LiMPO₄ and derived NaMPO₄ (M= Mn, Fe, Mg) with excellent electrochemical properties for lithium/sodium ion batteries

Bang-Kun Zou, Yu Shao, Zi-Yue Qiang, Jia-Ying Liao, Zhong-Feng Tang, Chun-Hua
Chen^{*}

*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*

Abstract

A simple two-step solid-state-reaction process is adopted to synthesize carbon-coated Mg-doped Li(Mn,Fe)PO₄ (LMMFP) nano-particles. As positive electrode materials for lithium-ion batteries, the carbon-coated LMMFP samples show excellent electrochemical properties in a temperature range from -20 to 55°C. For example, LiMn_{0.48}Fe_{0.5}Mg_{0.02}PO₄ can deliver a capacity of 146.2 mAh g⁻¹ at 3C rate and retain 95.3% after 450 cycles at 25°C. It can also deliver 160.7 mAh g⁻¹ at 1C and retain 97.7% after 100 cycles at 55°C. Even at -20°C, it gives a capacity of 109.5 mAh g⁻¹ with an average discharge voltage of 3.37 V at 0.2C. In Na/LMMFP cells, the LMMFP electrodes can be electrochemically converted into Mg-doped Na(Mn,Fe)PO₄ (NMMFP) electrodes for sodium-ion batteries (SIBs). Ex-situ XRD

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

proves that the derived NMMFP have an olivine-type structure and can reversibly extract and insert sodium ions. For example, $\text{NaMn}_{0.48}\text{Fe}_{0.5}\text{Mg}_{0.02}\text{PO}_4$ can deliver a reversible specific capacity of 126.9 mAh g^{-1} after 30 cycles at 0.1C with an average discharge voltage of 3.1 V. This study opens up a new direction on exploring olivine-type SIB cathodes.

Keywords: solid state reaction; lithium manganese iron phosphate; sodium manganese iron phosphate; magnesium doping; high and low temperature electrochemical performance.

1. Introduction

Driven by the demands for high performance lithium-ion batteries (LIBs), the increases in the power density and energy density are key objectives in current battery researches. Remarkably, the use of nano-structured electrode materials has been very effective in elevating the power density owing to the shortened diffusion distance in the electrodes [1]. The nanosizing strategy is particularly successful in the poorly conducting yet highly safe phosphate cathode material LiFePO_4 , which has been widely applied commercially. However, the low energy density of LiFePO_4 (578 Wh kg^{-1}) drives people looking for new electrode materials with still good safety characteristics, long cycle life, and low cost [2]. Up to now, olivine-type LiMnPO_4 (with a theoretical capacity of 697 Wh kg^{-1}) has been considered as one of the most promising cathode materials for LIBs, due to its higher voltage plateaus (4.1 V) than LiFePO_4 (3.4 V) against Li/Li^+ [3]. Unfortunately, it is difficult for LiMnPO_4 to achieve a desirable electrochemical performance due to its much lower electronic conductivity ($<10^{-10} \text{ S cm}^{-1}$) and lithium ion diffusivity ($<10^{-16} \text{ cm}^2 \text{ s}^{-1}$), and possible Mn-dissolution in the electrolyte (especially at elevated temperatures) [4, 5].

It is found that partial substitution of Mn^{2+} with Fe^{2+} in $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ (LMFP) ($0 < x < 1$) can largely increase the electrochemical activity [6-9]. Excellent electrochemical performance of LMFP can also be obtained through nano-crystallization, uniform carbon coating and cationic doping [10-16]. For example, electrochemically inactive Mg^{2+} is often adopted as a dopant because its ionic radius ($0.86 \text{ \AA}$) is between Mn^{2+} ($0.98 \text{ \AA}$) in the lithiated phase and Mn^{3+} (0.78

Å) in the delithiated phase. Therefore, a suppression of the volume change of Mg-doped LiMnPO_4 during lithiation/delithiation is believed to be achieved and experimentally observed. Some results also have shown that the kinetics and thermal stability of the crystals are improved for the Mg-doped samples [14, 17]. Most of these materials are synthesized by wet chemical routes, such as hydrothermal/solvothermal [7, 10, 18, 19], sol-gel [20] and co-precipitation [21] processes. Factors such as pH value, the type of solvent and even the adding sequence of the reactants have great influences on the morphology and structure of the product [22, 23]. However, these wet-chemical routes are not suitable for large-scale syntheses due to the high production cost. Therefore, the synthesis of LMFP via a solid-state-reaction route is desirable, but has not been very satisfactory mainly due to the non-uniform particle size and carbon coating layer [13, 24].

Herein, Mg-doped $\text{Li}(\text{Mn,Fe})\text{PO}_4$ is adopted to improve the kinetics and thermal stability of the crystals during chemical and electrochemical delithiation, nano-particles with a size of 50 nm and uniform carbon coating are obtained via a simple solid-state-reaction route. They show excellent cycling and rate performances in the temperature range from -20 to 55°C. Furthermore, the olivine-type $\text{Na}(\text{Mn,Fe})\text{PO}_4$ electrodes are also obtained by first de-lithiation from $\text{Li}(\text{Mn,Fe})\text{PO}_4$ and then sodium intercalation through electrochemical conversion. The derived $\text{Na}(\text{Mn,Fe})\text{PO}_4$ electrodes also possess impressive electrochemical performance for energy storage. This study opens up a new direction on olivine-type cathode materials for sodium ion battery (SIB).

2. Experimental

2.1 Synthesis of Materials

$\text{LiMn}_{0.98-x}\text{Fe}_x\text{Mg}_{0.02}\text{PO}_4$ ($x=0.2, 0.5$) powders were synthesized by a simple solid-state-reaction route. Firstly, 0.1 mol $\text{LiOAc}\cdot 2\text{H}_2\text{O}$, 2 mmol $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 0.1 mol $\text{NH}_4\text{H}_2\text{PO}_4$, 0.1x mol $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, (0.098-0.1x) mol $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ and 150 g agate balls were blended together with 200 mL acetone as a dispersing agent in a 500 mL agate jar. Then, the jar was sealed and placed on a planetary ball mill (SFM-1, MTI Corp.) for 10 h at 450 rpm. The mixed slurries were dried at 100°C for 12 h to obtain some mixed powders. Subsequently, the powders were calcined in a tubular furnace at 400°C for 10 h under N_2 atmosphere to obtain intermediate products (the first-step calcination). Then, the intermediate powder products were mixed with polyvinyl alcohol (PVA, the average molecular weight is about $1.1 \times 10^5 \text{ g mol}^{-1}$, 10 wt% of the intermediate products) in a mortar with some ethyl alcohol as the dispersant. Finally, the dried mixtures were calcined (i.e. the second-step calcination) at 260°C for 2 h and then 650°C for 10 h under N_2 atmosphere to obtain carbon-coated samples (named as “LMMFP-2” for $\text{LiMn}_{0.78}\text{Fe}_{0.2}\text{Mg}_{0.02}\text{PO}_4$ ($x=0.2$) and “LMMFP-5” for $\text{LiMn}_{0.48}\text{Fe}_{0.5}\text{Mg}_{0.02}\text{PO}_4$ ($x=0.5$)).

In order to study the de-intercalation behavior of Na^+ ions for NaMPO_4 as SIB cathodes, $\text{NaMn}_{0.78}\text{Fe}_{0.2}\text{Mg}_{0.02}\text{PO}_4$ (NMMFP-2) and $\text{NaMn}_{0.48}\text{Fe}_{0.5}\text{Mg}_{0.02}\text{PO}_4$ (NMMFP-5) samples were synthesized by the electrochemical conversion process. In brief, the lithium ions were removed from LMMFP by charging Li/LMMFP half cells to 4.5 V. Then, the cells were opened and the delithiated electrodes were used to

assemble half cells vs. Na. Thus, the NMMFP electrodes were obtained after the cells were first discharged to 2.0 V.

2.2 Characterization of Materials

High-power X-ray powder diffraction (XRD, Rigaku TTR-III, CuK α radiation) was used to characterize the crystal structures of the samples over a range of 2θ angles from 10° to 70° with 1° min^{-1} . Their morphologies were analyzed by scanning electron microscopy (SEM, JSM-6390 LA, JEOL) and (high resolution) transmission electron microscopy (TEM, HRTEM, JEM-2100F). Raman spectroscopy (Renishaw inVia Raman Microscope) on the condition of 532 nm diode laser excitation was carried out to analyse the carbon coating and an Infrared Carbon-sulfur analyzer (CS-8800C, Jinbo) was used to measure the carbon content. The specific surface area and the pore size distribution were measured by N₂-adsorption/desorption (Tristar II 3020M, Micromeritics).

2.3 Electrochemical Measurements

CR2032-type coin-cells were assembled to evaluate the electrochemical performances of the LMMFP and NMMFP electrodes. For the LMMFP samples, the as-prepared active materials were blended with carbon black and polyvinylidene fluoride binder at a weight ratio of 8:1:1 dispersed in N-methyl-2-pyrrolidone to form slurries, which were casted onto aluminium foils to make working electrodes. A lithium foil was used as the counter electrode, and Celgard 2400 polypropylene

membrane as a porous separator. The electrolyte was 1.0 M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v, Zhuhai Smoothway Electronics Materials Co. Ltd). The loading density of active materials was about 2 mg cm⁻². The cells were also galvanostatically cycled on a multi-channel battery test system (Neware BTS-2300, Shenzhen) in the voltage range from 2.2 to 4.5 V at temperatures from -20°C to 55°C. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the cells were performed on a CHI 660B electrochemical workstation. CR2032-type coin-cells Na/NMMFP were also assembled with a sodium foil as the counter electrode and glass fiber (Whatman Gf/D) as a porous separator. The electrolyte was 1.0 M NaClO₄ dissolved in EC and DMC (1:1, v/v) with 5 vol% fluoroethylene carbonate (FEC) as a film-forming additive. The cells were cycled in a voltage range from 2.0 to 4.3 V at room temperature.

3. Results and discussion

Fig. 1 presents the Rietveld refinement results for the XRD patterns of the LMMFP samples. It can be seen that all the diffraction peaks match well with the calculated curves with a relatively low R_{exp} (1.54%, 1.71%), R_{wp} (7.17%, 7.76%) and R_p (5.32%, 5.58%) for the LMMFP-2 and LMMFP-5, respectively, which are indexed as an olivine-type structure (PDF #81-1173). No impurity phase is detected with the doping of Mg ions in the samples. From the inserted table in **Fig. 1a**, it can be seen that the refined cell parameters of sample LMMFP-2 are: a=10.4164 Å, b=6.0803 Å, c=4.7329 Å. However, the refined cell parameters of sample LMMFP-5 are:

$a=10.3803 \text{ \AA}$, $b=6.0490 \text{ \AA}$, $c=4.7166 \text{ \AA}$ (Fig. 1b), suggesting a lattice contraction caused by the presences of less Mn^{2+} ions with larger ionic radius ($0.98 \text{ \AA}$) and more Fe^{2+} ions ($0.92 \text{ \AA}$) in LMMFP-5 than in LMMFP-2 [9].

Fig. 1 Rietveld refinement XRD patterns and the refined cell parameters (inserted) of LMMFP samples.

The morphologies of the LMMFP powders are analyzed by SEM and (HR)TEM, which are shown in Fig. S1 and Fig. 2. The LMMFP particles obtained from this simple solid-state-reaction route are homogeneously dispersed with a uniform particle size of about 30-60 nm (Fig. S1, Fig. 2a and 2d). The particle size of LMMFP-5 is slightly smaller than LMMFP-2. The possible reason is explained as following: in sample LMMFP-5, the Mn/Fe molar ratio is about 1:1, which means that in a uniform mixture of the starting materials, both the Mn salt and Fe salt particles are well

surrounded by the another salt (i.e. Mn-salt by Fe-salt and Fe-salt by Mn-salt). During the calculation step, the ferrous oxalate with low decomposition temperature ($\sim 190^{\circ}\text{C}$) starts to decompose, the surrounded manganese acetate ($>300^{\circ}\text{C}$) can prevent or hinder the agglomeration and growth of the decomposed particles. When the temperature reaches the decomposition temperature of manganese acetate, the decomposition product of ferrous oxalate acts as the similar "shielding" role. However, in sample LMMFP-2, the Mn/Fe ratio is about 4:1, the decomposition product of manganese acetate can agglomerate and grow up due to the much high content of Mn than Fe. From the enlarged TEM images shown in [Fig. 2b](#) and [2e](#), a uniform carbon coating layer can be clearly seen on the surface of LMMFP nano-particles. The HRTEM images in [Fig. 2c](#) and [2f](#) present that the thickness of the amorphous carbon coating layer is about 1.5-2 nm. The exhibited crystal planes with a d-spacing of 0.417 and 0.422 nm for LMMFP-5 and LMMFP-2, respectively, correspond to the (101) lattice planes. The slightly larger d-spacing of LMMFP-2 than LMMFP-5 is mainly caused by the higher Mn/Fe ratio, which is also consistent with the XRD results ([Fig. 1](#)). The synthesis of these nano-particles with uniform carbon coating can be benefited from three aspects. Firstly, acetate and oxalate are adopted as raw materials due to their substantial decomposition during the calcination. The different decomposition temperatures of acetate and oxalate can prevent or hinder the agglomeration and growth of the LMMFP nano-particles. Secondly, the two-step calcination procedure is necessary in this method because the low-temperature-calcination step is to remove the organic components and obtain the

intermediate products while the high-temperature-calcination is to form carbon coating and improve the crystallinity of the olivine products. Lastly, the uniform mixing of the two materials and thus the derived uniform carbon coating can be achieved by wet-grinding, when the PVA is mixed with the intermediate product powders, ethanol is used as a dispersant and the mixing is carried out in a long enough time (usually 10-30 min) until the ethanol is nearly evaporated, which can easily obtain a uniform carbon coating layer during the high-temperature-calcination, and the carbon layer can further prevent or hinder the agglomeration and growth of the olivine particles.

Fig. 2 TEM and HRTEM images of LMMFP-5 (a-c) and LMMFP-2 (d-f).

The existence of the carbon layer can also be proved by the Raman spectroscopy analysis shown in **Fig. 3a**. The peak at 948 cm^{-1} corresponds to the signal of PO_4^{3-} ions of the LMMFP samples, while the peaks located at 1353 and 1603 cm^{-1} are the characteristic peaks of carbon, which can be assigned to the D- and G- bands, respectively. The carbon mainly comes from the carbonization of PVA in the high-temperature-calcination step. The D and G bands are sequentially deconvoluted into four peaks (labeled peaks 1–4) by using the XPSPEAK 4.1 software [25], presented by **Fig. 3b-c**. The peaks located at 1341 cm^{-1} (2) and 1586 cm^{-1} (4) are related to sp^2 -type carbon, while the peaks at around 1184 cm^{-1} (1) and 1491 cm^{-1} (3)

are associated with sp³-type carbon. The integrated area ratio of sp³ to sp² (Asp³/Asp²) is calculated to be as low as 0.225 and 0.321 for LMMFP-2 and LMMFP-5, respectively, inferring that a high proportion of sp²-type carbon was coated onto the LMMFP samples. The carbon contents are about 1.95 wt% for both samples, which are measured by an infrared carbon-sulfur analyzer.

Fig. 3 Original (a) and deconvoluted (b-c) Raman spectra of LMMFP-2 and LMMFP-5.

Fig. 4 shows the N₂-adsorption/desorption results and the pore size distributions of the LMMFP samples. Both LMMFP-5 and LMMFP-2 give a type-IV isotherm from the N₂-sorption analysis (**Fig. 4a** and **4c**), with a similar BET specific surface area of

30.9 and 31.4 $\text{m}^2 \text{g}^{-1}$, respectively. The pore size distribution of LMMFP-5 (**Fig. 4b**) shows that both micropores (1.8 nm) and mesopores (3-100 nm) exist. The small mesopores with a size of 4 nm are within the pores within the nano-particles, and the big mesopores with an average size of 43 nm are from the spaces between the nano-particles. However, LMMFP-2 shows much more big mesopores and less small mesopores and micropores than LMMFP-5, suggesting a larger degree of particle aggregation caused by the higher Mn/Fe ratio.

Fig. 4 The N_2 -adsorption/desorption curves (a, c) and pore size distributions (b, d) of LMMFP samples.

Fig. 5 shows the electrochemical performance of LMMFP/Li half-cells at room temperature. All the cells were cycled for 3 times at 0.1C ($1\text{C}=160 \text{ mA g}^{-1}$) to activate the electrodes. From **Fig. 5a**, LMMFP-5 and LMMFP-2 can deliver reversible specific capacities of 152.2 and 141.6 mAh g^{-1} , with average discharge voltages of

3.61 and 3.77 V at 1C rate, respectively. The capacity retention remains at 98.8% and 94.5%, respectively, after 120 cycles for the two samples. The related discharge curves (**Fig. S2**) show that two obvious discharge plateaus at about 4.0 and 3.5 V are related to $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$ and $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ two-phase reactions. The capacity fading is mainly from the decay of Mn plateau, which is likely caused by the Mn^{2+} dissolution in the electrolyte. Even after 450 cycles at 3C charge/discharge current density, the specific capacities still remain at 139.3 mAh g⁻¹ (95.3%) and 112.4 mAh g⁻¹ (88.3%) for LMMFP-5 and LMMFP-2, respectively (**Fig. 5b**). The initial columbic efficiency of LMMFP-5 is 93.3% and the columbic efficiency in the following cycles is all about 100% for 450 cycles. From **Fig. 5c**, two obvious plateaus can also be clearly distinguished at 3C current density for LMMFP-5. **Fig. 5d-f** shows that both samples exhibit excellent rate performance. The discharge specific capacity of LMMFP-5 is 159.0, 154.3, 150.7, 145.6, 138.6, 132.3 and 123.3 mAh g⁻¹ at 0.5, 1, 2, 5, 10, 15 and 20C, respectively. And, it is 143.5, 142.2, 138.9, 132.8, 125.6, 115.8 and 102.9 mAh g⁻¹ for LMMFP-2, respectively. Such excellent electrochemical performance obtained with this simple solid-state-reaction route is superior to most reported data in the literature shown in **Table 1**. By comparing the electrochemical properties with the commercial LiFePO₄ listed in **Table S1**, the LMMFP-5 sample shows the optimal performance and can deliver about 8% higher energy density than LiFePO₄.

Fig. 5 The cycling performance of LMMFP electrodes at 1C rate (a) and 3C rate (b), the discharge curves of LMMFP-5 at 3C rate (c), the rate performance (d) and the discharge curves at different C rates (e, f) of LMMFP samples. All the cells are cycled at room temperature.

Fig. S3 shows the EIS results and CV curves of the LMMFP electrodes vs. Li/Li^+ . The EIS spectra of the electrodes after 3 cycles can be fitted as shown in **Fig. S3a** on the basis of an equivalent circuit (inset). The values of ohmic resistance attributed to the electrolyte solution (R_s) are both about 2.8 ohm, but the charge transfer resistance (R_{ct}) of LMMFP-5 (61.0 ohm) is smaller than LMMFP-2 (71.5 ohm). The EIS results are consistent with the rate performances of the electrodes, which prove that the kinetics is more difficult for Li^+ de-intercalation with the increased Mn/Fe ratio in LMMFP. From the CV curves, it can be seen that two couples of sharp redox peaks keep unchanged in the two electrodes in the initial four cycles (**Fig. S3b-c**). It is worth noting that the voltage gap between the $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ of LMMFP-2 (0.26 V) is higher than that of LMMFP-5 (0.18 V), which is also consistent with the EIS results. Nevertheless, the voltage gaps between the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ of the two electrodes are similar and they are both smaller than those for $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$. This implies that the

reaction $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ is kinetically more difficult than the reaction $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ [9, 12].

The chemical diffusion coefficient of Li^+ (D_{Li}) is also calculated for LMMFP-2 and LMMFP-5 (Fig. S4, Table S2), the values of D_{Li} range between 10^{-9} and $10^{-11} \text{ cm}^2 \text{ S}^{-1}$ compared with the results of olivine-type polyanion materials reported in the literatures using the similar calculated method [12, 25, 26]. The results show that LMMFP-5 possesses larger D_{Li} than LMMFP-8 at both the anodic and cathodic peaks of $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$. Therefore, LMMFP-5 shows higher specific capacity and better rate capability than LMMFP-2. At the same time, high Mn content in LMFP will lead Jahn-Teller effect and possible Mn-dissolution in the electrolyte, resulting in the worse cycling performance of LMMFP-2 than LMMFP-5.

Table 1 The comparison of electrochemical performance of the LiMPO_4 (M=Fe, Mn) electrodes between this work and previously reported ones.

LMFP electrodes	Synthetic method	Carbon content(wt%)	Rate stability (mAh g ⁻¹)	Refs
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Sol-gel	33	128 @1C; 86 @5C	[20]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Solvothermal	3.8	120 @1C; 60 @5C	[7]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Solvothermal	8	112 @1C; 81 @20C	[27]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Solid-state reaction	6	146 @1C	[13]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Solvothermal	4.4	148 @1C; 130 @5C	[28]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Solvothermal	1.84	135 @1C; 60 @20C	[9]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	Solvothermal	--	128 @1C; 114 @4C	[29]
$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	CVD assisted Solid-state reaction	2.95	143 @1C; 133 @5C	[30]
$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Solvothermal	2.11	146 @1C; 120 @20C	[9]
$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Hydrothermal	2.91	147 @1C; 105 @10C	[10]
$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Solid-state reaction	6.1	141 @1C; 121 @5C	[24]
$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Hydrothermal	2.7	120 @1C; 81 @20C	[31]
$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Solid-state reaction	2	156 @1C; 115 @10C	[32]

$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Solvothermal	2.7	140 @1C; 118 @5C	[8]
$\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$	Polyol reaction	5	140 @2C; 90 @10C	[6]
$\text{LiMn}_{0.78}\text{Mg}_{0.02}\text{Fe}_{0.2}\text{PO}_4$	Solid-state reaction	1.95	142 @1C; 103 @20C	This work
$\text{LiMn}_{0.48}\text{Mg}_{0.02}\text{Fe}_{0.5}\text{PO}_4$			154 @1C; 123 @20C	

The high-temperature cycling performance and low-temperature rate capability of the electrodes are also key challenges for the commercial applications of lithium-ion batteries, especially for LiMPO_4 . **Fig. 6a** shows the cycling performance of the LMMFP/Li half cells at 55°C. The initial discharge specific capacities are 160.7 and 149.3 mAh g⁻¹ for LMMFP-5 and LMMFP-2 at 1C rate, respectively, which are slightly higher than the values at room temperature. After 100 cycles, the capacity retention rates are 97.7% and 83.6%, respectively. The worse capacity decay of LMMFP-2 is mainly caused by the Mn dissolution in the electrolyte due to the higher content of Mn than LMMFP-5. The Mn dissolution rate is also evaluated by aging the electrode in the electrolyte at 25°C (or 55°C) for two weeks. The results are analyzed by ICP measurement as shown in **Fig. 6b**. The values of Mn content in the electrolyte of the two samples are both very small at 25°C. However, when aged at 55°C, the Mn dissolution rate is much faster, especially in LMMFP-2, increasing from 4.8 ppm at 25°C to 81.2 ppm at 55°C. Therefore, the high-temperature cycling performance of LMMFP-2 is much worse than LMMFP-5. Desirable low-temperature (-20°C) rate performance of LMMFP-5 is also shown in **Fig. 6c**, which can still maintain at 68.4% (109.5 mAh g⁻¹) with an average discharge voltage as high as 3.37 V at 0.2C. Even at 3C rate, it can deliver a high specific capacity of 71.9 mAh g⁻¹. Such excellent electrochemical performance is rarely seen and even better than commercial LiFePO_4 .

Fig. 6 The high-temperature (55°C) cycling performance of LMMFP samples (a), the contents of Mn dissolved in the electrolyte at 25°C and 55°C (b), and the discharge curves of LMMFP-5 at different C rates at -20°C.

The electrochemically active NMMFP electrodes derived from their corresponding LMMFP counterparts also show excellent sodium storage properties in SIBs. In **Fig. 7a**, NMMFP-5 can deliver a reversible specific capacity of 122.5 mAh g⁻¹ at the 2nd cycle at 0.1C (1C=160 mA g⁻¹), and remain at 126.9 mAh g⁻¹ after 30 cycles. The

average discharge voltage is 3.1 V, much higher than the value of NaFePO₄ (~2.4 V) [33, 34]. Thus, the NMMFP-2 electrode can deliver a specific capacity of 82.0 mAh g⁻¹ with an average discharge voltage of 3.3 V (Fig. 7b). The rate performance is also measured at a charge current density of 0.5C and discharged at different C rates (Fig. 7c). The discharge specific capacity of NMMFP-5 is 105.4, 102.0, 93.6, 79.5 and 49.1 mAh g⁻¹ at 0.5, 1, 2, 5 and 10C, respectively. And, it is 68.6, 62.8, 52.3, 35.8 and 12.3 mAh g⁻¹ for NMMFP-2, respectively. The EIS results and CV curves of NMMFP electrodes are similar to that of LMMFP (Fig. S5 vs. Fig. S3). A couple of redox peaks around 3.7 V correspond to the redox couple of Mn²⁺ ⇌ Mn³⁺, and the other redox peaks around 2.8 V correspond to Fe²⁺ ⇌ Fe³⁺.

Fig. 7 The charge-discharge curves of NMMFP-5 (a) and NMMFP-2 (b) at 0.1C, and the rate performance of NMMFP samples (c). All the cells are cycled at room temperature.

In order to further demonstrate the de-intercalation mechanism of NMMFP, the (HR)TEM images of the derived NMMFP-5 and its ex-situ XRD analysis at different states-of-charge are shown in **Fig. 8**. From **Fig. 8a-b**, it can be seen that NMMFP-5 keeps the uniform nano-particles and carbon coating layer as LMMFP-5. It exhibits crystal planes with a d-spacing of 0.384 nm, corresponding to the (111) lattice planes. Compared to the XRD patterns of LMMFP-5, the ex-situ XRD (**Fig. 8c**) shows that the electrochemically activated NMMFP-5 keeps the olivine-type structure. In the charge process, the XRD peaks (patterns a and c) shift to higher angles, indicating a lattice contraction caused by the Na^+ ions removed from the structure. Moreover, Na^+ ions can be reversibly inserted in the structure and cause the lattice expansion in the discharge process (patterns b and d). Overall, the XRD results prove that the synthesized NMMFP is an olivine-type polyanion material and can reversibly de-intercalate and intercalate Na^+ ions for SIB cathodes. To our knowledge, this is the first time to show the structure analysis and electrochemical performance of NaMPO_4 (M= Mn, Fe) although it is reported as a SIB cathode material before [35]. Compared to other cathode materials shown in **Table 2**, such NaMPO_4 (M= Mn, Fe) materials can not only deliver a higher energy density, but also open up a new research direction on olivine-type SIB cathodes.

Fig. 8 TEM and HRTEM images of NMMFP-5 (a-b), and the ex-situ XRD patterns (c) of NMMFP-5 at different states-of-charge (patterns a-b: NMMFP-5 is charged to 4.3 V and then discharged to 2.0 V in the initial cycle; patterns c-d: NMMFP-5 is charged to 4.3 V and then discharged to 2.0 V in the 2nd cycle).

Table 2 The comparison of electrochemical performance of the NaMPO₄ (M=Fe, Mn) electrodes with other SIB cathodes reported in literature.

Materials	Discharge potential (V)	Specific capacity and energy density	Refs
NaCrO ₂	~3.0 (2.0-3.6V)	120 mAh g ⁻¹ @0.5C; 360 Wh kg ⁻¹	[36]
Na _{0.38} Ni _{1/3} Mn _{1/3} Co _{1/3} O ₂	~2.7 (1.8-4.4V)	123 mAh g ⁻¹ @0.05C; 332 Wh kg ⁻¹	[37]
NaNi _{0.5} Mn _{0.5} O ₂	~3.0 (2.2-4.0V)	136 mAh g ⁻¹ @0.1C; 411 Wh kg ⁻¹	[38]
Na[Ni _{0.58} Co _{0.06} Mn _{0.36}]O ₂	~2.9 (1.5-3.9V)	157 mAh g ⁻¹ @0.1C; 455 Wh kg ⁻¹	[39]
Na _{0.44} MnO ₂	2.8 (2.0-4.0V)	123 mAh g ⁻¹ @0.2C; 344 Wh kg ⁻¹	[40]
Na _{0.44} [Mn _{0.44} Ti _{0.56}]O ₂	~2.6 (1.5-3.8V)	110 mAh g ⁻¹ @0.1C; 286 Wh kg ⁻¹	[40]
NaFePO ₄	2.45(1.5-3.75V)	148 mAh g ⁻¹ @0.2C; 363 Wh kg ⁻¹	[33]
NaFePO ₄	2.4 (1.5-4.5V)	135 mAh g ⁻¹ @0.2C; 324 Wh kg ⁻¹	[34]
Na ₃ V ₂ (PO ₄) ₃	3.4 (2.3-3.9V)	100 mAh g ⁻¹ @0.2C; 340 Wh kg ⁻¹	[42]
NaMn _{0.78} Mg _{0.02} Fe _{0.2} PO ₄	3.3 (2.0-4.3V)	82 mAh g ⁻¹ @0.2C; 271 Wh kg ⁻¹	This work
NaMn _{0.48} Mg _{0.02} Fe _{0.5} PO ₄	3.1 (2.0-4.3V)	127 mAh g ⁻¹ @0.2C; 394 Wh kg ⁻¹	

Conclusions

In summary, the LMMFP nano-particles are synthesized through a simple solid-state reaction route. The nano-particles with uniform carbon coating layer exhibit excellent electrochemical performance at temperatures from -20 to 55°C. Such promising properties can be anticipated for the next generation cathodes for high power LIBs. The olivine-type NMMFP materials are also successfully obtained through the electrochemical conversion of the LMMFP materials. They also possess impressive electrochemical performance for energy storage and open up a new research direction on olivine-type cathode materials for SIBs.

Acknowledgements

This study was supported by the National Science Foundation of China (grant no. 51577175), Hefei Center of Materials Science and Technology (2014FXZY006) and Education Ministry of Anhui Province (KJ2014ZD36). We are also grateful to Elementec Ltd in Suzhou.

References

- [1] D.P. Singh, F.M. Mulder, A.M. Abdelkader, M. Wagemaker, *Adv. Energy Mater.*, 3 (2013) 572-578.
- [2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.*, 144 (1997) 1188-1194.
- [3] D. Morgan, A. Van der Ven, G. Ceder, *Electrochem. Solid St. Lett.*, 7 (2004) A30-A32.

- [4] S.M. Oh, S.W. Oh, C.S. Yoon, B. Scrosati, K. Amine, Y.K. Sun, *Adv. Funct. Mater.*, 20 (2010) 3260-3265.
- [5] J. Moskon, M. Pivko, I. Jerman, E. Tchernychova, N.Z. Logar, M. Zorko, V.S. Selih, R. Dominko, M. Gaberscek, *J. Power Sources*, 303 (2016) 97-108.
- [6] H. Xu, J. Zong, F. Ding, Z.W. Lu, W. Li, X.J. Liu, *Rsc Adv.*, 6 (2016) 27164-27169.
- [7] Y. Hong, Z. Tang, Z. Hong, Z. Zhang, *J. Power Sources*, 248 (2014) 655-659.
- [8] L. Hu, B. Qiu, Y. Xia, Z. Qin, L. Qin, X. Zhou, Z. Liu, *J. Power Sources*, 248 (2014) 246-252.
- [9] B.K. Zou, R. Yu, M.M. Deng, Y.T. Zhou, J.Y. Liao, C.H. Chen, *RSC Adv.*, 6 (2016) 52271-52278.
- [10] Z.X. Chi, W. Zhang, X.S. Wang, F.Q. Cheng, J.T. Chen, A.M. Cao, L.J. Wan, *J. Mater. Chem. A*, 2 (2014) 17359-17365.
- [11] T. Liu, J. Xu, B. Wu, Q. Xia, X. Wu, *RSC Adv.*, 3 (2013) 13337-13341.
- [12] B.K. Zou, H.Y. Wang, Z.Y. Qiang, Y. Shao, X. Sun, Z.Y. Wen, C.H. Chen, *Electrochim. Acta*, 196 (2016) 377-385.
- [13] H.C. Shim, S. Bang, D.-M. Yoon, Y. Kong, T. Yu, *J. Alloys Compd.*, 649 (2015) 1315-1322.
- [14] Q. Lu, G. S. Hutchings, Y. Zhou, H.L. Xin, H. Zheng, F. Jiao, *J. Mater. Chem. A*, 2 (2014) 6368-6373.
- [15] L. Qin, Y. Xia, H. Cao, L. Luo, Q. Zhang, L. Chen, Z. Liu, *Electrochim. Acta*, 123 (2014) 240-247.

[16] S. Wi, J. Kim, S. Nam, J. Kang, S. Lee, H. Woo, M. Lee, C.H. Sonu, T. Moon, B. Park, *Curr. Appl. Phys.*, 14 (2014) 725-730.

[17] G.Y. Chen, A.K. Shukla, X.Y. Song, T.J. Richardson, *J. Mater. Chem.*, 21 (2011) 10126-10133.

[18] J. Schoiber, G. Tippelt, G.J. Redhammer, C. Yada, O. Dolotko, R.J.F. Berger, N. Hüsing, *Cryst. Growth Des.*, 15 (2015) 4213-4218.

[19] P. Zuo, L. Wang, W. Zhang, G. Yin, Y. Ma, C. Du, X. Cheng, Y. Gao, *Nanoscale*, 7 (2015) 11509-11514.

[20] B.Z. Li, Y. Wang, L. Xue, X.P. Li, W.S. Li, *J. Power Sources*, 232 (2013) 12-16.

[21] W. Yang, Y. Bi, Y. Qin, Y. Liu, X. Zhang, B. Yang, Q. Wu, D. Wang, S. Shi, *J. Power Sources*, 2275 (2015) 785-791.

[22] M.-S. Kim, J.-P. Jegal, K.C. Roh, K.-B. Kim, *J. Mater. Chem. A*, 2 (2014) 10607-10613.

[23] L. Wang, X.M. He, W.T. Sun, J.L. Wang, Y.D. Li, S.S. Fan, *Nano Lett.*, 12 (2012) 5632-5636.

[24] X. Zhou, Y. Xie, Y.F. Deng, X.S. Qin, G.H. Chen, *J. Mater. Chem. A*, 3 (2015) 996-1004.

[25] T.F. Hung, W.J. Cheng, W.S. Chang, C.C. Yang, C.C. Shen, Y.L. Kuo, *Chem. Eur. J.*, 22 (2016) 10620-10626.

[26] X.Y. Cao, J.J. Zhang, *Electrochim. Acta*, 129 (2014) 305-311.

[27] P.J. Zuo, L.G. Wang, W. Zhang, G. P. Yin, Y. L. Ma, C. Y. Du, X. Q. Cheng, Y. Z. Gao, *Nanoscale*, 7 (2015) 11509-11514.

- [28] L. Yang, Y. Xia, L. Qin, G. Yuan, B. Qiu, J. Shi, Z. Liu, *J. Power Sources*, 304 (2016) 293-300.
- [29] J. Xiong, Y. Wang, Y. Wang, J. Zhang, *Ceram. Int.*, 42 (2016) 9018-9024.
- [30] L. Yang, Y. Xia, X. Fan, L. Qin, B. Qiu, Z. Liu, *Electrochim. Acta*, 191 (2016) 200-206.
- [31] W. Xiang, Y.J. Zhong, J.Y. Ji, Y. Tang, H.H. Shen, X.D. Guo, B.H. Zhong, S.X. Dou, Z.Y. Zhang, *Phys. Chem. Chem. Phys.*, 17 (2015) 18629-18637.
- [32] C.-C. Yang, W.-H. Chen, *Mater. Chem. Phys.*, 173 (2016) 482-490.
- [33] C. Li, X. Miao, W. Chu, P. Wu, D.G. Tong, *J. Mater. Chem. A*, 3 (2015) 8265-8271.
- [34] J. Kim, D.H. Seo, H. Kim, I. Park, J.K. Yoo, S.K. Jung, Y.U. Park, W.A. Goddard, K. Kang, *Energy Environ. Sci.*, 8 (2015) 540-545.
- [35] R. Tripathi, S.M. Wood, M.S. Islam, L.F. Nazar, *Energy Environ. Sci.*, 6 (2013) 2257-2264.
- [36] C.Y. Yu, J.S. Park, H.G. Jung, K.Y. Chung, D. Aurbach, Y.K. Sun, S.T. Myung, NaCrO₂ cathode for high-rate sodium-ion batteries, *Energy Environ. Sci.*, 8 (2015) 2019-2026.
- [37] S. Ivanova, E. Zhecheva, R. Kukeva, G. Tyuliev, D. Nihtianova, L. Mihailov, R. Stoyanova, *J. Phys. Chem. C*, 120 (2016) 3654-3668.
- [38] E. de la Llave, V. Borgel, K.J. Park, J.Y. Hwang, Y.K. Sun, P. Hartmann, F.F. Chesneau, D. Aurbach, *ACS Appl. Mater. Inter.*, 8 (2016) 1867-1875.
- [39] J.Y. Hwang, S.M. Oh, S.T. Myung, K.Y. Chung, I. Belharouak, Y.K. Sun, *Nat.*

Commun., 6 (2015) 6865.

[40] K. Dai, J. Mao, X. Song, V. Battaglia, G. Liu, J. Power Sources, 285 (2015) 161-168.

[41] Y. Wang, J. Liu, B. Lee, R. Qiao, Z. Yang, S. Xu, X. Yu, L. Gu, Y.S. Hu, W. Yang, K. Kang, H. Li, X.Q. Yang, L. Chen, X. Huang, Nat. Commun., 6 (2015) 6401.

[42] J.F. Mao, C. Luo, T. Gao, X.L. Fan, C.S. Wang, J. Mater. Chem. A, 3 (2015) 10378-10385.

Figure captions:

Fig. 1 Rietveld refinement XRD patterns and the refined cell parameters (inserted) of LMMFP samples.

Fig. 2 TEM and HRTEM images of LMMFP-5 (a-c) and LMMFP-2 (d-f).

Fig. 3 Original (a) and deconvoluted (b-c) Raman spectra of LMMFP-2 and LMMFP-5.

Fig. 4 The N₂-adsorption/desorption curves (a, c) and pore size distributions (b, d) of LMMFP samples.

Fig. 5 The cycling performance of LMMFP electrodes at 1C rate (a) and 3C rate (b), the discharge curves of LMMFP-5 at 3C rate (c), the rate performance (d) and the discharge curves at different C rates (e, f) of LMMFP samples. All the cells are cycled at room temperature.

Fig. 6 The high-temperature (55°C) cycling performance of LMMFP samples (a), the contents of Mn dissolved in the electrolyte at 25°C and 55°C (b), and the discharge curves of LMMFP-5 at different C rates at -20°C.

Fig. 7 The charge-discharge curves of NMMFP-5 (a) and NMMFP-2 (b) at 0.1C, and the rate

performance of NMMFP samples (c). All the cells are cycled at room temperature.

Fig. 8 TEM and HRTEM images of NMMFP-5 (a-b), and the ex-situ XRD patterns (c) of NMMFP-5 at different states-of-charge (patterns a-b: NMMFP-5 is charged to 4.3 V and then discharged to 2.0 V in the initial cycle; patterns c-d: NMMFP-5 is charged to 4.3 V and then discharged to 2.0 V in the 2nd cycle).

Table 1 The comparison of electrochemical performance of the LiMPO₄ (M=Fe, Mn) electrodes between this work and previously reported ones.

Table 2 The comparison of electrochemical performance of the NaMPO₄ (M=Fe, Mn) electrodes with other SIB cathodes reported in literature.