Bibliographical Review on Inorganic Lithium Ion Conductors

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ABSTRACT

A bibliographical review of inorganic lithium ion conductors is presented with a focus on those potential candidates for lithium battery application. A wide variety of inorganic lithium ion conductors, both crystalline ceramics and non-crystalline glasses, are considered.

Key words : Solid electrolyte, Lithium ionic conductivity, Lithium batteries

S ince its invention by a Japanese company in 1990s, the lithium ion battery has attracted much attention both of consumers and different companies because of its performance merits of high open-circuit voltage and energy density, growing markets and rapid increases in production. Lithium ion secondary batteries have so far been used as a power source for portable electronic devices such as cellular telephones, notebook-type personal computers and video cameras.[1] The size of the commercially available battery is limited to 10 Wh, while large size lithium ion batteries are not yet available on the market on a commercial scale due to the difficulties in processing and safety issues. However, the demands for large scale batteries are increasing for reasons of saving energy and environment protection, i.e. development of electric vehicle, load-leveling of electric power, and supplementary systems for solar and wind power. In order to meet these special demands, many lithium ion cells are used in series or parallel combinations, and the use of larger amount of organic electrolytes is indispensable because most conventional lithium ion cells contain inflammable organic solvent as electrolytes. The presence of a large amount of organic liquid electrolytes could cause severe leakage or explosion of electrolytes.

One of the effective ways to overcome these safety problems is to replace the liquid electrolytes with nonflammable solid electrolytes. Among different solid electrolytes, solid polymer electrolyte has been considered to be an ideal alternative (to liquid electrolyte counterpart), and much work has been done to develop practical all-solid state batteries based on solid polymer electrolytes.[2-6] However, the studies on the shelf life of lithium polymer batteries show that the chemical stability between the polymer electrolytes and electrodes is usually difficult to be warranted.[7-10] Inorganic lithium ion conductors are able to pass the challenge of

chemical compatibility with electrodes and usually insensitive to hydrolysis,[11] thus the finding or synthesis more suitable inorganic Li solid electrolytes that can be employed in solid-state batteries has been of great interest.

Furthermore, besides the main commercial impetus for the development of large-scale lithium batteries, inorganic lithium ion conductors have also been attractive for use as solid electrolytes of various electrochemical gas sensors[12-17] because of their advantages of high selectivity and reproducibility, small size, simple structure, cheap cost and easy manipulation. This paper will highlight a number of recent developments on lithium solid electrolytes.

1. Lithium Ion Conductors with NASICON-type Structure

Among the several families of inorganic solids exhibiting lithium-ion conduction, lithium ionic conductors based on the NASICON structure (Fig. 1) are of special interest, because of their high conductivity combined with low activation energy. The general formula of NASICON-type compound is $(M')_n(M'')_m[A_2B_3O_{12}]$ with n=0~1 and m=0~3. The structure can be described as a covalent skeleton $[A_2B_3O_{12}]^-$ constituted of AO_6 octahedra and of BO_4 tetrahedra which form 3D interconnected channels and two types of interstitial spaces (M and M) where conducting cations are distributed.[18-21] The conducting cations move from one site to another through the bottlenecks the size of which depends on the nature of the skeleton ions and on the carrier concentration in both type of sites (M and M).[18]

The lithium-containing analogues, $LiM_2(PO_4)_3$ where M=Zr, Ti, Ge, Sn and Hf[22-24] also have a NASICON-type structure. Among all these compounds, $LiTi_2(PO_4)_3$ has the most suitable bottleneck size for Li^+ migration (the cell volume of 1309 $Å^3$) and a minimum activation energy of 0.28-0.3 eV for bulk conduction.[25] However, $LiTi_2(PO_4)_3$ only reveals the ionic conductivity of 2×10^{-6} Scm^{-1} at room tem-

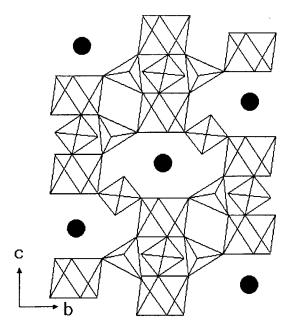**Fig. 1.** $LiM^{IV}_2(PO_4)_3$-NASICON structure showing the position of Li atoms within the $M^{IV}_2(PO_4)_3$ frame work.

perature due to its poor sinterability. But it was found that the conductivity and sinterability could be substantially improved with the addition of excess lithium compounds such as Li_2O, Li_3PO_4, Li_3BO_4 and $Li_4P_2O_7$.[25-27] It seems that the excess lithium compounds act as a flux to accelerate the sintering process and obtain high grain boundary conductivity.[26] Furthermore, it is also very effective for the enhancement of the conductivity to partially substitute M^{4+} with trivalent or aliovalent cations. Two types of solid solutions are available, with the general formula: $Li_{1-x}A_xM_{2-x}(PO_4)_3$ and $Li_{1+x}B_xM_{2-x}(PO_4)_3$. The substitution mechanisms are $A^{5+} = A^{.}_M + V^{'}_{Li}$ to form Li vacancies and $B^{3+} = B^{'}_M + Li^{.}_i$ to form lithium interstitials, respectively. The vacancy systems where Zr^{4+}, Ti^{4+} and Hf^{4+} are partially substituted by Nb^{5+} or Ta^{5+} have been investigated by Taylor and Chowdari et al.,[22,28] the maximum conductivity observed is 6×10^{-6} Scm^{-1} at 25°C for $Li_{0.1}Ta_{0.9}Zr_{1.1}(PO_4)_3$(x = 0.9), rising to 2×10^{-3} Scm^{-1} at 200°C.[28] In the last several years, Aono et al.[25-27,29] have conducted extensive studies on the interstitial solid solutions $Li_{1+x}B_xM_{2-x}(PO_4)_3$ where B = Al, Cr, Fe, Ga, Sc, In, Lu, Y and La, M = Ti, Ge, Hf, and Zr. The Ti systems with the compositions of $Li_{1.3}B_{0.3}Ti_{1.7}(PO_4)_3$ (B = Al or Sc) show the highest conductivity of 7×10^{-4} Scm^{-1} at room temperature, rising to 0.1 Scm^{-1} at 300°C,[26] and the activation energy is also very low, 0.35 eV decreasing to 0.2 eV above 200°C. However, it is not well clarified whether the high conductivities of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ and other trivalent metal-substituted systems are intrinsic to the structure or due to formation of secondary phases which favor sintering and decrease grain-boundary resistance.[25,26] Furthermore, for electrolyte application in lithium secondary battery, the Ti^{4+} should better be replaced by other metal ions that would be less susceptible to reduction by lithium metal.

The conductivities of Ge and Hf analogues, $LiGe_2(PO_4)O_3$ and $LiHf_2(PO_4)_3$[30,31] were also greatly enhanced by the addition of excess Li_2O or partial substitution of Ge^{4+} or Hf^{4+} with Cr, Fe, Sc, In, Lu, Y. The maximum conductivity of 1.7×10^{-4} Scm^{-1} at 25°C was attained in the composition of $Li_{1.2}Fe_{0.2}Hf_{1.8}(PO_4)O_3$, but further increasing the amount of dopants greatly reduces the ion conductivity.[32] Though these compounds are stable against lithium, they are significantly more costly to produce on an industrial scale. Another two analogues, $LiZr_2(PO_4)_3$ and $LiSn_2(PO_4)_3$ show even lower conductivity, because their structure was distorted to monoclinic rather than rhombohedral.[22] Recently, another NASICON-type compounds with the formula $LiM^{III}M^V(PO_4)_3$ (where M^V=Nb, Ta; M^{III}=Al, Fe, Cr) have been investigated by Thangadurai et al.[33] Among the Ta-containing compounds, $LiAlTa(PO_4)_3$ shows the highest ionic conductivity of 6.5×10^{-7} Scm^{-1} at 30°C, rising to 1.0×10^{-2} Scm^{-1} at 350°C. This material would not undergo a reduction in contact with lithium at elevated temperature, and it is comparatively cheap to produce on an industrial scale. Accordingly, this material deserves further attention to be tailored into suitable electrolyte materials for solid-state lithium batteries, especially for high temperature Li batteries. Furthermore, the compounds of $Li_2M^{III}M^{IV}(PO_4)_3$ (M^{III}=Cr, Fe, In; M^{IV}= Ti, Zr, Hf) have also been investigated,[34] the conductivities are in the range of 10^{-7}~10^{-8} Scm^{-1} at room temperature, rising to about 10^{-4} Scm^{-1} at 300°C.

2. Lithium Rare Earth Perovskites

Various studies on $La_{2/3-x}Li_{3x}TiO_3$[35-40] and $Ln_{1/2}Li_{1/2}TiO_3$ (Ln=La, Pr, Nd and Sm)[41-44] have been carried out in the last several years, since Inaguma et al.[35] reported the exciting discovery of high lithium ion conducting (10^{-3}~10^{-4} $S \cdot cm^{-1}$ at room temperature) in titanate-based solid solutions with a perovskite-related structure. The highest bulk conductivity reported in $La_{0.67-x}Li_{3x}TiO_3$ with x=0.11 is 1×10^{-3} Scm^{-1} at 25°C,[35] but the total conductivity is comparatively low, 2×10^{-5} Scm^{-1} due to grain boundary resistance. The electronic conductivity is estimated to be less than 1×10^{-8} Scm^{-1} at room temperature. The high ionic conductivity is considered to originate from the presence of a vacancy on the A-site and a lot of equivalent sites for lithium ions to occupy and move freely in the A-site perovskite. The following factors are considered to affect the ionic conductivity:

The carrier as well as vacancy concentration in A-site.[45,46] In A-site lattice, there are lithium ions, vacancies and skeletal ions (Ln) with larger ionic radius than lithium ions. When lithium ions migrate among the A-site lattices, the skeletal ions will behave as an obstacle to ion migration. So the distribution of lithium ions, vacancies and skeletal ions in A-site will strongly influence the ionic conductivity.

The subcell volume and the size of the bottleneck.[41,42,47] It is thought that conductivity decreases with the decrease of the bottleneck size, which is related to A-site ion substitutions and hydrostatic pressure. The substitutions of smaller

lanthanide ions such as Pr, Nd, and Sm for La in $La_{1/2}Li_{1/2}TiO_3$ decrease the ionic conductivity due to the decrease of the size of bottleneck. On the other hand, substitution of Sr with larger ionic radius for La in $La_{1/2}Li_{1/2}TiO_3$ increases the ionic conductivity due to the dilation of the subcell volume. Applying hydrostatic pressure to these perovskite compounds can suppress lithium ion migration and lead to a decrease of the conductivity.

The ordering of A-site.[37-41] The XRD results on $La_{1/2}Li_{1/2}TiO_3$[35] and $La_{2/3-x}Li_{3x}TiO_3$[37-41] showed that La^{3+} ions, Li^+ ions, and vacancies were to a small extent arranged in the alternate La-rich and Li-vacancy-rich layers along the c-axis, with formation of a tetragonal superlattice doubled along the c-axis with space group of P4/mmm. It was found that the ionic conductivity decreased with increasing the extent of ordering of La^{3+}. The decrease in ionic conductivity is attributed to an increase of activation energy for ionic conduction, which is presumably associated with the contraction of the lattice parameter a_p of the subcell.

The facilities of tilting of TiO_6 octahedron.[48] It is suggested that the tilting of TiO_6 octahedral actually occurs during lithium ion motion in the perovskite, and the conductivity increases with the increase of the tilting facilities of TiO_6 octahedron and vice versa.

The valency of both A-and B-site ions.[46,49] In peroviskite oxides, with a decrease in the average valence of A-site ions, i.e. with an increase in the average valence of B-sites ion, the site potential of A-site becomes shallow, and results in a decrease in the activation energy for the lithium ion migration and an increase of the ionic conductivity.

In all, the migration mechanism of lithium ion in these perovskite compounds has not been fully understood and more fundamental research works are still needed to clarify it. Furthermore, similar to Ti-based NASICON compounds, the perovskite-type compounds containing Ti^{4+} ions at the B-sites are easily reduced and become electronic conductors when they contact with lithium metal although they show high lithium ion conductivity at room temperature.[35,50] Therefore, it is a most important target to suppress the electronic conductivity while maintaining the high ionic conductivity. Those analogues containing Ta^{5+}[47,49,51-53] or Nb^{5+}[46,54-58] at the B-site have been of great interest due to their less susceptibility to reduction. The highest room temperature bulk conductivity of 7×10^{-3} Scm^{-1} was reported for $La_{1/3-x}Li_{3x}TaO_3$ with x = 0.06.[52] The solid solutions $Li_{2x}Sr_{1-2x}M_{0.5-x}Ta_{0.5+x}O_3$, where M = Cr, Fe, Co, Al, Ga, In and Y, have also shown high conductivities, the maximum conductivity observed is 1×10^{-4} Scm^{-1} at room temperature for $Li_{0.5}Sr_{0.5}Fe_{0.25}Ta_{0.75}O_3$ (x=0.25).[47] Furthermore, the electrical conductivities of Nb analogue $La_{1/3-x}Li_{3x}NbO_3$ have also been investigated by Belous and Martin et al.,[46,54] the highest bulk conductivity for x = 0.04 is 4.25×10^{-5} Scm^{-1} at 300 K,[54] and the ionic conductivity can be further enhanced by partial substitution of La with Sr, the maximum conductivity value of 7.3×10^{-5} Scm^{-1} at room temperature was attained for $(Li_{0.25}La_{0.25})_{1-x}Sr_{0.5x}NbO_3$ with x=0.125.[57]

3. Lithium Ion-conducting Glasses

Glassy materials have the following advantages for use as a solid state electrolyte: the easy formation of bulk samples without grain boundary, continuously variable compositions, isotropic properties for ion migration. Furthermore, the ability of glasses to be manufactured in thin film configuration enables them to make better contact with the electrodes in all solid state devices, which is particularly important for production of micro batteries and micro sensors.

It is well known that oxide glasses containing Ag^+ and Cu^+ ions are very conductive ionically at room temperature.[59,60] They are thus called superionic conducting glasses. However, the conductivity of oxide glasses containing alkali cation Li^+ is significantly lower than that of glasses containing Ag^+ even though the ionic radius of Li^+ is just half of that of Ag^+. The big difference in conductivity was thought to be resulted from the different electronic configurations between Ag^+ and Li^+.[59,60] The former has the complete d^{10} in the outermost orbitals and the latter has S^2, and thus Ag^+ are classified as a soft Lewis acid and Li^+ is classified as hard acid, and the soft acids as mobile ions are thought to be important to obtain highly conductive glasses.[61]

Up till now, several different lithium ion conducting glass systems have been investigated.[62-65] Two main strategies have been used to increase the ionic conductivity of lithium ion conducting glasses. The first is to use a combination of two anionic species, which has been known to be effective in enhancing the ionic conductivity due to the so-called mixed anionic effect.[64] The second strategy is to dissolve a highly ionic lithium salt in a conventional silicate, borate or phosphate. The enhancement of conductivity is attributed to a volume increasing effect of the dissolved ionic salt.[65] Although oxide-based glasses with a high concentration of lithium ions have been extensively studied to utilize as solid electrolytes of lithium batteries, the lithium ion conductivities of most oxide-based glasses are limited to 10^{-6} Scm^{-1} at room temperature.[63] Considerable enhancement in conductivity takes place when oxygen is replaced by the more polarizable sulphur (sulfide ions are classified as a soft acid). For example, the conductivity of the $60Li_2S.40SiS_2$ sulfide glass is on the order of 10^{-3} Scm^{-1} at room temperature,[66] increasing several folds when doped with lithium halides.[67] The button cells used Li_2S-SiS_2-LiI glass as electrolyte were commercialized and operated from ambient up to 180°C.[68,69] Besides SiS_2, the binary and ternary glasses in Li-S system have other glass formers, namely GeS_2,[70,71] B_2S_3[72,73] and P_2S_5.[74,75] Glasses in these systems also have high ionic conductivity comparable to the best crystalline ionic conductors and polymer electrolytes, in the ranges of $10^{-4} - 10^{-3}$ Scm^{-1} at room temperature.

However, there are several drawbacks in processing lithium sulfide glasses. One particular undesirable property is that glasses spontaneously devitrify, and the addition of lithium halides usually leads to a decrease of the decomposi-

tion voltage of the fabricated lithium batteries and a negative effect on glass stability[76] though it can enhance the ionic conductivity. Fortunately, the crystallization problem seems to be solved through adding some dopants. Kondo et al[77] have reported that the doping of Li_3PO_4 in Li_2S-SiS_2 based glasses can enhance the ionic conductivity without decreasing the decomposition voltage. Minami and Hayashi et al[78] discovered that the addition of small amount of Li_xMO_y (where M=Si, P,Ge, B, Al, Ga and In) to $60Li_2S.40SiS_2$ could improve the glass stability against crystallization and these Li_xMO_y-doped Li_2S-SiS_2 glasses also exhibited considerably high conductivity of 10^{-3} Scm^{-1}at room temperature. Furthermore, these glasses were proved to have good chemical and electrochemical stability in contact with Li metal and withstand high voltage application without decomposition.[79,80] So these oxysulfide glasses must be one of the most suitable lithium ion conductors as solid electrolytes for lithium secondary batteries. Recently, Bartholomew et al[81] have also reported that the addition of some oxides of groups IVA, VA, VB or VIA , such as SnS, SnS_2, TaS_2, BiI_3, As_2S_3, Sb_2O_3 and TeO_2 is helpful for the improvement of the stability of Li_2S-SiS_2, and the largest conductivity, 2.1×10^{-3} Scm^{-1} at room temperature, was obtained on the composition $60LiS_2$-$40SiS_2$-$2.79TaS_2$-$4.02LiI$. This conductivity value is the highest one recorded on inorganic lithium ion conductors at the room temperature to date.

Presently, the investigation on oxide based Li^+ ion conducting glasses has also made some progress. Glasses or glass-ceramics based on Li_2O-Al_2O_3-TiO_2-P_2O_5 have been reported to reveal a high ionic conductivity and high stability.[82] The maximum conductivity of 1.3×10^{-4} Scm^{-1} at room temperature was obtained on the composition of $14Li_2O$-$9Al_2O_3$-$38TiO_2$-$39P_2O_5$, this value is twice as large as the highest one of the sintered $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$.[82,26] This material has been successfully used as solid electrolyte for

CO_2 sensor.[83] However, glass formation of this particular composition is extremely difficult by simple air quenching techniques[84] as the glass transition temperature T_g and crystallization temperature T_c are relatively close. When the glass parent composition was adjusted to $50Li_2O$-$10TiO_2$-$40P_2O_5$, standard air quenching methods can be used in glass formation, however, the ionic conductivities of the glass samples with the general composition (50 + x) Li_2O-xAl_2O_3-$(10 - 2x)TiO_2$-$40P_2O_5$ ($0 \le x \le 4.5$) were decreased to 10^{-7}~10^{-8} Scm^{-1} at room temperature.[85]

4. Li_4SiO_4 and γ_{II}-Li_3PO_4 Structure Materials

While pure Li_4SiO_4 with a monoclinic structure, itself, is a poor lithium ion conductor with the conductivity of 2×10^{-5} Scm^{-1} at 300°C,[86] the ionic conductivity can be improved when it forms solid solutions with either Li_4GeO_4 or Li_4TiO_4, the best conductivity of 5×10^{-4} Scm^{-1} at 300°C was attained for the composition of $Li_4(Si_{0.6}Ti_{0.4})O_4$.[86] A more enhancement occurs when $Si^{4+}$was partially substituted by pentavalent cations such as P^{5+}, V^{5+} or As^{5+}, the maximum conductivity is observed for $Li_{3.6}(Si_{0.6}P_{0.4})O_4$, 1×10^{-4} Scm^{-1} at 100°C.[87]

Li_4SiO_4 can also be partially substituted by both divalent and trivalent cations. Main divalent cations include Zn, Mg, Co and Ni. The maximum conductivity for $Li_3Mg_{0.5}SiO_4$ is 2.3×10^{-5} Scm^{-1} at 200°C, rising to 1.5×10^{-2} Scm^{-1} at 400°C.[88-90] These materials are relatively easy to prepare, are stable in air and maintain their ionic conductivity for a very long time. Trivalent cations such as B, Al, Ga, Cr, Fe and In can partially substitute into Li_4SiO_4 giving rise to either interstitial or Li vacancy-based solid solutions of general formula: $Li_{4+x}M_xSi_{1-x}O_4$ ($Li^+ + M^{3+} \rightarrow Si^{4+}$) and $Li_{4-3y}M_ySiO_4$ ($3Li^+ \rightarrow M^{3+}$).[11,91-94] In forms of vacancy-based solid solution, generally, the conductivity decreases with increas-

Table 1. Solid Lithium Electrolytes for Possible Battery Application

Solid Electrolyte	Structure	Room temperature ionic conductivity (Scm⁻¹)		Stability with Li	Ref.
		σ_{bulk}	σ_{total}		
Lipon($Li_{3.3}PO_{3.9}N_{0.17}$)	Glass	–	2×10^{-6}	5.5 V vs Li	[2,139]
$0.95(0.6Li_2S$-$0.4SiS_2)$-$0.05Li_3PO_4$	Glass	–	9×10^{-4}	Stable with Li	[80]
$0.95(0.6Li_2S$-$0.4SiS_2)$-$0.05Li_4SiO_4$	Glass	–	10^{-3}	10 V vs Li/Ag,	[78,79]
$60Li_2S$-$40SiS_2$-$2.79TaS_2$-$4.02LiI$	Glass	–	2.1×10^{-3}	?	[81]
$Li_{0.29}La_{0.57}TiO_3$	Perovskite	10^{-3}	2×10^{-5}	1.7 V vs Li	[35-37,50]
$Li_{0.5}Sr_{0.5}M_{0.25}Ta_{0.75}O_3$ (M=Fe, Cr)	Perovskite	1×10^{-4}	6×10^{-5}	?	[47]
$Li_{1.3}M_{0.3}Ti_{1.7}(PO_4)_3$ (M=Al or Sc)	NASICON	3×10^{-3}	7×10^{-4}	2.4 V vs Li	[5, 25-27, 51]
$14Li_2O$-$9Al_2O_3$-$38TiO_2$-$39P_2O_5$	Glass	–	1.3×10^{-3}	?	[82]
$Li_{3.4}Si_{0.4}V_{0.6}O_4$	γ_{II}-Li_3PO_4	–	1×10^{-5}	Stable with Li	[101]
Li_9SiAlO_8	γ_{II}-Li_3PO_4	–	2.3×10^{-7}	6.5 V vs Li	[11]
Li_3N-KI	Tetragonal	–	1×10^{-4}	2.5-2.8 V (Decomposition voltage)	[109]

ing the size of M^{3+} [93] for a given amount of substitution. In interstitial solid solutions $Li_{4+x}M_xSi_{1-x}O_4$, except for B^{3+}, the ionic conductivity also decreases as the size of M^{3+} increases, and the Al^{3+} substituted compound $Li_{4.2}Al_{0.2}Si_{0.8}O_4$ shows the maximum conductivity of 1.58×10^{-3} Scm^{-1} at 300°C.[91] Another compound Li_9SiAlO_8 (x=0.5) exhibits an ionic conductivity of 2.3×10^{-7} Scm^{-1} at 25°C rising to 1.5×10^{-5} Scm^{-1} at 100°C, and it is stable versus metal lithium electrode up to 6.5 V below 100°C.[11] So this material may have a potential application in high voltage lithium cell.

In contrast to Li_4SO_4, the aliovalent doping of Li_4GeO_4 or Li_4TiO_4 leads predominantly to orthorhombic γ_{II}-Li_3PO_4 type phases. The compound $Li_{14}Zn$ $(GeO_4)_4$ which shows high conductivity at high temperature, e.g., 0.125 Scm^{-1} at 300°C, was firstly named LISICON.[95,96] (Lithium Super Ionic Conductor). But the room temperature conductivity of this compound is just 10^{-7} Scm^{-1}. One undesirable property for these LISICONs is that they usually show a remarkable reduction in ionic conductivity with time at low temperature, which is attributed to the trapping of mobile lithium ions by the immobile sublattice at low temperature via the formation of defect complexes.[97]

The solid solutions of Li_4AO_4-Li_3BO_4 (A=Si, Ge, Ti and B=P, As, V, Cr), with the general formula $Li_{3+x}A_xB_{1-x}O_4$, have also γ_{II}-Li_3PO_4 type phase structure,[98-101] the conductivities of most intermediate compositions are much higher than those of the end-members. Most of the compounds are thermodynamically stable and relatively insensitive to atmospheric attack. The maximum ambient conductivity of 4×10^{-5} Scm^{-1} was attained for $Li_{3.6}Ge_{0.6}V_{0.4}O_4$,[99] the silicate analogue, $Li_{3.4}Si_{0.4}V_{0.6}O_4$ shows slightly lower conductivity of 1×10^{-5} Scm^{-1} at room temperature.[101] It is stable in contact with lithium metal, and also it is less expensive to produce. So this material is an attractive candidate for use as solid electrolyte of lithium secondary batteries.

5. Li_3N and the Related Materials

Single crystals of lithium nitride Li_3N, with a layered crystal structure have very high ionic conductivity of 1×10^{-3} Scm^{-1} at room temperature, perpendicular to the c-axis (but two orders of magnitude less parallel to the c-axis), and the polycrystalline Li_3N also show ionic conductivity as high as 4×10^{-4} Scm^{-1} at 25°C.[102] Unfortunately, the practical applications of pure Li_3N are greatly limited due to its low theoretical decomposition potentials of 0.445 V[102] and its poor sinterability. A lot of attempts have been conducted to increase the decomposition voltage.[103-108] For example, the Al-doped compound, Li_3AlN_2 which is a cubic anti-fluorite type structure shows a decomposition of 0.85 V at 104°C.[103] However, the ionic conductivity is decreased to 5×10^{-8} Scm^{-1} at room temperature. LiMgN with the same anti-fluorite type structure exhibits even lower conductivity.[104] A mixture of Li_3N, LiI and LiOH, with the ratio of Li_3N:LiI:LiOH=1:2:0.77, shows a high conductivity of 0.95×10^{-4} Scm^{-1} at 25°C, and its decomposition voltage is also

increased to 1.6-1.8 V.[105] This material is, however, very hygroscopic and unsuitable for lithium battery application. Ternary lithium phosphorous nitrides $LiPN_2$ and Li_7PN_4 have the conductivities of 6.9×10^{-7} Scm^{-1} and 1.7×10^{-5} Scm^{-1} at 400 K respectively, which are two to three orders of magnitude less than that of Li_3N[106] and are of little interest. Lithium nitride chloride ($Li_9N_2Cl_3$), which crystallizes in a defect antifluorite structure with 10% of lithium sites vacant, shows the ionic conductivity of about 10^{-1} Scm^{-1} at 350°C. The electronic contribution to the total conductivity is smaller by a factor of less than 10^{-4}. These materials are thermodynamically stable against pure metallic lithium and have a decomposition voltage larger than 2.5 V.[107,108]

Recently, new intermediate compounds $3Li_3N$-MI(M=LI, Na, K, Rb) in the quasi-binary systems Li_3N-MI were synthesized.[109] They are isomorphous compounds with a tetragonal structure. The sintered samples exhibited high ionic conductivity of $1.1 \times 10^{-4} - 7.0 \times 10^{-5}$ Scm^{-1} at room temperature with activation energies of 0.32 – 0.34 eV. The decomposition voltages were approximately 2.5 – 2.8 V, much higher than those of Li_3N and Li_3N-LiI-LiOH electrolyte. The phosphorous analogue, Li_3P, has a room temperature conductivity of around 10^{-4} Scm^{-1} and it can be used up to 2.2 V against metal lithium electrode.[110] The composite electrolytes made of lithium phosphate (Li_3P) and lithium chloride were reported to be thermodynamically stable in contact with metal lithium electrode and had also a very high ionic conductivity of about 10^{-4} Scm^{-1} at room temperature.[111]

6. Lithium Metal Halides

Spinel-type ternary chlorides Li_2MCl_4 with M=Mg, Mn, Ti, Cd, Cr, Co and Fe have attracted a lot of interest due to their high ionic conductivities in the past two decades.[112-116] All these compounds crystallize with an inverse distribution with half of the lithium occupying tetrahedral sites and the other half occupying octahedral sites of space group $Fd\bar{3}m$. Almost all of these chlorides exhibit phase transition in the ranges of 300-500°C.[116] The low temperature cubic spinels such as Li_2MnCl_4, Li_2MgCl_4 and Li_2CdCl_4 transform to a defect NaCl-type structure at high temperature.[117] Other phases such as the Cr, Fe, and Co analogues are distorted spinel at low temperature due to the cation ordering and transform to cubic spinels at higher temperatures.[117] Generally, among all these ternary chlorides the cubic spinels showed highest conductivities. For example, Li_2MnCl_4 and Li_2MgCl_4 have shown an ionic conductivity of 0.14 Scm^{-1} at 400°C; Li_2CdCl_4 has a slightly higher value 0.3 Scm^1 at 400°C rising to 1.0 Scm^1 at 500°C,[112] but the practical application is greatly restricted due to its toxicity. However, partial substitution Na or Cu for Li in these ternary chlorides leads to reduction in the conductivity due to the mixed alkali effect.[116,117] Although the iodide system LiI-MI$_2$ (M=Mn, Cd, Pb) demonstrate a high ionic conductivity of 0.1 Scm^1 at 300°C for Li_2CdI_4, the monophase solid solution

existed only above 265°C.[117, 118] Upon cooling down they will decompose to form LiI and CdI_2 irreversibly, so they are unsuitable for battery applications.

7. Li_2SO_4 based Materials

Lithium sulphate is a well known ionic conductor which undergoes a phase transition from monoclinic (β-Li_2SO_4) to cubic (α-Li_2SO_4) at 848 K. The low temperature monoclinic β phase has low conductivity of 3.4×10^{-8} Scm^{-1} at 500°C and the high temperature face centred cubic α-phase has very high ionic conductivity of 1 Scm^{-1} at 575°C, increasing to 3 Scm^{-1} at 800°C.[119] So the suitable operating temperatures are usually higher than 300°C, these temperature are too high for most practical application, much work has been carried out to decrease the transition temperature without reducing the conductivity.

Studies of the binary Li_2SO_4-M_2SO_4 (M=Na, K, Ag) systems have shown that partially substituting Na, K or Ag for Li leads to the decrease of $\beta \Leftrightarrow \alpha$ phase transition temperature, i.e. from 850 K to 791 K for $LiNaSO_4$, and 688 K for $LiAgSO_4$.[120,121] In the meantime, the ionic conductivities were slightly increased, from 0.86 Scm^{-1} to 0.93 Scm^{-1} at 800 K for $LiNaSO_4$, and 1.17 Scm^{-1} at 688 K for $LiAgSO_4$. The operating temperature needed is still a little too high and the operating temperature range is rather narrow.

Attempts have also been made to substitute Li with a divalent ion thereby creating lithium vacancy. The system of Li_2SO_4-MSO_4 (M=Mg, Ca, Sr, Ba, Zd, Cd and Mn) shows limited solubility of MSO_4 in β-Li_2SO_4,[122-125] and the highest conductivity is correlated with the eutectic composition or the composition with minimum crystallite size.[125] But the ionic conductivity at low temperature of these divalent-cation-dopants-substituted β-Li_2SO_4 just increases by about an order of magnitude, and the decrease in the phase transition (monoclinic to cubic phase) temperature of these doped β-Li_2SO_4 are also very small.[124]

The system of Li_2SO_4-Li_3ASO_4 (A=P^{5+}, V^{5+}) also shows a limited solubility of Li_3ASO_4 in α-Li_2SO_4, and the ionic conductivity was reduced by partial substitution of S by P^{5+}or V^{5+}.[126-128]

8. Lithium Ion Conductor Composite Materials

Subsequent to Liangs discovery[129] that the dispersion of small Al_2O_3 particles into pure LiI enhances the Li^+ ion conductivity of the host, a number of experimental and theoretical studies have been devoted to this phenomenon. Different composite materials, such as $Li_{16-2x}Zn_x(GeO_4)_4$-ZrO_2,[130] Li_2SO_4-Al_2O_3,[131] Li_nX-Al_2O_3(X=F^-, Cl^-, Br^-, CO_3^{2-}),[132] and Li_3PO_4-Al_2O_3,[133] have been studied through either mechanical mixing or thermal decomposition of salts. The enhancement in ionic conductivity is ascribed to an increase in interfacial transport by one to two orders of magnitude. Generally, it is found that the ionic conductivity of the host

matrix varies substantially with the particle size of the dispersoids. Several models such as space-charge model,[134] percolation model[135-137] and surface morphology model[131] etc. have been proposed to explain this phenomenon. However, there is little high temperature conductivity data, relevant to battery application, available. Also the reported current density for lithium batteries using LiI-Al_2O_3 composite electrolytes are just about 100 μAcm^{-2},[138] which is a little low for practical battery application.

9. Concluding Remarks

Though lithium ion secondary batteries have been popularized as a power source for portable electronic devices such as cellular telephone and portable computers, it involves a serious safety problem especially when they are used as large-scale power sources for electric vehicles or energy storage for load leveling because of the presence of flammable organic solvent in the electrolytes. The substitution of solid electrolyte for the organic one should be a fundamental solution to decrease the safety problems and extend the application of lithium battery with high reliability. Besides improvement of safety, a solid electrolyte may effectively suppress the side reactions that deteriorate battery performances, thus greatly improve the cycle performance. Furthermore, as most inorganic lithium ion conductors can keep good chemical compatibility with electrode materials, so the choice for electrode materials becomes more flexible.

Solid electrolytes which are to be used in lithium secondary batteries should posses high ionic conductivity. Even for a thin film electrolyte of one micrometer thickness an ionic conductivity of more than 10^{-6} Scm^{-1} is usually required.[139] Furthermore, they should be stable in contact with the electrodes and be relatively simple and inexpensive to prepare. Besides solid polymer electrolytes, some of the inorganic lithium conductors outlined in Table1 appear to be good candidates for possible application as solid electrolytes, and the following systems may deserve particular attention in the future.

1. Li_2S-based glasses. The Li_2S-Si_2S glasses exhibit ambient temperature ionic conductivity as high as 10^{-3} Scm^{-1}, nearly comparable to that of liquid or polymer electrolytes. The glass stability (against crystallization) could be effectively improved by the addition of small amount of Li_xMO_y (where M=Si, P, Ge, B, Al, Ga and In) or some oxides of groups such as TaS_2, SnS, SnS_2, BiI_3, Sb_2O_3 etc. Furthermore, these glasses were proved to have good chemical and electrochemical stability in contact with elemental Li and withstand high voltage application without decomposition. So this kind of glasses may be one of the most suitable lithium ion conductors as solid electrolytes for lithium secondary batteries.

2. Lithium compounds with perovskite structure. They are easy to be fabricated into dense samples through the conventional mixed oxide process, and $Li_{0.29}La_{0.57}TiO_3$ also

reveal a high conductivity of 2×10^{-5} Scm^{-1} at room temperature. However, Ti-based compounds can intercalate lithium ions with the consequence reduction of Ti^{4+} to Ti^{3+} leading to the appearance of electronic conductivity, and the lithium-rich stability limit is just 1.7 V.[50] The Ta and Nb perovskites, La$_{1/3-x}$Li$_{3x}$TaO$_3$ and La$_{1/3-x}$Li$_{3x}$NbO$_3$ have nearly the same or slightly lower ionic conductivities at room temperature, but they are expected to be less susceptible to reduction in contact with elemental Li, thus deserve further attention toward tailing into electrolyte materials.

3. Lithium compounds with a NASICON structure. Even though Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ exhibits a high conductivity of 7×10^{-4} Scm^{-1} at room temperature, similar to Ti-based perovskite compounds, the use of this material as solid electrolytes are greatly limited by the fact the lower lithium-rich stability limit of 2.4 V.[139] The Ta-based analogues, Li$_{1+2x}$Ta$_{1-x}$Al$_{1+x}$(PO$_4$)$_3$ system exhibits slightly lower conductivity than that of LiTi$_2$(PO$_4$)$_3$, but they are stable against Li metal. So they are attractive candidates as solid electrolytes if the ionic conductivities can be sufficiently enhanced.

4. γ_{II}-Li$_3$PO$_4$ type structure compounds. Among the solid solution of Li$_4$AO$_4$-Li$_3$BO$_4$ (where A=Si, Ge; B=P,V), Li$_{4-x}$Si$_{1-x}$P$_x$O$_4$ system deserves special attention due to its high ionic conductivity, good stability in contact with lithium metal, moderate cost and ease to be prepared. Furthermore, the interstitial solid solutions Li$_{4+x}$Al$_x$Si$_{1-x}$O$_4$ also deserves further attention, although the room temperature conductivity of Li$_9$SiAlO$_8$ is remarkably small (just 2.3×10^{-7} Scm^{-1}), they are stable versus metal lithium electrode up to 6.5 V, making it a suitable candidate for high voltage lithium batteries application.

Acknowledgement

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