A single phase, well-crystallized Li4V(PO4)2F2/carbon nanocomposite has been prepared by an optimized solid-state route via oxidation of Li5V(PO4)2F2. The Li4V(PO4)2F2 composition exhibits lattice parameters close to those of the oxidized parent (a = 6.898 Å, b = 10.673 Å, c = 9.977 Å; β = 87.84°; V = 734.0 Å³). 1D 6Li solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) studies identified which of the six lithium ions are removed from the lattice of the parent Li5V(PO4)2F2. The results are in perfect accord with previous NMR-based predictions of which sites would be the most mobile and thereby most easily extracted upon cycling. Variable-temperature NMR studies and 2D exchange spectroscopy (EXSY) are used to probe the Li ion dynamics in Li4V(PO4)2F2. Importantly, our studies show that upon delithiation, the ion mobility was found to increase significantly vis-à-vis the parent Li5V(PO4)2F2. We ascribe this to the creation of lithium vacancies within the structure that open up pathways for ion transport.

Introduction

Lithium metal phosphates have attracted attention as lithium ion battery cathode materials since the late 1980’s. Goodenough and Delmas originally identified the potential viability of three-dimensional framework structures built from polyanions such as PO43− groups.1,2 The presence of the PO43− groups results in an “inductive effect” which gives a much higher redox-couple of the transition metal than the corresponding oxide.3 Lithium metal phosphates often possess high theoretical capacity, good reversibility and excellent thermal stability.4 Two promising materials that show capacities superior to layered metal oxides are LiFePO4 and monoclinic Li3V2(PO4)3.5,6 They have also been shown to have good ionic conductivity because the bulky PO43− units result in open pathways that can enable fast ion migration. This can be hindered in 1D frameworks such as olivine LiFePO4 by anti-site occupation in the channel pathways by Fe2+ ions,7,8 or by strong ion-electron coupling,9 but the understanding of such polyanion systems is still far from complete.

Lithium metal fluorophosphates are a novel class of insertion materials that also show promising lithium intercalation properties. The first example of a fluorophosphate recognized for use as a cathode was LiVPO4F.10 The effect of having fluoride in the coordination sphere of the transition metal was found to be beneficial to the operating voltage of the material. The V4+/V3+ redox couple in LiVPO4F was found to be 0.3 V higher in potential than in Li3V2(PO4)3. It displays a specific capacity of 165 mA h g−1 on removal of two lithium ions from the structure, very close to the theoretical capacity (170 mA h g−1).12 Removal of the second lithium ion is not a highly reversible process, however, possibly owing to distortions of the framework caused by the formation of the much smaller V3+ centres compared to V4+ in the parent.

Li3V(PO4)2F2 has six crystallographically distinct Li sites. In a previous paper, we used 6Li solid-state nuclear resonance (NMR) to study the local structure and mobility of the lithium ions.12 The six Li sites were resolved under fast magic-angle spinning (MAS) conditions (30 kHz), exhibiting chemical shifts of 2 ppm. The large chemical shift range results from the well-known Fermi-contact interaction. This phenomenon has been observed in many cathode materials and was first explored in detail by Grey et al.13,14 Li solid-state NMR provided a unique method for determining site-specific information about the exchange processes within this lattice. Two-Dimensional Exchange Spectroscopy (2D EXSY) was used to determine which pathway in the lattice is preferred for ion conduction.

Here, Li5V(PO4)2F2 was prepared by chemical oxidation of the parent compound. By determining the changes in the 6Li solid-state NMR spectra, it was possible to establish which sites...
are extracted on delithiation. The study of these vacancy-rich materials is essential for determining changes in ion dynamics as a function of lithium site occupancy, transition metal oxidation state, and accompanying structural changes caused by charging the lithium ion cell. Using variable-temperature and exchange-based NMR studies, the mobility of the Li ions is explored and is found to be superior to the fully lithiated structure.

**Experimental section**

**Sample preparation**

Single-phase microcrystalline samples of Li$_4$V(PO$_4$)$_2$F$_2$ were synthesized using VPO$_4$, Li$_3$PO$_4$ and a stoichiometric excess of LiF. Further details are described in a previous report. Li-enriched samples were prepared using pure $^6$Li$_3$PO$_4$ and $^7$LiF. The $\chi = 4$ composition was prepared by stoichiometric chemical oxidation of the parent compound, Li$_3$V(PO$_4$)$_2$F$_2$, using 1 M Br$_2$ in acetonitrile. The delithiated samples are extremely air and moisture sensitive and were stored and handled in an Ar-filled glovebox.

**Solid-state NMR**

$^6$Li and $^7$Li MAS NMR spectra were acquired at Larmor frequencies of 44.1 MHz and 116.6 MHz respectively on a Bruker AV-300 spectrometer. All room temperature experiments were carried out using a custom probe fitted to support 1.8 mm diameter rotors, spinning at frequencies up to 40 kHz. The $^7$Li variable-temperature studies were performed on a double-resonance probe supporting rotors of 2.5 mm outer diameter with a spinning frequency of up to 30 kHz. The temperature was calibrated using Sm$_3$Sn$_2$O$_7$ as a shift thermometer. The spectra are referenced to 1 M LiCl (aq) (0 ppm). All $^6$Li and $^7$Li NMR spectra were acquired using a one pulse experiment with a 90° pulse length of 2.5 $\mu$s. For studies of Li$_4$V(PO$_4$)$_2$F$_2$, the $^7$Li and $^7$Li recycle delays were both 50 ms. For Li$_3$V(PO$_4$)$_2$F$_2$, the $^7$Li and $^7$Li recycle delays were 1 s and 50 ms respectively. To be able to resolve the three resonances at lowest frequency, a Gaussian broadening value of 0.05 was used. $^6$Li spectral decompositions were performed using a xedplot program in the Bruker XwinNMR software. This allows variation of the peak position, peak height, line width and ratio of Gaussian to Lorentzian functions. 100% Lorentzian line shapes were used. The area was determined by integration, based on the peak height and the line width, using Maple 8.

$^7$Li 2D exchange spectra were acquired using mixing times between 1 $\mu$s and 15 ms and a recycle delay of 50 ms. The number of slices in the indirect dimension was 5120, with 256 transients averaged per slice. The increment for the slices in the indirect dimension is 1 $\mu$s. The $^7$Li 2D EXSY datasets took over 18 hours to collect. Although superior resolution was achieved with $^7$Li NMR, the much longer relaxation times for $^7$Li made this experiment prohibitively long (over a week). Gaussian broadening values of 0.0005 were used. Phase-sensitive detection in $t_1$ was achieved through the use of States-TPPI.

**Results and discussion**

**Synthesis and structure of Li$_4$V(PO$_4$)$_2$F$_2$**

The crystal structure of the parent phase, Li$_3$V(PO$_4$)$_2$F$_2$ (5122), is depicted in Fig. 1. The lithium atoms in Li$_3$V(PO$_4$)$_2$F$_2$ occupy the channels along the a axis (Li5 and Li6); the layers between the vanadium fluorophosphate sheets that lie at $a = 1/2$ in the (100) plane (Li1, Li2 and Li5); and the interstitial spaces within the framework (Li3 and Li4). The most likely pathways for lithium ion conduction are along the two-dimensional lithium sheets (Fig. 1i) and one-dimensional channels (Fig. 1ii), or a combination of these. The two paths intersect at Li4 and thus form a three-dimensional network. The Li1 and Li2 sites are located directly below vanadium atoms and are half occupied. Each of the six lithium sites is in distorted octahedral environments, namely surrounded by four oxygens and two fluorine atoms (see ESI†). Li3 and Li5 have two long Li-F bonds at 2.86 Å and 2.92 Å. Previous 2D EXSY studies of 5122 determined that Li ions exchange along the a-axis on a millisecond time scale. While Li5 and Li6 proved to be the most mobile ions, diffusion between channels (involving Li3 and Li4) is also possible. Surprisingly, exchange was not observed along the lithium layers that lie in the (100) plane. The ease of exchange was correlated to structural features such as the Li–Li internuclear distances and the channel dimensions, defined by a shared triangular face of the lithium polyhedra.

As we previously reported, on charging Li$_5$V$^{3+}$(PO$_4$)$_2$F$_2$, two well defined plateaus are observed. The first corresponds to the extraction of one lithium and oxidation of Li$_5$V$^{3+}$(PO$_4$)$_2$F$_2$ to Li$_5$V$^{4+}$(PO$_4$)$_2$F$_2$ at 4.15 V (4122). In earlier studies of Li$_5$V$_{5/3}$(PO$_4$)$_3$, Nazar et al. used chemical oxidation/reduction to simulate the processes that occur in the battery during electrochemical cycling. This method yielded bulk quantities of delithiated samples for analysis by powder X-ray diffraction and solid-state NMR. A similar approach was used to examine the delithiated samples here. However, the single-phase composition 4122 is signaled by a sloping step in the voltage profile, suggesting some degree of nonstoichiometry. To isolate this phase, Li$_5$V(PO$_4$)$_2$F$_2$ was treated with 1 M Br$_2$ which has a redox potential just above 4.1 V versus Li$^+$/Li, which is the voltage corresponding to the extraction of the first Li ion from the structure. Powder diffraction data acquired for the 4122 phase are shown in Fig. 2. It exhibits lattice parameters of $a = 6.898$ Å, $b = 10.673$ Å, $c = 9.977$ Å; $\beta = 87.84°$; $V = 734.0$ Å$^3$, as determined by indexing and a full pattern match in the same space group as the parent, $P2_1/c$. Comparison to those of the 5122 parent compound ($a = 6.350$ Å, $b = 10.797$ Å, $c = 10.406$ Å; $\beta = 90.003°$; $V = 713.4$ Å$^3$) reveals an anisotropic distortion. The
seen in layered structures upon removal of the Li+ ions that bind along the density from the paramagnetic vanadium centres through the contact interaction involves transfer of unpaired electron spin. 

To study the parent 5122 in terms of both structure and lithium ion dynamics, we turned to solid state NMR. Each factor of Li+ for X-rays, it was not possible to further refine the structure. This indicates that the oxidizing agent was not able to fully delithiate the material, and complicates the interpretation of the associated NMR data. Therefore, the study presented here focuses on the 4122 analogue, and its comparison to the parent 5122 in terms of both structure and lithium ion dynamics.

### One-dimensional $^6$Li NMR

Owing to the limitations of XRD for refinement of the lithium sites in the delithiated materials, and difficulties in obtaining high-resolution neutron diffraction patterns (free of impurity phases such as Li$_3$PO$_4$), it was difficult to refine the structure. This indicates that the oxidizing agent was not able to fully delithiate the material, and complicates the interpretation of the associated NMR data. Therefore, the study presented here focuses on the 4122 analogue, and its comparison to the parent 5122 in terms of both structure and lithium ion dynamics.

Fig. 3 compares 1D $^6$Li NMR spectra at 30 kHz and 7.1 T for (a) Li$_4$V(PO$_4$)$_2$F$_2$ and (b) Li$_5$V(PO$_4$)$_2$F$_2$. The inset is magnified by 6× to confirm the presence of site Li$_{1A}$. 

The Fermi-contact interaction is geometry dependent and the magnitude of the chemical shift is determined by the number of paramagnetic centres within the Li coordination environment and the Li–O(F)–V bond lengths and angles. It was anticipated that the transfer of electron density through the fluorine atoms would be less than for oxygen since the Li–F–V bond is more ionic than the Li–O–V bond. Attempting to assign multiple Li resonances to specific sites is a complex procedure that involves consideration of all of the aforementioned factors. There are two possible transfer mechanisms: delocalization and polarization. For V$^{3+}$ ($t_{2g}^2e_g^0$), the possible interactions are a 90° delocalization where the occupied $t_{2g}$ orbitals donate positive electron spin density to the lithium orbital or a 180° polarization transfer. There are no 180° bonding interactions between Li–O(F)–V and thus only the delocalization mechanism is considered in the assignment of the resonances.

The sites are labeled Li$_{1\alpha}$ where $\alpha$ is the crystallographic site number and $\beta$ is the resonance (A–F from highest to lowest frequency). It is clear that the six resonances undergo a change in chemical shift upon delithiation. The shift to lower frequency is expected because the vanadium centres lose electrons upon Li extraction, decreasing the transfer of electron density possible to the lithium nuclei. The resonances also broaden, corresponding to a small increase in structural disorder, as observed by the broadening in the diffraction pattern. While broadening could also indicate Li motion, this is unlikely given the time scales determined by exchange spectroscopy (vide infra). The resonance at highest frequency experienced the greatest amount of broadening and is difficult to distinguish in the spectra without magnification of the signal (inset in Fig. 3). As established for the parent compound, the $^6$Li line widths are much narrower because of the smaller quadrupole moment of $^6$Li compared to $^7$Li. Furthermore, the $^6$Li spectrum did not appear to have any spinning sidebands while third order spinning sidebands were


Assignment of the $^6$Li spectrum of Li$_4$V(PO$_4$)$_2$F$_2$

The spectral decomposition of the $^6$Li MAS spectrum of Li$_4$V(PO$_4$)$_2$F$_2$ is shown in Fig. 4. There are six well-defined Li sites so the deconvolution has been restricted based on this structural constraint. Intensity between Li$_{4c}$ and Li$_{6d}$ that is unaccounted for in this fitting is attributed to structural disorder or incomplete/inhomogeneous delithiation. For example, residual intensity/broadening at the Li$_{6d}$ site. To resolve the three resonances at lowest frequency, a broadening value of 0.05 was applied. Unlike the 4122 line shapes, the use of Gaussian line shapes at lowest frequency, a broadening value of 0.05 was applied.

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The spectral decomposition of the $^6$Li NMR spectra of 4122 shows evidence of Li$_3$PO$_4$ impurity (2-4%), the recycle delay chosen for the $^6$Li NMR spectra (1 s) does not favour the detection of diamagnetic impurities (typically with $T_1$ relaxation rates of hundreds of milliseconds).

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Table 1

<table>
<thead>
<tr>
<th>Li resonance</th>
<th>Chemical shift/ppm</th>
<th>$^6$Li line width/kHz</th>
<th>Relative area ratio</th>
<th>Chemical shift/ppm</th>
<th>$^6$Li line width/kHz</th>
<th>Relative area ratio</th>
<th>% Remaining$^b$</th>
</tr>
</thead>
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<tr>
<td>Li$_{1A}$</td>
<td>102</td>
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<td>0.5</td>
<td>90</td>
<td>2.00</td>
<td>0.4</td>
<td>100</td>
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<tr>
<td>Li$_{2B}$</td>
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<td>0.25</td>
<td>0.5</td>
<td>51</td>
<td>0.98</td>
<td>0.5</td>
<td>100</td>
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<tr>
<td>Li$_{4C}$</td>
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<td>0.27</td>
<td>1.0</td>
<td>26</td>
<td>0.51</td>
<td>1.0</td>
<td>100</td>
</tr>
<tr>
<td>Li$_{5D}$</td>
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<td>1.0</td>
<td>1</td>
<td>0.21</td>
<td>0.6</td>
<td>60</td>
</tr>
<tr>
<td>Li$_{5F}$</td>
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<td>1.0</td>
<td>$-3$</td>
<td>0.12</td>
<td>1.0</td>
<td>100</td>
</tr>
<tr>
<td>Li$_{6D}$</td>
<td>$-2$</td>
<td>0.12</td>
<td>1.0</td>
<td>$-6$</td>
<td>0.13</td>
<td>0.5</td>
<td>50</td>
</tr>
</tbody>
</table>

$^a$ Error estimates are $\pm$1 ppm in the chemical shift, $\pm$0.05 kHz in $^6$Li line width, $\pm$0.1 in relative area and $\pm$10% in percent remaining. $^b$ Percent remaining calculated by comparing the area of the Li$_4$V(PO$_4$)$_2$F$_2$ resonances to the area of the Li$_3$V(PO$_4$)$_2$F$_2$ resonances.

Fig. 4 The spectral decomposition of $^6$Li MAS spectrum of Li$_4$V(PO$_4$)$_2$F$_2$ at 30 kHz. The inset shows the fit of the lowest frequency resonances.
To determine the relative area of the resonances, the shift for Li\(_2\) was set to the expected occupancy (0.5). This site is the most clearly resolved and is assumed to have the most accurate fit. As shown in Table 1, it appears that Li\(_1\), Li\(_2\) and Li\(_4\) have the same relative areas as in Li\(_6\)V(PO\(_4\))\(_2\)F\(_2\). Thus, none of these Li ions has been removed by chemical oxidation. However, the three resonances at lowest frequency exhibited noticeable changes upon delithiation. The relative areas suggest that Li ions are equally removed upon oxidation from Li\(_6\)D and Li\(_5\)F. This corresponds to a total lithium loss of 18 ± 3%, consistent with the theoretical amount of lithium extracted (1/5 = 20%). Removal of these ions agrees with predictions from bond valence calculations and 2D EXSY results from Li\(_3\)V(PO\(_4\))\(_2\)F\(_2\) \(a\textsuperscript{12}\) and is completely consistent with the expansion in the \(a\)-axis (see above). Li\(_5\)F was found to exchange first with Li\(_6\)D at 500 \(\mu\)s. \(a\textsuperscript{12}\)

This assignment is further supported by examining the 2D EXSY data for the delithiated samples and considering structural changes. EXSY experiments take into account both the size of the voids where the ions reside and the channel dimensions, which are necessary to predict ion hopping between sites for long-range diffusion. \(a\textsuperscript{12}\)

Solid-state NMR has established which lithium ions are most likely to be removed from Li\(_3\)V(PO\(_4\))\(_2\)F\(_2\) upon electrochemical cycling. Upon oxidation to Li\(_3\)V(PO\(_4\))\(_2\)F\(_2\), our results show that Li\(_6\)D and Li\(_5\)F are partially extracted. While Rietveld refinements of the X-ray diffraction patterns of the delithiated samples were unable to provide conclusive structural information, the combination of fast MAS and \(^{6}\)Li-enriched samples allowed local information about each of the lithium sites to be determined using NMR spectra. The 2D EXSY results for Li\(_3\)V(PO\(_4\))\(_2\)F\(_2\) showed which Li ions are the most mobile and these same ions were proven to be extracted upon chemical oxidation. This confirms the utility of exchange studies to predict which sites will most easily be removed upon cycling. Another important consideration is the time scale of ion hopping. In the following subsections, variable-temperature and 2D EXSY studies are used to look at these dynamics in Li\(_4\)V(PO\(_4\))\(_2\)F\(_2\).

**One-dimensional variable-temperature studies**

Fig. 5 shows the \(^{6}\)Li one-dimensional variable-temperature studies for Li\(_3\)V(PO\(_4\))\(_2\)F\(_2\) and Li\(_4\)V(PO\(_4\))\(_2\)F\(_2\) from 310 to 364 K, with the sample temperature corrected to include the heating effects of spinning at 25 kHz. In both cases, the chemical shifts at high frequency display a linear dependence with temperature. This is consistent with the Curie–Weiss behaviour that is observed in paramagnetic materials. \(a\textsuperscript{12}\) None of the resonances appears to coalesce up to 364 K, the temperature limitation of the probe, in 4122 (Fig. 5a). Unlike the parent compound, the resonances in 4122 experience significant narrowing of the line shapes with temperature. Moreover, the resonances in 4122 for sites Li\(_2\) and Li\(_4\) start to undergo coalescence at 343 K. This corresponds to a Li ion hopping rate of greater than 300 \(\mu\)s between these two sites (hopping rate = \(1/(\pi\sigma\sqrt{2})\), where \(\sigma\) is the separation between the two resonances). The faster ion dynamics in the delithiated material, compared to the parent compound, was further investigated using 2D EXSY studies.

**2D EXSY studies: evidence and explanation for increased Li ion mobility**

The \(^{6}\)Li 2D EXSY spectrum for 4122 at room temperature with a mixing time of 15 ms is shown in Fig. 6. Comparing this spectrum to that of the parent compound, it is clear that there is an increase in the number of lithium sites that exchange. The resonances at low frequency are highly overlapped and it was necessary to look at the slices in the indirect dimension to resolve the cross-peaks. Through this careful analysis, it appears that all of the lithium sites exchange with each other at 15 ms. Exchange between Li sites at \(a = 1/2\) in the (100) plane, between the layers of vanadium fluorophosphates, is now observed. This suggests that while Li ion motion through this two-dimensional lithium layer is slow, it still occurs albeit impeded by diffusion bottlenecks and long internuclear distances. It is possible that these sites are also able to exchange in the fully lithiated sample, but the short \(T_1\) relaxation rate limited EXSY studies to mixing times shorter than 7 ms. Looking at the EXSY acquisition for 4122 with a mixing time of 7 ms (Fig. 7), a comparison can be made to

![Fig. 5](https://example.com/f5.png)
the dynamics in the parent compound. Here, in addition to the same sites that exchange in Li422, ion hopping is also evident between Li2B–Li4C and Li3E–Li4C. This exchange is clearly highlighted by using the slices extracted at (i) 60 and (ii) –3 ppm in the indirect dimension, showing both the diagonal and the off-diagonal resonances. This is emphasized by comparison to slices from the 100 μs mixing time, where only resonances from the diagonal are observed for these sites. This result is significant because lithium ions from the lithium layers in the (100) plane now participate in exchange.

This result is understood by considering the structural effects of removing Li6D and Li5F. Fig. 8 shows the Li2B–Li4C and Li3E–Li4C pathways that are made accessible by removal of the two ions, allowing exchange to occur. As well, the onset of ion hopping of the sites which were mobile in Li422 occurs earlier in Li4122. Li6E and Li5F started to exchange at 500 μs in Li422 while removing one lithium ion allows these two sites to exchange at a rate faster than 100 μs. The limitation imposed by the fast T1 relaxation rate of Li422 does not allow us to determine whether more sites are able to exchange in Li4122—but it is unequivocal that those that do exchange have much faster jump rates.

The two-dimensional lattice of the fully occupied Li422 is not conducive to rapid lithium exchange, probably because of the lack of vacancies and the high degree of ordering of the Li sites, which has been observed previously for Na2Al(PO4)2F2. However, partial lithium extraction increases the lithium mobility dramatically. The creation of vacancies between sites results in more free space, allowing facile ion exchange to take place.

The combination of fast MAS, low magnetic field and the choice of 6Li has made it possible to resolve resonances with a small separation (i.e. Li3E and Li5F are only 3 ppm apart). This allows site-specific information about ion dynamics to be obtained from complex 7Li 2D EXSY spectra. Chemical oxidation is a convenient method to prepare delithiated samples but the logical extension of this work is to study intermediate compositions (Li4–xV(PO4)2F2 where 5 ≥ x ≥ 3) prepared by electrochemical cycling. The use of 2D EXSY will determine at what composition the onset of increased mobility is achieved.

**Conclusion**

Chemical oxidation provided a method for producing delithiated Li4–xV(PO4)2F2 where x = 4. Using 6Li NMR, it was possible to determine which sites were extracted during delithiation. Li6D and Li5F were removed first. This agrees with bond valence...
calculations and was further supported by 2D EXSY studies. Exchange-based studies of Li$_5$V(PO$_4$)$_2$F$_2$ anticipated which sites would be the most mobile and thereby the most easily extracted upon charging. 1Li 2D EXSY experiments take into account both the site volume and the dimensions of the conduction pathway, giving an accurate prediction of the most mobile sites.

The lithium ion dynamics in the delithiated samples were found to be faster than in the parent compound. Ion hopping occurred on the microsecond time scale and could be explained by considering the structural changes induced by removal of lithium sites. The delithiated samples contain vacancies that play an important role in allowing rapid ion diffusion. These results help develop an understanding of important design properties for fast ion mobility. The vanadium fluorophosphate framework provides a promising specific capacity and could be optimized by creating vacancies in the lattice by doping with M$^{2+}$ ions to replace Li$. This would mimic the 4122 composition, hopefully the subject of our future investigations.

Acknowledgements

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References