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An environmentally benign and high-yield route is developed to synthesize hierarchical porous carbon for high-density energy storage.

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Hierarchical porous carbon (HPC) has attracted much attention in tackling down the global environmental and energy problems. For the state-of-the-art routes to synthesize HPC from organic compounds, the emission of carbon dioxide (CO₂) and gaseous pollutants is inevitable during thermal carbonization. Herein, we report an environmentally benign and high-yield route to synthesize HPC from CO₂ via H₂O-induced self-propagating reactions. By introducing an initiator of H₂O, CO₂ can react with lithium hydride (LiH) to produce HPC in 13 seconds at low temperatures. As-synthesized HPC exhibits interconnected micro-meso-macropore network structure with high porosity of 83%. The formation mechanism of HPC is discussed on the basis of the conversion reactions from CO₂ to C and the gas blowing effect in producing hierarchical porosity. The HPC evaluated as anode materials for lithium ion batteries not only delivers a high reversible capacity of ~1150 mAh g⁻¹ at a current density of 0.2 A g⁻¹, but also exhibits superior rate capability (~825 mAh g⁻¹ at 1.0 A g⁻¹) and excellent cycling properties (up to 2000 cycles). This research opens a new avenue both to synthesize HPC from CO₂ on a large scale and to mitigate greenhouse gas from the atmosphere.

Introduction

Ever-increasing consumption of fossil fuels has led to the global shortage of fossil fuels and environmental deterioration. The pursuit of a low-carbon economy has stimulated considerable effort in the development of efficient conversion and storage of the renewable energy including solar, wind, water and geothermal energy.¹⁻⁴ Lithium-ion batteries, which have come into powering hybrid electric vehicles and pure electric vehicles, are one of the most promising energy storage devices in terms of high energy density and good environmental compatibility. Currently, graphitic carbons are selected as the leading anode material for commercial lithium-ion batteries due to their low cost and good cycling stability. Unfortunately, the low lithium storage capacity (theoretical capacity of 372 mAh g^{-1}) and limited rate capability result in graphitic carbons failing to satisfy the requirements of the onboard lithium-ion batteries with higher energy density and power density.⁵⁻⁶ For the large-scale applications of onboard lithium-ion batteries, therefore, it is of importance to design and synthesize novel carbon materials with increased lithium storage capacity and superior rate capability.

HPC has been demonstrated to be the high-capacity and superior-rate anode material for lithium-ion batteries. $^{7\mathchar`-9}$ For

example, 3D hierarchical porous graphenes prepared by Zuo et al.¹⁰ deliver a reversible lithium storage capacity of 932 and 400 mAh g⁻¹ at the current density of 100 and 1000 mA g⁻¹, respectively, much higher than that of the commercial graphite⁵. The hierarchical porous structure and high specific surface area of hierarchical porous carbons are responsible for the improved electrochemical lithium storage properties. HPCs with a 1D to 3D network have been successfully synthesized from various carbonaceous sources by employing templates,¹¹⁻¹² chemical or physical activation,¹³⁻¹⁴ acidic etching,¹⁵⁻¹⁶ etc. Generally, the template synthesis of HPC is time-consuming, energy-intensive and environment-unfriendly because of the complicated synthesis procedure, limiting the industrial production. Recently, tremendous attention has been paid to synthesize HPC on a large scale via a template-free method.¹⁷⁻¹⁹

In order to achieve the environmentally benign synthesis of HPC, it is critical to select the green synthetic routes and pollutionfree carbonaceous sources. Organic compounds, such as fossilbased products,²⁰⁻²¹ polymers,²²⁻²³ biomass,²⁴⁻²⁵ and metal-organic frameworks,²⁶⁻²⁷ are the most important carbon precursor in the state-of-the-art synthesis of HPC. During the carbonization process, large amounts of CO₂, the most common greenhouse gas, and gaseous pollutants are released from the organic compounds. Anthropogenic emissions of CO₂ from organic compounds combustion are regarded as the major contributor to the continuing global warming.²⁸⁻²⁹ It was estimated that about 13 billion tonnes of CO₂ are produced from the consumption of fossil

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fuels each year.³⁰ Up to now, it is still challenging to reduce the anthropogenic emission of CO_2 into the atmosphere.

CO₂ has not been used as the carbonaceous source to produce HPCs because of its thermodynamically and kinetically stable nature. Herein, we develop a new strategy for the environmentally benign and efficient synthesis of HPC from CO₂ through a selfpropagating reaction between CO₂ and LiH. This self-propagating reaction can be easily initialized at room temperature (RT) by introducing a small amount of H2O. The H2O-induced selfpropagating synthesis of HPCs is an energy-saving and ultraefficient method as CO_2 can react with LiH to produce HPC in 13 seconds. Moreover, the as-synthesized HPC exhibits excellent electrochemical lithium storage properties with a high reversible capacity of \sim 830 mAh g⁻¹ at a current density of 1.0 A g⁻¹ and ultralong cycling life (over 2000 cycles). Our green and efficient strategy (Fig. S1) will open up a new avenue in tackling the longterm challenges of greenhouse effect, energy crisis and air pollution.

RESULTS AND DISCUSSION

Synthesis and characterization of HPC

Fig. 1 shows the key synthesis procedure of HPC from CO_2 . Firstly LiH powder was dispersed at the bottom of a homemade reactor

filled with gaseous CO₂, followed by introducing a small amount of H₂O into the reactor. Fig. 2a shows the time dependence of sample temperatures and gaseous pressures in the reactor. The temperature of the LiH-CO₂ mixture maintained at RT in the first stage, whereas it was raised from RT to 315 °C of the highest reaction temperature in 13 seconds as a small amount of H₂O was simultaneously mixed with LiH and CO2, indicating an exothermic nature of above synthesis reactions. The time dependence of gaseous pressures in the reactor is similar to that of the temperatures. These results imply that CO₂ was gradually consumed in the above exothermic process. The as-obtained solid residue was washed with hydrochloric acid, and then the postwashed solid residue (HPC) was collected for energy dispersive Xray spectroscopy (EDS) analysis (Fig. S2). Only C and O elements are identified. The weight ratio of C:O is calculated to be 95.3:4.7 for the HPC. The EDS result demonstrates that CO2 was successfully converted into carbon in above exothermic reaction process. The trace amount of O may be resulted from the oxygen absorbed by carbon.³¹⁻³²

A broad diffraction peak centered at 25.6° and a weak diffraction peak centered at 42.7°, which are close to the (002)



Fig. 1 Schematic illustration of the synthesis procedure of HPC.



Fig. 2 (a) Time dependence of temperatures and gaseous pressures in the reactor of the HPC synthesis process. (b) Raman spectrum of HPC.

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and (101) diffraction peaks of hexagonal graphite, respectively, were observed in the X-ray diffraction (XRD) pattern of HPC (Fig. S3), indicating that the HPC may not crystallize well. Raman spectrum was measured to study the degree of graphitization. Two peaks centered at 1350 and 1580 cm⁻¹ are observed in Fig. 2b, corresponding to the D band and G band modes of the sp^2 C–C bond, respectively.³³ The intensity ratio of the D to G band (I_D/I_G) is 0.86, implying low graphitization degree of HPC. This result is consistent with the XRD result. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were employed to evaluate the morphology. As shown in Fig. 3a and b, the as-synthesized carbon exhibits a HPC network morphology, in which the interconnected pores are randomly

distributed across the carbon sheets. The hierarchical porous morphology can be observed in TEM and high-resolution TEM image (Fig. 3c-e) as well. The porosity of HPC was further assessed by the nitrogen adsorption–desorption and Hg penetration measurements. A hysteresis loop (0.45<P/P₀<0.98) is observed in the nitrogen adsorption–desorption isotherms (Fig. 3f), which is a typical IV-type curve for mesoporous adsorbents, suggesting that the interconnected mesoporous channels are presented in HPC.³⁴ The pore diameter distribution of HPC is determined by the density functional theory (Fig. 3f) and Hg penetration method (Fig. 3g). The HPC exhibits a micro-meso-macropore structure. The micropores and macropores are centered at 1.45 and 151 nm,



Fig.3 (a, b) SEM images of HPC. (c, d) TEM images of HPC. (e) HRTEM image and SAED pattern of HPC. (f) Nitrogen adsorption-desorption isotherms and corresponding pore diameter distribution of HPC. (g) Pore diameter distribution of HPC calculated from the Hg penetration measurement.

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respectively. A continuous pore diameter distribution is found in the mesopores. From the Hg penetration analysis, the HPC possesses high porosity of 83% and high total pore volume of 9.51 $\text{cm}^3 \text{ g}^{-1}$. The specific surface area is calculated to be 334 m² g⁻¹ by the Brunauer Emmett Teller model. The crystalline characteristics of the HPC was further investigated by high-resolution TEM (Fig. 3e) and selected area electron diffraction (SAED, Fig. 3e), in good agreement with the results of XRD and Raman spectrum.

A static weighing method was used to estimate the yield of HPC. For a typical synthesis, a total of about 8.000 g LiH was used to react with CO_2 . Finally, *ca.* 2.768 g of HPC was obtained after washing and drying. The yield of HPC relative to the weight of LiH is about 34.6%. Even more important, the synthesis reaction of HPC occurred at a low temperature and a low gaseous pressure and completed within 13 seconds (Fig. 2a).

Formation mechanism of HPC

As shown in Fig. 4a, the XRD characteristic peaks of Li_2O and Li_2CO_3 phases were clearly detected in the as-obtained solid residue derived from the reaction between LiH, CO_2 and H_2O . The XRD peaks of C are not observed in Fig. 4a because of its poor crystallinity. The Rietveld refinement of XRD pattern shows that the weight ratio of Li_2O phase and Li_2CO_3 phase is 3:2, corresponding to *ca.* 3.7:1 of the molar ratio. These results

indicate that the crystalline Li_2O and poor crystalline C are the major phases in the as-obtained solid residue. As a result, it can be concluded that the direct chemical reaction between LiH and CO_2 may be responsible for the major products of Li_2O and C. To confirm our deduction above, the solid-gas mixture of LiH and CO_2 was gradually heated in a sealed reactor. The time dependence of sample temperatures and gaseous pressures in the reactor are presented in Fig. 4b. The sample temperature was elevated to 334 °C of the highest reaction temperature in 20 seconds when the solid-gas mixture of LiH and CO_2 was gradually heated to 212 °C. The mixture of LiH and CO_2 exhibits similar changes in the time dependence of sample temperatures and gaseous pressures with the mixture of LiH, CO_2 and a small amount of H_2O as shown in Fig. 2a, suggesting that the small amount of H_2O is not a required reactant for the conversion of CO_2 to carbon.

The solid product of LiH reacting with gaseous CO_2 was collected for XRD analysis (Fig. 4c). A major phase of Li_2O and a minor phase of Li_2CO_3 are observed in the XRD pattern. The Rietveld refinement of XRD pattern exhibits that the weight ratio of Li_2O phase and Li_2CO_3 phase is *ca.* 2.53:1, corresponding to *ca.* 6.25:1 of the molar ratio. After hydrochloric acid washing, the solid residue is carbon as determined by XRD and EDS analyses (Fig.



Fig. 4 (a) Rietveld refinement of the XRD pattern of the as-obtained solid residue of the LiH–CO₂ mixture with 0.09 g H₂O. (b) Time dependence of sample temperatures and gaseous pressures in the reactor of the LiH–CO₂ mixture heated from RT to 215 °C at a rate of 8 °C min⁻¹. (c) Rietveld refinement of the XRD pattern of the as-obtained solid residue of the LiH–CO₂ mixture heated from RT to 215 °C at a rate of 8 °C min⁻¹. (d) Temperature dependence of pressure difference of CO₂ for the Li₂O powder heated from RT to 310 °C.

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S4 and S5). The same products of C, Li_2O and Li_2CO_3 were identified in the as-obtained solid products of the LiH–CO₂ mixture with and without H₂O. Moreover, H₂ was detected in the gaseous reaction products of above two samples (Fig. S6). The chemical reaction between LiH and CO₂ can be proposed as follows:

$$4\text{LiH} + \text{CO}_2 \rightarrow \text{C} + 2\text{Li}_2\text{O} + 2\text{H}_2 \tag{1}$$

According to Equation 1, the theoretical yield of C is about 37.8%, which is very close to our experimental value of 34.6% relative to the weight of LiH.

The minor phase of Li₂CO₃ may be the product of the newly developed Li₂O reacting with CO₂ in the thermal process. The solid–gas mixture of Li₂O and CO₂ was heated from RT to 310 °C at a rate of 2 °C min⁻¹. The temperature dependence of pressure differences of CO₂ is plotted in Fig. 4d. The pressure differences of CO₂ remarkably decreased as the temperature was elevated to above 210 °C, implying that CO₂ was consumed at the temperature of above 210 °C. For the sample heated at 310 °C, a new phase of Li₂CO₃ was clearly detected in the XRD pattern (Fig. S7). These results prove our deduction that the newly developed Li₂O further reacted with CO₂ to produce the minor phase of Li₂CO₃ as shown in Fig. 4c.

$$Li_20 + CO_2 \rightarrow Li_2CO_3$$
 (2)

Combined with the Rietveld refinement results (Fig. 4a and c), it can be known that the content of Li_2CO_3 is not equal for the asobtained solid residues derived from the LiH–CO₂ mixture with and without H₂O. This result suggests that the content of Li_2CO_3 may relate to the amount of H₂O. For the LiH–CO₂ mixture reacting with various amounts of H₂O, the XRD patterns of asobtained solid residues were analyzed with the Rietveld refinement (Fig. 4a, 4c and Fig. S8–S11). The abundance of major phases of Li₂CO₃ and Li₂O are listed in Table. S1. It is obvious that the content of Li_2CO_3 can also be produced by the chemical reaction between LiH, H₂O and CO₂.

It is well known that LiH can react with H_2O to produce LiOH and give off H_2 at RT.³⁵ Gaseous CO₂ can be quickly absorbed by LiOH at RT (Fig. S12). Hence, the Li₂CO₃ derived from the LiH, H_2O and CO₂ mixture can be described by the following chemical reactions.

$\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$	(3)
$2\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$	(4)

The newly produced H_2O will exist in gas state because of the reactor temperature above its boiling point, preventing from the reaction between newly produced H_2O and LiH. On the basis of Equation 3 and 4, the theoretical content of Li₂CO₃ is 20.6 wt.%, which is less than the experimental value of 40.0 wt%, for the asobtained solid residue as shown in Fig. 4a. It can be concluded, therefore, that the chemical reactions (Equations 2, 3 and 4) are together responsible for the Li₂CO₃ formation from the LiH–CO₂ mixture with a small amount of H_2O .

The reaction heat of Equation 3 and 4 is calculated to be -111.2 and -133.2 kJ mol⁻¹ (Table. S2), respectively, suggesting that the

chemical interaction between LiH, H₂O and CO₂ is the exothermic reactions. As discussed above, it has been demonstrated that the reaction of Equation 1 can be initiated by heating the LiH-CO₂ mixture to 212 °C. For the LiH-CO₂ mixture with a small amount of H_2O , the heat released from the exothermic reaction (Equation 3) occurred at RT initiates the exothermic conversion reaction between LiH and CO₂. The adding H₂O acts as an initiator for the chain reactions between LiH and CO2. According to the standard enthalpies of formation of reactants and products (Table. S2), the heat released from Equation 1 is calculated to be -440.3 kJ mol⁻¹, implying an exothermic nature for the efficient synthesis of HPC from CO_2 , which is consistent with the experimental phenomenon as shown in Fig. 2a. However, the chemical reaction between LiH and CO_2 can occur only at the temperature above 212 $^{\circ}C$ (Fig. 4b), resulting from the high kinetic barrier. The reaction heat released from the exothermic reactions (Equations 3 and 4) is as high as 177.8 kJ mol⁻¹. As a consequence, this chemical reaction can be easily initiated by the reaction heat of the Equations 3 and 4.

As for the formation mechanism of HPC, the gas blowing effect plays a key role in producing hierarchical porosity.^{14,36} A series of simultaneous/consecutive reactions including Equations 1-4 occurred in the synthesis process of HPC. A lot of H₂ is released from these chemical reactions. The gas blowing effect of H₂ is responsible for the generation of interconnected macropores in HPC as the macroporous structure can be clearly observed in the as-obtained solid residue (Fig. 5a). Moreover, the C and O elements are shown to be homogeneously distributed within the as-obtained solid residue (Fig. 5b and c), indicating that the byproducts of Li₂O, Li₂CO₃ and LiOH are homogeneously dispersed into HPC. So, it can be concluded that the mesopores and micropores are probably produced during the removal of the byproducts (Li₂O, Li₂CO₃ and LiOH) and/or by the chemical/physical activation of LiOH and residual CO2. 37-38



Fig. 5 (a) SEM image of the as-obtained solid residue from the LiH– CO_2 mixture with a small amount of H₂O. (b, c) the corresponding elemental mappings of C and O.

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Fig. 6 (a) Cyclic voltammograms of HPC at a scan rate of 0.1 mV s^{-1} . (b) Galvanostatic charge and discharge curves of HPC at a current density of 0.2 A g⁻¹. (c) Cycling properties and Coulombic efficiency of HPC and commercial graphite at a current density of 0.2 A g⁻¹. (d) Galvanostatic charge and discharge curves of HPC at 0.2, 0.5, 1, 2 and 4 A g⁻¹. (e) Ultralong cycling life and rate performance of HPC and the cycling properties of commercial graphite cycled at 1 A g⁻¹.

Electrochemical lithium storage properties of HPC

The electrochemical lithium storage properties of HPC were evaluated using CR2032 coin-type half cells. Fig. 6a illustrates its cyclic voltammetry (CV) curves measured at a scanning rate of 0.1 mV s⁻¹. The electrochemical behaviors of the sample at the first cycle, particularly for the cathodic scan, are different from those at the subsequent cycles. In the first cathodic scan, two weak reduction peaks centered at ~0.65 V and 1.50 V, which were only detected in the initial lithiation process, are observed. The peak around 0.65 V can be attributed to the decomposition of the

electrolyte and the formation of the solid electrolyte interphase (SEI) layer in the carbon electrode. Another weak cathodic peak centered at ~1.50 V may originate from the irreversible reaction of lithium ions with functional groups on the surface of the carbon electrode.³⁹⁻⁴¹ These irreversible reactions are further confirmed by the galvanostatic discharge/charge result that a large irreversible capacity of 647 mAh g⁻¹ is found at the first cycle (Fig. 6b). The dominant peak at 0–0.5 V corresponds to the reversible lithium storage of HPC. From the second to third cycle, the CV curves have no obvious changes in voltages vs. Li/Li⁺ and peak current densities, demonstrating good reversibility of HPC for

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lithium storage. The redox peaks at 0.9/1.2 V can be clearly seen in the second and third cycles CV curves, which are associated with reversible lithium storage in the defects and pores of the HPC.^{18,42,43} The electrochemical behaviors of HPC are found to be similar to those of the non-graphitic carbon.

As shown in Fig. 6c, the HPC delivers a discharge capacity of 1160 mAh g^{-1} and a charge capacity of 513 mAh g^{-1} at a current density of 0.2 A g⁻¹ during first cycle, corresponding to an initial Coulombic efficiency of 44%. The low initial Coulombic efficiency can be attributes to form SEI layers on the large surface and interface areas of HPC and/or the irreversible lithium storage reaction of $\mathrm{Li}^{\scriptscriptstyle +}$ with functional groups on the surfaces. $^{\mathrm{18,44}}$ After several cycles, the HPC reaches a stable discharge capacity of ~ 470 mAh g^{-1} and high Coulombic efficiencies of ~99%. The capacity of HPC decreases at first several cycles may be mainly resulted from the gradual formation of the SEI layers on HPC electrode. It should be noted that the discharge capacity increases gradually with the cycle number in the continued cycling (Fig. 6c). The discharge capacity increases from 470 mAh g^{-1} to 558 mAh g^{-1} at the 100th cycle. This phenomenon has been also observed in other carbon materials. 43,45-47 The remarkable increase in discharge/charge capacity can be ascribed to the cycle-activating process of the carbon electrode during Li insertion/extraction.^{44,48} The HPC exhibits excellent cycling properties and superior rate capability. The long cycling properties were evaluated at the current density of 1.0 A g⁻¹ and the corresponding results are presented in Fig. 6e. It delivers a high reversible capacity of ~830 mAh g^{-1} after 1000 cycles, which is about 8 times and 10 times higher than that of the commercial graphite (Fig. 6e) and the amorphous activated carbon (Fig. S13), respectively. After the initial 1000 cycles discharged/ charged at the current density of 1.0 A g⁻¹, the HPC was cycled at various current densities (Fig. 6de). Its reversible capacity reaches as high as ~1150 mAh g^{-1} at the current density of 0.2 A g^{-1} . It is obvious that the reversible capacity of the HPC decreases with the increasing discharge/charge current density. The discharge capacities are ~1000, 825, 655 and 470 mAh g^{-1} , respectively, for the HPC cycled at the current densities of 0.5, 1.0, 2.0 and 4.0 A g^{-1} . When the current density is returned to 1.0 A g^{-1} after 100 cycles, the reversible capacity is recovered to \sim 815 mAh g⁻¹ without remarkable capacity fading after 100 cycles. To examine the longer cycling stability, the HPC was further cycled at the current density of 2.0 A g^{-1} . The reversible capacity of ~555 mAh g^{-1} is maintained up to 2000 cycles (Fig. 6e), corresponding to a high capacity retention of 85%.

Compared with commercial graphite and other carbonaceous materials reported, ^{7,10,18,41,45-47,48,49} the HPC exhibits a higher reversible capacity during the discharge/charge cycling and ultralong cycle life (Table. S3). The rate capability of the HPC is also superior to that of the commercial graphite and other carbon nanomaterials^{10,11,18,45-47} as depicted in Fig. S14. These superior electrochemical properties are assigned to the unique nanostructure of the HPC. It has been known that the reversible lithium storage capacity of the HPC is much greater than that of graphite (Fig. S14). The excess capacity may result from a high amount of extra lithium storage in the pores (including micropores,

mesopores and macropores) and surfaces/interfaces, which acts as reservoirs for electrochemical lithium storage.⁴⁴ Meanwhile, the hierarchical porous structure can buffer the large volumetric effect (about 10% for lithium storage in the graphite⁵⁰) during repeated intercalation and deintercalation of lithium ions in the HPC, contributing to excellent cycling stability. Of course, a large irreversible capacity is inevitable during first-cycle discharge/charge as shown in Fig. 6c because of the high surface/interface area of the HPC. For understanding the superior rate capability of HPC, the electrochemical impedance spectra (Fig. S15) were measured. The HPC has lower diffusion impedance and interfacial and charge transfer resistance than graphite at both open-circuit voltage and after forming stable SEI layers. It can be concluded that the interconnected porous nanostructure with high porosity of 83% not only promotes the continuous and rapid transport of electrons but also supplies fast transport channels for lithium ions. The synergistic effects of macropores, mesopores and micropores result in the superior rate capability of HPC.

Conclusions

In summary, we have developed an environmentally benign, efficient and high-yield route to synthesis HPC from greenhouse gas through H_2O -induced self-propagating reactions between CO_2 and LiH. The as-synthesized HPC exhibited the interconnected micro-meso-macropore network structure with high porosity of 83%. The formation mechanism of HPC was investigated with XRD, EDS, SEM, TEM, MS analyses and time dependence of sample temperature and gaseous pressure measurements. Owing to the unique hierarchical porous structure and high porosity, the HPC showed excellent electrochemical lithium storage properties with a reversible capacity of ~1150 mAh g⁻¹ at a current density of 0.2 A g⁻¹ and ~ 555 mAh g⁻¹ up to 2000 cycles even at a high current density of 2.0 A g⁻¹. Our results may provide a new avenue in tackling down the long-term challenges of greenhouse effect, energy crisis and air pollution.

Experimental Section

Chemical reagents

LiH (97%, Aladdin), CO₂ (>99.995%, Jingong), anhydrous ethanol (99.5%, Aladdin), Li₂O (97%, Aladdin) and hydrochloric acid (AR, Sinopharm) were used as received without further purification. To prevent air and moisture contamination of LiH and Li₂O, these reagents were handled in a MBRAUN glovebox filled with purified argon (>99.995%, Jingong).

Materials synthesis

The synthesis of HPC was performed in a homemade reactor equipped with 2 gas valves and a thermocouple. The sample temperatures and gaseous pressures in the reactor were monitored by the thermocouple and pressure transducer. The reactor was sealed with copper gasket. For a typical experiment, post-milled LiH powder (about 0.8 g) was loaded into a reactor in a glovebox (MBRAUN) filled with purified argon. About 6.5 bar CO_2 was introduced into the reactor to mix with LiH powder. The chemical reaction between LiH and CO_2 could be initialized by adding water and heating, respectively. In one case, a small amount of deionized water (e.g. 0.09, 0.18, 0.27, 0.36 and 0.45 g)

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was mixed with the solid–gas mixture LiH–CO₂ through a gas valve. In the other case, the solid–gas mixture LiH–CO₂ was heated from RT to 215 °C at a rate of 8 °C min⁻¹. At the end of the reaction, the reactor was gradually cooled to RT, followed by washing the solid product with excess hydrochloric acid (6 M). The suspension of solid products was filtered from the above solution by microfilter. Subsequently, the as-obtained solid products were washed by deionized water and absolute ethanol. This procedure was repeated several times. Finally, the solid products were dried at 80 °C in a vacuum oven.

Characterization

Crystal structures of samples were characterized by X-ray diffraction (XRD), in which the XRD patterns were measured on an X-ray diffractometer (PANalytical Xpert Pro, MiniFlex 600) with Cu Ka radiation at 40 kV and 15 mA. XRD patterns were recorded over a 2θ range of $10-80^{\circ}$. During XRD measurements, a homemade holder was applied to prevent samples from moisture contamination. The XRD patterns of crystalline products were refined with the Rietveld refinement program RIETAN-2000. Raman spectra were measured on a Renishaw Invia Reflex micro-Raman spectrometer using an excitation wavelength of 532 nm. Field emission scanning electron microscopy (FESEM), (energy dispersive X-ray spectroscopy (EDS)and transmission electron microscopy (TEM) were performed using a Carl Zeiss Auriga, Oxford X-Max 80 SDD and FEI Tecnai G2 F30, respectively. The composition of gases derived from the chemical reactions between LiH and CO₂ was analyzed using a mass spectrometer (QIC-20, Hiden). Nitrogen adsorption-desorption isotherms were performed on a Quantachrome Autosorb analyser at 77 K. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) model, and the pore diameter distribution was analyzed on an AutoPore IV 9500 by using mercury intrusion porosimetry.

Electrochemical measurement

Electrochemical properties of the working electrode were evaluated using CR2032 coin-type cells, which were assembled by using lithium foil as a counter electrode, Celgard membrane as a separator and 1 M LiPF₆ solution of ethylene carbonate and diethyl carbonate (1:1 by volume) as an electrolyte. The assembly of coin-type cells was carried out in an argon-filled glovebox (H₂O<1 ppm, O_2 <1 ppm). The active materials were mixed with polyvinylidene fluoride binder (85:15 by weight) in N-methyl-2pyrrolidinone to form slurry. The slurry was coated onto copper foil and then dried at 120 °C for 12 h. The galvanostatic charge and discharge tests were conducted on a Neware battery test system. The discharge/charge cycling properties were measured in the voltage range of 0.01–3.0 V versus Li/Li^{+} at ambient temperature. The cyclic voltammetry (CV) curves and electrochemical impedance spectra were tested on a CHI650B electrochemical workstation (Chenhua).

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