New lithium-ion conductors based on the NASICON structure†

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At present, there is a great interest to develop solid lithium-ion conductors for use as electrolytes in all-solid-state-lithium batteries. Availability of a suitable solid electrolyte material that could replace the currently used liquid electrolytes in lithium batteries would greatly contribute to the development of lithium battery technology by enabling fabrication of flexible, compact and leak-proof batteries of desired geometry. Two approaches are pursued for this purpose. One approach is to render liquid polymer electrolytes [such as polyethylene oxide (PEO) - lithium salt complexes] into solid composites by adding solid plasticizers (such as TiO₂ or Al₂O₃) without loss of conducting properties. The other approach is to synthesise lithium-containing solid compounds possessing the desired conducting properties.

Among the several families of inorganic solids exhibiting lithium-ion conduction, framework oxides based on the NASICON structure (Fig. 1) are of special interest, because materials exhibiting high conductivities combined with low activation energies have been reported for this structure. For example, the titanium-aluminium system, Li₁₋ₓTiₓAlₓ(PO₄)₃, exhibits a high conductivity (3.0 x 10⁻⁴ S cm⁻¹ at 25 °C) and a low activation energy (Eₐ = 0.2-0.3 eV) for x = 0.3. Despite these attractive features, there are several materials problems to be overcome before a lithium-ion conductor based on the NASICON framework could find application as electrolyte material. For instance, it is not clear whether the high conductivity of Li₁₋ₓTiₓAlₓ(PO₄)₃ and other such trivalent metal-substituted systems is intrinsic to the structure or due to formation of secondary phases that favour sintering and eliminate grain-boundary resistance. More importantly, for electrolyte application, the Ti⁺⁺ in the material should be replaced by other metal ions that would not undergo reduction by lithium. Towards this end, we examined lithium-ion conduction of mixed-metal NASICON-phases of the formula, LiₓM³⁺ₙM⁴⁺ₜ(PO₄)ₙ₋ₜ, where M³⁺ = Nb, Ta; M⁴⁺ = Al, Cr, Fe. We believed that once we obtain a stoichiometric NASICON-phase possessing intrinsic conducting properties similar to LiₓTiₓ(PO₄)₃ but without Ti⁺⁺, extraneous factors such as sinterability, grain boundary resistance, etc., could be tailored by appropriate means to obtain a favourable conducting material for application. Our results, which are reported in this paper, reveal that, among the phases investigated, LiTaAl(PO₄)₃ exhibits a total (bulk + grain boundary) conductivity of ca. 6.5 x 10⁻⁴ S cm⁻¹ at 30 °C and ca. 1.0 x 10⁻⁴ S cm⁻¹ at 350 °C. It must be mentioned that Nb- and Ta-containing NASICONs, LiₓNb₃₋ₓ₋ₜPO₄₃₋ₜ and AlₓTa₄₋ₓ₋ₜPO₄₃₋ₜ, have been investigated for their lithium-ion conductivity.

Experimental

LiₓM³⁺ₙM⁴⁺ₜ(PO₄)ₙ₋ₜ phosphates, where M³⁺ = Nb, Ta; M⁴⁺ = Al, Cr, Fe, were prepared by reacting stoichiometric mixtures of Li₂CO₃, M₃O₄, Al₂O₃, Cr₂O₃ and/or FeC₂O₄·2H₂O at 800 °C for 24 h in air as described in the literature. The phosphates were characterised by powder X-ray diffraction (XRD) (Siemens D50005 powder diffractometer, Cu-Kα radiation). Lattice parameters were derived from least-squares refinement of powder X-ray diffraction data (Fig. 2). Lithium-ion conductivities were measured on sintered pellets (sintered at 900 °C) coated with gold paste (cured at 600 °C for 6 h) using a HP4194A Impedance/Gain-Phase Analyzer over the frequency range 100 Hz-15 MHz in the temperature range 30-600 °C in air. For each sample, measurement was made for both heating and cooling cycles. Samples were equilibrated at constant temperature for about 1 h prior to each impedance measurement. Typical impedance plots are shown in Fig. 3. We see that, while the impedance plots [Fig. 3(a) and (b)] for

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low-conducting samples, LiNbFe(PO$_4$)$_3$ and LiTaFe(PO$_4$)$_3$, are neat semicircles, the corresponding plots [Fig. 3(c) and (d)] for the higher conducting samples, LiTaAl(PO$_4$)$_3$ and Li$_3$Ta$_2$Al$_6$(PO$_4$)$_10$, show a spike on the low-frequency side due to electrode polarisation. Similar behaviour has been reported for other lithium-ion conductors. Since it was not possible to separate bulk and grain boundary contributions to the total conductivity, we obtained the total ionic conductivity uniformly for all the samples, from the low frequency intercept of the impedance plots.

### Results and discussion

In Table 1, we list the compositions of LiM$_3$M$^{IV}$(PO$_4$)$_4$($M^IV$ = Nb, Ta; $M^III$ = Al, Cr, Fe) phosphates, their lattice parameters and conductivity data. For comparison, we also give the corresponding data for LiM$_3$M$^IV$(PO$_4$)$_4$ for $M^IV$ = Ti and Zr. All the LiM$_3$M$^{IV}$(PO$_4$)$_4$ phosphates investigated by us crystallise in the rhombohedral (R3c) NASICON structure (Fig. 1).

$$
\text{LiM}_3\text{M}^{IV}\text{(PO}_4)_4
$$

which has the smallest cell volume (1315 A$^3$) shows the highest total ionic conductivity ($\sigma_{tot}=6.5 \times 10^{-3} \text{ S cm}^{-1}$) at 30°C and which is a good lithium-ion conductor, we expected that members of LiM$_3$M$^{IV}$(PO$_4$)$_4$ would also exhibit similar lithium-ion conductivity.

Fig. 4 shows the Arrhenius plots for the lithium-ion conductivity of LiM$_3$M$^{IV}$(PO$_4$)$_4$ members and in Table 1, conductivity values at room temperature and at 350°C are given together with activation energy ($E_A$) values. We see that, between Nb$^{IV}$M$_3$ and Ta$^{IV}$M$_3$ members, the Ta$^{IV}$ members show a higher conductivity. Among the Ta$^{IV}$-containing members, the TaAl compound, LiTaAl(PO$_4$)$_4$ which has the smallest cell volume (1315 A$^3$) shows the highest total ionic (bulk + grain boundary) conductivity ($\sigma_{tot}=6.5 \times 10^{-3} \text{ S cm}^{-1}$) at 30°C and

![Fig. 2 Powder XRD patterns of (a) LiNbFe(PO$_4$)$_3$, (b) LiTaAl(PO$_4$)$_3$ and (c) Li$_3$Ta$_2$Al$_6$(PO$_4$)$_10$, at 300 °C.](image)

![Fig. 3 Typical impedance plots of (a) LiNbFe(PO$_4$)$_3$, (b) LiTaFe(PO$_4$)$_3$, (c) LiTaAl(PO$_4$)$_3$ and (d) Li$_3$Ta$_2$Al$_6$(PO$_4$)$_10$, at 300 °C.](image)

![Fig. 4 Arrhenius plots for total lithium-ion conduction of LiM$_3$M$^{IV}$(PO$_4$)$_4$. (a) LiNbFe(PO$_4$)$_3$, (b) LiTaFe(PO$_4$)$_3$, (c) LiTaAl(PO$_4$)$_3$, (d) Li$_3$Ta$_2$Al$_6$(PO$_4$)$_10$, (a) for comparison, the corresponding data for LiTa$_3$(PO$_4$)$_4$ are also shown (–) from ref. 14.](image)

### Table 1 Chemical composition, lattice parameters and total ionic conductivity data for NASICON-type phosphates LiM$_3$M$^{IV}$(PO$_4$)$_4$ ($M^IV$ = Nb, Ta, $M^III$ = Al, Cr, Fe)

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a_0$ (_{\text{Å}})</th>
<th>$c_0$ (_{\text{Å}})</th>
<th>$V_0$ (_{\text{Å}^3})</th>
<th>$\sigma_{\text{tot/298}}$, S cm$^{-1}$</th>
<th>$\sigma_{\text{tot/350}}$, S cm$^{-1}$</th>
<th>$E_A$, eV</th>
</tr>
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<tr>
<td>LiNbFe(PO$_4$)$_3$</td>
<td>8.593(3)</td>
<td>21.715(8)</td>
<td>1388</td>
<td>$&lt;10^{-4}$</td>
<td>$6.6 \times 10^{-4}$</td>
<td>0.85(200-400°C)</td>
</tr>
<tr>
<td>LiTaFe(PO$_4$)$_3$</td>
<td>8.542(6)</td>
<td>20.815(5)</td>
<td>1315</td>
<td>$6.5 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>0.47(30-250°C)</td>
</tr>
<tr>
<td>LiCrO(PO$_4$)$_3$</td>
<td>8.535(6)</td>
<td>21.515(8)</td>
<td>1360</td>
<td>$&lt;10^{-4}$</td>
<td>$3.7 \times 10^{-4}$</td>
<td>0.49(300-350°C)</td>
</tr>
<tr>
<td>LiTaAl(PO$_4$)$_3$</td>
<td>8.608(6)</td>
<td>21.753(6)</td>
<td>1395</td>
<td>$&lt;10^{-4}$</td>
<td>$3.0 \times 10^{-4}$</td>
<td>0.46(300-350°C)</td>
</tr>
<tr>
<td>Li$_3$Ta$_2$Al$_6$(PO$_4$)$_10$</td>
<td>8.531(4)</td>
<td>21.229(5)</td>
<td>1332</td>
<td>$6.5 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-3}$</td>
<td>0.51(30-250°C)</td>
</tr>
<tr>
<td>Li$_3$Ta$_2$Al$_6$(PO$_4$)$_10$</td>
<td>8.512</td>
<td>20.858</td>
<td>1310</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$6.3 \times 10^{-3}$</td>
<td>0.38(200-250°C)</td>
</tr>
<tr>
<td>LiTa$_3$(PO$_4$)$_4$</td>
<td>8.852</td>
<td>22.240</td>
<td>1508</td>
<td>$3.2 \times 10^{-3}$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>0.43(300-400°C)</td>
</tr>
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</table>

*aData taken from ref 13 and 14. The high temperature rhombohedral cell parameters are given. At low-temperatures, LiTa$_3$(PO$_4$)$_4$ has a monoclinic cell with $a=15.299(3)$, $b=8.940(3)$, $c=8.412(2)$, $\beta=125.98(12)$, $\gamma=97.6$°. (ref. 15).
to be a minimum (ca. 0.30 eV) when \( V \approx 1310 \AA^3 \), corresponding to that of LiTa(PO\(_4\)).

Among the LiM\(_x\)M\(_{3-x}\)(PO\(_4\))\(_2\) investigated here, LiTaAl(PO\(_4\))\(_2\) has the smallest \( V \approx 1315 \AA^3 \) and the \( E_a \) for this phase also happens to be the smallest (ca. 0.47 eV), although this value is considerably higher than that of LiTa(PO\(_4\)). This observation reveals that, while the activation energy for lithium-ion migration depends on the cell volume (optimal tunnel size), it also depends on the identity of M atoms constituting the M\(_x\)(PO\(_4\))\(_2\) framework.

Having identified a NASICON-phosphate, LiTaAl(PO\(_4\))\(_2\), that exhibits a lithium-ion conduction comparable to that of LiTa(PO\(_4\))\(_2\), but does not contain titanium(IV), we investigated the possibility of increasing its conductivity by appropriate substitution similar to that of Li\(_{1.0+2x}\)Ti\(_{2.9}\)Al\(_{1.0+2y}\)(PO\(_4\))\(_3\). For this purpose, we prepared the composition Li\(_{1.0+2x}\)Ta\(_{2.9}\)Al\(_{1.0+2y}\)(PO\(_4\))\(_3\) and investigated its ionic conductivity. We find that the conductivity of this phase is nearly the same as the parent LiTaAl(PO\(_4\))\(_2\), and investigated its ionic conductivity. Clearly, further work is required to understand the possibility of increasing its conductivity by appropriate substitution similar to that of Li\(_{1.0+2x}\)Ti\(_{2.9}\)Al\(_{1.0+2y}\)(PO\(_4\))\(_3\).

In conclusion, we have identified a new lithium-ion conducting NASICON phosphate, LiTaAl(PO\(_4\))\(_2\), that exhibits a conductivity behaviour comparable to that of LiTa(PO\(_4\))\(_2\), the best lithium-ion conductor among LiM\(_x\)M\(_{3-x}\)(PO\(_4\))\(_2\). Unlike LiTa(PO\(_4\))\(_2\), however, the new phosphate LiTaAl(PO\(_4\))\(_2\), containing stable Ta\(_4\) and Al\(_6\) valence states will not undergo a reduction in contact with lithium at elevated temperatures and, accordingly, the material deserves further attention towards tailoring electrolyte materials for solid-state lithium batteries.

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References