Three-Dimensional Graphene-Like Carbon Prepared from CO₂ as Anode Material for High-Performance Lithium-Ion Batteries

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As a typical greenhouse gas, carbon dioxide (CO₂) has significant negative impacts on the environment, and hence, harmless treatment of CO₂ has become very important. In this paper, we present a two-step approach for the preparation of three-dimensional graphene-like carbon (3D-GC) from CO₂. The 3D-GC sample had abundant micropores and nanopores on the carbon framework and its specific surface area was as high as 927 m²/g. Furthermore, the 3D-GC electrodes showed excellent electrochemical performance when used as the anode material in lithium-ion batteries. The reversible capacity was 705 mA h/g after 100 cycles at 100 mA/g and the rate capability was 252 mA h/g at 5000 mA/g.

Keywords: Three-dimensional graphene; Carbon dioxide; Anode material, Lithium-ion batteries

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1. Introduction

Carbon dioxide (CO₂) is a well-known carboxyl compound with low reactivity. With the rapid development of industries, increasing amounts of CO₂ are being released into the atmosphere, which adversely affects the earth's environment, for example, through the greenhouse effect. One of the most common and effective methods to overcome this serious problem is to store CO₂ in compressed form. However, this approach is associated with the risk of leakage and volume expansion. In recent years, many scholars have devoted themselves to research on the harmless treatment of CO₂, and some beneficial results have been obtained through effective approaches.¹⁻⁷ A significant development among them is the preparation of polycarbonate (PC) from CO₂ and epoxy compounds using aluminium or zinc-based catalysts.^{4,5}

In recent years, graphene has attracted considerable research interest owing to its superior mechanical flexibility, high electrical conductivity, high thermal conductivity, and large specific surface area.⁸ Various graphene composites have been developed for applications in many fields.^{12, 14-16} Three-dimensional (3D) graphene derived from graphene sheets finds widespread applications in environmental management, energy and catalysis fields.^{14, 17, 18} Thus, preparation of 3D graphene is expected to be beneficial for practical use. Sodium carbonate (Na₂CO₃) is a water-soluble, low-cost catalyst with high efficiency and selectivity, and it can be applied to fabricate carbon nanofibres and carbon nanotubes,^{19, 20} as well as an activator for carbon materials.^{21, 22}

In this study, we present the idea of three-dimensional graphene-like carbon prepared from CO₂ as anode material for high-performance

lithium-ion batteries, as shown in Fig. 1. We used Na₂CO₃ as a catalyst for the preparation of 3D graphene-like carbon (3D-GC) from CO₂ using a two-step reaction. The characterisation results show the presence of a mass of micropores and nanopores on the carbon framework, and the formation of 3D-GC with a high specific surface area. Furthermore, 3D-GC electrodes delivered enhanced electrochemical performances in terms of reversible capacity and rate capability for application as an anode material in lithium-ion batteries (LIBs).

2. Experimental

2.1 Fabrication of polycarbonate (PC)

The copolymerisation of CO₂ and propylene oxide (PO) can be carried

Fig. 1 The idea of three-dimensional graphene-like carbon (3D-GC) prepared from CO₂ as anode material for high-performance lithium-ion batteries.

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out according to a previously reported method^{23, 24} described as follows: Before polymerisation, The catalysts (Glutaric acid zinc, ZnGA) was dried at 100 °C for 24 h. Then, 0.4 g dried ZnGA was charged into a 100 ml autoclave equipped with a magnetic stirrer. The autoclave with ZnGA inside was connected to the reaction system with a vacuum line, and was further dried for 48 h under vacuum at 100 °C. After drying, the autoclave was purged with CO₂ and evacuated alternately three times. Then, 40 mL purified PO was added by a syringe, and CO₂ was filled until the pressure reaches 51.5 atm. Copolymerisation was performed at 60 °C for approximately 40 h at a stirring speed of approximately 100 rpm. After reaction, the autoclave was cooled to room temperature and the pressure was released. The mixture was taken out, dissolved in 200 mL of methylene chloride and transferred to a separating funnel. The catalyst residue was extracted from the copolymer using 200 mL of dilute hydrochloric acid (5% HCl). Then, the extraction was washed with water for several times, and the resulting copolymer solution was filtered and then dried in a vacuum oven at room temperature.

2.2 Fabrication of 3D-GC sample

10g as-prepared PC powder was mixed with the 20 g Na₂CO₃ powder (Guangzhou Chemical Reagent Factory) in 5ml deionized water for 15 min using a mechanical agitator. Then, the mixture was transferred into a 50 mL Teflon-lined autoclave, subsequently heated to 180 °C and maintained for 4 h. After cooling down to room temperature, the mixture was collected after being dried overnight in a vacuum oven at 80 °C. Then, the dry mixture was transferred into an oven and heated from ambient temperature to 700 °C at 5 °C/min and carbonised at this temperature for 4 h with flowing argon gas (99.99%, 200 cc/min). After cooling, the template was removed by rinsing with deionised water after several times, and the 3D-GC sample was obtained after being dried in a vacuum oven at 80 °C.

2.3 Characterisation

The samples were characterised by powder XRD (Rigaku, D/max 2200VPC X-Ray Diffractometer with Cu K α radiation), micro Raman spectroscopy (Renishaw inVia Raman Microscope) with 514 nm laser excitation at room temperature, field-emission scanning electron microscopy (FEI Quanta 400F Microscope) coupled with energy dispersive spectroscopy (EDS), TEM and high resolution TEM (JEOL, JEM-2010HR), and BET specific surface area test system (Micromeritics, ASAP 2460).

2.4 Electrochemical measurements

The working electrodes were prepared by mixing 75 wt% 3D-GC material with 15 wt% super-P as a conductive agent and 10 wt% polyvinylidene fluoride as a binder in a certain amount of N-methyl-2-pyrrolidinone to form a homogeneous slurry, which was painted onto copper foil. Subsequently, the as-prepared working electrodes were dried in a vacuum oven at 120 °C for over 12 h and then cut into Φ 14 wafers using a slicer. The CR2032 coin type half-cells were assembled in a high-purity argon gas filled glovebox, using the as-prepared 3D-GC wafers as working electrodes, lithium metal foil as counter electrode, LiPF₆ in ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate (EC/EMC/DMC in 1:1:1 volume ratio) as electrolyte, and Celgard 2400 as separator. The galvanostatic charge/discharge performances were evaluated using a battery testing system (LANHE CT2001) in the voltage range of 0.01–3.0 V versus Li/Li⁺ at different current densities. The EIS measurements (from 100 kHz to 0.01 Hz) and the CV tests (from 0.01 V to 3 V at a scan rate of 0.25 mV/s) were performed on an

electrochemical workstation (CHENHUA, CHI660E).

3. Results and discussion

Properties of as-prepared 3D-GC. Fig. 2(a) shows the schematic of the two-step approach for the synthesis of the 3D-GC sample. First, PC powder was synthesised using PO and CO₂ with ZnGA as a catalyst. The PC powder consists of white particles, as shown in the scanning electron microscopy (SEM) image in Fig. S1(a). The 3D-GC sample was prepared using PC powder as a carbon source and Na₂CO₃ as a catalyst. The preparation process involved heat dissolution, pyrolysis, and removal of the catalyst. The SEM image of the 3D-GC sample shows there are typical 3D structure of buck carbon framework (Fig. 2b) with a large variety of pores on the carbon framework (Fig. 2c). Moreover, the pores have a diameter of approximately 100 nm (in Fig. 2d). Transmission electron microscopy (TEM) images can reveal the microstructure of the 3D-GC sample more effectively. A representative 3D skeletal structure of carbon is observed in Fig. 2e, and abundant pores of approximately 100 nm diameter are evident in the carbon framework (as shown in the yellow circles). Furthermore, smaller pores are also observed on the carbon skeleton in Fig. 2f, and the diameter of these pores is approximately 5 nm (pink circles in Fig. 2g). Hence, we can confirm that the prepared 3D-GC is composed of mesopores and macropores.

The results of Brunauer-Emmett-Teller (BET) specific surface area analysis confirmed the presence of mesopores and macropores in the 3D-GC sample. Fig. 2h shows the N₂ adsorption/desorption isotherms of the sample. The isotherms exhibited a sharp capillary condensation step at high relative pressures ($P/P^\circ > 0.9$) and an adsorption/desorption hysteresis loop, indicating the existence of mesopores in the sample. Furthermore, the isotherm exhibited a changing curve with two sharp peaks (at ~5 and 45nm), as shown in Fig. 2i, which confirmed the existence of mesopores in the sample. The BET surface area of the 3D-GC sample (927 m²/g) was higher than that of some of the previously reported porous carbon materials and graphene samples.²⁵⁻²⁸

The crystal structure of the 3D-GC sample was characterised by X-ray powder diffraction (XRD) and laser Raman spectroscopy.^{29, 30} The XRD pattern is displayed in Fig. 2j. Two characteristic peaks of carbon at $2\theta = 23^\circ$ (002) and 43.5° (100, 101) are observed, which are indexed to non-graphitic carbon.³¹ In addition, the presence of two XRD diffraction peaks indicates that the sample is amorphous.³² The Raman spectra of the sample was used to confirm the carbon structure.^{30, 33} The two most intense features observed in the Raman spectrum (Fig. 2k) are the D peak at $\sim 1338\text{ cm}^{-1}$ and the G peak at $\sim 1590\text{ cm}^{-1}$. The D peak represents disordered carbon, and the G peak represents graphitic carbon. In accordance with the well-known empirical equation,²⁷ the large intensity ratio (I_D/I_G) of 0.82 indicates that the 3D-GC sample has a higher percentage of amorphous carbon, which is consistent with the XRD result. This is also in agreement with the results reported in other studies on porous carbon materials.^{26, 31, 34}

The Na₂CO₃ can be considered as a crucial role in the preparation of 3D-GC. First, Na₂CO₃ and PC powders can be distributed uniformly during heating. Second, after the PC sample was catalysed with Na₂CO₃ during pyrolysis to form the carbon material, the residual Na₂CO₃ can be easily removed by using pure water, and graphene-like carbon sample with a 3D structure can be obtained.²⁰ Furthermore, the formation of mesopores and the macropores on the sample could be attributed to the chemical activation of Na₂CO₃ during pyrolysis.²¹ The entire preparation process can be simplified as equation (1), and CO₂ can be efficiently converted to 3D-GC.

Fig. 2 (a) Schematic of the typical process for conversion of CO_2 to 3D-GC; (bd) SEM images of the 3D-GC sample; (ef) TEM images of the 3D-GC sample; (g) HRTEM image of the 3D-GC sample; (h) Nitrogen ($77\ \text{K}$) adsorption/desorption isotherms of the 3D-GC sample; (i) Pore size distribution of the 3D-GC sample; (j) XRD pattern of the 3D-GC sample; (k) Raman spectrum of the 3D-GC sample.

Universality of the procedure. To determine whether Na_2CO_3 can be used for the catalysis of other thermoplastic resins to prepare carbon materials, we used polyethylene terephthalate (PET) and polymethyl methacrylate (PMMA) as reagents replacing the PC precursor. The SEM images of the as-prepared samples showed that both PET and PMMA are beneficial to the formation of porous carbon (Fig. 3a and 3b).

We also determined whether sodium bicarbonate (NaHCO_3), sodium hydroxide (NaOH), or potassium hydroxide (KOH) can be used to replace Na_2CO_3 as the catalyst. As shown in Fig. 3c-e, graphene-like carbon sheets were obtained using NaHCO_3 , NaOH , or KOH as the catalyst. However, when NaHCO_3 was used as the catalyst, a small amount of CO_2 was inevitably produced during the preparation, suggesting that NaHCO_3 is not an ideal catalyst for the preparation of 3D-GC.

To understand the mechanism underlying the formation of 3D-GC, we prepared GC using different kinds of catalysts and carbon sources. We mainly exploited the catalytic function of the abovementioned catalysts and prompted the conversion of carbon sources to GC (sheets or 3D-structured carbon). When no catalyst was used, only bulk carbon was obtained during pyrolysis (Fig. 3f), even though the catalyst also acted as a template during the overall preparation process. As shown in Fig. 4 (a-f), the BET specific surface area value of the above resultant six specimens were respectively calculated to 758, 713, 466, 820, 727 and $166 \text{ m}^2/\text{g}$. Obviously, the BET specific surface area of the samples prepared by these catalysts were less than that of the 3D-GC. However, all samples showed a changing

curve sharp peak at 30–50 nm, indicated that the pore volume was dominantly contributed from mesopores in these specimens, consistent with the 3D-GC sample result.

Performance of 3D-GC as anode material of LIBs. The electrochemical performance of the 3D-GC sample as anode material in LIBs was studied, and the results are presented in Fig. 5. The first three cycles of the cyclic voltammetry (CV) tests are shown in Fig. 5a. In the reduction segments of the 1st cycle, a weak peak at $\sim 0.7 \text{ V}$ is observed. This peak is assigned to decomposition of the electrolyte and formation of a solid electrolyte interphase (SEI) layer,³⁵ which disappears after subsequent cycles. The de-lithiation reaction mainly occurs from 1.25 to 2.25 V, as evident from the two peaks observed in this range for the three cycles.³⁶ Fig. 5b shows that the initial three discharge/charge curves of the 3D-GC electrode at 100 mA/g have a potential window of 0.013 V (vs Li/Li^+). In the first discharge curve, a vague plateau is observed, which is consistent with the CV curve. This plateau disappears in the subsequent two cycles, implying the formation of a stable SEI layer on the electrode in the first discharge process. The discharge and the charge capacities are evaluated to be 1896 and 901 mA h/g, and the sample showed a low initial Coulombic efficiency ($\text{CE} = 47.52 \%$). The irreversible capacity loss can be mainly attributed to the reduction of electrolyte on the porous carbon, such as the irreversible reaction of lithium with residual electrochemically active surface groups in carbon materials and the decomposition of electrolyte to form an SEI layer.^{31, 37} In the subsequent cycles, the Coulombic efficiency of the sample increased up to 90%.

Fig. 5c displays the cycling performance of the 3D-GC electrode. The reversible charge capacity exhibits an initial specific capacity of 901 mA h/g at a current density of 100 mA/g, and the capacity tends to stabilise at 712 mA h/g after 35 cycles. Subsequently, the capacity is maintained at $\sim 705 \text{ mA h/g}$ for 100 cycles, which is much higher than the capacity retention of other carbon materials reported previously.^{34, 38, 39}

Fig. 3 SEM images of different samples prepared using different carbon sources and catalysts: (a) PET + Na_2CO_3 ; (b) PMMA + Na_2CO_3 ; (c) PC + NaHCO_3 ; (d) PC + NaOH ; (e) PC + KOH and (f) PC without catalyst.

Fig. 4 Nitrogen (77 K) adsorption/desorption isotherms and Pore size distribution of the resultant six specimens with different carbon sources and catalysts: (a) PET + Na₂CO₃; (b) PMMA + Na₂CO₃; (c) PC + NaHCO₃; (d) PC + NaOH; (e) PC + KOH and (f) PC without catalyst.

Fig. 5 Electrochemical performances of the 3D-GC sample half-cell. (a) Cyclic voltammograms of the first three cycles at a scanning rate of 0.1 mV/s. (b) Galvanostatic discharge/charge profiles of the first three cycles at 100 mA/g. (c) Cycling performance of the electrodes at a current density of 100 and 500 mA/g, respectively. (d) Rate performance of the electrode at various current densities. (e) Nyquist plots of the electrode during the 1st and the 50th cycles at a current density of 100 mA/g. (f) Nyquist plots of the electrode during the 1st and the 50th cycles at a current density of 100 mA/g.

Meanwhile, the electrode achieves an excellently long cycling life performance as demonstrated in Fig. 5d (at a current density of 500 mA/g). The specific capacity is maintained to 620 mA h/g after 500 cycles, and the Coulombic efficiency is above 99 %. In addition, we found that the change in the reversible capacity of the electrode at a current density of 500 mA/g is more stable than that at 100 mA/g in the first 100 cycles (Fig. S3). The galvanostatic charge/discharge results of the battery are exhibited in Fig. 5e. The discharge capacity of the electrode varies from 712 to 592, 522, 443, 389, 331, and 252 mA/g with increase in the current rate from 100 to 200, 500, 1000, 2000, 3000, and 5000 mA/g, respectively. The capacity recovers to 660 mA h/g when the current rate is reverted to 100 mA/g, and almost 92.6 % of the initial capacity is maintained at the same current density. The electrochemical impedance spectroscopy (EIS) results reveal the electrochemical characteristics of the electrode/electrolyte interface. Fig. 5f shows the Nyquist plot of the 3D-GC electrode during the 1st and the 50th cycle at a current density of 100 mA/g. It can be inferred that the resistance of the 1st cycle ($R \approx 31 \Omega$) is higher than that of the 50th cycle ($R \approx 20 \Omega$); this indicates the stable electrical conductivity of the electrode upon cycling,⁴⁰ and an equivalent circuit model was applied to fit the AC impedance spectra (insert, Fig. 5f). The as-prepared 3D-GC sample exhibits high capacity, excellent cycling stability and rate capability as an anode material for LIBs. This may be attributed to the 3D porous structure, which can shorten the Li⁺ diffusion distance and improve the electron transport rate for short path lengths during the discharge/charge processes.^{41,42} Meanwhile, the abundant mesopores and macropores are beneficial to increasing the electrode/electrolyte contact area for the realisation of a higher rate performance.^{36,41}

4. Conclusions

We have described a method for the fabrication of 3D-GC using CO₂ as a carbon source and Na₂CO₃ as a catalyst and template. The GC sample exhibited a 3D structure, and the BET specific surface area of the 3D-GC sample is 927 m²/g when the weight ratio of the carbon source to the template is 2. When the 3D-GC is applied as an anode material for LIBs, the electrode exhibited a high reversible capacity of 705 mA h/g after 100 cycles at a current density of 100 mA/g, outstanding lifespan (620 mA h/g after 500 cycles), and excellent rate capability (252 mA h/g) at 5000 mA/g. This work provides an efficient and green approach to fabricate 3D-GC on a large-scale using CO₂ as a precursor, and the GC material exhibits remarkable electrochemical performance for Li⁺ storage. Besides, the sample has potential applications in catalysis and adsorption.

Data Availability

The related supplementary data is in the part of supporting information.

Conflict of Interest

The authors declare no conflict of interest.

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