A thermodynamic investigation on the substitution mechanism of Mg-doped lithium vanadium phosphate

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ABSTRACT

Monoclinic lithium vanadium phosphate, Li₃V₂(PO₄)₃, is regarded as a potential cathode material for the next generation of high-performance lithium ion batteries, since it exhibits a high discharge voltage (up to ~4.1 V) and a large theoretical specific capacity (197 mAhg⁻¹). However, the low intrinsic electronic conductivity of Li₃V₂(PO₄)₃, which is a prevailing challenge for olivine type compounds, inhibits its use in commercial applications. Although the substitution of V³⁺ by other cation species is a common procedure to increase the conductivity and electrochemical performance of Li₃V₂(PO₄)₃, the underlying mechanisms for the improved properties are not yet well understood. Therefore, a thermodynamic approach is used in this work to investigate the influence of dopant, i.e. Mg²⁺ as well as vacancies on the V³⁺ site on the stability of the resulting materials. On the basis of the measured partial molar Gibbs energies, entropies and enthalpies of the electrochemical reaction, a detailed discussion of the substitution mechanisms and their influence on the electrochemical performance is presented.

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1. Introduction

Since around 2000, lithium vanadium phosphate (LVP) has attracted attention as a potential cathode material for lithium ion batteries due to its good thermal and chemical stabilities, relatively large Li diffusion coefficients and high discharge potentials [1–4]. However, the rather low intrinsic electrical conductivity of LVP tends to limit its cycling stability and electrochemical performance.

LVP can be prepared in the rhombohedral (NASICON-type) and the more thermodynamically stable monoclinic [5–9] crystallographic modifications. The crystal structure of monoclinic LVP is composed of corner connected PO₄ tetrahedra and VO₆ octahedra forming a loose framework into which Li ions can be easily incorporated. The two vanadium sites are distinct from each other due to the slight differences in their chemical surroundings, i.e. coordination and bond lengths [10]. At higher temperatures, however, the vanadium sites cannot be distinguished from each other, resulting in an increase in symmetry and an associated phase transformation to the high temperature rhombohedral γ-phase. Conversely, the three Li sites in the LVP crystal structure have distinctly different chemical surroundings. Due to the formation of several two-phase regions in the active cathode material during delithiation, clearly identifiable voltage plateaus are obtained when lithium is successively extracted from the respective crystallographic lattice sites. A theoretical specific capacity of 197 mAhg⁻¹ can be obtained when all three lithium ions are completely extracted, which is among the highest theoretical capacity values compared to other phosphate-based cathode materials. The electrochemical reactions taking place upon extraction/reinsertion of (Li⁺ + e⁻) [11] are summarized in Table 1.

The structural changes accompanied by the formation of different LiₓV₂(PO₄)₃ compounds during delithiation/lithiation were already investigated in detail by several groups [4,10,12,13]. However, the nature of the reactions taking place upon charging/discharging of LVP in the highest voltage region (i.e. Reaction IV on charge and IIIB on discharge in Table 1) are still not well understood and different mechanisms are proposed [10,13].

Currently, the low electronic conductivity of LVP poses a main challenge for its use in practical applications. Three approaches are usually employed to modify the LVP phase in order to improve its electrochemical performance properties i.e. carbon coating, nanostructuring, and doping. The latter approach is quite popular and research on this topic is still continuing [14]. For example, the electronic conductivity can be increased by p/n-type doping, and the use of hetero-valent cations to create intermittent electronic states between the conduction and valence band of the material.
has been proposed as a feasible approach [15–17]. Furthermore, inactive metal ions such as Bi$^{3+}$ [18] or Cr$^{3+}$ [19] were incorporated into the crystal lattice of LVP in order to stabilize the structure upon lithium insertion/extraction [18,19] and counteract the swelling/shrinking of the electrode material to improve cyclability.

Although much work has been performed on determining the processing-performance-property relationships for various doped LVP compounds, only limited knowledge is available on the substitution mechanisms governing the doping process. However, as mentioned by Rui et al. [5], a detailed understanding of the underlying principles of substitution are required in order to systemically tailor the LVP compound to optimize its performance.

2.2. Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM)

For XRD, the powdered samples were placed onto the sample holders according to the backloading technique. All measurements were conducted in a 2θ range of 5–120°, with step sizes of 0:033–0.20 and a dwell time of 400s/step. A PANalytical X’Pert Pro in Bragg-Brentano geometry with a Cu X-ray tube and a Ni filter was used for all measurements. Evaluation of the obtained diffraction patterns was performed by full-profile Rietveld analysis using the HighScore Plus software package.

For SEM analysis, a small amount of powder from the samples was distributed onto a double-sided conductive tape fixed on a sample carrier. SEM images were recorded using a ZEISS Supra 40 electron microscope with an Inlens detector and an acceleration voltage of 5 kV.

2.3. Inductively coupled plasma – optical emission spectroscopy (ICP-OES) and elemental analysis

ICP-OES measurements were performed to determine the Li, Mg, P, and V concentrations in the synthesized samples. About 50 mg of each sample was dissolved in a mixture of 35% HCl (conc.) and 65% HNO$_3$ (conc.) and the solutions were boiled for 1 h. After cooling, the solutions were diluted with deionized water to a volume of 50 ml. The thus obtained solutions were even further diluted for the ICP-OES measurements, which were conducted using a PerkinElmer ICP–OES type OPTIMA 7300 DV. Additionally, elemental analysis using a Carlo-Erba EA1108 CHNS-O was performed to determine the carbon content of the samples.

2.4. Particle size distribution (PSA analysis) and specific surface area

The particle size distributions were analyzed by laser diffraction using a CILAS-PSA190 device. The samples were dispersed in deionized water to which two drops of the dispersing agent Disperbyk-190 (BYK-Chemie GmbH) were added. Before each measurement, the dispersion was ultrasonicated for 10min to prevent particle agglomeration. The specific surface area of the powders was determined by N$_2$ physisorption using a Quantachrome Autosorb IQ Station. The samples were put into long glass capillaries, which were outgassed at 393 K under vacuum for 3 h. All measurements were conducted at a temperature of 77.35 K. The

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**Table 1**

Reactions taking place upon extraction/reinsertion of Li in Li$_3$V$_2$(PO$_4$)$_3$. The expected potentials were taken from the experimental results presented in this work.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging</td>
<td>E vs. Li/Li$^+$ [V]</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>$\text{Li}_3\text{V}_2\text{(PO}_4\text{)}_3 \rightarrow 0.5\text{Li} + \text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3$</td>
<td>Two-phase region</td>
</tr>
<tr>
<td>II</td>
<td>$\text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3 \rightarrow 0.5\text{Li} + \text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3$</td>
<td>Two-phase region</td>
</tr>
<tr>
<td>III</td>
<td>$\text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3 \rightarrow \text{Li} + \text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3$</td>
<td>Two-phase region</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3 \rightarrow \text{Li} + \text{V}_2\text{(PO}_4\text{)}_3$</td>
<td>Two-phase region</td>
</tr>
</tbody>
</table>

Discharging |
| IIB | $\text{V}_2\text{(PO}_4\text{)}_3 + 2\text{Li} \rightarrow \text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3$ | Solid solution |
| IIB | $\text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3 + 0.5\text{Li} \rightarrow \text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3$ | Two-phase region |
| IB | $\text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3 + 0.5\text{Li} \rightarrow \text{Li}_2\text{V}_2\text{(PO}_4\text{)}_3$ | Two-phase region |
commercial software ASiQwin as provided by Quantachrome was used to evaluate the data.

2.5. Electrochemical testing

Cathode materials were made by mixing the different LVP compounds with carbon black (TimCal, Super C45) and polyvinylidene fluoride (PVDF; Solvay, SOLFLEX® 5130) to achieve a weight ratio of (active material:carbon black: binder) = (8:1:1). First, the LVP-based sample powders were mechanically mixed with carbon black in an agate mortar using acetone as a rheological additive and then dried in a vacuum furnace for 30 min at 333 K to remove the remaining acetone. To make the slurries, a 5 wt% solution of PVDF in N-methyl-2-pyrrolidone (NMP; Sigma-Aldrich, 99.5% anhydrous) was added to the dried powders to achieve the desired 10 wt % binder ratio. Additional NMP could be added to reduce the viscosities of the slurries. Stirring was performed for approximately 24 h before coating on aluminum foil (MTI, >99.3%, thickness = 15 μm) using a doctor blade (120 μm) to make the electrodes. The electrodes were then dried under vacuum at 333 K for 2 h and then at 393 K for 4 h. The electrodes had a thickness of approximately 60 μm after drying. Upon calendaring, a thickness of about 50 μm was achieved. Electrodes with diameters of 15 mm were then punched out of the coated foils and dried at 393 K before introducing them directly into an inert atmosphere glovebox (H₂O < 0.1 ppm, O₂ < 0.1 ppm, Ar-supply: Ar 6.0) without any contact to air.

Coin cells (type 2016) were assembled inside the glovebox with Li discs (PI-KEM, 99.9%, thickness = 0.6 mm) as the negative electrode and a 1 M solution of LiPF₆ in a mixture of (ethylene carbonate: dimethyl carbonate) = (1:1) (RASF; Selectlyte: LP30) as the electrolyte. Additionally, Celgard 2500 (polypropylene film, thickness = 25 μm) was used as the separator. Electrochemical testing was performed using a Maccor battery tester (Maccor Series 4000), and the raw data were evaluated using the MIMs client provided by Maccor as well as the software Origin 2015G.

3. Results and discussion

3.1. Characterization of the synthesized compounds (XRD, ICP-OES and elemental analysis)

In order to estimate the homogeneity range of the monoclinic crystal lattice of LVP with respect to V vacancy formation and amount of Mg dopant, several compositions with varying nominal V and Mg contents were synthesized and analyzed by powder-XRD and Rietveld analysis of the measured diffraction data. The sample nomenclature, nominal stoichiometries, phases identified, refined lattice parameters of the phases and the references for the structural data are presented in Table 2.

The powder XRD data show that for the V-deficient samples, only sample LVP-V1 with a nominal composition of LiₓVₓ(PO₄)₃ was single phase. Similarly, for the Mg-doped samples, only sample LVP + Mg1 with nominal composition LiₓMg₁₋ₓVₓ(PO₄)₃ could be identified as being single phase. Impurities were detected in all other samples except the pristine compound LVP00. Decreasing the amount of V in LiₓVₓ(PO₄)₃ below x = 1.9 leads to the formation of two additional phases after the final heat treatment at 1073 K in Ar-5% H₂. These phases could be identified as LiV(P₂O₇)₂ and Li₃V₃(-P₂O₇)₃(PO₄)₂. Both of these compounds were already investigated structurally [21,22] and are electrochemically active [23–25]. Furthermore, since no diffraction peaks could be assigned to carbon in any of the samples, the carbon coating is assumed to be amorphous.

Although additional diffraction peaks were detected in the measured XRD patterns of the Mg-doped samples with x > 0.1 in LiₓMg₁₋ₓVₓ₋₃(PO₄)₃, thereby indicating the presence of extra phases, these phases could not be clearly identified. Nevertheless, the extra peaks assigned to these extra phases were identified at the same 2Theta values for all samples in question (LVP + Mg2, LVP + Mg3, and LVP + Mg4), showing that the extra phase/phases could be equilibrium ones for the synthesis conditions applied. The XRD patterns for all samples are shown in Fig. 1. The 2Theta values marked with dotted lines show emerging peaks assigned to impurity phases.

The stability limit of the monoclinic LVP phase with respect to V-vacancy formation and Mg incorporation according to the assumed stoichiometries LiₓV₂₋ₓ(PO₄)₃ and LiₓMgₓV₂₋ₓ(PO₄)₃, was thus determined as 0.2 < x < 0.1. Other values for the solubility limit of Mg-doped LVP can be found in the literature. These data are listed in Table 3 along with a short description of the synthesis procedure and the nominal compositions investigated. To enable a proper comparison of the data, the nominal compositions were converted to LiₓMgₓV₂₋ₓ(PO₄)₃ stoichiometries (last column in Table 3). Generally, the reported solubility ranges are all higher than the ones determined in this work. However, the experimental data cannot be directly related to each other since different synthesis procedures, temperatures and atmospheres (reducing/inert) were used. These are all strongly expected to influence the stability of the LVP phase with respect to Mg-incorporation. In fact, similar dependencies were reported for the phases in the Li-Fe-P₂O₇ system [26]. Furthermore, some inconsistencies were found in the data reported by Refs. [15,20]. For example, some samples were assumed to be single phase and well within the proposed solubility ranges although the respective XRD patterns showed unidentified peaks. These inconsistencies were not discussed, although they indicate that the experimentally determined solubility ranges may be much lower than presented, even better matching those of this work.

Since the samples LVP00 (pristine compound), LVP-V1 (V-deficient compound) and LVP + Mg1 (Mg-doped compound) were single phase according to the XRD results, only these three will be addressed in the rest of the article. The exact compositions of these samples were determined by ICP-OES (Li, V, Mg, P) and elemental analysis (C). The results, which are listed in Table 4, show no significant discrepancies from the expected stoichiometries. Only a minor Li loss in LVP00 and LVP + Mg1 and a slightly higher P concentration in all samples could be detected. These deviations, however, are assumed to be well within the accumulated errors resulting from the sample preparation, calibrations and instrumental limitations. The carbon content of all samples was determined by elemental analysis, and varies between 7 and 8 wt%.

3.2. Galvanostatic cycling

To determine the specific capacities of the three materials (pristine LVP00, V-deficient LVP-V1 and Mg-doped LVP + Mg1) and the effects of V-deficiency and Mg-doping on these parameters, galvanostatic cycling experiments were conducted in the potential range of 3.0–4.3 V. Three different current densities, i.e. 130 mAg⁻¹ (±1 C), 650 mAg⁻¹ (±5 C), 1300 mAg⁻¹ (±10 C), were subsequently applied for 100 cycles each. The results are shown in Fig. 2.

Since the specific charge and discharge capacities did not show any significant differences for all samples (high coulombic efficiency), only the discharge capacities are depicted in Fig. 2. At a current density of 130 mAg⁻¹, the specific capacities of the cathode materials range from 122 to 127 mAhg⁻¹, with LVP00 having the highest capacity and LVP + Mg1 the lowest. Generally, however, the capacity retention after 100 cycles is approximately 95% of the
theoretical value with respect to the pristine LVP compound (131.5 mAh/g). At higher current densities, the achievable specific capacities decrease continuously. For the LVP00 and LVP-V1 cathode materials, a 20 mAh/g decrease in capacity is observed when the current density is increased from 130 to 650 mAg/g and from 650 to 1300 mAg/g, respectively. However, in the Mg containing sample, the loss in specific capacity is only approximately 5 mAh/g.

Similar findings are reported in Ref. [27], who determined a specific capacity of 115 mAh/g for the compound Li3Mg0.1V1.9(PO4)3 at a C-rate of 5C. Other investigations [15,20,28] on Mg-doped LVP also show improved cycling performance and rate capabilities at elevated current densities. However, the mechanisms by which the Mg-ions influence the de-/lithiation reactions occurring during charging/discharging are not yet fully clarified. Dong et al. [20] state that the improved electric

Table 2
XRD results of the sample series Li3V2-x(PO4)3 and Li3MgxV2-x(PO4)3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal Stoichiometry</th>
<th>XRD Phases</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>Crystal structure data taken from the following references</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVP00</td>
<td>Li3V2(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60584</td>
<td>8.59567</td>
<td>12.0463</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP-V1</td>
<td>Li3V1.9(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60872</td>
<td>8.59524</td>
<td>12.04282</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP-V2</td>
<td>Li3V1.8(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60871</td>
<td>8.59437</td>
<td>12.04137</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP-V3</td>
<td>Li3V1.7(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.61041</td>
<td>8.59488</td>
<td>12.04082</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg1</td>
<td>Li3Mg0.1V1.9(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60455</td>
<td>8.59674</td>
<td>12.04537</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg2</td>
<td>Li3Mg0.2V1.8(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60445</td>
<td>8.59745</td>
<td>12.03797</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg3</td>
<td>Li3Mg0.3V1.7(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60198</td>
<td>8.59597</td>
<td>12.03571</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg4</td>
<td>Li3Mg0.4V1.6(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60445</td>
<td>8.59745</td>
<td>12.03797</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg5</td>
<td>Li3Mg0.5V1.5(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60747</td>
<td>8.59945</td>
<td>12.04137</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg6</td>
<td>Li3Mg0.6V1.4(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.61041</td>
<td>8.59488</td>
<td>12.04082</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg7</td>
<td>Li3Mg0.7V1.3(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60584</td>
<td>8.59567</td>
<td>12.0463</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg8</td>
<td>Li3Mg0.8V1.2(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60872</td>
<td>8.59524</td>
<td>12.04282</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg9</td>
<td>Li3Mg0.9V1.1(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.60871</td>
<td>8.59437</td>
<td>12.04137</td>
<td>[10]</td>
</tr>
<tr>
<td>LVP + Mg10</td>
<td>Li3Mg1V0.9(PO4)3</td>
<td>Li3V2(PO4)3</td>
<td>8.61041</td>
<td>8.59488</td>
<td>12.04082</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Table 3
Solubility limits and assigned stoichiometries of Mg doped LVP reported in literature.

<table>
<thead>
<tr>
<th>Assigned stoichiometry</th>
<th>Solubility range/limit reported</th>
<th>Transformed solubility range/limit for Li3Mg1V1.9(PO4)3</th>
<th>Method</th>
<th>Synthesis procedure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li3Mg0.1V1.9(PO4)3</td>
<td>0.2 &gt; x &gt; 0.1</td>
<td>0.4 &gt; x &gt; 0.2</td>
<td>Carbothermic reduction</td>
<td>Ball milling in pure ethanol, heated at 623 K (N2) and 1073 K (N2)</td>
<td>[27]</td>
</tr>
<tr>
<td>Li3Mg0.2V1.8(PO4)3</td>
<td>x = 0.27</td>
<td>x = 0.27</td>
<td>Sol-Gel</td>
<td>Drying at 353 K (air), heated at 573 K (70%Ar/30%H2), ground and pressed into pellets, heated to 1023 K (2 °C/min, 70%Ar/30%H2)</td>
<td>[20]</td>
</tr>
<tr>
<td>Li3Mg0.3V1.7(PO4)3</td>
<td>x &gt; 0.13</td>
<td>x &gt; 0.26</td>
<td>Carbothermic reduction</td>
<td>Ball milling in ethyl alcohol, heated at 573 K (Ar), ground and heated to 1073 K (90%Ar/10%H2)</td>
<td>[15]</td>
</tr>
<tr>
<td>Li3Mg0.4V1.6(PO4)3</td>
<td>0.45 &gt; x &gt; 0.3</td>
<td>--</td>
<td>Sol-Gel</td>
<td>Drying at 373 K (air), heated at 623 K (N2), heated at 1023 K (N2)</td>
<td>[28]</td>
</tr>
<tr>
<td>Li3Mg0.5V1.5(PO4)3</td>
<td>0.2 &gt; x &gt; 0.1</td>
<td>0.2 &gt; x &gt; 0.1</td>
<td>Sol-Gel</td>
<td>Heated at 573 K (95%Ar/5%H2), ground, heated to 1023 K (95%Ar/5%H2)</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of the sample series a) Li3V2-x(PO4)3 (x = 0, 0.1, 0.2, 0.3) and b) Li3Mg0.1V1.9(PO4)3 at a C-rate of 5C. Other investigations [15,20,28] on Mg-doped LVP also show improved cycling performance and rate capabilities at elevated current densities. However, the mechanisms by which the Mg-ions influence the de-/lithiation reactions occurring during charging/discharging are not yet fully clarified. Dong et al. [20] state that the improved electric
conductivity of Mg-containing LVP is the main contributing factor for the improved electrochemical properties of the cathode material, whereas Huang et al. [28] proposed that the structural integrity of the cathode material is enhanced. In another investigation [15], the reduction in particle size due to Mg-doping was assumed to be one of the main factors for the improved electrochemical performance. Therefore, in order to gain further insights into the influence of Mg-doping on the performance of the cathode materials in this work, a thorough investigation of the particle sizes, surface area, and morphology was conducted using laser diffraction, gas adsorption and SEM techniques.

3.3. Sample morphology (SEM, particle size distribution, specific surface area)

The particle size distributions of the cathode materials were determined by laser diffraction of the dispersed powders in water. According to the measurement results (Fig. 3), no significant differences could be observed in the particle sizes between the three cathode materials. The particle diameters range from 0.2 μm to 90 μm with a majority exhibiting a diameter of 38 μm. This is in accordance with the fact that sieving through a 40 μm mesh was performed prior to all measurements and investigations (cf. Section 2.1).

The specific surface areas of the cathode materials were determined by N₂ physisorption on 1.2828, 1.2937, and 2.0622 g samples of the LVP00, LVP-V1, and LVP + Mg₁, respectively. The pore volumes (Vₚore) and pore size distributions (dₚore) were also calculated from the desorption isotherms using the modified Kelvin equation according to the BJH (Barrett, Joyner and Halenda) method. The results of this analysis are presented in Fig. 4. It can be seen that the pore size distribution is quite narrow for the pristine compound, with an average dₚore of 4.943 nm. However, for the V-deficient and Mg-doped cathode materials, the pore size distribution is slightly broadened towards larger dₚore values, with a larger broadening effect observed for the Mg-doped samples. The average dₚore were determined as 5.460 nm and 5.873 nm for LVP00, LVP-V1, and LVP + Mg₁ cathode materials, respectively. The cumulative pore volumes amounted to 0.212 mg⁻¹, 0.153 mg⁻¹, and 0.146 mg⁻¹ for LVP00, LVP-V1, and LVP + Mg₁, respectively.

SEM micrographs of the samples confirm the results obtained by PSA and BET analysis. All three materials show similar particle shapes and surface constitutions, and the mesoporous character of all samples is clearly depicted (Fig. 5).

The slight differences in the surface morphologies can be attributed to the different amounts of remaining carbon in the materials. As was confirmed by elemental analysis, the higher carbon content in LVP00 is associated with a denser coating and smaller pore sizes, whereas the lower carbon content in LVP-V1 and LVP + Mg₁ resulted in increased pore volumes. Minor differences in the synthesis procedures, e.g. different amount of chemicals used during gelation (e.g. Mg(CH₃COO)₂), can influence the morphology of the resulting materials by altering e.g. the pH during the chemical reactions. Nevertheless, the morphological differences observed in LVP and the two derivative cathode materials are only minor and are not expected to have any significant effects on their electrochemical behaviors. Thus, it is not expected, that the improved cycling performance of LVP + Mg₁ results from the

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**Table 4**

Results of the ICP-OES measurements and elemental analysis of the synthesized samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li [wt.%]</th>
<th>Mg [wt.%]</th>
<th>P [wt.%]</th>
<th>V [wt.%]</th>
<th>C [wt.%]</th>
<th>Li:Mg:V:P (mole ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVP00</td>
<td>4.06 ± 0.003</td>
<td>–</td>
<td>20.075 ± 0.064</td>
<td>21.810 ± 0.1556</td>
<td>8.444 ± 0.010</td>
<td>2.97:0.00:2.00:3.03</td>
</tr>
<tr>
<td>LVP-V1</td>
<td>4.578 ± 0.019</td>
<td>–</td>
<td>20.75 ± 0.297</td>
<td>21.435 ± 0.233</td>
<td>7.789 ± 0.029</td>
<td>3.02:0.00:1.92:3.06</td>
</tr>
<tr>
<td>LVP + Mg₁</td>
<td>4.553 ± 0.019</td>
<td>0.532 ± 0.001</td>
<td>20.760 ± 0.028</td>
<td>21.525 ± 0.035</td>
<td>6.933 ± 0.003</td>
<td>2.96:0.10:1.91:3.03</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Galvanostatic cycling at 130 mAg⁻¹, 650 mAg⁻¹ and 1300 mAg⁻¹ for the different LVP-based materials. Due to conciseness, only the specific discharge capacities are shown.

**Fig. 3.** Particle size distributions of the samples LVP00, LVP-V1, and LVP + Mg₁; the maximum is indicated by the dotted line.

Evaluation of the adsorption isotherms by BET (Brunauer-Emmett-Teller) analysis yield specific surface areas of 73.324 m²g⁻¹, 77.949 m²g⁻¹, and 64.238 m²g⁻¹ for the LVP00, LVP-V1, and LVP + Mg₁ cathode materials, respectively. The pore volumes (Vₚore) and pore size distributions (dₚore) with respect to the pore diameter (dₚore) were also calculated from the desorption isotherms using the modified Kelvin equation according to the BJH (Barrett, Joyner and Halenda) method.

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### Reference

For detailed analysis and methodology, please refer to the cited literature and technical reports.
differences in the morphological properties.

3.4. Thermodynamic characterization of the delithiation reactions

The thermodynamics of the electrochemical cell reaction can also be used as a further tool to assess the influence of Mg-doping on the electrochemical performance of the cathode materials. Thermodynamic quantities such as the Gibbs free energy change $\Delta_rG_{Li}$, enthalpy change $\Delta_rH_{Li}$ and entropy change $\Delta_rS_{Li}$ of the cell reaction yield important information on the chemical potential of lithium in the cathode materials as a function of state of charge and the resulting driving forces for the various cell reactions.

Electrochemical measurements have become a frequently utilized tool to obtain thermodynamic data, mostly due to its feasibility. However, it has to be mentioned, that in order to enable the derivation of thermodynamic parameters, the enthalpies and entropies of formation are assumed to be temperature independent. Thus, the enthalpies and entropies of reaction are obtained by extrapolation of the data to 0 or 298 K, assuming a linear behavior in the whole temperature region. This results in a higher deviation compared to other, especially calorimetric methods. Nevertheless, a good agreement of data obtained by electrochemical means and e.g. calorimetry can be expected, as was shown by Wang and Navrotsky [30] and Godshall et al. [31], who both measured the thermodynamic properties of LiCoO$_2$ by calorimetric [30] and electrochemical [31] measurements and obtained comparable results.

For the general cell reaction $A Li_x + y Li \rightarrow B Li_{x+y}$, in which the lithiation of $A Li_x$ leads to the formation of a thermodynamically more stable second phase $B Li_{x+y}$, the partial Gibbs energy change due to the decrease in chemical potential of $Li$, $\Delta_rG_{Li}$, can be readily calculated from the measured e.m.f. of the general electrochemical cell $Li/Li^+/-$containing electrolyte$|A Li_x$, according to (1),

$$\Delta_rG_{Li} = -zFE$$

where $z$ is the stoichiometric coefficient of $Li$, $F$ is Faraday's constant (96485 Cmol$^{-1}$) and $E$ is the cell e.m.f. (always positive).

The partial entropy and enthalpy of reaction can be calculated...
using the following relations:

\[ \Delta G_{\text{Li}} = \Delta H_{\text{Li}} - T \Delta S_{\text{Li}} \]  

(2)

\[ -\frac{\partial \Delta G_{\text{Li}}}{\partial T} = zF \frac{\partial \Delta E}{\partial T} = \Delta S_{\text{Li}} \]  

(3)

\[ -zF \left( \Delta E + T \frac{\partial \Delta E}{\partial T} \right) = \Delta H_{\text{Li}} \]  

(4)

If the reverse reaction takes place due to the application of energy/work from an external source to the electrochemical cell system, i.e. \( \text{BLi}_{(x,y)} \rightarrow \text{ALi}_x + y \text{Li}_y \), then the increase in chemical potential of lithium can be determined according to equation (1) as:

\[ -\Delta G_{\text{Li}} = -zF \Delta E \]  

(5)

and equations (3) and (4) also change their sign accordingly. Thus, if the lithiation reaction has a negative value for \( \Delta G_{\text{Li}} \), then the delithiation reaction has a positive one.

For each of the sample materials (i.e. LVP90, LVP-V1, and LVP + Mg1), three electrochemical cells were assembled and tested to determine the thermodynamic properties of the cell reaction. All measurements were conducted inside a heating chamber which was set to 303 K unless otherwise stated. After assembly and an initial waiting time of 6 h, the electrochemical cells were galvanostatically cycled in a potential region of 3.0—4.3 V. This ensured the proper formation of the protective layer at the electrolyte/electrode interface (SEI layer). Five galvanostatic cycles were performed using a charge/discharge rate of 20 mAg\(^{-1}\). Afterwards, one additional cycle was conducted at a much lower rate, i.e. 2 mAg\(^{-1}\) and the data in this quasi-equilibrium cycle was used to determine the amount of electrical charge needed for each cell to reach the different voltage plateaux assigned to the three reactions to be investigated (Reactions I-III in Table 1).

The cells were then galvanostatically charged to the center of the first voltage plateau, which lies at about 3.6 V and the open circuit voltage was measured at a temperature \( T = 303 \) K. After an initial waiting period (equilibration time), the temperature of the heating chamber was increased by \( \Delta T \) and held at this temperature for approximately 6 h and then returned to the starting value of 303 K. Each step was repeated three times to ensure the reproducibility of the measurements. \( \Delta T \) values of 5, 10, 15 and 20 K were used for the investigations. Fig. 6, showing the voltage and temperature profile of the cell using LVP + Mg1 as a cathode material, is included to illustrate the measuring procedure. The red line shows the temperature profile of the heating chamber and the black line shows the cell voltage as a function of time. The voltage peak at the start of the measurement results from the initial charging to the corresponding potential plateau.

Evaluation of the temperature dependencies of the different voltage plateaux was done as follows. First, the voltages corresponding to the equilibrium state for the given reactions at 303 K were determined as the mean value of one hundred data points (300—500 min). This voltage was constant taking into account the accuracy of the method. The region used for determining the equilibrium potential at 303 K is shown in grey in Fig. 6. Then the baseline for each voltage increment was determined separately by fitting a linear function to the data points before and after the temperature change. The baseline was subtracted from the measured data to give the voltage change for each temperature step. These voltage changes were subsequently added to the equilibrium voltage at 303 K for the respective reactions to yield the absolute voltages for the corresponding temperatures.

This elaborate evaluation procedure proved to be necessary, since the time scales of the measurements were long for a single voltage plateau (up to 18 days), and the open circuit voltage of some cells may drift during such time scales. However, the relative voltage differences observed for a given temperature change \( \Delta T \) remained constant and are therefore more reliable.

3.5. Substitution mechanism

Before addressing the thermodynamic parameters governing the Reactions I-IV, the substitution mechanisms regarding the inclusion of vanadium vacancies (the LVP-V1 compound) or magnesium ions (the LVP + Mg1 compound) into the crystal structure should first be discussed. Since the substitution of \( \text{V}^{3+} \) by vacancies (\( \text{V}^{3+} \) in Kröger-Vink notation) or \( \text{Mg}^{2+} \) ions (\( \text{Mg}^{2+} \) in Kröger-Vink notation) is accompanied by a disruption of the charge balance in the crystal lattice, charge compensating mechanisms must take place to account for the lower charges of the substituents and retain electro-neutrality.

For the V-deficient compound, electro-neutrality can be maintained via a change in the oxidation state of some of the remaining vanadium ions or by the formation of anion vacancies. These reactions can be formulated in Kröger-Vink notation as follows:

\[ -x\text{V}^{4+} + x\text{V}^{3+} \rightarrow x\text{V}^{4+} + 3x\text{V}^{3+} \]  

(6)

\[ -x\text{V}^{4+} + x\text{V}^{3+} \rightarrow x\text{V}^{4+} + \frac{3}{2}x\text{V}^{3+} \]  

(7)

Since phase purity with respect to V-vacancies was only maintained for samples with a stoichiometric factor for Vanadium of 1.9, corresponding to \( x = 0.1 \) in the formula Li\(_3\)V\(_2\)-x(PO\(_4\))\(_3\), the stoichiometries according to the charge compensation mechanisms presented above are Li\(_3\)V(III)\(_1\)-xV(IV)\(_2\)-x(PO\(_4\))\(_3\) and Li\(_3\)V(III)\(_1\)-x(PO\(_3\))\(_3\) respectively.

From an analytic point of view, the two substitution mechanisms can be distinguished from each other via the concentration of oxygen vacancies in the final compound and the average oxidation state of the vanadium cations. For sample LVP-V1, the difference in oxygen concentration which would occur as a result of the two substitution mechanisms is only 0.28 wt%. Since the presence of physisorbed oxygen can influence the measurement results, determination of oxygen concentrations in the samples is a poor indicator to determine the substitution mechanism.

The second method by which the two mechanisms can be differentiated from each other is the determination of the oxidation state of V. In the case of anion vacancy formation, the V ions within the compound do not change their oxidation states and remain - III. However, when no anion vacancies are formed, 3x \( \text{V}^{3+} \) ions are oxidized to \( \text{V}^{4+} \) when \( x \) V-vacancies are introduced into the crystal lattice. Thus, the change in the oxidation state of V is expected to be a more feasible parameter to determine the substitution mechanism at hand. In this work, in order to explore the suitability of electrochemical measurements to determine the oxidation state of the vanadium ions and thereby further elucidate the substitution mechanism, charge-discharge tests of the cathode active materials were performed. In Fig. 7, the charge/discharge profile, conducted at 2 mAg\(^{-1}\), for the two samples LVP-V1 and LVP + Mg1 are shown. The theoretical capacities for the different stoichiometries resulting from charge balance by oxidation of \( \text{V}^{3+} \) to \( \text{V}^{4+} \) (dashed vertical lines) or by anion vacancies (solid vertical lines), are shown as vertical lines.

In the potential region of 3.0—4.3 V vs. Li/Li\(_+\), only the \( \text{V}^{3+}/\text{V}^{4+} \) redox couple is active [2,11]. Thus, a higher initial average oxidation state of V would yield a lower specific capacity within this potential
range, since less V$^{3+}$ ions are available for oxidation upon (Li$^{+}$ + e$^{-}$) removal. The theoretical capacities of compound LVP-V1, assuming electro-neutrality via oxidation of V$^{3+}$ to V$^{4+}$, i.e. Li$_3$V(III)$_{1.6}$V(IV)$_{0.3}$(PO$_4$)$_3$, is relatively low, and only amounts to 106.5 mAhg$^{-1}$. The experimentally determined value, however, far exceeds this theoretical limit. If, however, anion vacancies are assumed as the main mechanism for maintaining charge-balance, then the oxidation state of V remains unaltered (i.e. + III) and a higher value for the theoretical capacity can be expected (127.3 mAhg$^{-1}$). The observed specific capacity of 127 mAhg$^{-1}$ for the sample LVP-V1 is in good agreement with this value, as clearly depicted in Fig. 7, and thus the formation of anion vacancies is the more probable charge-compensation mechanism when vanadium vacancies are incorporated into the crystal structure. Therefore, it is proposed that the introduction of V-vacancies into the LVP crystal structure results in the formation of oxygen vacancies up to a concentration of x = 0.1 in Li$_3$V(III)$_{2-x}$ (PO$_4$-$3x/2$)$_3$. However, to further verify this mechanism, independent measurements of the oxidation state of V should be performed by other analytical techniques, which were beyond the scope of this work. Upon further increase of the V-vacancies, the reduced oxygen content of the sample results in the condensation of some of the phosphate groups and leads to the formation of diphosphates, following the reaction 2 PO$_4^{3-}$ + O$_2$ + P$_2$O$_7^{4-}$. This tendency can be seen in the formation of Li$_9$V$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$ for samples with x $>$ 0.1. Similar findings are valid for the Mg-containing sample LVP + Mg. For the substitution of V$^{3+}$ by Mg$^{2+}$, three mechanisms for maintaining charge balance are possible. The lower charge of the Mg-ions can be compensated by the concomitant oxidation of V$^{3+}$ to V$^{4+}$ as well as by the formation of anion vacancies. Additionally, however, the lower charge of the Mg-ions compared to the V$^{3+}$-ions cations can also be compensated by the inclusion of Mg interstitials. The three different substitution reactions can be written in Kroger-Vink notation as follows and are depicted in Fig. 8:

$$x\text{Mg} \rightarrow x\text{Mg}^{2+} + x\text{V}^{3+} \quad (8)$$

$$x\text{Mg} \rightarrow x\text{Mg}^{2+} + \frac{1}{2} x\text{V}_{\text{a}}^{0} \quad (9)$$

$$x\text{Mg} \rightarrow x\text{Mg}^{2+} + \frac{2}{3} x\text{V}_{\text{a}}^{0} \quad (10)$$

Partial oxidation of V$^{3+}$ ions to V$^{4+}$ is the predominantly assumed mechanism in literature [15,20]. As already discussed for LVP-V1, if partial oxidation of V$^{3+}$ to V$^{4+}$ is assumed, then a lower theoretical specific capacity of only 119.1 mAhg$^{-1}$ should be attained for LVP + Mg. According to Fig. 7, however, a far higher value was determined by galvanostatic cycling of the material in half-cells. Thus, only anion vacancy formation or the introduction of magnesium cation interstitials are probable mechanisms for maintaining charge-balance in Mg-doped LVP. These two mechanisms result in different stoichiometries for the compound, i.e.
According to our ICP-OES measurements, the proposed mechanisms is only 1.8%, since this factor is 1.90 for anion vacancy formation and 1.934 for cation interstitials incorporation. However, according to our ICP-OES measurements, the experimentally determined stoichiometric factor for V in LVP + Mg1 is 1.91, which is between the two cases. Therefore, no definite decision on the predominant mechanism governing the substitution of V$^{3+}$ with Mg$^{2+}$ can be made via these techniques.

3.6. Thermodynamic characterization of the delithiation reactions - results

The thermodynamic parameters for Reactions I-III as determined in this work are given in Table 5. Representative measurements are depicted in Figures A1-A3 Appendix. Reaction IV could not be adequately investigated since the potential plateau at voltages above 4.5 V is not stable. For example, after charging of the cathode materials up to 4.8 V, the open circuit voltage observed to slowly relax to a potential of 4.1 V over a 6 day period. Similar observations were reported in Ref. [11] and recently discussed in Ref. [13]. Two different explanations for this phenomenon were given by different authors. Saïdi et al. [11] suggest that significant structural changes occur upon switching from charging to discharging at x = 0 in Li$_x$V$_2$(PO$_4$)$_3$, leading to a change in the reaction mechanism from lithiation and delithiation. Kim et al. [13], on the other hand, propose that the different voltage profiles observed for lithiation and delithiation result from the low conductivity of the material at higher states of charge. During charging/discharging, a significant concentration gradient is formed perpendicular to the particle surfaces and time is required for the equilibration of the materials after a charge transfer process.

For the delithiation of the pristine compound (LVP00), the values for $\Delta_G^{r}$ are 172904 Jmol$^{-1}$, 176864 Jmol$^{-1}$ and 391495 Jmol$^{-1}$ for Reactions I-III, respectively. The observed increase in $\Delta_G^{r}$ reflects the higher overpotential needed for the delithiation reactions to occur.

Delithiation of Li$_x$V$_2$(PO$_4$)$_3$ leads to the formation of Li$_{2-x}$V$_2$(PO$_4$)$_3$ and Li$_x$V$(PO_4)_3$ and further to Li$_2$V$(PO_4)_3$ (cf. Table 1). The compound Li$_x$V$_2$(PO$_4$)$_3$ has been investigated in detail [10] and these authors found that the V$^{3+}$ and V$^{4+}$ ions are not randomly distributed within the crystal structure, but rather form a distinct pattern exhibiting long-range order. This charge ordering phenomenon has an impact on the entropic contribution to the driving force of the delithiation reactions, as can be seen in Table 5. The values for $\Delta_S^{r}$ in LVP00 are 2.923 Jmol$^{-1}$ K$^{-1}$, 0 Jmol$^{-1}$ K$^{-1}$ and 7.718 Jmol$^{-1}$ K$^{-1}$ for Reactions I-III respectively. The zero change in the partial molar entropies for Reaction II, i.e. the formation of the charge ordered Li$_2$V$_2$(PO$_4$)$_3$ phase, shows that the reduction in entropy associated with the formation of an ordered pattern of V$^{3+}$ and V$^{4+}$ ions compensates for the expected increase in entropy which should occur as a result of the looser framework upon lithium extraction.

The values for the thermodynamic parameters $\Delta_T^{r}$, $\Delta_H^{r}$, and $\Delta_S^{r}$ for sample LVP-V1 are almost the same as for the pristine compound. Therefore, it is concluded that the concomitant introduction of vanadium and anion vacancies into the crystal structure of LVP has no significant effect on the thermodynamic driving forces for the respective delithiation reactions. Thus, no improvement in the electrochemical properties is expected, which is in agreement with the galvanostatic cycling experiments discussed in Section 3.2.

In contrast, the measured entropy data for the LVP + Mg1 cathode material differ significantly to those from LVP00. The values of $\Delta_S^{r}$ are approximately 24–25% more positive than the respective values of LVP00. On the other hand, the $\Delta_H^{r}$ data for the two cathode materials are only nominally different to each other. Specifically, the change in $\Delta_H^{r}$ amounts to only 0.1–0.3% for Reactions I-III. The strong influence of Mg-doping on the entropic contributions to the thermodynamic driving forces for the delithiation reactions might stem from a disturbance in the charge ordering of the V-ions. The incorporation of Mg$^{2+}$ ions into the crystal lattice of LVP might inhibit the long-range ordering of the V ions, which was experimentally determined for Li$_2$V$_2$(PO$_4$)$_3$ [10], but which is also assumed to occur, at least to a lesser extent, in Li$_2$V$_2$(PO$_4$)$_3$ [12].

Compared to the V-deficient sample, Mg-doping has a far higher impact on the thermodynamic parameters of the de-/lithiation reactions. This impact is particularly observed in the entropies of reaction for the electrochemical cell. This might indicate a different charge balancing mechanism governing the substitution of V$^{3+}$ by Mg$^{2+}$. Thus, the retention of electro-neutrality in the magnesium doped compounds seem to be more probable by the introduction of cation interstitials than by the formation of anion vacancies. It is also expected that cation interstitials disturb the crystal lattice to a higher extent and thus have a higher impact on the overall entropy change of the compound which can lead to faster electrochemical reactions, such as Li insertion into/extraction from the system. Theoretical investigations via ab-initio calculations could help to further deduce the charge balancing mechanism of Mg-doped LVP. Nevertheless, it could be shown that Mg-doping of LVP leads to a

![Fig. 8.](image-url)
change in the entropy of the cell reaction $\Delta_S^{\text{r}}$ and further results in improved cycling performances, especially at higher rates.

### 4. Conclusion

The pristine compound Li$_3$V$_2$(PO$_4$)$_3$ (LVP00) and two derivatives thereof (V-deficient, LVP-V1; Mg-doped, LVP + Mg1), were successfully synthesized by a sol-gel route and the respective stability ranges were determined by XRD analysis. Characterization of the samples by SEM, N$_2$ adsorption measurements and PSA analysis showed that all samples have similar particle distributions and surface areas. Thus, no improvement in the electrochemical performance can be expected due to morphological differences.

A detailed discussion of the substitution mechanism was presented, and anion vacancies are assumed to be the main charge compensating mechanisms for the Mg-doped compound. Galvanostatic cycling between 3.0 and 4.3 V in half-cells showed an improved electrochemical performance for the Mg-doped sample, yielding high specific capacities (110 mAh g$^{-1}$) at high current densities up to 1300 mA g$^{-1}$ (~10C). However, the V-deficient sample showed no improvement in cycling stability compared to the pristine compound. To elucidate the effects of incorporation of Mg-ions into LVP, the partial molar Gibbs energies ($\Delta_G^{\text{r}}$), enthalpies ($\Delta_H^{\text{r}}$) and entropies ($\Delta_S^{\text{r}}$) of the electrochemical reactions were determined. The results show that V-deficiencies lead to no change in any of the thermodynamic parameters compared to the pristine compound. Mg-doping, however, strongly influences the entropy change of the cell reaction $\Delta_S^{\text{r}}$ with respect to the pristine LVP compound. In fact, a 24–25% increase in the entropy changes were measured in this work. In contrast, only a minor influence on $\Delta_H^{\text{r}}$ could be observed. These results may indicate that the nature of the charge-compensating substitution mechanism can be a driving factor for the increase in the electrochemical performance. In fact, several other elements were already investigated as a substituent for V$^{4+}$, i.e., Al$^{3+}$, Bi$^{3+}$, Ce$^{3+}$, Co$^{2+}$, Cr$^{4+}$, Cu$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Ge$^{4+}$, La$^{3+}$, Mg$^{2+}$, Mn$^{2+}$, Mo$^{6+}$, Nb$^{5+}$, Nd$^{3+}$, Ni$^{2+}$, Sn$^{4+}$, Ti$^{4+}$, Tm$^{3+}$, W$^{5+}$, Y$^{3+}$, Zn$^{2+}$, and Zr$^{4+}$ [14–20,27,28,32–58], and all of these investigations showed similar improvements in the electrochemical behavior of the material. In fact, optimized performances were obtained at low concentrations of the substituent; between $x = 0.05$ to 0.1 in a generalized stoichiometry of Li$_3$M$_x$V$_2$ (PO$_4$)$_3$ (with M $=$ substituent). Depending on the charge of the substituent, the stoichiometry should be adapted in order to maintain charge balance. Thus, for future applications in lithium ion batteries, the LVP compound should be doped with any abundant and low weight element to improve the cycling stability and high rate performance. The quality of the substituent however seems to be not as important.

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### Appendix A. Supplementary data

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### References

Li$_{(x)}$V$_{(1-x)}$(PO$_4$)$_3$ cathode materials, J. Power Sources 195 (2010) 5775.


M. Bini, S. Ferrari, D. Capsoni, V. Massarotti, Mn influence on the electrochemical behaviour of Li$_x$V$_{(2-x)}$(PO$_4$)$_3$ cathode material, Electrochim. Acta 56 (2011) 2648.

Y. Cheng, K. Feng, W. Zhou, H. Zhang, X. Li, H. Zhang, A Bi-doped Li$_x$V$_{(2-x)}$(PO$_4$)$_3$/C cathode material with an enhanced high-rate capacity and long cycle stability for lithium ion batteries, Dalton Trans. 44 (2015) 17579.

Y. Chen, Y. Zhao, X. An, L. Liu, Y. Dong, L. Chen, Preparation and electrochemical performance studies on Cr-doped Li$_x$V$_{(2-x)}$(PO$_4$)$_3$ as cathode materials for lithium-ion batteries, Electrochim. Acta 54 (2009) 5844.

Y.Z. Dong, Y.M. Zhao, H. Duan, The effect of doping Mg$^{2+}$ on the structure and electrochemical properties of Li$_x$V$_{(2-x)}$(PO$_4$)$_3$ cathode materials for lithium-ion batteries, J. Electroanal. Chem. 660 (2011) 14.


Q. Kuang, Y. Zhao, J. Xu, Synthesis, structure, electronic, ionic, and magnetic properties of Li$_{1-x}$Na$_x$Li$_x$V$_{(2-x)}$(PO$_4$)$_3$: a novel cathode material for lithium-ion batteries, Electrochim. Acta 36 (2011) 2201.

X. Lin, Y. Wang, B. Han, Q. Kuang, M. Wen, Layered Li-rich vanadium phosphate Li$_{(x)}$V$_{(2-x)}$(PO$_4$)$_3$: cathode and anode materials for lithium-ion batteries, Electrochim. Acta 191 (2016) 207.


J.S. Huang, L. Yang, K.Y. Liu, Y.F. Tang, Synthesis and characterization of Li$_{(x)}$V$_{(2-x)}$(PO$_4$)$_3$/C cathode material for lithium-ion batteries, J. Power Sources 195 (2010) 5013.


J. Yao, S. Wei, P. Zhang, C. Shen, K.-F. Aguey-Zinsou, L. Wang, Synthesis and properties of Li$_{(x)}$V$_{(2-x)}$Ce$_x$(PO$_4$)$_3$ cathode materials for Li-ion batteries, J. Alloy. Comp. 532 (2012) 49.

J. Liu, Y. Zhao, Q. Kuang, X. Li, Y. Dong, Z. Jing, S. Hou, Mixing transition-metal phosphates Li$_{(x)}$V$_{(2-x)}$Fe$_x$(PO$_4$)$_3$ (0 < x < 2): the synthesis, structure and electrochemical properties, Electrochim. Acta 196 (2016) 517.