Electrochemical Lithium Extraction and Insertion Process of Sol-Gel Synthesized LiMnPO_4 via Two-Phase Mechanism

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Abstract Text

Olivine-type LiMnPO_4 was synthesized via a citric-acid assisted sol-gel method. The structural evolution of the as-prepared material during calcination and the crystallization of LiMnPO_4 was investigated by XRD measurements. A reaction mechanism including two intermediate phases was derived for the synthesis. Furthermore, the electrochemical Li extraction and insertion processes were studied by *in situ/ex situ* XRD and MAS NMR measurements. The phase transition from LiMnPO_4 to MnPO_4 and *vice versa* proceeds via a two-phase mechanism. The ^{31}P MAS NMR spectra of MnPO_4 , which forms upon delithiation as confirmed by XRD patterns, shows a very broad signal. Possible explanations for the large width of this signal are given and evaluated.

Introduction Text

Phospho-olivines LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{and Ni}$) were discovered as potential cathode material for lithium-ion batteries 20 years ago.¹ Since then, a lot of effort has been put into this next-generation cathode material, especially LiFePO_4 (LFP).^{2,3} Among the olivine family, the iron compound emerged into the market and is utilized in power tools and electric vehicles, for example.

The attention toward these cathode materials is due to their high thermal safety, long cycle life, environmental sustainability, and potentially low cost. The energy density is related to the redox potential of the transition metal ion. Starting from $\text{Fe}^{3+}/\text{Fe}^{2+}$ in LFP (3.4 V vs. Li^+/Li) the energy density of the phospho-olivine increases with $\text{Mn}^{3+}/\text{Mn}^{2+}$ (4.1 V), $\text{Co}^{3+}/\text{Co}^{2+}$ (4.8 V), and $\text{Ni}^{3+}/\text{Ni}^{2+}$ (5.1 V).⁴ However, only the Fe- and Mn-compounds operate within the stability window of standard electrolytes. Furthermore, note that there are

discussions about the thermal stability of MnPO_4 (MP), the delithiated form of LiMnPO_4 (LMP). Earlier reports show a decomposition of MP evolving at 210 °C with oxygen release.^{5,6} Nevertheless, recent studies conclude that this decomposition is mostly dependent on the content of absorbed water (to a lesser extent on particle size) and can be suppressed by carbon coating.^{7,8}

There are also drawbacks for phospho-olivines like the low intrinsic electronic conductivity and the poor Li-ion mobility.⁴ The reason for these issues is the orthorhombic olivine-type structure with space group $Pnma$. On the one hand, the structure provides just 1-dimensional channels for the Li-diffusion with very limited jump rate between two neighboring channels. On the other hand, the transition metals form isolated chains of corner-sharing octahedra because of the $(\text{PO}_4)^{3-}$ tetrahedra interconnecting them.⁹ Moreover, LMP suffers from challenges associated with the manganese ion. First of all, the introduction of a Jahn-Teller distortion causes structural strain in the delithiated MnPO_4 .¹⁰ The cell volume shrinkage from LMP to MP is 9.5 %, whereas for LFP to FePO_4 (FP) the volume decreases only by 6.5 %.¹¹ Furthermore, Mn^{2+} ions are known to dissolve into the electrolyte after disproportion inside the MP structure ($2 \text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$), thus limiting the cycle life of the cathode.¹²⁻¹⁵

In order to overcome the main drawbacks of phospho-olivines, several methods have been described in literature that are aiming at synthesizing active LiMPO_4 . However, the underlying ideas are mostly the same: (i) reducing the particle size enhances the kinetics via shorter diffusion paths and (ii) applying conductive coatings promotes the electronic conductivity. Keeping this in mind, ball milling has proven to be inevitable.¹²⁻¹⁴ It decreases the particle size and enables an effective way for coating the cathode material. The cation ordering within the structure is also very important, because anti-site defects (M^{2+} on Li-site and *vice versa*) block the Li-diffusion paths.¹⁹ Furthermore, doping of LiMPO_4 on the transition metal site or the Li-site is often reported to enhance the electrochemical performance.^{9,20,21} Especially the mixed phospho-olivines $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ (with $0 \leq x \leq 1$; LFMP) are promising cathode materials showing higher energy densities compared to pure LFP.²²⁻²⁴

Phospho-olivines exhibit an outstanding high rate capability.²⁵ This was initially contradictory to their two-phase mechanism upon lithiation and delithiation. The formation of a second phase includes a nucleation step, structural rearrangement and furthermore, a movement of the phase boundary. Thus, a solid solution behavior is supposed to promote current rates of 10C and higher. Intensive research on phospho-olivines performed both *in situ* and *ex situ* revealed their versatile electrode phase transitions.²⁶⁻²⁹ The cathode material LFP undergoes a first-order phase transition at thermodynamic equilibrium during (de-)lithiation forming the two phases LiFePO_4 and FePO_4 . Near these end members, small solid solution regimes are observed.³⁰ Increasing the current rate leads to a metastable phase $\text{Li}_{1-x}\text{FePO}_4$ with cell parameters between those of the two end members. If high current rates are applied (10C to 60C), a fraction of the material is transforming via a solid solution transition. The amount of this fraction increases with increasing rates.³¹ It is also noted that the phase transformation mechanism is depending on the particle size. For micrometer-sized particles, the two-phase mechanism occurs, whereas for nanoparticles a solid solution transformation is observed. The ability of forming such a solid solution, which reacts via a single-phase transition, explains the high rate capability of LFP.

The behavior is different for LMP and LiCoPO_4 (LCP), which are less intensively investigated. To our knowledge, there is just one report on LMP addressing the phase transformation during electrochemical delithiation and lithiation from Chen *et al.*³² Their results indicate a small solid solution region near the end phase MnPO_4 and apart from that, a two-phase transition. The chemical delithiation of LMP leads to an amorphous phase $\text{MnH}_x\text{P}_2\text{O}_7$ induced by traces of water. However, if the particles are protected by a carbon coating, crystalline MP can be obtained.⁸

LCP reacts via an intermediate phase with composition $\text{Li}_{1-0.6}\text{CoPO}_4$ that shows solid solution-like behavior. The phase transformation proceeds via two subsequent two-phase steps (namely $\text{Li}_{1.0}\text{CoPO}_4$ to $\text{Li}_{1-0.6}\text{CoPO}_4$ and $\text{Li}_{1-0.6}\text{CoPO}_4$ to CoPO_4 (CP)).^{33–36} The intermediate phase is predicted to compensate the large volume misfit between the two end phases (here LCP and CP).

The mixed phospho-olivines $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ (LFMP, with $0 \leq x \leq 1$) indicate a phase transition depending on the amount of manganese. Generally, the (de-)insertion of Li-ions from LFMP and into $\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ (FMP) occurs via a third intermediate phase $\text{Li}_2\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$.^{37,38} This intermediate phase has a broad solubility range as evidenced by continuous shifts of the observed Bragg-reflections in X-ray diffraction. With higher Mn contents, the unit cell parameters of the intermediate phase and that of the starting phase LFMP converge. Finally, for Mn contents of 0.6 and 0.8 these two phases (LFMP and intermediate phase) are no longer separated and transform reversibly via solid solution mechanism (note that there is still the formation of the end phase FMP).¹¹

As already mentioned the reports for pure LMP are limited and so far, reveal no formation of an intermediate phase despite the large lattice mismatch. Therefore, we investigated olivine-type LiMnPO_4 as cathode material for Li-ion batteries. *In situ* synchrotron radiation diffraction was performed for the first electrochemical cycle of LMP. The data were verified by *ex situ* X-ray diffraction (XRD) and $^7\text{Li}/^{31}\text{P}$ magic-angle spinning (MAS) nuclear magnetic resonance (NMR) measurements.

Experimental

Synthesis

LiMnPO_4/C was prepared via a sol-gel method.³⁹ The starting materials were $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ ($\geq 99\%$, Sigma Aldrich). The molar ratio of the salts was 1.05:1.00:1.00, respectively. They were added subsequently to a vigorously stirred ethanol solution. After the addition of citric acid (1.2 eq, $\geq 99\%$, Merck) the reaction mixture was heated over night at 80°C to form a gel. The gel was dried in a muffle furnace at 120°C for 12 h in air. Afterwards, the brownish powder was ball milled (ZrO_2 balls and vial, 20 min duration, 700 rpm) with 10 wt% sucrose. The calcination was performed at 650°C for 4 h in flowing argon to obtain a black powder.

Materials Characterization

High-temperature XRD investigations were performed at the high-resolution powder diffraction beamline at PETRA-III (P02.1, DESY, Hamburg). The quartz glass capillaries with a diameter of 0.5 mm were filled inside the glovebox with the ground samples and

sealed air tight. The measurements were done stepwise with $\Delta T = 50$ K in a ceramic oven from room temperature to 700 °C.

In situ electrochemical XRD experiments were conducted in a special coin cell setup also at the high-resolution powder diffraction beamline at PETRA-III (P02.1, DESY, Hamburg). Details about the setup and the rotating coin cell holder were described elsewhere.^{40,41} The synchrotron radiation had a photon energy of approx. 60 keV ($\lambda = 0.20719$ Å) and was detected by a 2D flat panel detector (Perkin Elmer amorphous-Silicon detector). The obtained 2D images were integrated to 1D diffraction patterns using the X-ray image processing program Fit2D.⁴² All structure refinements were performed with Rietveld method using the Fullprof software package.⁴³

The electrodes for the coin cells (CR 2032) were prepared by mixing the active material with carbon black (Super P, Timcal) and polyvinylidene fluoride (PVDF) in a weight ratio of 80:13:7, respectively. N-methylpyrrolidone (NMP) was added to obtain a slurry, which was then cast on Al foil. After drying of the electrode film at 60 °C the electrodes were punched out with a diameter of 14 mm. The coin cells were assembled with polypropylene/polyethylene foil (Celgard 2325) as separator, LP-30 electrolyte (ethylene carbonate/dimethyl carbonate (EC/DMC), 1:1 (w/w), 1 M LiPF₆), and Li metal as counter electrode.

Electrochemical tests were performed in stainless steel Swagelok-type cells. The cathode material was ground with 20 % (w/w) carbon black (Super P, Timcal) and inserted into the Swagelok cell. Two sheets of Whatman GF/B separator, LP-30 electrolyte (EC/DMC 1:1 w/w, 1 M LiPF₆), and metallic lithium as counter electrode were used. The cells were prepared in an argon-filled glovebox and connected to a VMP3 multipotentiostat. The electrochemical characterization was performed with galvanostatic cycling in the voltage range of 2.5-4.6 V. For *ex situ* investigations on the cathode material, the Swagelok cells were disassembled in a glovebox and the electrodes were washed several times with DMC.

⁷Li and ³¹P MAS NMR measurements were performed on a Bruker Avance 200 MHz spectrometer ($B_0 = 4.7$ T) using 1.3 mm zirconia rotors in a dry nitrogen atmosphere. The reference for the chemical shift of ⁷Li was an aqueous 1M LiCl solution and the reference for ³¹P was H₃PO₄ (85 %). Typical values for the recycle delay and the $\pi/2$ pulse length were 1 s and 2 μ s, respectively. The experiments were performed at 298 K and a spinning speed of 60 kHz with a rotor synchronized Hahn-echo sequence ($\pi/2$ - τ - π - τ -acquisition).

Magnetization measurements of pristine LiMnPO₄ and products of delithiation/lithiation were performed using a SQUID magnetometer (MPMS) from Quantum Design. The temperature dependences of the magnetization were measured both in zero-field-cooled (ZFC) and in field-cooled (FC) mode between $T = 2$ and 330 K at 0.1 T and 1 T. Magnetic susceptibilities in the paramagnetic region were analysed in terms of the modified Curie-Weiss law with a temperature-independent paramagnetic contribution χ_0 : $\chi = C/(T-\theta) + \chi_0$, where the Curie constant $C = N_A \mu_{\text{eff}}^2 / 3k_B$ yields the effective paramagnetic moment μ_{eff} .

The carbon content of the calcined materials was determined via CHNS analysis (Elementar Vario MICRO CUBE). The morphology of the particles was analyzed by a scanning electron microscope (Merlin Gemini 2, Zeiss).

Results and Discussion

The carbon coated and calcined phospho-olivine LiMnPO_4/C (LMP/C) has an orthorhombic olivine-type structure. The XRD pattern shows a crystalline single-phase material with space group $Pnma$ (Fig. 1). No impurities such as Li_3PO_4 or $\text{Mn}_2\text{P}_2\text{O}_7$ are detected. They usually form due to an off-stoichiometry during synthesis.⁴⁴ Accordingly, the correct stoichiometry for our synthesis procedure is confirmed. The cell parameters $a = 10.453(2) \text{ \AA}$, $b = 6.106(1) \text{ \AA}$, $c = 4.747(1) \text{ \AA}$, and the unit cell volume $V = 302.98(9) \text{ \AA}^3$ were determined by Rietveld refinement. They are in good agreement with values from literature [$a = 10.449(1) \text{ \AA}$, $b = 6.105(1) \text{ \AA}$, $c = 4.746(1) \text{ \AA}$].⁸ The volume-weighted averaged crystallite size is 40 nm based on the refinement. The value was calculated by the Fullprof software using a dependency of $1/\cos\theta$ on the width of the reflections. In order to exclude contributions from the instrument, the instrumental resolution function was determined by a measurement on well-crystalline LaB_6 powder.

Fig. 1 Rietveld refinement based on the XRD pattern of carbon coated LiMnPO_4 (LMP/C).

The structural evolution of the material during calcination was investigated with synchrotron radiation (high temperature XRD, Fig. 2). The as-prepared powder (after sol-gel synthesis) was filled in a 0.5 mm glass capillary and sealed in Ar atmosphere. The XRD patterns were collected during stepwise heating the capillary up to 700 °C. Up to this temperature, the capillary was still intact. In the beginning, no distinct Bragg reflections are visible due to the amorphous structure of the sample. At 500 °C the first reflections begin to appear. They belong to three different phases: $\text{Mn}_3(\text{PO}_4)_2$, Li_3PO_4 , and LiMnPO_4 . When the calcination temperature is further increased, the reflections of LMP are increasing in intensity and those of the other phases vanish. Finally, at 600 °C only the orthorhombic olivine-type structure of LMP (space group $Pnma$) remains. The calcination temperature for the formation of LMP is within the range reported in literature (between 500-700 °C).^{39,45}

Fig. 2 High-temperature XRD patterns of LiMnPO₄ after sol-gel synthesis and drying at 120 °C.

Based on these results the chemical reaction proceeds as follows:

The starting materials react to amorphous Li₃PO₄ and Mn₃(PO₄)₂ under the synthesis conditions. At elevated temperatures, the crystallization of these two phases begin and LiMnPO₄ originates. There are also reports in literature on the formation of olivine-type LiMnPO₄.^{16,46} However, they are based on samples which have been successively calcined at different temperatures in contrast to our *in situ* calcination. Drezen *et al.* measured the evolution of olivine phases at 350 °C for sol-gel samples after the calcination for 5 h. If the temperature of the calcination is increased, LiMnPO₄ and small amounts of Li₃PO₄ are detected by XRD measurements.¹⁶ In contrast to our results, no Mn₃(PO₄)₂ was seen in the patterns and LiMnPO₄ forms directly without any intermediate phases. Consequently, LiMnPO₄ had to be formed during the sol-gel procedure. This can be ascribed to the control of the pH-value during synthesis. Nevertheless, another report on the solvothermal synthesis of LiMnPO₄, directly starting with Li₃PO₄ and Mn²⁺ ions, is emphasizing the formation of Mn₃(PO₄)₂ as an intermediate phase.⁴⁶ This finding is in agreement with our results. In summary, we investigated the evolution of LiMnPO₄ during calcination from the intermediate phases Li₃PO₄ and Mn₃(PO₄)₂, which have been formed during sol-gel synthesis. The XRD patterns acquired at higher temperatures (T ≥ 600 °C) show just slight changes, mainly the shift of the reflections towards smaller angles because of the increasing cell volume due to the higher temperatures.

The scanning-electron micrographs (Fig. 3) show the LMP material before and after ball milling. Before the milling procedure, large particles and agglomerates with sizes in the micrometer range are visible. They have disordered morphology and are irregular in size and shape. After milling the material for 20 min, the particles are spherical and have a homogeneous size distribution between 100 and 200 nm. 10 % sucrose (w/w) was added to the material before milling to prevent agglomeration and to introduce a further carbon source surrounding the particles. Nevertheless, the particles still form larger agglomerates. The as-prepared material contains 20 % (w/w) carbon, which reduces to 9 % (w/w) after calcination (650 °C for 4 h in flowing argon) in both cases: without prior ball milling (sample labeled as “LMP/no ball mill”) and with ball milling (sample labeled as “LMP/no sucrose”). The carbon content of the LMP/C material (with addition of sucrose) was determined after calcination to be 15 % (w/w). Compared to literature, this value is relatively high, but the LMP/C material exhibits superior electrochemical behavior in contrast to the sucrose free LMP sample.^{47–49}

Fig. 3 Scanning-electron micrographs of calcined LiMnPO_4 at different magnifications, (a) before ball milling and (b) after ball milling.

Electrochemical tests were performed for three different samples of LiMnPO_4 . One sample was taken after sol-gel synthesis and subsequent calcination (LMP/no ball mill). The other two samples were initially ball milled either with addition of sucrose or without (LMP/C and LMP/no sucrose). The first galvanostatic cycle of all three samples is depicted in figure 4a. The charge capacities range from 20 mAh/g for the directly calcinated LMP to 80 mAh/g for LMP/no sucrose and 135 mAh/g for LMP/C (theoretical capacity: 171 mAh/g). All values decreased during the first discharge by 25 %, reaching 15, 60, and 105 mAh/g, respectively. This irreversible capacity fade is ascribed to side reactions of the electrolyte at high potentials (> 4.3 V) with carbon and active material.^{50–53} The large difference in the capacity between

the three samples is attributed to the ball milling step, which reduces the particle size and introduces lattice disorder. On the other hand, the carbonization of sucrose enhances the electronic conductivity. Note that the specific capacities were calculated excluding the carbon content of the cathode material. The voltage profile of LMP/C clearly shows a flat plateau around 4.1 V assigned to the redox reaction of $\text{Mn}^{3+}/\text{Mn}^{2+}$. This flat plateau is a first indication for a two-phase mechanism of the re-insertion process. The polarization of 0.19 V is quite high and well known for olivine-type LiMnPO_4 .⁵⁴ Further electrochemical tests were performed with LMP/C. The rate capability of this material was investigated with a constant current cycling protocol up to 1C-rates (Fig. 4b). The specific capacity stabilizes during the first 10 cycles reaching more than 100 mAh/g and a coulombic efficiency of 97 %. The reversible capacities decrease for increasing C-rates, delivering 90 mAh/g for C/50, 70 mAh/g for C/5, and 47 mAh/g for 1C. The limited rate capability is attributed to the poor ionic and electronic conductivity. However, the capacity partially recovers after applying a rate of C/50 showing a good cycling stability.

Fig. 4 a) Electrochemical influence of ball milling and sucrose addition on LMP samples. Illustrated is the first galvanostatic cycle at a rate of C/100 between 2.5 and 4.6 V vs. Li^+/Li . b) Rate capability test of LMP/C at the same voltage window. The cathode material contains 9 %, 8 %, and 15 % (w/w) carbon for LMP/no ball mill, LMP/no sucrose, and LMP/C, respectively. In addition to that, 20 % (w/w) carbon black was added to each cathode material. The specific capacity is calculated without the carbon content to obtain a direct measure for the degree of active material access.

The structural changes of LMP/C during electrochemical cycling were investigated by *in situ* XRD. Furthermore, we prepared samples with different state-of-charge during the first cycle and investigated them via XRD and NMR methods (*ex situ* samples). In addition to the high background and strong Bragg reflections from the setup (aluminum foil and metallic lithium), the *in situ* XRD patterns show the orthorhombic $Pnma$ phase from the LMP/C cathode as expected (Fig. 5).

Fig. 5 *In situ* XRD measurement of the first electrochemical cycle of LMP/C. The figure shows the evolution of the 211/ 020 reflections as overlay (left) and as contour plot (right). The electrochemical cycling was performed with C/40 between 2.5-4.6 V. The red arrows indicate the changes observed during charging.

The intensity for this phase decreases during charge and increases again during discharge, while the reflections remain at their position. This behavior is characteristic for the two-phase mechanism, here between the two isostructural phases LMP and MP. For the second phase, the 020/ 211 reflections are clearly visible during the *in situ* measurement at 4.0° . They are very broad due to the decreased crystallite size and micro strain of the structure. The reflections appear during delithiation and vanish after lithiation. However, the intensity for these reflections remains quite low, since the cathode is only charged to a Li content of $x = 0.45$ in the *in situ* cell (derived from electrochemical data, here x denotes the overall Li content of the two-phase mixture). The value of 0.45 is in good agreement with the two reflections of LMP and MP (at 3.9° and 4.0° , respectively) which have a similar integrated intensity at the end of charge. After the first cycle, the pattern is very similar to the initial one, except for some loss of intensity. The deficit results from the uncompleted re-insertion to $x = 0.83$. Furthermore, the background increased at small angles ($\sim 2\text{-}4^{\circ}$) after the first charge (Fig. 6), indicating a partial amorphization of the cathode material. This increase seems to be more pronounced at the end of charge. These observations confirm the finding of the electrochemical measurement for side reactions of the cathode material with the electrolyte, especially at elevated voltages. The amorphization also contributes to the loss of intensity in the XRD pattern at the end of discharge.

Fig. 6 Partial amorphization of LMP/C during first charge observed by the increased background in the *in situ* pattern. For better visualization only six patterns with the same interval of 3.5 h are shown in the figure.

The *ex situ* XRD experiments confirm the two-phase mechanism as discussed before (Fig. 7). During charge, the intensity of the LMP phase decreases while that of the MP phase increases, and *vice versa* during discharge. The reflections of both phases do not shift significantly, revealing the absence of a solid solution region between them (Fig. 8).

Fig. 7 a) The voltage profile shows the corresponding state of charge of the *ex situ* samples, cycled with C/100 between 2.5-4.6 V vs. Li^+/Li . b) *Ex situ* XRD patterns of LMP/C at different states of charge as specified by x as overall Li content of the two-phase mixture. Dotted lines visualize the new Bragg reflections with hkl indices for MnPO_4 appearing during charge.

Fig. 8 Unit cell volumes of LMP/C and MP/C determined from the *ex situ* XRD measurements versus Li content (the Li content is based on electrochemical data assuming that the flow of one electron corresponds to the exchange of one Li-ion). Here x denotes the overall Li content of the two-phase mixture.

The marginal differences of the unit cell volume originate from the changing Li content of the material. The lattice parameters of MnPO_4 obtained from the pattern of the charged sample are $a = 9.661(4) \text{ \AA}$, $b = 5.925(2) \text{ \AA}$, $c = 4.783(1) \text{ \AA}$, and $V = 273.8(2) \text{ \AA}^3$ based on Rietveld refinement. The values are consistent with other reports from literature.^{7,55} Furthermore, no intermediate phase Li_xMnPO_4 forms during cycling as discussed in literature for olivine-type LFP,⁵⁶ LiCoPO_4 (LCP),^{33,34} and cation-mixed $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ (LFMP).³⁷ The first pattern of pristine LMP/C consists only of a single crystalline phase with the olivine-type structure (Fig. 7b). The second phase MP appears at a Li content of $x = 0.51$ (half charged) and increases in intensity until the end of charge at $x = 0.11$. At the same time, the LMP phase decreases in intensity, but is still present in the charged sample. The structural difference between the two phases results from the changed unit cell parameters for the delithiated MP. The lattice constants a and b decrease by 7.6 and 3.0 %, respectively, while c increases slightly by 0.8 %. MnPO_4 exhibits an anisotropic deformation causing structural strain of the lattice. The bond lengths and angles are distorted. The values based on Rietveld refinement are summarized in figure 9. Compared to theoretical values from literature, our experimental results show agreement.^{55,57}

Fig. 9 MnO₆ octahedron of initial LMP/C and deformation of the charged material MP/C due to Jahn-Teller distortion indicated by arrows (left). The symmetry of the octahedron is S_2 leading to equivalent bonds O3/O4 and O5/O6. Bond lengths and bond angles of initial LMP/C and the charged material are based on Rietveld refinement (right).

The cell parameters for both phases LMP and MP are only 2-5 % smaller and the ionic coordinates are similar to the DFT calculated values.⁵⁵ However, there is a difference for MP at the x and z coordinate on the O(8d) Wyckoff position. The x coordinate is 9 % and the z coordinate 12 % smaller compared to theoretical values. Concerning the structure of the Jahn-Teller distorted octahedron, this correlates with an elongated Mn-O5/O6 bond length (2.05 Å vs. 1.94 Å) and a narrowed O5-Mn-O6 bond angle (124.9° vs. 133.0°). Apart from that, the distortion of the structure agrees with literature. Upon discharge, the phase evolution is reversed. The amount of LMP increases and the amount of MP decreases until it disappears at $x = 0.61$. The relative intensities of the Bragg reflections coincide with the olivine-type structure of LMP/MP. Note that the intensities of MP during charge/discharge increase not linearly with respect to the amount of extracted/inserted lithium. When Li is extracted from the structure, the MP phase is not visible in the XRD pattern until the cell is half charged ($x = 0.51$). Upon further extraction of lithium, the intensity of MP increases disproportionately from $x = 0.27$ to 0.11. During re-insertion of lithium, the intensity of MP decreases almost completely until $x = 0.38$. It seems that the formation of crystalline MP is hindered in the beginning, maybe due to the strong rearrangements of the structure, resulting in an offset. For discharge, the crystalline MP declines very fast, indicating the instability and high energy of the material. In agreement with that, the *in situ* measurements also depict an offset for the formation of crystalline MP and the fast decrease during discharge. The *ex situ* XRD patterns were also analyzed with Rietveld refinement and examined with respect to an amorphization (Fig. 10). Therefore, the XRD patterns were measured with the same capillary type and the data were normalized. The pattern of the charged sample reveals an increased background, indicating the formation of an amorphous phase. Again, this agrees with previous results from electrochemical and *in situ* XRD measurements. The cathode material experiences amorphization at higher potentials during charge, because of side reactions with the electrolyte. The increase of the background is more pronounced in the *ex situ* pattern compared to *in situ* measurements, because of the slower applied C-rate (C/100 vs. C/40).

Fig. 10 Comparison of the XRD patterns of pristine ($x = 1$) and charged ($x = 0.11$) LMP/C showing the increased background, which is visualized by dashed lines.

The *ex situ* samples were also investigated by ^7Li and ^{31}P MAS NMR measurements. This method is very sensitive to the chemical environment of the observed nucleus, because of the interaction of electrons from the neighboring elements with the nucleus via bonds. Each environment corresponds to a distinct peak in the spectrum and modifications like the oxidation or reduction of the neighbors result in a shift of the peak. However, if the structure is amorphous or highly disordered, this can lead to a strong peak broadening because of multiple different overlapping environments around the nucleus. The two-phase mechanism and the absence of an intermediate phase can be confirmed by this technique. The ^7Li NMR spectrum of the pristine compound (Fig. 11a) is characterized by a strong peak at 67 ppm corresponding to LMP. The large shift is caused by the interaction of the Li nucleus with unpaired electron spin density of the paramagnetic Mn^{2+} ions via Li-O-Mn bonds.⁵⁸ The shift value is characteristic for the local environment inside the LiMnPO_4 olivine structure.^{57,59,60} As expected, the intensity of the Li signal at 67 ppm first decreases during the extraction of lithium from the structure and then increases with the insertion of lithium back into the material (Fig. 11a). The second phase MnPO_4 does not generate a new ^7Li peak, because it contains no lithium. However, an intermediate phase with partial Li content and mixed $\text{Mn}^{2+}/\text{Mn}^{3+}$ environment around the Li nucleus would form a new peak.^{33,37} The ^7Li MAS NMR spectra reveal no evolution of a new peak and thus confirm the absence of an intermediate phase. The peak position and the variation of intensities in the spectrum are similar to those in literature observed with *ex situ* ^7Li MAS NMR measurements on LFMP.³⁷ Furthermore, the peak does not shift and recovers after the first cycle, apart from a slightly smaller intensity. This verifies the two-phase mechanism and the absence of a solid solution. The solid solution mechanism would be characterized by peak shifts due to progressing alterations inside the structure towards the final lithium-free end-member phase. The pristine compound shows a peak at -1 ppm, which reveals the presence of Li in a diamagnetic compound such as LiOH or Li_2CO_3 . This phase disappears during cycling and the peak in the

fully charged sample (after one complete cycle) might just represent residues of the electrolyte salt.

The *ex situ* ^{31}P spectra (Fig. 11b) show a strong isotropic peak at 7955 ppm corresponding to LMP. Clement *et al.* measured a similar value for this material (7879 ppm)⁶¹ and theoretical calculations indicate a signal between 7250 and 8650 ppm.⁵⁷ Note that the exact peak position depends on the spinning speed, as it influences the exact sample temperature. We observed an increase in the ^7Li and ^{31}P NMR shifts by 3 % when the spinning speed is reduced from 60 kHz to 50 kHz, because the paramagnetic coupling increases with decreasing temperature according to Curie-Weiss law. This explains the small shift of the signals from sample to sample. While the isotropic peak at 7955 ppm shows only one broad resonance, the spinning sidebands at 8700 ppm suggest that it might consist of two overlapping peaks. During cycling, the peak at 7955 ppm decreases in intensity until it almost disappears for the completely delithiated sample and rises again for the relithiated ones. This behavior is very similar to the results of the ^7Li MAS NMR measurement. During delithiation, a very broad resonance is formed at about 7450 ppm, which becomes apparent only at the very end of charge. This peak can be assigned to the fully delithiated state MnPO_4 .⁸ For the pristine material, a narrow peak at 0 ppm is visible which represents P in a diamagnetic environment such as Li_3PO_4 . During cycling, this peak disappears and another resonance appears with a quite large negative shift of -157 ppm that might hint at H neighbors around the P, i.e. some Li-H exchange.^{62,63}

Fig. 11 a) ^7Li and b) ^{31}P MAS NMR spectra of LMP/C samples at different state of charge, acquired at a spinning speed of 60 kHz and a recycle delay of 1 s. Spinning sidebands are marked with an asterisk, a plus sign, and a cross. The intensity of the spectra is normalized with respect to the sample mass (in the range 1.9-4.2 mg) and the number of scans (7000-17000 for ^7Li and 60000-75000 for ^{31}P).

The total intensity for the ^{31}P spectra should remain constant since the phosphorus is not removed from the structure. This was already shown in literature for the LFP system^{64–66} and the LCP system.³³ Concerning the LMP system, Huang *et al.* investigated chemically delithiated MP and measured a ^{31}P MAS NMR signal around 7500 ppm for carbon coated MP,⁸ which is in good agreement with our result. Furthermore, a density functional theory (DFT)-based report calculated shifts in the range of 7589–9216 ppm.⁵⁷ In our case, for the electrochemically delithiated and carbon coated LMP, the NMR spectra show a very broad signal. The intensity of this signal cannot be easily determined due to the overlapping background and the limited signal-to-noise ratio. *Ex situ* XRD experiments revealed a crystalline contribution for MP and consequently a clear peak was expected in the ^{31}P NMR spectra. The large width of the ^{31}P NMR signal for the delithiated phase might be caused by multiple effects: (i) MnPO_4 was metastable and/or decomposed by the formation of an amorphous phase, leading to a flat peak in the NMR spectra. Note that the MAS NMR rotors are air tight, but generate a certain heat upon spinning. The decomposition was not investigated by XRD analysis after MAS NMR measurements; (ii) the structure of MnPO_4 is highly disordered due to the Jahn-Teller distortion, which leads to multiple different environments around the phosphorus atom. Furthermore, the environment consists of five unequal manganese sites that can be occupied by either Mn^{2+} or Mn^{3+} ions. This variety of contributions to the ^{31}P signal results in a broad and flat signal; (iii) the NMR signal is strongly broadened due to an intensive magnetic coupling between the Mn^{3+} moments. Therefore, we used SQUID measurements to observe the variation of the average magnetic moments during electrochemical cycling (Fig. 12).

Fig. 12 SQUID measurements of electrochemically cycled LMP/C at different states of charge. The data show a behavior in agreement with Curie-Weiss law (left) and the effective paramagnetic moments against the averaged Li content (right).

During delithiation, the average paramagnetic moment decreases in agreement with a simple model of co-existence of high-spin HS- Mn^{2+} and Mn-cations in a higher oxidation state in the material. For our calculations, we proposed the presence of HS- Mn^{3+} in the material.

However, this scenario is not straightforward because of a more delocalized character of electrons and, therefore, an increased temperature-independent Pauli-paramagnetism-like term in the total magnetization in Li-deficient materials. In conclusion, the first explanation seems not reliable, since XRD measurements on the aged material confirm the stability of the phase and since MnPO_4 is normally stable at least until 200 °C. The second explanation about the highly disordered structure of MnPO_4 is the most reliable one. The structure suffers from severe rearrangements during delithiation and reveal a distortion of the MnO_6 octahedra due to the Jahn-Teller effect, which in turn cause distortions in the local environment around P. Furthermore, the disorder of MnPO_4 is already indicated by broad reflections during the *in situ* XRD measurement resulting from micro strain.

Conclusions

After sol-gel synthesis the as-prepared material consists of Li_3PO_4 and $\text{Mn}_3(\text{PO}_4)_2$. During calcination, the two phases react completely to olivine-type LiMnPO_4 at 600 °C. Ball milling and the addition of sucrose as carbon precursor improve the electrochemical performance. The specific capacities are increased from 15 mAh/g to 105 mAh/g. Carbon coated LiMnPO_4 with particle sizes of 100-200 nm displays a two-phase reaction upon electrochemical extraction and insertion of lithium. Both phases LiMnPO_4 and MnPO_4 show distinct Bragg reflections in the XRD pattern without shifting, even at the end of charge/discharge. This confirms the absence of an intermediate phase and excludes a solid solution region. The cathode material experiences partial amorphization during cycling, because of side reactions with the electrolyte. The MAS NMR experiments confirm the two-phase mechanism and reveal the expected signals for LiMnPO_4 (^7Li : 67 ppm, ^{31}P : 7955 ppm). MnPO_4 is detected via ^{31}P MAS NMR only by a strongly broadened signal. This is attributed to the highly disordered structure of MnPO_4 , which results from the Jahn-Teller distortion, and from the micro strain inside the structure.

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