



# Ordered mesoporous carbon CMK-8 cathodes for high-power and long-cycle life sodium hybrid capacitors

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## ABSTRACT

Electrochemical energy storage (EES) devices with simultaneous high energy and high power output are critical in next-generation smart applications. Sodium hybrid capacitors (NHCs) are relatively new devices integrating the functions of batteries and capacitors. Research on capacitor-type carbon electrodes in NHCs is necessary to improve the energy-power behavior. Herein, we study ordered mesoporous carbon (OMC) materials synthesized at different temperatures (600 °C, 750 °C, and 900 °C) utilizing the KIT-6 silica template applied as adsorption cathodes for NHCs, paired with the superionic conductor Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> as the anode material. Raman measurement indicates that the degree of graphitization is maximized at 750 °C. As a result, the OMC carbonized at 750 °C delivered the best performance among three OMCs, with a high energy density (54 W h kg<sup>-1</sup>), high power (2200 W kg<sup>-1</sup>) and superior stability (5000 cycles). The current research demonstrates a new platform for utilizing OMCs as adsorption electrodes in NHCs to realize a high-energy, high-power, and highly stable storage devices.

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## 1. Introduction

The increased utilization of electrochemical energy storage (EES) devices is an obvious need in the current time of energy crises and environmental pollution. Lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs) exhibit the high energy densities, which are beneficial for large-scale commercialization. However, the limited specific powers and short cycle lifetimes of LIBs and NIBs restrict their further applications [1,2]. Meanwhile, supercapacitors possess high power densities and long-term stability for a million cycles, but low energy densities because of the physical adsorption–desorption mechanism [3]. Thus, hybrid capacitors that integrate the high energy density of batteries with the superior power density and long-term stability of supercapacitors are important for the development of EES devices.

Hybrid capacitor systems utilize conventional porous carbon electrodes as the cathodes to store anions via non-faradic sorption mechanisms and battery-type intercalation anodes to store cations via redox reactions. Based on the type of cation stored in the battery electrode, these systems can be classified as lithium or sodium

hybrid capacitors [4,5]. Sodium hybrid capacitors (NHCs) as emerging energy storage devices have recently been demonstrated as potential rivals to lithium hybrid capacitors (LHCs) in terms of both performance and cost. However, NHCs require deeper investigations for further improvements in their energy-power behaviors [6,7].

The energy-power behaviors of NHCs are greatly influenced by the cathodes, which are generally porous carbon materials. A large capacity difference between the anode and cathode in an asymmetric configuration can greatly affect the energy retention at high-power conditions [8–10]. The surface area and pore structure of the cathode are the critical factors affecting the charge storage capacity. Generally, a high-surface-area carbon-based material with many pores facilitates high electrochemical capacitance [11,12].

Among various carbon materials, ordered mesoporous carbon (OMC) materials have recently attracted much attention because they have well-ordered pore structures, extremely high surface areas and pore volumes, and good chemical and mechanical stability [13]. OMCs are generally synthesized by replication from mesoporous silica templates, including MCM-48 [14,15], SBA-1 [16], SBA-15 [17], and KIT-6 [18], named CMK-1, CMK-2, CMK-3, and CMK-8, respectively. By varying the pore structure of the mesoporous silica template, different types of carbon materials can be produced. Research on OMCs for NHCs is lacking to date. CMK-3, with a hexagonally ordered mesoporous structure synthesized

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using SBA-15 as a template, is among the most common electrode materials [13,19,20]. Although CMK-3 possesses a high energy storage capacity, it also exhibits low structural stability and poor ion mobility [21]. The 3D cubic mesostructure KIT-6 is a better candidate than SBA-15 to synthesize carbon-based materials for supercapacitors. CMK-8, synthesized via KIT-6, is expected to have high structural stability and high ion adsorption kinetics, thereby presenting good candidacy for use as NHC cathodes.

Herein, we report for the first time the utilization of OMCs derived from KIT-6 silica templates as the cathode for NHCs coupled with  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) as a sodium insertion host (anode). OMCs synthesized at various temperatures (600 °C, 750 °C, and 900 °C) were used as capacitor-type adsorption electrodes. The effects of the carbonization temperatures, pore structures, and textural properties on the electrochemical performance of the NHCs were deeply investigated. OMC used in hybrid capacitors can greatly enhance the high-power behaviors of NHCs, while providing good cyclability. The results also suggest the need for OMCs with strong carbon frameworks to enhance the energy output, power, and cyclability of NHCs.

## 2. Experimental section

### 2.1. Synthesis of mesoporous carbon

The mesoporous silica template KIT-6 was prepared according to a procedure reported elsewhere [22]. Typically, 9.6 g of the triblock copolymer P123 (Sigma-Aldrich) was mixed with 346.6 g distilled water and 18.8 g concentrated HCl (Daejung Chemical & Metal, South Korea). After the complete dissolution of P123, 9.6 g of butanol (Sigma-Aldrich) was added. The mixed solution was then stirred for 1 h at 35 °C, followed by the addition of 24.8 g tetraethyl orthosilicate (Sigma-Aldrich) and holding at 35 °C for 24 h. The mixture was then held at 100 °C for another 24 h. The white precipitate was collected, washed by distilled water several times, and dried at 100 °C. Mesoporous KIT-6 was obtained after calcination at 550 °C for 2.5 h.

The mesoporous carbon CMK-8 was synthesized by an incipient wetness method using the KIT-6 template. A certain amount of furfuryl alcohol (Sigma-Aldrich), corresponding to 80% of the pore volume of KIT-6 was used to impregnate 3.0 g of KIT-6 template. The impregnated sample was dried at 100 °C for 6 h and heated at 350 °C for 2 h in  $\text{N}_2$  with the heating rate of 1.3 °C/min. The impregnation process was repeated twice more with the volumes of furfuryl alcohol corresponding to 50% and 20% of the pore volume of KIT-6, respectively. After the third impregnation step, the mixture was carbonized at high temperatures of 600 °C, 750 °C, and 900 °C for 2 h in  $\text{N}_2$  flow. The black powder obtained after carbonization was washed with a solution of 2 M NaOH and deionized water to remove the silica template and then dried at 100 °C for 12 h. The OMCs carbonized at different temperatures are henceforth denoted as CMK- $x$ , where  $x$  is the carbonization temperature.

### 2.2. Characterization

The specific surface area and the total pore volume of the carbons were calculated by the  $\text{N}_2$  adsorption–desorption measurement using a TriStar II 3020 system (Micromeritics, USA). X-ray diffraction (XRD) measurements were performed on a Rigaku D-MAX 3 system with a  $\text{Cu K}\beta$  radiation. Transmission electron microscopy (TEM) (CM200, Philips) was used to characterize the morphology and the replica of the carbon specimens. Raman spectra were recorded by a LabRam HR800 instrument (Horiba Jobin-Yvon, France, installed at Korea Basic Science Institute),

equipped with an excitation laser of 515 nm in wavelength.

### 2.3. Electrochemical studies

Carbon-coated NVP and CMK- $x$  were used as the anode and cathode in the hybrid capacitor, respectively. The synthesis methodology, structural characterization, and sodium storage ability of NVP was briefly discussed in our previous publication [6]. The half-cell performances of CMK- $x$  with sodium metal as a counter electrode were shown in the supporting information (Fig. S1 and S2). The electrode composition used for the hybrid capacitor was 80 wt % of the active material, 10 wt% Ketjen black conductive additive, and 10 wt% Teflonized acetylene black binder. The slurry was cast over a stainless steel mesh under pressure and dried at 160 °C for 4 h under vacuum prior to cell fabrication. CR2032 coin-cells were assembled with NVP anodes and CMK- $x$  cathodes in a standard configuration within an Ar-filled glove box with the moisture content of <0.1 ppm. The mass ratio between NVP and CMK- $x$  was 1:2. The electrodes were separated by a porous polypropylene separator; the electrolyte was 1 M  $\text{NaClO}_4$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 vol/vol). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were performed using a Bio-Logic electrochemical work station (SP-150, France). Galvanostatic charge–discharge studies were executed with a Won-A-Tech Battery tester (WBCS 3000, Korea) with cycling between 0 and 3 V at different current densities in ambient conditions. The power density was calculated as  $P = (I/V/2m) \text{ W kg}^{-1}$ , where  $I$  is the current,  $V$  is the working potential of the system, and  $m$  is the mass of active material in both electrodes. The energy density was calculated as  $E = (P \cdot t) \text{ W h kg}^{-1}$ , where  $t$  is the discharge time [6].

## 3. Results and discussions

### 3.1. Characterization of mesoporous carbon

Fig. 1 shows the XRD patterns of the KIT-6 template and CMK- $x$ . In the low-angle XRD, similar to the pattern of the KIT-6 template, all patterns of CMK- $x$  show three clear diffraction peaks, indexed as the (211), (220), and (420) planes of a cubic  $la3d$  structure [13]. These indicate the successful replication of the KIT-6 mesoporous structure. When the carbonization temperature is increased, the intensity of the main peak is increased, and all the peaks are shifted to higher degree values. These changes may be due to the structural disorder and the framework shrinkage during the carbonization process, which can cause decreases of the cell parameters [23,24]. In addition, a prominent peak appears at  $2\theta = 23^\circ$  and a small broad peak around  $43^\circ$  in the wide-angle XRD patterns of CMK- $x$  (Fig. 1b), indicating that these materials are amorphous. The broad peak is assigned to the interlayer (002) diffraction resulting from stacks of parallel layer planes, and the intra-layer (100) peak from clusters of graphene sheets plus small amounts of disorganized carbon, respectively. The simultaneous presence of the (002) and (100) reflections suggest that CMK- $x$  possess both hexagonal and rhombohedral phases [13,18,25].

The as-synthesized carbon materials were further characterized by Raman spectroscopy, as shown in Fig. 2. The Raman spectra exhibit two peaks at approximately 1340 and 1600  $\text{cm}^{-1}$ . The first is attributed to the D band related to disordered carbon or defective graphitic structures, while the second is assigned to the G band corresponding to the typical graphitic structure [26]. Thus, higher intensity ratios of the G to D band ( $I_G/I_D$ ) indicate higher degrees of graphitization. The  $I_G/I_D$  ratio is maximized at 1.29 for CMK-750 compared to CMK-600 and CMK-900, demonstrating that carbonization at 750 °C produces the carbon material with the highest-

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