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Phase relations of Li₂O-MnO-P₂O₅ system and the electrochemical properties of Li_{1+x}Mn_{1-x}PO₄ compounds

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Abstract

The phase relations of Li₂O-MnO-P₂O₅ ternary system under reducing atmosphere have been systematically investigated by means of X-ray diffraction. Inferior to what we expected, no other new lithium manganese phosphates exist within the Li₂O-MnO-P₂O₅ ternary system under the reducing atmosphere. A high-pressure phase Mn₃(PO₄)₂ with graftonite Fe₃(PO₄)₂-type structure can be easily obtained in the MnO-P₂O₅ system under the ordinary solid-state reaction conditions in H₂/Ar atmosphere and its detail structure is presented. In addition, the solid solubility of Li_{1+x}Mn_{1-x}PO₄ is determined as $-0.05 \le x \le 0.03$. The lattice parameters and electrochemical properties of Li_{1+x}Mn_{1-x}PO₄ with *x* content are investigated. The electrochemical test results show that excess Li-ion (x > 0) or the excess Mn-ion (x < 0) in LiMnPO₄ has an unfavorable effect on the electrochemical properties caused by the deterioration of the lithium diffusion along the one-dimensional tunnels. *Keywords:* Solid-state reactions; $Li_2O-MnO-P_2O_5$ phase diagrams; X-ray diffraction; $Li_{1+x}Mn_{1-x}PO_4$ solid solutions.

1. Introduction

Since rechargeable lithium ion batteries became the most widely used and most advanced energy storage system, electrode materials are causing special concern [1-3]. For cathode materials, cobalt-based oxides are still utilized as the most common cathode material in commercial cells until now. However, its cost, toxicity, and poor thermal stability have become hinders of LiCoO₂ in large-scale applications in electrical vehicle (EV) and hybrid electric vehicles (HEV), which are considered as the tendency of the future application of lithium batteries. To satisfy the need for safer, environmental friendly and favorable performance cathode materials, a worldwide search for LiFePO₄ with three-dimensional polyanionic structures built of PO_4^{3-} tetrahedra and FO_6 octahedra has been carried out. The good thermal stability, comparable power density and flat voltage profile make LiFePO₄ to be a great potential candidate of the lithium battery cathode materials. In searching for new cathode materials, much work has also been performed on other lithium transition metal phosphate system [4-6]. To be noticed, typical studies have been reported on phosphates LiMPO₄ (M=Co, Ni, Mn, Cu) with isostructure of LiFePO₄ [7-10], where LiMnPO₄ appeals more interest due to its high redox potential which matches with the electrolyte window

in the present Li-ion batteries. Actually, much effort has been done to optimize LiMnPO₄ by coating with conductive materials or doping in Mn-site or Li-site [11-13]. Since its first reported by Adam.L et al. [14], manganese pyrophosphate (Li₂MnP₂O₇) has also been widely investigated in both experimental and theoretical calculation way [15, 16]. The manganese phosphates attract great attentions not only due to its high Mn^{2+}/Mn^{3+} redox potential, but also its multi valence states which show possibility to achieve beyond one-electron reaction just like Li₂MnSiO₄[17].

Besides the two manganese phosphates mentioned above, only a few manganese phosphates have been investigated, and ones still expecting there exist other new lithium manganese phosphates which may be as a candidate cathode material. Phase diagram is very important in searching for new materials and material synthesis [18]. To our knowledge, no phase diagram of the Li₂O-MnO-P₂O₅ system is available yet. To find the new lithium manganese phosphates, it will be very interesting to research the phase equilibria in the ternary Li₂O-MnO-P₂O₅ system under reducing atmosphere. Here, the phase relation of Li₂O-MnO-P₂O₅ ternary system has been systematically investigated by means of X-ray diffraction (XRD). In order to avoid the appearance of trivalent manganese, 95%Ar + 5%H₂ reducing atmosphere was used in the synthesis process of all samples. It will offer a better understanding for the phase relations of the Li₂O-MnO-P₂O₅ system and provide an experimental reference in searching of other new lithium manganese phosphates which may be as a candidate cathode

material. In addition, due to its much more attractive interests with high redox potential for Li-ion batteries, the solid solution region with excess lithium doping into manganese sites and reversely manganese doping into lithium sites in LiMnPO₄ (nominated as $Li_{1+x}Mn_{1-x}PO_4$) was determined as $-0.05 \le x \le 0.03$ and their corresponding lattice parameters were also reported here. Furthermore, the influence of manganese sites doping with excess lithium and lithium sites doping with excess manganese on the electrochemical performance of LiMnPO₄ were also investigated.

2. Experimental

A total of 50 specimens with different compositions were prepared by two-step solid-state method. There are 27 specimens for the two binary subsystems and 23 specimens for the ternary system.

Analytical grade Li_2CO_3 , MnCO₃ and NH₄H₂PO₄ were used as starting materials. The appropriate amounts of starting materials were grounded in an agate mortar for 30 min. The mixtures of the samples at P₂O₅ poor regions within the Li₂O-MnO-P₂O₅ system were preheated at 350 °C for 5 h in Ar atmosphere to expel NH₃, H₂O and CO₂. After cooling down to room temperature, the samples were reground again in the agate mortar for 30 min, pressed into pellets of about 10 mm in diameter and 2-3 mm in thickness, and then heated at 500-750 °C for 12 h in an alumina boat, depending on the samples composition. The samples finally cooled down to room temperature naturally. For the samples containing higher

mole ratio of P_2O_5 with lower melting temperatures of the reactants, the preheating was performed in a slow heating rate to prevent the precursor corroding with the alumina boat. In order to prevent forming of trivalent manganese, all samples were heated under the 95% Ar + 5% H₂ atmosphere.

The phase identification of these products was carried out by XRD using a D/Max-2400(Rigaku) diffractometer with Cu K α radiation. A graphite monochromator was used for diffracted beams. The Rietveld refinement of Li_{1+x}Mn_{1-x}PO₄ (-0.05 $\leq x \leq$ 0.03) samples and Mn₃(PO₄)₂ were performed by GSAS program.

The electrochemical characterization of $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO}_4$ (-0.05 $\leq x \leq$ 0.03) powders as cathode of the two-electrode electrochemical cells was measured by an automatic battery tester system (Land®, China). The cathode of the two-electrode electrochemical cells were fabricated by blending the prepared powder with acetylene black and polyvinylidiene fluoride (PVDF) binder in a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). The obtained slurry was coated on Al foil, dried at 90 °C for 24 h and pressed (5MPa), respectively. The electrodes fabricated were dried again at 90 °C for 12 h in vacuum and cut into 0.8 cm×0.8 cm in size. Two-electrode electrochemical cells were assembled in a Mikrouna glove box filled with high-purity argon, where the lithium metal foil were used as anode, Celgard® 2320 as separator, and 1M LiPF6 in EC:DMC (1:1 vol.%) were used as an electrolyte. The electrochemical capacity measurements were performed at the current rate of 5 mA/g between the voltage range of 2.0 and 4.5 V.

Cyclic voltammetric (CV) tests and electrochemical impedance spectroscopy (EIS) experiments were performed on an AUTOLAB PGSTAT100 type electrochemical workstation (Metrohm AG company). CV tests were carried out at a scan rate of 0.05mVs⁻¹ on the potential interval 2.5-4.5 V (vs. Li⁺/Li). All tests were performed at room temperature. Galvanostatic intermittent titration technique (GITT) was conducted by applied a series of constant current step (discharge or charge at 0.01 mA for 30 min) followed by an interrupt step (rest at 0 current for 240 min) to the cell.

3. Results and discussion

3.1. Binary systems

3.1.1. $Li_2O-P_2O_5$ system

Three compounds have been reported in the $Li_2O-P_2O_5$ system: $LiPO_3$, $Li_4P_2O_7$ and Li_3PO_4 . These three compounds have been verified by our group during the investigation of $Li_2O-P_2O_5$ -FeO ternary system [19], and here they were also confirmed again.

3.1.2. MnO- P_2O_5 system

Manganese phosphates are among the most wide spread minerals in the class of phosphates, and four compounds with manganese valence of +2 were reported, i.e. $MnP_4O_{11}[20-22], Mn_2(PO_3)_4[23,24], Mn_2P_2O_7[25], Mn_3(PO_4)_2$ [26-28]. Only three of them, $Mn_2(PO_3)_4$, $Mn_2P_2O_7$ and $Mn_3(PO_4)_2$, were confirmed here. Murashova et al. reported the new modification of manganese ultraphosphate MnP_4O_{11} compound by heating MnC_2O_4 with polyphosphoric acid (Mn:P = 2:11) at 550°C for 5 hours [20]. However, MnP_4O_{11} cannot exist under our synthesis condition, i. e., $MnCO_3$ and $NH_4H_2PO_4$ were used as the starting materials and solid-state method was adopted under the 95% Ar + 5% H₂ atmosphere. $Mn_2(PO_3)_4$ has a monoclinic system with the space group of C2/c (Z=4) or I2/a (Z=8) [23, 24]. Here we obtained $Mn_2(PO_3)_4$ with a space group of C2/c. And we observed $Mn_2P_2O_7$ existed under our experiment condition with a monoclinic symmetry belonging to the space group of C12/m1 as the report [25].

For Mn₃(PO₄)₂, a monoclinic system with three modifications was reported: a thermodynamically stable one at standard pressure, known as β '-phase, a high-pressure phase with graftonite Fe₃(PO₄)₂-type structure, called as α -phase[27], and γ -phase that can be synthesized under hydrothermal conditions[28]. All these three polymorphs adopt monoclinic system with same space group of P2₁/n or P2₁/c (SG No. 14) but different structural topology (crystallographical position) [28]. It has been reported that pure manganese graftonite (high-pressure α -phase) seems never to be prepared and solid solutions of the form (Mn_{1-x}M_x)₃(PO₄)₂ with graftonite-type structure can be formed, like a naturally occurring mineral with the chemical composition of (Fe, Mn, Ca, Mg)₃(PO₄)[27]. Under high pressure, the β '-phase can be transformed to be α -phase. A. G. Nord et al. obtained the α -phase Mn₃(PO₄)₂ by applying an extremely high pressure (2.5Gpa) to β '-phase Mn₃(PO₄)₂ at 600°C for 24

h, where the β '-phase Mn₃(PO₄)₂ were obtained by heating equimolar amounts of MnO and Mn₂P₂O₇ in an evacuated silica tube at 1100 °C for two weeks[27]. Interestingly, Mn₃(PO₄)₂ with the space group of P2₁/c (crystallized in a high-pressure α -phase) can be observed under our experiment condition, i.e., the mixture of MnCO₃ and NH₄H₂PO₄ heated in Ar atmosphere for a few hours firstly, pressed into pellets and annealed under the 95% Ar + 5% H₂ flow at 700 °C with intermediate grindings, and then furnace cooled to room temperature. Here, the existing of high-pressure α -Mn₃(PO₄)₂ in the Li₂O-MnO-P₂O₅ three-phase regions suggests that atmosphere can be somehow as an important factor which causing the formation of high-pressure phase under the ordinary solid-state reaction conditions.

In the literature, it only offered the index results (cell parameters) of x-ray powder diffraction data, and the detail structure of α -Mn₃(PO₄)₂ has not been reported yet [27,28]. Fig. 1 illustrates the X-ray diffraction patterns of α -Mn₃(PO₄)₂ obtained here, where the XRD patterns of β -Mn₃(PO₄)₂, γ -Mn₃(PO₄)₂, and graftonite Fe₃(PO₄)₂ which is isostructured with α -Mn₃(PO₄)₂ are also given for comparison. Here, the structure of α -Mn₃(PO₄)₂ was characterized, and the XRD patterns could be indexed to monoclinic structure. The number of chemical formulas per unit cell of the α -Mn₃(PO₄)₂ compound is 4. The cell parameters of a=8.817(7) Å, b=11.455(6) Å, c=6.244(5) Å, β =98.96(7) °, and V=155.7(4) Å³ for α -Mn₃(PO₄)₂ phase obtained from Rietveld refinement is shown in Table 1. In addition, the cell parameters obtained from the reference for Fe₃(PO₄)₂ [30], α -Mn₃(PO₄)₂ [27], β '-Mn₃(PO₄)₂ [26], γ -Mn₃(PO₄)₂ [28] are also given in Table 1 for comparison.

Preliminary refinements of the tetragonal structure were performed by Rietveld method [29] for α -Mn₃(PO₄)₂ compound, and the results are shown in Fig.2. The weighted pattern R factor, R_{WP}, is 2.54%. As illustrated in Table 2, all atoms of α -Mn₃(PO₄)₂ occupy the same Wyckoff site(4e), but different crystallographically sites. Table 3 contains interatomic distances computed from the nuclear positions listed in Table 2. Each Mn1 atom is surrounded by a polyhedron of 6 oxygen atoms. Mn2 and Mn3 are surrounded by 5 atoms respectively. The Mn1-O bond lengths extend from 1.99(4) Å to 2.581(25) Å, Mn2-O from 1.947(26) Å to 2.529(34) Å, and Mn3-O from 1.989(34) Å to 2.362(31) Å. Figure 3(a) shows the structure of α -Mn₃(PO₄)₂, projected along the c-aixs direction, where three manganese atoms form three distinct polyhedra with surrounding oxygen atoms. Mn2 and Mn3 are irregularly coordinated by five oxygen atoms, and Mn1 has six nearest oxygen atoms in the shape of highly distorted octahedron. As shown in Fig. 3 (b) of the assignment of coordination for phosphorus and manganese atoms, each oxygen atom is bonded to one phosphorus and two manganese atoms respectively.

3.1.3. MnO-Li₂O system

The MnO-Li₂O system in reducing atmosphere has been studied. In the system, only one compound was reported in literature: Li₂MnO₂, where manganese presents in the +2 oxidation state. It should be noted that without any other literatures reported about its existence under chemical condition except David's report [31], in which Li_2MnO_2 can be synthesized by using butyllithium and $LiMn_2O_4$ through a chemical

way in room temperature. In our experiment condition, there is no evidence of the existence of Li_2MnO_2 .

3.2. Ternary Li₂O–MnO–P₂O₅ system

3.2.1 Ternary compounds

In this system, 4 kinds of ternary compounds containing Mn^{2+} ion were verified in the literatures. These are LiMnPO₄, Li₂MnP₂O₇, Li₂Mn(PO₃)₄, LiMn(PO₃)₃. Here, all four compounds can be obtained by solid-state method. LiMnPO₄ was reported to have an orthorhombic system with space groups of Pmnb [32] or Pbnm [33] or Pnma[34,35]. In our experiment condition, LiMnPO₄ was observed with the space group of Pnmb. For Li₂MnP₂O₇, we obtained it with the space group of P2₁/a as reported in Ref. [36]. Li₂Mn(PO₃)₄ was observed to have an monoclinic system with the space group of Pnam in work [37], which is confirmed by our experimental result. Murashova et al [38] reported that LiMn(PO₃)₃ adopt an orthorhombic system with the space group of P2₁2₁2₁, and our X-ray diffraction analysis verified this conclusion. It should be noted that, inferior to what we expected, no other new lithium manganese phosphates exists within the Li₂O-MnO-P₂O₅ ternary system under the reducing atmosphere.

3.2.2 The subsolidus phase relations

No experimental work has been reported for ternary $Li_2O-MnO-P_2O_5$ phase diagram. We have prepared 50 different compositions samples by two-step solid-state

method under the reduction atmosphere (95% Ar + 5% H₂). The phase relations in the ternary Li₂O–MnO–P₂O₅ system were systematically investigated and shown in Table 4. The ternary LiO₂-MnO-P₂O₅ system can be divided into 15 three-phase regions under our experiment condition, as shown in Fig. 4, where the solubility of Li_{1-x}Mn_{1+x}PO₄ (-0.05 $\le x \le 0.03$) is also labeled.

3.3 The solid solutions of $Li_{1+x}Mn_{1-x}PO_4$

3.3.1 Phase identification

Fig.5 shows the X-ray diffraction patterns of $Li_{1+x}Mn_{1-x}PO_4$ compounds, and all the peaks can be indexed with single phase orthorhombic Pmnb. No impurity phase can be detected in the doping range of -0.05 $\leq x \leq 0.03$. Furthermore, the Rietveld refinement of the XRD data was carried out and a space group of Pmnb was chosen as refinement model. In the hypothesis that the formulas were as prepared stoichiometric $Li_{1+x}Mn_{1-x}PO_4$ (x = 0.03, 0.02, 0.00, -0.02, -0.04, -0.05) respectively. The occupancy of lithium and manganese sites were constrained not to exceed 100%, and the exceed lithium ions (or manganese ions) were set to occupy manganese site (or lithium site). The refinement results of $Li_{1.03}Mn_{0.97}PO_4$ and $Li_{0.95}Mn_{1.05}PO_4$ compounds were shown in Fig.6. The reasonably small refinement factors indicate that single phases of $Li_{1+x}Mn_{1-x}PO_4$ (-0.05 $\leq x \leq 0.03$) compounds were obtained in our work. These results indicate that there exists a solubility of $-0.05 \leq x \leq 0.03$ for $Li_{1+x}Mn_{1-x}PO_4$ samples. Comparing our results with that of Lin et al. [19], where the LiFePO₄ has much larger solid solubility with $-0.15 \leq x \leq 0.06$ than that of $-0.05 \leq x \leq$

0.03 in the $Li_{1+x}Mn_{1-x}PO_4$ compounds, the smaller solubility of LiMnPO₄ may be attributed to the relative larger difference of ionic radius between Li^+ ion (0.76 Å) and Mn^{2+} ion (0.83 Å) if one compare it of 0.76 Å to Li^+ ion and 0.78 Å to Fe^{2+} ion. Actually, the situation of solid solution in LiMPO₄ compounds is similar to the cation mixing phenomenon which was detected in hydrothermally prepared LiFePO₄ [39] and LiMnPO₄ [40]. Fang et al. [40] reported a suitable formula of Li_{0.828}Mn_{0.086}MnPO₄ for hydrothermally synthesized LiMnPO₄ sample, which exhibits a much large solubility of manganese ions substitution onto Li-site. The great difference in solubility of Li_{1+x}Mn_{1-x}PO₄ between the solid state method and hydrothermal method may be owing to the lower synthesis temperature and the liquid synthesized environment. However the cation mixing between lithium and manganese ions on the crystallographic 4a and 4c site of the olivine structure can be often observed which may be unfavorable for the electrochemical performance of the LiMnPO₄ sample. The olivine structure LiMnPO₄ consists of a distorted hexagonal close-packed oxygen framework with Li and Mn occupy octahedral site and P in the tetrahedral site [4]; this crystallographic environment makes one-dimensional tunnels through which lithium ions migrate. Partial occupation of Li⁺ lattice sites by Mn²⁺ will block the one-dimensional tunnels of lithium diffusion. Conversely, a partial occupation of Mn²⁺ lattice sites by Li⁺, in order to insure local charge neutrality, the stronger electrostatic attraction between oxygen and Li^+ (4a) ions will be unfavorable for lithium diffusion. In addition, the obviously difference of the ionic radius between Li⁺ and Mn²⁺ will lead to the distortions of the one-dimensional tunnels which can

hinder lithium diffusion.

Fig. 7 shows the corresponding lattice parameters as a function of content x obtained by the refinement results. It is noted that with the increasing of amount of excess Mn-ion (x < 0) in the structure, the lattice parameters show elongation of the c axis and shrinkage in the a and b axes and a consequent augment of the unit-cell volume. While, the inversed tendency of lattice parameters with the content x can be observed for the increase amount of excess Li-ion (x > 0). The difference gradient of the lattice parameters change between x > 0 and x < 0 may due to the different electronic environment caused by the different valence stage between the excess Mn²⁺-ion and Li⁺-ion, which will change the structure dependently.

3.3.2 Electrochemical properties of Li_{1+x}Mn_{1-x}PO₄

As we know that the low electronic conductivity($<10^{-10}$ S cm⁻¹) and low ionic diffusion coefficient($\sim 10^{-15}$ cm² s⁻¹) have been major obstacles hindering applications of LiMnPO₄. Strategies such as doping and conductive carbon coating that employed to LiFePO₄ have also been resolved to LiMnPO₄, expecting improvement in electrochemical performance. In the previous report [41], Chung et al. reported appropriate doping metal supervalent Nb to Li⁺ in LiFePO₄ enable forming black P-type conductors which leading to a significant improvement in electrochemical performance.

Here, the electrochemical capacities of $Li_{1+x}Mn_{1-x}PO_4$ (*x* = -0.05, -0.02, 0.00, 0.02, 0.03) solid-solution were compared. The electrochemical tests were performed at a

current density of 5 mA/g between the voltages of 2.0 V and 4.5 V. Their initial charge and discharge curves are shown in Fig.8. All Li_{1+x}Mn_{1-x}PO₄ samples exhibited charge plateaus at around 4.2 V and the discharge plateau at around 4 V, showing an average voltage of 4.1 V vs. Li/Li⁺. In addition, the initial discharge capacity of 93 mAhg⁻¹ was obtained for pristine LiMnPO₄ compound, which agrees well with that of Pieczonka's result [42]. As shown in Fig.8, a decrease of initial discharge capacity for solid solution $Li_{1+x}Mn_{1-x}PO_4$ compounds were observed. The discharge capacity of 76 mAhg⁻¹, 42 mAhg⁻¹, 72 mAhg⁻¹, 61 mAhg⁻¹ and 35 mAhg⁻¹ can be obtained with the x = 0.02, 0.03, -0.02, -0.04 and -0.05, respectively. For Li_{1+x}Mn_{1-x}PO₄ (x = 0.02, 0.03) compounds, the loss capacity may due to the decrease of the active plot of Mn^{2+} in $Li_{1+x}Mn_{1-x}PO_4$ after partial Mn^{2+} ion was substituted by Li^+ , which will decrease the capacity contribution of the $Mn^{2+} \leftrightarrow Mn^{3+}$ conversion compared to the pristine. In addition, the charge/discharge plateaus indicate that the solid solutions keep the phase transformation between LiMnPO4 and MnPO4 phase during the charge-discharge process. No matter excess Mn-ion doping in Li-site or excess Li-ion doping into Mn-site, the electrochemical curves of compounds show the same trend, which are gradual decrease in discharge capacity and more unconspicuous platform. The change of the platform in charge/discharge curves can be reflected more clearly in CV curves.

Fig. 9 shows the CV curves of the $Li_{1+x}Mn_{1-x}PO_4$ (x = -0.05, 0.00, 0.03) samples at a scan rate of 0.05 mVs⁻¹ on the potential interval 2.5-4.5 V (vs. Li^+/Li). We can find that the electrochemical response of doped samples, especially the deoxidization peaks, were weaker than the pristine one. It means the substitution in Li-site and Mn-site can not improve the electrochemical activity.

The cycle performance of the $Li_{1+x}Mn_{1-x}PO_4$ (-0.05 $\leq x \leq 0.03$) samples are given in Fig. 10. In order to investigate the rate capability during cycling, various current rates of 0.03C, 0.1C, 0.5C and 1C were applied to the working electrode. Here, the rate performance of $Li_{1+x}Mn_{1-x}PO_4$ samples in Fig. 10 indicated a remarkable degradation for the doping samples. It can be ascribed to the blocking effect caused by the cation mixing between Mn²⁺ and Li⁺. In order to understand influence of block effect on olivine phosphate LiMnPO₄, Electrochemical Impedance spectra (EIS) test have been performed for $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO}_4$ (-0.05 $\leq x \leq 0.03$), as shown in Fig. 11. The relevant parameters, including the Warburg impedance coefficient σ , the diffusion coefficient D, the double layer capacitance C_{dl} and the exchange current density i° , are calculated based on A. Y. Shenouda et. al's report and listed in table 5 [43,44]. With the increasing of the doping content, an obvious decrease of the value of the D can be observed for doped sample. Here, for the LiMnPO₄ sample, the value of the D is 2.62×10^{-13} cm²s⁻¹. For the Li_{1.03}Mn_{0.97}PO₄ and Li_{0.95}Mn_{1.05}PO₄ samples, the values of the D are 3.25×10^{-14} and 6.43×10^{-14} cm²s⁻¹ respectively. In order to confirm the result of the Li ion diffusion coefficient D, the GITT curves of $Li_{1+x}Mn_{1-x}PO_4$ in the voltage of 2.0-4.5V are also performed. The typical GITT results for $Li_{1+x}Mn_{1-x}PO_4$ samples with x = 0.00 and x = 0.03 are shown in Fig. 12. The diffusion coefficients obtained through GITT results are shown in Table 6 [45]. Compared with the EIS results, the same decreasing trend was observed. To conclude, the poor capacity for $Li_{1+x}Mn_{1-x}PO_4$ (x = -0.02, -0.04, -0.05) compounds in our experiment can be ascribed

to the blocking effect of Mn-ion after it occupied the Li-ion position, which will impede the diffusion of Li^+ during the electrochemical process, ultimately reduce the electrochemical activity.

4. Conclusions

The phase diagram of Li₂O-MnO-P₂O₅ ternary system under reduction atmosphere (95% Ar + 5% H₂) has been investigated. Four ternary compounds are verified and the solid solution ranges of $Li_{1+x}Mn_{1-x}PO_4$ (-0.05 $\leq x \leq 0.03$) is determined. Inferior to what we expected, no other new lithium manganese phosphates exist within the Li₂O-MnO-P₂O₅ ternary system under the reducing atmosphere. In MnO-P₂O₅ system, a high-pressure phase $Mn_3(PO_4)_2$ with graftonite Fe₃(PO₄)₂-type structure is easily obtained under our experiment condition and its detail structure is presented. In addition, the Rietveld refinement of the crystal structure reveals that the lattice parameters of $Li_{1+x}Mn_{1-x}PO_4$ solid solutions vary linearly with the increase amount of excess Li-ion ($x \ge 0$) or with the increase amount of excess Mn-ion (x < 0). In addition, the electrochemical properties of C-Li_{1+x}Mn_{1-x}PO₄ (-0.05 $\leq x \leq 0.03$) compounds are also compared at a current density of different current rates between 2.0 V and 4.5 V, and the results show that excess Li-ion ($x \ge 0$) or the excess Mn-ion ($x \le 0$) in LiMnPO₄ have an unfavorable effect on the electrochemical properties caused by the deterioration of the lithium diffusion along the one-dimensional tunnels.

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References

- [1] Y. Liu, R. Ma, Y. He, M. Gao, H. Pan, Adv. Funct. Mater. 24 (2014) 3944–3952.
- [2] Y. Wu, M. Gao, X. Li, Y. Liu, H. Pan, J. Alloys Compd. 608 (2014) 220-228.
- [3] M. Wang, X. Li, M. Gao, H. Pan, Y. Liu, J. Alloys Compd. 603 (2014) 158–166.
- [4] A. Yamada, Y. Kudo, K. Y. Liu, J. Electrochem. Soc. 148 (2001) A747-A754.
- [5] C. K. Back, R. Z. Yin, Y. S. Kim, J. Electrochem. Soc. 160 (2013) A1551-A1558.
- [6] J. Liu, W. Liao, A. Yu, J. Alloys Compd. 587 (2014) 133–137.
- [7] J. Wolfenstine, J. Read, J. L. Allen, Journal of Power sources 163 (2007) 1070-1073.
- [8] J. Wolfenstine, J. L. Allen, J. Power Sources 136 (2004) 150-153.
- [9] D. Morgan, A. van der Ven, G. Ceder, Electrochem. Solid-State Lett. 7 (2004) A30-A32.
- [10] K. Amine, H. Yasuda, M. Yamachi, Electrochem. Solid-State Lett. 3 (2000) 178-179.
- [11] X. Li, S. Liu, H. Jin, Y. Meng, Y. Liu, J. Alloys Compd. 614 (2014) 7–12.
- [12] Y. Gan, C. Chen, J. Liu, P. Bian, H. Hao, A. Yu, J. Alloys Compd. 620 (2015) 350–357.

- [13] Y. Zhang, Y. Zhao, Ionics 17 (2011) 457-461.
- [14] L. Adam, A. Guesdon, B. Raveau, J. Solid State Chem. 181 (2008) 3110-3115.
- [15] S. H. Lee, S. S. Park, Chem. Mater. 24 (2012) 3550-3557.
- [16] R. A. Shakoor, H. Kim, W. Cho, S. Y. Lim, H. Song, J. W. Lee, J. K. Kang, Y. T. Kim, Y. Jung, J. W. Choi, J. Am. Chem. Soc. 134 (2012) 11740-11748.
- [17] S. N. Lee, S. Baek, S. Amaresh, V. Aravindan, K. Chung, B. Cho, W. Yoon, Y. Lee, J. Alloys Compd. 630 (2015) 292–298.
- [18] S. Ping Ong, L. Wang, B. Kang, G. Ceder, Chem. Mater. 20 (2008) 1798-1807.
- [19] X. Lin, Y. Zhao, Y. Dong, Z. Liang, D. Yan, X. Liu, Q. Kuang, J. Mate. Sci. 50 (2015) 203-209.
- [20] L. K. Minacheva, M. A. Porai-Koshits, A. S. Antsyshkina, V. G. Ivanova, A. V. Lavrov, Koordinatsionnaya Khimiya 1 (1975) 421-428.
- [21] A. Olbertz, D. Stachel, I. Svoboda, H. Fuess, Zeitschrift fuer Kristallographie 209 (1994) 899-899.
- [22] A. Olbertz, D. Stachel, I. Svoboda, H. Fuess, Zeitschrift fuer Kristallographie 210 (1995) 220-220.
- [23] R. Glaum, H.Thauern, A. Schmidt, M. Gerk, Zeitschrift fuer Anorganische und Allgemeine Chemie 628 (2002) 2800-2808.
- [24] Natl. Bur. Stand. (U.S.) Monogr. 25 (1977) 21-21.
- [25] T. Stefanidis, A. G. Nord, Acta Crystallogr. C. 40 (1984) 1995-1999.
- [26] J. S. Stephens, C. Calvo, Canadian Journal of Chemistry 47 (1969) 2215-2225.
- [27] A. G. Nord, H. Annerstenb, Acta Chemica Scandinavica 41 (1987) 56-58.

- [28] W. Massa, O. V. Yakubovich, O. V. Dimitrova, Solid State Sci. 7 (2005) 950-956.
- [29] H. M. Rietveld, J. Appl. Cryst. 2 (1969) 65-71.
- [30] E. Kostiner, J. R. Rea, J. Inorganic Chemistry 13 (1974) 2876-2880.
- [31] W. I. F. David, J. B. Goodenough, M. M. Thackeray, M. G. S. R. Thomas, Revue de Chimie Minerale 20 (1983) 636-642.
- [32] S. Geller, J. L. Durand, Acta Cryst. 13 (1960) 325-331.
- [33] C. O. Bjoerling, A. Westgren, Geologiska Foereningens I Stockholm Foerhandlingar 60 (1938) 67-72.
- [34] O. Garcia-Moreno, M. Alvarez-Vega, F. Garcia-Alvarado, J. Garcia-Jaca, J. M. Gallardo Amores, M. L. Sanjuan, U. Amador, Chem. Mater. 13 (2001) 1570-1576.
- [35] J. M. Osorio-Guillen, B. Holm, R. Ahuja, B. Johansson, Solid State Ionics 167 (2004) 221-227.
- [36] L. S. Ivashkevich, K. A. Selevich, A. I. Lesnikovich, A. F. Selevich, Lyakhov, A.S. Zeitschrift fuer Kristallographie 221 (2006) 115-121.
- [37] M. T. Averbuch-Pouchot, A. Durif, Appl. Crystallogr. 5 (1972) 307-308.
- [38] E. V. Murashova, N. N. Chudinova, Kristallografiya 46 (2001) 1024-1029.
- [39] J. Chen, M. J. Vacchio, S. Wang, N. Chernova, P. Y. Zavalij, M. S. Whittingham, Solid State Ionics 178 (2008) 1676-1693.
- [40] H. Fang, Z. Pan, L. Li, Y. Yang, G. Yan, G. Li, S. Wei, Electrochem. Commun. 10 (2008) 1071-1073.
- [41] S. Y. Chung, J. T. Bloking, Y. M. Chiang, Nat. Mater. 1 (2002) 123-128.

- [42] N. P. W. Pieczonka, Z. Liu, A. Huq, J. H. Kim, J. Power Sources 230 (2013) 122-129.
- [43] A. J. Bard, L. R. Faulkner, Electrochemical Methods, second ed., John Wiley & Sons, New York, 2001.
- [44] A. Y. Shenouda, Hua K. Liu, J. Electrochem. Soc. 157 (2010) A1183-A1187.
- [45] X. Rui, N. Ding, J. Liu, C. Li, C. Chen, Electrochimica Acta 55 (2010) 2384–2390.

Captions for Figures and Tables

Table 1 Crystal data for α -Mn₃(PO₄)₂ and related compounds

Table 2 Atomic sites and coordinates of α -Mn₃(PO₄)₂ sample determined from

Rietveld refinement of power X-ray Diffraction at 300K

Table 3 Bond distances for manganese and phosphor polyhedral

Table 4 Phase regions and phase compositions in the Li₂O-MnO-P₂O₅ ternary system

Table 5 the related parameters calculated data from EIS plots

Table 6 the Li-ion diffusion coefficient D calculated from GITT test results.

Fig. 1 X-ray diffraction patterns of α -Mn₃(PO₄)₂ and related compounds.

Fig. 2 Rietveld refinement results of α -Mn₃(PO₄)₂ sample.

Fig. 3 (a) Structure of α -Mn₃(PO₄)₂, projected from the c-aixs direction; (b) Plot of α -Mn₃(PO₄)₂ crystal structure showing polyhedra linkage.

Fig. 4 Subsolidus phase relations of the LiO₂-MnO-P₂O₅ system: (A) $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO4}$ (-0.05 $\leq x \leq 0.03$); (B) $\text{Li}_2\text{MnP}_2\text{O}_7$; (C) $\text{Li}_2\text{Mn}(\text{PO}_3)_4$; (D) $\text{LiMn}(\text{PO}_3)_3$; dots: single phase; square: two phases; triangle: three phases.

Fig. 5 XRD patterns of $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO}_4$ (-0.05 $\leq x \leq 0.03$) solid solutions.

Fig. 6 Rietveld refinement results of Li_{1.03}Mn_{0.97}PO₄ and Li_{0.95}Mn_{1.05}PO₄ samples.

Fig. 7 Lattice parameters of $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO}_4$ (-0.05 $\leq x \leq 0.03$) samples as a function of *x* content.

Fig.8 The initial charge-discharge curves of $Li_{1+x}Mn_{1-x}PO_4$ (-0.05 $\leq x \leq 0.03$) samples.

(a) x = 0; (b) x = -0.02; (c) x = 0.02; (d) x = -0.04; (e) x = 0.03; (f) x = -0.05.

Fig.9 CV curves of the Li_{1+x}Mn_{1-x}PO4 (-0.05, 0.00, 0.03) samples

Fig.10 the cycle performance of the $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO}_4$ (-0.05 $\leq x \leq 0.03$) samples

Fig.11 Impedance spectra for $\text{Li}_{1+x}\text{Mn}_{1-x}\text{PO}_4$ (-0.05 $\leq x \leq 0.03$)

Fig. 12 the typical GITT results for $Li_{1+x}Mn_{1-x}PO_4$ samples with x = 0.00 and x = 0.03