

Heteroatom doping is attractive because it offers a means to modify surface polarity, electronic structure and electrochemical reaction sites without abandoning carbon's low-cost platform. N, S and P modification has improved both supercapacitor and sodium-storage performance in many biomass systems [29,44,45].

Yet adding heteroatoms should not be treated as automatically beneficial. In supercapacitors, excessive functionalization can reduce conductivity or structural stability. In hard carbon, additional reactive groups can increase first-cycle reactions even when they add reversible adsorption sites. The relevant objective is

therefore functional-site efficiency—reversible charge stored per unit of chemical complexity and irreversible reaction—rather than maximum dopant concentration.

Oil-palm residues offer an interesting opportunity because some heteroatoms and minerals are endogenous. PKS-derived carbon can retain P/S-related functionality after activation, while EFB contains silica and can be co-doped with N/S. This could reduce synthetic reagent requirements, but natural feedstock variability must be controlled if such endogenous chemistry becomes part of the product specification.

Laboratory Metrics Versus Practical Electrode Engineering

A recurring limitation across the literature is the gap between excellent material-level results and practical device requirements. High gravimetric capacitance or half-cell Na capacity does not alone establish industrial suitability. Thick electrodes introduce ionic and electronic transport gradients; increasing mass loading changes effective utilization; conductive additives and binders dilute active-material capacity; calendering alters pore accessibility; and full-cell balancing can reveal penalties invisible in half-cell tests [12,13]. Full-cell-focused analyses further caution that half-cell tests can overstate practical hard-carbon performance when finite sodium inventory and ultra-low anode potentials are not considered [46].

For supercapacitors, standardized reporting should include active mass per geometric area, electrode thickness, apparent density, two-electrode device performance, ESR and energy/power calculations based on total active material. For SIBs, essential variables include mass loading, electrode density, initial and average Coulombic efficiency, cutoff voltage, plateau fraction, full-cell cathode pairing, N/P balance and Na inventory.

Rate performance also requires careful interpretation in hard carbon. High surface-defect density can produce rapid pseudocapacitive-like Na uptake and attractive high-current capacity, but applications requiring maximum cell energy may value low-voltage plateau capacity and ICE more strongly. Fast-charging design therefore introduces additional trade-offs among defects, diffusion, plating risk and energy density [47,48].

Carbon Yield and the Hidden Denominator

Published electrochemical studies frequently normalize results per gram of final active carbon, but industrial manufacturing begins with kilograms or tonnes of wet biomass. Activation can substantially decrease mass yield. A material delivering exceptionally high F g^{-1} after severe KOH treatment may therefore require substantially more feedstock, activator and furnace energy for each kilogram of saleable electrode carbon.

Future studies should report at least three mass-normalized metrics: carbon yield from dry precursor, chemical consumption per kilogram of final carbon and electrode performance per kilogram of original biomass. These values would make it possible to compare high-performance activation with less aggressive routes such as one-step frond carbonisation.

The same reasoning applies to hard carbon. High-temperature pyrolysis may deliver superior ICE and plateau capacity but consume more energy and release additional volatile matter. If purification requires repeated acid washing, water and wastewater-treatment burdens must also be accounted for. A technology described as "green" solely because the carbon precursor is renewable can therefore be misleading.

Chemical Activation, Washing and Scale-Up

KOH is highly effective for producing microporosity, but industrial scale-up requires handling concentrated alkali, high-temperature corrosion, neutralisation and recovery of potassium-containing streams. H_3PO_4 and other chemical activators have different pore-development mechanisms but likewise require recovery and wastewater management. Physical activation avoids some chemical burdens but increases residence time and thermal demand [8,24,25]. Recent reviews of agricultural- and waste-biomass activated carbons likewise identify process optimisation, reagent intensity and environmental burden as core constraints on sustainable scale-up [49,50].

These factors create an important distinction between material sustainability and process sustainability. A renewable precursor can enter a resource-intensive conversion process. Consequently, future palm-derived electrode research should integrate process

mass balance, thermal demand and chemical recovery at an early stage rather than after electrochemical optimisation.

Integration with Palm-Oil Mills

Palm-oil mills already possess biomass logistics, boilers, steam systems and established handling of PKS, fibre and EFB. This infrastructure could reduce the logistical barrier to carbon production. However, residues currently have alternative functions, particularly PKS and fibre as fuels. Producing electrode carbon therefore incurs an opportunity cost: biomass diverted from steam or electricity generation must generate sufficient added value to justify replacement energy.

A cascaded strategy may be more realistic than complete diversion. Selected fractions with desirable composition could be routed to high-value carbon manufacturing while remaining biomass continues to supply process energy. Mill-derived waste heat or renewable electricity could contribute to drying and preprocessing, while centralized high-temperature carbonisation facilities could serve clusters of mills where economies of scale justify transport.

Circularity and Life-Cycle Assessment

Circularity should be evaluated using more than waste diversion. The relevant system includes residue generation, preprocessing, transportation, activator manufacture, furnace energy, washing, wastewater treatment, electrode fabrication, device lifetime and end-of-life pathways. Few palm-electrode studies currently integrate these dimensions.

Life-cycle assessment should therefore compare at least four scenarios: conventional residue combustion, conventional activated-carbon production, palm-derived supercapacitor carbon and palm-derived SIB hard carbon. Such comparison would reveal whether the climate and resource benefits of producing high-value carbon outweigh additional thermal and chemical processing. Techno-economic analysis should run in parallel because high-value products may justify more intensive processing where commodity fuel cannot.

Technology-Selection Framework

The evidence supports a staged technology-selection process rather than a single optimised recipe. The framework therefore treats feedstock selection, microstructure design, electrochemical validation and sustainability as sequential decision gates.

Stage 1: Feedstock Screening

Candidate residues should first be characterized for lignin, cellulose, hemicellulose, ash, silica, alkali metals, transition-metal impurities, moisture, bulk density and seasonal variability. PKS is attractive where dense carbon-rich shell material is available, EFB where fibrous and silica-containing architectures are useful, and frond material where low-chemical-input thermal conversion is feasible.

Stage 2: Application Assignment

If the precursor readily develops high accessible pore volume while preserving conductivity, a supercapacitor pathway may be preferable. If carbonisation produces stable turbostratic domains, controllable interlayer spacing and internal nanopores, the precursor may be more valuable as SIB hard carbon.

Stage 3: Processing Intensity

Supercapacitor pathways can employ chemical or physical activation depending on the required surface area and ion-transport architecture. Hard-carbon pathways should prioritize purification, controlled pyrolysis and closed-pore engineering, using activation only where it does not create excessive external surface.

Stage 4: Electrochemical Validation

Materials should progress from screening cells to realistic devices. Supercapacitors should be tested in two-electrode architectures at practical loading. Hard carbon should progress from Na-metal half-cells to full cells paired with realistic cathodes. In both cases, volumetric as well as gravimetric performance should be reported.

Stage 5: Manufacturing and Sustainability Filter

The final technology choice should incorporate carbon yield, energy consumption, reagent consumption, washing-water requirement, wastewater generation, furnace throughput, electrode processing, reproducibility and potential integration with mill infrastructure. A candidate that fails this final gate should not be prioritised for scale-up solely because it achieved a high laboratory metric.

Figure 5 converts these principles into a practical

decision framework. It integrates the two technological branches and shows where performance, manufacturability and environmental criteria enter the decision process.

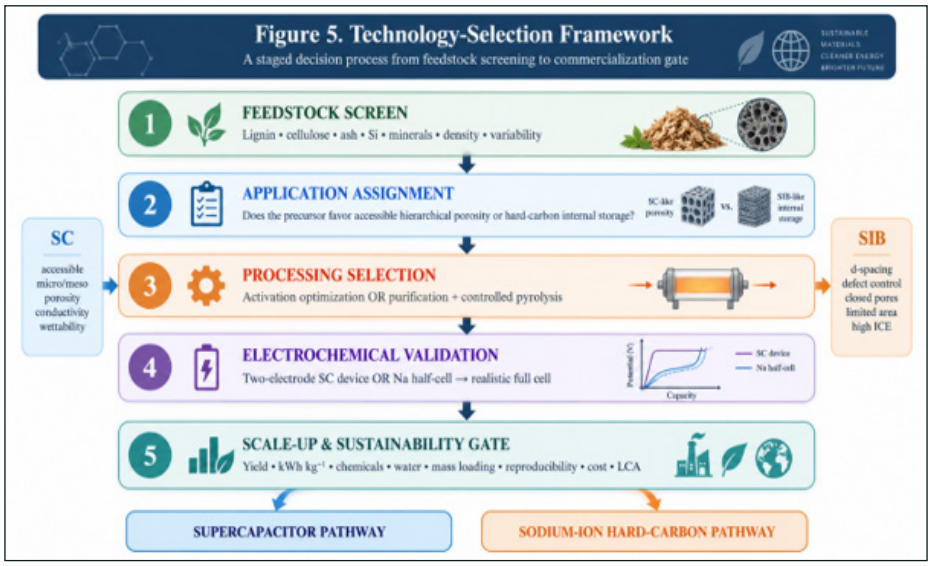

Figure 5: Technology-Selection Framework for Palm-Derived Electrode Carbon

Figure 5 illustrates that the framework prevents selection based exclusively on peak electrochemical values. Feedstock and application are screened together, after which processing is tailored to the intended storage mechanism. Only materials passing a manufacturing and sustainability gate advance toward commercialization.

Research Gaps and Future Research Agenda

Direct Comparison of Oil-Palm Residues

Most published studies optimize a single palm residue independently. This makes it difficult to determine whether superior performance arises from feedstock chemistry or from process optimisation. Future experiments should compare PKS, EFB, mesocarp fibre and frond under both standardized baseline conditions and individually optimised conditions.

Standardized Closed-Pore Characterization

Closed-pore engineering is emerging as a major hard-carbon strategy, yet characterisation methods remain inconsistent. BET analysis alone cannot adequately quantify internal inaccessible pores. Small-angle X-ray scattering, helium pycnometry, advanced adsorption methods, transmission electron microscopy and operando techniques should be integrated with electrochemical plateau analysis. Recent closed-pore-focused literature similarly argues that pore-construction routes, quantitative characterisation and Na-storage mechanisms should be evaluated together rather than inferred from BET area alone [51].

Mechanistic Separation of Slope and Plateau Capacity

Hard-carbon studies should report not only total reversible capacity but also slope and plateau contributions. This distinction would allow researchers to determine whether a modification primarily creates surface/defect adsorption sites or low-potential pore-filling capacity. Chen et al., Wu et al., and later reviews show that unresolved mechanistic ambiguity remains a major obstacle to universal hard-carbon design rules [10,11].

Higher Practical Mass Loading

Many laboratory electrodes are too thin to represent commercial transport constraints. Future palm-carbon studies should report performance at progressively increasing mass loading while monitoring areal capacity/capacitance, impedance and electrode density.

Full-Cell Sodium-Ion Validation

Palm-derived SIB studies remain disproportionately dependent on Na-metal half-cells. High ICE should be confirmed in full cells with realistic cathode materials and practical N/P ratios. Presodiation may provide additional flexibility, but its process safety and industrial compatibility should be assessed rather than treated as a laboratory correction for low ICE [13,18].

Low-Temperature and Fast-Charging Behaviour

Hard-carbon commercialization increasingly requires performance outside room-temperature low-rate tests. Low temperature changes electrolyte transport and Na diffusion, while aggressive fast charging can increase polarization and sodium-plating risk. Defect engineering, pore architecture and interfacial design should therefore be evaluated under application-relevant temperature and current ranges [47,48].

Reagent Recovery

Future activation studies should report not merely KOH/carbon ratios but actual recovery potential. Closed-loop alkali recovery, acid neutralisation and water recycling could determine whether high-surface-area palm carbon is economically and environmentally competitive.

Reproducibility and Feedstock Variability

Agricultural biomass varies with plantation age, soil, fertilizer regime, geographic origin and mill processing. Carbon-electrode studies typically treat feedstock as homogeneous. Multi-batch validation is needed to quantify how much raw-material variability can be tolerated without compromising electrode specifications.

Techno-Economic Assessment

Material cost should be modelled from the raw residue through drying, size reduction, purification, carbonisation, activation, washing, yield loss, grinding, electrode preparation and quality control. Cost per kilogram of precursor is insufficient because low-cost biomass can still produce expensive carbon after intensive processing.

Life-Cycle Assessment

Future claims of sustainability should be supported by cradle-to-gate or cradle-to-grave assessment. Relevant comparisons include greenhouse-gas emissions, cumulative energy demand, water consumption, chemical use, waste generation and avoided impacts from residue disposal or conventional carbon production.

Machine-Learning-Guided Process Optimization

The processing space is multidimensional: precursor chemistry, carbonisation temperature, heating rate, residence time, activator ratio, dopant level and washing intensity interact nonlinearly. Data-driven methods can identify combinations unlikely to be discovered through one-factor-at-a-time experiments. Ullah et al., have already introduced artificial-neural-network modelling into oil-palm-frond supercapacitor research, indicating that palm-derived carbon is well suited to this next stage of process optimization [40].

Conclusion

Oil-palm residues are no longer scientifically interesting merely because they are abundant biomass wastes. Their significance lies in their ability to be converted into structurally distinct advanced carbons for different electrochemical functions. Palm kernel shell, empty fruit bunch and oil-palm frond already demonstrate that feedstock chemistry, carbonisation, mineral control, activation, heteroatom functionality and pore engineering can generate electrode structures spanning highly accessible hierarchical carbon to closed-pore-rich hard carbon.

The evidence also shows that these materials should not be optimised under a single performance philosophy. Supercapacitors generally benefit from rapid electrolyte access, hierarchical open porosity, suitable surface functionality and low electronic resistance. Sodium-ion hard carbon instead requires a carefully controlled balance of turbostratic domains, expanded interlayer spacing, limited reactive surface, stable SEI formation, controlled defects and closed nanopores. Consequently, extreme activation can be beneficial for the former but detrimental to the latter.

The most promising industrial strategy is therefore a dual-pathway model in which palm residues are screened according to composition and assigned to application-specific processing routes. PKS is particularly attractive because evidence now supports both high-performance porous-carbon and hard-carbon pathways, while EFB and fronds expand the range of inherited morphologies and chemical functionalities available for engineering.

Commercial relevance will depend less on achieving another record laboratory capacitance or half-cell capacity than on combining strong electrochemical properties with high carbon yield, acceptable packing density, limited reagent consumption, realistic electrode loading, full-cell validation, reproducibility, chemical recovery and integration with existing palm-oil infrastructure. Future research should consequently move from "waste-derived carbon" toward specification-driven carbon manufacturing, where the residue is treated as an industrial precursor and processing is selected according to the storage mechanism required by the final device.

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