Concentration-gradient LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ cathode material for high performance lithium ion battery

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Highlights

- Concentration-gradient LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ is constructed through solvothermal method.
- The Mn dissolution of concentration cathode material is suppressed.
- The rate capability of this concentration material is improved.
- The cycle stability is improved, especially at elevated temperature.

Abstract

It is a great challenge to combine good cycling performance with high rate capability for LiM$_{1-x}$M$_x$PO$_4$ cathode materials owing to the Mn dissolution upon cycling and its low electronic/ionic conductivity. Here, we report a novel concentration-gradient structure of LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ material constructed by solvothermal treatment. This material shows a linear increase of Mn concentration from the edge to the particle centre, but the inverse trend for Fe concentration, which leads to the formation of Mn-rich phase in bulk and Fe-rich phase at surface. The Fe-rich phase effectively suppresses the corrosion from the electrolyte that minimizes the Mn dissolution and also improves the electronic/ionic conductivity of the surface that decreases the cathode/electrolyte interface resistance. Consequently, this concentration-gradient material achieves superior capacity retention with 98% after 50 cycles at 1 C even at elevated temperature, and also exhibits an excellent rate capability with the reversible capacity of 130 mA h g$^{-1}$ at 5 C rate. These results suggest that the concentration-gradient LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ is an ideal type of cathode material for high performance Lithium ion batteries.

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now admitted as one of the most promising cathode materials for Lithium ion batteries due to its stable working potential window (4.1 V vs. Li/Li$^+$) of a well-known carbonate ester-based electrolytes and similar theoretical discharge capacity (171 mA h g$^{-1}$) with LiFePO$_4$ [6,7]. However, its cycling performance and rate capability are still faced with serious challenges. In general, the capacity fade happens to LiMnPO$_4$ electrode during the cycling, especially at elevated temperature, which can be attributed to the Mn dissolution [8], like a Mn spinel (Li$_5$Mn$_2$O$_{12}$) [9], and while the poor rate performance is directly associated with the poor Lithium ion insertion/de-insertion kinetics induced by the Jahn-Teller lattice deformation [10,11]. Up to now, many efforts have been made to solve these problems.

Surface coating is an effective way to improve the electrochemical performance of the LiMnPO$_4$ cathode material [12–18]. Since LiFePO$_4$ that is regarded as an ideal surface coating material, has a strong resistance to the corrosion of electrolyte [8,18,19]. For instance, Oh et al. [8] synthesized a double-structured cathode material coating Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ with LiFePO$_4$. As a result, the coated material showed the enhanced cycling stability and rate capability, of which the reason was that the LiFePO$_4$ outer layer significantly improved the electron conductivity and protected the host material, while minimized the Mn dissolution. Zaghib et al. [19] also reported that LiMnPO$_4$ was encapsulated with the LiFePO$_4$ film, which could avoid the side reactions with the electrolyte since it does not degrade upon cycling. However, LiMnPO$_4$ core undergoes a phase transformation [20] due to the difference of ionic radius for Mn$^{2+}$ (9.7 Å) and Fe$^{2+}$ (9.2 Å) [21–24]. Therefore, a large void forms at core/shell interface after long-term cycling resulting that the core loses the path of Li ion for this kind of double-structured cathode material. Seriously, a decline of battery performance occurs [25,26]. Wang et al. tested the performance at low temperature of LiMnPO$_4$ material. The results showed that the polarization of the electrode increase with the decrease of temperature, which resulting in the decline of discharge capacity [27]. Previous studies also reported that this material were prone to arise Mn dissolution at elevated temperature leads to accelerate capacity fading during cycling [28,29].

Construction of a concentration-gradient structure base on cathode material has been extensively attracted attention, because it can minimize the mismatch between the surface and bulk phase [28–32]. Recently, Sun et al. [25] reported a Ni-rich concentration-gradient cathode material base on layered lithium transition-metal oxides, in which the Ni concentration decreases from the bulk toward the surface, and the Mn concentration increases linearly. It was found that the Ni-rich phase in bulk provided high capacity, and the Mn-rich stabilized the crystal structure. Moreover, this special surface structure limited the reactivity of bulk material with electrolyte resulting in outstanding performance of cycling [30]. For LiMnPO$_4$, suppression of Mn dissolution is critical to minimize capacity fade upon cycling. Therefore, it is highly desired to construct a concentration-gradient structure for LiMnPO$_4$ to protect the bulk material from directly contacting with electrolyte. On the basis of previous works [33–39], Fe-doped Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ [40–43], which can ensure high energy density with good electrochemical performance, is an ideal cathode material for modification.

In light of the above issue, we constructed a concentration-gradient structure based on Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ as illustrated in Scheme 1. The LiFePO$_4$ particle was coated on the surface and inserted into the internal space of Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ by solvothermal method. After calcining treatment, Fe$^{2+}$ was incorporated into the surface of Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ to form a new surface layer. This approach exploits the advantage of bulk doping to ensure high rate capability. At the same time, the new concentration-gradient surface layer protects the bulk Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ from electrolyte corrosion as a surface coating layer. Moreover, the phase separation is minimized owing to the structure similarity. Consequently, the material with concentration-gradient structure effectively improves the electrochemical performance in terms of cycling stability and rate capability.

### 2. Experimental section

#### 2.1. Synthesis of Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$

Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ (herein after referred to as LMFP) particles were prepared by the spray dry method. The details were as follows: an aqueous mixture with 10 wt. % glucose of LiOH·H$_2$O, MnCO$_3$, FeC$_2$O$_4$·2H$_2$O, NH$_4$H$_2$PO$_4$ in a molar ratio of 1:0.8:0.2:1 was vigorously stirred to form slurry with the solid content of 30 wt. %. The mixture was then spray dried at 120 °C with atmosphere of air and the as collected brownish powder was calcined at 650 °C for 8 h with the heating rate of 5 °C/min in an Ar atmosphere.

#### 2.2. Synthesis of concentration gradient materials

The concentration gradient cathode material (herein after referred to as CG–LMFP) was treated by solvothermal method. The as prepared Li$_{Mn_{0.8}Fe_{0.2}}$PO$_4$ mixed in PEG 400 solvent with strong magnetic stirring at room temperature in a beaker. Then the H$_3$PO$_4$ aqueous solution (1 M) and the LiOH aqueous solution (1 M) were dropped into the above mixture respectively under vigorous stirring. Subsequently, FeSO$_4$ aqueous solution (0.5 M) was dropped into the slurry slowly under stirring. The volume ratio between PEG 400 and H$_3$PO$_4$ was 1:40 and the molar ratio of H$_3$PO$_4$: LiOH: FeSO$_4$ was set at 1:3:1. The resulting slurry was transferred into a 100 ml Teflon-line stainless steel autoclave and heated at 180 °C for 12 h. The product was collected via filter and washed with ethanol and deionized water for several times. The obtained particles mixed in the solution with 10 wt. % glucose and the content of solid was about 30 wt. %. The mixture was then spray dried at 120 °C and the as collected brownish powder was calcined at 650 °C for 8 h with the heating rate of 5 °C/min in an Ar atmosphere. The carbon content in the final product is about 4.4 wt. %.

#### 2.3. Characterization

The crystalline structure of LMFP and CG–LMFP were identified using an X-ray powder diffraction (XRD, Bruker AXS, D8-Advance) that utilized Cu-K$_\alpha$ radiation ($\lambda = 1.54056 \ \text{Å}$). Data were collected over the 2θ range from 10° to 70° for 0.0067° s$^{-1}$ at ambient temperature. The Rietveld refinement was carried out using the MAUD software. XPS measurements were carried out with an X-ray photoelectron spectrometer (Kratoo AXIS Ultra DLD), using a focused monochromatized Al K$_\alpha$ radiation (1486.6 eV). Curve fitting of XPS spectra was carried out using a CasaXPS program and the binding scale was calibrated from the hydrocarbon contamination using the C 1s peak at 284.8 eV. HRTEM was carried out on FEI Tecnai F20 operated at 200 kV. The cross section was observed by field emission scanning electron microscope (FESEM, FEI Quanta FEG 250). Energy dispersive spectroscopy (EDXS) was employed in the SEM to investigate the distribution of elements. The chemical element composition of the product was examined quantitatively by inductive coupled plasma (ICP) with an emission spectrometer (Optima 5000 DV, Perkin–Elmer). The carbon content is measured by organic element analyzer (PE 2400iII).

The morphologies of samples were tested by SEM (Hitachi, S-4800). The specific surface area and particle size distribution was analysed by BET (Micromeritics, ASAP 2020M) and particle size
analyser (Microtrac, S3500), respectively.

2.4. Electrochemical measurements

The cathode electrodes were prepared by slurry with a mixture of 80 wt. % the active materials, 15 wt. % Super P carbon, and 5 wt. % polyvinylidene fluoride binder, which was dissolved in N-methyl-2-pyrrolidone. The resultant slurry was coated onto an Al foil, and then dried at 80°C for 12 h. The thickness was about 25 μm, and accordingly, the loading density of the electrode was 2.5–3.5 mg cm⁻². The 2032-type coin cell was assembled in an argon-filled glove box with lithium metal as anode and Celgard 2502 as the separator. The electrolyte consists of 1 M LiPF₆ which dissolved in ethylene carbonate and dimethyl carbonate with 3:7 volume ratios (Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd., P. R China). The cells were tested in a voltage range of 2.0–4.5 V (vs. Li⁰/Li⁺⁺) using a various constants-current constant-voltage (CCCV) protocol at various rates with a LAND-CT2001A battery test system (Jinnuo Corp., China). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with a Salartron400. The EIS measurements were carried out with the voltage amplitude of 5 mV after three cycles at 0.1°C at room temperature. For CV measurements, the cells were record in the potential range from 2.0 to 4.5 V at the scan rate of 0.1 mV s⁻¹.

3. Results and discussion

Fig. 1 shows the XRD patterns of LMFP and CG–LMFP. All the diffraction patterns can be well indexed to an orthorhombic space group Pnma (JCPDS No. 74–0375). Furthermore, the diffractions of CG–LMFP are all in the same places as the LMFP, which demonstrates that the two samples possess high crystallinity without impurity phase. Moreover, the parameters of LMFP and CG–LMFP were calculated with Rietveld refinement using Maud software as presented in Table 1. The reasonably small Rw and Rb factors indicate a good fitting. Compared to that of LMFP, the lattice parameter of CG–LMFP sample has a slight decrease, which could be attributed to the diffusion of Fe²⁺ ions (9.2 Å) into the olivine lattice of Mn²⁺ ions (9.7 Å) of LiMn₀.₈Fe₀.₂PO₄ [44,45].

The surface compositions of samples were measured by XPS as presented in Fig. 2. The core level spectra of Fe 2p (Fig. 2a, b) show that the Fe 2p₃/₂ binding energy for both samples is around 710.6 eV. The satellite peaks for two samples are around 724.1 eV as the multiple splitting of energy levels of Fe ion, which matches well with the Fe²⁺ [46,47]. Fig. 2c and d presents the core level spectra of Mn 2p for LMFP and CG–LMFP, respectively. Two peaks were observed about 653.9 eV for Mn 2p₁/₂ and 641.4 eV for Mn 2p₃/₂ with a spin–orbit splitting of 5.5 eV [48,49]. No significant difference is observed on the XPS spectra of the Fe 2p and Mn 2p for both

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<th>Table 1</th>
<th>Lattice parameters of LMFP and CG–LMFP.</th>
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<td>LMFP</td>
<td>6.0855</td>
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<td>CG–LMFP</td>
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samples. However, the surface composition of Fe for LMFP is 1.45 (atomic concentration %), which is lower than CG-LMFP (1.67), as listed in Table 2. On the contrary, the Mn atomic concentration at the particle surface of LMFP is higher than CG-LMFP. The results show that the transition metal concentration at the surface of the material has changed by this surface modification.

The particle morphologies of both LMFP and CG-LMFP samples were tested by SEM, as shown in Figs. S1 and S2. The microsphere LMFP and C-LMFP particles with the size about 20–30 μm are composed of agglomerated nanosized primary particles with the diameters of 40–50 nm. The specific surface area for LMFP and CG-LMFP are 25.93 m² g⁻¹ and 14.2 m² g⁻¹, as illustrated in the Table S1. Also, HRTEM was also used to investigate the surface microstructure of samples. As shown in Fig. 3a, the particle of LMFP was coated by amorphous carbon and well crystallized with the d-spacing of 1.03 nm, which corresponds to the (100) plane of LiMn₀.₈Fe₀.₂PO₄ [35]. In contrast, the CG-LMFP sample shows three sets of lattice fringes after surface modification, as illustrated in Fig. 3b. The outer layer has the d-spacing of 0.23 nm, which agrees well with the (012) plane in LiFePO₄ [50], and the d-spacing of the sub-surface layer is 0.37 nm, which corresponds to the (101) plane of LiMn₁₋ₓFeₓPO₄ (x = ~0.29) [51], while that of the inner layer is 0.30 nm, which associates with the (200) plane of LiMn₁₋ₓFeₓPO₄ (x = ~0.25) [52]. These results confirm that the surface structure evolved from uniform solid solution into Fe-rich phase.

Table 2
The atomic concentration of Fe and Mn for LMFP and CG-LMFP measured by XPS.

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<tr>
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<td>Fe</td>
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<td>LMFP</td>
<td>1.45</td>
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<td>CG-LMFP</td>
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Fig. 2. XPS spectra of Fe 2p for the LMFP (a) and CG-LMFP (b) samples; Mn 2p of LMFP (c) and CG-LMFP (d) samples. The dots and lines represent experimental data and fitting data, respectively.

Fig. 3. HRTEM images of LMFP (a) and CG-LMFP (b). Atomic concentration at the particle surface of LMFP is higher than CG-LMFP.
In order to further investigate the composition and distribution of Fe and Mn for two samples, energy dispersive X-ray mapping analysis (EDXS) was also carried out. Fig. 4a and c shows the cross sections of LMFP and CG–LMFP with particle diameter of nearly 15 μm. The EDXS line scanning map illustrates that the concentrations of Fe and Mn have no difference from one side to another for the LMFP sample as depicted in Fig. 4b. However, for the CG–LMFP, it clearly exhibits a concentration gradient about these two elements, in which the Fe concentration at the particle surface is higher than at the centre that decrease linearly, whereas the concentration of Mn on the surface is lower than the centre that increase linearly (Fig. 4d). These results indicate that the particle with concentration gradient structure has been constructed successfully by solvothermal treatment.

The cycling performances of CG–LMFP and LMFP at different temperature are illustrated in Fig. 5a and b. It can be seen that CG–LMFP sample shows an excellent cycling performance both at room temperature and at elevated temperature. However, for the CG–LMFP, it clearly exhibits a concentration gradient about these two elements, in which the Fe concentration at the particle surface is higher than at the centre that decrease linearly, whereas the concentration of Mn on the surface is lower than the centre that increase linearly (Fig. 4d). These results indicate that the particle with concentration gradient structure has been constructed successfully by solvothermal treatment.

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In order to confirm the above assumption, the electrochemical impedance and cyclic voltammetry spectroscopy were performed as presented in Fig. 7. The equivalent circuit shown in Fig. 7c [57,58] was used to fit the spectra, where $R_e$ is the electrolyte resistance, and $R_1$ and $CPE_1$ are the resistance and geometric capacitance of the anode solid-electrolyte interphase, respectively. $R_2$ represents the charge-transfer resistance, $CPE_2$ reflects the double-layer capacitance, and $W_0$ is the Warburg diffusion impedance. In the Nyquist plots as illustrated in Fig. 7a, each impedance spectrum consists of a depressed semicircle at high frequency, and a slope line at the low frequency range. The semicircle at high frequency region of impedance spectra can be assigned to the $R_1CPE_1$ and $R_2CPE_2$ elements. As shown in Table 3, $R_1$ and $R_2$ of CG-LMFP electrode was decreased by surface
modification, which contributes to the suppression of Mn dissolution protected the SEI from destruction and the Fe-rich phase also maintained the surface structure that preserved the transportation channel of Lithium ion. The low frequency region represents the Warburg impedance related to the Li\textsuperscript{+} diffusion. The lithium ion diffusion coefficient can be calculated according the following equation:

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^2F^2C^2\sigma^2}$$

Where R is the gas constant (8.314 J mol\textsuperscript{-1} k\textsuperscript{-1}), T is the absolute temperature (K), A is the contact area of the electrode (1.32665 cm\textsuperscript{2}), n is the number of the electrons per molecule (n = 1, for Fe\textsuperscript{3+}/Fe\textsuperscript{2+} and Mn\textsuperscript{3+}/Mn\textsuperscript{2+} redox pair), F is the Franday constant (96486 C mol\textsuperscript{-1}), C is the concentration of the Lithium ion (6.38 \times 10\textsuperscript{-3} mol cm\textsuperscript{-3}) (ratio between the tap density of the prepare material and the molecular weight) \cite{59} and the σ is the Warburg coefficient (obtained from Fig. 7b) \cite{60,61}. The σ is equal to the slope of the straight line as illustrated in Fig. 7b. Through calculation, the diffusion coefficient is calculated to be about 2.4 \times 10\textsuperscript{-13} cm\textsuperscript{2} s\textsuperscript{-1} for LMFP and 1.2 \times 10\textsuperscript{-12} cm\textsuperscript{2} s\textsuperscript{-1} for CG–LMFP, respectively. Based on this, it demonstrates that the surface Fe-rich composition is benefit to the Li\textsuperscript{+} migration. Fig. 7d displays the CV curves of the CG–LMFP and LMFP at 0.1 mV s\textsuperscript{-1}, which show the oxidation and reduction peaks of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} and Mn\textsuperscript{3+}/Mn\textsuperscript{2+}. The peak current density for CG–LMFP is much higher than LMFP. Moreover, and the difference between the anodic peaks and cathodic peaks of Mn and Fe for CG–LMFP are smaller than that of LMFP. These results show that the concentration gradient surface layer could improve the conductivity and weaken the polarization of the cathode. All of these results further validate that construction of concentration-gradient structure in LiMn\textsubscript{0.8}Fe\textsubscript{0.2}PO\textsubscript{4} cathode material could significantly decrease interface resistance and improve the Lithium ion diffusion kinetics.

4. Conclusions

We have developed a concentration-gradient structure cathode material based on LiMn\textsubscript{0.8}Fe\textsubscript{0.2}PO\textsubscript{4} with excellent electrochemical performance by solvothermal treatment. This structure takes advantage of anticorrosion of surface Fe-rich phase from electrolyte and stability of this surface structure, resulting in superior cycling performance. Moreover, the Fe-rich phase at the surface of LiMn\textsubscript{0.8}Fe\textsubscript{0.2}PO\textsubscript{4} also benefits for electronic/ion kinetics, which leads to an excellent rate performance. As a consequence, the concentration-gradient electrode exhibited high rate capability with outstanding cycle stability, maintaining 98% discharge capacity retention after 50 cycles at 1 C rate at elevated temperature. Therefore, it is anticipated that this novel concentration-gradient LiMn\textsubscript{0.8}Fe\textsubscript{0.2}PO\textsubscript{4} should be one of the most promising candidates for advanced Lithium ion batteries.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.11.037.

References