Microporous 3D Graphene-Like Carbon as Iodine Host for Zinc-Based Battery–Supercapacitor Hybrid Energy Storage with Ultrahigh Energy and Power Densities

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Zinc (Zn)-based aqueous battery-supercapacitor hybrid (BSH) devices are considered promising energy storage devices benefiting from their high energy and power densities, low-cost, safety, and environmental benignity. However, challenges remain in the development of efficient BSH electrodes due to poor reversibility in battery electrodes and lack of efficient supercapacitor electrodes to solve the problems of low power and energy densities. Herein, the loading of iodine (I_2) in the nanopores of 3D graphene-like carbon (3DGC) for the fabrication of BSH electrodes and their device application with Zn are reported. The uniform micropores of 3DGC serve as nanocages to stabilize I_2, the high surface area of 3DGC maximizes the dispersion, and the high conductivity of 3DGC provides a path for fast electron transfer. The resultant I_2-loaded 3DGC (I_2/3DGC) is applied to evaluate Zn-based battery and BSH performance. The I_2/3DGC-based electrode exhibits excellent performance with ultrahigh energy and power densities resulting from the high reversibility of I_2 and supercapacitance of 3DGC. The device exhibits high cyclic stability in both battery and supercapacitor modes due to the confinement of I_2 in the micropores. It is demonstrated that this combination of 3DGC with I_2 provides an easy way to fabricate durable and economical BSH electrodes.

1. Introduction

The development of materials for energy storage devices, such as batteries and supercapacitors, has attracted significant interest due to the limited availability of fossil fuels and the continuous increase of environmental pollution and resultant abrupt climate change.[13] In general, batteries deliver high energy density but suffer from low power density and low cyclic stability due to the poor reversibility and stability of the battery materials.[2] In contrast, supercapacitors can deliver high power density with high cyclic stability but suffer from low energy density due to their surface-limited charge storage mechanism.[3–5] Therefore, an efficient energy storage device with a combination of the high energy density of a battery and the high power density of a supercapacitor is highly desirable for complex electrical systems, such as high-power electronics and electric vehicles, for which controllable performance is required simultaneously.[6,7] In this regard, battery–supercapacitor hybrid (BSH) electrodes and devices were recently reported to exhibit both high energy and power densities, fast charge/discharge capability, and excellent cycling stability for on-demand applications.[8–10] The working principle of a BSH electrode involves both an oxidation/reduction reaction (i.e., in a battery) and ion adsorption/desorption on the electrode surface (i.e., in a capacitor).[6,10] Therefore, by selecting a suitable battery-type electrode material that works in the given potential range and by utilizing the full capacitance of a capacitive electrode material in a BSH electrode, the output voltage of a full-cell device can be increased, resulting in an increase in its energy and power densities. Therefore, a combination of redox-active molecules and high-surface-area carbon materials is the ideal choice for the fabrication of BSH electrodes.

Transition metal–based electrode materials have been widely investigated as battery electrode materials because of their multiple oxidation states, superior redox activity, and high theoretical capacity.[13–19] However, they show unsatisfactory performance in energy storage applications because of their low electrochemical stability in real operating conditions.[19] Recently, as a battery cathode material, iodine (I_2) has stimulated great interest due to its high volumetric energy density, low cost, and high abundance compared with traditional transition metal–based cathode materials.[12,13] Furthermore, conversion of iodine to the iodide ion is one of the most efficient redox processes, with fast kinetics and high reversibility.[14–17] Nonetheless, despite the various advantages of the iodine species, the poor intrinsic electronic
conductivity of elemental iodine and the high solubility of discharge products (iodide and polyiodide ions) have usually hindered device energy storage performance.\textsuperscript{[18, 19]}

To overcome the poor electronic conductivity and solubility of iodine species, a lot of effort has been devoted to confining iodine in conductive carbon matrices to enhance the conductivity and suppress iodine leaching.\textsuperscript{[20–22]} Recently, various carbon-based materials, including carbon cloth,\textsuperscript{[23–25]} activated carbon,\textsuperscript{[19, 23–25]} mesoporous carbon (2–50 nm in pore diameter),\textsuperscript{[21]} polyaniline,\textsuperscript{[26]} N-doped carbon,\textsuperscript{[27, 28]} metal–organic frameworks,\textsuperscript{[29]} and MXenes,\textsuperscript{[30]} have been used as host materials to confine I\textsubscript{2} for metal–iodine battery application.\textsuperscript{[31]} Although an I\textsubscript{2}-based cathode has been used for battery application, the BSH performance of the I\textsubscript{2} cathode has not been explored yet probably due to the low surface area of the host material, which limits the full utilization of the I\textsubscript{2} species and accessibility of electrolyte ions, resulting in low performance. Therefore, it is highly desired to develop a carbon-based host material with high conductivity and high surface area and possessing high iodine loading for BSH application.\textsuperscript{[1b, 32]} In this regard, 3D graphene-like carbons (3DGCs) are a potentially promising host material for I\textsubscript{2}. Recently, our group developed a scalable production method for 3DGC via zeolite-templated synthesis.\textsuperscript{[33, 34]} The synthesized 3DGC exhibited a large accessible surface area and high electrical conductivity that originated from the graphene-like frameworks constituting the 3D interconnected pore structure, thereby presumably resulting in full utilization of iodine species.\textsuperscript{[33, 35]} In addition, 3DGC has been reported to exhibit high electrical double-layer capacitor (EDLC) performance originating from its high surface area and high conductivity, which makes this an ideal candidate as a host for redox molecules (i.e., battery material) in the fabrication of BSH electrodes.\textsuperscript{[36, 37]}

Herein, we developed a novel BSH electrode material using I\textsubscript{2} as the battery material and 3D GC as the capacitive material by simple sublimation of I\textsubscript{2} into the micropores (<2 nm in pore diameter according to the IUPAC nomenclature) of 3DGC. The hydrophobic carbon surfaces of 3DGC provide favorable adsorption of I\textsubscript{2} into the micropores of 3DGC. The battery and BSH devices were assembled using I\textsubscript{2}-loaded 3DGC as the cathode and zinc metal (Zn) as the anode; Zn was used because it is abundant in nature, inexpensive, and has a high energy density. The I\textsubscript{2} entrapped in the carbon micropores provides a reversible I\textsubscript{2}/2I\textsuperscript{−} redox reaction, which acts as an electron relay during the charge/discharge process. 3DGC has graphene-like carbon frameworks that can provide conductive paths for electrons and an interconnected pore structure, thereby enhancing the diffusion and storage of electrolyte ions. The synergistic effect between the confined I\textsubscript{2}/2I\textsuperscript{−} redox couple and the EDLC capacitance of 3DGC at the cathode leads to a remarkable enhancement in both the energy density and power density of the Zn-based BSH device.

2. Results and Discussion

2.1. Synthesis and Characterization of I\textsubscript{2}-Loaded 3DGC

The carbon product obtained from Ca\textsuperscript{2+} ion–exchanged beta zeolite is denoted as 3D graphene-like carbon, or 3DGC, because of its graphenic frameworks, which constitute a 3D interconnected porous structure.\textsuperscript{[31]} The formation of electrode materials involves the encapsulation of I\textsubscript{2} molecules into the micropores of 3DGC (Figure 1a). As 3DGC is hydrophobic in nature and possesses an ordered microporous structure with pore diameters less than 1 nm, the entrapment of I\textsubscript{2} molecules in the micropores of 3DGC is favored because I\textsubscript{2} is also hydrophobic and the molecular diameter is around 0.5 nm.\textsuperscript{[18]} Figure 1b shows the Ar adsorption/desorption isotherms of 3DGC. The adsorption isotherm of 3DGC exhibited a type-I isotherm with a very sharp increase in the relative pressure region of P/P\textsubscript{0} < 0.05. This increase of the adsorbed amount can be interpreted as being due to Ar filling of the microporous structure of 3DGC. The corresponding pore size distribution, derived using quenched solid density-functional theory (QSDFT) and assuming a slit-shaped pore geometry,\textsuperscript{[39]} showed a sharp peak centered at 0.9 nm (Figure S1, Supporting Information).

Table 1 shows the BET surface area and micropore volume of the carbon and carbon-iodine composite samples. 3DGC has a high Brunauer–Emmett–Teller (BET) specific surface area of 3050 m\textsuperscript{2} g\textsuperscript{−1}. From the Ar adsorption/desorption isotherms of I\textsubscript{2}-loaded 3DGC (I\textsubscript{2}/3DGC), it was deduced that iodine infiltration into 3DGC caused a distinct decrease in the amount of Ar adsorption in the low-pressure region (Figure 1b). The pore size distribution of I\textsubscript{2}/3DGC (Figure S1, Supporting Information) showed the disappearance of the 0.9 nm micropore peak. The surface area of I\textsubscript{2}/3DGC was 220 m\textsuperscript{2} g\textsuperscript{−1} and its micropore volume was 0.09 cm\textsuperscript{3} g\textsuperscript{−1} (Table 1). For comparison of the I\textsubscript{2} loading capacity of other types of carbon, I\textsubscript{2} was loaded in carbon mesostructured by KAIST (CMK) (Figure S2, Supporting Information) and microporous activated carbon (Figure S3, Supporting Information) in the same manner as in the case of I\textsubscript{2}/3DGC. The textual properties of both I\textsubscript{2}-loaded CMK (I\textsubscript{2}/CMK) and I\textsubscript{2}-loaded activated carbon (I\textsubscript{2}/AC) were measured (Figure S2b,c and Figure S3b,c, Supporting Information) and are shown in Table 1, in which it can be observed that both CMK and AC have much lower surface areas than 3DGC and that their second composite (I\textsubscript{2}/CMK and I\textsubscript{2}/AC) also has a lower surface area than that of I\textsubscript{2}/3DGC. The X-ray powder diffraction (XRD) pattern of 3DGC, as shown in Figure 1c, displays well-resolved peaks at 2θ = 7.8° and 14.9°, suggesting an ordered microporous structure inherited from the beta zeolite template.\textsuperscript{[39]} After the loading of I\textsubscript{2} in 3DGC, the peaks at 2θ = 7.8° and 14.9° corresponding to 3DGC micropores completely disappeared because the micropores were filled with I\textsubscript{2}. The wide-angle region of the XRD of I\textsubscript{2}/3DGC displays no crystalline iodine peaks as I\textsubscript{2} is confined in the micropores of 3DGC (Figure 1c). Here, the structural collapse of 3DGC in I\textsubscript{2}/3DGC cannot be ruled out as the XRD peak intensity decreases significantly. We revealed that after the removal of I\textsubscript{2} by heating in N\textsubscript{2}, the structural ordering of 3DGC was the same as in the case of pristine ZTC (Figure S4, Supporting Information).

Figure 2a shows scanning electron microscope (SEM) images of the resultant I\textsubscript{2}/3DGC samples. The SEM images reveal that, after the iodine loading, the carbon samples maintained their original morphology without observable bulk iodine crystals on the surface, indicating the encapsulation of I\textsubscript{2} molecules into the porous structure of 3DGC. The SEM images measured at a low magnification do not show any observable bulk iodine...
crystals (Figure S5, Supporting Information). Figure 2b provides high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images and Figure 2c,d provides the corresponding STEM–energy-dispersive X-ray spectroscopic (EDS) mapping images for elemental C and I in I₂/3DGC. In the iodine–carbon hybrid samples, the resultant mapping images show the uniform distribution of iodine across the carbon particles. Thus, SEM and STEM investigations indicated that iodine

Table 1. Textural properties of carbons and iodine–carbon hybrids.

| Samples    | S_{BET} | V_{total} | V_{micro} | V_{meso} |
|------------|---------|-----------|-----------|----------|
| 3DGC       | 3050    | 1.49      | 1.21      | 0.28     |
| CMK-3      | 854     | 1.28      | 0.15      | 1.03     |
| AC         | 1420    | 1.33      | 0.47      | 0.86     |
| I₂/3DGC    | 220     | 0.15      | 0.09      | 0.06     |
| I₂/CMK-3   | 163     | 0.21      | 0.04      | 0.05     |
| I₂/AC      | 132     | 0.19      | 0.04      | 0.15     |

*BET surface area was calculated from the adsorption branch in the region of \( P/P_0 = 0.05–0.15; \) total pore volume was determined at \( P/P_0 = 0.97; \) micropore volume was determined from the cumulative volume in the pore diameter range of \( d < 2 \text{ nm}; \) mesopore volume was calculated by subtracting the micropore volume from the total pore volume.

Figure 2. Electron microscopic observation and elemental mapping analysis of iodine–carbon hybrids. a) SEM image of I₂/3DGC. b) HAADF-STEM image of I₂/3DGC and corresponding atomic-resolution STEM-EDS mapping images for c) C and d) I elements.
completely infiltrated the pore interior of the carbon samples. Based on these results, it was reasonable to conclude that contact between iodine and the graphene-like carbon framework was good. In addition, the X-ray photoelectron spectroscopy (XPS) survey spectrum of I2/3DGC shows the presence of elemental iodine in 3DGC (Figure S6, Supporting Information).

The thermogravimetric analysis (TGA) under N2 gas flow. As shown in Figure 3, no mass loss of I2 occurred below 155 °C, revealing the high thermostability of I2/3DGC. We compared the TGA profile of I2/3DGC with those of other composites of I2/CMK-3 and I2/AC. The TGA profiles of I2/CMK-3 and I2/AC exhibited a mass loss of I2 at around 120 °C (Figure 3). These TGA results reveal that the thermostability of iodine in I2/3DGC was higher than those of I2/AC and I2/CMK-3. The higher stability of iodine in I2/3DGC arises from the strong bonding between iodine and the graphene-like carbon framework was evident from the XPS survey spectrum of I2/3DGC shows the presence of elemental iodine in 3DGC (Figure S6, Supporting Information).

Finally, after 200 minutes, all the iodine was completely removed from the three samples, leaving only carbon. The measured iodine loadings were 58 ± 2.4, 55 ± 2.4, and 70 ± 2.5 wt% in I2/3DGC, I2/CMK-3, and I2/AC, respectively.

2.2. Zn–I2 Battery Performance of I2/3DGC BSH Electrode

The battery performance of the I2/3DGC electrode was evaluated by fabricating a Zn–I2 battery using I2/3DGC as the cathode and Zn as the anode. The cyclic voltammetry (CV) curve of the Zn–I2 battery with five repetitive scans in the range of 1.7–0.9 V at a scan rate of 1 mV s⁻¹ shows a pair of stable redox peaks with peak-to-peak separation (ΔE_p) of 100 mV (Figure 4a), corresponding to the redox reaction of the I2/2I⁻ redox couple. The peak at 1.25 V corresponds to the reduction of I2 to 2I⁻ and the peak at 1.35 V corresponds to the oxidation of I⁻ to I2. The stable and low ΔE_p value in the CV of the I2/3DGC electrode in the Zn–I2 battery reveals the high electrochemical stability of iodine species and the favorable electron transfer process in I2/3DGC due to the confinement of iodine species in the micropores of 3DGC. The CV at different scan rates (0.5–2 mV s⁻¹) reveals that the peak current increases without change in peak potential, implying the high reversibility and fast electron transfer of the I2/2I⁻ redox process (Figure 4b). However, at a higher scan rate (>5 mV s⁻¹) the peak potential shifts (Figure S7a, Supporting Information) and the peak currents are proportional to the square roots of the scan rates, indicating that the reaction process is diffusion-controlled (Figure S7b, Supporting Information).

The performance of the cell was evaluated by the charge/discharge curve (Figure 4c) measured under a constant current density of 0.4 C (1 C = 211 mA h g⁻¹) in the potential range of 0.9–1.65 V (determined from the CV curve). The discharge curve of the I2/3DGC-based Zn–I2 battery displays a flat plateau around 1.27 V and the initial discharge capacity reaches 342 mA h g⁻¹ (Figure 4c). Both CMK-3 and AC have relatively low surface areas, which hinder the full utilization of iodine (Figure 4c). As both CMK-3 and AC have relatively low surface areas, which hinder the full utilization of iodine (Figure 4c).

In addition, the low capacities of I2/AC and I2/CMK-3 are due to the much lower peaks and capacitive currents of both I2/AC and I2/CMK-3, as evident from the CV measurements (Figure S8, Supporting Information). However, recent works of literature reported the high capacity of a Zn–I2 battery with our I2/AC-based cathodes in the lower potential range of 1.6–0.5 V.[24,25] When we tested the Zn–I2 battery with our I2/AC-based cathode in the potential range of 1.65–0.5 V at 0.1 C rate, it showed a higher capacity of 166 mA h g⁻¹, close to the value reported in the literature (Figure S9a, Supporting Information).[25] However, the 3DGC-based electrode showed anomalous high capacity (>600 mA h g⁻¹) at 0.1 C because of the high-capacitance behavior of 3DGC (Figure S9b, Supporting Information). Figure 4d shows the charge/discharge curves of the Zn–I2 battery with I2/3DGC electrode at different C-rates. At the 0.4 C rate, the

![Figure 3](image-url) a) TGA profiles and b) corresponding derivative weight signals of I2/3DGC (black), I2/CMK-3 (red), and I2/AC (blue).
capacity was 342 mA h g⁻¹ and decreased with the increase in the C-rate from 0.4 to 3.2 C. At the 1 C rate, the discharge capacity was 250 mA h g⁻¹, which is higher than the theoretical capacity of 211 mA h g⁻¹. The higher capacity of I₂/3DGC arises due to the capacitance behavior of 3DGC. To know the contribution of the capacitance of 3DGC in the Zn–I₂ battery, we investigated the CV of the Zn–I₂ battery with I₂/3DGC cathode at the scan rate of 1 mV s⁻¹ (Figure S10, Supporting Information). As shown in Figure S10, Supporting Information, the shaded area arises due to the capacitance behavior of 3DGC, which contributes 40% to the total capacity of the Zn–I₂ battery with I₂/3DGC cathode. Moreover, the capacity contribution of each component in the I₂/3DGC-based electrode to the capacity of the Zn–I₂ battery has also been studied by preparing cathodes with only 3DGC and only I₂ on a carbon foam (CF) sheet, which was used as a current collector (Figure S11a, Supporting Information). From Figure S11a, Supporting Information, it is observed that the CF sheet/Zn system shows a low OCV of 0.978 V and the CF sheet has negligible capacity contribution (1.3 mA h g⁻¹, Figure S11b, Supporting Information) because of the very low capacitance current (Figure S11c, Supporting Information). The bare I₂-based electrode in the Zn–I₂ battery (OCV of 1.212 V, Figure S12a, Supporting Information) delivers only 17.5 mA h g⁻¹ (Figure S12b, Supporting Information) because of poor I₂ utilization due to the absence of any support material. The I₂ utilization efficiency was only 7.6% in the I₂/Zn battery. The CV of the I₂/Zn battery (Figure S12c, Supporting Information) also shows a lower capacitive current and peak current corresponding to the I₂/2I⁻ redox reaction with high ΔE_p of 270 mV, revealing the sluggish electron transfer process in the absence of 3DGC, resulting in the decrease in capacity of the I₂/Zn battery. Figure S13, Supporting Information, shows the performance of the 3DGC/Zn system with an OCV of 1.149 V (Figure S13a, Supporting Information). From Figure S13b, Supporting Information, it is observed that 3DGC contributed significantly (100 mA h g⁻¹) to the total capacity of the I₂/3DGC/Zn battery because its supercapacitance behavior originated from its extremely high surface area (3050 m² g⁻¹). The CV of the Zn/3DGC system also shows a high capacitive current, revealing its supercapacitance property (Figure S13c, Supporting Information). Because of the high surface area of 3DGC, the capacity contribution from I₂ is also as high as 150 mA h g⁻¹ due to the high accessibility of confined I₂ (I₂ utilization efficiency of 71%) in the micropore of 3DGC. As 3DGC contributed 100 mA h g⁻¹, the resultant capacity of I₂/3DGC in the Zn–I₂ battery (250 mA h g⁻¹ at 1 C) is higher than the theoretical capacity (211 mA h g⁻¹). At the 3.2 C rate, the Zn–I₂ battery with I₂/3DGC electrode delivers a capacity of 205 mA h g⁻¹, which is only 3% lower than the theoretical capacity of the Zn–I₂ battery (211 mA h g⁻¹). The average discharge voltage at all C-rates is 1.27 V. The Zn–I₂ battery with I₂/3DGC electrode delivers an ultrahigh energy density of 434 Wh kg⁻¹ at a power density of 85 W kg⁻¹, which is higher than that of the currently most efficient Zn–I₂ battery reported (Table S2, Supporting Information).
Information). It also delivers a high energy density of 260 W h kg\(^{-1}\) at a high power density of 872 W kg\(^{-1}\). The cycling performance of I\(_2\)/3DGC was evaluated at different C-rates of 0.4, 0.8, 1.6, and 3.2 C, as shown in Figure 4e. At 0.4 C rate, the initial capacity was 342 mA h g\(^{-1}\); after 50 cycles, the capacity decreased to 300 mA h g\(^{-1}\) with a capacity retention of 87%. At 0.8 C, the initial capacity was 280 mA h g\(^{-1}\) and exhibited 96% (270 mA h g\(^{-1}\)) capacity retention after 50 cycles of operation. At 1.6 C, the initial capacity was 230 mA h g\(^{-1}\), and after 50 cycles, the capacity slightly decreased to 228 mA h g\(^{-1}\) (99% capacity retention). At 3.2 C, the initial capacity was 205 mA h g\(^{-1}\) and stable capacity was exhibited even after 400 cycles of operation with >99% capacity retention. When the current density switched to the initial current density of 0.4 C, the capacity rapidly reverted to 300 mA h g\(^{-1}\). The high capacity retention of the I\(_2\)/3DGC electrode in the Zn–I\(_2\) battery is due to the strong confinement of iodine species in the micropore of 3DGC (vide infra). In addition, the Coulombic efficiency values at 0.4, 0.8, 1.6, and 3.2 C were \(\approx 80\%\), \(\approx 94\%\), \(\approx 98\%\), and \(\approx 99\%\), respectively (Figure 4e). At a low C-rate, the lower Coulombic efficiency may be due to the slow diffusion of the electrolyte in the micropore of 3DGC,[40] causing the higher charging capacity. The stabilized electrochemical impedance spectrum of the cell shows two semicircles (Figure S14, Supporting Information), which implies the presence of two different microstructures of 3DGC and I\(_2\).[41]

### 2.3. BSH Performance of I\(_2\)/3DGC BSH Electrode

The device using I\(_2\)/3DGC as the cathode and Zn as the anode can be termed an asymmetric BSH (I\(_2\)/3DGC//Zn) cell. The OCV of the I\(_2\)/3DGC//Zn device was 1.381 V (Figure S15, Supporting Information), which is higher than the theoretical OCV of the Zn–I\(_2\) battery (i.e., 1.30 V), as described in the following equations.

\[
\text{Anode: } \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad E^0 = 0.763 \text{ V} \tag{1}
\]

\[
\text{Cathode: } I_2 + 2e^- \rightarrow 2I^- \quad E^0 = 0.54 \text{ V} \tag{2}
\]

\[
\text{Overall: } \text{Zn} + I_2 \rightarrow \text{ZnI}_2 \quad E^0 = 1.303 \text{ V} \tag{3}
\]

The higher OCV of the I\(_2\)/3DGC//Zn BSH than that of the Zn–I\(_2\) battery is due to the supercapacitance behavior of 3DGC. Figure 5 shows the electrochemical performance of the I\(_2\)/3DGC//Zn BSH cell. Figure 5a shows the CV curve of the I\(_2\)/3DGC//Zn BSH cell in a potential range 0–1.7 V at a scan rate of 5 mV s\(^{-1}\). The CV curve had a deviated rectangular shape having a high capacitive current with a redox process at 1.22/1.36 V corresponding to the I\(_2\)/2I\(^{-}\) redox couple, as in the case of the Zn–I\(_2\) battery. The CV curves of the I\(_2\)/CMK-3//Zn and I\(_2\)/AC//Zn BSH cell also had a redox process at 1.3/1.52 V corresponding to the I\(_2\)/2I\(^{-}\) redox couple, with low current densities because of their low surface area. Figure 5b shows the

![Figure 5](https://www.advancedsciencenews.com/)

**Figure 5.** a) CV curve at 5 mV s\(^{-1}\) and b) charge/discharge at 0.5 A g\(^{-1}\) of I\(_2\)/3DGC//Zn, I\(_2\)/CMK-3//Zn, and I\(_2\)/AC//Zn BSH devices. c) Charge/discharge at different current densities (1–10 A g\(^{-1}\)) and d) illustration of the Zn\(^{2+}\) ion storage mechanism of I\(_2\)/3DGC//Zn BSH device.
galvanostatic charge/discharge curves of I$_2$/3DGC/Zn, I$_2$/CMK-3/Zn, and I$_2$/AC/Zn BSH cells at 0.5 A g$^{-1}$. From Figure 5b, it can be observed that the I$_2$/3DGC-based BSH exhibited significantly higher capacitance (345 F g$^{-1}$) than those of I$_2$/AC (170 F g$^{-1}$) and I$_2$/CMK-3 (160 F g$^{-1}$) based BSH electrodes. Figure 5c shows the capacitances of the I$_2$/3DGC//Zn BSH device at different current densities in ampere per gram. The I$_2$/3DGC BSH electrode delivers specific capacitances of 278, 252, 216, 190, 170, and 147 F g$^{-1}$ at 1, 2, 4, 6, 8, and 10 A g$^{-1}$, respectively. The I$_2$/3DGC//Zn BSH device delivers an ultrahigh power density of 8.94 kW kg$^{-1}$ at an energy density of 59 W h kg$^{-1}$, which is higher than or comparable to the most efficient BSH devices reported thus far (Table S3, Supporting Information). It also delivers a high energy density of 111 W h kg$^{-1}$ at a high power density of 847 W kg$^{-1}$.

The charge/discharge curves of the BSH device clearly have a curve-shaped slope at $\approx$1–1.4 V and a linear curve at 0–1 V versus Zn/Zn$^{2+}$ at various current densities of 1–10 A g$^{-1}$ due to the battery behavior of the I$_2$/21- redox couple and the supercapacitive behavior of 3DGC, respectively (Figure 5c). These results indicate that the hybrid device combines the mechanisms of a battery and supercapacitor, as shown in Figure 5d. To distinguish the contribution of the battery and supercapacitor in the BSH performance, we examined the CV measured at 5 mV s$^{-1}$ (Figure S16, Supporting Information). In Figure S16, Supporting Information, the dotted areas, which arise due to the battery behavior of I$_2$/21-, contribute $\approx$25% in BSH performance. To understand the mechanism of the charge/discharge process, the discharge products at different voltages were analyzed with XPS measurement (Figure S17, Supporting Information). The XPS results for the electrode materials at charged state (1.7 V) mainly indicate the presence of iodine species in the I$_2$ state, with negligible amounts of I$^-$/I$_2$ species. The discharge product at 1 V, where most of the I$_2$ to ZnI$_2$ conversion takes place, shows high proportions of both I$^-$/I$_2$ and Zn$^{2+}$/Zn$^{2+}$ species. When we measured the XPS of the discharge product at 0 V, we obtained the signature of I$^-$, as in the case of discharge products at 1 V (Figure S17a, Supporting Information). However, compared to the discharge product at 1.6 and 1 V, the proportion of Zn$^{2+}$/Zn$^{2+}$ species significantly increased in the discharge product at 0 V because of the absorption of Zn$^{2+}$ in 3DGC at <1 V (Figure S17b, Supporting Information). These results indicate that the discharge process in the BSH device combines the mechanisms of a battery (i.e., the formation of ZnI$_2$ in the micropore of 3DGC) and a supercapacitor (i.e., adsorption of Zn$^{2+}$/Zn$^{2+}$ in the micropore of 3DGC). More precisely, the charge/discharge process in the Zn/I$_2$/3DGC BSH device involves a “rocking-chair”-type mechanism,[42] in which the Zn anode oxidizes, yielding the Zn$^{2+}$ ions, which are transferred to the I$_2$ center to form ZnI$_2$ and also absorbed in the micropores of the I$_2$/3DGC cathode. During the charging process, ZnI$_2$ and 3DGC expel the Zn$^{2+}$ ions that are transferred and reduced at the Zn electrode.

The cycle stability of the I$_2$/3DGC/Zn BSH cell was evaluated at the current density of 1 A g$^{-1}$ (Figure 6a). The I$_2$/3DGC/Zn BSH cell exhibits a capacity retention of 75% even after 2700 cycles, revealing its high cyclic stability (Figure 6a). To understand the high cyclic stability, we examined the charge/discharge curves of the 2nd and 2700th cycles of the I$_2$/3DGC//Zn BSH cell (Figure 6b). Figure 6b shows that the pattern of the discharge curve, which includes the contribution from the battery material (iodine species) in the capacitance of the I$_2$/3DGC//Zn BSH cell remains the same even in the 2700th cycle. We also analyzed the electrode materials post cyclic stability test with the STEM-EDS mapping (Figure 6c); we did not observe any iodine species on the external surfaces of 3DGC, indicating that the high durability is due to the strong confinement of iodine species in the micropores of 3DGC. The confinement behavior of iodine in the BSH electrode was further studied by UV–vis spectroscopic measurements and color change after soaking the electrode materials in an aqueous ZnSO$_4$ electrolyte (Figure 6d). Figure 6d shows that iodine powder gradually dissolves in the electrolyte solution, and thus the solution exhibits multi-UV–vis absorption peaks ($\lambda_{\text{max}}$ (H$_2$O) nm$^{-1}$, 291, 358, and 443). In contrast, the electrolyte obtained after soaking of I$_2$/3DGC does not show any characteristic peak of I$_2$ nor did the color of the electrolyte change even after 1 month (inset of Figure 6d). From these results, we demonstrate that the dissolution of iodine was highly impeded by the confinement effect of iodine species within the ordered microporous structure of 3DGC, which led to an increase of the cyclic stability in both battery and BSH systems. The slight decrease of the capacitance in BSH at a high cycle number may be due to partial structural damage of 3DGC.$^{[37]}

3. Conclusion

In summary, we have demonstrated the high performance of an iodine cathode prepared by embedding iodine in microporous 3D graphene-like carbon via the conventional melt-diffusion method in Zn–I$_2$ battery and Zn-based BSH device applications. The uniform micropores of 3DGC serve as nanocages to stabilize the iodine species, the high-surface-area 3DGC maximizes the iodine dispersion, and the electrically conductive framework of 3DGC serves as a path for fast charge transfer. The developed iodine–carbon hybrid-based electrode exhibited a high capacity of 342 mAh g$^{-1}$ and ultrahigh energy density of 434 W h kg$^{-1}$ at a power density of 85 W kg$^{-1}$ in the Zn–I$_2$ battery mode; these values are much higher than those of conventional mesoporous carbon CMK- and activated carbon–based iodine cathodes. In the BSH device anode, the I$_2$/3DGC exhibited a high capacitance of 278 g$^{-1}$ at a current density of 1 A g$^{-1}$, with a high energy density of 111 W h kg$^{-1}$ at a power density of 847 W kg$^{-1}$. The I$_2$/3DGC BSH electrode exhibited a high power density of 8.94 kW kg$^{-1}$ at an energy density of 59 W h kg$^{-1}$. In both battery and BSH device modes of operations, the I$_2$/3DGC electrode exhibited excellent cyclic stability due to the strong confinement of I$_2$ in the micropores of 3DGC. Taking the remarkable battery and supercapacitance performance into account, the proposed strategy using zeolite-templated microporous carbon as a matrix will be advantageous for developing a high-performance iodine cathode for Zn–I$_2$ and other possible metal–halogen-based energy storage devices.

4. Experimental Section

Materials: An H$^+$ form of beta zeolite (HSZ-931HQA, Si/Al = 14, powder, Tosoh), ethylene (C$_2$H$_4$, 99.9%, Rigas) and nitrogen (N$_2$, 99.999%,
Joongang gas), HCl (>35%, Daejung), NaOH (>97.0%, pellet, Junsei), ethanol (Merck), CF sheet (280 mm width x 280 mm length x 0.454 mm thickness, MTI), carbon black (Super P, TIMCAL Graphite & Carbon, MTI), zinc foil (100 mm width x 100 mm length x 0.05 mm thickness, MTI), and glass microfiber filters (Grade GF/D 2400, Whatman) were purchased and used as received. Activated charcoal (Darco KB-B, wet powder), CaCl₂·6H₂O (98%), iodine (>99.8%, solid), sodium carboxymethyl cellulose (average M₆₀ ≈ 250,000, degree of substitution 1.2), and ZnSO₄·H₂O (>99.9%) were purchased from Sigma-Aldrich.

**Templated Synthesis of Carbons:** Prior to carbon synthesis, the zeolite sample was ion-exchanged with CaCl₂·6H₂O in a previously reported manner.[34] After Ca²⁺ exchange, the zeolites were filtered, washed with water, and dried. In a typical synthesis of 3DGC, 1 g of CaCl₂·6H₂O in a previously reported manner.[35] The gas flow was controlled at 75 cm³ min⁻¹ under N₂ gas flow. At 650 °C, the N₂ flow was combined with C₂H₄ flow and switched to pass through a water bubbler before reaching the zeolite bed. The temperature of the bubbler was kept at 30 °C for constant steam flow. The N₂/C₂H₄/H₂O volumetric ratio was controlled at 77/19/4 by mass flow controllers (Line-Tech M3030V). The total gas flow was controlled at 75 cm³ min⁻¹. The gas flow at 650 °C was maintained for 2 h for carbon deposition. After completion of the carbon deposition, the gas flow was switched back to dry N₂. The temperature of the sample was increased to 900 °C and maintained for 1.5 h. To remove the zeolite template, the resultant zeolite/carbon composite was collected after cooling to room temperature and treated with 2.0 M NaOH and 1.0 M HCl solutions in a sequential manner.[37] The NaOH–HCl–washed carbon product was acquired by filtration with washing and drying at 100 °C.

For use as a comparison group, a mesoporous carbon CMK-3 sample was synthesized using mesoporous silica SBA-15 as a hard template, following the procedure in the literature.[41]

**I₂ Loading into Carbons:** The solid iodine was crushed and ground with an agate mortar and pestle set (Silico & Chemico Porcelain Works). Then, an individual carbon sample of 0.1 g was homogeneously mixed with the iodine powder at a weight ratio of 2/3 in the mortar. The physical mixture was sealed in a glass tube and heated to 135 °C (heating rate: 5 °C min⁻¹) for 12 h under vacuum. After cooling to room temperature, iodine–carbon composite samples were obtained.

**Characterization:** Argon adsorption–desorption isotherms were obtained at liquid Ar temperature (≈87 K), using a Quantachrome Autosorb iQ volumetric adsorption analyzer. XRD data were obtained on a Rigaku SmartLab diffractometer with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA. SEM images were taken with an FEI Verios 460 instrument operated at an acceleration voltage of 5 kV. HAADF-STEM images were obtained with an FEI Titan cubed G2 60-300 instrument operated at an acceleration voltage of 300 kV at the KAIST Analysis Center for Research Advancement. EDS analyses were performed in diffraction mode using an FEI Super-X detector. Using a TA Instrument TGA Q50 analyzer, TGA was conducted by increasing the temperature to 800 °C at a heating rate of 5 °C min⁻¹ in N₂ flow of 40 cm³ min⁻¹. For XPS measurements, a Thermo Scientific K-alpha spectrometer was used with a degree of ultrahigh vacuum of 10⁻⁸–10⁻⁹ mbar. XPS spectra were obtained using monochromatized Al Kα radiation.

Figure 6. Cyclic stability of I₂/3DGC electrode for BSH applications. a) Change in the capacitance with the number of cycles and b) charge/discharge curve of 2nd and 2700th cycles of I₂/3DGC electrode in the BSH device, revealing its high cyclic stability. c) STEM-EDS analysis results of the I₂/3DGC electrode after 2700 cycles of operation. The images do not show any iodine species on the external surface of 3DGC, revealing the strong confinement of I₂ in the micropore of 3DGC. d) UV–vis spectra and corresponding optical images (inset in (d)) of (A) I₂ powder and (B) I₂/3DGC after being immersed in the aqueous 1 M ZnSO₄ electrolyte solution for 5 d.
UV–vis spectroscopy was conducted with a Shimadzu UV-2600 spectrometer.

Electrochemical Measurements: For battery and BSH device performance measurements, working electrodes were prepared by slurry coating. Specifically, Zn foil was used as the counter electrode. For the preparation of working electrodes, I2-loaded carbon was used as an active material. Super P and sodium carboxymethyl cellulose were also used as the conductive agent and binder, respectively. These powder samples were blended homogeneously in a certain amount of doubly distilled water using the agate mortar. The weight ratio of the active material, conducting agent, and binder was 8/1/1. The prepared slurry was coated on the CF sheet and dried at 60 °C for 8 h. The areal iodine loading was ≈2 mg cm⁻². For electrochemical measurements, the film was punched out to make disc-type electrodes with 15 mm diameter. The bare I2 cathode was prepared using I2 solution prepared in hexane and dropcast on CF sheet and dried at room temperature. To fabricate electrochemical cells, the disc electrodes were transferred to a split test cell (MTI, EQ-STC-MTI). A glass microfiber filter was used as the separator. An aqueous 1 M ZnSO₄ solution was used as the electrolyte. CV and galvanostatic charge/discharge (GCD) measurements were performed at 298 K using an Autolab PGSTAT302N workstation. The cyclic stability test was conducted after the CV measurements at 298 K with a WonAtech WBCS3000 battery cycler. The voltage window for battery mode operation was 0.9–1.7 V and the current density was the current divided by the electrode mass of the active material. For GCD curves of both battery and supercapacitor mode of operation, the second scan was always considered.

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
Research data are not shared.

Keywords
battery–supercapacitor hybrids, energy densities, iodine hosts, power densities, zinc–iodine batteries, 3D graphene-like carbons

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