Electrical conductivity in lithium orthophosphates

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Abstract

The electrical conductivity of lithium orthophosphates was investigated as a function of the nature of the transition-metal cation. LiMPO4 (M = Mn, Co, Ni) compounds and their derivatives were investigated. The enhancement in ionic conductivity appeared for compounds containing manganese cations. A relationship between crystal structure and ionic conductivity was established and discussed.

Keywords: Olivine-type compounds; Lithium orthophosphates; Electrical conductivity

1. Introduction

Recently, solid-state ionics gains intensive development, especially in the energy storage related field, due to the potential applications of solid electrolyte and electrode materials as well. Extensive works have been carried out for the search of superior fast lithium-ion conductors as membrane in advanced batteries has been carried out [1,2]. It has been shown by Goodenough et al. that frameworks built up from PO4 or from P2O7 polyamions are good candidates for the use of solid electrolytes [3] and electrode materials [4] in rechargeable lithium cells. The low atomic weight of lithium and the high negative Gibbs energies of formation of many lithium compounds, which may be formed in the course of discharge, are very promising in this respect.

Previous studies of the crystal chemistry and ion transport properties of alkali-based phosphates A xB2(PO4)3, with A = Li, Na and B = transition-metal, have shown that the sodium members have a Nasicon-type structure [5], while lithium compounds have been shown to exhibit various structures depending on the substitution at the B site [6]. Lithium orthophosphates LiMPO4 (M = Mn, Co, Ni) [7,8] adopt an olivine-related structure, which consists of a hexagonal closed-packing (HCP) of oxygen atoms with Li+ and M2+ cations located in half of the octahedral sites and P5+ cations in 1/8 of tetrahedral sites. This structure may be described as chains (along the c direction) of edge-sharing MO6 octahedra which are cross-linked by the PO4 groups forming a three-dimensional network (Fig. 1). Tunnels perpendicular to the [0 1 0] and [0 0 1] directions contain octahedrally coordinated Li+ cations (along the b axis), which are mobile in these cavities.

The ionic conductivity of Li3Sc2(PO4)3 ceramics was optimized to \(2 \times 10^{-9} \text{ S cm}^{-1}\) at room temperature [9]. The increase of the conductivity was also obtained in Li3Sc2(PO4)3 by the substitution of the scandium with aluminium and yttrium. Recently, orthorhombic phospho-olivine were investigated as high-voltage positive electrode active materials for lithium secondary batteries. LiCoPO4 exhibited the highest 4.8 V discharge plateau of 100 mA h g \(^{-1}\) vs. Li/Li+ [10,11]. In contrast, LiNiPO4 and LiMnPO4 had no voltage plateaus in their discharge profiles even after initial charging to 5.2 V but the observed irreversible capacity is attributed to the poor electronic conductivity [10]. Thus, it is an important issue to collect data on electrical transport in these compounds.
The aim of this paper was the study of the electrical transport properties of lithium orthophosphates LiMPO$_4$ (M = Mn, Co, Ni) and their mixed compounds Li(M, M')PO$_4$ with M' = Co, Ni. The conductivity measurements were carried out by impedance spectroscopy. The relationship between transport properties and microstructure is discussed.

2. Experimental

All the lithium orthophosphates LiMPO$_4$ (M = Mn, Co, Ni) and mixed samples Li(M, M')PO$_4$ (with M' = Co, Ni) were synthesized by solid-state reaction. Ammonium phosphate (NH$_4$)$_2$HPO$_4$ was mixed with stoichiometric amounts of high purity Li$_2$CO$_3$, MCO$_3$ (M = Mn, Co) and NiO. The mixture was ground thoroughly in an agate mortar followed by calcination at 800 °C for 48 h. The reaction products and the structure were identified by X-ray powder diffraction (XRPD) using a Philips diffractometer with a cobalt anticathode. High purity silicon powder was used as an internal standard and lattice parameters were computer refined.

A.c. conductivity measurements were carried out on compact discs prepared with ionically blocking gold electrodes using a frequency-response analyser (model Solartron FRA 1255) and a broadband dielectric converter (model BDC-N Novocontrol). Samples 5 mm in diameter and 2-mm thick were formed by pressing solid powders at 4 ton cm$^{-2}$ and placed in a holder Novocontrol™. Measurements were carried out in the frequency range 0.001–1000 kHz and monitored in the temperature range 373–573 K. Overall system was controlled by computer using the win-deta™ program from Novocontrol. Thus, our bench apparatus is able to measure electrical conductivity in the range from 0.1 to $10^{-18}$ S cm$^{-1}$. Here, one can neglect the difference in stoichiometry of the sample near electrodes because the voltage at the electrodes was chosen to be in the order of 10 mV and the current in the sample was very small (nA) during the measurements. Data analysis of the conductivity measurements was conducted assuming an equivalent circuit for the materials to be a parallel combination of conductance $G$ and a constant phase element (CPE), assuming the power law $Z = A(j\omega)^{-n}$. The $A$ and $n$ parameters were calculated by the nonlinear-least-squares (NLLS) method [12].

3. Results and discussion

3.1. Structural properties

The XRPD diagrams showed that all lithium orthophosphate compounds studied are isomorph to the related olivine structure with a HCP oxygen array and tetrahedral sites occupied P$^{5+}$ formed PO$_4$ oxo-anions. XRPD of Li(M, M')PO$_4$ were indexed, assuming the orthorhombic system with the space group Pmnb. Cell parameters refined from the X-ray diffraction patterns using the least-squares method are gathered in Table 1. These results are in good agreement with values reported in Ref. [13]; as an example, the LiCoPO$_4$ phase was indexed with unit cell parameters of $a = 5.920$ Å, $b = 10.213$ Å, and $c = 4.701$ Å. The evolution of the lattice parameters as a function of the mean ionic radii of transition-metal cation [14] is shown in Fig. 2. We remark that the increase of the size of the divalent cation is accompanied by an increase of the lattice parameters and by the linear variation the molar volume as well. These results agree well with the structural model for the substitution of the M$^{2+}$ cation for smaller M$^{2+}$ cation in lithium orthophosphates. Furthermore, the olivine structure is preserved because the similarities of the size for small cations as Li$^+$ and M$^{2+}$. Such a behavior was currently observed for numerous compounds of the LiMPO$_4$ group [11]. Moreover, the olivine structure has orthorhombic symmetry with alternate $a$–c planes of Li and M occupying the octahedral sites, which makes it possible for there to be the two-dimensional Li diffusion paths between the HCP oxygen layers.

3.2. Electrical conductivity studies

Impedance measurements (a.c. conductivity) for LiMPO$_4$ and Li(M, M')PO$_4$ compounds have been carried out as a function of the temperature in the range 100–300 °C. As an example, both Nyquist and Bode plots at 300 °C of the LiNiPO$_4$ sample are shown.

Fig. 1. Schematic representation of the crystal structure of LiMPO$_4$ compounds showing the HCP oxygen array with MO$_6$ and PO$_4$ groups.
The impedance diagrams of the other Li(M, M')PO_4 materials are of the same type. All the spectra are characterized by the presence of a clearly distinguished semi-circle. In the first order approximation, the equivalent circuit of the cell can be presented by to be a parallel combination of conductance (G) and a CPE. The latter can originate from anomalous diffusion processes tacking place in the bulk material [15].

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a \pm 0.004 ) (( \text{Å} ))</th>
<th>( b \pm 0.006 ) (( \text{Å} ))</th>
<th>( c \pm 0.004 ) (( \text{Å} ))</th>
<th>( V \pm 0.3 ) (( \text{Å}^3 ))</th>
<th>( &lt; r_i &gt; ) (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNiPO_4</td>
<td>5.859</td>
<td>10.038</td>
<td>4.681</td>
<td>275.3</td>
<td>0.69</td>
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<tr>
<td>Li(Co, Ni)PO_4</td>
<td>5.896</td>
<td>10.123</td>
<td>4.692</td>
<td>280.3</td>
<td>0.72</td>
</tr>
<tr>
<td>LiCoPO_4</td>
<td>5.920</td>
<td>10.213</td>
<td>4.701</td>
<td>284.2</td>
<td>0.74</td>
</tr>
<tr>
<td>Li(Mn, Ni)PO_4</td>
<td>5.968</td>
<td>10.220</td>
<td>4.711</td>
<td>287.3</td>
<td>0.76</td>
</tr>
<tr>
<td>Li(Mn, Co)PO_4</td>
<td>6.006</td>
<td>10.311</td>
<td>4.730</td>
<td>292.9</td>
<td>0.79</td>
</tr>
<tr>
<td>LiMnPO_4</td>
<td>6.108</td>
<td>10.449</td>
<td>4.744</td>
<td>302.8</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Fig. 2. Variation of (a) the lattice parameters and (b) the unit cell volume as a function of the mean ionic radii of M elements in Li(M, M')PO_4 orthophosphates.

in Fig. 3(a–b). The impedance diagrams of the other Li(M, M')PO_4 materials are of the same type. All the spectra are characterized by the presence of a clearly distinguished semi-circle. In the first order approximation, the equivalent circuit of the cell can be presented by to be a parallel combination of conductance (G) and a CPE. The latter can originate from anomalous diffusion processes tacking place in the bulk material [15].

Fig. 4 presents the experimental results of the electrical conductivity for all orthophosphate samples in the standard Arrhenius plot \( \sigma = \sigma_0 \exp(-E_a/k_B T) \), where \( E_a \) is the activation energy. These results show an increase of the conductivity with increasing temperature for all compounds indicating a characteristic activated behavior over the complete temperature range studied. Because of the very large values of resistance, it was impossible to obtain dispersion curves at temperatures lower than 100 °C.

Fig. 3. (a) Bode plot and (b) Nyquist plot for LiNiPO_4 at 300 °C.
Furthermore, plots of log(σ) vs. 1/T were found to be linear in the temperature range considered. From impedance measurements, the total conductivity activation energies, $E_a$, were derived, yielding an activation energy of 0.6 eV for LiMPO$_4$ compounds and their derivatives Li(M, M')PO$_4$. Fig. 5 displays the variation of $E_a$ vs. unit cell volume. These results are similar to those found for other lithium fast-ion conductors. For example, LiMnPO$_4$ exhibits an activation energy of $E_a = 0.6$ eV [16].

We can ascertain that the activation energy decreases weakly with the decrease of the volume molar, as shown in Fig. 5. This phenomenon has been observed by Subramanian et al. for the substituted LiZr$_2$(PO$_4$)$_3$ system [6]. The change in the activation energy was attributed to a shrinking lattice effect. It is suggested that, for smaller lattice, the decreasing size of the cavities in the olivine framework, in which the lithium ions reside, brings these cations closer the M$^{2+}$ ions. Consequently, the increasing repulsion between Li$^+$ and M$^{2+}$ cations reduces the strength of the Li–O bonds resulting in lower activation energy and higher conductivity.

Data analysis of the a.c. conductivity measurements was conducted assuming an equivalent circuit for the materials to be a parallel combination of conductance $G$ and a CPE. Frequency-dependent conductivity is interesting in that it has been observed in disordered semiconductors, insulators or fast-ion conductors in which conduction can take place among localized states by a mechanism of carrier hopping [17]. Fig. 6 shows the plots of the conductivity vs. frequency for Li(M, M')PO$_4$ samples. In the high-frequency domain, the conductivity dispersion follows the power law dependence as observed in many hopping ion-conductors [18]. To evaluate the qualitative behavior, it is assumed a power law $\sigma(\omega) = \sigma_0 + A(\omega)^n$, where $\sigma_0$ is the d.c. term, $A$ is a constant, and $n$ is the slope of high-frequency dispersion calculated by the NLLS method. It is found that the power factor $n$ is weakly temperature dependent with a mean value $n = 0.86$ for the Li(M, M')PO$_4$ samples (Table 2). Furthermore, the high-frequency dispersion parameter seems to be relatively unaffected by the transition-metal substitution.

Bearing in mind that the weakly temperature dependent exponent is lying below unity and that the activation energy has a high value of $\sim 0.65$ eV, these experimental results suggest that the electrical conduction in lithium orthophosphates is presumably caused by the hopping of Li$^+$ ions. Such general trends have been reported for the Li–B–O system for which the activation energies were found in the range 0.6–0.7 eV and the power factor was estimated to be between 0.6 and 0.8 [19]. Considering the occupancy of Li atoms in octahedral sites, we must consider the interstitial network connected in three dimensions that provides the pathway for Li$^+$-ion diffusion. It is obvious that, upon the
transition-metal substitution in the LiMPO$_4$ olivine phase, the shrinkage of the lattice results in a decreasing size of the cavities, in which lithium ions reside, and in a decreasing ion-diffusion due to the stiffening of the Li–O chemical bonds.

4. Conclusion

Crystallochemical studies of the mixed lithium orthophosphates Li(M, M’)PO$_4$ have shown that these compounds are solid solution isostructural to olivine. The electrical measurements displayed the change in the electrical conductivity with the size of the cavities allowing free motion of the Li$^+$ ions. Even these compounds exhibit poor conduction properties, it was instructive to determine the effect of the cavity size on conductivity for various M$^{2+}$ substitutions. The change in the activation energy was attributed to a shrinking lattice effect. It is suggested that, for smaller lattice, the decreasing size of the cavities, in which the lithium ions reside, brings these cations closer the M$^{2+}$ ions. Consequently, the increasing repulsion between Li$^+$ and M$^{2+}$ cations reduces the strength of the Li–O bonds resulting in lower activation energy and higher conductivity. Analysis of the frequency-dependent conductivity suggests that the electrical conduction in lithium orthophosphates is presumably caused by the hopping of Li$^+$ ions between octahedral sites of the olivine framework.

References