Porous carbon matrix-encapsulated MnO *in situ* derived from metal-organic frameworks as advanced anode materials for Li-ion capacitors

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ABSTRACT Conversion-type anode materials hold great potential for Li⁺ storage applications owing to their high specific capacity, while large volume expansion and poor electrical conductivity limit their rate and cycling performances. Herein, a bimetal ZnMn-based metal-organic framework (ZnMn-MOF) is engineered for *in situ* conversion of MnO-encapsulated porous carbon (MnO/PC) composite. The templating and activation effects of coordinated Zn endow the converted PC matrix with a highly porous structure. This enhances the compatibility of PC matrix with MnO particles, resulting in the full encapsulation of MnO particles in the PC matrix. More significantly, the PC matrix provides enough void space to buffer the volume change, which fully wraps the MnO without crack or fracture during repeated cycling. As a result, MnO/PC shows high charge storage capability, extraordinary rate performance, and long-term cycling stability at the same time. Thus MnO/PC exhibits high delithiation capacities of 768 mA h g⁻¹ at 0.1 A g⁻¹ and 487 mA h g⁻¹ at a high rate of 0.7 A g⁻¹, combined with an unattenuated cycling performance after 500 cycles at 0.3 A g⁻¹. More significantly, MnO/PC demonstrates a well-matched performance with the capacitive activated carbon electrode in a Li-ion capacitor (LIC) full cell. LIC demonstrates a high specific energy of 153.6 W h kg⁻¹ at 210 W kg⁻¹, combined with a specific energy of 71.8 W h kg⁻¹ at a high specific power of 63.0 kW kg⁻¹.

Keywords: Li-ion capacitors, MnO/porous carbon composites, metal-organic frameworks derivant, conversion-type anode materials

INTRODUCTION

The ever-increasing electric energy storage/delivery demands in consumer electronics and electric vehicles have stimulated significant interest in seeking advanced rechargeable energy storage devices with both high-energy and high-power performances [1–8]. In this context, hybrid supercapacitors have been developed to bridge the energy and power performance gaps between batteries and supercapacitors [9–11]. When a Li-ion battery (LIB) anode is assembled with a supercapacitor cathode, the hybrid system, also called Li-ion capacitor (LIC) [12–15], shows a enhanced power performance while maintaining a preminent energy density comparable to LIBs. To date, LICs have been constructed using an activated carbon (AC) cathode combined with a great deal of transition metal oxide (TMO) anodes including Li₄Ti₅O₁₂ [16], TiO₂ [17], Nb₂O₅ [18,19], and MoO_x

[20]. However, poor electrical conductivity and huge volume expansion during lithiation render these TMOs low rate capability and unsatisfactory cycling stability, resulting in mismatch power and cycling performances with the capacitive electrode. Therefore, these disadvantages limit the utilization of TMOs from high-performance LICs.

Carbonaceous materials are very ideal as composite media to enhance the Li⁺ storage performance of TMOs owing to their high electrical conductivities, flexible structures and low cost. Compared with surface binding of TMOs on high surface carbons (graphene, carbon nanotubes, etc.), inner inclusion of these materials in a carbon matrix is more effective [21–24]. The carbon matrix can enhance the electrical conductivity and prevent agglomeration of the inclusive TMOs. The MnO composites have received more and more research attention owing to high theoretical capacity (756 mA h g⁻¹), low operational potential, and environmental friendliness of MnO anode material. However, huge volumetric expansion during the lithiation brings a critical problem because of the crack and fracture of the carbon. The separation of MnO with coated carbon was found after only 100 cycles [25], resulting in unsatisfactory cycling stability. Therefore, novel strategies should be developed to improve the structural integrity of the carbon for stable hosting of MnO.

To date, extra void spaces have been introduced into the carbon matrix to relieve the strain caused by the huge volume change of MnO. Jiang *et al.* [25] reported a peapod-like MnO/carbon heterostructure with internal void space which exhibited a stable cycling performance for 1000 cycles. Xiao *et al.* [21] found that MnO nanoparticles encapsulated within a foam-like carbon matrix maintain a specific capacity of 1212 mA h g⁻¹ after 1000 cycles. The large void spaces reduce the contact area with the carbon matrix, bringing about extra resistance for charge transfer. In addition, the void spaces in these composites are designed elaborately using a multistep process which is time-consuming and with low efficiency. Therefore, new strategies for the successful inclusion of MnO with increased void spaces in the carbon matrix are still urgently needed.

Porous carbon (PC) can provide enough void spaces owing to their highly porous structures which can buffer the volume change of TMOs during the lithiation/delithiation process. The interconnection of inner nanopores can serve as pathways for Li⁺ diffusion. To achieve the application of PC as a carbon matrix, composites should be prepared by constructing the porous structure while maintaining the performance of TMO. This is still very challenging and robust methods of synthesis

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should be developed.

Metal-organic frameworks (MOFs) are robust precursors to derive TMO-based nanocomposites. The organic linkers of MOFs can be used as the carbon source for conversion of carbon matrices with coordinated metal ions/clusters converted TMOs *in situ* encapsulated [26,27]. MOF-derived composites have achieved applications in supercapacitors and Li, Na, K and Zn ion-based batteries [26–28], but their utilization for LICs is still very limited. The carbon matrix converted by decomposition of MOFs is still very solid. If a volatile element is involved in the MOF, derived carbon in the nanocomposite can be templated and activated to a highly porous matrix in the pyrolysis process, with TMOs encapsulated. However, to the best of our knowledge, no attempt has been made to construct volatile element-involved MOF to derive MnO-encapsulating PC anode for LIC applications.

Here, MnO-encapsulating PC was *in situ* derived from ZnMn-MOF for the first time with volatile Zn as the templating and activation agent for the formation of PC matrix, which was used as high-performance anode materials for LICs. The highly porous PC matrix provides enough void space to buffer the volume change and improve the electrical conductivity of MnO, resulting in superior Li^+ storage performance. The MnO/PC displays high charge storage capability, extraordinary rate performance and long-term cycling stability at the same time. More importantly, the MnO/PC is used to assemble an LIC cell with a commercial AC electrode, and the resulting LIC exhibits both high-energy and high-power performances.

EXPERIMENTAL SECTION

Synthesis of the MnO/PC composite

ZnMn-MOF was synthesized as a precursor using the hydrothermal method. Manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 2 mmol) and 1 mmol of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) were dissolved into 68 mL of a mixed solvent of dimethylformamide, ethanol and deionized water with a volume ratio of 15:1:1, and then 3 mmol of trimesic acid was dissolved into the solution. The solution was transferred into a 100-mL Teflon-lined autoclave and heated at 180°C for 3 h. The ZnMn-MOF was repeatedly washed using ethanol and deionized water by centrifugation and collected after being dried at 60°C . The ZnMn-MOF powder obtained was annealed at 1000°C for 6 h with a slow ramping rate of 3°C min^{-1} in 10 vol% H_2 and Ar mixed gas.

Synthesis of the MnO/C composite

Mn-MOF was also synthesized using the same hydrothermal method with 3 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as the single metal ion source. The Mn-MOF powder was converted to the Mn/C composite by annealing at 800°C for 6 h in H_2 and Ar mixed gas with the same ramping rate.

Material characterization

The crystal structure of the sample was measured by X-ray diffraction (XRD; Rigaku, Ultima IV) using a Cu $\text{K}\alpha 1$ source. Field-emission scanning electron microscope (FESEM; JEOL, JSM-7800F) and transmission electron microscope (TEM; JEOL, JEM-2100 plus) were used to characterize the morphologies and microstructures of the samples. Elemental distribution images were tested by the energy dispersive spectrometer (EDS) map-

ping equipped on the FESEM. The chemical compositions of the samples were recorded on an X-ray photoelectron spectroscopy (XPS; Kratos, AXIS-ULTRA, DLD-600 W). Thermogravimetric analyser (TGA) was recorded on an SDT Q600 in air with a temperature range from room temperature to 800°C and a heating rate of $10^\circ\text{C min}^{-1}$. N_2 adsorption/desorption isothermal was measured using a Quantachrome Autosorb-IQ-MP/XR surface area and pore analyzer. The Raman spectra were collected on a Renishaw inVia Raman spectrometer measured using a laser wavelength of 532 nm.

Electrochemical measurements

Electrochemical measurements of active materials were conducted *via* the assembly of CR 2016 coin-type cells with a Li counter/reference electrode while using 1 mol L^{-1} LiPF_6 in a mixture of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (EC:DMC:EMC = 1:1:1, v/v/v) as the electrolyte. The working electrode was fabricated by a slurry-coating method according to the following procedure. Firstly, the active material, carbon black (super P), and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 were grinded in *N*-methyl-2-pyrrolidone (NMP) to form a slurry. Then, the slurry was coated on Cu foil using a scraper. After being vacuum-dried at 110°C for 10 h, the Cu foil-supported electrode was cut into disk electrodes with a diameter of 1.2 cm. The mass loading of anode material in each electrode was controlled at 1.5–2.0 mg. For LICs testing, MnO/PC was used as the anode material and the commercial available AC (SPC-02S, Fujian Xinsen Carbon, Co., Ltd.) was used as the cathode material. The MnO/PC electrode was pre-lithiated in a half cell at a specific current of 0.1 A g^{-1} prior to the assembly of LICs. Capacity values were measured by the galvanostatic charge and discharge (GCD) method on a Neware battery tester at a constant temperature of 30°C . The cyclic voltammetry (CV) electrochemical impedance spectroscopy (EIS) tests were measured on a CHI 660E electrochemical workstation (Shanghai Chenhua, China). EIS were tested in the frequency range from 0.01 Hz to 100 kHz at the open-circuit potential with an alternating current perturbation of 5 mV.

RESULTS AND DISCUSSION

The synthesis process of the MnO/PC nanocomposite and its derived mechanism from ZnMn-MOF are illustrated in Fig. 1. Firstly, the ZnMn-MOF is synthesized as the self-sacrificial precursor for the conversion of MnO/PC. As illustrated in Fig. 1a, trimesic acid serves as the organic ligand to coordinate Zn and Mn ions under the hydrothermal condition, resulting in the formation of ZnMn-MOF. Subsequently, the ZnMn-MOF is transformed to MnO/PC by annealing following a mechanism illustrated in Fig. 1b. The organic ligand of ZnMn-MOF is carbonized into a carbon matrix while the coordinated Zn and Mn are converted to their oxide particles. The templating effect of ZnO particle endows the carbon matrix with a highly porous structure. The ZnO was reduced into volatilizable Zn by carbothermic reduction at elevated temperatures, and during this process, the carbon matrix got activated to be more porous. The carbon matrix and MnO particles were both *in situ* transformed from ZnMn-MOF, which ensured full encapsulation of MnO particles into the carbon matrix.

Fig. 2a shows XRD patterns of ZnMn-MOF and MnO/PC. The XRD pattern of ZnMn-MOF demonstrates its crystalline state, indicating well-aligned coordination of trimesic acid with

Figure 1 Schematic illustration of the (a) formation process and (b) conversion mechanism from the ZnMn-MOF of the MnO/PC.

Figure 2 (a) XRD patterns of the ZnMn-MOF and MnO/PC. FESEM images of the (b) ZnMn-MOF and (c) MnO/PC. (d–g) TEM images at different magnifications and (h) EDS mapping image of the MnO/PC.

Zn and Mn ions. The XRD pattern of MnO/PC displays diffraction peaks which can be fully assigned to the cubic MnO (JCPDS no. 07-0230), indicating full conversion of ZnMn-MOF to MnO/PC. The morphologies of ZnMn-MOF and MnO/PC were characterized by FESEM. It is found that ZnMn-MOF is constituted by many nanorods with diameters around 50 nm

(Fig. 2b). MnO/PC shows a morphology of MnO particles encapsulated in PC matrix with all the MnO particles fully wrapped into the PC matrix. Similarly, MnO/C is transformed from Mn-MOF as a control sample. The conversion temperature is reduced to 800°C to avoid the formation of Mn_7C_3 phase (Fig. S1). Mn-MOF shows the same morphology of nanorods

while the converted MnO/C shows a morphology of a mixture of MnO particles and carbon (Fig. S2). The sizes of MnO particles are much larger than those in MnO/PC, and the MnO particles cannot be fully wrapped in the carbon matrix. Therefore, the inclusion of Zn reduces aggregation and increases dispersion of MnO in the carbon matrix owing to the more porous structure of carbon matrix which can better encapsulate the MnO particles.

The morphology of MnO/PC was also characterized by TEM. As shown in Fig. 2d–f, the PC serves as a matrix for the encapsulation of MnO particles. The PC matrix can prevent mutual contact of MnO particles. More significantly, owing to the templating and activation effects of ZnO, the PC matrix is enriched with mesopores and micropores, and the highly porous structure is very flexible to buffer volume change of the MnO. The high-resolution TEM image in Fig. 2g shows the MnO is crystallized with long range lattice fringes, and the PC is amorphous as its lattice fringes are irregularly arranged. The EDS mapping image of MnO/PC (Fig. 2h) shows the existence of Zn, Mn, O and C elements. However, the EDS signal from Zn element is very weak, indicating its ignorable amount.

Fig. 3a shows the TGA curve of MnO/PC annealed in air at temperatures ranging from room temperature to 800°C. The composite shows 2.11% weight loss when the temperature increases from room temperature to 67°C owing to evaporation of adsorbed water. Then, the composite experiences conversion to manganese oxides with different oxidation states and burning of PC with elevation of the temperature. As shown in Fig. 3a, the TGA curve shows gradually increased weight retention when temperature ranges from 67 to 372°C, which can be ascribed to oxidation of MnO to Mn₃O₄. PC is burned away when the temperature further increases, causing a rapid weight loss in the range of 372–470°C. However, the oxidation of Mn₃O₄ to MnO₂ leads to another region of weight rises, when the temperature ranges from 470 to 650°C. MnO₂ can be gradually transformed

to Mn₂O₃ when the temperature is higher than 650°C, and the TGA curve displays a gradually reduced weight retention as the temperature further rises. According to the equation $2\text{MnO} + \text{O}_2 = 2\text{MnO}_2$, it can be calculated that 122.55% of the weight retention will be maintained after the MnO is converted to MnO₂. However, MnO/PC demonstrates 98.38% of the weight retention at 650°C when MnO is converted to MnO₂, which can be ascribed to the burning of PC. The weight ratio of MnO in MnO/PC can be calculated to be 82.01%.

Fig. 3b shows the Raman spectrum of MnO/PC with signals from both MnO and PC detected. The Raman peak at 646.9 cm⁻¹ can be assigned to stretching vibration mode of Mn–O chemical bond [29]. The Raman signal from carbon can be best fitted into I, D, G and D' bands of the carbon [30]. The D and G bands show a higher intensity ratio of 1.04 than the reported carbon matrix [31,32], which is indicative of the carbon with abundant defects and in good agreement with the characteristic of PC. The N₂ adsorption/desorption isotherm (Fig. 3c) shows a hysteresis loop owing to the existence of mesopores and a straight line at low pressure region from the N₂ adsorption/desorption of micropores. The density functional theory (DFT)-based pore size distribution curve of the MnO/PC shown in the inset of Fig. 3c verifies the coexistence of mesopores (2–50 nm) and micropores (<2 nm), indicating the formation of hierarchical porous structure of the PC matrix. The Brunauer-Emmett-Teller (BET) area of the MnO/PC is 112 m² g⁻¹, which is larger than reported MnO-based composites, such as carbon-coated MnO microspheres (45.6 m² g⁻¹) [33], MnO/C nanopeapods (103 m² g⁻¹) [25], MnO quantum dots embedded in carbon nanotubes (65.2 m² g⁻¹) [34], MnO/reduced graphene oxide (RGO) (33.6 m² g⁻¹) [35]. The high specific area of MnO/PC can be ascribed to the highly porous structure of PC matrix. The high-resolution Mn 3s XPS spectrum shows two peaks with a splitting binding energy of 6.0 eV, which is the typical feature of the Mn²⁺ [36]. Except for the XPS peaks from C–C, the high-

Figure 3 (a) TGA curve, (b) Raman spectrum, and (c) N₂ adsorption/desorption isotherm and the corresponding pore size distribution curve of the MnO/PC. High-resolution (d) Mn 3s, (e) C 1s and (f) O 1s XPS spectra of the MnO/PC.

resolution C 1s spectrum also exhibits intense photoelectron signals from oxygenated functional groups of C–O–C and O–C=O (Fig. 3e), indicating enriched defects in the carbon. The O 1s spectrum (Fig. 3f) also exhibits peaks from the metal oxides and oxygenated functional groups of carbon. The XPS test confirms the successful synthesis of the MnO/PC composite.

The kinetics for Li⁺ storage of MnO/PC was analyzed. Fig. 4a shows the CV curves at different scan rates of MnO/PC. It is found that each CV curve exhibits a pair of redox peaks owing to the reversible reaction of $2\text{Li}^+ + \text{MnO} + 2\text{e}^- = \text{Li}_2\text{O} + \text{Mn}$ [29]. Besides current response of the redox peaks, a background current exists in the whole potential region, which is indicative of the coexistence of charge storage from both diffusion-controlled redox process and surface-induced capacitive process. The latter process is more favourable for fast Li⁺ storage [20]. The CV curves show similar shapes at scan rates ranging from 0.1 to 1 mV s⁻¹, indicating high rate performance of the MnO/PC. To verify the existence of the capacitive behaviour, peak currents of the CV curves for both cathodic and anodic scans were analyzed using the following equations [37,38]:

$$i = av^b, \quad (1)$$

$$\log i = b \log v + \log a, \quad (2)$$

where, i is the peak current, v is the scan rate, and a and b are constants for a fixed electrode. By fitting the relationship of $\log i$ vs. $\log v$ (Fig. 4b), it is found that the MnO/PC electrode shows b values of 0.67 and 0.72 for the redox peaks under cathodic and anodic scans, respectively, indicating surface-induced capacitive behaviour occurring in addition to the diffusion-controlled battery reaction. The overall contributions from the two differ-

ent mechanisms were quantitatively analyzed according to the following equations [39,40]:

$$i = k_1 v + k_2 v^{1/2}, \quad (3)$$

$$i/v^{1/2} = k_1 v^{1/2} + k_2. \quad (4)$$

By fitting specific currents at each potential according to Equation (4), the contributions for the diffusion and capacitive processes can be separated. Fig. 4c compares the CV curves with the circled area from the capacitive contribution. By calculation of the specific capacity using the formula $Q = \int (i/v) dv$ [41], it can be found that the capacitive behaviour takes 75.3% of the charge storage capacity. The capacitive contributions at different scan rates are plotted in Fig. 4d, and it increases from 65.8% to 85.5% as the scan rates increase from 0.1 to 1.0 mV s⁻¹. Therefore, it is obvious that the charge storage of the MnO/PC is mainly from the capacitive contribution, and thus high-rate performance can be anticipated.

Fig. 5a compares the cycling stability of fresh MnO/PC and MnO/C electrodes at a specific current of 0.1 A g⁻¹. It can be found the MnO/PC electrode displays higher specific capacity and better cycling stability than the MnO/C electrode. The MnO/PC exhibits an initial lithiation/delithiation capacity of 1260/781 mA h g⁻¹ with a coulombic efficiency of 62.0%. The low coulombic efficiency at the initial cycle can be ascribed to the formation of solid electrolyte interface (SEI) and irreversible conversion of Li⁺ to its oxide. The MnO/PC electrode shows a coulombic efficiency as high as 96.6% with a lithiation/delithiation capacity of 813/786 mA h g⁻¹ at the second cycle, indicating high reversibility of MnO/PC for Li⁺ storage after the initial cycle. After being cycled at 0.1 A g⁻¹ for 60 cycles, the

Figure 4 (a) CV curves at different scan rates of the MnO/PC, and (b) relationship and linear fitting results of the cathodic and anodic peak currents and scan rate used to determine the b value. (c) Separation of the capacitive and diffusion-controlled contributions of MnO/PC at a scan rate of 0.5 mV s⁻¹. (d) The percentage of capacitive and diffusion-controlled contributions at different scan rates.

Figure 5 (a) Cycling performance at 0.1 A g⁻¹ of MnO/PC and Mn/C, and the coulombic efficiency of MnO/PC. (b) GCD curves for the initial five cycles of the MnO/PC. (c) Rate performance at specific currents ranging from 0.1 to 0.7 A g⁻¹ of MnO/PC and Mn/C. (d) Typical GCD curves at different specific currents of MnO/PC. (e) Long-term cycling performance at a high specific current of 0.3 A g⁻¹ of MnO/PC and MnO/C.

MnO/PC electrode maintains a lithiation/delithiation capacity of 868/851 mA h g⁻¹. The MnO/C electrode only maintains a lithiation/delithiation capacity of 450/445 mA h g⁻¹. Therefore, excellent cycling stability is achieved by MnO/PC. Fig. 5b compares the initial five cycles of GCD curves at a specific current of 0.1 A g⁻¹ of MnO/PC. After the first lithiation process, the MnO/PC electrode shows nearly overlapped GCD curves, which is indicative of stable performance for Li⁺ storage. The rate performance of MnO/PC is also compared with that of MnO/C under stepped specific currents. As shown in Fig. 5c, the MnO/PC electrode shows higher specific capacity than the MnO/C electrode under these specific currents. The MnO/PC electrode shows a lithiation/delithiation capacity of 805/768 mA h g⁻¹ at 0.1 A g⁻¹ after being tested at stepped specific currents of 0.1, 0.2, 0.3, 0.5 and 0.7 A g⁻¹, indicating its excellent cycling stability at different rates. The MnO/PC electrode also displays an average delithiation capacity of 487 mA h g⁻¹ at 0.7 A g⁻¹, indicating its high-rate performance. The GCD curves at different specific currents are compared in Fig. 5d, which all

demonstrate similar GCD curves owing to stable performance at different rates. The MnO/PC electrode is also cycled at a high specific current of 0.3 A g⁻¹ to further demonstrate its long-term cycling stability. As shown in Fig. 5e, the MnO/PC electrode displays an initial delithiation capacity of 598 mA h g⁻¹ with an increased specific capacity of 758 mA h g⁻¹ being maintained after 500 cycles. The activated performance during cycling has been disclosed by many reported MnO-based materials [21,28,32,42,43], which can be ascribed to the further oxidation of Mn(II) to Mn(IV) and the interfacial lithium storage [42,43]. By contrast, the MnO/C electrode exhibits fast declined specific capacity during long-term cycling, and only 59 mA h g⁻¹ is retained after 300 cycles. Based on the aforementioned results, it is obvious that the MnO/PC demonstrates combined merits of high specific capacity, good rate performance and excellent cycling stability for Li⁺ storage.

To better understand improved performance of MnO/PC, the electrode cycled at 0.1 A g⁻¹ for 50 cycles was measured by *ex situ* TEM technique. As shown in Fig. 6a, the MnO particles are still

fully encapsulated in the PC matrix. The lithiation/delithiation of MnO gives rise to huge volume expansion, resulting in erosion, fracture and pulverization of MnO, as shown by the TEM images in Fig. 6b–d. However, as illustrated in Fig. 7, the porous structure of PC matrix provides enough void space to buffer the volume change of MnO for Li^+ storage, and the PC matrix can fully wrap MnO without crack or fracture during repeated cycling. As a result, stable cycling performance can be obtained. In addition, the encapsulation of MnO in PC prevents the aggregation of MnO particles, which can increase the electroactive sites and shorten the diffusion distance of Li^+ . In the meantime, the EIS spectra of MnO/PC (Fig. S3) exhibit rapidly reduced semicircle diameters in the high-frequency region during repeated cycling, indicating low charge transfer resistance can be achieved by MnO/PC during long-term cycling. Therefore, MnO/PC shows excellent Li^+ storage performance.

MnO/PC was used as the anode material to assemble LICs with the AC electrode for further indication of superior Li^+ storage performance. Fig. 8a illustrates the structure of the MnO/PC//AC LICs. The AC electrode stores charge *via* achieving electrical double-layer capacitance, which is surface-related with high-rate and stable performances. Owing to sluggish reaction kinetics and low redox reversibility of battery reactions, traditional anode materials cannot match the high-rate and stable performance of the capacitive electrode at high rates and long-term cycling, respectively. However, MnO/PC displays well matched performance with AC in LICs. Fig. 8b shows the CV curves at different scan rates of an LIC. It is found that the LIC displays a voltage as high as 4.2 V owing to supplemental working potentials for the MnO/PC and AC electrodes. The CV curves at different scan rates are all nearly rectangular and the GCD curves at different specific currents are nearly linear (Fig. 8c), indicating the capacitive charge storage behaviour of LIC. The LIC shows a specific capacity of 62.7 F g^{-1} at a specific current of 0.1 A g^{-1} with a specific capacity of 29.3 F g^{-1} maintained at high specific current of 30 A g^{-1} . The specific capacity and specific current were both calculated referring to the total mass of active materials in MnO/PC and AC electrodes, so high-capability and high-rate performances

Figure 6 TEM images of the MnO/PC tested after being cycled at a specific current of 0.1 A g^{-1} for 50 cycles: (a) overall morphology, and enlarged images showing (a) erosion, (b) fracture and (c) pulverization of MnO particles.

Figure 7 Schematic illustration of the mechanism for the porous structure of AC used to buffer the volume change of MnO during Li^+ storage.

were achieved at the same time using current LIC. The LIC was cycled at a specific current of 10 A g^{-1} . As shown in Fig. 8d, the LIC demonstrates 80% of the capacity retention after 1000 cycles, corresponding to a very small capacity degradation of 0.01 mA h g^{-1} per cycle. The LIC also shows high charge/discharge reversibility with a coulombic efficiency higher than 99%. An LIC cell can simultaneously drive 10 blue light-emitting diodes (LEDs) for 5 min (Fig. 8e), indicating high-energy and high-power performances have been achieved. The specific energy and specific power of the LIC were calculated from the GCD curves, and it is found that LIC shows a maximum specific energy of $153.6 \text{ W h kg}^{-1}$ at 210 W kg^{-1} combined with a specific energy of 71.8 W h kg^{-1} at a high power of 63.0 kW kg^{-1} . As compared in Fig. 8f, the specific energy performance of our LIC is higher than MnO/RGO/porous N-doped carbon (127 W h kg^{-1} at 125 W kg^{-1} , $83.25 \text{ W h kg}^{-1}$ at 25 kW kg^{-1}) [44], porous NiCo_2O_4 //AC (39 W h kg^{-1}) [45], manganese carbodiimide (MnNCN)//AC (103 W h kg^{-1}) [46], MnO nanoparticles/PC//AC (less than 35 W h kg^{-1} at 2608 W kg^{-1}) [47], Mn_3O_4 /graphene//AC (142 W h kg^{-1} at 648 W kg^{-1} , 20 W h kg^{-1} at 6.5 kW kg^{-1}) [48], Mn_3O_4 /3D-graphene//polyaniline-derived AC (97.2 W h kg^{-1} at 62.5 W kg^{-1} , 5 W h kg^{-1} at 6250 W kg^{-1}) [49], mesocrystal MnO//AC (less than 20 W h kg^{-1} at 2952 W kg^{-1}) [50], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /AC hybrid nanotubes//AC (90 W h kg^{-1} at 50 W kg^{-1} , 32 W h kg^{-1} at 6000 W kg^{-1}) [51], and B-Si/ SiO_2 /C//porous spherical carbon (128 W h kg^{-1} at 1229 W kg^{-1} , 89 W h kg^{-1} at 9704 W kg^{-1}) [52]. These results indicate both high-energy and high-power performances of our LIC.

CONCLUSIONS

Highly PC matrix is found very robust to buffer the volume change and improve the electrical conductivity of conversion-type anode materials. Results on MnO/PC show high charge storage capability, extraordinary rate performance and long-term cycling stability at the same time. MnO/PC is *in situ* converted from bimetal ZnMn-MOF with the templating and activation effects of volatile Zn to construct the PC matrix. Owing to high rate and stable cycling performances, MnO/PC is well-matched in performance with the capacitive AC electrode in an LIC full cell. The MnO/PC-based LIC demonstrates both high-energy and high-power performances. Our work demonstrates that the PC matrix is robust enough to improve Li^+ storage performance of conversion-type anode materials, and

Figure 8 (a) Schematic illustration of the structure, (b) CV curves at scan rates ranging from 0.5 to 10 mV s^{-1} , (c) GCD curves at specific currents ranging from 0.1 to 30 A g^{-1} , and (d) long-term cycling performance and the coulombic efficiency of the MnO/PC//AC LIC. (e) Photographs of an LIC cell used to drive 10 blue LEDs at different durations. (f) Ragone plots of the MnO/PC//AC LIC and previously reported LICs.

the ZnMn-MOF can be used as robust precursor for *in situ* conversion of high-performance MnO/PC composites.

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Author contributions Jiang S and Chen H conceived the idea and wrote the manuscript. Jiang S, Yun S and Zhang Z performed the experiments. Cao H designed the schematic diagram. Feng H helped with the energy storage performance test. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

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金属有机框架结构原位衍化多孔炭基体封装的MnO颗粒及其锂离子电容器应用

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摘要 转换型阳极材料因较高的比容量在储锂方面具有较大的应用潜力, 但是严重的体积膨胀和低电导率限制了此类电极材料的倍率和循环性能. 本研究设计了一种双金属锌锰基金属有机骨架(ZnMn-MOF)材料, 并成功地将其转化成多孔炭封装的MnO颗粒(MnO/PC)复合电极材料. 配位锌组元的模板和活化作用赋予PC基体多孔结构, 能够显著地提高PC基体与MnO颗粒的相容性, 导致MnO颗粒完全封装于PC基体中. 更重要的是, PC基体的多孔结构为缓冲MnO的体积变化提供了足够的空间, 经过反复的充放电循环后MnO仍完全封装于PC基体而不发生破裂乃至破碎. 研究表明, MnO/PC同时具有较高的电荷储存容量、优异的倍率性能和超长的循环稳定性. MnO/PC在 0.1 A g^{-1} 时具有 768 m A h g^{-1} 的比容量, 在 0.7 A g^{-1} 时其比容量仍能保持 487 m A h g^{-1} , 并且在 0.3 A g^{-1} 循环500次后性能未衰减. 值得关注的是, MnO/PC在锂离子电容器中与电容型活性炭电极表现出良好的匹配性, 组装的锂离子电容器在比功率为 210 W kg^{-1} 时实现了 $153.6 \text{ W h kg}^{-1}$ 的比能量, 并且在比功率为 63.0 kW kg^{-1} 时仍能维持 71.8 W h kg^{-1} 的比能量.