Graphene encapsulated spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates for high-performance Li-ion batteries

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ABSTRACT: the electrochemical performance of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ material is further enhanced via synergistic strategies including crystal orientation growth, microspherical self-assembly and graphene encapsulation. The crystal orientation growth of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ with plate-like morphology not only reduces the Li-ion transport length, but also enlarges the (010) surface, and leads to the improvement of Li-ion diffusion. The self-assembled spherical hierarchical superstructures can effectively prevent the plane-plane stacks of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates during spontaneously aggregating, providing more (010) surface for Li^+ insertion/extraction. The graphene encapsulation can build a 3D conductive network as well as stabilize the microspherical aggregations, resulting in superior electronic conductivity and stability. As a consequence of the synergistic effects, the as-obtained $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ sample exhibits excellent rate capability ($141.1 \text{ mA h g}^{-1}$ at 5 C, $126.5 \text{ mA h g}^{-1}$ at 10 C, $107.7 \text{ mA h g}^{-1}$ at 20 C) and outstanding cyclability (25 °C, 94.6% capacity retention after 500 cycles at 1 C). The synergistic strategy involving crystal orientation growth, microspherical self-assembly and graphene encapsulation provides a fascinating candidate to obtain superior olivine-type cathode materials with excellent rate capability and cycling stability, and holds the potential to be extended to the controlled preparation of other electrode materials.

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1. Introduction:

Better batteries with higher energy, faster charge-discharge rate, longer cycle life are in urgent need on the condition of rapid development of electric vehicles (EVs) and hybrid electric vehicles (HEVs)[1-3]. As the most potential candidate for cathode materials of power batteries, olivine-type LiFePO_4 -based materials have drawn massive attention, and tremendous advances on high-rate capability have been achieved in recent years[4, 5]. However, the low theoretical specific energy of LiFePO_4 material becomes to be an insurmountable hurdle, which severely impedes its applications in power batteries for EVs or HEVs[6, 7]. Spontaneously, another olivine-type material of LiMnPO_4 has come to the field of view of researchers due to its moderate operate voltage of 4.1 V (vs. Li/Li^+), resulting in high energy density compared with LiFePO_4 [8]. Moreover, LiMnPO_4 takes advantages of low cost, good safety and environmental benign, considered to be an emerging cathode material for power batteries. Unfortunately, LiMnPO_4 suffers from even lower electronic conductivity ($\sim 10^{-10} \text{ S cm}^{-1}$) and Li-ion diffusivity ($\sim 10^{-16} \text{ cm}^2 \text{ s}^{-1}$) than LiFePO_4 does, which lead to its inferior specific capacities and high-rate capability[6, 9]. Furthermore, sharp degradation of LiMnPO_4 crystal structure during charge-discharge process results in poor capacity retention because of the excessive interface strain between LiMnPO_4 phase and MnPO_4 phase resulting from John-Teller distortion[10, 11].

Many efforts have been made to overcome these drawbacks so as to improve the electrochemical performance of LiMnPO_4 [12-15]. Recent researches show that an appropriate substitution of Mn with Fe in LiMnPO_4 can form $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($0 \leq x \leq 1$) compounds, which improve the electronic and ionic conductivity as well as reduce John-Teller distortion[16]. Just like in olive-structural LiFePO_4 crystallite, Li-ions in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ crystallite preferably diffuse along the b-axis rather than along the a- or c-axes. Therefore, it is very effective to improve the rate capability of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ by architecting a plate-like structure with preferred (010) facet as LiFePO_4 does[17,

18]. J. Vittal et al.[19] have synthesized pure phase LiMnPO_4 and $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0.5, 0.75$) nanoplates by using a simple solvothermal route, confirming that substitution of Fe^{2+} for the Mn^{2+} site has been found to improve the electrochemical activity of the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple significantly. Hu et al.[12] have reported that $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ nanoplates synthesized by solvothermal method deliver excellent discharge capacities, which is attributed to the fast Li diffusion in the diffusion path of [010] crystallographic axis along the short radial direction of the nanoplates. However, the plate-like $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ easily aggregates through plane-plane stacking, resulting in a rapid decline of Li-ion diffusion distance and reaction rate of Li^+ insertion/extraction. The self-assembled spherical hierarchical superstructures can effectively prevent the plane-plane stacking of $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ nanoplates during spontaneously aggregating, thus providing more (010) surface for the Li^+ insertion/extraction[20, 21]. Furthermore, such an open porous microspherical structure is expected to possess low interfacial energy, high reactivity, high power density and better fluidity characteristics[22, 23]. Therefore, microspherical self-assembly is considered to be a good strategy to architect advance materials for Li-ion batteries. Carbon coating is another effective way to improve the electrochemical performance of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ by compensating its low conductivity[24-26]. Recently, hybrid coating by carbon and graphene has been used as a high-efficient carbon coating technique for modifying olivine-structured $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ material[27-29]. Due to the synergistic effect of amorphous carbon and graphene, hybrid coating can construct a thin, tightly attached, and continuous 3D conductive network by wrapping $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, resulting in superior high-rate capability and excellent cycling stability[30]. Besides the improvement of electronic conductivity, well-organized carbon layers can effectively prevent the dissolution of manganese, which plays crucial role on determining the cyclability of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ [10, 31]. Based on the investigation results above mentioned, it's clearly that reducing b-axis thickness, enlarging (010) surface, forming well-organized carbon coating and architecting 3D conductive network are very crucial for high performance $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ material. On the other hand, although there are controversial conclusions on the unclear structure (a solid solution or a two-phase structure) and the

underlying mechanism (different optimal Fe/Mn ratios with different synthetic methods), several studies have proved that $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ possesses best electrochemical performance among the different Fe/Mn ratios by first-principles calculations and electrochemical tests[32]. Therefore, to develop a novel, multifunctional and synergistic architecture for $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ material with small b-axis length, large (010) surface and uniform carbon layer is a great effective strategy to prepare high performance cathode materials for Li-ion batteries.

Herein, graphene encapsulated spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates are prepared via synergistic strategy involving crystal orientation growth, microspherical self-assembly and graphene encapsulation for the first time, which provides a fascinating candidate to obtain superior olivine-type cathode materials with excellent rate capability and cycling stability. The binary solvent (EG:H₂O=1:1 v/v) plays a crucial role on crystalline orientation of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates during hydrothermal process. The surface tension and electrostatic force facilitate the $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates to form microspherical aggregations during the self-assembled process. Water-soluble starch and graphene oxide play a key role on the encapsulation of microspherical aggregations. Amylose is used as crosslinking factor to bridge GO based on the dehydration/condensation reaction, helping GO to form 3D continuous conductive network. Amylopectin is likely to form a thin, tightly attached and uniform film on $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ surface, resulting in a well-organized carbon layer during the carbothermal reduction reaction. Owing to this unique structure, the as-prepared $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ material exhibit excellent high-rate capability and cyclability, which may offer a good selection of power batteries for EVs or HEVs.

2. Experimental section

2.1 Preparation of GO nanosheets: GO nanosheets were prepared with an improved method proposed by JM Tour and his co-workers[33]. Typically, a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) was added to a mixture of 3.0 g graphite flakes (120 μm) and 18.0 g KMnO₄, resulting in a slight exotherm to 35~40 °C. Subsequently, the reaction was thermostat-controlled to 50 °C and stirred for 12 h. After that, the obtained-slurry was cooled to room temperature and slowly poured onto specially-made

ice with 400 mL H₂O and 3 mL H₂O₂ (30 wt%,). Then, the mixture was filtered through paper filters and the filter cake was washed repeatedly by deionized water, 30% HCl and ethanol, respectively. Afterwards, the filter cake was dried overnight at 50 °C in a vacuum oven to get graphite oxide powder. Finally, 0.4 g graphite oxide powder was added into 200 mL H₂O, and the complete delamination of graphite oxide into GO was achieved by ultrasonic treatment. The suspension of GO with a content of 2.0 mg mL⁻¹ was preserved for later use.

2.2 Preparation of LiFe_{0.75}Mn_{0.25}PO₄ samples: graphene encapsulated spherical hierarchical superstructures self-assembled by LiFe_{0.75}Mn_{0.25}PO₄/C nanoplates were prepared by a combination route of solvothermal method, self-assembly and carbon coating. The detailed preparation process was described in Fig. S1† (see ESI). Firstly, FeSO₄·7H₂O and MnSO₄ were dissolved into 100 mL H₂O, subsequently H₃PO₃ solution was added, and then LiOH·H₂O aqueous solution was added slowly in constant stirring. Following the addition of LiOH·H₂O, the mixed solution changed into suspension. After that, 100 mL EG was added as solvent to obtain precursor suspension. The concentration of Li⁺ in the precursor suspension was controlled to be 0.15 mol L⁻¹. The molar ratio of the Li: Fe: Mn: P in the precursor solution was 3:0.75:0.25:1. Secondly, the precursor suspension was put into a Teflon-lined Parr reactor, and then was heated at 160 °C for 5 h. After the hydrothermal reaction, the precipitation was washed with deionized water and ethanol, followed with drying at 100 °C for 12 h under vacuum to obtained LiFe_{0.75}Mn_{0.25}PO₄ nanoplates. Thirdly, 2.0 g LiFe_{0.75}Mn_{0.25}PO₄ nanoplates were dispersed into 200 mL GO suspension by mechanical stirring and ultrasonic dispersing. Then, 3.42 g water-soluble starch was added and the suspension was poured into reactor and heated to 80 °C for 2 h under N₂. After that, the suspension was cooled down and the precipitation was washed with deionized water and ethanol, and the filter cake was dried at 100 °C for 12 h under vacuum to obtained LiFe_{0.75}Mn_{0.25}PO₄ powder. At last, the dried powder for carbon coating and further crystallizing was calcinated under Ar atmosphere at the temperature of 700 °C for 12 h. For comparison, a reference LiFe_{0.75}Mn_{0.25}PO₄ sample was synthesized through the

same process without using graphene oxide. The as-obtained $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples without or with graphene were labelled as LFMPa and LFMPb, respectively.

2.3 Characterization of physical: The crystalline structures of LFMPa and LFMPb were studied by X-ray diffractometer (XRD, D8 focus, Germany Bruker company) with Cu K_α radiation at 40 kV, 40 mA, step size of 0.02° , and a count time of 0.6 s per step between $2\theta=10^\circ$ and 80° . Scanning electron microscope (SEM) images were taken after aurum coating by using a field emission scanning electron microscope (Hitachi, S-4300) operated at 10 kV. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were taken by a field emission transmission electron microscopy (JEOL, JEM-2100F). SEM was used for observing the morphology of the prepared powders. High resolution TEM (HRTEM) and SAED were applied to detect the crystal lattice of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$. Meanwhile, the morphous of carbon layer on the surface of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4/\text{C}$ crystallite was observed by HRTEM. Fourier Transform Infrared Spectroscopy (FTIR) has been used to detect the presence and variation of functional groups in carbon sources (starch, graphene oxide), $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ precursor, and $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$. The structural variations of carbonaceous material in LFMPa and LFMPb were identified by Raman spectroscopy (Renishaw Raman Microscope, 532 nm HeNe Laser). The carbon contents of LFMPa and LFMPb were detected by a simple chemical method. Typically, 0.2 g $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ sample accurated to 0.0001 g was dissolved into 50 mL 1.0 mol L^{-1} HCl, followed by stirring for 6 h. Then, the mixture was filtered through paper filters and the residual was washed repeatedly by deionized water. At last, the residual was dried at 60°C under vacuum for carbon analysis and the filtrate was diluted for elemental analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian 710-ES). The electron conductivity of LFMPa and LFMPb were measured by the four-probe conductivity meter (RTS-8). In the conductivity test, 5.0 g $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ powder was pressed into a nummular platelet with a diameter of 2 cm and a thickness of ~ 0.5 cm under a pressure of 10 MPa.

2.4 Measurement of electrochemical properties: For the preparation of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ cathode electrodes, $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ sample and acetylene black

were blended and grind for 30 min, then 10 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone was added in and stirred for 10 min. Typically, the weight ratio of active material, conductive additive and PVDF was 80:10:10. Subsequently, the resultant slurry, pasted on Al foil, was dried at 80 °C under vacuum for 12 h. The loading of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ material including carbon and graphene in cathode electrode was 2.0 mg cm^{-2} . Electrochemical tests were performed using CR2032 type coin cells with lithium anode assembled in an Argon filled glove box. The electrolyte was 1.0 mol L^{-1} LiPF_6 in EC + DEC +DMC (1:1:1 vol.%). Charge–discharge cycling at a constant current mode was carried out between 2.5 and 4.5 V at various rate from 0.1 to 20 C. Cyclic voltammograms (CVs) were obtained over the voltage range from 2.92 to 4.42 V at a scanning rate of 0.1 mV/s using an electrochemical working station (CS310). Electrochemical impedance spectroscopies (EIS) were also test at room temperature using CS310 in the frequency ranged from 100 to 0.1 kHz at an open-circuit voltage of 3.42 V with an amplitude of 5 mV on the electrode.

3. Result and discussion

3.1 structure and morphology

The crystallinity and the phase information of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples have been confirmed with the XRD method. Fig. 1b and Fig. 1c show the XRD profiles of LFMPa and LFMPb, respectively. The diffraction peaks are indexed according to olive-structural LiFePO_4 with space group *Pnma*. All the peaks of LFMPa and LFMPb can be well assigned to those of the standard XRD pattern (JCPDS 83-2092) as shown in Fig. 1c. No obvious carbon has been detected in LFMPa and LFMPb due to its low content and crystallinity, even though the presence of carbon is confirmed by SEM and HRTEM. Additionally, the strong and narrow diffraction peaks indicate high crystallinity of the as-obtained $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples. However, compared with standard XRD patterns of LiFePO_4 , the diffraction peaks of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples slightly shift toward lower diffraction angles, which is compatible with increased lattice parameters of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples justified by the larger ionic radius of the Mn^{2+} respect to the Fe^{2+} (0.97 vs 0.92 Å)[32]. Table S1† presents the lattice parameters of

$\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples based on the calculation using MDI Jade 5.0 software, which are in coincidence with the chemical compound of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$. To better evaluate the compositions of the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, ICP-AES is applied to confirm the mole ratio of Fe/Mn. The mole ratios of Fe/Mn in LFMPa and LFMPb are 3.04:1 and 3.03:1, respectively (see in Table 1), indicating an approximate chemical composition of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$.

On the other hand, the relative intensities of the peaks are obvious different between the prepared $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples (Fig. 1b, Fig. 1c) and the standard orthorhombic LiMPO_4 (Fig. 1a, Fig. 1d). The XRD patterns of LiMPO_4 are dominated by the four (101), (111), (020), and (311) lines, and the (311) line possess the largest intensity. However, the XRD profiles of LFMPa and LFMPb are dominated by the strongest (020) diffraction line, which suggests that the crystallites of LFMPa and LFMPb have a preferred lattice plane of (010) facet. According to the relative peak intensities of (020) line to (111) line calculated from XRD patterns (see Table S1[†]), the ratio of $I_{(020)}/I_{(111)}$ of LFMPb is larger than that of LFMPa. The result demonstrates that the degree of orientation of LFMPb is larger than that of LFMPa, which is probably owing to the effect of graphene encapsulation, protecting the high degree of orientation via the suppression of crystal growth.

Fig. 2a and Fig. 2b give the panoramic SEM images of microspherical aggregation of LFMPa and LFMPb, respectively. Self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates, the microspherical aggregation without or with graphene encapsulation is about 5 μm in size. However, the morphology of graphene encapsulated microspherical aggregation is much different from that of the microspherical aggregation without graphene. Without the encapsulation of graphene, the nanoplates in LFMPa further grow under the action of Ostwald ripening, resulting in a quasi-spherical structure of assembled aggregation (Fig. 2a). Furthermore, the magnified SEM images in Fig. 2c and Fig. 2d clearly exhibit the differences between LFMPa and LFMPb. The fuzzy silky substances wrapped on the surface of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates in Fig. 2d are identified as reduced graphene oxide, which are absent in Fig. 2c. The lattice fringes of graphene presented in HRTEM photographs of LFMPb demonstrate that the

microspherical aggregation is encapsulated by graphene (Fig. 2f). Additionally, the HRTEM photographs exhibit clear lattice fringes indicating single crystallinity of the $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates in Fig. 2e and 2f, which are corresponding to the SAED in their inset, respectively. Additionally, the HRTEM photographs of LFMPa and LFMPb present a same lattice fringes spacing of 0.301 nm. The results indicate that the largest exposed plane of nanoplates in LFMPa and LFMPb is the (010) lattice plane, giving the strongest (020) line in the X-ray pattern (Fig. 1b, Fig. 1c).

FTIR techniques have been used to detect the presence and variation of functional groups in carbon sources (starch, graphene oxide), $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ precursor, and $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ as shown in Fig. 3. In FTIR spectrum of starch, three characteristic peaks appear between 1000 and 1200 cm^{-1} , related to C–O bond stretching of starch [34]. Furthermore, the characteristic peak at 1640 cm^{-1} is attributed to the tightly bound water in the starch [35]. The infrared absorption bands of graphene oxide located at 1730 , 1615 , 1409 and 1050 cm^{-1} demonstrates the presence of C=O (carboxyl), C=O (carbonyl) and C–O (alkoxy)[36–38]. Based on above, we can deduce the presence of carbon sources in LFMPa and LFMPb precursor. Moreover, compared with graphene oxide, the assymetric stretching vibrations of C=O bond for LFMPb precursor shifts from 1615 to 1632 cm^{-1} . This may demonstrate that the C=O group of graphite oxide has been influenced by the anhydroglucose ring of starch, thus confirm that amylose play as bridge to crosslink GO nanosheets based on the dehydration/condensation reaction (see in Fig. 5). After thermal treatment, obvious variations are detected for both LFMPa and LFMPb, giving significant information for the variation of function groups. The characteristic absorption peak around 1000 cm^{-1} assigned to the symmetric stretching of the P–O bond in the PO_4 tetrahedron is obviously presented in FTIR spectra of LFMPa and LFMPb, which is covered by C–O bond stretching of starch for LFMPa and LFMPb precursor. Furthermore, compared with LFMPb precursor, the free O–H groups ($3600\sim 3200\text{ cm}^{-1}$), the C = O stretching vibrations of carboxyl groups (1720 cm^{-1}), and C–O stretching vibrations of epoxy groups (1050 cm^{-1}) in LFMPb almost disappear, which indicates that GO is almost reduced and starch is almost carbonized in the thermal treatment conditions.

The surface compositions of LFMPa and LFMPb are investigated by Raman spectroscopy in the range of 500 - 2000 cm^{-1} as shown in Fig. S2†. It's obviously that two peaks located at 1600 and 1358 cm^{-1} are revealed in the spectrum of LFMPa and LFMPb. The Raman peaks at 1600 and 1358 cm^{-1} are attributed to the G band (graphitized carbon) and D band (disordered carbon), respectively. Thus the peak intensity ratio (I_D/I_G) between 1358 and 1600 cm^{-1} in Raman shifts is calculated to be an index of the degree of disordering [39]. As shown in Fig. S2†, the I_D/I_G ratio of sample LFMPa is larger than that of LFMPb, indicating that the introduction of graphene increases the conductivity of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ sample. Moreover, it's worth noting that the spectra of LFMPa presents a low-intensity band at $\sim 950 \text{ cm}^{-1}$ belonging to the PO_4 stretching vibration [40], which is absent in the spectra of LFMPb. This result indicates that LFMPb are completely coated and hardly detected by Raman spectroscopy due to the encapsulation effect of graphene.

3.2 Possible formation mechanism of graphene encapsulated spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates

According to the above results, it is indeed found that spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates without/with graphene encapsulation are synthesized through the same preparation process in the absence or in the presence of GO, respectively.

In order to investigate the formation process of graphene encapsulated spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates, the morphology and structural information of representative products at different stages are characterized as shown in Fig. S3†. According to the evolution from precursor to $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates, we can conclude that $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates are synthesized from $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ precipitation under the orientation function of EG during hydrothermal reaction. In the course of thermostatic reaction, the self-assembly of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates and the encapsulation of GO are accomplished, resulting in a superior architecture of graphene encapsulated spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates, which is extremely benefitted for the electrochemical performance.

On the basis of the analysis above, the possible formation mechanisms of spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates without/with graphene encapsulation are proposed as follow: (1) the precipitation in the precursor suspension dissolves and re-crystallizes to form the nuclei of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoparticles during the early stage. (2) During the later stage of hydrothermal process, the long chain $(\text{EG})_n$ molecules adsorbed on the (010) face of preformed nanoplates facilitate the orientation of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates. (3) During the thermostatic reaction, the $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates start to assemble microspherical aggregations due to the effect of surface tension and electrostatic force. (4) At the same time, two different processes generate when GO is absent or present. In the absence of GO, the spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates further grow to form quasi-spherical aggregations by Ostwald ripening, which makes small crystals dissolve and large crystals grow. But, in the presence of GO, spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates are encapsulated by GO, which inhibits further growth of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates by Ostwald ripening. (5) Lastly, after further crystallizing and carbon coating of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples under high temperature, the spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates without/with graphene encapsulation are acquired. The formation mechanisms of spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates without/with graphene encapsulation are schematically shown in Fig. 4.

As shown in Fig. 5a, it's obvious that the graphene encapsulated superior architecture has an inner carbon layer on the surface of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates and an outer 3D graphene layer around the microspherical aggregation. According to our hypothesis, amylopectin is likely to form a thin, tightly attached and uniform film on $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ surface due to the adsorption of H- bond, resulting in a well-organized carbon layer on the surface of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates. Moreover, amylose play a key role on the encapsulation of graphene, because amylose is likely to bridge GO based on the dehydration/condensation reaction, helping GO to form 3D

continuous conductive network around the microspherical aggregation after heat treating. The bridging mechanism of graphene nanosheets is schematic in Fig. 5b.

3.3 electrochemical properties

The evaluation of electrochemical properties of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples is performed in a $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4 \parallel \text{LiPF}_6$ (EC, DEC, DMC) $\parallel \text{Li}$ cell. The Fig. 6a and Fig. 6b respectively present the charge-discharge profiles of LFMPa and LFMPb at different rate from 0.1 C to 20 C rate in the voltage range of 2.5-4.5 V vs. Li/Li^+ . For both LFMPa and LFMPb, the discharge curves at 0.1 C exhibit two perfect plateau voltages of 3.42 and 3.92 V vs. Li/Li^+ , corresponding to the redox plateau potentials of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$. The spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates without graphene encapsulation exhibit a reversible special capacity of $164.8 \text{ mA h g}^{-1}$ at 0.1 C which is sharply down to 17 mA h g^{-1} at 20 C. By contrast, the graphene encapsulated spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates exhibit a reversible special capacity of $164.9 \text{ mA h g}^{-1}$ at 0.1 C which remains up to $107.7 \text{ mA h g}^{-1}$ at 20 C. As shown in Fig. 6c, LFMPb shows a similar lithium storage performance at 0.1 C, but exhibit a high special capacity at elevated rate (0.5~20 C) compared with LFMPa. Furthermore, the difference of capacity retention between LFMPb and LFMPa (see inset in Fig. 6c) is getting larger with the rise of charge-discharge rate. Obviously, LFMPb shows more excellent rate capability than LFMPa. Fig. 6d shows that the capacity retention of LFMPb remains 94.6% after 500 cycles at 1 C rate, which is much higher than that of LFMPa. The inset in Fig. 6d exhibits an apparent difference between the specific capacities of LFMPa and LFMPb. The specific capacities at different C-rate and capacity retention after 500 cycles for LFMPa and LFMPb are list in Table S2†. The charge-discharge curves of LFMPa and LFMPb at different cycles are also employed to demonstrate their cyclability. As shown in Fig. 6e and Fig. 6f, the profile of charge-discharge curves at different cycles is consistent for both LFMPa and LFMPb. However, we can see that the charging plateau rises and the discharging plateau declines with the increasing cycles, probably resulting from the increasing impedance during cycles. With a close observation, the plateau voltages of charging and

discharging for $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox is clearly revealed in the insets of Fig. 6e and Fig. 6f. As we can see, the plateau voltage differences of LFMPb is smaller than those of LFMPa at different cycles, resulting in a remarkable cyclability of LFMPb. The detailed values of plateau voltage differences is clearly shown in Fig. S4†. The excellent high-rate capability and remarkable cyclability of LFMPb are mainly attributed to synergistic strategies of crystal orientation growth, microspherical self-assembly and graphene encapsulation.

In order to understand the synergistic strategies leading to the superior rate capability of LFMPb, CV measurements are carried out to evaluate the electrochemical activity of the two $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples. Fig. 7 shows the CV profiles of the LFMPa and LFMPb at a scan rate of 0.1 mV s^{-1} . The CV curves show two distinct redox peaks with midpoint potentials of 3.42 and 3.92 V, which are consistent with the two-plateau charging-discharging profiles at 0.1-5 C (see Fig. 7a and Fig. 7b), respectively. The first anodic and cathodic peaks are attributed to the redox of $\text{LiFePO}_4/\text{FePO}_4$, and the second anodic and cathodic peaks are attributed to the redox of $\text{LiMnPO}_4/\text{MnPO}_4$. Compared with LFMPa, LFMPb shows strong and narrow redox peaks. LFMPb exhibits higher peak currents (i_p) than LFMPa, indicates that the LFMPb possesses higher activities of oxidation reduction than LFMPa. Furthermore, the decrease of potential shifts (V_{ps}) away from midpoint potentials from LFMPa to LFMPb indicates that the polarizations of cathode electrodes from LFMPa to LFMPb are decreased. All these results demonstrate the kinetics of LFMPb are enhanced compared with LFMPa, which is attributed to fast Li-ion diffusion of plate-like $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ with preferred (010) facet and superior electronic conductivity of 3D continuous networks with graphene and carbon. The values of i_p and V_p of oxidation peaks in CVs are listed in Table S3†.

The EIS measurements are carried out to further study the kinetics of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ samples. Fig. 8a shows the Nyquist plots of LFMPa and LFMPb electrodes with lithium content of 50% after a cycle. The Nyquist plots show basically similar characteristics, including a semicircle in high-to-medium frequency region and straight lines in low frequency region. In order to interpret the impedance spectrum, an

equivalent circuit is present in Fig. 8b. In the equivalent circuit, R_s represents bulk resistance of the cell, reflecting the overall ohmic resistance of the electrolyte and electrodes; R_{ct} and CPE respectively represent the charge transfer resistance and constant phase element, corresponding to the semicircle at high-to-medium frequencies; The straight line in the low frequency region indicates the Warburg impedance Z_w , which is related to Li-ions diffusion in the electrodes. By comparing the diameters of the semicircles in high-to-medium frequency region, it is found that the impedance of LFMPb electrode is smaller than that of LFMPa, resulting in an improvement of electronic conductivity of LFMPb electrode owing to the thin, tightly attached, and continuous 3D conductive network by hybrid coating of carbon and graphene.

In order to better understand the factors leading to the superior cyclability of LFMPb electrode, further EIS tests are performed after different cycles of 100, 200 and 400 cycles (see Fig. 8b). Obviously, the new semicircle appeared at the high frequency indicates the solid-electrolyte interphase impedance (R_{sei}) and constant phase element (CPE1), attributed to the newly formed solid electrolyte interface film after long cycled. The corresponding equivalent circuit is shown in Fig. 8d. According to the fitting results listed in Table S4[†], we can see that R_{sei} and R_{ct} of LFMPb electrode are 38.6 and 30.8 Ω , respectively, which are much smaller than those of LFMPa at 100 cycles. Furthermore, the R_{sei} and R_{ct} of LFMPb increase only a little (3.2 and 5.7 Ω after 200 cycles, 8.0 and 11.1 Ω after 400 cycles, respectively) with the increase of cycle number, while those of the LFMPa raise largely (17.3 and 25.9 Ω after 200 cycles, 37.4 and 64.9 Ω after 400 cycles, respectively). The small R_{sei} indicates slowly growth of SEI film owing to graphene encapsulation of LFMPb, reducing the contact between $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ crystal and electrolyte. It's reported that well-organized carbon layers can effectively inhibit the dissolution of manganese, resulting in a good cyclability. Table 2 gives the ICP-AES results of manganese dissolution in the electrolyte for the two samples after long cycled. The manganese contents in the electrolyte of LFMPa are 45.2, 73.5 and 128.6 ppm after cycling for 100, 200 and 400 cycles, respectively, which are much more than those of LFMPb. Therefore, the

superior cycling performance of LFMPb is owed to the completely and uniformly coated carbon layers and well-organized graphene encapsulation. The small R_{ct} proves that hybrid carbon coating enhances the electronic conductivity of LFMPb, which is consistent with measurement results of four probe conductivity meter. The electronic conductivities of LFMPa and LFMPb are 1.6×10^{-1} and $3.4 \times 10^{-3} \text{ S cm}^{-1}$, separately.

These remarkable properties of graphene encapsulated microspherical assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates, such as superior specific capacity, high rate capability, and excellent cyclability should be attributed to the following factors: (i) the smaller thickness in [010] direction for $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates would effectively reduce the path length of Li^+ ion diffusion and electronic conduction, (ii) the larger (010) surface of spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates would effectively increase reaction rate of Li^+ insertion/extraction, (iii) the completely and uniformly coated carbon layers and stable 3D conducting network constructed by amorphous carbon and graphene can provide continuous electronic transport paths, (iv) the encapsulation of graphene can stabilize the microspherical aggregations and inhibit the dissolution of manganese, and (v) the hierarchical architecture of microspherical aggregations consisted of $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates could possess low interfacial energy, high reactivity, high special capacity and better fluidity characteristics.

4. Conclusion

Graphene encapsulated spherical hierarchical superstructures assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates are synthesized via synergistic strategies of crystal orientation growth, microspherical self-assembly and graphene encapsulation for the first time, which provide a fascinating approach to obtain superior olivine-type cathode materials with excellent rate capability and cycling stability. Compared with spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates without graphene encapsulation, the graphene encapsulated spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates possess short diffusion distance, high (010) surface, well-organized carbon coating and excellent stability, resulting in an excellent high-rate capability and cyclability. The graphene encapsulated

spherical hierarchical superstructures self-assembled by $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ nanoplates deliver a high specific capacity of $107.7 \text{ mA h g}^{-1}$ at 20 °C and superior capacity retention of 94.6% after 500 cycles, which make it have great applied value for high performance Li-ion batteries. Moreover, the synergistic strategies of crystal orientation growth, microspherical self-assembly and graphene encapsulation provide a fascinating approach to obtain advanced olivine-type cathode materials for power batteries used in HEVs or EVs.

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References

- [1] J.-M. Tarascon, M. Armand, *Nature*, 414 (2001) 359-367.
- [2] M. Armand, J.-M. Tarascon, *Nature*, 451 (2008) 652-657.
- [3] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energ Environ Sci*, 4 (2011) 3243-3262.
- [4] Y.G. Wang, P. He, H.S. Zhou, *Energ Environ Sci*, 4 (2011) 805-817.
- [5] K. Zaghib, A. Guerfi, P. Hovington, A. Vijh, M. Trudeau, A. Mauger, J.B. Goodenough, C.M. Julien, *J Power Sources*, 232 (2013) 357-369.
- [6] V. Aravindan, J. Gnanaraj, Y.S. Lee, S. Madhavi, *J Mater Chem A*, 1 (2013) 3518-3539.
- [7] K. Zaghib, M. Trudeau, A. Guerfi, J. Trottier, A. Mauger, R. Veillette, C.M. Julien, *J Power Sources*, 204 (2012) 177-181.
- [8] Y. Wan, Q.J. Zheng, D.M. Lin, *Acta Chim Sinica*, 72 (2014) 537-551.
- [9] J. Sugiyama, H. Nozaki, M. Harada, K. Kamazawa, Y. Ikeda, Y. Miyake, O. Ofer, M. Mansson, E.J. Ansaldi, K.H. Chow, G. Kobayashi, R. Kanno, *Phys Rev B*, 85 (2012).
- [10] X.H. Yang, Y.Y. Mi, W.D. Zhang, B.R. Wu, H.H. Zhou, *J Power Sources*, 275 (2015) 823-830.
- [11] R. Hanafusa, Y. Oka, T. Nakamura, *J Electrochem Soc*, 162 (2015) A3045-A3051.
- [12] L.J. Hu, B. Qiu, Y.G. Xia, Z.H. Qin, L.F. Qin, X.F. Zhou, Z.P. Liu, *J Power Sources*, 248 (2014) 246-252.
- [13] S. Liu, H.S. Fang, B. Yang, Y.C. Yao, W.H. Ma, Y.N. Dai, *J Power Sources*, 230 (2013) 267-270.
- [14] Z. Yang, G.S. Cao, J. Xie, X.B. Zhao, *J Solid State Electr*, 16 (2012) 1271-1277.
- [15] D.Z. Chen, W. Wei, R.N. Wang, X.F. Lang, Y. Tian, L. Guo, *Dalton T*, 41 (2012) 8822-8828.
- [16] H. Yi, C. Hu, X. He, H. Xu, *Ionics*, 21 (2015) 667-671.
- [17] R.G. Mei, X.R. Song, Y.F. Yang, Z.G. An, J.J. Zhang, *Rsc Adv*, 4 (2014) 5746-5752.
- [18] A. Paoletta, G. Bertoni, E. Dilella, S. Marras, A. Ansaldi, L. Manna, C. George, *Nano letters*, 14 (2014) 1477-1483.
- [19] K. Saravanan, V. Ramar, P. Balaya, J.J. Vittal, *J Mater Chem*, 21 (2011) 14925-14935.
- [20] J. Su, X.-L. Wu, C.-P. Yang, J.-S. Lee, J. Kim, Y.-G. Guo, *The Journal of Physical Chemistry C*, 116 (2012) 5019-5024.

- [21] F. Yu, S. Ge, B. Li, G. Sun, R. Mei, L. Zheng, *Current Inorganic Chemistry*, 2 (2012) 194-212.
- [22] D.W. Xu, X.D. Chu, Y.B. He, Z.J. Ding, B.H. Li, W.J. Han, H.D. Du, F.Y. Kang, *Electrochim Acta*, 152 (2015) 398-407.
- [23] Y.Y. Mi, P. Gao, W. Liu, W.D. Zhang, H.H. Zhou, *J Power Sources*, 267 (2014) 459-468.
- [24] S. Tao, W.F. Huang, G.X. Wu, X.B. Zhu, X.B. Wang, M. Zhang, S.H. Wang, W.S. Chu, L. Song, Z.Y. Wu, *Electrochim Acta*, 144 (2014) 406-411.
- [25] Q. Xia, T. Liu, J. Xu, X. Cheng, W. Lu, X. Wu, *J Mater Chem A*, 3 (2015) 6301-6305.
- [26] L. Bao, G. Xu, H. Zeng, L. Li, R. Zhao, G. Shen, G. Han, S. Zhou, *Crystengcomm*, 18 (2016) 2385-2391.
- [27] X. Zhou, Y. Deng, L. Wan, X. Qin, G. Chen, *J Power Sources*, 265 (2014) 223-230.
- [28] R. Cheruku, S. Bhaskaram, G. Govindaraj, L. Vijayan, in: *SOLID STATE PHYSICS: Proceedings of the 59th DAE Solid State Physics Symposium 2014*, AIP Publishing, 2015, pp. 050136.
- [29] J. Duan, G. Hu, Y. Cao, K. Du, Z. Peng, *Ionics*, (2016) 1-9.
- [30] X.F. Zhou, F. Wang, Y.M. Zhu, Z.P. Liu, *J Mater Chem*, 21 (2011) 3353-3358.
- [31] X. Zhou, Y. Xie, Y.F. Deng, X.S. Qin, G.H. Chen, *J Mater Chem A*, 3 (2015) 996-1004.
- [32] W.F. Huang, S. Tao, J. Zhou, C. Si, X. Chen, W. Huang, C.H. Jin, W.S. Chu, L. Song, Z.Y. Wu, *J Phys Chem C*, 118 (2014) 796-803.
- [33] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, *ACS nano*, 4 (2010) 4806-4814.
- [34] X. Ma, J. Yu, N. Wang, *Macromol Mater Eng*, 292 (2007) 723-728.
- [35] J. Fang, P. Fowler, J. Tomkinson, C. Hill, *Carbohydrate polymers*, 47 (2002) 245-252.
- [36] T. Szabó, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanakis, D. Petridis, I. Dékány, *Chemistry of Materials*, 18 (2006) 2740-2749.
- [37] G. Wang, B. Wang, J. Park, J. Yang, X. Shen, J. Yao, *Carbon*, 47 (2009) 68-72.
- [38] V. Chandra, J. Park, Y. Chun, J.W. Lee, I.-C. Hwang, K.S. Kim, *Acs Nano*, 4 (2010) 3979-3986.
- [39] J. Ha, S.-K. Park, S.-H. Yu, A. Jin, B. Jang, S. Bong, Y.-E. Sung, Y. Piao, *Nanoscale*, 5 (2013) 8647-8655.
- [40] M. Bousa, O. Frank, L. Kavan, *Electroanalysis*, 26 (2014) 57-61.