

Research Papers

Scalable synthesis of biomass-derived three-dimensional hierarchical porous activated carbons for electrochemical energy storage and hydrogen physisorption

Aravindha Raja Selvaraj^{a,b}, Nikolaos Kostoglou^c, Rajmohan Rajendiran^a, Inho Cho^a, Claus Rebholz^d, Nagarajan Deepan Chakravarthi^a, Kandasamy Prabakar^{a,*}

^a Department of Electrical Engineering, Pusan National University, 2 Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 46241, Republic of Korea

^b School of Chemical, Biological and Battery Engineering, Gachon University, Seongnam-si 13120, Gyeonggi-do, Republic of Korea

^c Department of Materials Science, Montanuniversität Leoben, 8700 Leoben, Austria

^d Department of Mechanical and Manufacturing Engineering, University of Cyprus, 2109 Nicosia, Cyprus

ARTICLE INFO

Keywords:

Hierarchical porous carbons
Supercapacitor energy storage
Hydrogen storage
Pouch cell
QSDFT gas sorption analysis

ABSTRACT

Pore structure properties such as specific surface area, pore volume, and pore size distribution are important considerations when using nanoporous carbons as electrochemical energy storage and H₂ storage materials. In this work, the Quenched Solid Density Functional Theory (QSDFT) analysis is employed to study the nanopore structure of hierarchical porous carbon (HPC) materials derived from bamboo chopsticks (BCS) by adopting a few-step chemical activation method. The effect of carbonization temperature (600–800 °C) and inorganic activator ratio on the surface chemistry and properties of HPC materials are investigated along with the way this influences the energy storage and H₂ storage performances. The as-prepared materials exhibit high surface area (1439–1940 m² g⁻¹) and porosity, which is achieved even with a low KOH:BCS ratio. The supercapacitor (SC) HPC material processed at 800 °C and a KOH:BCS of 2:1, showed a good capacitive performance of 360 F g⁻¹ at a current density of 0.5 A g⁻¹ and exhibited a superior rate characteristic along with excellent electrochemical stability. A symmetrical SC reached a specific energy of over 75.3 Wh kg⁻¹ and a specific power of 375 W kg⁻¹ in an organic electrolyte. Furthermore, pouch cell type SC devices are fabricated to light LEDs. The hydrogen uptake of all the HPC samples is above 2 wt% (at 77 K and 1 bar) with the highest being 2.3 wt% for the sample processed at 700 °C due to its higher micropore volume. This study proposes a feasible low-cost method to convert waste biomass and exploit the desired hierarchical porous carbon material for multifunctional storage applications.

1. Introduction

There has been growing interest in waste management systems for the sustainable development of energy production and storage application [1,2]. In this sense, reduction, reuse, and recycling are three elementary building blocks to accelerate the sustainable development goals and attain a fossil-fuel free civilization [3]. Solid waste materials (biomass) can be recycled into biochar, which could be used in energy storage applications as sustainable resources for renewable energy applications [4]. The growing need for renewable energy sources has sparked a lot of research interest recently in energy storage technologies due to contemporary civilization development [5,6]. Researchers are

especially relying on supercapacitors (SCs) due to their high-power density, fast charge-discharge capability, and cyclic stability [7]. SCs may be divided into two types based on their operating mechanisms: pseudo-capacitors (PCs), that employ faradaic processes to store charge on the electrode, and electrochemical double layer capacitors (EDLCs) which use reversible ion electrosorption at the surface or inside pores to store charge [7,8]. On the other hand, hydrogen (H₂) gas is the ideal energy carrier for long-term energy storage applications and the most promising alternative solution to fossil fuels due to its higher gravimetric energy density and environmentally friendly nature [9,10]. Hydrogen can be stored in multiple ways such as in compressed or liquefied form, incorporated in metal hydrides via chemical storage or stored in porous

* Corresponding author.

E-mail address: prabakar@pusan.ac.kr (K. Prabakar).

<https://doi.org/10.1016/j.est.2024.112085>

Received 16 November 2023; Received in revised form 9 January 2024; Accepted 12 May 2024

Available online 28 May 2024

2352-152X/© 2024 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

adsorbents through a solid-state physisorption process [11]. A plethora of nanoporous materials have been proposed for H₂ storage since they have high H₂ uptake, reversible charge/release behavior and fast kinetics while drastically minimizing the occupied H₂ volume needed [8,11].

To fulfill the requirement of both SCs and hydrogen adsorption characteristics, nanoporous carbon materials have been synthesized with tuned characteristics such as large specific surface area (SSA), specific pore volume (SPV), pore size distribution (PSD) and good ion/gas sorption behavior [11–13]. The nitrogen adsorption at 77 K characterization technique is widely used to evaluate the pore structure properties of nanoporous carbons by measuring the adsorption of nitrogen gas on the carbon surface [14,15]. The adsorption data are normally analyzed using isotherm models such as the Brunauer–Emmett–Teller (BET) method [16]. Despite its widespread use, the classical BET method may not be applicable for microporous materials [17]. Therefore, in this work, we have analyzed the pore structure properties of nanoporous carbons by the Quenched Solid Density Functional Theory (QSDFT) model, which considers the energetic and geometrical heterogeneities of nanoporous carbon surfaces [12,18]. The biomass derived activated carbon (AC) structure's graphitization degree, surface wettability and its surface functionalization can be tailored through various contemporary pyrolysis techniques methods [19–22]. Moreover, the hierarchical porosity (a combination of micro, meso or macropores) is believed to enhance the energy storage performance (specific capacitance, energy, and power densities) and H₂ uptake of porous carbon electrodes [23–25]. The electrochemical characteristics of electrode materials are significantly influenced by the carbon's hierarchical pore structure. The accumulation of electrical charge at the electrode/electrolyte interface is the primary mechanism for the charge storage in porous carbons with significant micropores (<2 nm), which offer high surface area and hence yields significant specific capacitance and a substantial energy density [26,27]. Furthermore, the large ion-transport pathways are favored by the superior mesopores (250 nm) and a certain quantity of macropores (>50 nm), which shorten the transmission distances, ensuring high-rate capability and high-power density of supercapacitors [26,28]. Modern research has focused on increasing the energy density of AC electrodes without losing their inherent high-power density and long cycle life, since many AC electrode materials have low energy density in symmetric supercapacitors (SSC), which limits their potential practical applications [29,30]. The energy density of SSC is determined not only by the electrodes used but also the electrolyte utilized, since the aqueous electrolyte suffers from low operational voltage due to water decomposition [30,31]. Even though a neutral aqueous electrolyte was initially used in this study with the potential window maximum of 2.0 V for a full cell, it was further increased beyond 2.0 V in symmetric supercapacitors with an organic electrolyte with improved cell voltage and the energy density ($E = 0.5 \text{ CV}^2$) [29,32].

With all these comprehensive considerations in mind, choosing raw materials and their activation is the crucial factor to achieve high SSA and bimodal porosity [4,21]. Disposed bamboo wooden chopsticks can be used as raw material for biochar due to its abundant natural source, cheap availability and high yield through put of carbon [30,31,33,34]. In this study, mandarin bamboo chop sticks (BCS) have been successfully converted into hierarchical porous activated carbon (HPC) through a simple and cost-effective activation process. The influence of chemical activator inorganic salt and activation temperature for the tuning of the structure, morphology and PSD have been investigated. Additionally, the SSA, SPV and PSD were analyzed by the QSDFT technique. The highest specific capacitance of 360 F g^{-1} has been achieved by the HPC processed at 800°C with an energy density of 75.3 W h kg^{-1} at 375 W kg^{-1} for a symmetrical SC in an organic electrolyte. In addition, HPC processed at 700°C shows the largest gravimetric hydrogen uptake of 2.3 wt% at 1 bar and 77 K.

2. Experimental section

2.1. Materials & preparation of HPCs

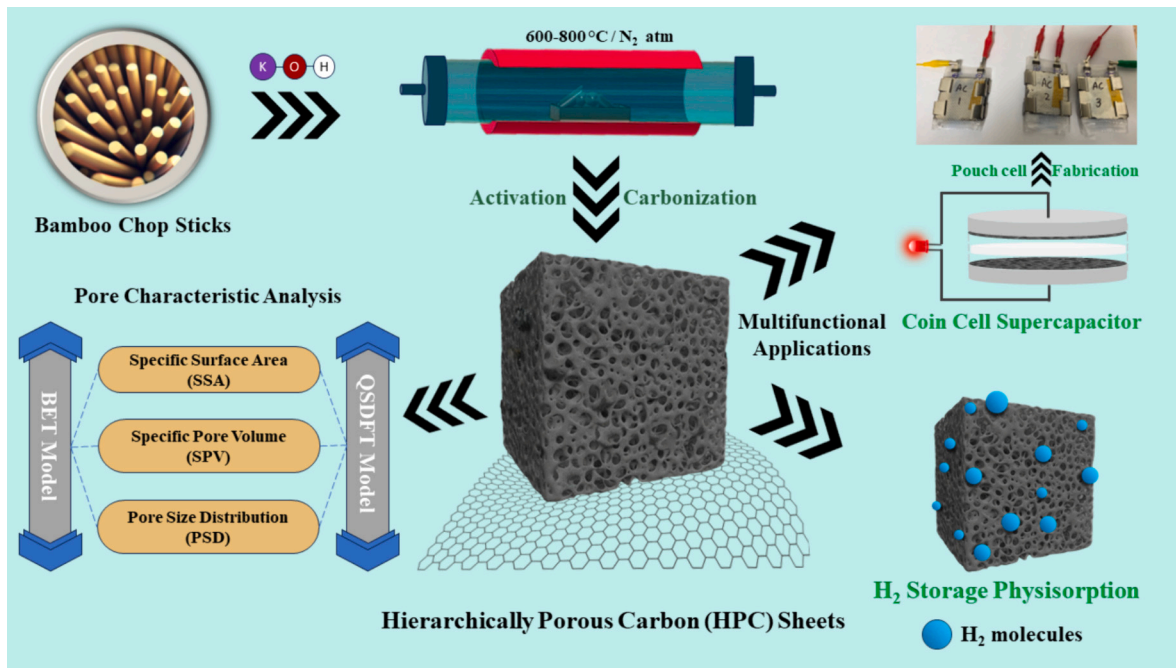
KOH, hydrochloric acid (HCl), poly-vinylidene fluoride (PVDF) and N-methyl-2-pyrrolidinone were purchased from Sigma Aldrich and carbon cloth (CC) was received from MTI Corporation, South Korea. All reagents were of analytical grade and used as received without further purification. The BCS were gathered from local restaurants (Busan City, South Korea). The preparation process schematic for HPC is demonstrated in Scheme 1. The raw sticks were cut into smaller sticks, rinsed repetitively in double distilled (DD) water, and dried overnight in an air-dry oven at 100°C . In a mortar, the dry wood was then ground into a fine powder. In the next step, it was pre-carbonized in a muffle furnace at 300°C for 4 h and subsequently the pre-carbonized samples were mixed with KOH flakes at a mass ratio of 1:1. The mixture was transferred to an alumina crucible and carbonized in a tubular furnace to 600°C , 700°C , and 800°C at a rate of 3°C min^{-1} for 4 h under an N₂ atmosphere. The activated samples were then washed with 10 % HCl and DD water until they reach a neutral pH. After that, the samples were dried overnight at 100°C . These ACs are marked as HPC-600, HPC-700 HPC-800 and HPC-800(2), where the first number represents the activation temperature and (n) the mass ratio of KOH to the raw carbon material (see Table TS1 in SI).

2.2. Physicochemical characterization

The morphologies of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, S-2400, Hitachi) under 20 kV and using high-resolution transmission electron microscopy (HRTEM, JEOL 3010, 200 kV). The structures, composition, and elemental analysis were performed by XRD (Rigaku, Powder XRD measurement), Raman (XperRam 200 (Nano Base, Korea) and XPS (ESCALab 250). The low-pressure (0–1 bar) gas adsorption and desorption isotherms were recorded at 77 K using an Anton Paar QuantaTech Autosorb-iQ³ manometric gas sorption analyzer and ultrapure (99.999 %) N₂ and H₂ as adsorbates. Prior to the gas sorption measurements, carbon powder samples of ~40 mg were degassed under high vacuum (10^{-6} mbar) at 250°C for 24 h with the aim to remove physisorbed species from their external surface and internal pore structure. The SSA was calculated by applying the multipoint BET method, following the BET consistency criteria (ISO 9277:2010) for the N₂ adsorption data in the relative pressures (P/P_0) between 0.005 and 0.15, as well as the QSDFT method using the N₂-carbon adsorption transition kernel at 77 K for slit and cylindrical pores. The total pore volume (TPV), micropore volume, PSD and mean pore size were also estimated using the QSDFT method. The ASiQWin software provided by Anton-Paar QuantaTec was used for QSDFT analysis. The contact angle (CA) of water and electrolytes were measured with a contact angle instrument (DSA100 KRÜSS). The XRD, XPS, and FESEM at the Korea Basic Science Institute (KBSI-Busan).

2.3. Electrochemical characterization

All electrochemical measurements were carried out using a biologic electrochemical workstation (Biologic SP150). The electrochemical behavior of all HPC electrode materials were characterized by conventional three electrode configurations with 6 M KOH electrolyte, whereas two-electrode coin cell SSC were assembled with 1 M LiPF₆ organic electrolyte for the electrochemical measurements, including galvanostatic charge/discharge (GCD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and cyclic longevity. The electrode preparation, electrochemical measurement methodologies and electrochemical calculations are given in the Supplementary Information (SI) [35].



Scheme 1. Schematic of the synthesis and fabrication of the HPC nanosheets derived from bio-wastes.

3. Results and discussion

3.1. Material characterization

3.1.1. Gas sorption and material structure analysis

The N_2 adsorption–desorption measurements were used to evaluate the pore structure characteristics of the carbon samples at different activation steps (Fig. 1). Fig. 1a shows the nitrogen adsorption–desorption isotherms recorded at 77 K for the HPC materials. All carbons demonstrate combined Type I and Type IV isotherms, according

to the IUPAC classification [36], which describe microporous (pore sizes below 2 nm) and mesoporous (pore sizes between 2 and 50 nm) materials, respectively [37]. The enhanced N_2 adsorption behavior at lower relative pressures is clearly attributed to dominant microporosity, while the characteristic Type H4 hysteresis loop formed between the adsorption and desorption branches at higher relative pressures is related to capillary N_2 condensation due to mesoporosity [37,38]. The characteristic “step-down” at the closure point of the hysteresis loop implies that the desorption mechanism involves cavitation induced N_2 evaporation from the mesopores via spontaneous formation of vapor bubbles in the

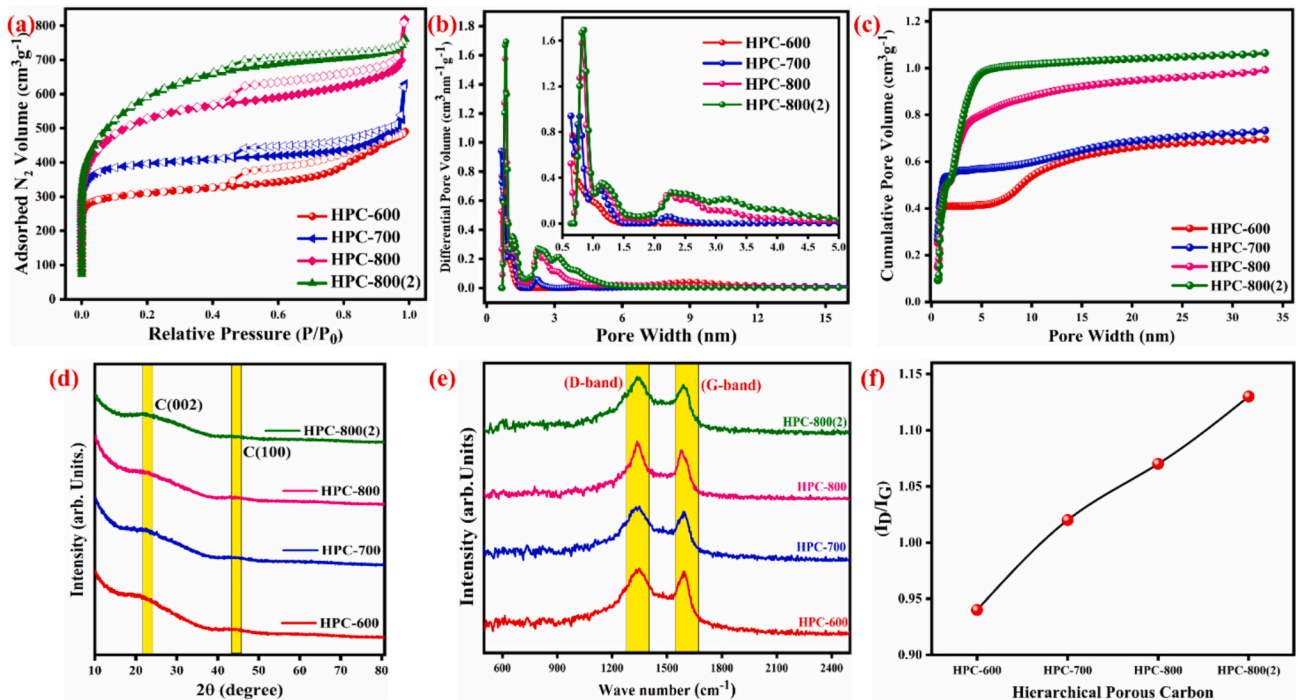


Fig. 1. (a) N_2 adsorption-desorption isotherms, (b) PSD curves, (c) SPV with different ranges of pore size (d) powder XRD patterns, (e) Raman spectra and (f) comparison of I_D/I_G ratio for the HPC at various temperatures.

condensed N₂ [39]. All the isotherms do not reach a clear saturation plateau at the maximum relative pressure because of N₂ condensation in macropores (pore sizes beyond 50 nm) and/or adsorption onto external surfaces. The Fig. 1b and c depict the differential PSD analysis and the cumulative pore volume as a function of the pore size, respectively, as derived by the QSDFT method. In Fig. 1b, HPC-600 shows a distinctive maximum at ~0.65 nm followed by two very broad/low-intensity peaks centered at 4.3 and ~9 nm, thus revealing the presence of ultra-micropores and mesopores, while HPC-700 has a four-modal distribution at ~0.65, ~0.8, ~1.1 and ~2.3 nm, thus highlighting mainly the presence of ultra-micropores and super-micropores [40]. The samples activated at 800 °C (HPC-800 and HPC-800(2)) demonstrate comparable peak maxima at ~0.85, ~1.15, ~2.3 and ~3.2 nm, as observed in Fig. 1b, thus indicating the existence of super-micropores and small mesopores [18,39]. However, these samples exhibit the highest cumulative pore volumes for pore sizes below 35 nm, as evidenced in Fig. 1c. The pore structure properties of the activated carbon materials, including SSA, SPV, micropore volume and average pore width, are also summarized in Table 1. The HPC-800 and HPC-800(2) samples exhibit the highest surface area and pore volume values and the largest mean pore widths among all studied carbons, as derived by the BET and QSDFT methods. However, HPC-700 combines the highest micropore volume fraction (72 %) and the smallest mean pore width (0.75 nm) among all studied samples. It should be noted that the absolute micropore volume of HPC-700 is comparable to the micropore volumes of the samples activated at 800 °C, despite its lower total pore volume. In addition, the lowest surface area and pore volume sample, HPC-600, demonstrates the second highest micropore volume fraction (58 %) and the second smallest mean pore width (0.85 nm). Hence, both HPC-700 and HPC-600 have a higher relative micropore content compared to the samples activated at 800 °C where the contribution of mesopores seems to be more significant.

The XRD patterns (Fig. 1d) provide further information on the phase structure of the HPC samples. All HPC materials display a broad diffraction peak at around $2\theta = 23.7^\circ$ and a weak diffraction peak at around 44.1° , indicating the turbostratic form of the carbonaceous material [28,41]. The broad diffraction peaks indicate the amorphous and porous nature of the HPC materials [27]. To learn more about the graphitic structure of the HPC materials, Raman spectra were collected and analyzed (Fig. 1e). Characteristic peaks observed at around $1340\text{--}1350\text{ cm}^{-1}$ (D-band) and $1582\text{--}1590\text{ cm}^{-1}$ (G band) is attributed to the defective sp³ carbon crystallites and the vibration of sp² carbon graphitic structure, respectively [41]. The relative intensity ratio of the D-band to the G-band (I_D/I_G) are extensively adopted to evaluate the graphitization degree of HPC materials. The calculated I_D/I_G values for HPC-600, HPC-700, HPC-800, and HPC-800(2) were 0.94, 1.02, 1.07

and 1.13, respectively. Fig. 1f indicates that the obtained carbon materials treated at higher activation temperatures possess a lower graphitization degree and higher amount of crystal defects [41]. The higher I_D/I_G value for HPC-800(2) signifies the higher degree of carbon material disorder with high porosity. The defects in hierarchical porous carbons can improve wettability, i.e., are greatly beneficial for the improvement of electrolyte ion adsorption [42].

3.1.2. Morphological studies

The pre-carbonized BCS display a sheet-like graphitic carbon structure with a smooth surface having only macropores as illustrated in Fig. S1a. Fig. 2 depicts the microstructure evolution in KOH activated HPCs materials. After pyrolysis (Fig. 2a), a substantial number of tiny pores emerged at the surface/edges of the carbon skeleton in HPC-600 due to the thermal decomposition/reaction of intercalated metallic potassium over the surface/edges of graphitic carbon [42,43]. An increase in annealing temperature (HPC-700, HPC-800), i.e., a prolonged continuous activation process, resulted in interconnected hierarchical porous carbon sheets with honeycomb-like structure [44]. The addition of KOH salt (HPC-800(2)) also catalyzes the porous formation as shown in Fig. 2d, since a thick sheet-like structure has been preserved with hierarchical porosity.

The HRTEM images of the HPCs processed at different temperatures (Fig. 3(a–d)) further confirm the hierarchical porous sheet-like structure of the HPCs. From the HRTEM image shown in Fig. 3a, one can see that a small number of pores are present at the surface of the carbon skeleton, indicating that the sample is moderately porous. With an increase in carbonization temperature (700 °C), HPC-700 (Fig. 3b) showed a hierarchical porous sheet structure with the additional white spots (see Fig. 3f) on the carbon surface, which clearly indicates dominant microporosity [41,42]. Further increasing the temperature (HPC-800), there is also the formation of disorderiness in the edges of carbon layers along with the large amounts of white spots (micropores) on the hierarchical porous carbon sheets (Fig. 3f), which suggests that abundant macropores and mesopores exist in the activated carbon. It is ascribed that the intercalated metallic K compounds (KOH activation) easily react with graphitic layers in carbon structure at a specific temperature, a high degree of porous disordered structure [45,46].

Even after doubling the activating agent, the honeycomb-like hierarchical porous sheet-like structure (Fig. 3d) is still preserved in HPC-800(2). Also, HPC-800(2) (Fig. 3h) showed an interconnected network diverging into two distinct regions, one with visible graphitic ribbons in the surface of the edge's region (see red circles), indicating a higher degree of graphitization, as well as an abundance of homogeneous amorphous micropores (see blue circles) and a certain amount of irregular mesopores on the surface of carbon [42,47]. This is consistent with the gas sorption results. The HRTEM EDAX maps of the HPC samples shown in Fig. S2(a–d), demonstrate the uniform distribution of C, O, N and a small amount of K within the samples. The incorporation of O and N on the carbon samples indicates the successful incorporation of high-density oxygenated functional groups, which are helpful for increasing the wettability of the carbon electrodes [48,49]. According to morphological studies, these hierarchical pores are connected by meso- and micropores that are embedded in the walls of the macropores. This porous structure allows the electrolyte to permeate the bulk particles and create three-dimensional channels for the efficient transportation of cations, which is useful for effective EDLC storage [47]. This is due to the removal of metallic K⁺ and its derivatives from the carbon skeleton which are helpful for the formation of supplementary micropores and in turn helpful for the enhanced physisorption of H₂ molecules via weak van der Waals interactions on the surface of the pores [50].

3.1.3. Elemental composition and chemical state of the HPC

XPS analysis was carried out to identify and quantify the surface composition of the HPCs. After activation and carbonization, only the presence of C1s, O1s and a trace amount of N1s could be observed in the

Table 1

Summary of pore structure properties deduced from N₂ adsorption data recorded at 77 K.

Sample	S_{BET} (m ² /g)	S_{QSDFT} (m ² /g)	V_{QSDFT} (cm ³ /g)	V_{QSDFT} (MP) (cm ³ /g)	V_{QSDFT} (MP)/ V_{QSDFT} (%)	$d_{50\text{-QSDFT}}$ (nm)
HPC-600	1218	1439	0.69	0.40	58	0.85
HPC-700	1564	1723	0.73	0.53	72	0.75
HPC-800	1747	1813	0.99	0.52	52	1.41
HPC-800 (2)	2147	1940	1.06	0.53	50	2

S_{BET} : Brunauer-Emmet-Teller (BET) area, S_{QSDFT} : cumulative surface area for pores smaller than 33 nm in width calculated by the Quenched Solid Density Functional Theory (QSDFT) method for slit and cylindrical pores, V_{QSDFT} : cumulative pore volume for pores smaller than 33 nm in width derived by the QSDFT method, $V_{\text{QSDFT(MP)}}$: cumulative micropore volume derived by the QSDFT method, $V_{\text{QSDFT(MP)}/V_{\text{QSDFT}}}$: percentage of micropore volume to total pore volume ($(V_{\text{QSDFT(MP)}/V_{\text{QSDFT}}}) \times 100\%$), $d_{50\text{-QSDFT}}$: volume-weighted median of the pore width as derived by the cumulative pore volume.

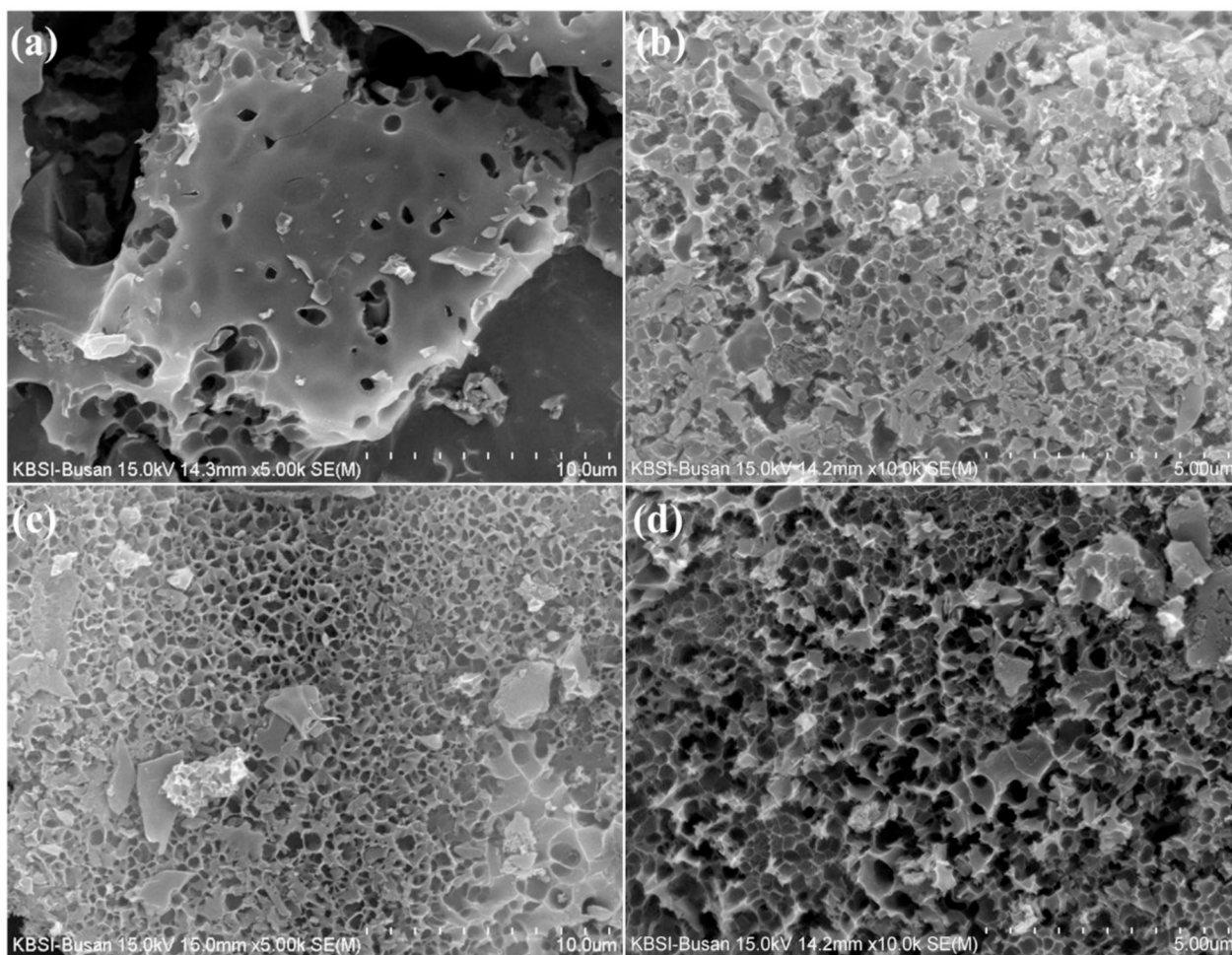


Fig. 2. Evolution of BCS derived HPC: FE-SEM images of the as-synthesized (a) HPC-600, (b) HPC-700, (c) HPC-800 and (d) HPC-800(2).

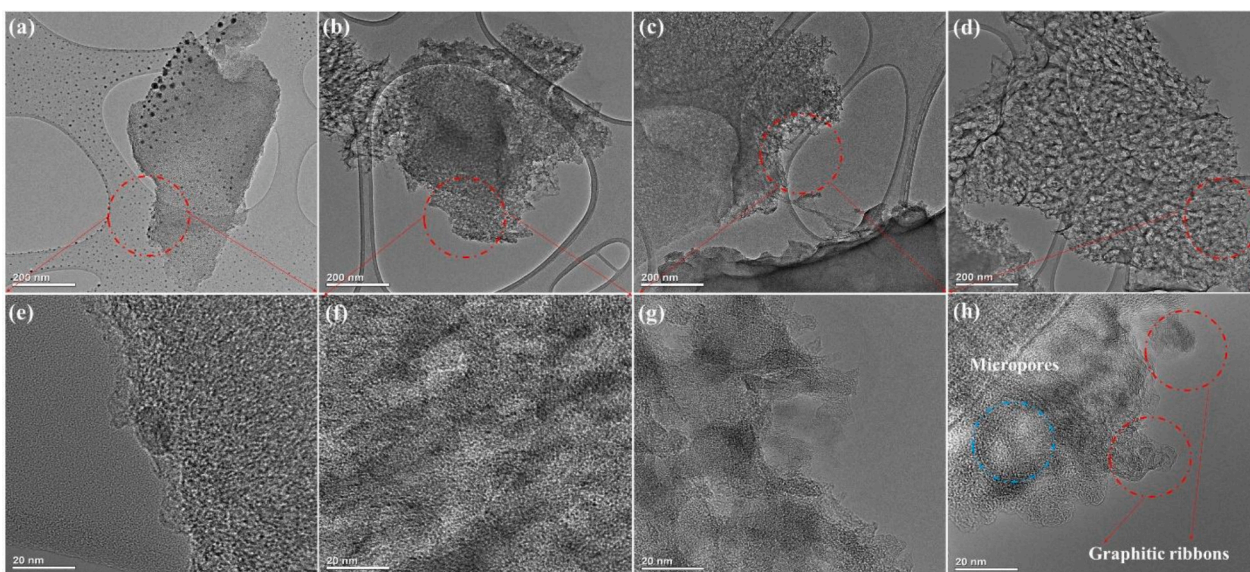


Fig. 3. HRTEM images of BCS derived HPCs at different pyrolysis temperatures, (a) HPC-600, (b) HPC-700, (c) HPC-800, (d) HPC-800-2 and (e, f, g, h) higher magnification images of respective HPCs.

studied materials (Fig. S3 and Table TS3). The deconvoluted C1s and O1s XPS spectra are shown in Fig. 4. The high-resolution C 1s spectrum (Fig. 4a) was deconvoluted into five peaks and it shows a major peak at

284.5 eV, revealing the presence of hybridized sp^3 C—C/ sp^2 C=C graphitic carbon, belonging to the carbon skeleton of the material [50,51]. The presence of other peaks such as C—OH/C—H (285.8 eV),

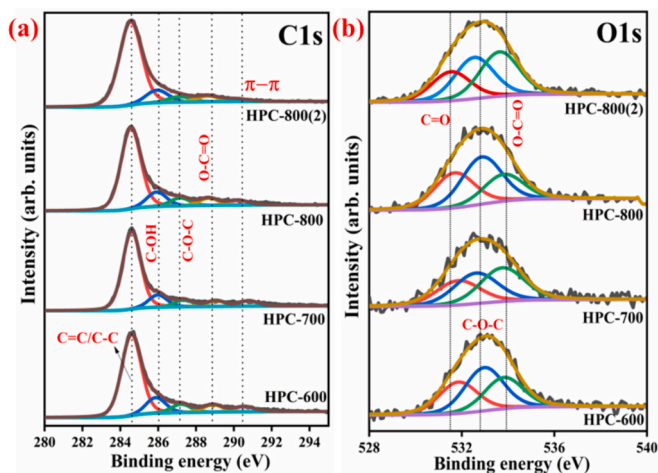


Fig. 4. High-resolution HPC XPS spectra of (a) C1s, and (b) O1s at different temperatures.

C—O—C (287.4 eV), O—C=O (288.6 eV) and a satellite peak of $\pi-\pi^*$ (291.6 eV) in the higher-binding energy region indicates the formation of abundant conjugated systems during the annealing process [42,50]. The O 1s XPS spectra (Fig. 4b) shows three peaks located at 531.53 eV, 532.54 eV and 533.63 eV attributable to the C=O, C—O—C and C—OH functional groups [50,52]. A sizable number of oxygen functional groups have formed on the surface of the HPCs after carbonization and activation [48,53]. As the pyrolysis temperature increased (see Table TS4), the ratio of functional groups containing oxygen increased, indicating that the HPCs were oxidized during the KOH activation process [42,50]. As a result of the oxygen functional groups favoring the electrode material's wettability, the electrolyte ions distribute at the surface of the active material quickly, improving the performance and high-rate capability of electrode materials [42,54].

The wettability of HPCs and pre-carbonized BCS was evaluated by contact angle measurements (Fig. S4). The measurements clearly show the hydrophobicity of the pre-carbonized-BCS ($\sim 125.3^\circ$) electrode and the contact angles in all HPCs are substantially changed into hydrophilic nature, displaying significantly reduced contact angles of 88.3° , 73.2° , 64.1° and 57.7° for HPC-600, HPC-700, HPC-800, and HPC-800(2), respectively (Fig. S4). The decrease in the contact angles clearly demonstrates that the affinity of the electrode material towards the electrolyte improved significantly after activation and high temperature carbonization [42,55]. The superior wettability of the carbon material with the electrolyte promotes the rapid charge transfer from the bulk phase to the electrode/electrolyte interface, which is beneficial to its electro-sorption performance [53,56].

3.1.4. Electrochemical behavior of HPC

The electrochemical capacitive performance of HPC electrodes was assessed using a 6 M KOH aqueous electrolyte and is presented in Fig. 5. The HPC electrodes were initially quantified by CV (Fig. 5a) at a scan rate of 20 mV s^{-1} , which displays a relatively rectangular shape without redox peaks evidently reflecting their excellent double layer capacitance (EDLC) [46,57]. The HPC-800(2) has the largest integrated area of the CV curve, indicating the highest specific capacitance [41,50]. In addition, quasi-rectangular CV curves were observed and preserved even at higher scan rate of 500 mV s^{-1} for the HPC-800(2) material as shown in Fig. 5b, indicating the EDLC behavior with fast discharge/charge kinetics [57]. In Fig. 5c, the relationship between the scan rate vs. discharge current density at mid voltage (0.5 V) at different scan rates ($2\text{--}500 \text{ mV s}^{-1}$) is shown to comprehend the diffusion process. All HPC electrodes display linear current characteristics, which suggest improved ion transport into porous HPCs [42,58], among them the HPC-800(2) material evidently displays linear and superior discharge current

behavior with improved rate capability at high rate due to better electrolyte ion diffusion and sorption behavior [42,59].

Galvanostatic charge/discharge (GCD) tests were further carried out to determine the capacitive behaviors of the HPCs. The GCD profiles (Fig. 5d) of the electrodes at a current rate of 0.5 A g^{-1} exhibit nearly isosceles triangles and reaffirm the EDLC behavior [41,60]. Among the electrodes, HPC-800(2) showed an extended charge/discharge due to its higher porosity/pore volume. The GCD curves (Fig. 5e) of HPC-800(2) at various current densities maintained the symmetric triangular shapes even at a very high current density (5 A g^{-1}), which implies that the HPCs possess an outstanding electrochemical reversibility and EDLC nature [42,51]. The GCD tests (rate capability) of all HPCs at different current densities are plotted in Fig. 5f and clearly show that HPC-800(2) has the highest C_{SC} capacitance value (calculated by GCD by Eq. 1 in SI) of 359.4 F g^{-1} at 0.5 A g^{-1} . Even at a rate of 5 A g^{-1} , an intriguing capacitance value of up to 207 F g^{-1} was observed and clearly showed superfast rate behavior (84.2 % retention) mainly due to the multilevel meso-porosity of HPC-800(2), which facilitates a faster ion transfer pathway than other carbon electrodes [42,61]. Moreover, it should be noted that (from Fig. S5) comparatively HPC-600 has a lower specific capacitance and retention rate (124.4 F g^{-1} and 69.7 %). When the activation temperature and KOH ratio was increased, a far superior capacitance and rate capability was achieved due to the large SSA and pore volume which can boost the ion electro-sorption behavior [25,61]. The hierarchical porous structure with a high meso-/macropore volume helps for sufficient ion transportation and nano-sized sheet-like structures serve as short diffusion pathways to reach the adsorption sites (micropores) [46]. Also from Fig. S5, it is also worth emphasizing that the relationship between the capacitive and rate performance is linear to surface area and porosity, which is because all the pores and surface areas of the materials are effective in charge transmission and storage.

Electrochemical impedance spectra (in KOH electrolyte) were collected to gain insights into the electrochemical storage behaviors of HPC electrodes. Nyquist plots (insets: magnified view of the high-frequency region) of HPC electrodes are compared in Fig. 5g. All electrodes show steep linear curves in the low-frequency region (with an angle approximately 90°) and perfect EDLC capacitive behavior [51,62]. Furthermore, the length of the Warburg line distinguishes the resistance of electrolyte diffusion at the electrode-electrolyte interface, namely the Warburg resistance (Z_w) [42,51]. Among the HPC electrodes, HPC-800(2) has a low Warburg tail compared to the other HPC electrodes relative to the real axis, indicating that the electrode promotes rapid ion transport [42]. The inset of Fig. 5g shows the semicircle in the intermediate to high frequency region which is related to interfacial charge transfer resistance (R_{ct}). Additionally, the equivalent circuit was fitted by the Randles method (inset Fig. 5g). As seen in Table TS5, HPC-600 electrode exhibits the largest equivalent series resistance (R_s) $> 1.7 \Omega$ due to its low meso-/micropores, resulting in an ESR increase [57]. The HPC-800(2) electrode exhibits a negligible $R_{ct} = 0.07 \Omega$, and series resistance (R_s) which is lower than that of the other HPC electrodes, clearly implying their typical capacitive characteristics [59,63]. In addition, the Bode plot (Fig. 5h) clearly shows that the low frequency phase angle for all HPC electrodes is approaching 90° , indicating the double layer charge storage property [42,58]. Furthermore, the phase angle is lowered with increasing activation temperature, which proves high capacitive behavior owing to short diffusion pathways of the electrolyte ions to the electrodes [42]. According to the EIS analyses, low R_{ct} , R_s and Warburg impedance are attributed to the favorable hierarchical porous structure as well as the cohesive influence of substantial defect sites, higher graphitization degree, excellent porous channel with improvement of electronic conductivity and wettability, which can endow the HPC-800(2) material with enhanced polarization and rapid electrolyte ion/charge transportation [51,64]. Furthermore, the cyclability was investigated by continuous GCD process (5 A g^{-1}) for all HPC electrodes. The electrode HPC-800(2) retained 94.3 % cyclic stability with minimal capacitance loss, whereas other HPC electrodes

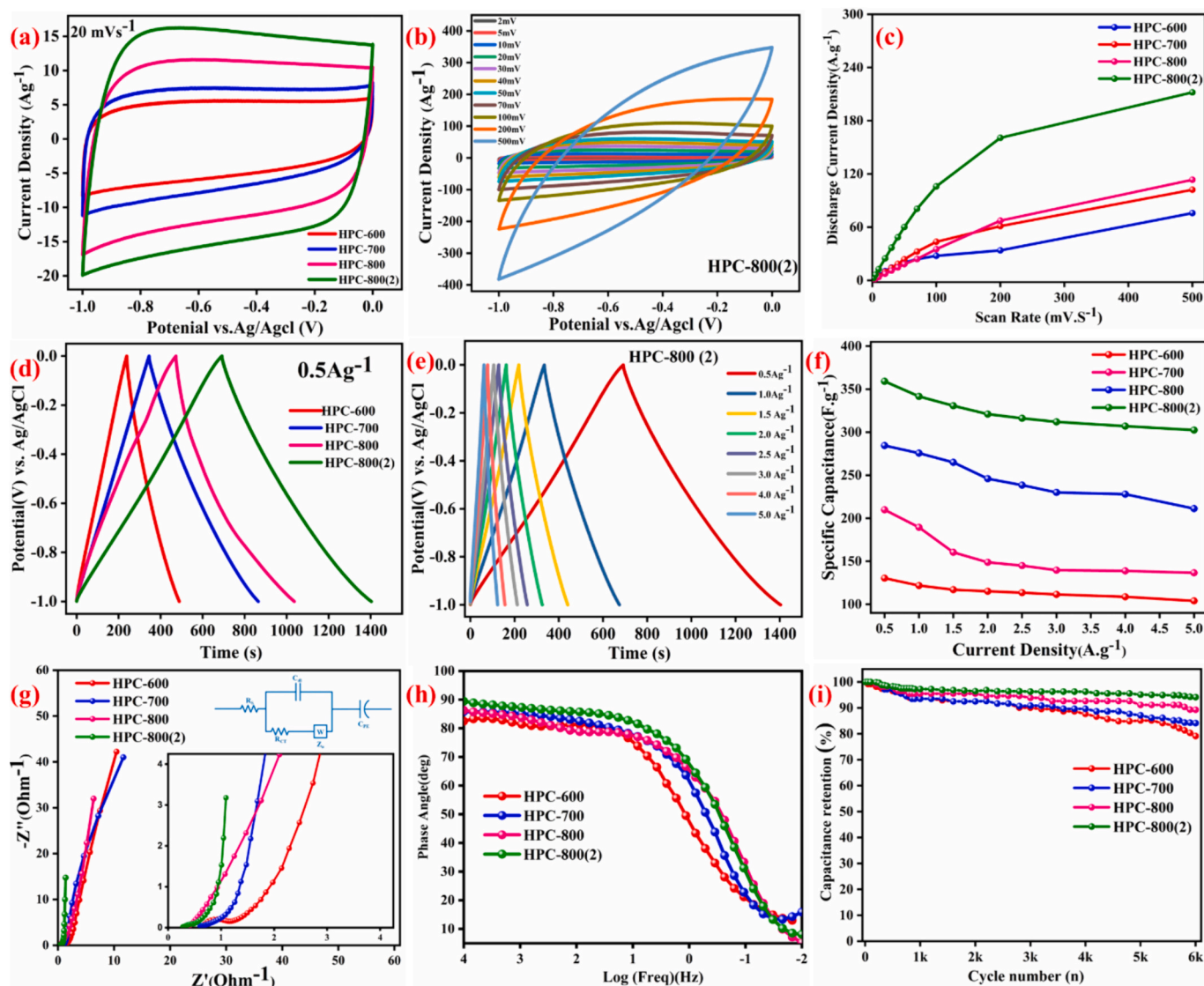


Fig. 5. Electrochemical performance of HPCs in a three-electrode system: (a) comparative CV curves at 20 mV s^{-1} , (b) CV curves of HPC-800(2) at diversified scan rates, (c) discharge current density vs. scan rate, (d) comparative GCD curves of HPC, (e) GCD curves of HPC-800(2) at current density between 0.5 and 5 A g^{-1} , (f) comparison of gravimetric specific capacitances of different HPCs, (g) Nyquist plots (inset: high-frequency region), (h) Bode plots of phase angle and impedance versus frequency and (i) cyclic stability of HPC electrodes.

(see Table TS6) retained much lesser than the initial capacitance after 6000 cycles. The high electronic conductivity and improved wettability of HPC-800(2) electrode demonstrated improved cyclic stability. The synthesized HPC-800(2) electrode showed enhanced specific capacitance, long cyclic life and rate capability values compared to that of many recent biomasses derived porous carbons (Table TS7) due to the synergistic effect of outstanding SSA and porosity, the sheet-like hierarchical pore structure ranging from macropore to mesopore and micropore along with the abundant high oxygen content on the surface, making it a promising candidate in charge storage applications.

3.1.5. Fabrication of organic symmetric supercapacitor (SSC) device

To further validate the advantages of HPC-800(2) electrochemical performance in real-time applications, the coin cell SSC was assembled with 1 M LiPF_6 organic electrolyte. To confirm the operating voltage range of this device, the CV at a scan rate of 20 mV s^{-1} (Fig. 6a) and GCD (Fig. 6b) at a current density of 1 A g^{-1} were initially assessed at various voltage ranges from 1.5 to 3.0 V at room temperature. Both rectangular shaped CV curves and symmetrical isosceles shaped charge discharge profiles were observed, suggesting ideal double layer behavior and

outstanding reversibility across the entire potential window (0 – 3.0 V) [65,66]. Furthermore, the good rectangular shape can be seen in the CV curve (Fig. 6c) of the fabricated symmetric SCs at increased sweep rates (2 to 200 mV s^{-1}) reaffirms the robustness of the electrodes. As the sweep rate increases, the current obtained is also enhanced without apparent deformation, illustrating the outstanding rate capability of the electrode materials and the synergistic effects of the high SSA and the hierarchical porous structure [27]. In Fig. 6d, the GCD curves at different specific currents (2 mA to 20 mA) demonstrated a symmetric/linear behavior over entire specific currents, thus confirming a good capacitive reversibility, which is characteristic of electrical double layer capacitance [65,67]. The long-term stability (Fig. 6e) of the HPC-800(2) coin cell SC was assessed using repeated GCD testing (at 5.0 A g^{-1}). Even after 10,000 cycles, the capacitance retention is 89.4% , demonstrating robust energy storage stability. As seen from Fig. 6f, Nyquist plots of coin cell has very low $R_s = 4.7 \Omega$ due to the intrinsic resistance of carbons and the charge transfer process at the carbon electrode-organic electrolyte interfaces [65]. In addition, a straight line is observed at the low frequency region at an angle $\sim 45^\circ$ relative to the real axis related to Warburg resistance (W) caused by the semi-ionic diffusion-controlled

process [67]. To evaluate the overall performance, the energy and power densities of coin cell SSC were calculated and presented on the Ragone plot in Fig. S6a. HPC exhibited a maximum power density (375 W kg^{-1}) along with a maximum energy density (75.3 Wh kg^{-1}) than those of other reported carbon materials, as summarized in Table TS8. This implies that the carbon material having a high SSA with optimized hierarchical pore structure and PSD improves the ability of the carbon electrode material to accept electrolyte ions and enhances the development of high-performance EDLCs [61]. To estimate the real-time practical applications of the symmetric pouch cell, the supercapacitor device was fabricated with both positive and negative electrodes coated on a stainless steel (Fig. S6b). Furthermore, it is seen that the series connected pouch cell supercapacitors can power a LED (see Fig. S6c, d & Video S1), indicating a cost-effective energy storage technology.

3.1.6. H_2 storage studies

Besides the electrochemical energy storage performance of the HPC materials, their H_2 storage capability was also studied. Low-pressure (0–1 bar) H_2 adsorption–desorption isotherms were collected at 77 K to evaluate the H_2 storage performance of the carbon samples at different activation steps (Fig. 7a). All samples demonstrate a fully reversible H_2 adsorption–desorption behavior, characteristic of the H_2 physisorption mechanism at super-critical temperatures. The HPC-700 showed the highest H_2 uptake at 1 bar (i.e., 2.3 wt% or $\sim 11.6 \text{ mmol/g}$), followed by HPC-800(2) and HCP-800 (i.e., $\sim 2.2 \text{ wt\%}$ or $\sim 11.2 \text{ mmol/g}$ for both) and HPC-600 (i.e., $\sim 2 \text{ wt\%}$ or $\sim 9.9 \text{ mmol/g}$). This is most likely because HPC-700 combines the highest micropore volume fraction (72 % of the total pore volume) and the smallest mean pore width (0.75 nm) among all samples, as determined by gas sorption analysis and observed in Fig. 7b and c. It should be noted that pores of sub-nanometer sizes/widths act as “strong” adsorption sites for molecular H_2 due to the overlapping potential fields of the opposite pore walls [68]. The H_2 storage capacities of the activated carbon materials, expressed in different units, are also summarized in Table TS9. The gravimetric H_2 uptake values presented in this work (i.e., 2–2.3 wt% at 77 K and $\sim 1 \text{ bar}$) are comparable to those of other bamboo-derived

carbons reported in the literature [69–73].

4. Conclusion

In summary, we have demonstrated a one-step synthetic strategy for the synthesis of hierarchical porous carbon with high surface areas (up to $2000 \text{ m}^2 \text{ g}^{-1}$), large pore volumes ($1.06 \text{ cm}^3 \text{ g}^{-1}$) and porosity inside the micropore-mesopore range for high energy density supercapacitors and hydrogen adsorption. Furthermore, the QSDFT method was used to investigate the micro- and mesoporosity, surface area and pore volume that are principally responsible for the ion electrosorption (supercapacitors) and hydrogen physisorption (hydrogen storage). The higher activation/carbonization temperature applied HPC-800(2) electrode exhibits a larger surface area, a tunable pore structure and improved surface wettability, and hence shows enhanced specific capacitance (360 F g^{-1} at 0.5 A g^{-1}), excellent rate capacity and cycling stability. Additionally, HPC-700 exhibits the largest hydrogen storage capacity of $\sim 2.3 \text{ wt\%}$ due to its high proportion of micropores (82.7 %) and smallest pore width (0.75 nm). Finally, we assembled symmetrical SCs from HPC-800(2), which delivered an energy density as high as 75.3 Wh kg^{-1} at a gravimetric power density of 375 W kg^{-1} . As consumed bamboo chopsticks are broadly and readily available all over the world, their collection through effective waste management systems may provide a new precursor for efficient hierarchical porous carbon materials, which are of great significance for their multifunctional applications.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.est.2024.112085>.

CRediT authorship contribution statement

Aravindha Raja Selvaraj: Data curation, Writing – original draft, Conceptualization. **Nikolaos Kostoglou:** Formal analysis, Resources, Writing – review & editing, Investigation. **Rajmohan Rajendiran:** Software, Visualization. **Inho Cho:** Validation, Visualization. **Claus Rebholz:** Writing – review & editing. **Nagarajan Deepan Chakravarthi:** Visualization. **Kandasamy Prabakar:** Funding acquisition, Project

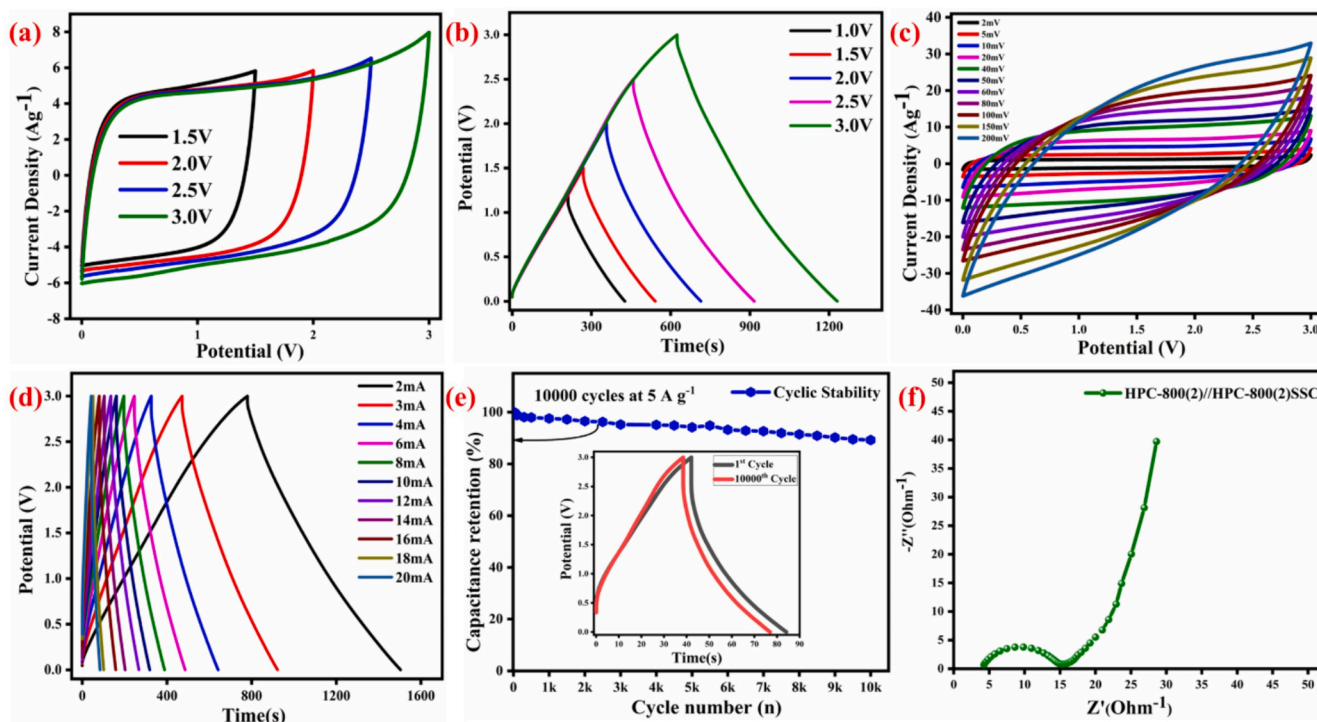


Fig. 6. Electrochemical behavior of HPC-800(2) for SSCs: (a) CV curves at various voltage windows, (b) GCD under various voltage windows, (c) CV at different scan rates, (d) GCD at different current densities, (e) cycling performance with inset showing GCD profiles at 5 A g^{-1} , (f) Nyquist plot in 1 M LIPF_6 organic electrolyte.

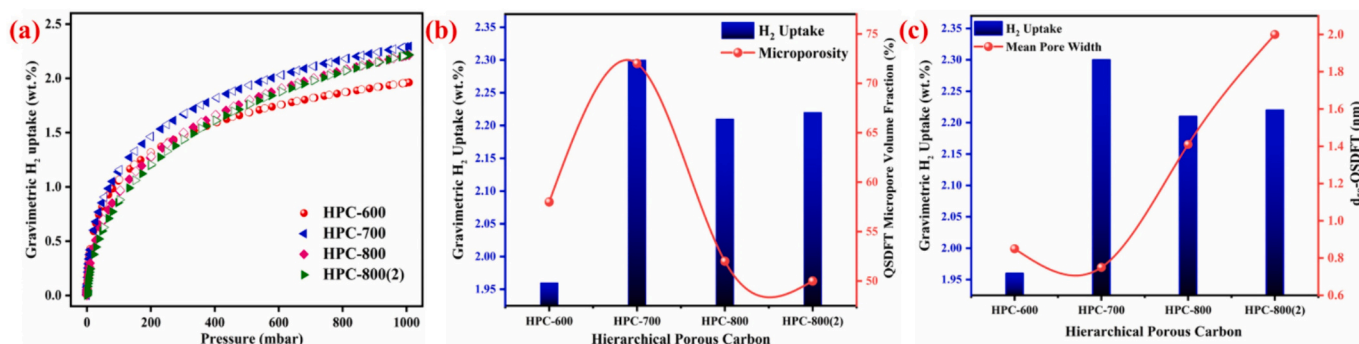


Fig. 7. (a) H₂ adsorption/desorption isotherms at 77 K, (b) correlation plot between gravimetric H₂ uptake and the micropore volume fraction as derived by the QSDFT method and (c) correlation plot between gravimetric H₂ uptake and mean pore width as derived by the QSDFT method.

administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research work was supported by the research project (NRF-2022R11A3066168) from Basic Research Laboratory through the National Research Foundations of Korea funded by the Ministry of Science, South Korea.

This work also supported by BK21 plus, Creative Human Resource Education and Research programs for ICT convergence in the 4th Industrial Revolution, Pusan National University, Busan, South Korea.

N.K. would like to thank Prof. Christian Mitterer and Prof. Oskar Paris from the Montanuniversität Leoben for providing resources and access to experimental equipment.

References

- [1] P. Newell, R. Lane, A climate for change? The impacts of climate change on energy politics, *Camb. Rev. Int. Aff.* 0 (2018) 1–18, <https://doi.org/10.1080/09557571.2018.1508203>.
- [2] M.Z. Jacobson, Review of solutions to global warming, air pollution, and energy security, *Energy Environ. Sci.* 2 (2009) 148–173, <https://doi.org/10.1039/b809990c>.
- [3] J. Green, P. Newman, Disruptive innovation, stranded assets and forecasting: the rise and rise of renewable energy, *J. Sustain. Fin. Invest.* 7 (2017) 169–187, <https://doi.org/10.1080/20430795.2016.1265410>.
- [4] K.K. Yadav, S. Krishnan, N. Gupta, S. Prasad, M.A. Amin, M.M.S. Cabral-Pinto, G. K. Sharma, R. Marzouki, B.H. Jeon, S. Kumar, N. Singh, A. Kumar, S. Rezaia, S. Islam, Review on evaluation of renewable bioenergy potential for sustainable development: bright future in energy practice in India, *ACS Sustain. Chem. Eng.* 9 (2021) 16007–16030, <https://doi.org/10.1021/acssuschemeng.1c03114>.
- [5] X. Li, J. Wang, One-dimensional and two-dimensional synergized nanostructures for high-performing energy storage and conversion, *InfoMat* 2 (2020) 3–32, <https://doi.org/10.1002/inf2.12040>.
- [6] M. Sevilla, R. Mokaya, Energy storage applications of activated carbons: supercapacitors and hydrogen storage, in: *Energy & Environmental Science*, Royal Society of Chemistry, 2014, pp. 1250–1280, <https://doi.org/10.1039/c3ee43525c>.
- [7] W. Raza, F. Ali, N. Raza, Y. Luo, K.H. Kim, J. Yang, S. Kumar, A. Mehmood, E. E. Kwon, Recent advancements in supercapacitor technology, *Nano Energy* 52 (2018) 441–473, <https://doi.org/10.1016/j.nanoen.2018.08.013>.
- [8] V. Augustyn, P. Simon, B. Dunn, Pseudocapacitive oxide materials for high-rate electrochemical energy storage, *Energy Environ. Sci.* 7 (2014) 1597, <https://doi.org/10.1039/c3ee4164d>.
- [9] Z.J. Baum, L.L. Diaz, T. Kononova, Q.A. Zhou, Materials research directions toward a green hydrogen economy: a review, *ACS Omega* 7 (2022) 32908–32935, <https://doi.org/10.1021/acsomega.2c03996>.
- [10] P. Ramirez-Vidal, R.L.S. Canevesi, G. Sdanghi, S. Schaefer, G. Maranzana, A. Celzard, V. Fierro, A step forward in understanding the hydrogen adsorption and compression on activated carbons, *ACS Appl. Mater. Interfaces* 13 (2021) 12562–12574, <https://doi.org/10.1021/acsami.0c22192>.
- [11] T. Rimza, S. Saha, C. Dhand, N. Dwivedi, S.S. Patel, S. Singh, P. Kumar, Carbon-based sorbents for hydrogen storage: challenges and sustainability at operating conditions for renewable energy, *ChemSusChem* 15 (2022), <https://doi.org/10.1002/cssc.202200281>.
- [12] N.M. Musyoka, B.K. Mutuma, N. Manyala, Onion-derived activated carbons with enhanced surface area for improved hydrogen storage and electrochemical energy application, *RSC Adv.* 10 (2020) 26928–26936, <https://doi.org/10.1039/d0ra04556j>.
- [13] A. Ariharan, K. Ramesh, R. Vinayagamoorathi, M.S. Rani, B. Viswanathan, S. Ramaprabhu, V. Nandhakumar, Biomass derived phosphorous containing porous carbon material for hydrogen storage and high-performance supercapacitor applications, *J. Energy Storage* 35 (2021), <https://doi.org/10.1016/j.est.2020.102185>.
- [14] K. Sing, The use of nitrogen adsorption for the characterisation of porous materials, www.elsevier.nl/locate/colsurfa, 2001.
- [15] C. Schlumberger, M. Thommes, Characterization of hierarchically ordered porous materials by physisorption and mercury porosimetry—a tutorial review, *Adv. Mater. Interfaces* 8 (2021), <https://doi.org/10.1002/admi.202002181>.
- [16] R. Bardestani, G.S. Patience, S. Kaliaguine, Experimental methods in chemical engineering: specific surface area and pore size distribution measurements—BET, BJH, and DFT, *Can. J. Chem. Eng.* 97 (2019) 2781–2791, <https://doi.org/10.1002/cjce.23632>.
- [17] F. Ambroz, T.J. Macdonald, V. Martis, I.P. Parkin, Evaluation of the BET theory for the characterization of meso and microporous MOFs, *Small Methods* 2 (2018), <https://doi.org/10.1002/smt.201800173>.
- [18] A.V. Neimark, Y. Lin, P.I. Ravikovitch, M. Thommes, Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons, *Carbon* 47 (2009) 1617–1628, <https://doi.org/10.1016/j.carbon.2009.01.050>.
- [19] Z. Gao, Y. Zhang, N. Song, X. Li, Biomass-derived renewable carbon materials for electrochemical energy storage, *Mater. Res. Lett.* 5 (2017) 69–88, <https://doi.org/10.1080/21663831.2016.1250834>.
- [20] Z. Bi, Q. Kong, Y. Cao, G. Sun, F. Su, X. Wei, X. Li, A. Ahmad, L. Xie, C.M. Chen, Biomass-derived porous carbon materials with different dimensions for supercapacitor electrodes: a review, *J. Mater. Chem. A Mater.* 7 (2019) 16028–16045, <https://doi.org/10.1039/c9ta04436a>.
- [21] M.L. Divya, S. Natarajan, Y.S. Lee, V. Aravindan, Biomass-derived carbon: a value-added journey towards constructing high-energy supercapacitors in an asymmetric fashion, *ChemSusChem* 12 (2019) 4353–4382, <https://doi.org/10.1002/cssc.201901880>.
- [22] S. Kumar, G. Saeed, L. Zhu, K.N. Hui, N.H. Kim, J.H. Lee, OD to 3D carbon-based networks combined with pseudocapacitive electrode material for high energy density supercapacitor: a review, *Chem. Eng. J.* 403 (2021), <https://doi.org/10.1016/j.cej.2020.126352>.
- [23] M. Sevilla, G.A. Ferrero, N. Diez, A.B. Fuertes, One-step synthesis of ultra-high surface area nanoporous carbons and their application for electrochemical energy storage, *Carbon* 131 (2018) 193–200, <https://doi.org/10.1016/j.carbon.2018.02.021>.
- [24] G.A. Yakaboylu, C. Jiang, T. Yumak, J.W. Zondlo, J. Wang, E.M. Sabolsky, Engineered hierarchical porous carbons for supercapacitor applications through chemical pretreatment and activation of biomass precursors, *Renew. Energy* 163 (2021) 276–287, <https://doi.org/10.1016/j.renene.2020.08.092>.
- [25] S. Bi, Z. Li, D. Xiao, Z. Li, T. Mo, G. Feng, X. Zhang, Pore-size-dependent capacitance and charging dynamics of nanoporous carbons in aqueous electrolytes, *J. Phys. Chem. C* 126 (2022) 6854–6862, <https://doi.org/10.1021/acs.jpcc.2c01121>.
- [26] M.H. Kim, K.B. Kim, S.M. Park, K.C. Roh, Hierarchically structured activated carbon for ultracapacitors, *Sci. Rep.* 6 (2016) 2–7, <https://doi.org/10.1038/srep21182>.
- [27] L. Peng, Y. Liang, J. Huang, L. Xing, H. Hu, Y. Xiao, H. Dong, Y. Liu, M. Zheng, Mixed-biomass wastes derived hierarchically porous carbons for high-performance

- electrochemical energy storage, *ACS Sustain. Chem. Eng.* 7 (2019) 10393–10402, <https://doi.org/10.1021/acssuschemeng.9b00477>.
- [28] H. Zhou, Y. Zhou, L. Li, Y. Li, X. Liu, P. Zhao, B. Gao, Amino acid protic ionic liquids: multifunctional carbon precursor for N/S codoped hierarchically porous carbon materials toward supercapacitive energy storage, *ACS Sustain. Chem. Eng.* 7 (2019) 9281–9290, <https://doi.org/10.1021/acssuschemeng.9b00279>.
- [29] B. Pal, S. Yang, S. Ramesh, V. Thangadurai, R. Jose, Electrolyte selection for supercapacitive devices: a critical review, *Nanoscale Adv.* 1 (2019) 3807–3835, <https://doi.org/10.1039/c9na00374f>.
- [30] C.-F. Liu, Y.-C. Liu, T.-Y. Yi, C.-C. Hu, Carbon materials for high-voltage supercapacitors, *Carbon* 145 (2019) 529–548, <https://doi.org/10.1016/j.carbon.2018.12.009>.
- [31] X. Zang, C. Shen, M. Sanghadasa, L. Lin, High-voltage supercapacitors based on aqueous electrolytes, *ChemElectroChem* 6 (2019) 976–988, <https://doi.org/10.1002/celec.201801225>.
- [32] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, Carbons and electrolytes for advanced supercapacitors, *Adv. Mater.* 26 (2014) 2219–2251, <https://doi.org/10.1002/adma.201304137>.
- [33] K. Chaturvedi, A. Singhane, M. Dhangar, M. Mili, N. Gorhae, A. Naik, N. Prashant, A.K. Srivastava, S. Verma, Bamboo for producing charcoal and biochar for versatile applications, *Biomass Convers. Biorefin.* (2023), <https://doi.org/10.1007/s13399-022-03715-3>.
- [34] T. Phuangchik, P. Shanmugam, S. Kandasamy, S. Bunnag, S. Boonyuen, Investigating six types of bamboo charcoal for eco-friendly renewable energy generation, *Biomass Convers. Biorefin.* (2023), <https://doi.org/10.1007/s13399-023-05200-x>.
- [35] I. Cho, A.R. Selvaraj, J. Bak, H. Kim, K. Prabakar, Mechanochemical pretreated M_n+1AX_n (MAX) phase to synthesize 2D- $Ti_3C_2T_x$ MXene sheets for high-performance supercapacitors, *Nanomaterials* 13 (2023), <https://doi.org/10.3390/nano13111741>.
- [36] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* 87 (2015) 1051–1069, <https://doi.org/10.1515/pac-2014-1117>.
- [37] T.J. Mays, A new classification of pore sizes, *Stud. Surf. Sci. Catal.* (2007) 57–62, [https://doi.org/10.1016/S0167-2991\(07\)80009-7](https://doi.org/10.1016/S0167-2991(07)80009-7).
- [38] M. Thommes, K.A. Cychoz, Physical adsorption characterization of nanoporous materials: progress and challenges, *Adsorption* 20 (2014) 233–250, <https://doi.org/10.1007/s10450-014-9606-z>.
- [39] N. Kostoglou, C. Koczwara, S. Stock, C. Tampaxis, G. Charalambopoulou, T. Steriotis, O. Paris, C. Rebholz, C. Mitterer, Nanoporous polymer-derived activated carbon for hydrogen adsorption and electrochemical energy storage, *Chem. Eng. J.* 427 (2022), <https://doi.org/10.1016/j.cej.2021.131730>.
- [40] S. Stock, N. Kostoglou, J. Selinger, S. Spirk, C. Tampaxis, G. Charalambopoulou, T. Steriotis, C. Rebholz, C. Mitterer, O. Paris, Coffee waste-derived nanoporous carbons for hydrogen storage, *ACS Appl. Energy Mater.* 5 (2022) 10915–10926, <https://doi.org/10.1021/acsaem.2c01573>.
- [41] A.R. Selvaraj, D. Chinnadurai, I. Cho, J.-S. Bak, K. Prabakar, Bio-waste wood-derived porous activated carbon with tuned microporosity for high performance supercapacitors, *J. Energy Storage* 52 (2022) 104928, <https://doi.org/10.1016/j.est.2022.104928>.
- [42] A.R. Selvaraj, A. Muthusamy, H.-J. Inho-Cho, K. Kim, K. Prabakar Senthil, Ultrahigh surface area biomass derived 3D hierarchical porous carbon nanosheet electrodes for high energy density supercapacitors, *Carbon* 174 (2021) 463–474, <https://doi.org/10.1016/j.carbon.2020.12.052>.
- [43] H. Zhang, X.L. Zhou, L.M. Shao, F. Lü, P.J. He, Hierarchical porous carbon spheres from low-density polyethylene for high-performance supercapacitors, *ACS Sustain. Chem. Eng.* 7 (2019) 3801–3810, <https://doi.org/10.1021/acssuschemeng.8b04539>.
- [44] B. Yang, D. Zhang, W. She, J. Wang, S. Gao, Y. Wang, K. Wang, Remarkably improving the specific energy of supercapacitor based on a biomass-derived interconnected hierarchical porous carbon by using a newly-developed mixed alkaline aqueous electrolyte with widened operation voltage, *J. Power Sources* 492 (2021), <https://doi.org/10.1016/j.jpowsour.2021.229666>.
- [45] D. Gu, R. Ma, Y. Zhou, F. Wang, K. Yan, Q. Liu, J. Wang, Synthesis of nitrogen-doped porous carbon spheres with improved porosity toward the electrocatalytic oxygen reduction, *ACS Sustain. Chem. Eng.* 5 (2017) 11105–11116, <https://doi.org/10.1021/acssuschemeng.7b03046>.
- [46] S.Y. Lu, M. Jin, Y. Zhang, Y.B. Niu, J.C. Gao, C.M. Li, Chemically exfoliating biomass into a graphene-like porous active carbon with rational pore structure, good conductivity, and large surface area for high-performance supercapacitors, *Adv. Energy Mater.* 8 (2018) 1–9, <https://doi.org/10.1002/aenm.201702545>.
- [47] H. Liu, X. Liu, H. Wang, Y. Zheng, H. Zhang, J. Shi, W. Liu, M. Huang, J. Kan, X. Zhao, D. Li, High-performance sodium-ion capacitor constructed by well-matched dual-carbon electrodes from a single biomass, *ACS Sustain. Chem. Eng.* 7 (2019) 12188–12199, <https://doi.org/10.1021/acssuschemeng.9b01370>.
- [48] M. Moloudi, M.S. Rahmani, A. Noori, X. Chang, R.B. Kaner, M.F. Mousavi, Bioinspired polydopamine supported on oxygen-functionalized carbon cloth as a high-performance 1.2 V aqueous symmetric metal-free supercapacitor, *J. Mater. Chem. A Mater.* 9 (2021) 7712–7725, <https://doi.org/10.1039/d0ta12624a>.
- [49] Y. Zhang, Y. Liu, Y. Bai, Y. Liu, E. Xie, Boosting the electrochemical properties of carbon materials as bipolar electrodes by introducing oxygen functional groups, *RSC Adv.* 10 (2020) 35295–35301, <https://doi.org/10.1039/d0ra06888h>.
- [50] R. Rajendiran, M. Nallal, K.H. Park, O.L. Li, H.J. Kim, K. Prabakar, Mechanochemical assisted synthesis of heteroatoms inherited highly porous carbon from biomass for electrochemical capacitor and oxygen reduction reaction electrocatalysis, *Electrochim. Acta* 317 (2019) 1–9, <https://doi.org/10.1016/j.electacta.2019.05.139>.
- [51] A.R. Selvaraj, I.S. Raja, D. Chinnadurai, R. Rajendiran, I. Cho, D.W. Han, K. Prabakar, Electrospun One Dimensional (1D) Pseudocapacitive nanorods embedded carbon nanofiber as positrode and graphene wrapped carbon nanofiber as negatode for enhanced electrochemical energy storage, *J. Energy Storage* 46 (2022) 1–11, <https://doi.org/10.1016/j.est.2021.103731>.
- [52] A.R. Selvaraj, H.J. Kim, K. Senthil, K. Prabakar, Cation intercalated one-dimensional manganese hydroxide nanorods and hierarchical mesoporous activated carbon nanosheets with ultrahigh capacitance retention asymmetric supercapacitors, *J. Colloid Interface Sci.* 566 (2020) 485–494, <https://doi.org/10.1016/j.jcis.2020.01.117>.
- [53] M. Wang, Z. Yang, W. Li, L. Gu, Y. Yu, Superior sodium storage in 3D interconnected nitrogen and oxygen doped carbon network, *Small* 12 (2016) 2559–2566, <https://doi.org/10.1002/sml.201600101>.
- [54] F. Chen, Y. Zhang, M. Zheng, Y. Xiao, H. Hu, Y. Liang, Y. Liu, H. Dong, Preparation of high-performance porous carbon materials by citric acid-assisted hydrothermal carbonization of bamboo and their application in electrode materials, *Energy Fuels* 36 (2022) 9303–9312, <https://doi.org/10.1021/acs.energyfuels.2c01828>.
- [55] X. Liu, C. Lai, Z. Xiao, S. Zou, K. Liu, Y. Yin, T. Liang, Z. Wu, Superb electrolyte penetration/absorption of three-dimensional porous carbon nanosheets for multifunctional supercapacitor, *ACS Appl. Energy Mater.* 2 (2019) 3185–3193, <https://doi.org/10.1021/acsaem.9b00002>.
- [56] J. Wei, Y. Li, D. Dai, F. Zhang, H. Zou, X. Yang, Y. Ji, B. Li, X. Wei, Surface roughness: a crucial factor to robust electric double layer capacitors, *ACS Appl. Mater. Interfaces* 12 (2020) 5786–5792, <https://doi.org/10.1021/acsaami.9b18799>.
- [57] J. Yang, Z. Chen, H. Lin, P. Feng, Y. Xie, Y. Liang, M. Zheng, X. Liu, Y. Liu, Y. Xiao, Exfoliating waste biomass into porous carbon with multi-structural levels for dual energy storage, *ACS Appl. Energy Mater.* 5 (2022) 12090–12098, <https://doi.org/10.1021/acsaem.2c01517>.
- [58] S.T. Senthilkumar, R.K. Selvan, Y.S. Lee, J.S. Melo, Electric double layer capacitor and its improved specific capacitance using redox additive electrolyte, *J. Mater. Chem. A* (n.d.), doi:<https://doi.org/10.1039/c2ta00210h>.
- [59] S.T. Senthilkumar, R.K. Selvan, J.S. Melo, C. Sanjeeviraja, High performance solid-state electric double layer capacitor from redox mediated gel polymer electrolyte and renewable tamarind fruit shell derived porous carbon, *ACS Appl. Mater. Interfaces* 5 (2013) 10541–10550, <https://doi.org/10.1021/am402162b>.
- [60] P. Cheng, T. Li, H. Yu, L. Zhi, Z. Liu, Z. Lei, Biomass-derived carbon fiber aerogel as a binder-free electrode for high-rate supercapacitors, *J. Phys. Chem. C* 120 (2016) 2079–2086, <https://doi.org/10.1021/acs.jpcc.5b11280>.
- [61] M. Dvoyashkin, D. Leistenschneider, J.D. Evans, M. Sander, L. Borchardt, Revealing the impact of hierarchical pore organization in supercapacitor electrodes by coupling ionic dynamics at micro- and macroscales, *Adv. Energy Mater.* 11 (2021), <https://doi.org/10.1002/aenm.202100700>.
- [62] W. Hu, J. Huang, P. Yu, M. Zheng, Y. Xiao, H. Dong, Y. Liang, H. Hu, Y. Liu, Hierarchically porous carbon derived from *Neolamarckia cadamba* for electrochemical capacitance and hydrogen storage, *ACS Sustain. Chem. Eng.* 7 (2019) 15385–15393, <https://doi.org/10.1021/acssuschemeng.9b02734>.
- [63] K.V. Sankar, R. Kalai Selvan, Improved electrochemical performances of reduced graphene oxide based supercapacitor using redox additive electrolyte, *Carbon* 90 (2015) 260–273, <https://doi.org/10.1016/j.carbon.2015.04.023>.
- [64] B.-A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, Physical interpretations of Nyquist plots for EDLC electrodes and devices, *J. Phys. Chem. C* 122 (2018) 194–206, <https://doi.org/10.1021/acs.jpcc.7b10582>.
- [65] Y. Yao, Y. Zhang, L. Li, S. Wang, S. Dou, X. Liu, Fabrication of hierarchical porous carbon nanoflakes for high-performance supercapacitors, *ACS Appl. Mater. Interfaces* 9 (2017) 34944–34953, <https://doi.org/10.1021/acsaami.7b10593>.
- [66] R. Thangavel, A.G. Kannan, R. Ponraj, V. Thangavel, D.W. Kim, Y.S. Lee, Nitrogen- and sulfur-enriched porous carbon from waste watermelon seeds for high-energy, high-temperature green ultracapacitors, *J. Mater. Chem. A Mater.* 6 (2018) 17751–17762, <https://doi.org/10.1039/c8ta05248d>.
- [67] J. Yang, J. Liu, Y. Chen, B. Chang, X. Zhang, X. Wang, Insight into the supercapacitive behavior of activated hollow porous carbon spheres in different electrolytes, *ACS Appl. Energy Mater.* 4 (2021) 13766–13775, <https://doi.org/10.1021/acsaem.1c02502>.
- [68] D.P. Broom, C.J. Webb, G.S. Fanourgakis, G.E. Froudakis, P.N. Trikalitis, M. Hirscher, Concepts for improving hydrogen storage in nanoporous materials, *Int. J. Hydrogen Energy* 44 (2019) 7768–7779, <https://doi.org/10.1016/j.ijhydene.2019.01.224>.
- [69] C. Rodríguez Correa, C. Ngamyang, D. Klank, A. Kruse, Investigation of the textural and adsorption properties of activated carbon from HTC and pyrolysis carbonizates, *Biomass Convers. Biorefin.* 8 (2018) 317–328, <https://doi.org/10.1007/s13399-017-0280-8>.
- [70] L. Luo, T. Chen, W. Zhao, M. Fan, Hydrothermal Doping of Nitrogen in Bamboo-based Super Activated Carbon for Hydrogen Storage, n.d.
- [71] W. Zhao, L. Luo, H. Wang, M. Fan, Activated C for H_2 -storage, 2017.
- [72] W. Zhao, M. Fan, H. Gao, H. Wang, Central composite design approach towards optimization of super activated carbons from bamboo for hydrogen storage, *RSC Adv.* 6 (2016) 46977–46983, <https://doi.org/10.1039/c6ra06326h>.
- [73] H.S. Jang, J. Mun, W.G. Hong, S.M. Lee, J.W. Jeon, C.Y. Lee, H.J. Kim, B.H. Kim, The performance of green carbon as a backbone for hydrogen storage materials, *Int. J. Hydrogen Energy* 45 (2020) 10516–10522, <https://doi.org/10.1016/j.ijhydene.2019.03.084>.