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Carbon Inverse Opal Macroporous Monolithic Structures as Electrodes for Na-ion and K-ion Batteries

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Highly ordered three-dimensionally structured carbon inverse opals (IOs) produced from sucrose are stable electrodes in sodium-ion and potassium-ion batteries. The walls of the ordered porous carbon structure contain short-range graphitic areas. The interconnected open-worked structure defines a conductive macroporous monolithic electrode that is easily wetted by electrolytes for Na-ion and K-ion systems. Electrochemical characterization in half-cells against Na metal electrodes reveals stable discharge capacities of 25 mAh g⁻¹ at 35 mA g⁻¹ and 40 mAh g⁻¹ at 75 mA g⁻¹ and 185 mA g⁻¹. In K-ion half cells, the carbon IO delivers capacities of 32 mAh g⁻¹ at 35 mA g⁻¹ and ~25 mAh g⁻¹ at 75 mA g⁻¹ and 185 mA g⁻¹. The IOs demonstrate storage mechanisms involving both capacitive and diffusion-controlled processes. Comparison with non-templated carbon thin films highlights the superior capacity retention (72% for IO vs 58% for thin film) and cycling stability of the IO structure in Na-ion cells. Robust structural integrity against volume changes with larger ionic radius of potassium ions is maintained after 250 cycles in K-ion cells. The carbon IOs exhibit stable coulombic efficiency (>99%) in sodium-ion batteries and better coulombic efficiency during cycling compared to typical graphitic carbons.

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The growing demand for large-scale lithium-ion battery (LIB) production for electric vehicles and smart grids is constrained by limited lithium resources and high costs.^{1–3} Sodium-ion batteries (SIBs) emerge as a promising alternative due to abundant sodium resources.^{4–7} Despite the vast abundance of sodium and potassium compared to lithium, potassium-ion batteries (PIBs) have received less attention until recently.^{8–10} PIBs offer advantages such as abundant resources and a closer redox potential to Li/Li⁺ than SIBs, suggesting higher voltage plateau and energy density. However, PIBs face challenges, such as the larger size of K⁺ ions hindering efficient intercalation into some electrode materials.¹¹ The performance of SIBs and PIBs therefore depends on electrode materials, prompting focused efforts to develop materials with specific properties, such as mechanical strength, chemical stability, high surface area, and conductivity.^{12–15}

Among various electrode materials, carbon materials, with their chemical stability, large specific surface, high electrical conductivity, and cost-effectiveness, have garnered attention. The development of nanostructured carbons, such as carbon nanotubes,¹⁶ graphene,¹⁷ carbon nanowires, porous carbons,¹⁸ and hollow carbon spheres,¹⁹ has become an important material set for rechargeable battery anodes. While graphite has been used universally as an anode for LIBs exhibiting a capacity of 370 mAh g⁻¹, it does not work well in SIBs (35 mAh g⁻¹).²⁰ While K-ions can insert into graphite, the theoretical capacity is lower for PIBs than LIBs and repeated cycling can cause extensive volume expansion (~60%) and pulverization of the graphite structure.²¹ Hard carbons, a prospective anode for SIBs,^{22,23} exhibit reversible capacities of 296–353 mAh g⁻¹ in Na-ion cells with heated-treated variants reaching ~430 mAh g⁻¹.^{24,25} In potassium-ion batteries, the hard carbon electrode falls short of the theoretical KC₈ capacity (280 mAh g⁻¹), highlighting the need

for increased potassiation capacity to demonstrate higher energy density.²⁶

Three-dimensionally ordered macroporous structures can be useful as electrode materials for sodium-ion and potassium-ion batteries, and as a model system to see how porosity and interconnected structure can affect the overall cycling behavior compared to thin films or random slurries of various carbon types. These structures, previously explored in lithium-ion batteries, have demonstrated their capacity to enhance rate performance and longevity.^{27–31} The ordered macroporous design offers advantages such as improved structural integrity, providing a stable framework that mitigates volume expansion during charge-discharge cycles. This inherent stability contributes to sustained electrochemical performance over extended cycles. Translating these benefits to Na-ion and K-ion batteries holds significant potential, addressing challenges posed by the larger size of sodium and potassium ions. Specifically in K-ion batteries, capacity fading has been reported due to suspected large volume changes with cycling.^{32,33} The ordered macroporous architecture facilitates efficient ion diffusion and electrolyte permeation, factors critical for optimizing the electrochemical performance of Na-ion and K-ion batteries. By harnessing the structural advantages observed in lithium-ion batteries, three-dimensional ordered macroporous structures^{34–36} emerge as a promising avenue for advancing the capabilities of Na-ion and K-ion batteries, aligning with the growing demand for sustainable and high-performance energy storage solutions.

In this report, we present a three-dimensionally porous inverse opal structure of carbon and systematically evaluate its performance in sodium and potassium ion cells. Our investigation delves into the influence of this unique macroporous structure on the electrochemical behavior of these cells, specifically examining galvanostatic charge/discharge profiles and distinguishing between capacitive and diffusion-controlled processes. By studying the intricate interplay between the 3D inverse opal structure and the electrochemical characteristics in sodium and potassium ion cells, our aim is to discern the potential of these macroporous structures as versatile

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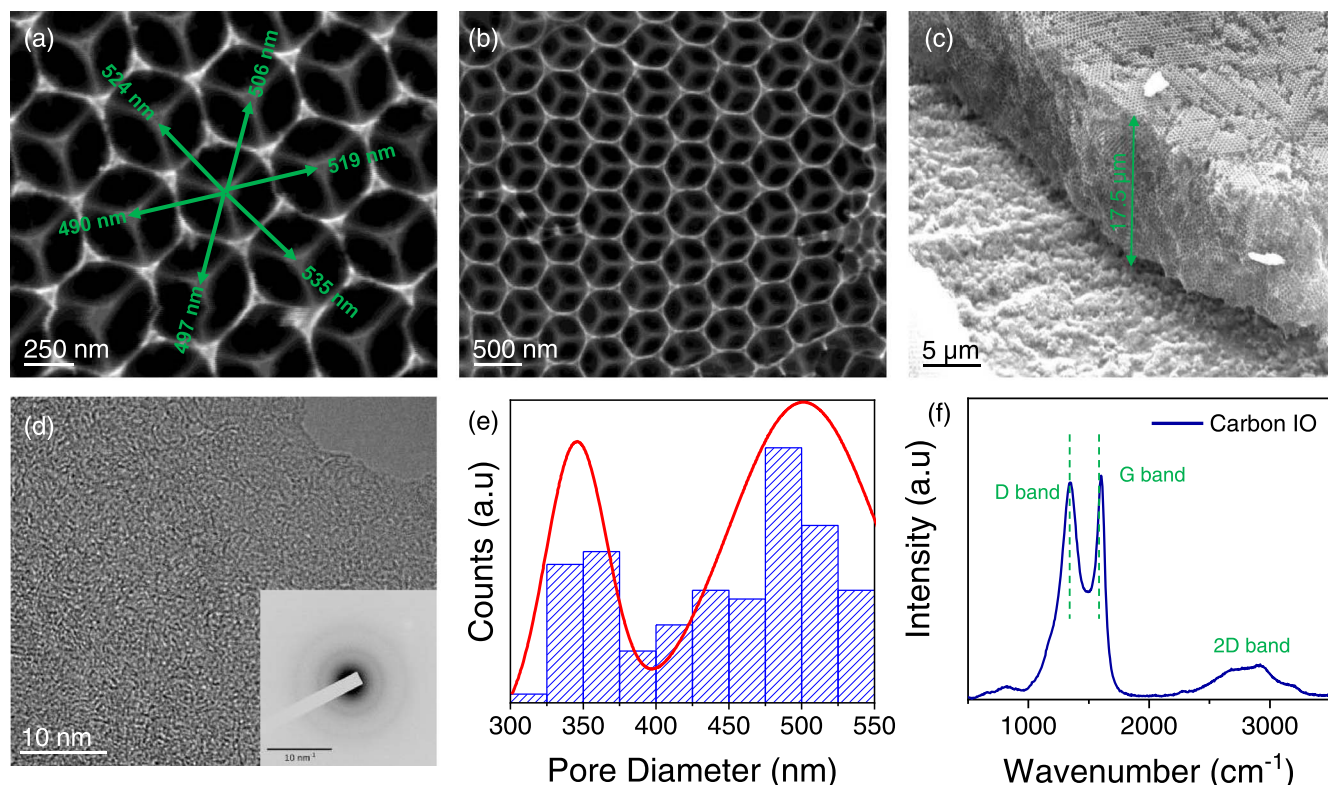


Figure 1. SEM images of carbon inverse opals at various magnitudes highlighting (a) pore size, (b) high degree of order and (c) thickness. (d) HRTEM of carbon IOs. (Inset) SAED showing diffuse rings corresponding to (100) and (110) planes of localized layered graphitic regions. (e) Histogram showing bimodal distribution of pore diameters. (f) Raman spectrum of carbon IOs.

scaffolding or model architectures. This investigation could be useful in unlocking the potential of porous structures in “post-lithium” technologies, contributing to the ongoing evolution of advanced energy storage systems.

Experimental

Materials preparation.—Stainless steel (SS) discs (grade 304) with a diameter of 15.5 mm were used as substrates. The opal template was fabricated using the evaporation induced self-assembly (EISA) method, which involved suspending the SS discs in a 0.2% solution of polystyrene spheres (500 nm diameter, Polysciences GmbH) and deionized water. The suspended discs were placed in a convection oven at 60 °C overnight. The dried PS spheres were infiltrated with ~35 μl of the sucrose solution before being placed in a convection oven at 70 °C for 25 min. The carbon samples were then heated to 100 °C for 5 h in air before being heated to 900 °C at a ramp rate of 5 °C min⁻¹ under Ar and held for 2 h. Carbon electrodes in thin film form were prepared using the same method, excluding the use of polystyrene spheres as a structural template.

Material characterization.—SEM analysis was performed on FEI Quanta 650 FEG high resolution SEM at an accelerating voltage of 10 kV. SEM images and feature dimensions were analyzed using ImageJ software. Raman scattering was performed on an Ocean Optics QE65PRO Raman Spectrometer using a 40 mW Ar⁺ laser at 532 nm excitation. The laser was focused onto the samples using a 40× objective lens and spectra were collected using a CCD camera. TEM analysis was conducted using a JEOL JEM-2100F TEM operating at 200 kV.

Electrochemical characterization.—All electrochemical characterization was performed using BioLogic VSP Potentiostat/Galvanostat. The mass loading of active materials was between 0.5 mg–0.8 mg for all electrodes, corresponding to 0.27–0.43 mg cm⁻² on stainless steel

discs (grade 304) with a diameter of 15.5 mm. The carbon inverse opal material was investigated in a half cell configuration against a pure Li, Na, or K counter electrode using a stainless-steel PAT cell from EL-Cell in a two-electrode configuration. The electrolyte used was 1.0 M LiPF₆ in EC/DMC = 50/50 (v/v) (Sigma Aldrich), 1.0 M NaClO₄ in PC with 5 wt% fluoroethylene carbonate (FEC) additive, and 1.0 M KPF₆ in EC/DMC = 50/50 (v/v) for the lithium, sodium, and potassium cells, respectively. The separator used was glass microfiber from Whatman Grade GF/A cut to size. All electrochemical tests were investigated in a potential window of 2.0 V–0.014 V.

Results and Discussion

Material characterization.—The carbon inverse opal (IO) samples were grown by calcination of a sacrificial self-assembled opal film infiltrated with a sucrose solution. Details of the structure and morphology are demonstrated by scanning electron microscopy (SEM) images in Figs. 1a and 1b. The images show IOs on the current collector, and the morphology is typically islands of three-dimensional ordered macroporous architecture. These IOs are characterized by highly ordered interconnected layers of carbon with face-centred cubic (FCC) symmetry. The growth of the opal template is perpendicular to the (111) plane of the FCC lattice,³⁷ with the various layers seen through the pores of the samples. Cross-sectional SEM imaging of the carbon IO in Fig. 1c shows the thickness of the material is ~17.5 μm. High resolution transmission electron microscopy (HRTEM) is shown in Fig. 1d, a disordered nanostructure was observed in the carbon inverse opal samples featuring curved, short-range graphitic areas within the IO walls. Selected area electron diffraction (SAED) pattern shows dispersive diffraction rings. The disordered microstructure of the carbon IOs is characterized by local regions of puckered layered graphitic structures and their relative orientations contribute to the (100) and (110) planes in the polycrystalline SAED pattern.³⁸ Structural measurements were extracted from the SEM images, captured at various

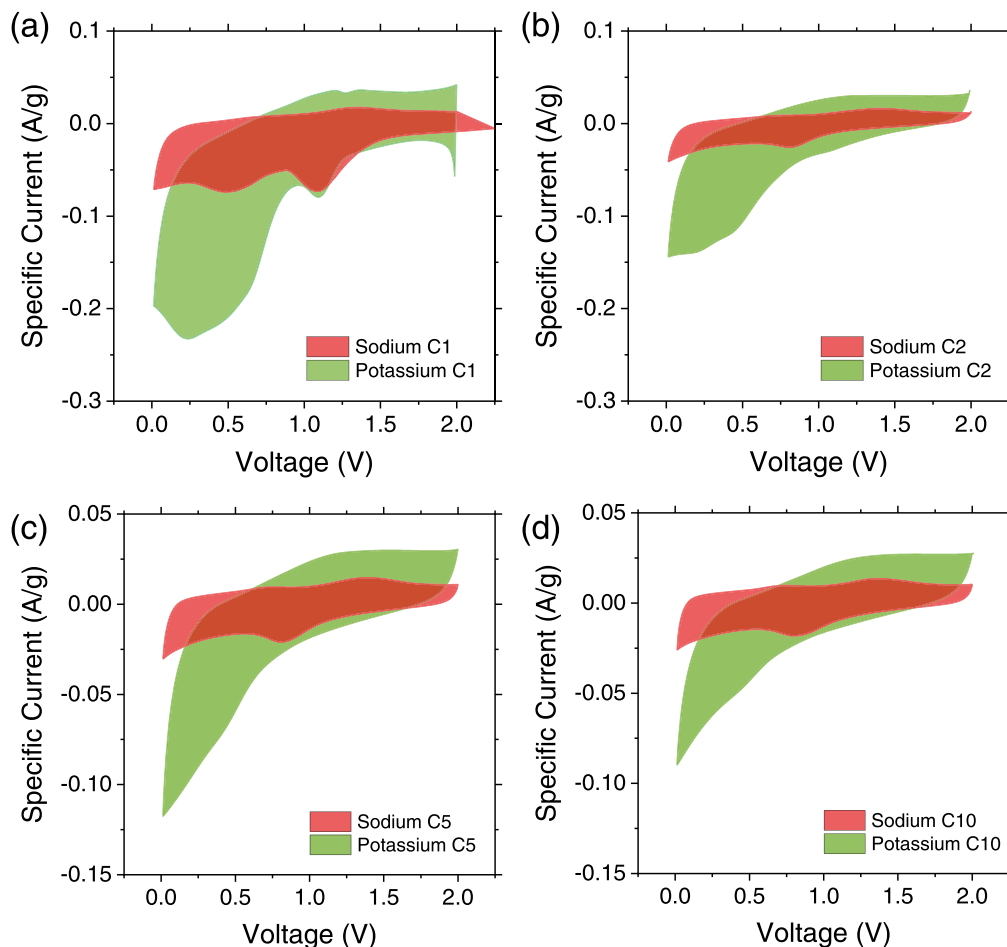


Figure 2. Cyclic voltammograms of (a) 1st scan (C1), (b) 2nd scan (C2), (c) 5th scan (C5) and (d) 10th scan (C10) for carbon inverse opals in sodium and potassium half cells.

locations across the sample surface. To mitigate the influence of potential isotropic swelling, measurements were systematically obtained from various directions across each feature, as seen in Fig. 1a. The material had a bimodal distribution in recorded pore diameter, as shown by the histogram in Fig. 1e, from the regions examined this equates to 68% of the pores being ~ 495 nm in diameter and 32% being ~ 355 nm in diameter. A histogram of wall thickness measurements can be found in the Supplementary materials, Fig. S1, where the thickness is measured to be ~ 26 nm on average.

The macroporosity induces a high surface area-to-volume ratio, offering ample space for optimal electrolyte infiltration. The specific surface area is approximated by considering the ratio of average macropore diameters (68% at 495 nm, and 32% at 355 nm), assuming perfect FCC symmetry and disregarding micropores and mesopores within the IO walls. With each FCC unit cell containing 4 macropores with the area per pore is equal to $4\pi r^2$ and a volume approximated as a^3 (where $a = D\sqrt{2}$), the specific surface area per unit volume is derived as $10.17 \text{ m}^2 \text{ cm}^{-3}$. Using the density of hard carbon (1.5 g cm^{-3})³⁹ and the volume fraction of perfectly ordered FCC arranged inverse opals,⁴⁰ the specific area per unit mass was calculated to be $25.59 \text{ m}^2 \text{ g}^{-1}$. With an average mass loading of 0.65 mg, yields a specific surface area of 0.02 m^2 for these electrodes. While this approximation yields a lower specific surface area compared to other calculations based on N_2 adsorption for carbon IOs,^{41–43} it is worth noting that this calculation does not consider any potential additional meso-/microporosity of the surface and is a lower bound value for the geometrical surface area of the

electrode. Such porosity often constitutes a significant contribution to the surface area values determined by gas adsorption.^{44,45}

Raman spectroscopy, Fig. 1f, shows clear peaks at $\sim 1347 \text{ cm}^{-1}$ and $\sim 1604 \text{ cm}^{-1}$ for the D (disorder) and G (graphitic) bands of carbon, respectively. These bands are associated with the vibrational modes of carbon atoms, the D band is characteristic of disorder induced by sp^3 hybridization and is activated in the presence of structural defects, disorder, or the presence of amorphous carbon.⁴⁶ The G band is associated with the E_{2g} vibrational mode of sp^2 -bonded carbon atoms present in graphitic structures, the intensity of the D band compared to the G band (I_D/I_G), which was 0.97, suggests a combination of ordered and disordered regions in the carbon IO.⁴⁷ The full width at half maximum for the D and G bands are 174.3 cm^{-1} and 72.7 cm^{-1} based on Gaussian models, which could indicate the coexistence of amorphous carbon/disordered regions with graphitic structures.^{48–50} This observation agrees with the HRTEM and SEAD data where the IO structural walls comprise carbon interspersed with localized regions of layered graphitic structures. The broad peak at 2810 cm^{-1} is known as the 2D peak and originates from second order two phonons process, with the weak intensity and broad width indicating defects in the IO.⁵¹

Electrochemical characterization in Na-ion and K-ion cells.—

The electrochemical behavior of the material was characterized in a half cell system against either a Na or K metal counter electrode. Figure 2 shows the cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s^{-1} in the potential window 2 V–0.014 V. The first cycle for carbon IO vs sodium, Fig. 2a, shows cathodic peaks at 1.08 V and

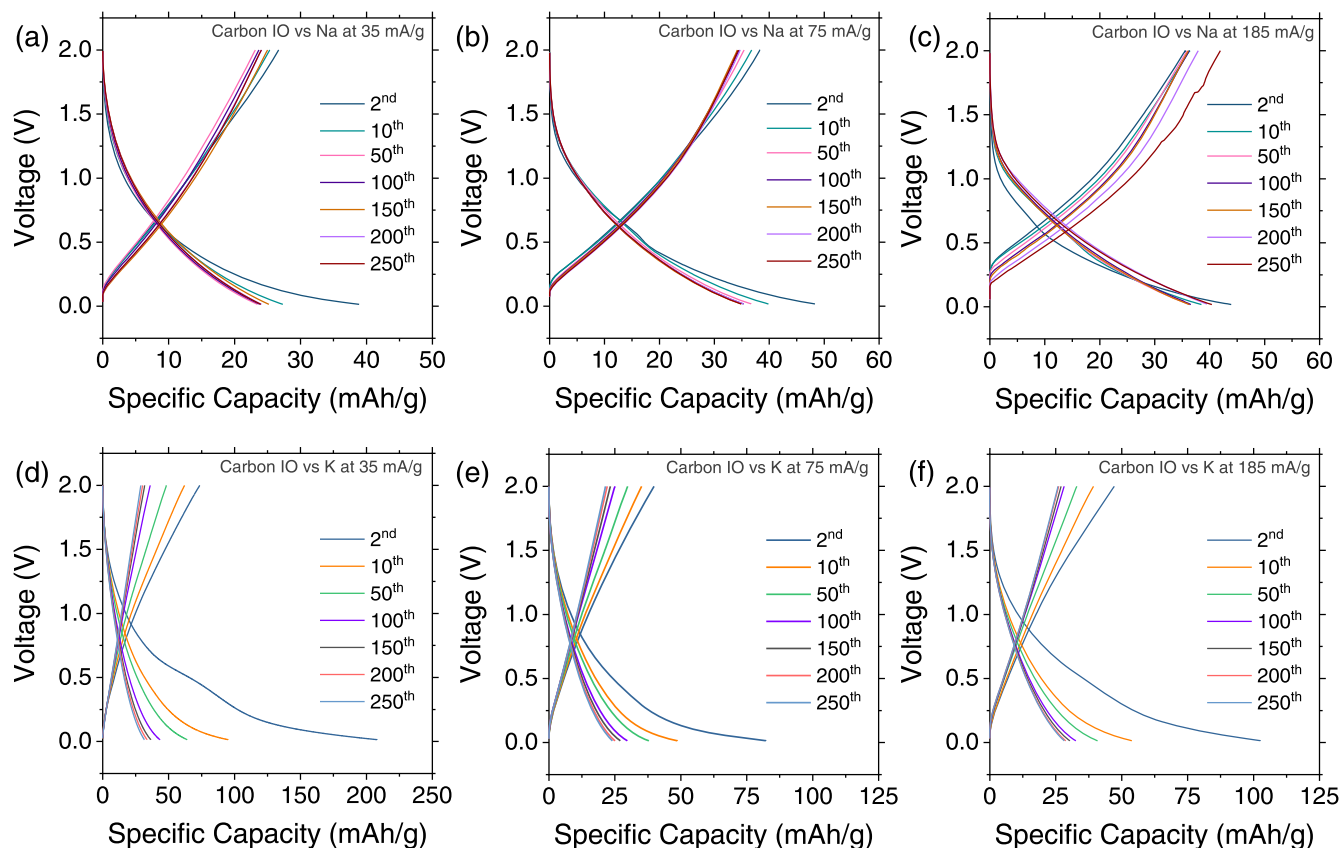


Figure 3. Galvanostatic charge–discharge profiles between 2.0–0.014 V for carbon IOs vs sodium at (a) 35 mA g^{−1}, (b) 75 mA g^{−1}, (c) 185 mA g^{−1}. Charge–discharge profiles for carbon IOs vs potassium at (d) 35 mA g^{−1}, (e) 75 mA g^{−1}, and (f) 185 mA g^{−1}.

0.49 V that disappear in subsequent cycles, and are ascribed to the irreversible reaction between sodium ions and surface functional groups, the decomposition of the electrolyte, the SEI layer formation, and various irreversible side reactions.^{52–54} The cathodic peak at 0.02 V is attributed to the sodium insertion into carbon materials.⁵⁵ From the 2nd cycle onwards, Figs. 2b–2d, a broad cathodic peak at 0.7 V can be seen in the cathodic scan, this is seen for reversible sodiation of oxides on the surface, and the corresponding anodic peak at 1.4 V.⁵⁶ For the desodiation of carbon, a broad peak from 0.014 V – 0.9 V is observed, indicating the extraction of sodium takes place across a wide potential range.⁵⁷

The CVs for the carbon IO vs potassium are shown in Fig. 2 (in green), the initial scan shows cathodic peaks at 1.08 V and a broad peak from ~0.7 V–0.2 V. This broad peak contains a peak at ~0.6 V which is associated with the irreversible reactions such as SEI layer formation and decomposition of electrolyte, the peak at 1.08 V is also ascribed to the SEI layer, as these disappear after the first and second cycle. The potassiation of carbon appears to occur from 0.2 V–0.014 V, with the depotassiation occurring over a wide voltage range similar to that observed in the sodium system. A higher current density is seen in the voltage region of 1.0 V–1.5 V, this has been observed in graphene oxide materials^{58–60} and could indicate extraction reactions with surface oxides as seen compared to the same measurements in the Na-cell.

The electrochemical storage performance of the carbon IOs was examined using galvanostatic cycling for both systems, and the data is shown in Fig. 3. Three rates were examined, 35 mA g^{−1}, 75 mA g^{−1}, and 185 mA g^{−1}, with all cells cycled 250 times to analyze specific capacities and stability in sodium-ion and potassium-ion battery cells. The initial discharges of all cells can be found in the Supplementary materials, Fig. S2. Figures 3a–3c show carbon IO vs Na from the 2nd to the 250th cycle, while the initial discharge was 255 mAh g^{−1} at a current density of 35 mA g^{−1}, this fell to ~40

mAh g^{−1} for the 2nd discharge with a coulombic efficiency of 68%. The specific capacity was stable by the 10th cycle at 27 mAh g^{−1} and maintained this capacity for the 250 cycles with an average coulombic efficiency of 98.6%. The 2nd cycle at 75 mA g^{−1}, shown in Fig. 3b, displayed a discharge and charge capacity of 48.5 mAh g^{−1} and 38.5 mAh g^{−1}, respectively, with a coulombic efficiency of ~79%. The discharge capacity after the 10th cycle was 40 mAh g^{−1} which remained stable over the next 240 cycles, falling to 35 mAh g^{−1} which equated to a 12.5% loss in capacity. When the current density was 185 mA g^{−1}, the carbon IOs showed impressive capacity retention for the 250 cycles, losing just over 1% in specific capacity from 38.5 mAh g^{−1} at the 10th cycle to 38 mAh g^{−1} at the 250th cycle. This was accompanied by a coulombic efficiency of 99.7% on average, indicating stable and reliable cycling at the 185 mA g^{−1} current density.

For the potassium-ion system, carbon inverse opals were cycled at the same rates as outlined for the sodium-ion cells, these are seen in Figs. 3d–3f. A weak plateau was observed during the second cycle at 35 mA g^{−1} (Fig. 3d), from 0.7–0.4 V, followed a sloping region from 0.4 V–0.42 V, and another sloping region extending to the lower potential limit, which is in close agreement with the cathodic peaks observed in the CV. However, capacity fading is more obvious in the K-ion battery compared to the Na-ion, with an initial discharge capacity of 1667 mAh g^{−1} (ICE of ~5%) (Supplementary materials, Fig. S2d), which falls to 208 mAh g^{−1} for the 2nd cycle and continues to fade reaching 32 mAh g^{−1} for the 250th cycle with an average Coulombic efficiency of ~83%. The 75 mA g^{−1} rate shows an initial discharge capacity of 554 mAh g^{−1} with an ICE of ~9%, which is lower than other carbon materials reported for potassium-ion batteries.^{58,61} The 2nd, 10th, and 50th cycles show discharge capacities of 82 mAh g^{−1}, 49 mAh g^{−1} and 38 mAh g^{−1}, respectively. The capacity fades to 24 mAh g^{−1} for the 250th cycle, however the Coulombic efficiency continuously improves reaching

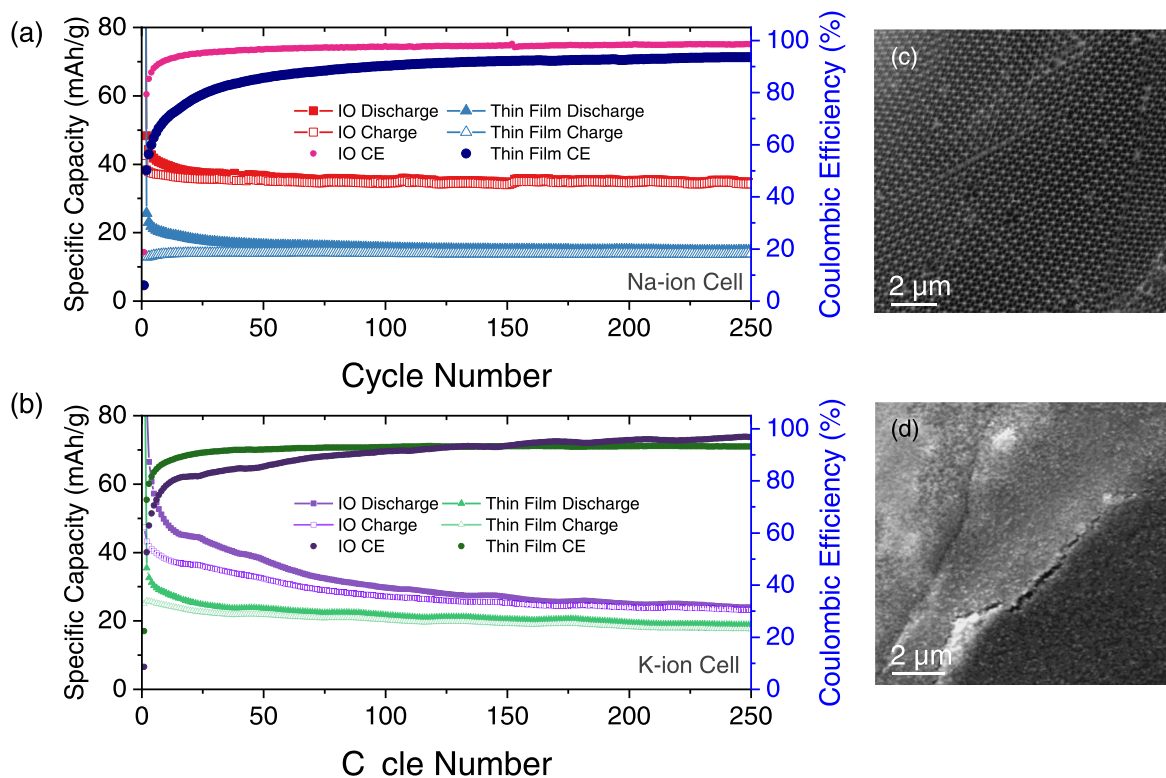


Figure 4. Comparison of (a) carbon IO and carbon thin film vs sodium at 75 mA g^{-1} , and (b) carbon IO and carbon thin film vs potassium at 75 mA g^{-1} . SEM images showing morphology of (c) carbon IO electrode, and (d) carbon thin film electrode.

97% by the 250th cycle. The 185 mA g^{-1} rate, Fig. 3f, showed slightly higher ICE ($\sim 13\%$) with specific capacities of 421 mAh g^{-1} and 53 mAh g^{-1} for the discharge and charge, respectively. The carbon IOs exhibited a discharge capacity of 28 mAh g^{-1} , with a charge capacity of 26 mAh g^{-1} after 250 cycles, showing a Coulombic efficiency of $\sim 92\%$.

The carbon IOs demonstrated a disparity in the K-ion batteries relative to their efficacy in Na-ion batteries. Previous studies have suggested that defects in the electrode structure can enhance specific capacity.^{62,63} While the capacities achieved may not match those recorded for other hard carbon structures ($100\text{--}300 \text{ mAh g}^{-1}$),^{64,65} incorporating heteroatom-doping or composite additions could prove beneficial in this context, leading to an enhancement in specific capacity.^{66,67}

As a comparison, we also acquired galvanostatic charge-discharge curves of the carbon IOs for lithium-ion half cells at current densities of 75 mA g^{-1} and 185 mA g^{-1} , and the data are shown in the Supplementary materials, Fig. S3. At a 75 mA g^{-1} current density, the cell shows an initial Coulombic efficiency of 32% for the carbon inverse opals vs Li, corresponding to a discharge and charge capacity of 731 mAh g^{-1} and 234 mAh g^{-1} , respectively. However, this low Coulombic efficiency is limited to the first few cycles, averaging out to 99% for the 250 cycles. A stable specific capacity is obtained after 10 cycles with a reversible capacity of $\sim 100 \text{ mAh g}^{-1}$. For the 185 mA g^{-1} rate, a lower ICE of 27% was recorded with capacities of 383 mAh g^{-1} and 102 mAh g^{-1} for the discharge and charge. Similar curves are observed for the carbon IOs in all three systems with a sloping voltage region exhibited at $\sim 1.5 \text{ V}$, which is generally associated with surface electrochemical reactions; these processes involve interactions with edge and defect sites as well as adsorption onto the surface of pores.^{68,69} Lithium readily intercalates into the interlayer spacing of graphite, forming LiC_6 at full charge.⁷⁰ However, sodium faces challenges due to its larger ionic radius, leading to thermodynamically unstable graphitic intercalation compounds (GICs).⁷¹ Potassium intercalation is further hindered, and while sodium interactions are described by an “adsorption–intercalation–pore

filling” mechanism, potassium storage in hard carbons is primarily attributed to surface adsorption.^{69,72–74}

To examine how the macroporous structure affected electrochemical behavior, non-templated carbon thin films were tested vs sodium and potassium at a current density of 75 mA g^{-1} , shown in Figs. 4a and 4b. SEM images showing the difference in morphology of the carbon inverse opal and carbon thin film is shown in Figs. 4c and 4d. Additional SEM images showing the morphology of carbon thin films are shown in the Supplementary materials, Fig. S4. Initial Coulombic efficiencies showed an improvement for the IOs in the sodium ion cell, registering 19% ICE for the carbon IO and 6% ICE for the carbon thin film. Comparable discharge capacities of approximately 215 mAh g^{-1} are noted for both materials in the first cycle. However, the thin film exhibits more significant capacity fading, recording 26 mAh g^{-1} in the 2nd discharge compared to 48 mAh g^{-1} in the carbon IO-containing cell. Impressively, the IO maintains consistent discharge capacities of 40 mAh g^{-1} , 35 mAh g^{-1} , and 35 mAh g^{-1} for the 10th, 100th, and 250th cycles, while the thin film shows 20 mAh g^{-1} , 16 mAh g^{-1} , and 15 mAh g^{-1} for the same cycles. This equates to a 28% loss in capacity, from the 2nd to 250th cycle, for the IO structure versus 42% loss in capacity for the thin film. Coulombic efficiencies recorded from the 2nd to the 250th cycle show improved reversibility for the carbon IO with an average CE of 97% while the thin film averaged 89% Coulombic efficiency. Notably, the macroporous carbon doubles the specific capacity relative to the thin film, potentially attributed to the inverse opal structure’s improved electrolyte penetration, shorter diffusion distances, and a higher surface area that is electrochemically accessible, providing additional charge compensation sites for sodium. The IO architecture enables efficient mass transport of ions and electrodes which promotes uniform electrochemical reactions and improves Coulombic efficiency.^{75–77}

Figure 4b illustrates the comparison between the carbon thin film and carbon IO in a potassium-ion half-cell. Notably, the initial coulombic efficiency is higher in the thin film, reaching 22%,

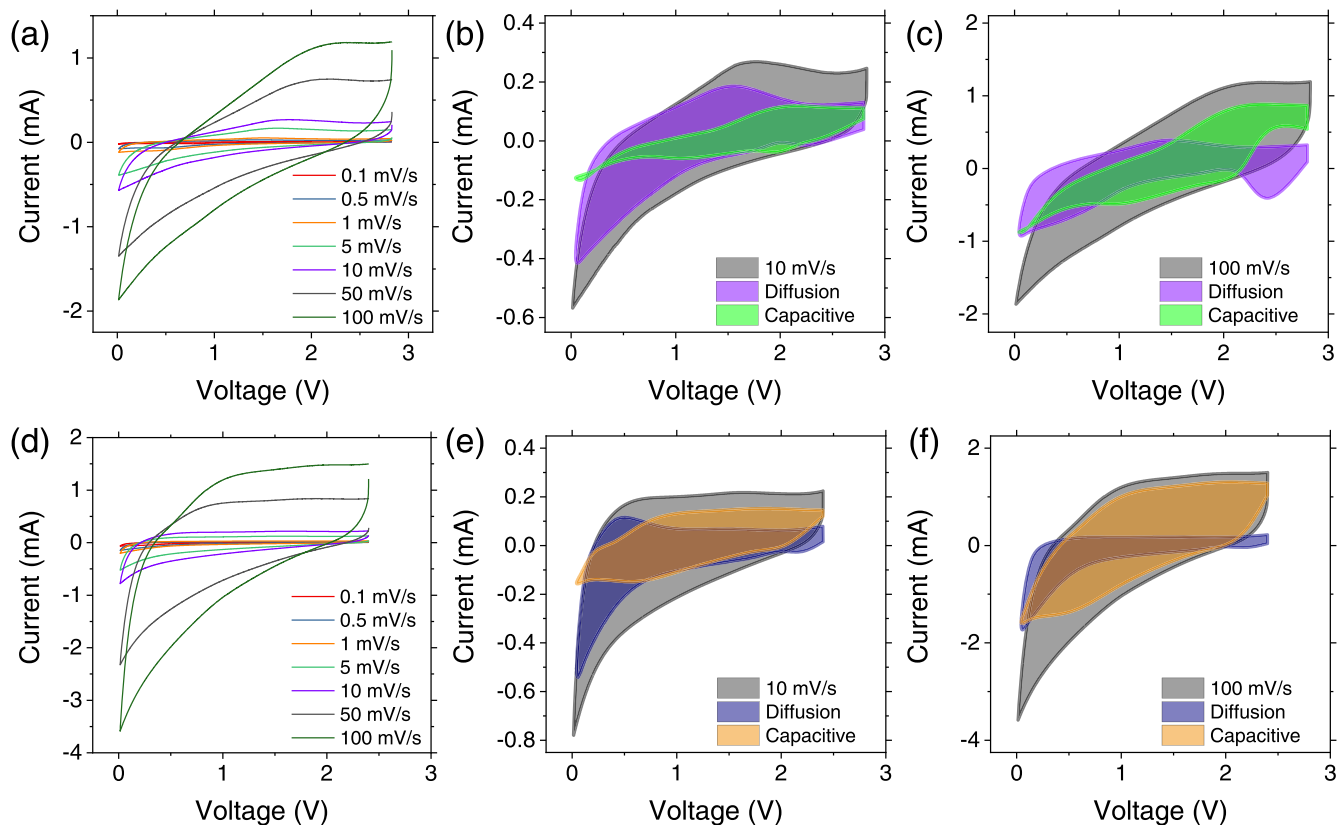


Figure 5. (a) CV of carbon IO in Na-ion cell at various scan rates. Intercalation (purple) and capacitive (green) contributions to the total measured current (grey) for carbon IO at scans rates of (b) 10 mV s⁻¹ and (c) 100 mV s⁻¹. The sum of these contributions at each potential equals the actual measured current. (d) CV of carbon IO in K-ion cell. (e) Intercalation (blue) and capacitive (orange) processes compared to the total measured current (grey) for carbon IO in K-ion cell at scans rates of (b) 10 mV s⁻¹ and (c) 100 mV s⁻¹.

compared to the carbon IO's 9%. Despite the IO exhibiting higher 1st and 2nd discharge capacities (554 mAh g⁻¹ and 82 mAh g⁻¹) in contrast to the thin film (112 mAh g⁻¹ and 35 mAh g⁻¹), a more pronounced capacity fading is observed in the IO material. The carbon IO retained 30% capacity from the 2nd cycle to the 250th, compared to the thin film's retention recorded at 51%. This observation implies potential structural stresses or damage to the IO walls. Notably, this marks the first report of carbon inverse opals being tested in potassium-ion batteries. The potential reason for the IO wall damage could be attributed to the larger ionic radius of potassium compared to lithium and sodium, for which carbon IOs have previously demonstrated efficacy.^{29,78,79} However, a noteworthy trend emerges as the IO structure consistently improves in reversibility throughout the 250 cycles, surpassing the Coulombic efficiency of the thin film. The final Coulombic efficiencies are recorded as 97% for the IO and 93% for the thin film.

Electrochemical kinetics.—To further analyze the storage mechanism for carbon inverse opals in Na-ion and K-ion batteries, CV techniques were employed. The CV curves for carbon IO at various scan rates from 0.1–100 mV s⁻¹ are shown in Fig. 5. While the CVs were set in a potential window of 2 V–0.014 V, a drift to higher voltages at the end of each cycle is observed. The curves for both systems exhibit a consistent shape with redox peaks in a lower potential region and a rectangular shape in a high potential region. These features are attributed to the diffusion-controlled intercalation process and surface-induced double layer capacitance, respectively.⁸⁰ To assess the specific contribution of these processes,⁸¹ capacitive effects were analyzed using the power-law formula:

$$i(V, t) = av^b \quad [1]$$

where i is the current (mA), v is the scan rate (mV/s) and a , b are adjustable values. The b -values can be derived from a plot of $\log(i)$ vs $\log(v)$ a log on both sides of Eq. 1. A value of $b = 0.5$ signifies a current that is diffusion-controlled, indicative of a Faradaic intercalation process.^{82,83} On the other hand, when $b = 1$, it denotes a capacitive response, where the capacitive current shows a linear proportionality to the scan rate. The b -values at the end of the voltage window (0.014 V) were found to be 0.65 and 0.59 for the carbon IOs in Na-ion and K-ion systems, respectively, this plot can be found in the Supplementary materials, Fig. S5. These values indicate that both double-layer capacitance and Faradaic intercalation processes are utilized with more current coming from the diffusion-controlled processes.⁸⁴

The measured currents arising from capacitive and diffusion processes can be explicitly determined using the following equation:

$$i(V, t) = k_1v + k_2v^{1/2} \quad [2]$$

where i represents the current, v is the scan rate, and k_1 and k_2 are coefficients corresponding to the capacitive and diffusion-controlled processes, respectively. Figure 5 shows the calculated contributions from Faradaic and non-Faradaic processes, at scan rates of 10 mV s⁻¹ and 100 mV s⁻¹, in both Na-ion and K-ion cells. Calculated contributions for all scan rates can be found in Supplementary materials, Figs. S5, S6, and S7. For the carbon IOs in Na-ion cells, diffusion-controlled processes account for 97%, 85%, 83% 70%, and 67% of the current contribution for scan rates

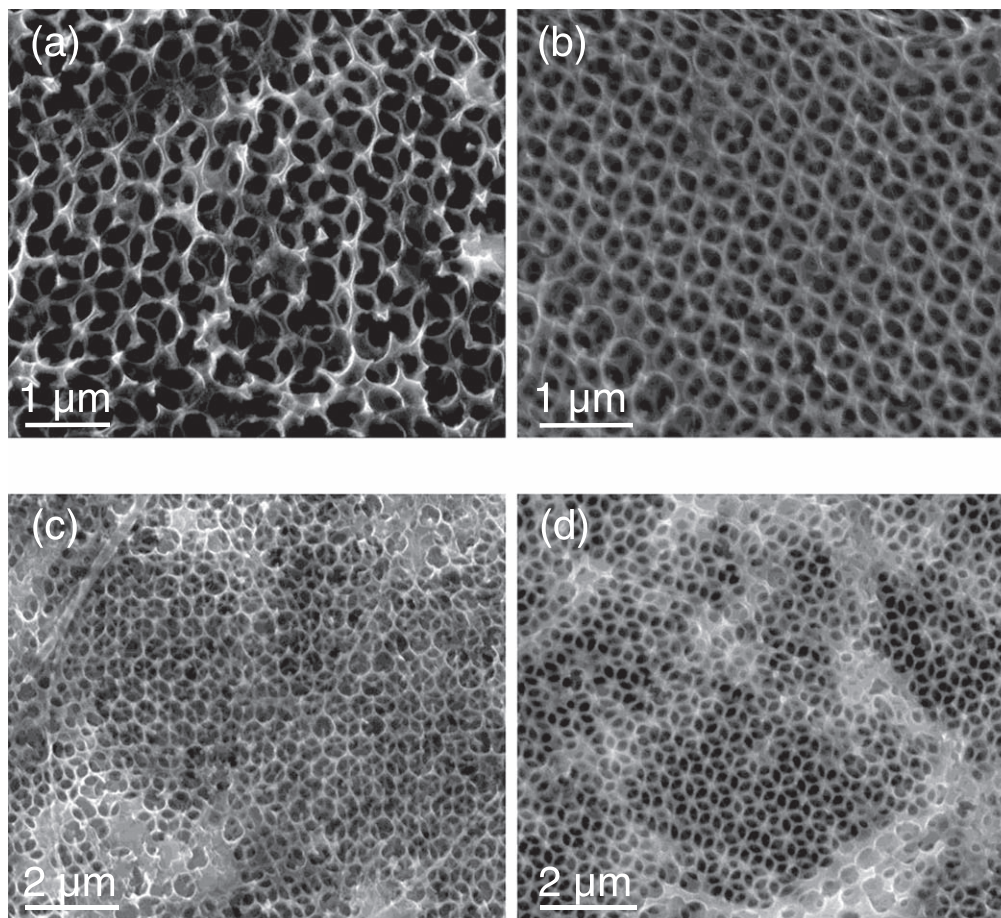


Figure 6. Post-mortem SEM analysis of carbon inverse opals after 250 cycles at (a) 75 mA g^{-1} vs Na, (b) 185 mA g^{-1} vs Na^+/Na , (c) 75 mA g^{-1} vs K, (d) 185 mA g^{-1} vs K^+/K .

0.1, 0.5, 1, 5, and 10 mV s^{-1} . Once the scan rate reaches 50 mV s^{-1} in these tests, we note the onset of a greater current contribution from capacitive reactions, which account for 54% of the current response and increase to 60% for 100 mV s^{-1} , see Supplementary materials, Fig. S7. On the other hand, double-layer capacitance accounts for a larger proportion of the current response for the carbon IOs in the K-ion cell. As can be seen from Figs. 5e and 5f, a large portion of the current response at the higher voltage region is from capacitive processes. For each scan rate, diffusion-controlled processes accounted for 87%, 78%, 76%, 72%, 48%, 29% and 24% for the 0.1, 0.5, 1, 5, 10, 50, and 100 mV s^{-1} scan rate, respectively (Supplementary materials, Fig. S7).

Post-mortem structural analysis.—Post-mortem analysis involved SEM examination of the structural integrity of carbon IOs in sodium and potassium-ion cells. Given the substantial specific surface area and interconnected pore structure that demonstrated durability in lithium-ion cells, we sought to assess their performance in sodium and potassium-ion cells. After 250 cycles at 75 mA g^{-1} and 185 mA g^{-1} rates, cells were disassembled, washed with electrolyte solution, and examined. For sodium-ion cells (Figs. 6a and 6b), despite observing distortion and slight swelling after cycling in sodium-ion cells, the structural integrity of the inverse opal remained. Significantly, the structural integrity persisted despite volume expansion of the inverse opal walls. Initially measured at 26.5 nm before cycling, the wall thickness increased by 40% (to $\sim 37 \text{ nm}$) and 77% (to $\sim 47 \text{ nm}$) at rates of 75 mA g^{-1} and 185 mA g^{-1} , respectively.

The carbon inverse opals after potassiation are shown in Figs. 6c and 6d. The carbon IOs exhibited more pronounced volume

expansion during cycling relative to the sodium-ion cell. Measurements from SEM images indicated a wall thickness of $\sim 48 \text{ nm}$ after 250 cycles at the 75 mA g^{-1} rate and 55 nm for the 185 mA g^{-1} rate. While the majority of the electrode maintained its structure, SEM images revealed localized swelling and breakage in certain areas, as depicted in Supplementary materials, Fig. S8. Additional SEM images of all electrodes post-cycling can be found here as well. Intriguingly, this structural breakdown occurred primarily at the slower rate of 75 mA g^{-1} , despite a wall thickness swelling of only 81%, compared to the faster rates showing an $\sim 106\%$ increase.

This structural integrity is innate to the interconnected inverse opal architecture, evident in the accommodation of volumetric swelling within the macropores during cycling, as illustrated in SEM images. Previously, inverse opal structures have been shown to withstand thousands of cycles in lithium-ion batteries,²⁹ and reports have shown resistance to volumetric swelling over 500 cycles in sodium-ion cells.⁸⁵ This report extends the scope by showcasing their resilience against potassium ions, which exhibit larger ionic radii and are more susceptible to cause volume expansion.⁸⁶ These findings contribute valuable insights into the potential viability of inverse opal structures for sustained performance and longevity in “beyond-lithium” battery applications.

Conclusions

Carbon inverse opals were synthesized from sucrose to produce highly ordered, three-dimensional macroporous architecture. The macroporous structure was characterized by interconnected layers with face-centred cubic (FCC) symmetry, providing a high surface

area-to-volume ratio. High-resolution transmission electron microscopy (HRTEM) revealed a disordered nanostructure with curved, short-range graphitic areas, and selected area electron diffraction (SAED) confirmed the disordered microstructure. Structural measurements indicated two mean averages of pore diameters of ~ 495 nm and ~ 355 nm, and an electrode coating thickness of approximately $17.5\ \mu\text{m}$.

The electrochemical characterization of the carbon IOs in sodium-ion (Na-ion) and potassium-ion (K-ion) battery cells showed promising behavior during cycling, particularly at the faster rates. Cyclic voltammetry analysis exhibited reversible sodiation and potassiation processes. Galvanostatic cycling at various rates demonstrated stable specific capacities and Coulombic efficiencies in Na-ion cells. However, in K-ion cells, a more pronounced capacity fading was observed, suggesting potential challenges associated with the larger ionic radius of potassium.

Electrochemical kinetics analysis indicated that both diffusion-controlled intercalation and surface-induced double-layer capacitance contributed to the charge storage mechanism. Post-mortem structural analysis revealed the remarkable structural integrity of the carbon IOs, even after 250 cycles in both Na-ion and K-ion cells. The inverse opal architecture accommodated volumetric swelling within the macropores, showcasing resilience against the challenges posed by repeated sodium and potassium ion intercalation.

These findings underscore the potential of three-dimensional ordered macroporous structures, such as carbon inverse opals, as promising electrode structures for “beyond-lithium” battery technologies and also provide an electrode structure that allows examination of charge storage mechanisms and fundamental response to charging and discharging in the absence of physical additives such as additional conductivity enhancers or binders. The unique architecture not only facilitates stable electrochemical performance in sodium-ion cells but also demonstrates notable durability and resistance to structural breakdown, even in the presence of larger potassium ions.

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