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Tuning Internal Accessibility via Nanochannel Orientation of Mesoporous Carbon Spheres for High-Rate Potassium-Ion Storage in Hybrid Supercapacitors

Jongyoon Park, Kangseok Kim, Eunho Lim,* and Jongkook Hwang*

Enhancing the accessibility and utilization of active sites through mesopores in carbon anode materials is crucial for developing high-power potassium-ion hybrid supercapacitors (PIHCs). Here, a multiscale phase separation method combining block copolymer (BCP) microphase- and homopolymer (HP) macrophase-separation is utilized to produce two model carbon materials with controlled mesopore orientation: open-end (oe-MCS) and closed-end mesoporous carbon sphere (ce-MCS). BCPs form identical cylindrical micelles, and HPs encapsulate these cylindrical micelles within spheres and control their orientations relative to the interface. This approach manipulates only the degree of mesopore openings in the MCS materials while maintaining all other factors at similar levels. Opening mesopores in carbon anode materials primarily enhances K⁺ adsorption capacity, reduces K⁺ diffusion length, and improves ion transport. Thus, oe-MCS anode exhibits a higher specific capacity with a significant capacitive-controlled contribution. The resulting PIHC device displays maximum energy and power densities of 103 Wh kg⁻¹ and 12 300 W kg⁻¹, respectively, along with capacity retention of 86.1% after 20 000 cycles at 2.0 A g^{-1} . This study significantly advances the understanding of mesopore design to improve capacitive K⁺ storage in hard carbon materials, paving the way for the development of high-power PIHCs.

1. Introduction

The demand for high-power energy storage is growing, especially in applications such as stabilizing renewable energy variability

J. Park, K. Kim, J. Hwang Department of Energy Systems Research Ajou University Suwon 16499, Republic of Korea E-mail: jongkook@ajou.ac.kr E. Lim Department of Chemical & Biochemical Engineering Dongguk University Seoul 04620, Republic of Korea E-mail: eunholim@dgu.ac.kr J. Hwang Department of Chemical Engineering Ajou University Suwon 16499, Republic of Korea

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in energy storage systems and personal mobility devices (e.g., mobility scooters and electric bicycles).^[1] To reduce the heavy reliance on Li and its high price volatility,^[2] potassium-ion hybrid supercapacitors (PI-HCs) have been proposed as promising high-power alternatives. This is because of the abundance of K resources and low redox potential of K⁺/K (-2.93 V vs the saturated hydrogen electrode (SHE), which is comparable to that of Li⁺/Li of -3.04 V vs SHE), in addition to the high ionic conductivities of their carbonate electrolytes.^[3] A PIHC comprises a battery-type anode and capacitor-type cathode, which could yield high energy and power densities and an extended cycle life. However, this hybrid approach often poses significant challenges in balancing the "slow" Faradaic reactions at the anode and the "rapid" non-Faradaic electrosorption at the cathode.^[4] The anode (e.g., graphite or metal alloys), in particular, is a bottleneck in realizing a high rate capability and a long lifespan.^[5] This is due to the large ionic size of K^+ (1.38 Å vs 0.76 Å for Li⁺), which

leads to slow kinetics in solid-state diffusion and significant volume changes during repeated (de)potassiation processes.

To address anode-related problems in PIHCs, a wide variety of carbon materials such as expanded graphite,^[6] hollow carbon,^[7] porous carbon,^[8] and hard-soft hybrid carbon^[9] have been developed. Among these, porous hard carbon has recently emerged as a promising material, providing high reversible capacity and long-cycle stability due to its large interlayer spacing and porous structures, which relieve the stresses associated with volume changes.^[10] Engineering porous architectures of carbon greatly improve the overall K⁺ capacity and modulates the contribution of two K⁺ storage mechanisms (surface-driven adsorption and diffusion-controlled intercalation).^[11] Hierarchical micro/mesoporous structures have been of particular interest because they combine the advantages of two different pore systems. Micropores increase the contact area between the electrode and the electrolyte, thereby increasing the concentration of surface-driven adsorption sites. Mesopores further improve ion transport capability and increase the accessibility to active sites present near micropores.^[8] However, the exact role of each pore, especially mesopores, remains unidentified. For example, Qian



et al. and Wu et al. argued that mesopores are responsible for increasing the capacitive K⁺ adsorption.^[12] Conversely, other researchers claimed that the introduction of mesopores shortened the solid-state K⁺ diffusion path, thereby primarily enhancing the intercalation process.^[13] This controversy mainly arises from the absence of suitable model carbons that have controlled mesopores while keeping other factors constant. Furthermore, conventional approaches mostly rely on the stepwise use of multiple templates or activation processes, often involving various chemicals (e.g., acid leaching) or thermal treatments (e.g., pyrolysis at different temperatures).^[14] These methods simultaneously impact various factors such as the degree of graphitization, content of heteroatoms/functional groups, particle size, and morphologies.^[15] As a result, understanding how mesopores affect K⁺ storage mechanisms and utilization of active sites remains a great challenge. Moreover, there are no studies to date that examine the impact of mesopore orientation (i.e., degree of mesopore opening) on K⁺ storage behavior.

Herein, we synthesized two model mesoporous carbon spheres (MCSs) in which only the orientation of the mesopore channels was manipulated, while other factors were consistently controlled. We utilized multiscale phase separation in a blend of block copolymers (BCPs) and homopolymers (HPs).^[16] The BCPs underwent microphase separation to form cylindrical BCPcarbon precursor micelles, while the macrophase separation of the HPs led to these BCP micelles to evolve into spherical morphologies with controlled orientations. Depending on the type of HP used, identical cylindrical BCP micelles self-assembled in orientations parallel or perpendicular to the HP interface. This led to the formation of open-end MCS (oe-MCS), where both ends of the nanochannels were fully exposed, and closed-end MCS (ce-MCS), where the nanochannel walls were exposed to the exterior, limiting access to the interiors of the carbon particles. As anode materials for use in PIHCs, oe-MCS exhibited a specific capacity that was 1.5-fold higher than that of ce-MCS, along with superior rate capabilities across all current densities. Quantitative analysis using cyclic voltammetry (CV) revealed that opening the cylindrical mesopore channels enhanced the surface-driven adsorption capacity rather than the intercalation capacity. This was primarily due to reducing the K⁺ diffusion length and enhancing ionic transportation. As a result, the higher specific capacity and large capacitive contribution of oe-MCS enabled the fabrication of PIHCs with higher energy and power densities and cycle stability compared to those of PIHCs prepared using ce-MCS.

2. Results and Discussion

2.1. Preparation of MCS with a Controlled Mesopore Orientation

To fabricate MCS materials with controlled mesopore orientation, we utilized the phase behavior in a blend of A-*b*-B block copolymer and A-homopolymer (Figure S1, Supporting Information). The polymer blend undergoes mainly two different types of phase separations depending on the ratio (r_N) of the degree of polymerization of homopolymer A ($N_{A, homo}$) to that of the A-block in the A-*b*-B BCP ($N_{A, BCP}$).^[17] At $r_N << 1$, the low-molecular-weight A-homopolymer is selectively solubilized within the A block of BCP and co-assembled together via microphase separation at a size scale of 5–50 nm. Therefore, an $r_N \ll 1$ is a required condition for the synthesis of conventional ordered mesoporous materials (Figure S1a, Supporting Information).^[18] When $r_N >>1$, the high-molecular-weight A-homopolymer is completely segregated from A-*b*-B phases and forms independent macrophases larger than 100 nm. This behavior corresponds to macrophase separation via spinodal decomposition (SD) which can control the macroscopic particle morphology of the polymer blends (Figure S1b, Supporting Information).

Based on these phase separation criteria in the polymer blend, we conducted preliminary experiments to selectively control microphase- and macrophase-separation in the synthesis of model carbon materials. The abbreviations used in this paper are listed in Table S1, Supporting Information. We used poly(ethylene oxide)-*block*-polystyrene (PEO-*b*-PS, $M_n =$ 31.4 kg mol-1, with 15.9 wt.% PEO) as a structure-directing agent, prehydrolyzed aluminosilicate (AS) sol as a reinforcer, and phenol-formaldehyde (PF) resin with low-molecular-weight of 500 g mol⁻¹ as a carbon precursor. To induce macroscale SD, we used high-molecular-weight HPs (996 kg mol⁻¹) of either homo-poly(methyl methacrylate) (HPMMA) or homopolystyrene (HPS). All components were homogeneously dissolved in a mixture of tetrahydrofuran (THF) and CHCl₂. First, we optimized the conditions for the synthesis of conventional bulk mesoporous carbon using PEO-b-PS, PF, and AS sol via microphase separation (Figure S2, Supporting Information). Oligomeric PF and AS are hydrophilic because of their abundant methylol and hydroxyl groups, making them selectively miscible with the hydrophilic PEO blocks of the BCPs via hydrogen bonding.^[19] When the solvents were evaporated at 50 °C, the homogeneous solution became thermodynamically unstable, leading to spontaneous phase separation. During this process, the PEO-b-PS and the precursors underwent microphase separation into PF-AS/PEO and PS block domains, forming cylindrical micelles through cooperative assembly (Figure S2a, Supporting Information). Annealing at 100 °C is then performed to polycondense the AS and PF, enhancing the overall structural stability, with the AS framework serving as reinforcement to prevent structural collapse during carbonization.^[20] Pyrolysis of the PEO-b-PS at 900 °C and acid etching of AS resulted in the formation of ordered mesoporous carbon with irregular micrometer sizes and ill-defined morphologies (Figure S2, Supporting Information). We then investigated the conditions to prepare the carbon sphere via macroscale SD (Figure S3, Supporting Information). We prepared a blend consisting of an excess amount of hydrophobic HPMMA (or HPS) and the PF and AS sol, without using the PEO-b-PS. The high-molecular weight of HPMMA makes it immiscible with the BCPs and precursors due to significant conformational entropy loss.^[21] The hydrophilic PF and AS are incompatible with the hydrophobic HPMMA, leading to the complete segregation of HPMMA from the PF and AS phases. Consequently, the blend spontaneously phase separates into structures that reduce the total interfacial area and energy:^[16c] a minority PF and AS phase with spherical shapes confined within the majority HPMMA matrix (Figure S3, Supporting Information). Subsequent carbonization completely decomposed the HPMMA matrix (Figure S4, Supporting Information), yielding a mesoporefree microporous carbon sphere (meso-free-CS). These results indicate that PEO-b-PS is necessary to obtain ordered mesopores





Figure 1. Schematic of the fabrication of the MCS materials.



(ce-MCS)

and that hydrophobic HPs work as in-situ generated molds that shape the hydrophilic precursor phases into spheres.

Combining the aforementioned nanoscale BCP self-assembly and macroscale SD of the HP, we designed a multiscale phase separation method for the synthesis of MCS materials with controlled mesopore orientation (Figure 1). The microphase separation of PEO-b-PS and precursors (PF and AS) led to the formation of identical cylindrical mesopores, while the macrophase separation between BCP phases and HP phases resulted in a spherical particle morphology with different orientations of the cylindrical mesopores (Figure S5, Supporting Information). These orientations depended on the type of HP used, which tuned the enthalpic interactions at the BCP-HP interface. When using an HP-MMA matrix, it provides an enthalpically neutral surface for the PEO/precursor and PS-block microdomains, aligning both microdomains perpendicular to the HPMMA interface (Figure S6a, Supporting Information). After carbonization, oe-MCS was produced with both ends of the nanochannels fully exposed. Conversely, the HPS matrix provides an enthalpically favorable surface for the PS-block microdomains, leading to the preferential interactions of the PS blocks with the surrounding HPS matrix (Figure S6b, Supporting Information). Consequently, the PS blocks within the BCPs are situated on the outermost layers of the BCP/precursor phases, aligning the cylindrical micelles parallel to the HPS interface. This arrangement produced *ce*-MCS, wherein the "walls" of the nanochannel cylinders are exposed, but the "mesopore ends" of these cylinders are mostly sealed from the exterior.

To confirm the formation of the structure via multiscale phase separation of the blend, the as-prepared oe-MCS hybrids were sectioned into specimens with thicknesses of 100 nm and observed using transmission electron microscopy (TEM). Figure 2a shows that the PF-AS/BCP domains (dark areas) are encapsulated by the HPMMA matrix (bright areas). The PF-AS/BCP domains adopt the shapes of spherical particles within the internal nanocylinders arranged perpendicular to the HP-MMA matrix. This is because HPMMA serves as a thermodynamically neutral surface for the PF-AS/PEO and PS block segments of the BCPs, which ensures that the interfacial energy between each BCP microdomain and the HPMMA matrix is equally balanced and neutralized (Figure S6a, Supporting Information).^[22] This behavior is further theoretically supported by the fact that the Flory-Huggins interaction parameters for the PEO/PMMA and PS/PMMA blends are nearly identical under our synthesis conditions.^[23] During carbonization at 900 °C, the HPMMA matrix decomposes completely, the PF-AS/PEO is converted to carbon walls, and the PS-blocks decompose to form mesopores (Figure S4, Supporting Information). This process results in the formation of oe-MCS with cylindrical mesopores, with their ends fully exposed to the exterior (Figure 2b; Figure S7a-c, Supporting Information). Scanning electron microscopy (SEM) images reveal that oe-MCS exhibits highly accessible open mesopores with no recognizable mesopore blocking (Figure 2c).

When HPS is utilized as the matrix instead of HPMMA, the PF-AS/BCP domains exhibit similar spherical particle morphologies but with significant differences in the orientations of the internal nanocylinders (Figure 2d).^[16c] The cylindrical BCP microdomains are curved and mostly aligned parallel to the HPS interface, which is due to the immiscibility of HPS with PF-AS/PEO and the enthalpically favorable interactions of HPS with the PS blocks of the BCPs. Self-assembly is directed to minimize the contact between HPS and PF-AS/PEO, while maximizing the contact between HPS and the PS blocks, thereby forming cylindrical micelles with the outermost PS-block layers in contact with the HPS interface (Figure S6b, Supporting Information). Subsequent carbonization leads to the generation of ce-MCS with welldeveloped internal cylindrical mesopores, and the openings of these pores at the cylindrical ends are mostly sealed from the exterior (Figure 2e; Figure S7d-f, Supporting Information). The TEM and SEM images of ce-MCS clearly show a thin carbon layer covering the outermost surface (Figure 2e,f). The surface carbon layer is partially peeled off, likely owing to the gas pressure generated during pyrolysis partially tearing the completely enclosed surface. The particle size and size distribution were determined by analyzing 200 particles in the SEM images, and oe-MCS and



Figure 2. a) Cross-sectional TEM image of an as-prepared (PF-AS/PEO-*b*-PS) domain confined within the HPMMA matrix. b) TEM and c) SEM images of *oe*-MCS. d) Cross-sectional TEM image of an as-prepared (PF-AS/PEO-*b*-PS) domain confined within the HPS matrix. e) TEM and f) SEM images of *ce*-MCS.

ce-MCS exhibit uniform particle size distributions with average particle sizes of 420 and 440 nm, respectively (Figure S8, Supporting Information).

The identical cylindrical mesopore structures with different orientations (i.e., different mesopore apertures) of oe-MCS and ce-MCS were further corroborated via small-angle X-ray scattering (SAXS) and N₂ physisorption at 77 K. In the SAXS pattern of *oe*-MCS (Figure 3a), the primary peak is observed at a q_1 value of 0.246 nm⁻¹, accompanied by higher-order reflections at angular positions of $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{7}$ relative to the first-order maximum. This sequence of spacing indicates a hexagonal arrangement of cylindrical mesopores.^[24] ce-MCS exhibits a set of reflections that correspond to the same hexagonal symmetry as that of *oe*-MCS, with an almost identical primary peak position of $q_2 =$ 0.240 nm⁻¹. Despite displaying the same cylindrical mesopores, distinctly different N2 ad-/desorption isotherms are observed for these carbon particles (Figure 3b; Figure S9, Supporting Information). The hysteresis loop generated by the N₂ ad-/desorption isotherms at 77 K provides information regarding the levels of connectivity/accessibility of the mesopores within the MCS materials. *oe*-MCS exhibits type H1 hysteresis, indicating a porous material with a narrow distribution of uniform cylindrical mesopores with open ends. Conversely, ce-MCS displays type H2 hysteresis owing to pore-blocking effects that cause deviations from type H1 hysteresis.^[25] The desorption of *oe*-MCS at higher pressures ($P/P_0 = 0.8$) is associated with the facile evaporation of liquid N₂ from the open mesopores (Figure S9b, Supporting Information). Conversely, the blocked mesopores within ce-MCS remain filled until they are emptied via cavitation, leading to delayed desorption at low pressures close to $P/P_0 = 0.5$ (Figure S9d, Supporting Information). The pore size distributions of the MCS materials, which were derived from the adsorption branches of the isotherms, were estimated using the quenched solid density

functional theory (QSDFT) method. *oe*-MCS and *ce*-MCS exhibit uniform pore size distributions, with identical peak pore sizes of 10 nm (Figure 3c). Based on the SAXS and QSDFT pore sizes, the wall thicknesses of the cylindrical nanochannels are ≈ 20 nm. This value is consistent with the carbon layer thickness of *ce*-MCS observed using TEM (Figure 2e), further confirming that the outermost carbon originates from the parallel orientations of the cylindrical PF-AS/BCP micelles. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) and total pore volumes are also comparable: 1,137 m² g⁻¹/0.79 cm³ g⁻¹ and 1,150 m² g⁻¹/0.86 cm³ g⁻¹ for *oe*-MCS and *ce*-MCS, respectively (Table S2, Supporting Information).

Other factors that affect K⁺ storage in amorphous hard carbon were investigated using X-ray diffraction (XRD), highresolution TEM (HR-TEM), and Raman and X-ray photoelectron spectroscopy (XPS). The broad XRD peaks at $2\theta = 24$ and 43° originate from the (002) and (100) planes of the disordered graphitic layers, respectively, which typically occur in amorphous hard carbon (Figure 3d).^[8] Based on the Bragg equation and the (002) peak, the respective average interlayer spacings of these graphitic layers are 0.379 and 0.378 nm for oe-MCS and ce-MCS, which are almost identical. The HR-TEM images corroborate these findings, revealing disordered graphitic layers with similar interlayer spacings (Figure S10, Supporting Information). Raman spectroscopy reveals two broad peaks at \approx 1,350 and 1,600 cm⁻¹, corresponding to the D and G bands (Figure 3e).^[26] The I_D/I_G intensity ratios of *oe*-MCS and ce-MCS are 1.0 and 0.96, respectively, indicating comparable degrees of graphitization. High-resolution XPS confirms the presence of O and C atoms at similar concentrations in both MCS materials (Figure S11a, Supporting Information). As the C=O groups are active sites for capacitive K⁺ adsorption via CO + K⁺ + $e^- \leftrightarrow$ C-O-K, the O 1s spectra are deconvoluted into three peaks at

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Figure 3. Characterization of the MCS materials. a) SAXS patterns, b) N_2 physisorption isotherms, c) pore size distributions, d) XRD patterns, e) Raman spectra, and f) contents of O-containing functional groups, as determined using XPS.

532.5, 532.9, and 534.0 eV, corresponding to C=O, C–OH or C–O–C, and COOH groups, respectively (Figure S11b-c, Supporting Information).^[8,27] The content of each functional group is quantified, as shown in Figure 3f, revealing similar C=O concentrations within *oe*-MCS (1.88 at.%) and *ce*-MCS (1.93 at.%).

Based on these results, we successfully synthesized model carbon anode materials by exclusively manipulating the cylindrical mesopore orientation while consistently controlling all other factors (pore size and structure, wall thickness, surface area, particle size, and particle morphology, interlayer spacing, degree of graphitization, and C=O content) at similar levels (Table S2, Supporting Information). The major difference between *oe*-MCS and *ce*-MCS is their internal accessibility via mesopores, which are determined by the orientations of the cylindrical nanochannels. Consequently, this enables the investigation of the relationship between mesopore orientations and their impact on the K⁺ storage behavior.

2.2. Electrochemical Performances of the Anode Half-Cells

The electrochemical performances of the MCS samples as an ode materials were initially evaluated via galvanostatic charge discharge (GCD) (i.e., depotassiation-potassiation) measurements at a current density of 0.05 A g⁻¹. Owing to the irreversible side reactions and the formation of solid electrolyte interphase layers in the first cycle, *oe*-MCS, and *ce*-MCS exhibit almost identical low initial Coulombic efficiencies of 27% (**Figure 4**a,b). Aside from the first cycle, the subsequent cycles almost over-

lap, and a similar trend is observed in the CVs in the potential range 0.01–3.0 V (vs K⁺/K) (Figure S12, Supporting Information). Hard carbon anodes store K⁺ mainly via two different mechanisms: surface-driven capacitive adsorption at a potential of >0.5 V (vs K^+/K) and diffusion-controlled intercalation at a potential of <0.5 V (vs K⁺/K).^[10a,28] We thus estimated the adsorption and intercalation capacities of oe-MCS and ce-MCS based on the discharge (potassiation) profiles at a current density of 0.05 A g⁻¹ (Figure 4c). *oe*-MCS exhibits a higher intercalation capacity (98 mAh g^{-1}) compared to that of *ce*-MCS (78 mAh g^{-1}). Notably, the adsorption capacity of *oe*-MCS is 120 mAh g^{-1} , which is $\approx 67\%$ higher than that of *ce*-MCS (72 mAh g^{-1}), and thus, the overall specific capacity of *oe*-MCS is 1.5-fold higher than that of *ce*-MCS. Therefore, opening the mesopores contributes to enhancing the intercalation and adsorption capacities, with a more significant influence on the adsorption capacity. A large adsorption capacity with a sloping potential profile is favorable in realizing an excellent rate capability. Figure 4d shows the rate capabilities of the anodes at various current densities from 0.05 to 1.0 A g⁻¹. oe-MCS delivers reversible capacities of 210, 184, 144, 129, and 109 mAh g⁻¹ at 0.05, 0.1, 0.3, 0.5, and 1.0 A g⁻¹, respectively (Figure S13; Table S3, Supporting Information). In addition, oe-MCS exhibits higher areal and volumetric performances than those of ce-MCS at all current densities (Figure S14, Supporting Information).

Electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) analyses were performed. Figure 4e shows the Nyquist profiles of *oe*-MCS and *ce*-MCS after 10 cycles at a current density of 0.05 A g^{-1} . The semicircle represents the charge-transfer resistance (R_{ct}),

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Figure 4. GCD curves of a) *oe*-MCS and b) *ce*-MCS at 0.05 A g^{-1} . c) Potential-dependent capacities obtained from the GCD profiles during potassiation at a current density of 0.05 A g^{-1} . d) Rate performances of the MCS materials at current densities ranging from 0.05 to 1.0 A g^{-1} . e) Nyquist plots of the MCS anodes. f) GITT profiles and g) calculated internal resistances of the MCS anodes. h) Cycle stabilities of the MCS materials at 1.0 A g^{-1} over 500 cycles. Before the long-term cycling study, the anodes were first activated using GCD at a current density of 0.05 A g^{-1} for 5 cycles.

representing the migration of ions at the electrode interface.^[29] The semicircle of *oe*-MCS is smaller than that of *ce*-MCS, suggesting that *oe*-MCS displays a lower interface resistance and faster K⁺ kinetics at the electrode interface. Similar characteristics of *oe*-MCS are further confirmed via GITT measurements (Figure 4f). The change in the potential during each relaxation period indicates the overpotential at the respective ion-storage stage. The *oe*-MCS electrode exhibits a smaller overpotential than that of the *ce*-MCS electrode (Figure 4f). Consequently, *oe*-MCS exhibits a lower internal resistance (Figure 4g) and a higher K⁺ diffusion coefficient (D_{K+}) (Figure S15, Supporting Information) compared to *ce*-MCS, especially in the potential range where K⁺ adsorption dominates over K⁺ intercalation.^[10a,28] The results of EIS and GITT indicate the enhanced charge transport kinetics of *oe*-MCS. In addition, the long-term cycling performances of

oe-MCS and ce-MCS were evaluated at a high current density of 1.0 A g⁻¹ (Figure 4h). The oe-MCS electrode maintains a higher specific capacity compared to that of the ce-MCS electrode. After 500 cycles, oe-MCS and ce-MCS show capacity retentions of \approx 87% and 75%, respectively, indicating the excellent reversibility and structural stability of the oe-MCS electrode.

Therefore, *oe*-MCS exhibits a significantly improved specific capacity and low charge-transfer resistance, and an excellent rate capability compared to those of *ce*-MCS. As a control sample, we compared the electrochemical performance of *meso-free*-CS, which shows significantly lower specific capacity, rate capability, and cycle stability compared to *oe*-MCS and *ce*-MCS (Figure S3; Figure S16, Supporting Information). These results further suggest that enhancing the interior accessibility of the anode enables the efficient utilization of active sites, improves ionic

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Figure 5. CVs of a) *oe*-MCS and b) *ce*-MCS at scan rates from 0.1 to 1.0 mV s⁻¹. c) *b* values of the MCS electrodes as functions of potential for the cathodic (potassiation) process. d) Capacitive contributions of the MCS materials at scan rates from 0.1 to 1.0 mV s⁻¹. e) Capacitive- and diffusion-controlled K⁺ storage capacities of *oe*-MCS (pink) and *ce*-MCS (green) in the cathodic process, as calculated using the CVs at a scan rate of 0.1 mV s⁻¹. f,g) Nyquist and h) Bode plots of the MCS materials, as obtained from the results of EIS using symmetric cells with non-intercalating electrolytes.

transportation, and reduces $K^{\!+}$ diffusion length, ultimately improving the overall electrochemical $K^{\!+}$ storage performance.

2.3. Kinetics and Mechanism of K⁺ Storage

The kinetics and K⁺ storage mechanisms of the electrode materials were investigated via CV at scan rates of 0.1–1.0 mV s⁻¹ (**Figure 5**a,b). The power-law relationship between the scan rate and measured current follows Equation (1):

$$i = av^b \tag{1}$$

where *i* and *v* are the measured current (A g^{-1}) and scan rate (mV s⁻¹), respectively, and *a*, *b* are adjustable variables. *b* is determined from the slope of the linear curve obtained by plotting log

(*i*) versus log (*v*). Based on *b*, as the first approximation, we can analyze the capacitive- (b = 1) and diffusion-controlled currents (b = 0.5).^[8] *oe*-MCS consistently exhibits a higher *b* than that of *ce*-MCS across the entire potential range (Figure 5c), and the *b* values at the anodic peaks are also higher for *oe*-MCS (Figure S17, Supporting Information). These results suggest that K⁺ storage within *oe*-MCS is dominated by capacitive-controlled adsorption compared to that within *ce*-MCS. This effect is particularly pronounced at >0.5 V (vs K⁺/K), suggesting that the fully exposed mesoporous channels of *oe*-MCS show a significant influence in improving the capacitive-controlled adsorption.^[10a,28] We quantitatively separate the capacitive- and diffusion-controlled contributions at a fixed potential (V) using Equation (2):

$$i = k_1 \nu + k_2 \nu^{1/2} \tag{2}$$

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Figure 6. a) Schematic of the MCS//MSP20 PIHC device. CVs of b) *oe*-MCS//MSP20 and c) *ce*-MCS//MSP20 at scan rates from 0.5 to 3.0 mV s⁻¹. GCD profiles of d) *oe*-MCS//MSP20 and e) *ce*-MCS//MSP20 at current densities of 0.05–1.0 A g⁻¹. f) Rate performances and g) power densities of MCS//MSP20 at current densities from 0.05 to 10.0 g⁻¹. h) Cycle stability of MCS//MSP20 at 2.0 A g⁻¹ over 20,000 cycles.

where $k_1 v$ and $k_2 v^{1/2}$ represent the capacitive- and diffusioncontrolled currents, respectively, e.g., the shaded region shown in Figure S18 (Supporting Information) displays the capacitive current $(k_1 v)$ used to calculate the capacitive K⁺ capacity based on the CVs.^[30] At a scan rate of 0.1 mV s⁻¹, oe-MCS shows a considerably higher specific capacity than both meso-free-CS and ce-MCS (Figure S19, Supporting Information). The introduction of accessible mesopores leads to an enhancement in specific capacity and capacitive-controlled contribution (Figure 5d,e; Figure S19, Supporting Information). More specifically, as the degree of mesopore opening increases from ce-MCS to oe-MCS, the capacitive-controlled capacity increases from 71 to 112 mAh g⁻¹ (i.e., a 58% improvement), whereas the diffusion-controlled capacity increases from 66 to 92 mAh g⁻¹ (i.e., a 39% improvement). All results indicate that opening mesopores simultaneously increases the concentrations of kinetically accessible active sites for capacitive- and diffusion-controlled processes, with a more pronounced effect on the capacitive-controlled process (Figure S19, Supporting Information). Notably, the capacitivecontrolled capacity remains unchanged across the different scan rates, in contrast to the diffusion-controlled capacity, which decreases markedly as the scan rate increases (Figure 5d). As the capacitive process mostly operates via "fast" surface-driven K⁺ adsorption, the capacitive-controlled capacity can naturally only be utilized at high scan rates (Figure 5d). Consequently, *oe*-MCS exhibits higher specific capacities with larger capacitive-controlled contributions at all scan rates compared to those of *ce*-MCS (Figure 5e), and these characteristics of *oe*-MCS are advantageous in fabricating high-power PIHCs.

Additional insights were obtained from the EIS data measured using MCS//MCS symmetric cells containing a non-intercalating electrolyte, i.e., $0.1~_{\rm M}$ tetrabutylammonium



perchlorate (TBAClO₄) in ethylene carbonate: diethyl carbonate (EC:DEC, 1:1, v/v, refer to the experimental section for details).^[31] Symmetric cells were utilized to exclusively study the non-Faradaic processes, thereby revealing the characteristics of solvated ion mass transport within the pores. In the Nyquist plot (Figures 5f,g), the semicircle observed in the high-frequency range corresponds to the interfacial contact resistance between the electrode and current collector, as well as among electrode particles. This semicircle is similar for both oe-MCS and ce-MCS cells, suggesting that they have comparable interfacial contact resistance (Figure 5g). In the middle-frequency range, represented by the linear slope at $\approx 45^{\circ}$ angle from the Z'-axis, the ionic resistance for ce-MCS was estimated to be 17.9 Ohm, which is twice as high as that for oe-MCS (9.4 Ohm). This difference indicates that oe-MCS has more efficient K⁺ transport within the pores. Furthermore, a nearly perpendicular straight line from the Z'-axis is observed at 1.26 Hz for oe-MCS and at 0.4 Hz for ce-MCS, respectively, suggesting that K⁺ mass transport is enhanced in oe-MCS compared to ce-MCS.[31] This finding is also supported by the data presented in the Bode plot (Figure 5h). In the presence of a non-Faradaic reaction at the electrode, the Bode phase angle tends to approach -90° . As a straight line perpendicular to the Z'-axis indicates the occurrence of a non-Faradaic reaction at the electrode. This result suggests that the formation of an electric double layer on the electrode surface begins more rapidly on oe-MCS.[31b,32] The EIS results from symmetric cells reveal the faster K⁺ ion kinetics within the pores of *oe*-MCS compared to those within the pores of *ce*-MCS. From this perspective, opening the mesopores is an effective method of improving the rate capability of a carbon anode, and it displays significant potential in the field of high-power PIHCs.

2.4. Performance Evaluations of PIHC Devices

Before assembling the PIHCs, commercial activated carbon (MSP20) was evaluated as the cathode in a half-cell against K metal in the potential range 1.8–4.0 V (vs K⁺/K). MSP20 exhibits a large S_{BET} of 2,664 m² g⁻¹ (Figure S20a, Supporting Information), which renders it a suitable capacitor-type cathode. The GCD measurements show that MSP20 exhibits a linear sloping potential profile (Figure S20b, Supporting Information) and delivers respective specific capacities of 96, 93, 86, 83, 78, 71, and 51 mAh g⁻¹ at 0.05, 0.1, 0.3, 0.5, 1.0, 2.0, and 5.0 A g⁻¹ (Figure S20c, Supporting Information). The rectangular shapes of the CVs also indicate a typical capacitor-like behavior (Figure S20d, Supporting Information), suggesting that MSP20 operates via the non-Faradaic electrosorption of bis(fluorosulfonyl)imide anions (FSI⁻).^[33]

PIHC full-cell devices were fabricated using *oe*-MCS or *ce*-MCS as the anodes and MSP20 as the cathodes, and they are denoted *oe*-MCS//MSP20 and *ce*-MCS//MSP20, respectively. To optimize the specific capacity balance between MCS and MSP-20 and to achieve maximum electrochemical performance, the working voltage and the anode-to-cathode mass ratio were carefully controlled (Figure S21, Supporting Information, refer to experimental section for details). In a PIHC, the cathode reversibly stores FSI⁻ via non-Faradaic reactions while the anode reversibly stores K⁺ via the Faradaic reaction (**Figure 6**a). This hybridized

charge storage mechanism results in asymmetric CVs for the PIHC (Figure 6b,c).^[34] Notably, the CVs of oe-MCS//MSP20 at various scan rates are more rectangular (Figure 6b) than those of ce-MCS//MSP20 (Figure 6c). A similar trend is observed in the GCD profile, where the oe-MCS//MSP20 (Figure 6d) shows higher charge storage capacity at lower voltages (0.01-1.0 V) compared to the ce-MCS//MSP20 (Figure 6e). These differences are attributed to *oe*-MCS exhibiting a high potential sloping profile and a high capacitive-controlled capacity (Figure S22, Supporting Information), which is advantageous in balancing the chargestorage capacity and electrode kinetics with those of a capacitortype cathode. As a result, oe-MCS//MSP20 exhibits an excellent rate capability, with a high energy density of 103 Wh kg⁻¹ at a power density of 113 W kg⁻¹. This device even maintains an energy density of 7 Wh kg^{-1} at an ultrahigh power density of 12,300 W kg⁻¹ (Figure 6f,g). Such an excellent rate capability and outstanding energy and power densities are comparable to those of numerous state-of-the-art PIHCs, as shown in Figure 6h and Table S4 (Supporting information).^[7,8,35] Furthermore, oe-MCS//MSP20 exhibits an outstanding long-term cyclability, with a retention of 86.1% at 2.0 A g^{-1} over 20,000 cycles, even after cycling at a harsh current density of 10.0 A g^{-1} (Figure 6i).

3. Conclusion

The microphase separation of PF-AS/PEO-b-PS led to the formation of identical cylindrical mesopores, whereas the macrophase separation between PF-AS/PEO-b-PS and HP resulted in a spherical particle morphology. The orientations of the cylindrical mesopores (i.e., internal accessibility) could be controlled by changing the type of HP (HPMMA or HPS) to tune the enthalpic interactions at the BCP-HP interface. This method enabled the syntheses of oe-MCS and ce-MCS with controlled mesopore orientation while maintaining all other factors (pore size and structure, wall thickness, surface area, particle size and morphology, interlayer spacing, degree of graphitization, and C=O content) at similar levels. This enabled exclusive investigation into the influence of mesopore openings on the K⁺ storage behavior. Opening the cylindrical mesopores of MCS improved the intercalation and adsorption capacities, with a more pronounced effect on the adsorption capacity. When used as an anode material in a PIHC, oe-MCS exhibited a higher reversible capacity with a larger capacitive-controlled contribution and reduced charge-transfer resistance, and an improved rate performance compared to those of ce-MCS. These features of the oe-MCS anode were highly advantageous in balancing the charge-storage capacity and electrode kinetics with those of a capacitor-type cathode, enabling the fabrication of high-power PIHC full-cells. The oe-MCS//MSP20 PIHC exhibited a maximum energy density of 103 Wh kg⁻¹ at a power density of 113 W kg⁻¹. This device even maintained an energy density of 7 Wh kg⁻¹ at an ultrahigh power density of 12 300 W kg⁻¹. Moreover, excellent long-term cycling stability was observed, with a capacity retention of 86.1% after 20000 cycles at 2.0 A g⁻¹. These results suggest that the introduction of highly accessible mesopores into the hard carbon can improve the electrochemical performance, particularly in terms of the capacitivecontrolled capacity. Moreover, this study demonstrates that the efficient utilization of active sites via mesopore engineering displays significant potential in the field of high-power PIHCs.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

high power density, mesopore orientation, mesoporous carbon sphere, multiscale phase separation, potassium-ion hybrid supercapacitor

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