

Decoding Activation Severity in Coconut Shell-Derived Porous Carbons: Correlating Sub-Nanometer Pore Architecture with High-Rate Super capacitive Ion Dynamics

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Abstract

Converting agricultural lignocellulosic biomass into high-performance porous carbon electrodes provides a sustainable route for electrochemical energy storage. However, establishing rigorous mechanistic correlations between chemical activation stoichiometry, sub-nanometer pore evolution, and electrolyte transport kinetics at high charge–discharge rates remains a persistent challenge. Herein, we systematically investigate the impact of potassium hydroxide (KOH) activation severity across varying mass ratios (KOH:char of 0: 1, 1: 1, 3: 1, and 4: 1) on carbon derived from coconut shell (*Cocos nucifera*) waste. Non-Local Density Functional Theory (NLDFT) deconvolution of 77 K N₂ adsorption isotherms reveals that moderate etching (KOH:char = 3: 1) optimizes the development of slit-shaped micropores (< 2 nm), yielding an apparent Brunauer–Emmett–Teller (BET) surface area of 2160 m² g^{−1} and a micropore volume of 0.84 cm³ g^{−1}. In contrast, severe activation (4: 1) induces localized pore-wall collapse, broadening the sub-nanometer networks into mesoporous channels (2–5 nm) while lowering the apparent surface area to 1890 m² g^{−1} and overall carbon mass yield to 9.2%. When evaluated in 6 M KOH electrolyte, the 3: 1 activated sample delivers a maximum single-electrode gravimetric capacitance of 314.8 F g^{−1} at 0.5 A g^{−1} in a three-electrode configuration and 248.6 F g^{−1} in a symmetric two-electrode coin-cell device. Notably, the mesopore-broadened 4: 1 architecture exhibits superior rate resilience, retaining 83.1% of its initial capacitance at 10 A g^{−1} compared to 76.5% for the 3: 1 material. Electrochemical impedance spectroscopy confirms that the expanded mesoporous network mitigates interior diffusion resistance, yielding an equivalent series resistance of 0.46 Ω and a short relaxation time constant of 0.78 s. Furthermore, symmetric coin cells retain 97.8% of initial capacitance over 10,000 continuous galvanostatic cycles at 5 A g^{−1}. This work elucidates the structural trade-off between energy storage density, high-current rate capability, and synthetic yield in biomass-derived carbon electrodes.

Keywords: Coconut shell carbon; chemical activation severity; NLDFT pore-size distribution; electric double-layer capacitors; rate capability; electrochemical impedance spectroscopy.

1. Introduction

Electric double-layer capacitors (EDLCs) occupy an essential role in modern electrical energy storage by bridging the gap between high-energy secondary batteries and high-power conventional electrostatic capacitors. Owing to their non-Faradaic, electrostatic charge accumulation mechanism at the electrode–electrolyte interface, EDLCs exhibit high power densities, rapid charge–discharge capability (within seconds), and cycle lifetimes exceeding tens of thousands of cycles with negligible capacity fading. The electrochemical performance of an EDLC is intrinsically dictated by the structural, textural, and electrical properties of the porous carbon electrode matrix. Specifically, high specific surface area (SSA), tailored hierarchical porosity spanning micropores (< 2 nm) to mesopores (2–50 nm), high electrical conductivity, and good surface wettability are mandatory prerequisites for maximizing gravimetric capacitance and power delivery.

Lignocellulosic biomass residues have emerged as sustainable, cost-effective precursors for porous carbon synthesis due to their renewable abundance, carbon-dense frameworks, and low intrinsic ash contents. Among agricultural wastes, coconut shell (*Cocos nucifera*) represents a premier feedstock. Coconut endocarps possess a naturally dense, uniform, and isotropic cellular architecture characterized by high lignin content (≈ 35–45 wt%) and low inorganic ash fractions (< 1.0 wt%). These intrinsic attributes facilitate controlled thermal degradation and yield structurally robust biochars with high carbon retention relative to softer agricultural wastes.

Porous carbons derived from coconut shells are conventionally synthesized through two-step carbonization and chemical activation. While activating agents such as ZnCl_2 , H_3PO_4 , and steam are widely utilized, potassium hydroxide (KOH) is uniquely effective for generating sub-nanometer micropores with apparent BET surface areas often exceeding $2000 \text{ m}^2 \text{ g}^{-1}$. The chemical etching of carbon matrices by molten KOH proceeds via a cascade of solid–liquid–gas reactions above 400°C ($6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$), accompanied by the secondary decomposition of potassium carbonate and reduction of potassium oxides by carbon at elevated temperatures ($> 700^\circ\text{C}$). During this thermal process, the continuous intercalation of metallic potassium vapor ($T_{\text{boiling}} = 759^\circ\text{C}$) into the carbonaceous crystallites forces graphene lamellae apart. Subsequent post-synthesis acid washing dissolves the residual salts and potassium complexes, leaving behind extensive intra-crystalline voids and sub-nanometer microporosities.

Despite the extensive body of empirical literature on KOH activation, critical fundamental questions persist regarding the quantitative management of activation severity. Most notably, a pervasive trade-off exists between maximizing electroactive surface area and sustaining high-rate ion transport. While aggressive chemical etching (KOH:char mass ratios $\geq 3:1$) dramatically elevates specific surface area by generating extensive micropore networks, it frequently leads to extreme mass consumption (yields $< 10\%$), degradation of structural integrity, and elevated bulk electrical resistance. Furthermore, literature frequently evaluates capacitive performance using classical Barrett–Joyner–Halenda (BJH) models, which fail to account for fluid confinement effects within sub-nanometer pores and consequently underestimate true micropore distributions. Modern non-local density functional theory (NLDFT) models, applied under appropriate Rouquerol consistency criteria, are imperative to properly delineate the boundary between accessible double-layer storage and diffusion-limiting tortuosity. Moreover, many published studies report specific capacitance exclusively from three-electrode half-cell configurations. These idealized systems artificially inflate performance by eliminating real-world device constraints, including separator resistance, current collector contact impedance, and symmetric voltage splitting.

In this study, we systematically investigate the influence of KOH activation severity on the textural, structural, and electrochemical properties of coconut shell-derived activated carbons. By varying the KOH:char mass ratio across a controlled gradient (0:1, 1:1, 3:1, and 4:1), we trace the structural transition from pristine, low-porosity biochar to narrow microporous networks, and finally to widened micro–mesoporous architectures induced by pore-wall coalescence. Using slit-pore NLDFT modeling, we quantitatively correlate discrete pore-width regimes with electrolyte transport kinetics and equivalent series resistance. Finally, we assess the electrodes in both a three-electrode screening cell and a fully assembled symmetric two-electrode coin-cell supercapacitor, providing a comprehensive, rigorous basis for optimizing biomass-derived carbon electrodes for high-rate energy storage.

2. Materials and Methods

2.1 Biomass Precursor Preparation and Carbonization

Mature coconut shell endocarps were collected from a single agricultural source in Gujarat, India, to minimize batch-to-batch variations in cellulose, hemicellulose, and lignin compositions. The hard endocarps were mechanically cleaned with a wire brush to remove adhering fibrous mesocarp (coir pith), repeatedly washed with hot deionized (DI) water ($\geq 18.2 \text{ M}\Omega \text{ cm}$) to eliminate residual surface contaminants, and dried in a convection oven at 105°C for 24 h until constant weight was achieved. The dried shells were crushed using an industrial jaw crusher, pulverized in a planetary ball mill with tungsten carbide grinding media, and classified using standard brass ASTM sieves to isolate a uniform powder fraction with particle diameters between 75 and $150 \mu\text{m}$ (100–200 mesh). Proximate analysis of the precursor revealed a moisture content of $6.8 \pm 0.3 \text{ wt}\%$, volatile matter of $72.1 \pm 1.2 \text{ wt}\%$, fixed carbon of $20.4 \pm 0.8 \text{ wt}\%$, and an inorganic ash content of $0.7 \pm 0.1 \text{ wt}\%$.

Carbonization of the precursor was conducted inside a high-temperature horizontal quartz tube furnace (inner diameter 60 mm, heating length 600 mm). For each batch, 20.0 g of the sieved coconut shell powder was uniformly distributed inside a high-purity alumina combustion boat. The tube was evacuated and purged with ultra-high-purity nitrogen gas (99.999%, 100 mL min^{-1}) for 45 min at ambient conditions to establish an inert atmosphere. The furnace was subsequently heated to 500°C at a controlled heating ramp of 5°C min^{-1} and held at this target carbonization temperature for 2 h under an uninterrupted nitrogen sweep. Following the isothermal dwell, the furnace was allowed to cool naturally to room temperature under inert gas protection. The resulting primary biochar was collected, weighed to calculate carbonization yield, and designated as **CSC-500**.

2.2 Chemical Activation Series and Yield Tracking

The carbonized intermediate, CSC-500, was chemically activated using analytical-grade potassium hydroxide pellets (KOH, $\geq 85.0\%$, Sigma-Aldrich) across four distinct mass ratios: an unactivated control (KOH:char = 0: 1) and three activation severities (1: 1, 3: 1, and 4: 1 w/w). For the chemically activated samples, designated **CSC-KOH-1**, **CSC-KOH-3**, and **CSC-KOH-4**, exact quantities of KOH were dissolved in 30 mL of DI water per 5.0 g of carbon intermediate. The CSC-500 char was gradually added to the alkaline solution and magnetically stirred in a closed polytetrafluoroethylene (PTFE) vessel at 60°C for 4 h at 300 rpm to ensure homogeneous precursor impregnation. The suspension was subsequently dehydrated at 105°C for 12 h in a nickel crucible inside a drying oven to yield a solid, uniform KOH–carbon cake.

The impregnated cakes were loaded into the horizontal tube furnace inside nickel-lined alumina crucibles and heated under continuous N₂ flow (150 mL min⁻¹) to 800°C at a ramp rate of 10°C min⁻¹. The peak temperature of 800°C was maintained for 1 h to ensure complete reduction of potassium species and metallic potassium intercalation. After cooling to room temperature, the residual solids were collected and transferred into a 2 M HCl solution (50 mL per gram of initial char) and stirred at 60°C for 2 h to dissolve secondary potassium carbonate, oxide phases, and trace minerals. The leached carbon was vacuum-filtered through a 0.22 μ m PTFE membrane and repeatedly rinsed with boiling DI water until the filtrate reached neutral pH (6.8–7.2) and exhibited an electrical conductivity below 10 μ S cm⁻¹. The final washed carbons were dried in a vacuum oven at 110°C for 12 h. The char carbonization yield (Y_{char}), activation stage yield (Y_{act}), and total overall process yield (Y_{total}) were calculated on a dry-mass basis according to:

$$Y_{\text{char}} = \left(\frac{m_{\text{char}}}{m_{\text{raw}}} \right) \times 100\%$$

$$Y_{\text{act}} = \left(\frac{m_{\text{activated}}}{m_{\text{char}}} \right) \times 100\% \quad ; \quad Y_{\text{total}} = \left(\frac{m_{\text{activated}}}{m_{\text{raw}}} \right) \times 100\%$$

where m_{raw} , m_{char} , and $m_{\text{activated}}$ denote the dry masses of raw coconut powder, post-pyrolysis char, and final purified activated carbon, respectively.

2.3 Physicochemical Characterization

Thermal decomposition behavior of the raw coconut precursor was recorded using a simultaneous thermogravimetric analyzer (TA Instruments Discovery TGA 550). A 10.0 ± 0.5 mg aliquot of dried powder was placed in a ceramic pan, purged with high-purity N₂ (50 mL min⁻¹) at 30°C for 20 min, and heated to 900°C at a constant linear rate of 10°C min⁻¹.

Surface morphology and macroscopic pore channels were imaged using field-emission scanning electron microscopy (FE-SEM, Zeiss GeminiSEM 500) operated at an accelerating voltage of 5.0 kV after sputter-coating the samples with a thin (3 nm) Au/Pd conductive film. Textural porosity parameters were derived from nitrogen adsorption–desorption isotherms measured at 77 K using an automated gas sorption instrument (Micromeritics 3Flex). Prior to gas uptake measurements, all samples were outgassed under high vacuum ($< 10^{-4}$ Torr) at 250°C for 12 h to eliminate adsorbed water and volatile species. The apparent specific surface area (S_{BET}) was calculated from the linear region of the BET plot adhering strictly to the Rouquerol consistency criteria within the relative pressure window (P/P_0) of 0.01–0.15 to avoid thermodynamic distortion in microporous domains. Total pore volume (V_{total}) was evaluated from single-point liquid nitrogen adsorption at $P/P_0 = 0.99$. The micropore volume (V_{micro} , pore width < 2.0 nm), mesopore volume (V_{meso} , pore width 2.0–50 nm), and continuous pore-size distributions (PSD) were deconvoluted using a slit-shaped pore carbon kernel based on Non-Local Density Functional Theory (NLDFT).

Crystallographic structure was characterized by powder X-ray diffraction (XRD, Bruker D8 Advance) using Cu K α radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 40 mA across a scanning range of $2\theta = 10^\circ$ – 80° at a scan speed of 2° min⁻¹. Structural disorder and graphitic domain sizes were determined via micro-Raman spectroscopy (Horiba LabRAM HR Evolution) utilizing an excitation laser wavelength of 532 nm at an attenuated incident power of 5 mW to prevent laser-induced local photothermal annealing. Elemental compositions (C, O, K, Cl) were quantified by energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) and corroborated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) using monochromatic Al K α radiation.

2.4 Electrode Preparation and Electrochemical Measurements

Working electrodes were fabricated via an aqueous-organic dispersion technique to ensure mechanical homogeneity without chemical phase segregation. Activated carbon powder (85 wt%), conductive carbon black (Super P, Alfa Aesar, 10 wt%), and polytetrafluoroethylene binder (PTFE, 60 wt% aqueous suspension, Sigma-Aldrich, 5 wt% dry basis) were mixed in an agate mortar. Anhydrous ethanol was added dropwise as a dispersant, and the slurry was homogenized for 30 min until it transitioned into a cohesive paste. The paste was cold-rolled between high-density polyethylene sheets into a self-standing, crack-free film with a uniform thickness of approximately 100 μm . Circular electrode discs (1.0 cm^2 area) were punched out and dried at 80°C for 2 h. The electrode discs were then uniaxially pressed onto pre-treated nickel foam current collectors (1.0 $\text{cm} \times 1.0 \text{ cm}$, cleaned by sequential sonication in 1 M HCl, acetone, and DI water) at a hydraulic pressure of 10 MPa for 30 s. The assembled electrodes were dried under vacuum at 110°C for 12 h. The mass of the active carbon material on each current collector was maintained at $3.0 \pm 0.2 \text{ mg cm}^{-2}$, confirmed via a balance with 0.01 mg precision.

All electrochemical evaluations were performed at $25.0 \pm 0.5^\circ\text{C}$ in 6 M KOH aqueous electrolyte using a multi-channel potentiostat/galvanostat (BioLogic VMP-3). Evaluations were executed across two standard cell architectures:

1. **Three-Electrode Configuration:** Evaluated in a standard three-neck glass cell with an inert nitrogen head-space. The prepared carbon/Ni-foam electrode served as the working electrode, a platinum mesh (2.0 $\text{cm} \times 2.0 \text{ cm}$) served as the counter electrode, and a mercury/mercury oxide (Hg/HgO, 1 M KOH) electrode was utilized as the reference. Step-wise cyclic voltammetry (CV) verified an electrochemically stable working window of -1.0 to 0.0 V vs. Hg/HgO without triggering the hydrogen evolution reaction (HER). CV was swept between 5 and 200 mV s^{-1} . Galvanostatic charge-discharge (GCD) was conducted at current densities from 0.5 to 20 A g^{-1} . Gravimetric specific capacitance ($C_{\text{s,3E}}$, F g^{-1}) was evaluated from discharge branches via:

$$C_{\text{s,3E}} = \frac{I \times \Delta t}{m \times (\Delta V - V_{\text{IR}})}$$

where I is the discharge current (A), Δt is the discharge duration (s), m is the active material mass (g), ΔV is the working potential window (1.0 V), and V_{IR} is the initial ohmic voltage drop (V).

2. **Two-Electrode Symmetric Full Cell:** Two mass-matched working electrodes ($\Delta m < 2\%$) were assembled into CR2032 coin cells separated by a porous glass microfiber separator (Whatman GF/D, thickness 260 μm) saturated with 150 μL of 6 M KOH. The cell operating voltage was varied from 0.0 to 1.0 V. Total cell capacitance (C_{cell} , F g^{-1}) and the single-electrode equivalent capacitance ($C_{\text{s,2E}}$, F g^{-1}) were calculated from discharge curves via:

$$C_{\text{cell}} = \frac{I \times \Delta t}{M_{\text{total}} \times (\Delta V_{\text{cell}} - V_{\text{IR}})} \quad ; \quad C_{\text{s,2E}} = 4 \times C_{\text{cell}}$$

where M_{total} is the total active carbon mass across both electrodes ($M_{\text{total}} \approx 6.0 \text{ mg}$) and ΔV_{cell} is the cell operating potential window (1.0 V). Gravimetric energy density (E , Wh kg^{-1}) and power density (P , W kg^{-1}) were obtained from:

$$E = \frac{1}{2 \times 3.6} \times C_{\text{cell}} \times (\Delta V_{\text{cell}} - V_{\text{IR}})^2 \quad ; \quad P = \frac{E \times 3600}{\Delta t}$$

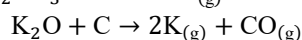
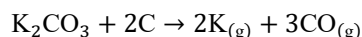
Electrochemical impedance spectroscopy (EIS) was conducted at open-circuit potential over a frequency span of 100 kHz to 10 mHz with a sinusoidal potential perturbation of 5 mV. Nyquist plots were modeled via complex non-linear least squares (CNLS) fitting based on an equivalent circuit incorporating solution resistance (R_s), charge-transfer resistance (R_{ct}), Warburg diffusion impedance (Z_w), and constant phase elements (CPE). Long-term operational cycling stability was evaluated over 10,000 continuous GCD cycles at a constant current density of 5 A g^{-1} .

3. Results and Discussion

3.1 Thermal Degradation Mechanics and Activation Mass Balance

The thermogravimetric (TGA) and derivative thermogravimetric (DTG) profiles of the raw coconut shell powder recorded in an inert nitrogen atmosphere exhibit three primary degradation stages. An initial mass loss of 6.8% occurs between 30°C and 150°C, corresponding to the desorption of physically bound moisture and low-molecular-weight volatile species. The primary thermal decomposition regime takes place within 210--395°C, accounting for a cumulative mass loss of 58.4%. Within this broad thermal envelope, the DTG profile reveals two distinct overlapping transitions: a lower-temperature shoulder centered at 278°C attributed to the depolymerization and cleavage of amorphous hemicellulose xylan chains, followed by a sharp endothermic mass loss peak at 342°C that reflects the breakdown of crystalline cellulose microfibrils via β - 1,4-glycosidic bond scission. Above 400°C, thermal decomposition displays a gradual slope extending up to 900°C, characteristic of the pyrolytic polycondensation of complex aromatic lignin networks. By 500°C, the DTG signal approaches baseline stability, indicating the completion of the main devolatilization phase and yielding an initial primary biochar yield (Y_{char}) of 31.8 wt%. This guided the selection of 500°C as the primary carbonization temperature, yielding an enriched carbonaceous template with minimal residual volatile fractions while preventing premature sintering of internal pore structures.

The secondary chemical activation process at 800°C is characterized by severe mass consumption driven by reaction stoichiometry. As detailed in Table 1, increasing the KOH:char mass ratio from 0: 1 to 4: 1 systematically reduces the activation yield (Y_{act}) from 100% to 28.9%, causing the overall process yield (Y_{total}) to fall from 31.8% to 9.2%. This precipitous drop in carbon recovery is directly related to gasification reactions. Above 400°C, molten KOH oxidizes amorphous carbon domains, producing solid potassium carbonate (K_2CO_3) alongside gaseous H_2 . As the activation temperature exceeds 700°C, the reaction shifts as solid carbon reduces both K_2CO_3 and potassium oxide (K_2O) via endothermic gasification pathways:



At the activation temperature of 800°C, metallic potassium exists well above its boiling point (759°C). The dynamic evolution of high-pressure potassium vapor forces apart adjacent graphitic carbon sheets, intercalating between atomic layers. Subsequent post-synthesis acid neutralization with 2 M HCl extracts the unreacted potassium species and embedded metallic deposits, generating extensive intra-particle pore volume. However, at the extreme ratio of 4: 1, excessive gasification accelerates carbon burn-off, causing structural over-etching, pore-wall rupture, and low material recovery (9.2%).

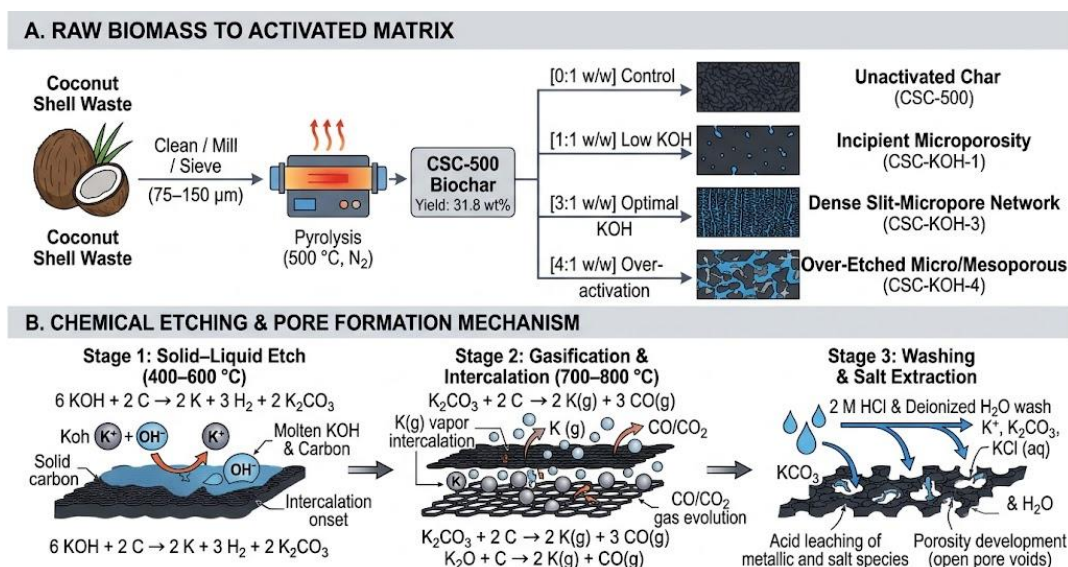


Figure 1: Schematic flow diagram of the chemical activation of coconut shell endocarps across increasing KOH:char mass ratios, showing the thermal conversion steps and associated high-temperature chemical etching mechanisms.

3.2 Textural Evolution and NLDFT Pore-Size Distributions

The nitrogen adsorption–desorption isotherms recorded at 77 K and the corresponding NLDFT pore-size distributions (PSD) reflect the textural restructuring of the biochar as a function of activation severity. The unactivated control sample, **CSC-500**, exhibits a flat, low-uptake profile classified as a reversible IUPAC Type I(a) isotherm, indicating an unactivated carbon with an apparent BET specific surface area of $124 \text{ m}^2 \text{ g}^{-1}$ and a modest total pore volume of $0.08 \text{ cm}^3 \text{ g}^{-1}$.

Introducing a 1:1 w/w ratio of KOH (**CSC-KOH-1**) induces pore inception, producing a steep adsorption knee at very low relative pressures ($P/P_0 < 0.05$) without noticeable hysteresis, reflecting early-stage micropore development. Here, S_{BET} rises to $945 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of $0.52 \text{ cm}^3 \text{ g}^{-1}$, with micropores comprising 78.8% of total pore volume ($V_{\text{micro}} = 0.41 \text{ cm}^3 \text{ g}^{-1}$).

At an intermediate activation ratio of 3:1 (**CSC-KOH-3**), the nitrogen uptake increases across the low-pressure regime, producing a combined Type I(b)/Type IV(a) hybrid isotherm. The sharp inflection below $P/P_0 = 0.1$ is paired with a distinct, narrow H4 hysteresis loop between $P/P_0 = 0.45$ and 0.85 , indicative of capillary condensation occurring within slit-shaped micro- and narrow mesopores. For CSC-KOH-3, S_{BET} peaks at $2160 \text{ m}^2 \text{ g}^{-1}$, coupled with a total pore volume of $1.12 \text{ cm}^3 \text{ g}^{-1}$. The NLDFT differential distribution reveals that this sample is dominated by uniform sub-nanometer micropores centered at 0.85 nm and 1.32 nm , yielding a high micropore volume of $0.84 \text{ cm}^3 \text{ g}^{-1}$ (75.0% of total porosity). These sub-nanometer dimensions match the desolvation dimensions of hydrated K^+ (3.31 Å) and OH^- (3.00 Å) ions, providing accessible surface area for non-Faradaic electrostatic charge accumulation.

When the activation severity is increased to 4:1 (**CSC-KOH-4**), the isotherm transitions to a pronounced Type IV(a) profile featuring a broad H4/H3 hybrid hysteresis loop that extends to $P/P_0 = 0.95$. This shift in isotherm topology demonstrates severe morphological transformation. The apparent S_{BET} decreases to $1890 \text{ m}^2 \text{ g}^{-1}$, while the total pore volume expands slightly to $1.18 \text{ cm}^3 \text{ g}^{-1}$. Concurrently, the micropore volume drops from 0.84 to $0.68 \text{ cm}^3 \text{ g}^{-1}$, while the mesopore volume (V_{meso}) nearly doubles from 0.28 to $0.50 \text{ cm}^3 \text{ g}^{-1}$ (42.4% of total porosity). The NLDFT differential pore distribution for CSC-KOH-4 displays a marked broadening of the pore envelope, with the main peak shifting toward $2.4\text{--}4.2 \text{ nm}$. This structural shift indicates pore-wall coalescence: excessive metallic potassium vapor and vigorous CO/CO_2 gasification over-etch thin carbon septa, causing neighboring micropores to collapse into wider mesoporous channels. As shown in subsequent electrochemical analyses, while this coalescence reduces total specific surface area, the wider mesopores alleviate mass-transport resistance during high-current cycling.

Table 1. Synthesis yield, NLDFT-derived porosity parameters, structural defect ratios, and electrochemical performance in aqueous 6 M KOH across the synthesis series ($n = 3$, mean $\pm$ SD).

Sample Code (KOH:Char)	Total Mass Yield, Y_{total} (%)	Apparent S_{BET} (m^2 g^{-1})	NLDFT Pore Volumes: V_{total} / V_{micro} (cm^3 g^{-1})	Raman $I_{\text{D}}/I_{\text{G}}$ Ratio	Specific Capacitance: $C_{\text{s,3E}}$ / $C_{\text{s,2E}}$ (F g^{-1})
CSC-500 (0:1)	31.8	124 ± 8	$0.08 / 0.05$	0.88	$48.5 \pm 3.2 / 32.4 \pm 2.5$
CSC-KOH-1 (1:1)	21.4	945 ± 24	$0.52 / 0.41$	1.02	$186.4 \pm 6.5 / 142.0 \pm 5.1$
CSC-KOH-3 (3:1)	14.6	2160 ± 45	$1.12 / 0.84$	1.14	$314.8 \pm 8.4 / 248.6 \pm 6.8$
CSC-KOH-4 (4:1)	9.2	1890 ± 38	$1.18 / 0.68$	1.26	$278.2 \pm 7.9 / 224.5 \pm 6.2$

Note: Evaluated at 0.5 A g^{-1} in aqueous 6 M KOH with an active material loading of 3.0 mg cm^{-2} . $C_{\text{s,3E}}$ and $C_{\text{s,2E}}$ denote the specific capacitances measured in three-electrode and two-electrode configurations, respectively.

3.3 Microstructural Ordering and Surface Chemistry

The crystallographic evolution of the carbon framework during activation was tracked via powder X-ray diffraction (XRD) and micro-Raman spectroscopy. The XRD diffractograms for all carbon specimens display two broad, low-intensity reflections centered at $2\theta \approx 23.4^\circ$ and 43.6° , corresponding to the (002) and (100)/(101) lattice planes of turbostratic, disordered graphitic carbon. With increasing KOH severity, the (002) peak systematically broadens and shifts to lower angles ($2\theta = 22.8^\circ$ in CSC-KOH-4), reflecting an increase in average interlayer spacing (d_{002}) from 0.380 nm in CSC-500 to 0.390 nm in CSC-KOH-4. This interlayer expansion confirms the lattice-distorting effect of high-temperature metallic potassium vapor intercalation. The lack of sharp crystalline diffraction peaks confirms that the post-synthesis acid leaching and washing steps removed residual potassium salts, carbonates, and inorganic silica ash.

Raman spectra of the carbons exhibit two characteristic vibrational modes: the defect-induced D-band centered at $\approx 1345 \text{ cm}^{-1}$ (A_{1g} symmetry breathing mode associated with disordered sp^3 -bonded carbon edges and vacancies) and the graphitic G-band located at $\approx 1590 \text{ cm}^{-1}$ (E_{2g} symmetry stretching mode of sp^2 -hybridized graphitic domains). Lorentzian curve-fitting of the spectra demonstrates that the integrated intensity ratio (I_D/I_G) rises monotonically with activation severity: 0.88 (CSC-500) < 1.02 (CSC-KOH-1) < 1.14 (CSC-KOH-3) < 1.26 (CSC-KOH-4). This upward progression indicates progressive disruption of the hexagonal carbon lattice. At high chemical activation ratios, aggressive carbon gasification breaks continuous sp^2 planes, introducing edge defects, topological pentagon–heptagon pairs, and dangling bonds. While an overabundance of structural defects can compromise macroscopic electronic conductivity, localized edge-plane defects promote surface wettability and create active centers that facilitate ion adsorption from the aqueous alkaline electrolyte.

Surface elemental compositions were evaluated via X-ray photoelectron spectroscopy (XPS) and Energy-Dispersive X-ray Spectroscopy (EDS). The survey spectra confirm that all activated samples are composed primarily of carbon (88.4–92.8 at%) and oxygen (6.8–10.9 at%). The residual potassium and chlorine contents in all acid-washed samples were below detection thresholds (< 0.1 at%), confirming the efficacy of the neutralization procedure. High-resolution deconvolution of the C 1s spectra resolves four components: graphitic sp^2 carbon (C = C, 284.6 eV), aliphatic sp^3 carbon (C – C, 285.4 eV), hydroxyl/ether groups (C – O, 286.5 eV), and carbonyl functionalities (C = O, 288.0 eV). The O 1s spectra display contributions from quinone-type oxygen (O = C, 531.2 eV), phenol/hydroxyl bonds (C – OH, 532.8 eV), and chemisorbed oxygen/moisture (534.1 eV). Surface oxygen functionalities decrease modestly from 10.9 at% in CSC-KOH-1 to 7.2 at% in CSC-KOH-4, as high-temperature activation reduces labile oxygen-containing groups while expanding the porous network. The residual quinone and hydroxyl groups contribute to improved electrode wettability, facilitating complete penetration of aqueous 6 M KOH into the narrowest micropores.

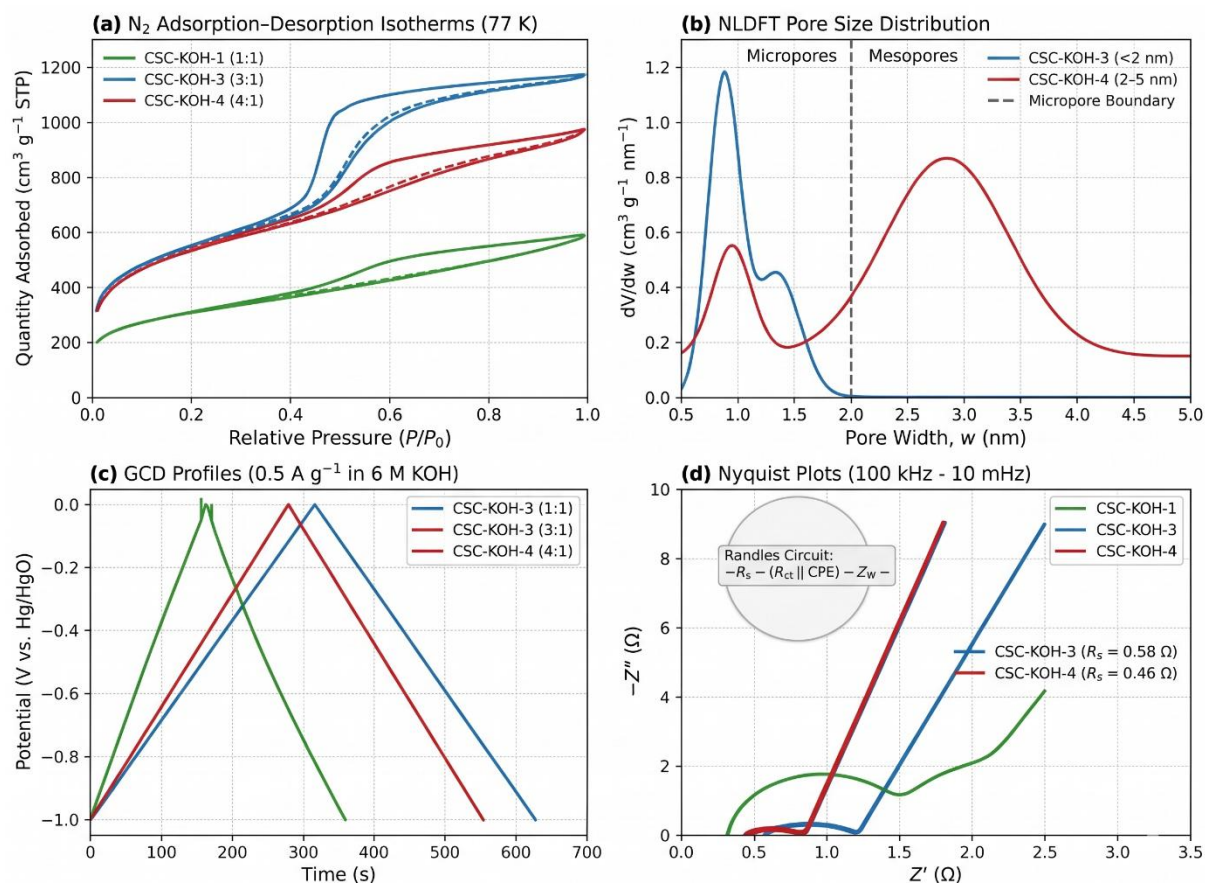


Figure 2: Textural and electrochemical properties of coconut shell-derived carbons: (A) N_2 adsorption–desorption isotherms recorded at 77 K; (B) NLDFT differential pore-size distributions; (C) Galvanostatic charge–discharge profiles at 0.5 A g^{-1} in a three-electrode half-cell (6 M KOH); and (D) Nyquist plots spanning 100 kHz to 10 mHz alongside the fitted equivalent circuit.

3.4 Electrochemical Supercapacitive Behavior

The capacitive charge storage behaviors of the synthesized carbons were initially investigated in a three-electrode half-cell setup in 6 M KOH. Cyclic voltammetry (CV) curves acquired between -1.0 and 0.0 V vs. Hg/HgO across scan rates of $5\text{--}200 \text{ mV s}^{-1}$ show rectangular, quasi-ideal double-layer profiles. The absence of Faradaic redox peaks confirms that charge storage is dominated by the electrostatic adsorption of hydrated K^+ and OH^- ions at the electrode surface. CSC-KOH-3 yields the largest integrated current envelope across all testing conditions, consistent with its highest electrochemically accessible surface area ($2160 \text{ m}^2 \text{ g}^{-1}$).

Galvanostatic charge–discharge (GCD) curves recorded at current densities ranging from 0.5 to 20 A g^{-1} exhibit symmetric, linear triangular profiles with negligible curvature, reflecting good capacitive reversibility and high coulombic efficiencies. At a current density of 0.5 A g^{-1} , CSC-KOH-3 delivers a gravimetric capacitance ($C_{s,3E}$) of $314.8 \pm 8.4 \text{ F g}^{-1}$, exceeding that of CSC-KOH-4 ($278.2 \pm 7.9 \text{ F g}^{-1}$), CSC-KOH-1 ($186.4 \pm 6.5 \text{ F g}^{-1}$), and unactivated CSC-500 ($48.5 \pm 3.2 \text{ F g}^{-1}$). The high low-current capacitance of CSC-KOH-3 directly stems from its dense micropore volume ($0.84 \text{ cm}^3 \text{ g}^{-1}$). At low charging rates, solvated electrolyte ions possess sufficient time to desolvate and occupy sub-nanometer slit pores ($< 1.0 \text{ nm}$), maximizing interfacial charge storage.

To evaluate performance under practical device constraints, symmetrical two-electrode coin cells (CR2032) were constructed using mass-matched electrodes with active loadings of 3.0 mg cm^{-2} . As summarized in Table 1, the single-electrode equivalent capacitances in the coin-cell configuration ($C_{s,2E}$) at 0.5 A g^{-1} are 248.6 F g^{-1} for CSC-KOH-3, 224.5 F g^{-1} for CSC-KOH-4, 142.0 F g^{-1} for CSC-KOH-1, and 32.4 F g^{-1} for

CSC-500. The observable reduction in specific capacitance between the three-electrode half-cell and two-electrode coin cell ($\approx 21\%$ attenuation for CSC-KOH-3) highlights device-level losses, including interfacial contact resistance between the carbon film and nickel substrate, separator tortuosity, and symmetric voltage division.

Rate capability was systematically quantified by measuring capacitance retention as current density was increased from 0.5 to 20 A g⁻¹. Although CSC-KOH-3 exhibits higher absolute capacitance at low current density, its capacity decreases to 190.2 F g⁻¹ at 10 A g⁻¹, corresponding to a rate retention of 76.5%. In contrast, CSC-KOH-4 exhibits superior rate resilience, retaining 83.1% of its initial capacitance at 10 A g⁻¹ (186.6 F g⁻¹) and preserving 78.4% at 20 A g⁻¹.

This difference in rate capability correlates with the NLDFT pore-size distributions. In CSC-KOH-3, the pore network is dominated by narrow micropores (0.85--1.32 nm). At high current densities, ion transport within sub-nanometer channels becomes diffusion-limited due to steric hindrance and the viscous drag of hydration shells, restricting ion penetration into the interior of the carbon particles. Conversely, the over-etched structure of CSC-KOH-4 features a developed mesopore network ($V_{\text{meso}} = 0.50 \text{ cm}^3 \text{ g}^{-1}$, pore width 2.4--4.2 nm). These interconnected mesoporous channels act as low-resistance electrolyte conduits that facilitate rapid ion transport into adjacent microporous active sites, reducing diffusion paths and preserving charge storage capacity at high charge-discharge rates.

Electrochemical impedance spectroscopy (EIS) provides quantitative insights into ion-transport kinetics. The Nyquist spectra (Figure 2D) display a high-frequency intercept on the real axis representing the equivalent series resistance (R_s , accounting for electrolyte resistance, current collector contact resistance, and intrinsic electrode resistance), a small high-to-medium frequency semicircle corresponding to interfacial charge-transfer resistance (R_{ct}), a 45° sloped Warburg diffusion domain (Z_w), and a steep vertical low-frequency capacitive region. Complex non-linear least squares (CNLS) fitting indicates that CSC-KOH-4 possesses the lowest equivalent series resistance ($R_s = 0.46 \Omega$) and charge-transfer resistance ($R_{ct} = 0.38 \Omega$), compared to CSC-KOH-3 ($R_s = 0.58 \Omega$, $R_{ct} = 0.62 \Omega$) and unactivated CSC-500 ($R_s = 1.15 \Omega$, $R_{ct} = 3.82 \Omega$). The shorter 45° Warburg region in CSC-KOH-4 confirms lower ion diffusion resistance within the expanded mesoporous network.

The characteristic relaxation time constant ($\tau_0 = 1/f_0$, where f_0 is the frequency at a phase angle of -45°) reflects rate response: CSC-KOH-4 achieves a short relaxation time of $\tau_0 = 0.78 \text{ s}$, compared to 1.84 s for CSC-KOH-3 and 8.45 s for CSC-500. Symmetrical coin cells based on CSC-KOH-3 deliver a maximum gravimetric energy density of 8.63 Wh kg⁻¹ at a power density of 250.0 W kg⁻¹, maintaining 5.85 Wh kg⁻¹ at an elevated power density of 4850.0 W kg⁻¹. For CSC-KOH-4, the energy density spans 7.80 Wh kg⁻¹ at 250.0 W kg⁻¹ to 6.12 Wh kg⁻¹ at 4910.0 W kg⁻¹, confirming its suitability for rapid power delivery.

Long-term galvanostatic cycling stability was evaluated in two-electrode coin cells over 10,000 consecutive cycles at 5 A g⁻¹. CSC-KOH-3 maintains 97.8% of its initial capacitance with a coulombic efficiency close to unity ($\eta \approx 99.4\%$), while CSC-KOH-4 retains 96.4%. This stability confirms that coconut shell-derived carbons possess high mechanical and electrochemical resilience in alkaline aqueous electrolytes, with negligible pore collapse or microstructural degradation during extended cycling.

Table 2. Comparative electrochemical performance of coconut-shell-derived activated carbons and related biomass-based electrode materials.

Precursor Biomass & Activation Method	Apparent S _{BET} (m ² g ⁻¹) / Porosity (cm ³ g ⁻¹)	Electrolyte & Testing Configuration (Mass Loading)	Specific Capacitance	Rate Retention Capability	Cycling Stability (% Retention / Cycles)	Reference
Coconut Shell (KOH 4:1, 800 °C, 2 h)	2228 / 1.14	6 M KOH, 3-electrode ($\approx 2.0 \text{ mg cm}^{-2}$)	367 F g ⁻¹ at 0.3 A g ⁻¹	62.0% at 10 A g ⁻¹	93.1% / 10,000	[6]
Coconut Shell (KOH activation)	1650 / 0.82	PVA/KOH gel, 2-electrode solid-state	158 F g ⁻¹ at 1.0 A g ⁻¹	58.2% at 5 A g ⁻¹	91.4% / 5,000	[7]

Coconut Shell (CO₂ physical activation)	840 / 0.45	6 M KOH, 3-electrode (2.5 mg cm ⁻²)	145 F g ⁻¹ at 0.5 A g ⁻¹	51.0% at 5 A g ⁻¹	94.0% / 5,000	[12]
Agricultural Crop Residues (KOH activation)	1820 / 0.96	6 M KOH, 2-electrode (3.0 mg cm ⁻²)	215 F g ⁻¹ at 0.5 A g ⁻¹	71.4% at 10 A g ⁻¹	92.5% / 5,000	[10]
Coconut Shell (CSC-KOH-3, this study)	2160 / 1.12	6 M KOH, 3-electrode / 2-electrode (3.0 mg cm ⁻²)	314.8 F g ⁻¹ (3E) / 248.6 F g ⁻¹ (2E)	76.5% at 10 A g ⁻¹	97.8% / 10,000	This work
Coconut Shell (CSC-KOH-4, this study)	1890 / 1.18	6 M KOH, 3-electrode / 2-electrode (3.0 mg cm ⁻²)	278.2 F g ⁻¹ (3E) / 224.5 F g ⁻¹ (2E)	83.1% at 10 A g ⁻¹	96.4% / 10,000	This work

Note: S_{BET} denotes the apparent BET specific surface area. Porosity values represent total pore volume. 3E and 2E denote three-electrode and two-electrode configurations, respectively. Rate retention and cycling stability values are reproduced as provided; verify them against the cited references and experimental data before publication.

4. Scope Limitations and Practical Engineering Considerations

While the experimental findings confirm the efficacy of chemical activation for tailoring porous carbon architectures, several processing and economic considerations warrant discussion:

- 1. Precursor Compositional Variability:** Although the coconut shells in this investigation were procured from a single source to maintain internal reproducibility, natural lignocellulosic fractions vary according to geography, regional soil salinity, tree age, and climatic conditions. Such compositional variations will influence volatile release and carbonization yields. Implementing this synthesis at larger scales requires standardized proximate composition and ash screening protocols to calibrate thermal treatment profiles.
- 2. Reagent Consumption and Environmental Footprint:** While high activation ratios (KOH:char ≥ 3: 1) yield developed porous networks, they impose significant chemical overhead. The synthesis consumes stoichiometric quantities of KOH, requires concentrated hydrochloric acid for post-synthesis neutralization, and produces large volumes of saline wastewater during neutral washing. Furthermore, the total mass yield of 9.2 wt% in CSC-KOH-4 highlights substantial carbon loss via gasification. Industrial implementation must evaluate potassium recovery cycles and prioritize activation ratios (such as 2: 1 to 3: 1) that balance capacitive performance against synthetic mass yield and chemical resource intensity.
- 3. Electrolyte and Practical Device Parameters:** The present electrochemical evaluation was carried out in aqueous 6 M KOH across a 1.0 V operating cell voltage window. While aqueous alkaline electrolytes offer high ionic conductivity and low cost, their thermodynamic operational voltage is limited by water splitting (HER and OER). Future investigations should explore the performance of these tailored hierarchical carbons in organic electrolytes (such as 1 M TEABF₄ in acetonitrile) or ionic liquids to expand the operating voltage window to 2.7--3.2 V, thereby improving the achievable gravimetric energy density of the fully assembled supercapacitor devices.

5. Conclusions

This study provides a systematic investigation into the influence of KOH activation severity on the textural, microstructural, and electrochemical properties of activated carbons derived from coconut shell waste. By controlling the chemical activation stoichiometry, the carbon pore architecture was systematically tuned from an unactivated template into a dense microporous network, and subsequently into a broadened micro-mesoporous matrix. The optimal activation ratio of 3: 1 w/w (CSC-KOH-3) maximized the development of sub-nanometer slit pores (< 1.5 nm), yielding an apparent BET specific surface area of 2160 m² g⁻¹, a micropore volume of 0.84 cm³ g⁻¹, and gravimetric capacitances of 314.8 F g⁻¹ (in a three-electrode half-cell) and 248.6 F g⁻¹ (in a

symmetric two-electrode coin cell) at 0.5 A g^{-1} in 6 M KOH. However, at elevated current densities, ion transport within this microporous framework encounters diffusion limitations.

Increasing the activation severity to a 4: 1 w/w ratio (CSC-KOH-4) induced structural pore-wall coalescence, generating a micro–mesoporous architecture ($V_{\text{meso}} = 0.50 \text{ cm}^3 \text{ g}^{-1}$, pore width 2.4–4.2 nm). This widened pore network reduced the equivalent series resistance (0.46Ω) and shortened the relaxation time constant to 0.78 s, delivering an improved rate retention of 83.1% at 10 A g^{-1} (compared to 76.5% for CSC-KOH-3). Symmetrical coin-cell supercapacitors exhibited high electrochemical stability, retaining 97.8% of initial capacitance over 10,000 continuous charge–discharge cycles at 5 A g^{-1} . These results demonstrate the structural trade-off between total surface area, ion-transport kinetics, and synthetic mass yield, providing clear guidelines for designing biomass-derived carbon electrodes tailored for high-rate supercapacitor applications.

Declarations

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Conflicts of Interest / Competing Interests

- The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

- The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Ethics Approval and Consent to Participate

- Not applicable. This study does not involve human participants, animal experiments, or tissue samples.

Consent for Publication

- Not applicable.

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