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LiFePO₄/reduced graphene oxide hybrid cathode for lithium ion battery with outstanding rate performance

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Lithium iron phosphate (LFP)/reduced graphene oxide (rGO) hybrid has been prepared using a homogeneous coprecipitation method followed by heat treatment. As a cathode material for lithium ion battery, the hybrid demonstrates a specific capacity of higher than 170 mA h g^{-1} . The excess capacity of

¹⁰ more than the theoretical value of LFP is attributed to the reversible reduction-oxidation reaction between lithium ions and rGO nanosheets. The highly conductive rGO sheets on which LFP particles are uniformly and closely anchored assist the electron migration, lithium ions transfer and prevent the aggregation of LFP particles during charging and discharging, leading to an initial coulombic efficiency of more than 100% with the content of rGO between 7% and 25 % in the hybrid. LFP with 15 % rGO ¹⁵ shows a high discharge capacity of 172 mA h g⁻¹ at 0.06 C, and the capacity remains 139 mA h g⁻¹ at 11.8

C, as well as with an excellent cycling stability.

Introduction

Lithium ion batteries (LIBs) have been considered as alternative energy sources for electrical vehicles and hybrid electrical ²⁰ vehicles.¹⁻³ In order to meet the strong demand in higher-capacity storage systems, the capacity and rate capacity must be improved, urging the discovery of novel cathodes.^{4, 5} As one of the most promising cathode materials for LIBs, LiFePO₄ (LFP) has received a substantial interest due to its low cost, environmental ²⁵ compatibility, relatively large capacity, good thermal stability and

- excellent safety.^{6, 7} However, the intrinsic electronic conductivity and Li⁺ ion diffusion coefficient in LFP are low, which limit its rate performance.⁸ To circumvent these problems, many approaches have been proposed, such as carbon coating,⁹⁻¹¹ ³⁰ metallic cation doping,^{12, 13} and LFP particle size reduction.^{14, 15}
- As the most common and the most effective way, carbon coating can increase electron migration during charging and discharging. Various conductive carbon-based additives have been reported to

enhance the electrical conductivity, such as carbon black,16, 17 35 graphite,^{18, 19} pyrolytic carbon,²⁰ and carbon nanotubes.^{21, 22} In comparison to the carbon materials mentioned above, graphene can offer an improved interfacial contact because of its superior conductivity, flexible two-dimensional structure, and high surface area.²³ These promising advantages make graphene a great 40 candidate potentially for use in electrode materials for LIBs.²⁴ One approach to large-scale graphene synthesis is to reduce chemically exfoliated graphite oxide or graphene oxide (GO) obtained by Hummers' (or modified Hummers') method.²⁵ Several studies have demonstrated enhanced electrochemical 45 performances using LFP/reduced graphene oxide (rGO) hybrids as cathode materials for LIBs, in which the cathode was prepared either by mechanically mixing rGO with LFP particles,²⁶ or by pyrolyzing GO/rGO with either LFP precursor or LFP particles.²⁷, Because of enhanced electron transportation contributed by the 50 rGO sheets in the cathode, the LFP in the hybrids is able to deliver a specific capacity ranging between 146~165 mA h g⁻¹ in a charging/discharging rate of 0.05 to 0.1 C. A good electrical contact between LFP particles and graphene platelets is critical to ensure a high rate performance while keeping the carbon content 55 low.

Herein, we developed an *in-situ* approach to the LFP/rGO hybrid synthesis via a homogeneous coprecipitation method combined with calcinations. The process involves nucleation and growth of FePO₄ (FP) nanoparticles on graphene oxide (GO) ⁶⁰ platelets using urea, subsequently mixing with LiOH, and finally annealing. The resultant LFP/rGO hybrid contains LFP particles uniformly anchored on the surface of the rGO sheets. The hybrid

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consisting of interconnected rGO sheets and LFP particles prevents the aggregation of LFP particles, thus provides more channels for the rapid diffusion of Li ions during charging and discharging, which usually occurs for LFP particles simply mixed s with binders and conductive additives. Our results show that the

s with binders and conductive additives. Our results show that the hybrid with 15 wt% rGO remains a high capacity of 139 mA h g⁻¹ at a charging/discharging rate of 11.8 C (1C=170 mA/g), compared to 93 mA h g⁻¹ for commercial LFP powder (9 wt% carbon) measured at the same C-rate, indicating an excellent rate to capability.

Experimental

Synthesis of graphite oxide

Graphite oxide was synthesized from natural graphite by a modified Hummers' method. Briefly, graphite powder (2 g; 500

- ¹⁵ mesh, Sinopharm Chemical Reagent Co., Ltd) and NaNO₃ (1 g; >
 99 wt%) were mixed, then put into concentrated H₂SO₄ (96 ml;
 98 wt%) in an ice bath. Under vigorous stirring, KMnO₄ (6 g;
 99.5 wt%) was gradually added and the temperature of the mixture was kept below 20 °C. After being removed from the ice
- $_{20}$ bath, the mixture was stirred at 35 °C in a water bath for 18 h. During the reaction, the mixture became pasty with a brownish color. Successively, 150 ml H₂O was slowly added into the mixture and temperature of the mixture was kept below 50 °C. After being diluted with 240 ml H₂O, 5 ml 30 wt% H₂O₂
- ²⁵ (Sinopharm Chemical Reagent Co., Ltd) was added to the mixture; then the solution color changed to brilliant yellow along with bubbling. After continuously stirring for 2 h, the mixture was filtered and washed with HCl aqueous solution (250 ml, 1:1 by volume), DI water and ethanol (anhydrous) to remove other ³⁰ ions. Finally, the solid obtained was dried by vacuum.

Preparation of LFP/rGO

The LFP/rGO was prepared as the following steps: (1) homogeneous coprecipitation, (2) pre-annealing and (3) annealing. In a typical experiment, 10 mmol $Fe(NO_3)_3$ (2.42 g; 99

- ³⁵ wt%, dissolved in 100 H₂O) and 10 mmol NH₄H₂PO₄ (1.15 g; 99 wt%, dissolved in 100 H₂O) were slowly and sequentially added to 100 ml mixed suspension of 8 mg ml⁻¹ GO and 300 mmol urea (18.01 g; 99 wt%). After being exposed to ultrasound in an ultrasonic bath for 30 min, the mixture was heated at 90 °C for
- $_{40}$ 1.5 h under stirring. When cooled to room temperature, the sample was collected by filtration, washed with DI water, and pre-annealed at 400 °C for 4 h under the atmosphere of Ar + H₂ (1:0.05 by volume). Finally, the LFP/rGO was obtained by annealing the sample at 800 °C for 8 h at the same atmosphere.
- ⁴⁵ The content of rGO in the LFP/rGO was measured by a chemical method. 200 mg LFP/rGO was added to 100 ml of HCl (1:10 by volume) solution for stirring. When LFP was dissolved from the hybrid completely, the suspension was filtered and washed by DI water several times. The content of rGO in the hybrid was
- 50 calculated by weighing the residuals after drying.

Characterization

The structure of the as-prepared LFP/rGO was characterized by X-ray diffraction (XRD, CuK α radiation; λ =0.15414 nm) at the scan rate of 2° min⁻¹ in the 2 θ range of 5 and 80°. Scanning ⁵⁵ electron microscopy (SEM) was performed using JSM-6700F

(field emission gun; specimen chamber pressure of about 10⁻⁵ Pa; accelerating voltage 10 kV; working distance 8 mm). Transmission electron microscopy (TEM, JEM - 2010F; 200 keV) was used to study the morphology and microstructure of the hybrid. Raman spectrum measurements were carried out using INVIA (RENISHAW, England) system with a 514.5 nm wavelength incident laser light. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos AXIS Ultra DLD XPS equipped with a 180° hemispherical energy analyzer.

 $_{65}$ Photoelectron was stimulated by monochromated Al K α radiation (1486.6 eV) with an operating power of 150 W. It was operated in the analyzer mode at 80 eV for survey scans and 20 eV for detailed scans of core level lines.

Electrochemical characterization

- ⁷⁰ Electrochemical experiments were performed using 2032 cointype cells. The working electrode consisted of 85 wt% active material, 10 wt% carbon black and 5 wt% polytetrafluoroethylene (PTFE) binder. The electrolyte was a solution of 1 M LiPF₆ in EC/DEC (1:1 by volume) (purchased from Zhangjiagang Guotai-
- ⁷⁵ Huarong new chemical materials Co. Ltd). Pure Li foil was used as the counter electrode. Celgard 2300 was used as a separator. Cyclic voltammogram (CV) was done using 2032 coin cell between 2 and 3.8 V at a scan rate of 0.1 mV/s by CHI650A (Shanghai CH Instrument Company, China). The cells were
- ⁸⁰ charging and discharging at room temperature using a Land battery tester (China). The testing voltage in the constant current mode is between 2.0 and 3.8 V, and the cells were charged in the constant voltage mode at 3.8 V until the current reached 0.05 C.

Results and discussion

 $_{95}$ CO(NH₂)₂+3H₂O \rightarrow 2NH₄⁺+CO₂+2OH⁻

- 85 As shown in Fig. 1, graphite oxide prepared by a modified Hummers' method,²⁹ was sonicated in water to form a suspension of graphene oxide platelets. For the synthesis of the FP/rGO hybrid, Fe(NO₃)₃ and NH₄H₂PO₄ were added in the graphene oxide suspension in the presence of urea. Then the mixed solution
- ⁹⁰ was put in an oil bath at 90 °C under a continuous stirring for 1.5 h. The molar ratio of $Fe(NO_3)_3$ to urea was 1:30. In the suspension, urea slowly releases hydroxyl ions and results in the uniform formation of $FePO_4$ as suggested by the following reactions:

 $Fe(NO_3)_3 + NH_4H_2PO_4 + 3OH^- \rightarrow FePO_4 + 3NO_3^- + 2H_2O + NH_3$



Fig. 1 Scheme of LFP/rGO synthesis.

During this process, Fe^{3+} may be first absorbed on the ¹⁰⁰ negatively charged surface of GO and then nucleate in the

(1)

(2)

(3)

presence of $PO_4^{3^2}$. As the nuclei grow, FP nano-crystals are anchored on the GO sheets. After FP coprecipitated and grew up on the surface of rGO completely, the mixture was cooled to the room temperature, and FP/GO was collected by filtration. Fig. 2a

- ⁵ shows that there are no diffraction peaks in the X-ray diffraction (XRD) pattern of FP/GO, indicating an amorphous nature of the FP nanoparticles on GO. Scanning electron microscopy (SEM) (Fig. 2b) and transmission electron microscopy (TEM) (Fig. 2c and d) indicate that the FP particles are spherical with an average
- ¹⁰ diameter of about 20 nm. We can see that the FP particles evenly distribute on and closely contact with the GO sheets. The selected area electron diffraction (SAED) pattern of the FP nanoparticles (inset of Fig. 2d) shows typical rings of FP, further indicating that FP is amorphous. After being washed with water and ethanol
- ¹⁵ three times to remove the excess ions, the as-obtained sample was mixed with LiOH by grinding. Then the mixture was subject to a pre-annealing at 400 °C for 3 h under Ar + H₂ (1:0.05 by volume) atmosphere and to a further annealing at 800 °C for 8 h under the same atmosphere to form LFP/rGO. During this process, LFP ²⁰ was made following the reaction:

$$2\text{LiOH} + 2\text{FePO}_4 + \text{H}_2 \rightarrow 2\text{LiFePO}_4 + 2\text{H}_2\text{O}$$

At the same time, graphene oxide (GO) was converted to reduced graphene oxide (rGO). In the process, the LFP particles are tightly distributed on the surface of rGO by oxygen-²⁵ containing functional groups, and are partially wrapped by rGO which is favor to enhancing the electrochemical performance of the hybrid.^{30, 31}



Fig. 2 The as-prepared FP/GO. (a) XRD pattern, (b) SEM, (c) and (d) TEM.

Fig. 3a shows XRD pattern of the LFP/rGO hybrid. The XRD pattern exhibits a single phase of LFP. All the diffraction peaks are in accordance with ordered LFP olivine structure indexed by orthorhombic P_{mna} (JCPDS No. 81-1173), indicating a high ³⁵ crystallinity of the LFP. There are no obvious rGO diffraction peaks at ~26° in the LFP/rGO hybrid, which could be due to its low content and/or well-exfoliated morphology. Graphene in the hybrid was further confirmed by Raman spectroscopy, as shown in Fig. 3b. Two peaks at 1353.1 and 1590.5 cm⁻¹ are attributed to ⁴⁰ the D and G bands of graphene, respectively.³² The D band is an indication of disorder-allowed zone-edge modes of graphite, along with amorphous carbon species.³³ The intensity ratio of D to G band (I_D/I_G) was about 1.30, indicating that the hybrid has a high degree of disorder in carbon arrangement.³⁴ It was suggested

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 $_{45}$ that the LFP/rGO hybrid with high I_D/I_G value in carbon Raman spectra might outperform good electrochemical properties. 35 Fig.

3c shows the binding energy profile of carbon in the hybrid measured by X-ray photoelectron spectroscopy (XPS). The observation of C1s binding energies at 286.7 eV (C-OH), 287.7 ⁵⁰ eV (C=O) and 289.7 eV (O=C-OH), suggests that some oxygencontaining functional groups remain in rGO, and the atomic percentages of various carbons derived from the fitted peak areas are indicated in the figure. By chemical method (See experimental for details), the content of rGO in the LFP/rGO ⁵⁵ hybrid was determined as 15 wt%.

Fig. 3d-f show SEM and TEM images of LFP/rGO. Fig. 3d exhibits a curled morphology of rGO sheets, consisting of thin wrinkled 'paper-like' structures. It can also be seen from SEM that the LFP nanoparticles are also uniformly distributed on the ⁶⁰ surface of rGO (similar to FP particles). The TEM image in Fig. 3e shows that the typical LFP particle size is ~100 nm in diameter. The HRTEM image shows the crystal lattice fringes of

the LFP nanoparticles with a d-spacing of 0.29 nm (Fig. 3f), corresponding to the (020) plane of orthorhombic LFP crystals. The high crystallinity of the LFP nanoparticles has been further confirmed with the SAED pattern (inset of Fig. 3f). It is worth

s noticing the rGO and the LFP nanoparticle have an atomically close interface, benefiting to the efficient electron transfer during charging and discharging, as will be discussed below.



Fig. 3 LFP with the content of 15 wt% rGO. (a) XRD pattern, (b) Raman spectrum, (c) C1s binding energy profile measured by XPS, (d) SEM, (e and f) TEM.

Fig. 4a shows the cyclic voltammetry curves of LFP/rGO at the scan rate of 0.1 mV/s. A pair of redox peaks associated with ¹⁵ Fe²⁺/Fe³⁺ couple was observed at 3.54 V for anodic direction, and at 3.34 V for cathodic direction, corresponding to the extraction and insertion of lithium ion in LFP, which reveals a singleelectron reaction mechanism. The charging/discharging characteristics of the LFP/rGO hybrids in the voltage window of ²⁰ 2.0~3.8 V are shown in Fig. 4b. There are flat plateaus over the voltage range of 3.4~3.5 V for the LFP/rGO hybrids, which is typical for the single-phase transition of lithium iron phosphate to iron-phosphate as shown by the equation: LiFePO₄ \rightarrow Li⁺ + e + FePO₄

LiFePO₄ → Li⁺ + e + FePO₄ (4)
As an example, the hybrid with the content of 15 wt% rGO has capacities of 160.2 and 172 mA h g⁻¹ (normalized to the mass of LFP) for the first charge and discharge, respectively. The results indicate an initial coulombic efficiency (discharge to charge) of 107.5%, higher than 100% for the common coulombic ³⁰ efficiency of LFP cathode materials. In addition, the LFP/rGO hybrids deliver specific capacities of 161, 172 and 189.5 mA h g⁻¹, depending on the weight percentage of rGO with 7, 15 and 25

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wt%, respectively. The high initial coulombic efficiency and the increase in the specific capacity with rGO content suggest that rGO nanosheets contribute to Li^+ ion storage in the LFP/rGO hybrid, and the storage mechanism is reversible. In a control

- ⁵ experiment, pure rGO has given a specific capacity of 48 mA h g⁻¹ as cathode materials at the same condition (see Figures S1 and S2), which is much less than 2000 mA h g⁻¹ for graphene reported in the literature.³⁵ One possible reason is that the rGO restacks during charging and discharging, leading to the aggregation and
- ¹⁰ thus increase in the polarization and decrease in their surface area. In the LFP/rGO hybrids, however, rGO nanosheets are separated by LFP particles, possibly leading to a larger surface

area for storing Li⁺ ions. When the content of rGO in the LFP/rGO hybrid is increased from 7 to 25 wt%, the initial ¹⁵ coulombic efficiency is increased from 102 to 117 % (Fig. 4b). The LFP/rGO with the content of 25 wt% rGO has 117% of an initial coulombic efficiency, and 189.5 mA h g⁻¹ of the first discharge capacity, higher than those reported.^{28, 36, 37} The initial coulombic efficiency increase with the rGO content is attributed ²⁰ to the enhancement of Li⁺ ion storage capacity of rGO, especially below the voltage of 3.0 V. But very high rGO content will result in a low density of the hybrid, which is not favour for its practical application. Further research work will focus on the optimum content of rGO for its practical application.



Fig. 4 (a) Cyclic voltammogram of LFP with 15 wt% rGO at a scan rate of 0.1 mV/s in the voltage range of 2.0~3.8 V, (b) Comparison of the first charge and discharge profiles for LFP with 7, 15, and 25 wt% rGO, respectively, (c) The rate performance of LFP with 15 wt% rGO at various current densities after the first cycle, (d) Ragone plot correlating the gravimetric densities of energy and power of LFP/rGO|Li half cells containing 1 M LiPF₆ in EC and DEC (1:1 by volume).

Long-term charging and discharging cycling was performed for the LFP/rGO hybrid with the content of 15 wt% rGO (see Figure S3). After 50 cycles, the hybrid still delivered a specific capacity of 168 mA h g⁻¹, which has 97.5% retention of the first ³⁵ discharge specific capacity 172 mA h g⁻¹. The coulombic efficiencey has 98~100% after the first cycle. Obviously rGO has greatly enhanced the electrochemical performance of LFP during charging and discharging, leading to an excellent cycling performance. The improvement may be ascribed to two main ⁴⁰ factors: one is the contribution from rGO nanosheets because lithium ions can be inserted in or extracted from both sides of rGO nanosheets; the other factor is that, highly conductive rGO nanosheets on which LFP particles are anchored serve as a fast path for electron and Li⁺ ions migration during charging and

45 discharging, possibly benefitting to the improvement in the

kinetics and reversibility of lithium insertion/extraction cycles. Furthermore, morphology of rGO wrapped LFP particles may lead to a better rate performance, since electron transfer could be fast on the surface of LFP to withstand high discharging/charging ⁵⁰ rate. At the same time, because Li⁺ ions can be inserted/extracted on the rGO surface, the rGO can act as a medium to transfer Li⁺ ions between the boundary of LiFePO₄/FePO₄, resulting in fast Li⁺ ions transportation during charging and discharging. Fig. 4c shows the rate performance of LFP/rGO with the content of 15 ⁵⁵ wt% rGO at different current densities. When the current density is increased from 0.06 C to 11.8 C, the discharge capacity is decreased from ~172 to ~139 mA h g⁻¹ (81% retention). The discharge capacity of 139 mA h g⁻¹ at 11.8 C is significantly higher than ~ 93 mA h g⁻¹ of commercial LFP (~9 wt% carbon, 60 Beijing Easpring Co. Ltd) at 11.8 C. A comparison indicates that 60 8

the high C-rate specific capacity (~139 mAh g⁻¹ at 11.8 C) is higher than those previously reported, such as graphene-coated commercial carbon-coated LFP (125 mA h g⁻¹ of at 10 C),³⁵ LFP/graphene (75 mA h g⁻¹ at 10 C),³⁸ and ultrthin graphite

- ⁵ foam/LFP (70 mA h g⁻¹ at 7.53 C).³⁹ Furthermore, as long as the current reverts back to 0.06 C, the original capacity of LFP/rGO is recovered. When charged to 3.8 V (in state of charge), LFP becomes FePO₄. TEM shows that the particle of FePO₄ is smaller and separated by rGO sheets (See Figure S4); when discharged to
- ¹⁰ 2.0 V (in state of discharge), FePO₄ is changed to LFP again with the original olivine crystallinity (See Figure S5), indicating that rGO nanosheets are tolerant to varied charge and discharge currents; such a merit is highly desirable for electrode materials in lithium ion batteries. The Ragone plot (Fig. 4d) highlights the
- ¹⁵ excellent rate performance of the LFP/rGO hybrid in the rate range of 0.06 to 11.8 C. At a power density of 6 kW/kg, the LFP/rGO delivers an energy density of 425 Wh/kg, 50% higher than that of commercial samples, indicating that most of the energy stored in the LFP/rGO is available for utilization, less
- ²⁰ dependent on the rate of energy extraction (power). This property shed light on rapid charge/discharge applications when the LFP/rGO hybrid is used in Li-ion batteries. At the same time, the coulombic efficiency of LFP/rGO maintains in 98~100% for various current densities.

25 Conclusions

In summary, the LFP/rGO hybrid has been prepared by a homogeneous coprecipitation and followed heat treatment. The content of rGO varies from 7 to 25% in the hybrid and the LFP particles are closely anchored on the surface of rGO sheets. The

- ³⁰ hybrid with 15% rGO can deliver a capacity of 172 mA h g-1. It has an energy density of up to 569 Wh/kg, which is higher than the typical 500 Wh/kg of LFP. More importantly, the addition of rGO has improved the rate performance of the existing LFP electrode materials, leading to a high capacity of 139 mA h g-1 at
- ³⁵ 11.8 C. With a wide range of rGO's redox potential, the preparation approach may be potentially extended to other electrode materials with low conductivity and capacity for lithium ion batteries.

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