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NMR STUDIES OF MODIFIED NASICON-LIKE, LITHIUM CONDUCTING SOLID ELECTROLYTES

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Abstract

^{27}Al, ^{31}P and ^{7}Li NMR measurements have been performed on lithium conducting ceramics based on the $LiTi_2(PO_4)_3$ structure with Al, V and Nb metal ions substituted for either Ti or P within the framework NASICON structure. The ^{27}Al magic angle spinning NMR measurements have revealed that, although Al is intended to substitute for octahedral Ti sites, additional substitution into tetrahedral environments (presumably phosphorous sites) occurs with increasing amount of Al addition. This tetrahedral substitution appears to occur more readily in the presence of vanadium, in $Li_{1+x}Al_xTi_{2-x}(PO_4)_{2.9}(VO_4)_{0.1}$, whereas similar niobium additions (in place of vanadium) appear to stifle tetrahedral substitution. ^{7}Li static NMR spectra reveal quadrupolar structure with Cq approximately 42kHz, largely independent of substitution. Measurement of the ^{7}Li central transition linewidth at room temperature reveals a relatively mobile lithium species (300-900Hz) with linewidth tending to decrease with Al substitution and increase with increasing V or Nb. This new structural information is discussed in the context of ionic conduction in these ceramics.

Introduction

Solid state lithium ion conductors are being extensively investigated in the hope of developing materials with high ionic conductivity, good electrochemical stability and useful mechanical properties. Such materials would have many applications in energy storage and other

electrochemical devices. Lithium ion conducting ceramics and glasses have the advantage over, for example, polymer based systems, in that the conduction can be solely attributed to the lithium species. In addition, high room temperature conductivities (up to $1x10^{-3}$ S/cm) have been reported in several cases (1-3). One such class of materials are those based on $LiM_2(PO_4)_3$ (4) where, for example, M = Ti, Ge, Zr. Further substitutions, as in for example $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ where M = Al, Sc (5,6) and $Li_{1+x}Al_xTi_{2-x}(PO_4)_{3-y}(MO_4)_y$ where M = V, Nb, Y (7) can lead to improved conductivities and sinterability. All of these compounds have a NASICON type structure, consisting of MO_4 tetrahedra and $M'O_6$ octahedra linked through bridging oxygens. This results in a system of three dimensional 'channels' in which the Li ions reside. It has been previously stated (4) that the ionic conductivity can be altered by controlling the channel sizes via one or more of the above substitutions since, although the overall crystal symmetry remains the same, the lattice dimensions depend on the size of the structural cations(4).

Significant improvements in conductivity (both bulk and grain boundary) have been observed when Al is substituted into the parent $LiTi_2(PO_4)_3$ (LTP) lattice. This has previously been explained by the fact that the sintering of the pellets becomes significantly easier on substitution, resulting in a reduction of porosity from nearly 40% to only 4%. Gromov et al. (7) have suggested that the addition of vanadium and/or niobium to the LATP structure also results in conductivity enhancements. The changes in macroscopic properties such as conductivity and density have not been well correlated to microstructural changes upon substitution. Only x-ray diffraction analyses have been reported and these show that the long range order is unaffected in most cases and only the cell lattice parameters change upon substitution.

Our previous characterization work using [27]Al, ^{31}P and ^{7}Li solid state NMR measurements (8,9) in $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ systems has shown that, at the molecular level, substitution of LTP with (say for example) Al does not necessarily lead to the expected local order. Two ^{27}Al NMR peaks were observed which were indicative of both tetrahedral as well as octahedral coordination for aluminium. [7]Li linewidth measurements suggested significant ion motion was present thus averaging out the dipole-dipole interactions and resulting in relatively narrow central transition linewidths. In order to further investigate the structural effects, we undertake in this paper a systematic investigation of the effect of substitution (specifically of Al, V and Nb) on the local order and dynamics in the structure $Li_{1+x}Al_xTi_{2-x}(PO_4)_{3-y}(MO_4)_y$, using solid state NMR.

Experimental

Detailed descriptions of the material preparation are given elsewhere (see for example Best et al. in this proceedings and ref (10)). In brief, appropriate ratios of $(NH_4)_2HPO_4$, TiO_2, Li_2CO_3, Al_2O_3 and V_2O_5 or Nb_2O_5 were combined and heat treated appropriately to produce the desired ceramics. Complete reaction was confirmed via XRD analysis.

NMR experiments were conducted using a 7.1T superconducting magnet and a modified Bruker CXP 300 spectrometer operated by a Tecmag interface. Spectra were recorded at 116.615, 121.47 and 78.45MHz for ^7Li, ^{31}P and ^{27}Al respectively. Room temperature static and MAS spectra were acquired. For the MAS spectra the sample was enclosed in a 4mm zirconia rotor spinning at a maximum speed of 14kHz. Typical rf pulses of 4.3μs, 2μs and 0.6μs were used for ^7Li, ^{31}P and ^{27}Al respectively. Shifts were externally referenced to $[Al(H_2O)_6]^{3+}$ in aqueous $Al(NO_3)_3$ and 85%H_3PO_4.

Results and Discussion

^{27}Al NMR

Figure 1 presents the ^{27}Al MAS NMR spectra for $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ and $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$ for x=0.1 and x=0.3. It is clear that, at the lower concentrations of aluminium, only one resonance is observed (15ppm). This is consistent with ^{27}Al in an octahedral environment in phosphates (11). With increasing substitution however, a second resonance appears at -40ppm, which is assigned to a tetrahedrally substituted aluminium. In the case of ceramics containing vanadium, even the lowest aluminium content samples show evidence of this latter peak. This is more clearly seen in figure 2 which gives the ratio of tetrahedral to octahedral substituted aluminium (Al_t/Al_o) for a number of different compositions. This figure shows that, after an initial onset region where all aluminium atoms appear to occupy octahedral sites, the tetrahedrally coordinated aluminium resonance increases in a monotonic manner. At the highest concentrations, the ratio Al_t/Al_o does not appear to be influenced by the presence of vanadium. The ^{27}Al NMR spectrum for $Li_{1+x}Al_xTi_{2-x}(NbO_4)_{0.1}(PO_4)_{2.9}$ was also obtained and showed that niobium substitution, when added instead of vanadium, suppresses the Al_t environment.

Given that aluminium substitution was intended for the titanium atoms, the presence of tetrahedrally coordinated aluminium suggests that some phosphorous is being replaced instead

of titanium. This will have two effects - the resultant material is unlikely to be stoichiometric, with several octahedral site vacancies needed to maintain electrical neutrality and some small fraction of phosphorous must be expelled from the overall LATP structure. This is discussed in greater detail below.

^{31}P NMR

^{31}P MAS NMR spectra are shown in figure 3 as a function of aluminium content at constant vanadium content of 0.1. The unsubstituted LTP structure is also included for comparison and shows the presence of more than one phosphorous site. This is unusual since crystallographic evidence in the parent NASICON structure (12) suggests only a single phosphorous site. The NMR evidence here suggests the possibility of at least three closely associated sites (only slight differences in chemical shifts are seen) which are likely to be due to tetrahedral bond distortions in the phosphorous site leading to slightly different chemical shifts. Upon addition of aluminium, broadening is seen to occur which is consistent with Al substitution resulting in the presence of P-O-Al interactions and the likely distortion of the -O-P bond from a perfect tetrahedral angle. When vanadium is present, a further small resonance is observed at approximately -25ppm. This is assigned to P-O-V type phosphorous since vanadium is significantly different in its electronegativity from P or Al. Our other work has confirmed that the intensity of this peak depends on vanadium content (13). In the series of samples which do not contain vanadium, as aluminium content increases the peaks broaden in exactly the same manner as those shown in figure 3. However, in addition, the integrated intensities for this series suggest that the content of phosphorous is decreasing with increasing aluminium. The integrated intensities are shown in figure 4 for samples with and without vanadium as a function of aluminium content. The effect of decreasing phosphorous intensity is not as significant when vanadium is present.

The ^{31}P NMR experiments presented above confirm the interpretations inferred from the ^{27}Al data above. The broadening and asymmetry of the ^{31}P resonance is consistent with the presence of Al_t and the decrease in the integrated intensity with aluminium substitution agrees with the idea that Al_t substitution requires loss of some phosphorous. Since no other ^{31}P peaks were evident it is suggested that the excess phosphorous may occur as a glassy phase in the intergranular regions (eg P_2O_5 or Li_3PO_4). This is also consistent with the increasing ease of sinterability of the ceramics and an increasing grain boundary conductivity (5).

^7Li NMR

An example of the ^{7}Li static NMR spectra obtained in this work is presented in figure 5. All spectra have a similar appearance with a relatively narrow central transition. The first order satellite transitions indicate a quadrupolar coupling constant, C_q, of approximately 42kHz, consistent with prior results for LTP at room temperature (14). The sharpness of these satellite transitions appears to be dependent on the substitution of vanadium and aluminium as well as extent of processing, consistent with some distribution of the electric field gradient (efg) experienced by individual lithium ions. Substitution does not, however, appear to have a major effect on the magnitude of the efg, as seen in figure 6, where only the addition of aluminium appears to cause a very slight but steady increase in C_q (from 42kHz to 43.2kHz). Previous investigation of ^{7}Li in LTP have suggested that this value of C_q corresponds to lithium being present predominantly in the A1 site in the NASICON structure; that is, the site in which lithium ions are coordinated by six oxygens in a tetrahedral arrangement and in which the efg is relatively symmetric, as compared with the A2 site (14). The slight increase in C_q upon addition of aluminium may be a result of some Al_t substitution as well as contraction of the overall cell volume.

Since ionic conductivity is due to high lithium ion mobility, the correlation between ^{7}Li linewidth and conductivity was examined by measuring the full width at half maximum (FWHM) of the central ^{7}Li transition as a function of composition. Figure 7 indicates changes in FWHM for ^{7}Li as a function of Al, V and Nb content. It can be seen that aluminium substitution causes a slight decrease in linewidth whilst both vanadium and niobium result in increased linewidths.

To the firs order, ^{7}Li central transition linewidths are governed by two effects (i) the strength of the dipole-dipole interaction and (ii) the lithium ion mobility which can effectively average these interactions. Therefore, since FWHM increases with increasing vanadium and niobium, this implies either that the lithium ion mobility is decreasing (which should correlate with a decrease in conductivity) or that the strength of the dipole-dipole interaction (most likely Li-P (14)) is increasing. The latter effect may occur if the effective Li-P distance is decreased. This can either occur because the tunnel size is decreased, as would be the case if the overall cell volume is decreased due to substitution of smaller atoms (eg Al for Ti), or because an increase in the tunnel size (as may occur for V and Nb substitutions) causes the lithium ion to skew towards one of the O-P interactions rather than remaining in the centre of the tunnel. This latter effect, however, could also be expected to decrease the lithium ion mobility since the Li-O interaction would be stronger.

Previous work has suggested that substitution of aluminium in the LTP structure increases conductivity, which is consistent with the ^{7}Li FWHM trend, although the latter changes are only small. Vanadium and niobium substitutions to LATP have also been suggested to enhance ionic conductivity (7), although this is not confirmed by our recent work (10). The increased ^{7}Li linewidths certainly do not correlate with an enhancement in bulk ionic conductivity.

Conclusions

Multinuclear solid state NMR experiments have shown that significant microstructural changes take place in the lithium ion conductor, LTP, upon substitution with ions such as Al^{3+}, V^{5+} and Nb^{5+}. It has been shown that addition of aluminium to LTP results in some tetrahedrally coordinated aluminium (in contrast to the expected octahedral substitution). This probably leads to non-stoichiometric compounds due to the presence of octahedral cation vacancies and the expulsion of some phosphorous containing compound. The lack of any evidence for such a compound in the ^{31}P NMR suggests this may be a glassy phase or some volatile phase that was lost during the preparation and processing. The notion of a glassy phase is favored since this would enhance the sinterability of the ceramic and lead to higher grain boundary conductivities, as has indeed been observed. ^{7}Li NMR does not show any distinct correlation between linewidths (attributed to lithium ion motion) and previously reported conductivity data.

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Figure Captions

Figure 1. ^{27}Al MAS NMR spectra for $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ at x=0.1 and x=0.3

Figure 1b. ^{27}Al MAS NMR spectra for $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$ as a function of aluminium content.

Figure 2. The ratio of tetrahedral to octahedral 27Al sites (Al_t/Al_o) in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ and $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$ as a function of aluminium content, calculated from the NMR spectra.

Figure 3. ^{31}P MAS NMR spectra for $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$ as a function of aluminium content.

Figure 4. Changes in the integrated intensities of ^{31}P spectra as a function of aluminium content in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ and $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$. Numbers are in arbitrary units.

Figure 5. ^{7}Li static NMR spectra for $Li_{1.3}Al_{.3}Ti_{1.7}(PO_4)_3$ and $Li_{1.3}Al_{.3}Ti_{1.7}(VO_4)_{0.1}(PO_4)_{2.9}$ showing central transition and first order satellites with Cq ~ 42kHz.

Figure 6. The first order quadrupolar coupling constant Cq for ^{7}Li as a function of increasing aluminium content in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$ and $Li_{1+x}Al_xTi_{2-x}(NbO_4)_{0.1}(PO_4)_{2.9}$.

Figure 7. ^{7}Li full width at half maximum (FWHM) central transition linewidths in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, $Li_{1+x}Al_xTi_{2-x}(VO_4)_{0.1}(PO_4)_{2.9}$ and $Li_{1+x}Al_xTi_{2-x}(NbO_4)_{0.1}(PO_4)_{2.9}$ as a function of aluminium content.