Enhanced ionic conductivity of Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ with addition of lithium borate

Dawei Wang $^{a}$, Guiming Zhong $^{a}$, Yixiao Li $^{a}$, Zhengliang Gong $^{b}$, Matthew J. McDonald $^{a}$, Jin-Xiao Mi $^{c}$, Riqiang Fu $^{d}$, Zhicong Shi $^{c}$, Yong Yang $^{a,⁎}$

$^{a}$ Collaborative Innovation Center of Chemistry for Energy Materials, State Key Lab of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
$^{b}$ National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, USA
$^{c}$ Department of Material Science and Engineering, Xiamen University, Xiamen 361005, China
$^{d}$ College of Energy, Xiamen University, Xiamen 361005, China
$^{⁎}$ Corresponding author. Tel./fax: +86 592 2185753.
E-mail address: yyang@xmu.edu.cn (Y. Yang).

1. Introduction

Inorganic solid electrolytes have attracted much interest as the range of applications of lithium ion batteries widens. The replacement of dangerously flammable organic electrolytes by non-flammable, inorganic solid electrolytes can go a long way to ameliorating the safety problems that have plagued lithium ion batteries as of late, and they are expected to play an important role in the future development of large-scale, solid state lithium ion battery systems with enhanced safety features.

Li$_5$SiO$_4$–Li$_3$PO$_4$ solid solutions have been reported as lithium ion conductors with a γ–Li$_3$PO$_4$ structure [1–4]. With an ionic conductivity of $3 × 10^{-6}$ S cm$^{-1}$ at room temperature (RT), the composition Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ had the best showing of all the solid solution compounds xLi$_5$SiO$_4$–(1–x)Li$_3$PO$_4$. In addition, the Li$_5$SiO$_4$–Li$_3$PO$_4$ system showed excellent chemical and electrochemical stability, which was paired with relatively simple and convenient synthesis procedures. For these reasons, Li$_5$SiO$_4$–Li$_3$PO$_4$ solid electrolytes are capable of competing with LiPON glasses, which also showed an ionic conductivity on the order of $10^{-5}$ S cm$^{-1}$ at RT [5].

In order to increase the ionic conductivity in the Li$_5$SiO$_4$–Li$_3$PO$_4$ system, Zhang et al. [6] added small amounts of LiBO$_2$ and its precursors to the 0.6Li$_5$SiO$_4$–0.4Li$_3$PO$_4$ system and investigated their effects. They found that the ionic conductivity showed a moderate increase (less than 30%) after the addition of LiBO$_2$ and/or its precursors, but then decreased after further addition of LiBO$_2$ because of the formation of a Li$_3$SiO$_4$ impurity phase. The lithium borate was speculated to play a role as a sintering assistant, but no direct evidence was given in their study. Much earlier, Masquelier et al. [7] had successfully doped silicon with boron up to $x = 0.5$ in Li$_{3.5}$B$_x$Si$_{1-x}$O$_4$ solid solutions and confirmed the formation of solid solutions from a linear decrease in crystal parameters after the addition of boron. However, further measurements on ionic conductivity were not taken in their study.

In this work, in order to study the form of boron in the Li$_5$SiO$_4$–Li$_3$PO$_4$ phase, or more precisely, whether boron atoms insert into the crystal structure or play a role as a sintering assistant, we perform a systematic study on the formation and microstructure of a series of compounds with different ratios of B:(Si$_{0.5}$P$_{0.5}$), using various characterization techniques such as XRD, SEM and solid-state nuclear magnetic resonance (NMR) techniques. We further discuss the origin of the improved ionic conductivity of the compounds.

© 2015 Elsevier B.V. All rights reserved.
2. Experimental

A series of \( \text{Li}_x\text{BO}_3-(1-x)\text{Li}_2\text{SiO}_3\text{P}_0\text{.5O}_4 \) (0 ≤ x ≤ 0.2) compounds were prepared via a conventional solid reaction. The starting materials Li2CO3, H2BO3, NH4H2PO4 (purities of 98.0%, 99.5% and 99.0% respectively, all from the Sinopharm Chemical Reagent Co., Ltd) and SiO2 (purity of 99.8%, Alfa Aesar) were mixed together and ball-milled using ethanol as a grinding reagent. To compensate for lithium loss during calcination at high temperature, 5 mol% extra lithium was added for lithium borate added Li2SiO3P0.5O4 and 10% for the pristine sample. The precursors were dried after 4 h of ball-milling, then calcined at 900 °C for 10 h. This was followed by grinding, with the obtained powders being pressed into pellets under 5 MPa of pressure. For the lithium borate added samples, pellets were sintered at a temperature of 850 °C for 10 h and were then annealed to RT in the furnace, while the pristine Li2SiO3P0.5O4 pellets were sintered at 1000 °C for 10 h and were annealed to RT in accordance with the procedures in the literature [1,2].

X-ray powder diffraction (XRD) technique was used to characterize the phases and their purities, using Cu Kα radiation (1.54178 Å) on a Panalytical X’Pert (Philip, Netherlands) instrument. Normally, XRD patterns for Rietveld refinement were collected at 20 ppm with a step of 0.0167°, and 10 s per step. The XRD patterns for Rietveld refinement were collected from 10–50°, with a step of 0.0083°, and 30 s per step. GSAS software was used for Rietveld refinement of XRD data. The apparent density was measured by finding the weight and dimensions of pellets, and relative density was calculated by comparing the apparent density with the theoretical density. A Hitachi S-4800 scanning electron microscope was also used to check the cross-section morphology of samples.

AC impedance measurements were made in order to measure the conductivity of samples, using a Solartron 1260 impedance analyzer with the frequency range of 1 to 10^6 Hz and an amplitude of 100 mV. The measurement cell was constructed as follows: first, silver slurry was spread onto the surfaces of pellets and cured at 600 °C for 30 min in order to vaporize organic solvent. Following this, the silver-coated pellets were placed between two pieces of steel for testing. Test temperatures were varied from 50 to 150 °C at 10 °C intervals to study the temperature dependent relationship. The electronic conductivity was then measured using the DC polarization method with a Solartron 1287 electrochemical analyzer with a polarization potential of 0.1 V and a holding time of 10,000 s.

High-resolution magic angle spinning nuclear magnetic resonance (MAS NMR) was used to characterize the chemical environments of atoms (such as P and B). 31P MAS NMR spectra was undertaken at 162.0 MHz on a Bruker Avance 400 MHz NMR spectrometer using a small angle pulse of 1.4 μs and a delay time of 10,000 s. The resulting spectra were indexed peak positions were negligibly shifted with the addition of lithium borate. In order to investigate in more detail, Jade 5 software was used to calculate the lattice parameters of the samples. It was found that the lattice parameters were not consistently changed with increased boron content and any variations were due to experimental error.

3. Results and discussion

Both Li2SiO3 and Li3PO4 have a similar structure ([Li2SiO3: P21/m, Li3PO4: Pnma]) [9,10]. Therefore, they are likely to form solid solutions with each other in a wide stoichiometric range. The usual formulas are \( (1-x)\text{Li}_2\text{SiO}_3\text{P}_0\text{.5O}_4 \) (0 ≤ x ≤ 0.25) with a Li2SiO3 structure and \( (1-x)\text{Li}_3\text{PO}_4\text{–xLi}_2\text{SiO}_4 \) (0.5 ≤ x ≤ 1) with a \( \gamma \)-Li3PO4 structure [11]. Since boron shows only a slightly smaller ionic radius (0.11 Å) than silicon (0.26 Å) and phosphorus (0.17 Å) while tetrahedrally coordinated [11], it could possibly replace Si and/or P by B and form a series of solid solutions. In addition, lithium borates are good sintering assistants which can improve the bulk properties of ceramic materials. Thus, it is necessary to identify the role of boron in Li2SiO3P0.5O4.

Fig. 1 shows the XRD patterns of lithium borate added samples. The diffraction results indicate that the main sample phase was crystallized in an orthorhombic structure, which is the structure of crystal Li3PO4. Traces of Li2CO3 were detected due to the extra lithium source. No crystalline lithium borates could be found from the XRD patterns, and the indexed peak positions were negligibly shifted with the addition of lithium borate. In order to investigate in more detail, Jade 5 software was used to calculate the lattice parameters of the samples. It was found that the lattice parameters were not consistently changed with increased boron content and any variations were due to experimental error.

It is difficult to conclude whether the boron played a role as a substitutional atom or as the sintering assistant from the XRD data alone, as XRD focuses on a long range order and is more sensitive to heavy atoms. In contrast, NMR is a technique that is sensitive at a short range order and can gather information on the local atmosphere of individual atoms. Therefore, it is possible to understand the behavior of each atom in a sample.

Fig. 2 shows 31P NMR spectra of xLi2BO3–(1–x)Li2SiO3P0.5O4 (0 ≤ x ≤ 0.2) samples with the chemical shift at around 9 ppm, indicating that P is tetrahedrally coordinated in all compositions. No peaks attributable to P–O–P (Q1 = –4.4 ppm, Q2 = –22.7 ppm) or P–O–B (–16 ppm) bridges were observed in the 31P NMR spectra, confirming that Li3PO4 and Li2O–B2O3–P2O5 glasses do not exist in this system [12].

Fig. 3 shows the 11B MAS NMR spectra of xLi2BO3–(1–x)Li2SiO3P0.5O4 (0 ≤ x ≤ 0.2). There are two groups of peaks in the spectra, whose chemical shifts are approximately 20 ppm and 2 ppm. The peaks at 20 ppm clearly show the second-order quadrupolar line-broadening, resulting from non-spherical charge distribution interacting with the electric field gradient (EFG), V, at the boron nucleus. This indicates that the boron exist in a non-symmetric environment at grain boundaries in the form of B03 having a large EFG. In contrast, the boron peak at 2 ppm is narrow and does not have apparent second-order quadrupolar line-broadening effects, implying that such a boron locates in a
symmetric tetrahedral coordination, i.e. having a BO₄ structural unit at this site (Fig. 4). This kind of boron might exist at grain boundaries in the form of lithium borate glass, or has successfully replaced Si/P and inserted into the crystal lattice.

For different compositions of \( x \) \( \text{Li}_3\text{BO}_3 - (1-x)\text{Li}_3.5\text{Si}_0.5\text{P}_0.5\text{O}_4 \) (0 \( \leq x \leq 0.2 \)), the line-shapes for the peak at \( \sim 20 \) ppm are rather complex, implying that there exist complex environments for boron and thus the existence of different lithium borate glasses with different numbers of oxygen bridges[13]. Interestingly, as \( x \) increases from 0.15 to 0.2, the line-shape gradually becomes the typical second-order quadrupolar line-broadening with the asymmetry parameter \( \eta_Q = (V_{xx} - V_{yy})/V_{zz} \sim 0 \), where \( V_{xx}, V_{yy}, \) and \( V_{zz} \) are referred to the EFG’s principal elements. In other words, when \( x \geq 0.2 \), there exists only one dominant boron in the form of BO₃ having the EFG asymmetry parameter \( \eta_Q \sim 0 \) in the bulk of the system. In order to obtain the line-shape of the second order quadrupolar effect for the boron having the EFG asymmetry parameter \( \eta_Q \sim 0 \), we subtracted the spectrum for \( x = 0.15 \) (Fig. 3c) from the one for \( x = 0.2 \) (Fig. 3d). This difference spectrum, as shown in Fig. 3e, is considered to represent the typical quadrupolar effect and likely describes only one boron local atmosphere with increased boron content (\( x \geq 0.2 \)). On the other hand, the line-shape for \( x = 0.05 \) (Fig. 3a) appears to be reasonably fitted using the asymmetry parameter \( \eta_Q \sim 1 \), indicating that there exists a dominant boron in the form of BO₃ having the EFG asymmetry parameter \( \eta_Q \sim 1 \) in the bulk of the system when \( x < 0.05 \). Therefore, it is obvious that there are two distinct boron environments in the form of BO₃ in the LISICON electrolyte system, one having the EFG asymmetry parameter \( \eta_Q \sim 1 \) while another one having the EFG asymmetry parameter \( \eta_Q \sim 0 \). The \( ^{11}\text{B} \) line-shape for the former can be represented by Fig. 3a (\( x \leq 0.05 \)) while for the latter one is shown by Fig. 3e (\( x > 0.2 \)). Apparently, the line-shapes for \( x = 0.1, 0.15, \) and 0.2 are resulted from the overlapped line-shapes from these two distinct boron environments in the system. Fig. 3f, g, and h shows the superimposed spectra from Fig. 3a and e by adjusting the relative ratio of their spectra for \( x = 0.1, 0.15, \) and 0.2. Clearly, the fitted spectra for \( x = 0.1, 0.15, \) and 0.2 agree very well with their corresponding experimental spectra, implying that there are indeed two distinct forms of boron associated with these peaks. On the other hand, the integrated areas of the peaks at \(-20 \) ppm and \( 2 \) ppm suggest that majority of boron exists at grain boundaries in the form of BO₃ (at \(-20 \) ppm), and only a small fraction of the boron is present in the form of BO₄ (2 ppm peak).

Fig. 5 presents the cross section morphologies of samples with different lithium borate contents. It was observed that a small amount of
voids existed in the samples, which may have been due to the moderate pressure while producing pellets or the sintering method employed. The cross sections of the pristine and Li$_3$BO$_3$ glass added samples all exhibited intra-crystalline structure, which indicated a good sintering behavior as well as a low grain boundary resistance. There was no any difference between the pristine and Li$_3$BO$_3$ glass added samples from a macro-morphological perspective. Therefore, it was difficult to judge any change in ionic conductivity from SEM imaging of grain boundaries.

Fig. 5f shows a photo of a lithium borate added LISICON sample, with the translucent appearance indicating a good sintering behavior and a high level of grain boundary contact.

The relative density of a sample is a key characteristic of its mechanical properties and plays an important role in ionic conductivity. The relative densities of samples increased from 86% to more than 90% after the addition of lithium borate (the relative density is 91%, 91%, 93%, 93% as x = 0.05, 0.1, 0.15, 0.2, respectively). As well, the sintering temperature of Li$_3$BO$_3$ glass added Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ was 850 °C, 150 °C lower than that of pristine Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$. This decrease was mostly due to Li$_3$BO$_3$ glass having acted as a sintering assistant, improving the sintering properties, in particular relative densities.

With a moderate mobile lithium ion concentration and a suitable crystal structure, Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ had the highest ionic conductivity of the set of Li$_3$PO$_4$–Li$_4$SiO$_4$ solid solutions [1,2]. Here, Rietveld refinement of XRD data was used to fit the crystal structure parameters. The structural model proposed by Rabadanov [14] was used in the refinements, utilizing GSAS software with the occupancies of Si–P and oxygen set to unity. The refinement patterns are shown in Fig. 6 with the structural information given in Table 1. From this information it can be seen that Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ had more lithium sites existing in its crystal structure than that of Li$_3$PO$_4$, which had two fully occupied lithium sites [10].

![Fig. 5. Morphologies of cross sections of xLi$_3$BO$_3$–(1–x)Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ pellets with (a) x = 0.0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15, and (e) x = 0.2. (f) Photo of a lithium borate added LISICON sample.](image)

![Fig. 6. XRD refinement of Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$, collected at room temperature.](image)
The lithium sites were not fully occupied, which facilitated lithium migration from one site to another, leading to the Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ sample having a much higher ionic conductivity than Li$_3$PO$_4$.

Fig. 7 shows the Nyquist plots of Ag||LiSICONs||Ag simulation cells. There was one semicircle at the high frequency range and one tail at the low frequency range which corresponded to the total resistance and electrode polarization, respectively. It was difficult to distinguish the bulk resistance and grain boundary resistance from impedance spectra, thus only total conductivity is discussed here. The high frequency semicircle decreased and vanished with increasing test temperature, leaving just a dispersive line at the low frequency side. Because of this, (RQ)Q and RQ equivalent circuits were used to fit the Nyquist plots at low and high temperatures. The varied shapes of tails were mainly due to the different interfaces between the samples and electrodes [15]. The conductivity of pristine Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ was about $6 \times 10^{-6}$ Sc m$^{-1}$ at room temperature, a result comparable with the literature [1,3,4]. After lithium borate addition, the conductivity improved to about $6.5 \times 10^{-6}$ Sc m$^{-1}$ at room temperature, while the differences among xLi$_2$BO$_3$-(1-x)Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ (0 ≤ x ≤ 0.2) samples were not obvious.

The conductivities of samples at different temperatures fit Arrhenius plots well (Fig. 8). The equation used was $\sigma = A \exp(-\Delta H / RT)$, where $\sigma$ is the conductivity, $A$ is the pre-factor, $R$ is the ideal gas constant, $T$ is the temperature in Kelvins, and $\Delta H$ is the activation energy. The activation energies and pre-factors of xLi$_2$BO$_3$-(1-x)Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ (0 ≤ x ≤ 0.2) calculated from Arrhenius plots, are given in Table 2. The overall activation energy increased slightly after the addition of lithium borate, since Li$_2$BO$_3$ glass which existed in the grain boundaries had a larger activation energy than the pristine material [16]. A high activation energy would have negative effects on the ionic conductivity, the observed increase in ionic conductivity must therefore have been due to the increase in pre-factor. This increase in pre-factor was mainly due to the observed increase in relative density.

An ideal solid electrolyte must be solely an ionic (i.e., not an electronic) conductor in case of short circuit in a lithium ion battery. In order to check the transference numbers of samples, electronic conductivities were measured by the DC polarization method (Fig. 9). The polarization time was 10,000 s, in order to eliminate any ionic effect due to the moderate lithium migration rate. The current drop at the beginning of the process was due to capacitance effects of space charge regions on the electrodes. The electronic conductivities of the samples were at about $10^{-8}$ S cm$^{-1}$, calculated from the final current at 10,000 s, and the calculated transference numbers of lithium mobile ions $t^+$ were more than 0.996 for all the Li$_2$BO$_3$ added Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ samples (Table 2), which confirmed that conduction was dominated by lithium ions.

In order to explore the possible interaction of solid electrolytes with cathode materials, XRD patterns were measured of mixtures of cathode and Li$_2$BO$_3$ added samples, before and after heat-treatment at 900 °C for 10 h (Fig. 10). There were no changes observed in the XRD data before and after calcination, which indicates that Li$_2$BO$_3$ added LiSICONs were stable when matched with LiCoO$_2$ and lithium rich materials such as 0.5LiMnO$_3$.0Co$_{0.2}$Ni$_{0.8}$O$_2$–0.5Li$_2$MnO$_3$, at least up to 900 °C. This good thermal stability with cathode materials may yield opportunities for constructing solid state batteries requiring high energy density cathode materials such as LiCoO$_2$ [17].

Table 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyck.</th>
<th>Site</th>
<th>S.O.F</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U[Å$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>8d</td>
<td>1</td>
<td>0.68</td>
<td>0.16400</td>
<td>−0.00270</td>
<td>0.23110</td>
<td>0.0104</td>
</tr>
<tr>
<td>Li2</td>
<td>4c</td>
<td>m</td>
<td>0.84</td>
<td>0.07420</td>
<td>1/4</td>
<td>0.68850</td>
<td>0.0196</td>
</tr>
<tr>
<td>P/Si</td>
<td>4c</td>
<td>m</td>
<td>1</td>
<td>0.14248</td>
<td>1/4</td>
<td>0.32783</td>
<td>0.0106</td>
</tr>
<tr>
<td>O1</td>
<td>8d</td>
<td>1</td>
<td>1</td>
<td>0.34400</td>
<td>1/4</td>
<td>0.27319</td>
<td>0.0200</td>
</tr>
<tr>
<td>O2</td>
<td>4c</td>
<td>m</td>
<td>0.68</td>
<td>0.05400</td>
<td>1/4</td>
<td>0.28318</td>
<td>0.0198</td>
</tr>
<tr>
<td>O3</td>
<td>4c</td>
<td>m</td>
<td>0.68</td>
<td>0.05400</td>
<td>1/4</td>
<td>0.28318</td>
<td>0.0198</td>
</tr>
<tr>
<td>Li1a</td>
<td>8d</td>
<td>1</td>
<td>0.32</td>
<td>0.17100</td>
<td>0.03700</td>
<td>0.19400</td>
<td>0.0085</td>
</tr>
<tr>
<td>Li2a</td>
<td>4c</td>
<td>m</td>
<td>0.13</td>
<td>0.09500</td>
<td>1/4</td>
<td>0.84400</td>
<td>0.0177</td>
</tr>
<tr>
<td>Li3</td>
<td>4c</td>
<td>m</td>
<td>0.04</td>
<td>0.21000</td>
<td>1/4</td>
<td>0.09000</td>
<td>0.0058</td>
</tr>
<tr>
<td>Li4</td>
<td>8d</td>
<td>1</td>
<td>0.13</td>
<td>0.02100</td>
<td>−0.04600</td>
<td>0.42800</td>
<td>0.0170</td>
</tr>
</tbody>
</table>

Fig. 7 Nyquist plots of xLi$_2$BO$_3$-(1-x)Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ (0 ≤ x ≤ 0.2) samples measured at room temperature.

Fig. 8 Arrhenius plots of xLi$_2$BO$_3$-(1-x)Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ (0 ≤ x ≤ 0.2) samples.

4. Conclusion

A series of xLi$_2$BO$_3$-(1-x)Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ (x = 0.0, 0.05, 0.1, 0.15, 0.2) samples were synthesized by solid state reaction. The lithium borate glasses settled at grain boundaries in the structure of BO$_3$ and BO$_4$, and played a role as sintering assistant. It was shown that the
conductivities of the samples were dominated by Li\textsuperscript{+} ionic conductivity with a transference number t\textsubscript{Li\textsuperscript{+}} ≥ 99.6%, i.e. 6.5 × 10\textsuperscript{-6} S cm\textsuperscript{-1} after Li\textsubscript{3}BO\textsubscript{3} addition, which is about two times that of pristine Li\textsubscript{3.5}Si\textsubscript{0.5}P\textsubscript{0.5}O\textsubscript{4} (~3.6 × 10\textsuperscript{-6} S cm\textsuperscript{-1} at room temperature). This increase of conductivity was due to the addition of lithium borate, which increased the relative densities of the samples from 85% to more than 90% of samples. It was also demonstrated that Li\textsubscript{3}BO\textsubscript{3} added samples were thermally stable together with both LiCoO\textsubscript{2} and the lithium rich material 0.5LiMn\textsubscript{0.6}Co\textsubscript{0.4}O\textsubscript{2}Ni\textsubscript{0.6}O\textsubscript{2}–0.5Li\textsubscript{3}MnO\textsubscript{3} up to 900 °C. The improvement of lithium borate added LISICONs with respect to their sintering behavior, ionic conductivity and chemical stability against cathode materials gives prominence to another material with great potential for constructing solid state batteries.

Acknowledgments

Financial support from the National Basic Research Program of China (973 program, Grant No. 2011CB935903) and the National Natural Science Foundation of China (Grant Nos. 21233004 and 21021002) is gratefully acknowledged. The \textsuperscript{11}B MAS NMR experiments were carried out at the National High Magnetic Field Laboratory (NHMFL), supported by the National Science Foundation Cooperative Agreement (DMR-1157490) with the State of Florida.

References


![Fig. 9. DC polarization characterization of xLi\textsubscript{3}BO\textsubscript{3}–(1–x)Li\textsubscript{3.5}Si\textsubscript{0.5}P\textsubscript{0.5}O\textsubscript{4} (0 ≤ x ≤ 0.2) samples.](image)

![Fig. 10. XRD patterns of samples: mixture of LiCoO\textsubscript{2} and 0.1Li\textsubscript{3}BO\textsubscript{3}–0.9Li\textsubscript{3.5}Si\textsubscript{0.5}P\textsubscript{0.5}O\textsubscript{4} (a) before and (b) after heat-treatment at 900 °C for 10 h; a mixture of 0.5LiMn\textsubscript{0.6}Co\textsubscript{0.4}O\textsubscript{2}Ni\textsubscript{0.6}O\textsubscript{2}–0.5Li\textsubscript{3}MnO\textsubscript{3} and 0.2Li\textsubscript{3}BO\textsubscript{3}–0.8Li\textsubscript{3.5}Si\textsubscript{0.5}P\textsubscript{0.5}O\textsubscript{4} (c) before and (d) after heat-treatment at 900 °C for 10 h. # denotes XRD peaks of LiCoO\textsubscript{2}, + represents XRD peaks of 0.5LiMn\textsubscript{0.6}Co\textsubscript{0.4}O\textsubscript{2}Ni\textsubscript{0.6}O\textsubscript{2}–0.5Li\textsubscript{3}MnO\textsubscript{3}, the remaining peaks can be attributed to lithium borate added LISICONs.](image)

### Table 2

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Activation energy/kJ mol\textsuperscript{-1}</th>
<th>Pre-factor RT × 10\textsuperscript{-6}/S cm\textsuperscript{-1}</th>
<th>Conductivity/DC-conductivity/Transference number (t\textsubscript{Li\textsuperscript{+}})</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>46.8</td>
<td>5.19</td>
<td>3.6</td>
<td>–</td>
</tr>
<tr>
<td>0.05</td>
<td>48.4</td>
<td>5.70</td>
<td>6.31</td>
<td>2.80</td>
</tr>
<tr>
<td>0.10</td>
<td>48.9</td>
<td>5.73</td>
<td>6.23</td>
<td>2.76</td>
</tr>
<tr>
<td>0.15</td>
<td>49.4</td>
<td>5.86</td>
<td>6.56</td>
<td>2.47</td>
</tr>
<tr>
<td>0.20</td>
<td>49.8</td>
<td>5.92</td>
<td>6.31</td>
<td>0.67</td>
</tr>
</tbody>
</table>