Graphical Abstract for:

Mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ nanopowders with excellent high rate and low temperature performances for lithium-ion batteries

Bang-Kun Zou^a, He-Yang Wang^a, Zi-Yue Qiang^a, Yu Shao^a, Xin Sun^a, Zhao-Yin Wen^b, Chun-Hua Chen^{a,*}

- a. CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Anhui Hefei 230026, China*
- b. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*

Ascorbic acid acts as both an antioxidant and a surfactant to form organic groups (first carbon source) on the surface of as-solvothermal products, in which the -OH (or H_2O) groups of glucose (second carbon source) are closely bonded to the surface to form a uniform adsorption layer. Uniform mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ nanopowders are formed after calcination, which demonstrate excellent electrochemical performances.

1 **Mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ nanopowders with excellent high rate and**
2
3 **low temperature performances for lithium-ion batteries**
4
5

6 Bang-Kun Zou^a, He-Yang Wang^a, Zi-Yue Qiang^a, Yu Shao^a, Xin Sun^a, Zhao-Yin Wen^b, Chun-Hua
7

8
9 Chen^{a,*}
10

- 11
12
13
14 *a. CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science*
15
16 *and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology,*
17
18 *University of Science and Technology of China, Anhui Hefei 230026, China*
19
20
21
22 *b. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
23
24
25
26
27

28 **Abstract**
29
30

31 A novel solvothermal approach with ascorbic acid as both an antioxidant and a
32
33 first-time carbon coating source is developed to synthesize $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$
34
35 nano-particles with a uniform particle size distribution around 150 nm. A calcination
36
37 step for the second-time carbon coating and further crystallization is adopted
38
39 following the solvothermal step. The structures and electrochemical properties of the
40
41 obtained samples are studied by X-ray diffraction, scanning electron microscopy,
42
43 transmission electron microscopy, Raman spectroscopy, Fourier transformation
44
45 infrared, Infrared carbon-sulfur analyzer and galvanostatic cell cycling. Ascorbic acid
46
47 plays a crucial role in the formation of uniform carbon layer and nano-particles.
48
49 Compared with single-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ without adding ascorbic acid,
50
51
52
53
54
55
56
57
58
59

60
61 Corresponding authors: E-mail: chchen@ustc.edu.cn; Phone: +86-551-63606971; Fax: (+86)551-63601592.
62

1 the mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ shows much better electrochemical
2
3 performance. It can deliver specific capacities of 154.8 and 128.5 mAh g^{-1} at 1C and
4
5
6 20C, respectively, at 25°C. Even at -20°C, its specific capacities are 106.6 and 68.8
7
8
9 mAh g^{-1} at 0.2C and 5C, respectively.

10
11 **Keywords:** lithium manganese iron phosphate; ascorbic acid; mixed carbon coating;
12
13
14 lithium ion batteries; electrochemical performance.
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1. Introduction

Olivine-structured LiMPO_4 ($\text{M}=\text{Fe}, \text{Mn}$) as one of the representative cathode materials for lithium-ion batteries (LIBs) are widely investigated after J. B. Goodenough and co-workers first reported in 1997 [1-5]. With the substitution of Fe^{2+} in LiFePO_4 by Mn^{2+} , 20% higher energy density can be achieved for LiMnPO_4 due to the higher $\text{Mn}^{2+}/\text{Mn}^{3+}$ voltage plateau (4.0 V vs. Li/Li^+) than $\text{Fe}^{2+}/\text{Fe}^{3+}$ voltage plateau (3.4 V vs. Li/Li^+) [6, 7]. Since the common organic electrolyte systems are electrochemically very stable at this 4.0 V voltage, LiMnPO_4 is considered as the next generation cathode material for LIBs [8]. Unfortunately, researches have shown that LiMnPO_4 not only suffers from the intrinsic lower electronic conductivities ($10^{-10} \text{ S cm}^{-1}$) and lithium ion diffusion coefficient ($<10^{-9} \text{ cm}^2 \text{ s}^{-1}$) than LiFePO_4 ($10^{-9} \text{ S cm}^{-1}$ and $10^{-8} \text{ cm}^2 \text{ s}^{-1}$) [9-12], but also degrades fast due to Jahn-Teller effect between LiMnPO_4 and MnPO_4 in the charge-discharge process [6, 13]. In response to these limitations of LiMnPO_4 , researchers have found that making nano-particles and partial substitution of Mn^{2+} by other transition metal ions (such as Fe, Ni, Mg and so on) [14-19] are helpful for improving the electrochemical activity. Lu et al. [15] have synthesized $\text{LiMg}_{0.05}\text{Mn}_{0.95}\text{PO}_4$ nanofiber through an electrospinning method, good electrochemical performance can be achieved (107 mAh g^{-1} at 5C). Nano-sized carbon and grapheme nanoplates are also used to improve the electronic conductivity and thus the rate performance of the carbon-coated LiMnPO_4 [9, 20-22]. Dong et al. [23] have reported Li_3VO_4 -coated LiMnPO_4 can have a relatively stable capacity and a moderate rate performance (71.2 mAh g^{-1} at 2C). However, compared with those of

commercial LiFePO_4 materials, these electrochemical performances of LiMnPO_4 are far from real applications [24].

Recently, $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ (LMFP) ($0 < x < 1$) has attracted wide attention because the partial substitution of Mn^{2+} by Fe^{2+} does not decrease the specific capacity compared with $\text{LiMn}_{1-x}\text{M}_x\text{PO}_4$ ($0 < x < 1$, $\text{M} = \text{Mg}$, Ti and Cu) [25-30]. For example, a carbon nanotube-loaded $\text{LiFe}_{0.6}\text{Mn}_{0.4}\text{PO}_4/\text{C}$ synthesized by a spray drying method shows excellent rate performance (114.4 mAh g^{-1} at 20°C) [31]. Currently, co-precipitation and hydrothermal process are the mainstream synthetic methods for LMFP. Nevertheless, a co-precipitation process usually results in particle size in the order of microns, which is not beneficial to rate performance of LMFP. For a hydrothermal/solvothermal process to prepare LMFP, factors such as the choice of solvent, pH value and even the adding sequence of the reactants have a great influence for the morphology of the product [22, 32, 33]. Even ascorbic acid, PEG, CTAB etc. are often used as the additives or carbon sources in the synthesis of olivine-type materials, the functional mechanism of the additive is often ignored in the hydrothermal process [34]. Simultaneously, carbon coating layer is also one of the principal factors to influence the electrochemical performance. Basically, the uniform carbon coating is hardly to be achieved from the simply mixed nano-LMFP with organic matters except for the high amount of the organics [21, 26, 34-40], the residual high amount carbon after carbonization is electrochemical inert, which can reduce the specific capacity of active materials.

In this work, the uniform carbon coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ with less than 2 wt% carbon content is synthesized by a two-step carbon coating method. Firstly, a well-designed solvothermal method is adopted to synthesize $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ with a mixed solvent of deionized water and ethylene glycol. The ethylene glycol works as the main solvent while the deionized water can increase the solubility of the reactants. Simultaneously, ascorbic acid is adopted as an antioxidant, which can prevent the low-valence metal ions (Fe^{2+} and Mn^{2+}) from the oxidation. Uniform LMFP particles around 150 nm with adsorbed organic groups ($\text{C}=\text{C}$, $-\text{CH}_x$, $-\text{OH}$) can be obtained under the synergy of the mixed solvent and ascorbic acid. After mixing with an appropriate amount of glucose, a uniform adsorption layer can be formed due to the adsorbed organic compound can act as a sort of surfactant and closely bond to the $-\text{OH}$ (or H_2O) groups of glucose, ascorbic acid and glucose act as the first and second carbon sources after a post-heat treatment, the obtained mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ sample shows improved electrochemical performance than the single-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ without adding ascorbic acid. For example, the mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ sample owns a specific capacity of 127.9 mAh g^{-1} at 20C at 25°C and 68.8 mAh g^{-1} at 5C at -20°C.

2. Experimental

2.1 Synthesis of Materials

$\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ nanoparticles were synthesized by a novel solvothermal method. Firstly, 6 mmol LiOH was dissolved in the mixture solvent of 10 mL deionized water

1 and 25 mL ethylene glycol to obtain solution A. 2.2 mmol H_3PO_4 was added in 10 mL
2
3 ethylene glycol to obtain solution B. 0.4 g ascorbic acid was dissolved in the mixture
4
5 solvent of 5 mL deionized water and 30 mL ethylene glycol, followed by adding 0.8
6
7
8 mmol $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 1.2 mmol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to obtain solution C. Then, solution
9
10
11 B was added into solution A under vigorous magnetic stirring to obtain a milky white
12
13 suspension D. Subsequently, solution C was added dropwise into suspension D under
14
15 stirring to obtain a precursor suspension E. Finally, the suspension E was transferred
16
17
18 into a 100 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was put
19
20
21 into an electric oven and kept at 180°C for 10 h. The solvothermal precursor
22
23
24 $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ (named as “DP-LMFP”) was collected by centrifuging and washing
25
26
27 for several times with deionized water and absolute alcohol.
28
29
30

31 The solvothermal product was mixed with glucose (0 wt% and 8 wt% of the
32
33 solvothermal products) in the mortar with some deionized water and ethyl alcohol as
34
35 the dispersants until they were dried, and then, the mixtures were calcined in a tube
36
37 furnace at 350°C for 2 h and 650°C for 8 h under Ar/H_2 (5 vol% H_2) atmosphere to
38
39 obtain the mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ samples (named as “D0-LMFP” for
40
41
42 0 wt% glucose and “D8-LMFP” for 8 wt% glucose).
43
44
45
46

47 In order to study the effect of ascorbic acid, another $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ sample was
48
49 synthesized using the same solvothermal process without adding ascorbic acid. Here
50
51
52 we assign “SP-LMFP” for the as-solvothermal product, the solvothermal product was
53
54
55 then calcined in the tube furnace at 350°C for 2 h and 650°C for 8 h under Ar/H_2 (5
56
57
58
59
60
61
62
63
64
65

1 vol% H₂) atmosphere to obtain single-carbon-coated LiMn_{0.4}Fe_{0.6}PO₄ samples (named
2
3 as “S0-LMFP” for 0 wt% glucose and “S8-LMFP” for 8 wt% glucose).
4
5
6
7

8 9 2.2 Characterization of Materials

10
11 The crystal structure of the samples was characterized using powder X-ray power
12 diffraction (XRD, Rigaku TTR-III, CuK α radiation) over a range of 2 θ angles from
13
14 10° to 70°. Raman spectra (Renishaw inVia Raman Microscope) were recorded on the
15
16
17 condition of 532 nm diode laser excitation. Their morphologies were analyzed by
18
19
20 scanning electron microscopy (SEM, JSM-6390 LA, JEOL) and (high resolution)
21
22
23 transmission electron microscopy (TEM, HRTEM, JEM-2010). The carbon content
24
25
26 was measured by Infrared Carbon-sulfur analyzer (CS-8800C, Jinbo). Fourier
27
28
29 transformation infrared (FTIR, Magna-IR 750 spectrometer) spectroscopy was also
30
31
32 conducted in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹.
33
34
35
36
37
38

39 2.3 Electrochemical Measurements

40
41 The electrochemical performances of the LMFP products were evaluated using
42
43 CR2032-type coin-cells, which were assembled in an argon filled glove box (MBraun
44
45 Labmaster 130). The working electrodes were made by casting a slurry of 80 wt%
46
47
48 active materials, 10 wt% carbon black and 10 wt% polyvinylidene fluoride binder
49
50
51 dispersed in N-methyl-2-pyrrolidone onto an aluminum foil. A lithium foil acted as
52
53
54 the counter electrode, and Celgard 2400 polypropylene membrane acted as a porous
55
56
57 separator. The loading density of active materials was about 2 mg cm⁻². The
58
59
60
61
62
63
64
65

electrolyte was 1 M LiPF_6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v, Zhuhai Smoothway Electronics Materials Co. Ltd). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the cells were employed on a CHI 660B electrochemical workstation. The cells were also galvanostatically cycled on a multi-channel battery test system (Neware BTS-2300, Shenzhen) at both room temperature ($25\pm 2^\circ\text{C}$) and low temperature (-12°C and -20°C).

3. Results and discussion

3.1 Structures and Morphologies

The XRD patterns of the LMFP samples are shown in **Fig. 1**. All of the diffraction peaks can be indexed into a well-crystalline olivine-type structure of LiFePO_4 (PDF #40-1499) without any impurity phase except for the diffraction peaks shift to smaller angles, suggesting the lattice contraction caused by the larger ionic radius of Mn^{2+} (80 pm) than Fe^{2+} (76 pm). It should be noted that the as-solvothermal samples are found to be well-crystallized olivine LMFP already (**Fig. 1a-b**). The purpose of the subsequent heat treatment is to carbonize the ascorbic acid and glucose. Yet the diffraction peaks of carbon cannot be detected probably due to the amorphous nature or small amount (**Fig. 1c-d**).

Fig. 2 shows the morphologies of the S8- and D8- LMFP samples. From the SEM and TEM images, it can be seen that the particles of the obtained S8-LMFP become larger and aggregate more together (**Fig. 2a-b**) compared with D8-LMFP (**Fig. 2e-f**) if

ascorbic acid is not added in the solvothermal process. The shape of D8-LMFP particles look like nanorods with a diameter of 30-50 nm and a length of 100-150 nm. Obviously, D8-LMFP sample is composed of homogeneous particles with a narrow size distribution. Therefore, ascorbic acid not only prevents the oxidation of the metal ions, but also reduces the particle size and improves the dispersion. In order to get the in-sight understanding of the synthesis process, more careful investigations are performed. Apparently, TEM and HRTEM analyses also provide clear evidence for the carbon coatings. For S8-LMFP, a non-uniform carbon coating can be seen on the LMFP particles (**Fig. 2d**). The carbon thickness varies from 1 to 4 nm, while some free carbon can be detected (**Fig. 2c**). To the contrast, uniform carbon coating is achieved on D8-LMFP sample with 2 nm thickness of the carbon coating layer (**Fig. 2g and 2h**). No lattice fringes can be seen for these carbon coatings due to the amorphous phase. Hence, mixed carbon coating is necessary and the first carbon source ascorbic acid has a significant impact on the morphology of the particles and the quality of carbon coating.

3.2 Reaction Mechanisms

Fig. 3 shows the Raman spectra of LMFP samples at different stages of the synthetic process. The as-solvothermal samples SP- and DP- LMFP have only the strong peaks of PO_4^{3-} without any other characteristic peaks. After the heat treatment of as-solvothermal samples at 650°C without glucose, the obtained D0-LMFP has not only the peaks of PO_4^{3-} , but also the D and G bands of carbon, which is not appeared

1 in S0-LMFP sample. Thus, the surface of DP-LMFP particles must have adsorbed
2
3 some organic groups coming from the adding ascorbic acid, which can be carbonized
4
5 at high calcination temperature 650°C in D0-LMFP. The peaks of PO_4^{3-} become much
6
7
8 weaker when the second carbon source glucose is used in S8- and D8-LMFP due to
9
10 the formation of much thicker carbon coating layer.
11
12

13
14 FTIR spectra of ascorbic acid and LMFP samples at different stages of the synthetic
15
16 process are shown in **Fig.4**. For DP-LMFP, a broad signal at 3445 cm^{-1} can be
17
18 attributed to $-\text{OH}$ coming from possible crystal water or some organic compound on
19
20 the surface of as-solvothermal product. The signals at 2920 and 1643 cm^{-1} correspond
21
22 to the $-\text{CH}_x$ ($x=1, 2, 3$) and $\text{C}=\text{C}$ groups, respectively, which may simply come from
23
24 ascorbic acid, suggesting the adsorbed organic compound is ascorbic acid and its
25
26 derivatives. However, for SP-LMFP sample synthesized under similar solvothermal
27
28 conditions but without using ascorbic acid, FTIR signals of $-\text{CH}_x$ or $\text{C}=\text{C}$ groups
29
30 cannot be detected. After the 650°C heat treatment, the signals disappear in both
31
32 D0-LMFP and D8-LMFP due likely to the carbonization of organic compound. This is
33
34 consistent with the results of Raman analysis (**Fig. 3**).
35
36
37
38
39
40
41
42
43

44
45 **Fig. S1** shows the photos of the LMFP samples synthesized with and without
46
47 ascorbic acid at different stages of the synthetic process. The color of both the
48
49 as-solvothermal samples SP- and DP- LMFP are canary yellow (**Fig. S1a** and **S1d**).
50
51 After the 650°C heat treatment, the ascorbic acid derived samples D0- and D8- LMFP
52
53 are all darker black than their counterparts synthesized without ascorbic acid S0- and
54
55 S8-LMFP (**Fig. S1e** vs. **S1b**, **S1f** vs. **S1c**). Of course, the samples with a second-time
56
57
58
59
60
61
62
63
64
65

1 carbon coating with glucose, i.e. S8- and D8-LMFP, are also darker than the samples
2
3 without using glucose, i.e. S0- and D0-LMFP due to the effect of glucose
4
5 carbonization. The carbon content is only 1.82 wt% and 1.96 wt% for S8- and D8-
6
7 LMFP, respectively. The contribution carbon content of the adsorbed ascorbic acid
8
9 and its derivatives in D8-LMFP is about 0.07-0.10 wt% measured by Infrared
10
11 Carbon-sulfur analyzer. It is also noted that the tapping density of D8-LMFP is as
12
13 high as 1.2 g mL⁻¹.
14
15
16
17
18
19

20 Based on above analyses, a schematic mechanism of chemical reactions is proposed
21
22 for the formation of carbon coatings on LMFP nanoparticles (Fig. 5). Firstly, ascorbic
23
24 acid is a highly soluble antioxidant in a polar solvent (water and ethylene glycol here),
25
26 which can prevent the low-valence metal ions (Fe²⁺ and Mn²⁺) from being oxidized.
27
28 During the solvothermal process, organic groups (C=C, -CH_x, -OH) coming from
29
30 ascorbic acid and its derivatives are absorbed on the surface of LMFP precursor
31
32 nano-particles. When glucose is mixed with as-solvothermal powders, the adsorbed
33
34 organic compound can act as a sort of surfactant and closely bond to the -OH (or H₂O)
35
36 groups of glucose to form a uniform adsorption layer. During the heat treatment, this
37
38 layer can be carbonized to form a uniform carbon layer on the surface of LMFP
39
40 particles. Simultaneously, the adsorbed organic layer can also act as a physical
41
42 separation to prevent the growth and agglomeration of the nano-particles during the
43
44 solvothermal process and the high temperature treatment. However, if without
45
46 ascorbic acid, only few -OH groups coming from the crystal water are absorbed on
47
48 the surface of LMFP particles. Thus, subsequently, glucose is unevenly distributed on
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

the particle surface, leading to a non-uniform carbon coating layer and the agglomeration of the nano-particles.

3.3 Electrochemical Properties

Fig. 6 shows the CV curves and EIS results of S8- and D8-LMFP electrode vs. Li/Li^+ . It can be seen that the separate redox peaks are all very sharp and keep unchanged in the initial four cycles. A couple of redox peaks around 4.0 V correspond to the transformation of $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$, and the other redox peaks around 3.5 V correspond to $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$. Generally, the reaction $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ is kinetically more difficult than the reaction $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ so that the potential difference between the cathodic and anodic peaks of the former is usually greater than the latter. It is true for sample S8-LMFP where the voltage gaps between the $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ and $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ redox peaks are 150 mV and 130 mV (**Fig. 6a**), respectively. However, it decreases to both 100 mV for D8-LMFP (**Fig. 6b**). The result is also consistent with the EIS spectra (**Fig. 6c**) which can be fitted with an equivalent circuit (inset in **Fig. 6c**). The Nyquist plots give similar spectra consisting of a depressed semicircle in the medium-frequency region and a straight line in the low-frequency region [34]. The values of ohmic resistance (R_s) for S8- and D8- LMFP are both at 2-4 ohm, but the charge transfer resistance (R_{ct}) of D8-LMFP (69.0 ohm) is much smaller than S8-LMFP (149.4 ohm). Both the CV and EIS results demonstrate that the smaller particles size and more uniform carbon coating layer of D8-LMFP than S8-LMFP indeed provides more efficient electron/ion transport.

The results of galvanostatic cycling of S8- and D8- LMFP/Li half-cells at room temperature are shown in Fig. 7. The D8-LMFP shows the optimal rate capability than S8-LMFP (Fig. 7a). The specific discharge capacity of D8-LMFP is as high as 156.8, 155.8, 154.0, 150.5, 145.1, 140.1 and 128.5 mAh g⁻¹ at 0.5, 1, 2, 5, 10, 15 and 20C discharge current density (0.5C charge), respectively. However, the specific discharge capacity of S8-LMFP is 143.1, 141.3, 137.6, 133.1, 124.7, 117.6 and 109.2 mAh g⁻¹, respectively. The specific capacity and the capacity retention ratio of S8-LMFP are both worse compared with D8-LMFP (Fig. 7b). Obviously, non-uniform carbon coating layer (especially the thick carbon layer) in S8-LMFP seriously hinders the diffusion of lithium ions; on the other hand, the larger and aggregate particles increase the difficulty of reaction kinetics. The charge-discharge curves of D8-LMFP at different rates show two obvious plateaus during the discharge process even when the current increases from 0.1C to 5C (Fig. 7c). Two pairs of plateaus related to Mn²⁺/Mn³⁺ and Fe²⁺/Fe³⁺ redox couples at 4.0 V and 3.4 V, respectively, are clearly seen at low current density. The contribution ratio of the capacity from the two voltage plateaus is approximately equal to the Mn/Fe molar ratio in the D8-LMFP samples, which is also demonstrated by the CV curves. The cycling performance is shown in Fig. 7d at 1C rate, S8- and D8- LMFP can deliver a specific discharge capacity of 137.5 mAh g⁻¹, 154.5 mAh g⁻¹ at the 1st cycle, and retain 97.6% (134.2 mAh g⁻¹), 96.8% (149.6 mAh g⁻¹) after 130 cycles, respectively.

The initial coulombic efficiency of D8-LMFP is 93.7% at 0.1C, and the upcoming coulombic efficiency is all 99-100% (Fig. 7d). From Table 1, it should

be noted that such excellent cycling and rate performance of D8-LMFP with less carbon content (1.96 wt%) is superior to most reported data in the literature.

Another key challenge for the wide applications of lithium-ion batteries requires the electrode materials with desirable low temperature electrochemical performance. The cycling performance and the charge-discharge curves of samples D8-LMFP at -12 and -20°C are shown in **Fig. 8**. The sample D8-LMFP can deliver 122.0 mAh g⁻¹ with a discharge voltage as high as 3.486 V at 50% SOC at 0.2C and -12°C (**Fig. 8a-b**). It is worth noting that the discharge capacity is 106.6 mAh g⁻¹ at 0.2C and -20°C (**Fig. 8c-d**). Even at 5C rate, the specific capacity can still maintain at 68.8 mAh g⁻¹. When the temperature returns to 25°C from -20°C, the cell can recover its original capacity at room temperature. Such excellent electrochemical properties of D8-LMFP are even better than the commercial LiFePO₄, but also with much higher energy density.

CV scanning at various scan rates from 0.1 to 2.0 mV s⁻¹ was carried out to further explain the different electrochemical behaviors of S8- and D8- LMFP samples. From **Fig. 9a**, obvious redox peaks of D8-LMFP can be seen even for the highest sweeping rate of 2.0 mV s⁻¹, and the Mn²⁺ ↔ Mn³⁺ peaks is much stronger than that of S8-LMFP (**Fig. 9b**). It is also worth mentioning that some extra cathodic peaks (between 3.2 and 3.7 V) can be observed at high scan rates, which is consistent with the discharge curves shown in **Fig. 7c, 8b** and **8d**. This phenomenon is also observed by others groups [38, 43]. According to their study, the possible reason is that Li intercalation in MnPO₄ is initially incomplete due to its slow kinetics at high rates so that some

Mn³⁺-containing FePO₄ is formed. This Mn³⁺-containing FePO₄ can be intercalated with Li at about 3.6 V vs. Li/Li⁺ to form some intermediate LiFePO₄. Because MnPO₄/LiMnPO₄ has higher thermodynamic potential than LiFePO₄, the un-reacted MnPO₄ would simultaneously oxidize the intermediate LiFePO₄ in to FePO₄ while it becomes LiMnPO₄. As can be seen in Fig. 9c-d, the peak current (I_p) is proportional to the square root of the scan rate (v), which can be used to calculate the chemical diffusion coefficient of Li⁺ (D_{Li}) using the Randles–Sevcik equation (T=298 K):

$$I_p = (2.69 \times 10^5) n^{3/2} C_{Li} A v^{1/2} D_{Li}^{1/2}$$

where n is the number of electrons per reaction species, C_{Li} is the bulk concentration in moles per cubic centimeter (0.0228 mol cm⁻³), A is the surface area of the electrode (cm²), v is the potential scan rate (V s⁻¹) and D_{Li} is the diffusion coefficient (cm² s⁻¹). The calculated results for the two samples are listed in Table 2, which are between 10⁻¹⁰ and 10⁻¹² cm² s⁻¹, being similar to those reported literature [38, 41]. The results show that D8-LMFP possesses larger D_{Li} than S8-LMFP, especially at the peak of Mn²⁺ ⇌ Mn³⁺, indicating faster Li⁺ insertion/extraction reactions, which is consistent with the smaller R_{ct} obtained from the EIS result.

4. Conclusions

In summary, the LiMn_{0.4}Fe_{0.6}PO₄ nano-powders are synthesized through a novel solvothermal method by using mixed solvent and ascorbic acid as both antioxidant and the first carbon source. Under the synergy of mixed solvent and antioxidant ascorbic acid, the obtained sample has a uniform particle size distribution around 150 nm. After mixing with 8 wt% glucose as the second carbon source and a calcination

1 step at 650°C, the obtained mixed-carbon-coated $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ sample shows
2
3 excellent electrochemical performance at -20°C to 25°C. Such $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$
4
5 nano-powders are promising cathode materials for high performance lithium-ion
6
7
8
9 batteries.

10 11 12 13 14 **Acknowledgments**

15
16
17 This study was supported by National Science Foundation of China (grant no.
18
19 51577175), Hefei Center of Materials Science and Technology (2014FXZY006) and
20
21 Education Ministry of Anhui Province (KJ2014ZD36). We thanks for the help from,
22
23 Dr. Xin Liang and Mr. Fei Xia in the samples measurement. We are also grateful to
24
25
26
27
28 Elementec Ltd in Suzhou.
29
30
31
32

33 34 **References**

- 35
36 [1] M. Armand, J.M. Tarascon, Building better batteries, Nature 451 (2008) 652.
37
38 [2] A.S. Arico, P. Bruce, B.Scrosati, J.M. Tarascon, W.V. Schalkwijk,
39
40 Nanostructured materials for advanced energy conversion and storage devices,
41
42 Nat. Mater. 4 (2005) 366.
43
44
45 [3] C. Liu, F. Li, L.P. Ma, H.M. Cheng, Advanced materials for energy storage,
46
47 Adv. Mater. 22 (2010) E28.
48
49
50 [4] Y.G. Guo, J.S.Hu, L.J. Wan, Nanostructured Materials for Electrochemical
51
52
53
54
55
56 Energy Conversion and Storage Devices, Adv. Mater. 22 (2008) 2878.
57
58
59
60
61
62
63
64
65

- [5] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, Phospho-olivines as positive-electrode materials for rechargeable lithium batteries, *J. Electrochem. Soc.* 144 (1997) 1188.
- [6] L.X. Yuan, Z.H. Wang, W.X. Zhang, X.L. Hu, J.T. Chen, Y.H. Huang, J.B. Goodenough, Development and challenges of LiFePO_4 cathode material for lithium-ion batteries, *Energ. Environ. Sci.* 4 (2011) 269.
- [7] J. Li, L. Zhang, L.F. Zhang, W.W. Hao, H.B. Wang, Q.T. Qu, H.H. Zheng, In-situ growth of graphene decorations for high-performance LiFePO_4 cathode through solid-state reaction, *J. Power Sources* 249 (2014) 311.
- [8] V. Aravindan, J. Gnanaraj, Y.S. Lee, S. Madhavi, LiMnPO_4 - A next generation cathode material for lithium-ion batteries, *J. Mater. Chem. A* 1 (2013) 3518.
- [9] S.M. Oh, S.W. Oh, C.S. Yoon, B. Scrosati, K. Amine, Y.K. Sun, High-Performance Carbon- LiMnPO_4 Nanocomposite Cathode for Lithium Batteries, *Adv. Funct. Mater.* 20 (2010) 3260.
- [10] Y.R. Wang, Y.F. Yang, Y.B. Yang, H.X. Shao, Enhanced electrochemical performance of unique morphological LiMnPO_4/C cathode material prepared by solvothermal method, *Solid-State Commun.* 150 (2010) 81.
- [11] D. Morgan, A. Van der Ven, G. Ceder, Li conductivity in Li_xMPO_4 ($\text{M} = \text{Mn, Fe, Co, Ni}$) olivine materials, *Electrochem. Solid-State Lett.* 7 (2004) A30.
- [12] R. Amin, P. Balaya, J. Maier, Anisotropy of electronic and ionic transport in LiFePO_4 single crystals, *Electrochem. Solid-State Lett.* 10 (2007) A13.

- [13] E. Stura, C. Nicolini, New nanomaterials for light weight lithium batteries, *Anal. Chim. Acta* 568 (2006) 57.
- [14] T. Liu, B.B. Wu, X.D. Wu, Realizing Fe substitution through diffusion in preparing $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4\text{-C}$ cathode materials from $\text{MnPO}_4\cdot\text{H}_2\text{O}$, *Solid-State Ionics* 254 (2014) 72.
- [15] Q. Lu, G.S. Hutchings, Y. Zhou, H.L. Xin, H. Zheng, F. Jiao, Nanostructured flexible Mg-modified LiMnPO_4 matrix as high-rate cathode materials for Li-ion batteries, *J. Mater. Chem. A* 2 (2014) 6368.
- [16] L.F. Qin, Y.G. Xia, H.L. Cao, L.J. Luo, Q. Zhang, L.P. Chen, Z.P. Liu, Effects of Ti additive on the structure and electrochemical performance of LiMnPO_4 cathode material, *Electrochim. Acta* 123 (2014) 240.
- [17] X.L. Li, S. Liu, H.C. Jin, Y. Meng, Y.F. Liu, Ionothermal synthesis and electrochemical analysis of Fe doped LiMnPO_4/C composites as cathode materials for lithium-ion batteries, *J. Alloys and Compd.* 614 (2014) 7.
- [18] S. Wi, J. Kim, S. Nam, J. Kang, S. Lee, H. Woo, M. Lee, C. H. Sonu, T. Moon, B. Park, Enhanced rate capability of $\text{LiMn}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ nanoplates by reduced graphene oxide/carbon double coating for Li-ion batteries, *Curr. Appl. Phys.* 14 (2014) 725.
- [19] S. Akimoto, I. Taniguchi, Synthesis and characterization of $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3}\text{PO}_4/\text{C}$ nanocomposite cathode of lithium batteries with high rate performance, *J. Power Sources* 242 (2013) 627.

- [20] J.G. Duan, Y.B. Cao, J.B. Jiang, K. Du, Z.D. Peng, G.R. Hu, Novel efficient synthesis of nanosized carbon coated LiMnPO_4 composite for lithium ion batteries and its electrochemical performance, *J. Power Sources* 268 (2014) 146.
- [21] J. Zong, X.J. Liu, Graphene nanoplates structured LiMnPO_4/C composite for lithium-ion battery, *Electrochim. Acta* 116 (2014) 9.
- [22] M. Zhao, Y. Fu, N. Xu, G.R. Li, M.T. Wu, X.P. Gao, High performance LiMnPO_4/C prepared by a crystallite size control method, *J. Mater. Chem. A* 2 (2014) 15070.
- [23] Y.Z. Dong, Y.M. Zhao, H. Duan, Z.Y. Liang, Enhanced electrochemical performance of LiMnPO_4 by Li^+ -conductive Li_3VO_4 surface coatings, *Electrochim. Acta* 132 (2014) 244.
- [24] F.J. Chen, F. Tao, C.M. Wang, W.L. Zhang, L. Chen, The influence of improved carbon coating layer with nanometer-sized CeO_2 interconnector on the enhanced electrochemical performance of LiMnPO_4 , *J. Power Sources*, 285 (2015) 367.
- [25] Y. Hong, Z.L. Tang, Z.J. Hong, Z.T. Zhang, $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ ($x = 0, 0.1, 0.2$) nanorods synthesized by a facile solvothermal approach as high performance cathode materials for lithium-ion batteries, *J. Power Sources* 248 (2014) 655-659.
- [26] L.J. Hu, B. Qiu, Y.G. Xia, Z.H. Qin, L.F. Qin, X.F. Zhou, Z.P. Liu, Solvothermal synthesis of Fe-doping LiMnPO_4 nanomaterials for Li-ion batteries, *J. Power Sources* 248 (2014) 246.

- [27] W.F. Huang, S. Tao, J. Zhou, C. Si, X. Chen, W. Huang, C.H. Jin, W.S. Chu, L. Song, Z.Y. Wu, Phase Separations in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$: A Random Stack Model for Efficient Cathode Materials, *J. Phys. Chem. C* 118 (2014) 796.
- [28] M.S. Kim, J.P. Jegal, K.C. Roh, K.B. Kim, Synthesis of $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ microspheres using a microwave-assisted process with a complexing agent for high-rate lithium ion batteries, *J. Mater. Chem. A* 2 (2014) 10607.
- [29] W.C. Yang, Y.J. Bi, Y.P. Qin, Y. Liu, X.H. Zhang, B.C. Yang, Q. Wu, D.Y. Wang, S.Q. Shi, $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ cathode material synthesized via co-precipitation method with superior high-rate and low-temperature performances for lithium-ion batteries, *J. Power Sources* 275 (2015) 785.
- [30] S.M. Oh, S.T. Myung, J.B. Park, B. Scrosati, K. Amine, Y.K. Sun, Double-Structured $\text{LiMn}_{0.85}\text{Fe}_{0.15}\text{PO}_4$ Coordinated with LiFePO_4 for Rechargeable Lithium Batteries, *Angew. Chem. Int. Edit* 124 (2012) 1889.
- [31] Y.Y. Mi, P. Gao, W. Liu, W.D. Zhang, H.H. Zhou, Carbon nanotube-loaded mesoporous $\text{LiFe}_{0.6}\text{Mn}_{0.4}\text{PO}_4/\text{C}$ microspheres as high performance cathodes for lithium-ion batteries, *J. Power Sources* 267 (2014) 459.
- [32] L. Wang, X.M. He, W.T. Sun, J.L. Wang, Y.D. Li, S.S. Fan, Crystal Orientation Tuning of LiFePO_4 Nanoplates for High Rate Lithium Battery Cathode Materials, *Nano Lett.* 12 (2012) 5632.
- [33] M.K. Devaraju, I. Honma, Hydrothermal and Solvothermal Process Towards Development of LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}$) Nanomaterials for Lithium-Ion Batteries, *Adv. Energy Mater.* 2 (2012) 284.

- [34] P. Zuo, G. Cheng, L. Wang, Y. Ma, C. Du, X. Cheng, Z. Wang, G. Yin, Ascorbic acid-assisted solvothermal synthesis of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanoplatelets with enhanced electrochemical performance for lithium ion batteries, *J. Power Sources* 243 (2013) 872.
- [35] L.H. Liao, H.T. Wang, H. Guo, P.Y. Zhu, J. Xie, C.H. Jin, S.C. Zhang, G.S. Cao, T.J. Zhu, X.B. Zhao, Facile solvothermal synthesis of ultrathin $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ nanoplates as advanced cathodes with long cycle life and superior rate capability, *J. Mater. Chem. A* 3 (2015) 19368.
- [36] Y. Hong, Z.L. Tang, S.T. Wang, W. Quan, Z.T. Zhang, High-performance LiMnPO_4 nanorods synthesized via a facile EG-assisted solvothermal approach, *J. Mater. Chem. A* 3 (2015) 10267.
- [37] W. Liu, P. Gao, Y. Mi, J. Chen, H. Zhou, X. Zhang, Fabrication of high tap density $\text{LiFe}_{0.6}\text{Mn}_{0.4}\text{PO}_4/\text{C}$ microspheres by a double carbon coating–spray drying method for high rate lithium ion batteries, *J. Mater. Chem. A* 1 (2013) 2411.
- [38] X. Zhou, Y. Xie, Y.F. Deng, X.S. Qin, G.H. Chen, The enhanced rate performance of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ cathode material via synergistic strategies of surfactant-assisted solid state method and carbon coating, *J. Mater. Chem. A* 3 (2015) 996.
- [39] S.-Y. Yan, C.-Y. Wang, R.-M. Gu, M.-W. Li, Enhanced kinetic behaviors of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ cathode material by Fe substitution and carbon coating, *J. Solid State Electrochem.* 19 (2015) 2943.
- [40] W. Xiang, E.H. Wang, M.Z. Chen, H.H. Shen, S.L. Chou, H. Chen, X.D. Guo,

B.H. Zhong, X.L. Wang, Hierarchical structured $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ spheres synthesized by template-engaged reaction as cathodes for high power Li-ion batteries, *Electrochim. Acta* 178 (2015) 353.

[41] X. Yang, Y. Mi, W. Zhang, B. Wu, H. Zhou, Enhanced electrochemical performance of $\text{LiFe}_{0.6}\text{Mn}_{0.4}\text{PO}_4/\text{C}$ cathode material prepared by ferrocene-assisted calcination process, *J. Power Sources* 275 (2015) 823.

[42] H. Shen, W. Xiang, X. Shi, B. Zhong, H. Liu, Hierarchical $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ nanorods with excellent electrochemical performance synthesized by rheological phase method as cathode for lithium ion battery, *Ionics* 22 (2015) 193.

[43] K. Wang, M. Hou, S. Yuan, H. Yu, Y. Wang, C. Wang, Y. Xia, An additional discharge plateau of Mn^{3+} in $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ at high current rates, *Electrochem. Commun.* 55 (2015) 6.

Figure captions:

Fig. 1 XRD patterns of SP- (a), DP- (b), S8- (c), D8- (d) LMFP, respectively.

Fig. 2 SEM and (HR)TEM images of samples S8-LMFP (a-d), D8-LMFP (e-h).

Fig. 3 Raman spectra of LMFP samples at different stages of the synthetic process.

Fig. 4 FTIR spectra of ascorbic acid and LMFP samples at different stages of the synthetic process.

Fig. 5 Schematic illustration of the synthesis process and reaction mechanism.

Fig. 6 The cyclicvoltammetry (CV) curves of S8- (a) and D8-LMFP (b) electrodes at a scan rate of 0.1 mV s^{-1} , Electrochemical impedance spectra (EIS) of half cells Li/ S8- and D8-LMFP after 3

cycles at 0.1C rate (c).

Fig. 7 The electrochemical performance of S8- and D8- LMFP at 25°C.

Fig. 8 The electrochemical performance of D8-LMFP at -12°C and -20°C.

Fig. 9 CV curves at different scan rates of samples D8-LMFP (a) and S8-LMFP (b), the linear relationship of I_p vs. $v^{1/2}$ of D8-LMFP (c) and S8-LMFP (d).

Table 1 The comparison of electrochemical performance of the LMFPelectrodes between this work and previously reported ones.

LMFP electrodes	Carboncontent (wt%)	Cycling stability (mAh g ⁻¹)	Rate stability (mAh g ⁻¹)	Refs
LiMnPO ₄	25	130 @0.05C (93.5%, 40 cycles)	133 @0.1C 119 @1C	21
LiMn _{0.5} Fe _{0.5} PO ₄	2.7	147 @1C (≈100%, 100 cycles)	140 @1C 118 @5C	26
LiMn _{0.4} Fe _{0.6} PO ₄	3.5	145 @1C (98%, 200 cycles)	148.7 @1C 114.4 @10C	31
LiMn _{0.9} Fe _{0.1} PO ₄	10-12	51 @10C (75%, 100 cycles)	125 @0.5C 80 @5C	34
LiMn _{0.85} Fe _{0.15} PO ₄	9	118 @1C (75%, 500 cycles)	138.0 @5C 120.9 @20C	35
LiMnPO ₄	2.49	136.8 @0.5C (94.5%, 100 cycles)	138 @1C 110 @10C	36
LiMn _{0.4} Fe _{0.6} PO ₄	3	140 @2C (≈100%, 100 cycles)	138 @1C 106.3 @20C	37
LiMn _{0.5} Fe _{0.5} PO ₄	6.1	132 @1C (95%, 500 cycles)	140 @1C 120 @5C	38
LiMn _{0.5} Fe _{0.5} PO ₄	5.17	120 @1C (92.3%, 150 cycles)	130 @1C 105 @20C	39
LiMn _{0.5} Fe _{0.5} PO ₄	3.2	100 @1C (90.7%, 150 cycles)	116.0 @1C 81.5 @20C	40
LiMn _{0.4} Fe _{0.6} PO ₄	1.92	140 @3C	150.8 @1C	41

		(96%, 100 cycles, 60°C)	120.7 @20C	
		120 @1C	133 @1C	
	LiMn _{0.5} Fe _{0.5} PO ₄	1.99	(89.23%, 100 cycles)	78 @20C
				42
	LiMn _{0.4} Fe _{0.6} PO ₄	1.96	149.6 @1C	154.8 @1C
			(96.8%, 130 cycles)	128.5 @20C
				This work

Table 2 The Li⁺ diffusion coefficient (D_{Li}) of S8- and D8- LMFP samples.

LMFP electrodes	Anodic peaks	Diffusion coefficient (D _{Li} , cm ² s ⁻¹)
	Fe	7.59*10 ⁻¹⁰
D8-LMFP		
	Mn	8.75*10 ⁻¹¹
	Fe	6.62*10 ⁻¹⁰
S8-LMFP		
	Mn	1.80*10 ⁻¹¹

Figure 1

Figure 2

Figure 3

(a)

(b)

Figure 4

(a)

(b)

Figure 5

First carbon source

adhesion

calcination

nonuniform

Single-carbon-coating

uniform

Mixed-carbon-coating

calcination

adsorption

D-(+)- glucose

Second carbon source

Figure 6a

(a)

Figure 6b

(b)

Figure 6c

(c)

Figure 7

Figure 8

Figure 9