Thin film Li electrolytes for all-solid-state micro-batteries

Hui Xia, Hai Long Wang, Wei Xiao, Man On Lai and Li Lu*

Department of Mechanical Engineering,
9 Engineering Drive 1,
National University of Singapore,
117576, Singapore
Fax: +65 6516 2242 E-mail: jasonxiahui@gmail.com
E-mail: wanghailong@nus.edu.sg E-mail: mpexw@nus.edu.sg
E-mail: mpelaimo@nus.edu.sg E-mail: mpeluli@nus.edu.sg
*Corresponding author

Abstract: All-solid-state thin film lithium micro-batteries have attracted more and more interests due to their potential applications as power sources for microelectronic devices. Thin film Li electrolyte, as the key part in the thin film batteries, is very important to the performance of the thin film batteries. This paper reviews a wide range of lithium ion conductors including glassy electrolytes and crystalline electrolytes for potential application in the micro-batteries. The thin film Li electrolytes reported in the literatures are reviewed with a focus on their ionic and electronic conductivity, chemical stability, and compatibility with electrode materials.

Keywords: thin film; lithium ion conductors; Li electrolyte; lithium-ion batteries; all-solid-state micro-batteries; thin film batteries; ionic conductivity; electronic conductivity.


Biographical notes: Hui Xia is a research fellow at the Materials Science Laboratory in the Department of Mechanical Engineering, National University of Singapore. He received his PhD Degree from the Advanced Materials for Micro- and Nano- System (AMM&NS) Program of Singapore-MIT Alliance (SMA). He has won two prestigious awards while pursuing his PhD (President Graduate Fellowship of National University of Singapore and Chinese Government Award for Outstanding Self-financed Students Abroad). His research interests span the fields of energy storage and conversion materials: electrodes for advanced Lithium-ion batteries, nano-structured electrodes for supercapacitors, fabrication of all-solid-state microbatteries for microelectronics.

Hai Long Wang is pursuing his PhD at the Materials Science Laboratory, in the Department of Mechanical Engineering, National University of Singapore. He received his Master’s Degree from the School of Materials Science and Engineering, Tsinghua University. He is currently engaged in studies on the synthesis, and characterisation of nano-structured cathode materials for lithium-ion batteries.
1 Introduction

There is a strong growing interest to develop next-generation batteries with lightweight, long cycle life and high energy density due to the ever increasing micro- and nano- devices such as smart cards, implantable medical devices, Complementary Metal Oxide Semiconductor (CMOS) memory chips, micro-electro-mechanical systems and so on (Bates et al., 2000; Dudney, 2005). In contrast to the conventional lithium-ion batteries found in the mass market, the cathode, electrolyte and anode in the thin film micro-batteries are fabricated in micro-metre or sub-micro-metre thickness, using thin film technology as shown in Figure 1, where the thin films of electrodes, solid electrolyte and current collectors are sequentially grown on a substrate using different kinds of deposition techniques.

The solid electrolyte is the most critical component in all solid-state thin film batteries. One of the main constraints in the commercialisation of solid-state lithium batteries is the unsatisfactory solid electrolyte (Robertson et al., 1997). The specifications for an appropriate electrolyte material should meet following criteria:

- the lithium ion conductor should have ionic conductivity higher than $10^{-7}$ S/cm at room temperature
- it has a unity transference number for conduction by Li$^+$ ions, $t_{\text{ion}} > 0.99 \gg t_{\text{electron}}$
- it should be chemically stable against metallic lithium and cathode materials
• it has a high electrochemical decomposition voltage (higher than 5.5 V vs. Li)
• it can be easily synthesised and fabricated (Thangadurai and Weppner, 2006).

Solid electrolytes for Li ion conductors are generally divided into organic polymer-based and inorganic-based ones. However, organic polymer-based electrolytes are not common in thin film-type electrolytes and, therefore, they are not included in this review. Inorganic electrolytes may be classified into non-oxide or oxide in terms of materials, and glassy or crystalline in terms of material structure. Thin films of solid electrolyte can be prepared by conventional deposition methods such as Radio Frequency (RF) sputtering (Ohtsuka and Yamaki, 1989a, 1989b), Pulsed Laser Deposition (PLD) (Zhao et al., 2002), thermal evaporation (Kbala et al., 1984), Electron Beam (EB) evaporation (Li et al., 2006), sol-gel spin coating (Kitaoka et al., 1997) and so on. The aims of this review are to report recent advances in development of the Li thin film electrolytes for micro-batteries and identify new thin film electrolytes as potential candidates for next-generation micro-batteries.

Figure 1  Schematic illustration of a thin film micro-battery structure (see online version for colours)

2 Glass electrolytes

Glassy lithium ion conductors have been extensively studied as electrolytes for solid-state lithium-ion batteries for the last two decades. Compared with crystalline ceramic electrolytes, the glassy electrolytes have particular advantages including:
• a wide range selection of compositions
• isotropic ion conduction
• ease of fabrication as dense thin films
• no grain boundaries.

Generally, glassy lithium ion conductors are composed with three compounds:
• a network former (normally covalent oxides or sulphides such as SiO$_2$, P$_2$O$_5$, B$_2$O$_3$, SiS$_2$, P$_2$S$_5$, etc.)
• a network modifier (Li$_2$O or Li$_2$S to break the oxygen or sulphide bridges)
• a doping salt (Li$_n$X (X = F, Cl, Br, I for n = 1, SO$_4$ for n = 2))
(Duclo and Souquet, 2001).

Glassy lithium ion conductors are generally classified into two types depending on the host material, oxide glass and sulphide glass.
2.1 Oxide glass electrolytes

There are not many reports on pure oxide glasses in recent years, probably due to their relatively poor ionic conductivity at room temperature. The advantages of the lithium oxide glasses over sulphide glass are that they are less hygroscopic, and more chemically stable in air. It has been proved that oxide glass does not react with electrode materials during Li intercalation/deintercalation, which is very beneficial for cycle performance of batteries (Cho et al., 2006, 2007). Although oxide electrolytes show relatively low ionic conductivity, they can be easily deposited by conventional physical vapour deposition methods in thin film form, which can reduce the internal resistance due to the extremely small thickness. Therefore, for micro-battery applications, extensive effort has been focused on the fabrication of lithium oxide glass thin film electrolytes and improvement of the ion conductivity of the oxide glass film.

Hundreds of different glass compositions have been developed, starting from binary systems such as Li2O-B2O3 to ternary systems, such as Li2O-SiO2-P2O5. However, only limited reports have been published on the solid electrolyte films. The ionic conduction properties of thin film glasses reported in the literature are summarised in Table 1. Among these thin film electrolytes, recent research has focused on two: Li2O-SiO2-V2O5 (LVSO) and Li2O-P2O5+N2 (LiPON), due to their high lithium ionic conductivity and successfully application in micro-batteries.

Table 1 Ionic conductivity of Li thin film glassy electrolytes

<table>
<thead>
<tr>
<th>Electrolyte system</th>
<th>Deposition method</th>
<th>Ionic conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2O–B2O3</td>
<td>Thermal evaporation</td>
<td>10^-8–10^-10 (Ito et al., 1983; Balkanski et al., 1989, 1994)</td>
</tr>
<tr>
<td>Li2O–B2O3–P2O5</td>
<td>Flame pyrolysis deposition</td>
<td>10^-7 (Cho et al., 2007)</td>
</tr>
<tr>
<td>Li2O–SiO2–ZrO2</td>
<td>RF-sputtering</td>
<td>10^-6 (Miyauchi et al., 1983)</td>
</tr>
<tr>
<td>Li2O–SiO2–V2O5</td>
<td>RF-sputtering</td>
<td>10^-8 (Ohtsuka and Yamaki, 1989a, 1989b)</td>
</tr>
<tr>
<td>Li2O–P2O5–SiO2</td>
<td>RF-sputtering</td>
<td>10^-6 (Kanehori et al., 1986)</td>
</tr>
<tr>
<td>Li2O–P2O5–Nb2O5</td>
<td>RF-sputtering</td>
<td>10^-8 (Chowdari and Radhakrishnan, 1991)</td>
</tr>
<tr>
<td>Li2O–P2O5–SiO2</td>
<td>Thermal evaporation</td>
<td>10^-7 (Chowdari and Radhakrishnan, 1990)</td>
</tr>
<tr>
<td>Li2O–P2O5–LiI</td>
<td>Thermal evaporation</td>
<td>10^-6 (Levasseur et al., 1983)</td>
</tr>
<tr>
<td>B2O3–Li2O–Li2SO4</td>
<td>RF-sputtering</td>
<td>10^-6, 10^-7 (Meunier et al., 1989; Joo et al., 2003)</td>
</tr>
<tr>
<td>BPO4–Li2O</td>
<td>Electron beam evaporation</td>
<td>10^-6–10^-8 (Jones and Akridge, 1994)</td>
</tr>
<tr>
<td>Li2O–P2O5+N2</td>
<td>RF-sputtering</td>
<td>10^-6 (Bates et al., 1992)</td>
</tr>
<tr>
<td>Li2O–P2O5–SiO2+N2</td>
<td>Pulsed Laser Deposition</td>
<td>10^-7 (Zhao et al., 2002)</td>
</tr>
<tr>
<td>Li2O–P2O5–SiO2+N2</td>
<td>RF-sputtering</td>
<td>10^-5 (Lee et al., 2003a)</td>
</tr>
<tr>
<td>Li2SO4+N2</td>
<td>RF-sputtering</td>
<td>10^-5 (Joo et al., 2004)</td>
</tr>
</tbody>
</table>
2.1.1 LVSO thin film electrolyte

The Li$_2$O-V$_2$O$_5$-SiO$_2$ thin film electrolyte has shown high lithium ion conductivity. Among these solid solutions, the specific composition Li$_{3.4}$V$_{0.6}$Si$_0.4$O$_4$ exhibits the highest conductivity of $1 \times 10^{-5}$ S/m at room temperature (Robertson et al., 1997). The LVSO thin film electrolyte was first fabricated using RF-sputtering by Ohtsuka and Yamaki (1989a, 1989b). Although the film is deposited at room temperature, it is partially crystallised, exhibiting an ionic conductivity of about $1 \times 10^{-6}$ S/cm with activation energy of 0.5 eV and an electronic conductivity about $10^{-10}$ S/cm. It was found that the conductivity of the annealed LVSO thin film, which is crystalline, is higher than that of the as-sputtered film, which has a low degree of crystallinity. It is speculated that the amorphous Li$_2$O in the film reacts with H$_2$O or CO$_2$ in the air forming LiOH or Li$_2$CO$_3$ and, thus, lowers the conductivity of the film. By using the LVSO thin film as the solid state electrolyte, Ohtsuka and Sakurai (2001) successfully developed the micro-battery with Li film as the anode and MoO$_3$ thin film as the cathode. This micro-battery can work between 1.5 V and 3.5 V delivering a discharge capacity about 60 µAh/cm$^2$µm with 1-µm thickness cathode. Zhao and Qin (2003) successfully prepared the LVSO thin film by PLD. The LVSO thin film deposited by PLD shows amorphous state, exhibiting an ionic conductivity of about $3 \times 10^{-7}$ S/cm and electronic conductivity of about $10^{-11}$ to $10^{-12}$ S/cm. However, the electrochemical stability test of the film by Zhao et al. (2002) reveals that the LVSO film has a low voltage window around 3.5 V and it is probably suitable for those micro-batteries with low working voltages. After Zhao and Qin (2003), Kawamura et al. (2004) also fabricated the amorphous LVSO film by PLD with an ionic conductivity of about $2.5 \times 10^{-7}$ S/cm and an electronic conductivity of about $10^{-13}$ S/cm. The ionic conductivity of the LVSO films prepared by PLD is one order smaller than that of the sputtering LVSO film and two orders smaller than that of the crystalline LVSO sample.

The difference is probably due to the different degrees of crystallinity and different compositions between the films and bulk material. The Pulsed Laser Deposited (PLDed) LVSO film is completely amorphous and has an obvious lithium deficiency in the film with a composition of Li$_{2.2}$V$_{0.54}$Si$_0.46$O$_{3.4}$, which probably leads to a lower ionic conductivity. Although the PLDed LVSO film exhibits a lower ionic conductivity, it is stable to humidity and high temperature and the film is smooth and dense without any pinholes or cracks showing excellent quality as a solid electrolyte separating cathode and anode materials. By using a LVSO thin film electrolyte, Kuwata et al. (2006) first successfully fabricated SnO/LVSO/LiCoO$_2$ and SnO/LVSO/LiMn$_2$O$_4$ micro-batteries only by PLD.

2.1.2 LIPON thin film electrolyte

In 1980s, the Li$_2$O-P$_2$O$_5$-SiO$_2$ system attracted some interest as the thin film electrolyte for micro-batteries as earlier reports indicated that films with suitable conductivity and apparent stability with contact with lithium could be deposited by RF-sputtering of targets containing Li$_2$SiO$_4$ and Li$_2$PO$_4$ (Kanehori et al., 1986). However, the ORNL group found that, although films with high lithium content had conductivities higher than $10^{-4}$ S/cm at room temperature, none of the films selected for cell measurement were stable in contact with lithium (Bates et al., 1992). At the same time, the researchers from ORNL developed a new glass electrolyte, the lithium phosphorous oxynitride glass,
commonly referred to as ‘LIPON’ (Yu et al., 1997), which quickly gained attention and is widely used in the micro-batteries. The LIPON films, first reported by Bates et al. (1992) are typically deposited by RF-sputtering from a high purity Li$_3$PO$_4$ target in nitrogen plasma. A small amount of N incorporated into the films from the plasma can effectively stabilise the film in contact with lithium and enhance the ionic conductivity 40-fold compared to amorphous Li$_3$PO$_4$ films prepared by sputtering (Yu et al., 1997). The high ion conductivity is due to either the formation of additional cross-linking between phosphate groups or a decrease of the electrostatic energy when P-O is replaced by P-N bonds. The maximum reported ionic conductivity is $3.3 \times 10^{-6}$ S/cm with an activation energy of 0.55 eV for the composition of Li$_{2.9}$PO$_{3.3}$N$_{0.46}$. The LIPON film also exhibits negligible electronic conductivity ($\sim 10^{-14}$ S/cm) and excellent electrochemical stability from 0 to 5.5 V against lithium metal (Yu et al., 1997).

Although high quality LiPON films can be prepared by RF-sputtering, the deposition rate achieved by sputtering is very low (1–10 nm/min) due to the low working pressure and low power needed to avoid cracking of the target (Bates and Yu, 1996; Yu et al., 1997). Therefore, different deposition methods have been utilised to prepare LiPON thin films. Vereda et al. (2002) at Tuffs explored the use of a nitrogen Ion Beam Assisted Deposition (IBAD) of thermally evaporated Li$_3$PO$_4$ as an improved method. Although the growth rate of LiPON film using IBAD can reach up to ~66 nm/min with a good conductivity and electrochemical stability, it appears that the film is prone to crack due to the large tensile stresses, leading to electrical shorting in metal/LiPON/metal test cells. A similarly high deposition rate is achieved by PLD which yields amorphous film with comparable properties (Zhao et al., 2002). However, the LiPON film deposited by PLD had a very rough surface morphology, limiting its application in micro-batteries. The LiPON films have also been successfully fabricated by nitrogen plasma-assisted deposition of E-beam reactive evaporated Li$_3$PO$_4$ (Liu et al., 2004). The EB evaporation prepared films had an ionic conductivity of $\sim 10^{-7}$–$10^{-8}$ S/cm and the film growth rate can reach about 8.33 nm/min. Another EB evaporation based approach, a Plasma-Assisted Directed Vapour Deposition (PA-DVD), was also successfully utilised to prepare LiPON films (Kim and Wadley, 2008). The deposition rate by PA-DVD can reach up to 45 times of those reported for RF-sputtering method, and the ionic conductivity at room temperature for the film is about $10^{-7}$–$10^{-8}$ S/cm. Manipulation of the plasma-enhanced process conditions can also control the pore morphology and significantly affect the ionic conductivity of the films. Therefore, it appears that the PA-DVD method is promising for more economical deposition of LiPON films since the deposition rate can be improved without sacrificing other properties of the electrolyte.

It seems to be a trend that the ionic conductivity increases with N/P ratio in the LiPON film. Several groups have reported improved ionic conductivity when more N content is incorporated in the film (Bates and Yu, 1997; Dudney, 2003; Choi et al., 2002; Hamon et al., 2006). However, this trend is not valid when we compare the ionic conductivity of LiPON films prepared by different groups. As shown in Table 2, the highest N/P ratio in the LiPON film prepared by different groups ranges from 0.46 to 1.49. However, there is no consistent trend showing the increase in ionic conductivity with increasing N/P ratio. To achieve an N-rich LiPON composition, Dudney and Jang (2003), used codeposition of Li$_3$PO$_4$ along with Li$_3$N. They found that the enhancement of lithium ion conductivity with increasing N content is modest. When the increasing nitrogen content is compensated for by additional lithium ions, the ionic conductivity will degrade with an increase in the activation energy. Driven by the same
Kim et al. (2002) performed nitrogen-implantation on the as-deposited LiPON film to incorporate excessive nitrogen concentration. Similar to Dudney’s finding, no apparent trend in the change of ionic conductivity was found. From the Nuclear Magnetic Resonance (NMR) studies of IBAD prepared LiPON films, Stallworth et al. (2005) conclude that nitrogen incorporation via the IBAD process occurs in two ways:

- the formation of larger chain-like structures linked through the replacement of oxygen by ‘network’ nitrogen
- the implantation of molecular N₂.

In the case of incorporation of molecular N₂, the increased nitrogen concentration in the LiPON film may not further improve lithium ion conductivity. Therefore, a clear analysis of variation of the lithium ion conductivity with nitrogen incorporation is still lacking, probably due to the difficulty of precisely determining the film composition. The relationship between lithium ion conductivity and atomic-scale microstructures in LiPON is complicated. The lithium ion conductivity of LiPON films depends on the nitrogen concentration, bonding configuration (doubly or triply coordinated nitrogen) and structural relaxation in the amorphous film. It has been found that an increase of 2–4 times in the lithium ion conductivity may occur when the LiPON film is annealed briefly at temperatures of 150–250°C (Neudecker et al., 2000).

### Table 2

<table>
<thead>
<tr>
<th>Bates et al., RF-sputtering</th>
<th>Dudney et al., cosputtering</th>
<th>Choi et al., RF-sputtering</th>
<th>Hamon et al., RF-sputtering</th>
<th>Kim et al., PA-DVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Li₂₃PO₃.₅N₀.₆₆</td>
<td>Li₂₃PO₂.₅N₁₂</td>
<td>Li₃.₉⁷PO₁.₃₇N₁.₂₅</td>
<td>Don’t know</td>
</tr>
<tr>
<td>N/P ratio</td>
<td>0.46</td>
<td>1.2</td>
<td>1.25</td>
<td>1.4</td>
</tr>
<tr>
<td>Conductivity</td>
<td>3.3 × 10⁻⁶</td>
<td>4.1 × 10⁻⁷</td>
<td>1.67 × 10⁻⁶</td>
<td>~1.6 × 10⁻⁶</td>
</tr>
</tbody>
</table>

The big success of LiPON thin film electrolyte lies not only in its high ionic conductivity but also in its excellent electrochemical stability and negligible electronic conductivity. The LiPON electrolyte exhibits good electrochemical stability with both metallic lithium and transition metal oxide cathodes at cell potentials up to 5.5 V vs. Li. In addition, the electronic resistivity of the LiPON film is >10¹⁶ Ω·cm, which greatly minimises the short circuit self-discharge of the battery. The chemical stability of LiPON in contact with lithium metal may be attributed to the reducing character of the oxynitride glass matrix. Due to the good electrochemical stability of LiPON electrolyte, many all-solid-state micro-batteries have been developed using different anodes and cathodes as shown in Table 3. Among all these micro-batteries, the Li/LiPON/cLiCoO₂ micro-batteries exhibit the best performance, having the highest capacity in the voltage window 3.5–4.2 V, cycle life up to 10,000, and highest energy and power densities (Bates and Yu, 1996). With a 4 µm thick LiCoO₂ cathode, the micro-batteries can provide 1 mWh/cm² energy at a 1 mW/cm² power discharge (Dudney and Jang, 2003). When discharged at higher rates, the energy decreases due to the polarisation induced by the battery resistance. Although the ionic conductivity of LiPON film is still low, the thickness of LiPON film is only 1 µm and the resistance of thin film batteries is mainly contributed by the cathode.
and the cathode/electrolyte interface. Wang et al. (1996) summarise that the capacity loss of the thin film batteries during cycling is caused primarily by an increase in the cell resistance, which is largely due to the increase in cathode/electrolyte interface resistance (Wang et al., 1996). Therefore, reducing the cathode/electrolyte interface resistance is crucial to further improve the power density and cycle life of thin film batteries. Thermal treatment (normally 150–250°C) is an effective way to reduce the interface resistance and, hence, to reduce the reactivity of the thin film battery. As explained by Iriyama et al. (2005), the thermal treatment does not change the activation energy of the charge transfer reaction but increases the number of electrochemically active sites at the cathode/electrolyte interface. Jeong et al. (2006) deposited a buffer layer of Al2O3 between LiCoO2 and LiPON film and found the thermal treatment at 400ºC with Al2O3 can reduce the interface resistance.

Table 3 Different types of micro-batteries with their working voltage and highest capacity under small current

<table>
<thead>
<tr>
<th>Micro-battery configuration</th>
<th>Working voltage (V)</th>
<th>Capacity (µAh/cm²–µm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/LiPON/cLiCoO2</td>
<td>3.5–4.2</td>
<td>69</td>
<td>Bates et al. (2000)</td>
</tr>
<tr>
<td>Sn3N4LiPON/cLiCoO2</td>
<td>2.7–4.2</td>
<td>50</td>
<td>Bates et al. (2000)</td>
</tr>
<tr>
<td>Zn3N2/LiPON/cLiCoO2</td>
<td>2.7–4.2</td>
<td>40</td>
<td>Bates et al. (2000)</td>
</tr>
<tr>
<td>SiSn0.37O3Ni1.72/LiPON/cLiCoO2</td>
<td>2.7–4.2</td>
<td>40</td>
<td>Bates et al. (2000)</td>
</tr>
<tr>
<td>Li/LiPON/cLiMn2O4</td>
<td>3–4.5</td>
<td>60</td>
<td>Dudney (2005)</td>
</tr>
<tr>
<td>Li/LiPON/nLi1.15Mn2.5O4</td>
<td>2.5–4.5</td>
<td>120</td>
<td>Bates et al. (2000)</td>
</tr>
<tr>
<td>Li/LiPON/aV2O5</td>
<td>1.5–3.5</td>
<td>120</td>
<td>Bates et al. (1994)</td>
</tr>
<tr>
<td>Li/LiPON/cV2O5</td>
<td>2.5–3.5</td>
<td>60</td>
<td>Bates et al. (1994)</td>
</tr>
<tr>
<td>Al/LiPON/cLi2MMn3O8 (M = Fe, Co)</td>
<td>3–5</td>
<td>40</td>
<td>Schwenzel et al. (2006)</td>
</tr>
<tr>
<td>Li/LiPON/cLiCoPO4</td>
<td>3.5–5.2</td>
<td>12</td>
<td>West et al. (2003)</td>
</tr>
</tbody>
</table>

2.1.3 Other promising thin film electrolytes

As shown in Table 1, the lithium ionic conductivity of some thin film electrolytes prepared in the last two decades is actually comparable to that of LVSO and LiPON films. The problem limiting wide application of the electrolytes in micro-batteries is its poor electrochemical stability. Considering the successful example of the LiPON electrolyte, it may be an effective way to improve the electrochemical stability by incorporating nitrogen into these oxide electrolytes. Preliminary results for a sputter deposited lithium boron oxyinitride electrolyte film have been reported. However, the incorporation of nitrogen in the LiBO2 film does not improve its ionic conductivity, but it does improve its chemical stability against air and moisture (Birke et al., 1996). The electrochemical stability has not been evaluated, but may be comparable to that of the phosphate material. Incorporation of nitrogen seems to be especially effective in the phosphate materials. Nitrogen-incorporated lithium silicophosphate thin film electrolytes have been reported by Lee et al. (2003a, 2003b). Nitrogen incorporation in the Li2O-SiO2-P2O5 system (LiSiPON) not only improves its lithium ionic conductivity to $1.24 \times 10^{-5}$ S/cm but also improves its electrochemical stability, making this film stable
Thin film Li electrolytes for all-solid-state micro-batteries

up 5.5 V against Pt metal. A Si_{0.7}V_{0.3}/Li_{1.9}Si_{0.28}P_{1.0}O_{1.1}N_{1.0}/LiCoO_2 thin film battery has been successfully fabricated, showing a high reversible capacity about 50 µAh/cm^2-µm between 2 and 3.9 V and very small capacity fade up to 1500 cycles. Another thin film solid electrolyte, Lithium Sulphur Oxynitride (LISON), was fabricated by RF-sputtering from a Li_2SO_4 target in N_2 atmosphere (Joo et al., 2004). The Li_{0.29}S_{0.28}O_{0.35}N_{0.09} film exhibits a lithium ionic conductivity of 2 × 10^{-5} S/cm and is stable up to 5.5 V vs. Li/Li^+. However, no result on the full cell test has been reported. Another example is the Li_2O-B_2O_3-Li_2SO_4 (LBSO) system prepared by sputtering, forming Li/LBSO/TiS_2O_y thin film battery (Meunier et al., 1989). Here, the LBSO film can only reach a lithium ionic conductivity of about 3 × 10^{-7} S/cm. Later studies show that the ionic conductivity increases with Li_2SO_4 content. Recently, Joo et al. (2003) prepared a LBSO thin film electrolyte by sputtering with a high Li_2SO_4 content (0.7Li_2SO_4-0.3LiBO_2). The film shows a high lithium ionic conductivity of about 2.5 × 10^{-6} S/cm, a low electronic conductivity about 10^{-13} S/cm, and very high electrochemical stability (stable up to 5.8 V vs. lithium metal). This LBSO film has been utilised in the Li/LBSO/TiS_2 thin film battery, showing good cycle performance. It is promising to use this thin film electrolyte to develop new thin film batteries with higher energy and power densities by using LiCoO_2 or LiMn_2O_4 cathodes.

2.2 Sulphide and oxysulphide glass electrolytes

One of the important discoveries for creating high lithium conducting glassy electrolyte is that the lithium ion conductivity can be greatly enhanced by changing the oxygen matrix to a sulphide matrix (Minami et al., 2006). Oxide glasses show lithium ion conductivity in the range from 10^{-8} to 10^{-5} at room temperature while sulphide glasses show higher ionic conductivity of 10^{-3}-10^{-4} S/cm. The impressive conductivities and low activation energies of sulphide glasses are attributed to the weaker bonding of lithium with the non-bridging sulphur anions. However, these glasses have not been widely used because they are difficult to handle and synthesise due to the corrosive chemical, and highly hygroscopic, nature of sulphur. Being both highly reactive with air and highly corrosive with silica containers, great care and a highly efficient glove box are required synthesise and fabricate the sulphide glasses.

Though there are many studies for synthesising sulphide bulk glasses by melt quenching, only a few studies can be found for sulphide thin films because of the difficulty of preparation. Table 4 shows the lithium ionic conductivity of thin film glassy sulphide electrolytes prepared by different groups. Due to the low ionic conductivity of the glassy oxide electrolytes, Khala et al. (1984) started the research on thin films of glassy sulphide electrolytes. The thin films obtained with glasses of the B_2S_3-Li_2S and B_2S_3-Li_2S-LiI systems, using a vacuum evaporation in the glove box have been investigated. In each system, the thin films and starting glasses have the same composition and similar conductivities, about 10^{-4} and 10^{-5} S/cm respectively at room temperature. For all samples, the electronic conductivity is lower than 10^{-8} S/cm at room temperature. It was found that the presence of lithium iodide in the ternary system causes an increase in the ionic conductivity after appropriate annealing. This enhancement may be attributed to the structural imperfections at the film/substrate interface (Au/thin film glass/Au) induced by the heat treatment, which probably lowers down the interfacial migration enthalpy and improves the ionic conductivity. To improve ionic conductivity, Creus et al. (1989) used vacuum evaporation to prepare thin film electrolytes using the
Li$_2$S-SiS$_2$ binary glass and its ternary derivative Li$_2$S-SiS$_2$-P$_2$S$_5$. The electrolytes showed an ionic conductivity in the range from $10^{-6}$ to $10^{-5}$ S/cm and micro-batteries with the configuration Li/Li$_2$S-SiS$_2$(-P$_2$S$_5$)/V$_2$O$_5$-TeO$_2$ were thereafter fabricated. It was found that the sulphide electrolytes have high reactivity with lithium metal, forming a resistive film, causing a large increase in cell resistance. A good solution to the electrolyte instability is to use a LiI protective layer between the electrolyte and lithium metal as proposed by Creus et al. (1989). This idea was used to great advantage by Jones and Akridge (1995) from Eveready Battery Company (EBC) to develop Li-TiS$_2$ thin film batteries with outstanding performance. The electrolyte was deposited by RF-sputtering of a target with the composition of 6LiI-4Li$_3$PO$_4$-P$_2$S$_5$, and the protective LiI layer was deposited by thermal evaporation. The total ionic conductivity (glassy electrolyte + LiI) was estimated to be $2 \times 10^{-6}$ S/cm, which correctly falls between the $10^{-7}$ S/cm conductivity of the LiI layer and the $10^{-5}$ S/cm conductivity of the oxysulphide electrolyte layer. These EBC micro-batteries could normally be cycled more than 1000 cycles between 1.4 and 2.8 V with greater than 90% cathode utilisation at current densities as high as 300 µA/cm$^2$.

The thin films of Li$_2$S-GeS$_2$-Ga$_2$S$_3$ glass system prepared by RF-sputtering were reported by Yamashita et al. (1996) and Yamashita and Yamanaka (2003). The ionic conductivity is almost identical to that of bulk glasses with similar compositions, which increases with increasing Li$_2$S content. The film possesses an ionic conductivity of about $1.4 \times 10^{-4}$ S/cm at room temperature, with the highest lithium content. However, the electrochemical stability of the film and the performance of the full thin film battery have yet to be investigated. Compared to vacuum evaporation, sputtering could easily produce a well-adhered dense film. However, to reduce the contact between the sulphide film and air, a special sputtering apparatus with closed chamber is required.

<table>
<thead>
<tr>
<th>Electrolyte system</th>
<th>Deposition method</th>
<th>Ionic conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_2$S$_3$-Li$_2$S</td>
<td>Vacuum evaporation</td>
<td>$10^{-4}$ S/cm</td>
</tr>
<tr>
<td>B$_2$S$_3$-Li$_2$S-LiI</td>
<td>Vacuum evaporation</td>
<td>$10^{-4}$ S/cm</td>
</tr>
<tr>
<td>Li$_2$S-SiS$_2$</td>
<td>Vacuum evaporation</td>
<td>$10^{-5}$-10$^{-6}$ S/cm (Creus et al., 1989)</td>
</tr>
<tr>
<td>Li$_2$S-P$_2$S$_5$-SiS$_2$</td>
<td>Vacuum evaporation</td>
<td>$10^{-5}$ S/cm</td>
</tr>
<tr>
<td>LiI-Li$_3$PO$_4$-P$_2$S$_5$</td>
<td>RF-sputtering</td>
<td>$10^{-5}$ S/cm</td>
</tr>
<tr>
<td>Li$_2$S-GeS$_2$-Ga$_2$S$_3$</td>
<td>RF-sputtering</td>
<td>$10^{-4}$ S/cm</td>
</tr>
</tbody>
</table>

### 3 Crystalline electrolytes

Generally speaking, crystalline materials should have higher ionic conductivity and better stability over the corresponding glasses if their crystal structures have been well designed for high ionic conduction. However, it is not the case in case of crystalline lithium ionic conductors whose ionic conductivities and electrochemical decomposition potentials are usually lower than glassy materials. The advantage of crystalline lithium ion conductors is their high temperature stability. Therefore, a fully crystalline, high temperature-annealed electrolyte is appealing for solid-state systems where a high-temperature process step is desirable for cathode improvement and electrode/electrolyte interfacial quality enhancement. The material search for new crystalline
Thin film Li electrolytes for all-solid-state micro-batteries

lithium ion conductors continues. Some compounds have been found which exhibit promising lithium ionic conductivity at room temperature and they are promising for use as thin film electrolyte for micro-batteries.

3.1 NASICON-type electrolytes

The lithium analogues based on sodium superionic conductor (NASICON) structure have been widely studied as lithium ion conductors for batteries. The interest in the NASICON type of compounds stems from their special properties: high ionic conductivity, high temperature stability, low thermal expansion behaviour, and large surface area (Robertson et al., 1997; Thangadurai and Weppner, 2006). In general, the properties of the NASICON-type lithium ion conductor compounds strongly depend on their chemical stoichiometry and the thermal treatment. Different systems with the general formula LiM\textsuperscript{IV} \textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (M\textsuperscript{IV} = Ti, Zr, Hf, Ge, Sn and etc.) or LiM\textsuperscript{V}M\textsuperscript{III} \textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (M\textsuperscript{V} = Nb, Ta, Sb, and V and M\textsuperscript{III} = Al, Cr and Fe) have been reported (Robertson et al., 1997; Thangadurai and Weppner, 2006). The structure consists of PO\textsubscript{4} tetrahedra and MO\textsubscript{6} octahedra linked at corners to form open 3D tunnels with lithium ions located in interstitial sites (Figure 2, where M = Ti). The M = Ti system is probably the most studied system because the smaller tunnels formed with the Ti\textsuperscript{4+} cations are a better fit for the lithium conductors. The lithium ion conductivity of LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} is about 10\textsuperscript{−5} S/cm at room temperature and it may be increased, by at least two orders of magnitude, by partial substation of Ti\textsuperscript{4+} by trivalent cations such as Al, Ga, In, Ti, Sc, Y, La, Cr, Fe etc. (Manso et al., 2003). The enhancement of the overall ionic conductivity can be attributed to a higher charge carrier number and to a lower porosity of the pellets. The lithium ion conductivity for Li\textsubscript{1+x}Ti\textsubscript{2−x}Al\textsubscript{x}(PO\textsubscript{4})\textsubscript{3} can reach as high as 10\textsuperscript{−3} S/cm at room temperature (Fu, 1997). However, the potential for lithium insertion compensated by the reduction of the M cation may prohibit their use with most lithium anode materials. Especially for Ti-based system, Ti\textsuperscript{4+} is readily reduced to Ti\textsuperscript{3+} when contacted with lithium metal, which may result in a significant electronic conductivity. Nevertheless, other systems like Al, Ta or Al, Ge compositions are expected to be electrochemically stable with lithium (Xu et al., 2007; Rambabu et al., 2006). Unfortunately, neither full cell testing nor voltammetry studies have been done to evaluate their electrochemical stability.

Figure 2 Crystal structure of NASICON LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (see online version for colours)
The high lithium ionic conductivity of \( \text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x\text{(PO}_4\text{)}_3 \) system realises its utilisation in all-solid-state batteries. Birke et al. (1999) and his coworkers successfully fabricated the solid state battery \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{(PO}_4\text{)}_3/\text{LiMn}_2\text{O}_4 \) and it was operated successfully at room temperature. Due to the instability between the lithium metal and Ti\(^{4+}\)-containing the NASICON electrolyte, \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) was selected as the anode and a sintering additive \( \text{LiBO}_2\cdot\text{LiF} \) was added to block undesired reactions between electrodes and electrolyte. Although \( \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{(PO}_4\text{)}_3 \) has a lithium insertion instability limit of about 2.4 V vs. lithium, the electronic conductivity is still low and becomes an unimportant factor for practical battery use once the sintering additive is used, since the time scale for lithium insertion may be enlarged from weeks to years (Birke et al., 1999). Both \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and \( \text{LiMn}_2\text{O}_4 \) thin films have been prepared on the \( \text{Li}_{1+\delta}\text{Ti}_{2-\delta}\text{Al}_\delta\text{(PO}_4\text{)}_3 \) (LTP) plate by the sol-gel coating method (Hoshina et al., 2005; Dokko et al., 2007). The interface between the electrode and electrolyte was studied by fabricating the solid state battery \( \text{Li}_4\text{Ti}_5\text{O}_{12}(\text{or } \text{LiMn}_2\text{O}_4)/\text{LTP}/\text{PMMA}/\text{Li}, \) where PMMA is the poly(methylmethacrylate) gel polymer, to avoid direct contact between LTP and lithium metal. It was found that the battery performance is mainly controlled by the electrode/electrolyte contact. However, the sol-gel coating process easily led to a porous film with a rough surface, which induces a bad contact between the electrode and the electrolyte and, hence, a big charge transfer resistance at the interface. For fabricating thin film micro-batteries, the use of RF-sputtering or PLD to deposit the electrode and electrolyte films should be considered because they can easily prepare dense films with smooth surfaces. By far, there is only one report on \( \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{(PO}_4\text{)}_3 \) thin films prepared by the sol-gel annealing method (Wu et al., 2003). The films prepared by sol-gel annealed between 750°C and 900°C by this method are of pure \( \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{(PO}_4\text{)}_3 \) phase with good crystallinity. The ionic and electronic conductivities of the film annealed at 800°C are \( 1.5 \times 10^{-5} \) and \( 5 \times 10^{-11} \) S/cm, respectively. Similar to the bulk electrolyte, the thin film electrolyte with a thickness about 1 µm exhibited redox reactions with lithium at about 2.4 V. Further studies on the thin film electrolytes of this NASICON-type materials are required and attention should be focused on the Ti-poor or Ti-free NASCIONS, such as \( \text{Li}_{1+\delta}\text{Al}_{\delta}\text{Ge}_x\text{Ti}_{2-x-\delta}\text{(PO}_4\text{)}_3 \) and \( \text{Li}_{3-2x}\text{Cr}_{2-x}\text{Ta}_x\text{(PO}_4\text{)}_3 \) systems.

### 3.2 Lisicon-type electrolytes

Solid solutions between two end members of types (a) \( \text{Li}_x\text{XO}_4: \text{X} = \text{Si, Ge, Ti} \) and (b) \( \text{Li}_y\text{YO}_4: \text{Y} = \text{P, As, V, Cr} \); \( \text{Li}_z\text{M}_{x}\text{O}_4: \text{M} = \text{Zn, Mg} \); \( \text{Li}_2\text{ZO}_4: \text{Z} = \text{S, W} \) lead to the \( \gamma\text{Li}_3\text{PO}_4 \) type phases, the so-called LISICONs (lithium super ionic conductor), which exhibit high levels of lithium ionic conductivity (Robertson et al., 1997). The first material given the name LISICON was \( \text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4 \), which is a member of the solid solution \( \text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4 \) \( (–0.36 \leq x \leq 0.87) \). The family of \( \text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4 \) lithium ion conductors is derived from the parent \( \gamma\text{Li}_2\text{ZnGeO}_4 \) phase, by \( \text{Zn}^{2+} \rightarrow 2\text{Li}^+ \) substitution (Sebastian et al., 2003). The structure of \( \text{Li}_2\text{ZnGeO}_4 \) consists of a distorted hcp anion array wherein Li, Zn and Ge ions occupy one-half of the tetrahedral sites. \( \text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4 \) \( (x = 0.75) \) adopts the same structure where the substitution \( \text{Zn}^{2+} \rightarrow 2\text{Li}^+ \) introduces extra (interstitial) lithium ions occupying the octahedral sites, as shown in Figure 3. In the bulk material, two compositions \( \text{Li}_{1+\delta}\text{Ge}_{0.8}\text{V}_{0.2}\text{O}_4 \) and \( \text{Li}_{3+\delta}\text{Si}_{0.8}\text{V}_{0.2}\text{O}_4 \) attracted a lot of interest due to their high lithium ionic conductivities at room temperature \( (4 \times 10^{-3} \text{ for } \text{Li}_{1+\delta}\text{Ge}_{0.8}\text{V}_{0.2}\text{O}_4 \) and \( 1 \times 10^{-3} \text{ S/cm for } \text{Li}_{3+\delta}\text{Si}_{0.8}\text{V}_{0.2}\text{O}_4 \) (Robertson et al., 1997). As mentioned in the previous part, the LVSO thin films have
Thin film Li electrolytes for all-solid-state micro-batteries

been prepared by both PLD and RF-sputtering. Although the annealed film with a high degree of crystallinity shows higher lithium ionic conductivity than that of the as-deposited film with a low degree of crystallinity or amorphous character (Ohtsuka and Yamaki, 1989a), only the as-deposited film was successfully utilised in the full solid thin film batteries. However, there is excess Li$_2$O incorporated in the highly disordered film (as-deposited) which compromises the electron transference number and induces appreciable self-discharge current in the thin film batteries (Ohtsuka and Yamaki, 1989b). Annealing after electrolyte film deposition on the thin film cathode is normally not recommended in order to avoid the interfacial reactions between the cathode and the electrolyte and crack formation due to the difference of thermal expansion.

Whitacre and West (2004) fabricated the all-solid-state battery by depositing Li film and LiCoO$_2$ thin film on the each side of a crystalline Li$_3$PO$_4$/Li$_2$SiO$_3$ electrolyte chip. The electrolyte/cathode stack was annealed at 700ºC to obtain the cathode crystallisation. The high temperature annealing does not induce any deleterious interfacial reactions and the full solid cell works well. Therefore, further studies on developing all-solid-state thin film batteries using crystalline LISICON thin film electrolytes are recommended.

Figure 3  Crystal structure of LISICON Li$_{3.5}$Zn$_{0.25}$GeO$_4$ (see online version for colours)

In addition to oxide compounds, a number of sulphide compounds with a LISICON structure have been recently reported. The new thio-LISICON found in the Li$_2$S-GeS$_2$, Li$_2$S-GeS$_2$-ZnS, Li$_2$S-GeS$_2$-Ga$_2$S$_3$, and Li$_2$S-GeS$_2$-P$_2$S$_5$ systems have the structures related to the $\gamma$-Li$_3$PO$_4$ type (Kanno et al., 2000; Kanno and Murayama, 2001). Among these compounds, the new thio-LISICON Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$, which was derived from the lithium germanium sulphides, Li$_4$GeS$_4$, exhibited a high lithium ionic conductivity of $2.2 \times 10^{-3}$ S/cm at 25ºC, high electrochemical stability (~5 V vs. lithium), no reaction with lithium metal, and no phase transition up to 500ºC (Kanno and Murayama, 2001). By using PLD, Ohta et al. (2005) successfully deposited the Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ thin films on the sapphire substrates. The as-deposited film exhibits weak XRD peaks, indicating the low degree of crystallinity of the film. The lithium ionic conductivity of the as-deposited film is about $1.7 \times 10^{-3}$ S/cm, which is one-fifth of that of the bulk material. The author attributes the decrease in the conductivity of the film to the increased lithium content in the film, which reduces the number of lithium vacancy in
the LISICION structure and probably causes the decrease of conductivity. Although the thin film electrolyte exhibited a promising lithium ionic conductivity at room temperature, the electronic conductivity, electrochemical stability and full thin film battery test have yet to be done.

3.3 Perovskite electrolytes

Extensive researches have been carried out on polycrystalline lithium electrolytes with perovskite structure because of the high lithium ionic conductivity linked to the crystallographic structure (Robertson et al., 1997). The perovskite (ABO$_3$)-type lithium lanthanum titanate (LLTO) La$_{2/3-x}$Li$_{3x}$TiO$_3$ (La, Li at A site, and Ti at B site) has attracted most of interest because the highest lithium ionic conductivity of $10^{-3}$ S/cm at room temperature has been reported for the LLTO materials (Stramare et al., 2003). The crystalline structure of the La$_{2/3-x}$Li$_{3x}$TiO$_3$ materials has a three-dimensional framework of corner-sharing TiO$_6$ octahedra with alternate stacks of La-rich and La-deficient layers along the c-axis (as shown in Figure 4). The lanthanum ions, larger in ionic size, are the main contributors to the stabilisation of the perovskite-type structure while the lithium ions moving along A-site vacancies are the charge carriers responsible for high electrical conductivity. Although LLTO exhibits very high lithium ionic conductivity at room temperature, its use as an electrolyte is not applicable due to its instability when contact directly with lithium metal (Thangadurai and Weppner, 2006). As we mentioned before, the titanate based electrolytes undergo fast lithium insertion with consequent reduction of Ti$^{4+}$ to Ti$^{3+}$, leading to high electronic conductivity. The choice of electrodes is also limited because either lithium metal or any intercalated electrodes having a cathodic potential of more than 2.8 V will react with the electrolyte (Ahn and Yoon, 2005). Nevertheless, researchers are still trying to prepare the LLTO thin film electrolyte for thin film batteries. Table 5 shows the properties of LLTO thin films prepared by different method. LLTO thin films were first reported by Kitaoka et al. (1997) by sol-gel method. The lithium ionic conductivity of the sol-gel prepared LLTO thin films is about $10^{-8}$~$10^{-7}$ S/cm, much lower than the value of bulk material, which was attributed to the high porosity, small crystalline size of the films. There were also attempts to prepare the LLTO thin films by RF-sputtering but they failed to make a high quality film with high lithium ionic conductivity (Lee et al., 2006). The most successful LLTO thin films were prepared by PLD. The highest lithium ionic conductivity of the LLTO film prepared by PLD is $8.2 \times 10^{-4}$ S/cm at room temperature, very close to the value of bulk material (Maqueda et al., 2008). Ahn and Yoon (2005) proposed that the amorphous LLTO film, instead of the crystalline one, may be suitable for thin film batteries, as the electronic conduction produced by the insertion of lithium may be alleviated by blocking the conducting path of electronic carriers. The LLTO films prepared by them were claimed to be amorphous and they found that the electronic conductivity of the LLTO films does not change when contact with lithium metal. Recently, Maqueda et al. (2008) pointed out that the PLD prepared LLTO films that exhibit amorphous features from XRD characterisation actually exhibit nano-crystalline character with tetragonal perovskite structure observed by HRTEM. However, no work on thin film batteries directly using LLTO thin film electrolyte has been reported so far. Boyle et al. (2002) from Sandia National Laboratories have even tried to fabricate SnO/LLTO/LiCoO$_2$ thin film batteries by the spin-cast method. All thin film battery samples they prepared got electrically shorted finally and they
attributed the issue to some adatom mixing during processing or some defect in the LLTO layer over a large area. Due to the instability of LLTO electrolyte, attempts are being made to use LiPON coated LLTO thin film electrolyte to enhance its electrochemical stability. By introducing a LiPON interlayer, the LiPON/LLTO/LiPON sandwich structure is stable in the operating potential range between 0 V and 5.5 V (Lee et al., 2006). An all-solid-state Li/LiPON/LLTO/LiCoO₂ cell using e-beam evaporated LLTO thin film electrolyte was successfully fabricated and the cell showed promising charge/discharge performance (Li et al., 2006).

Figure 4 Crystal Structure of Perovskite La₀.₆₂Li₀.₁₆TiO₃ (see online version for colours)

It would be attractive to synthesise perovskite-type solid solutions containing no Ti ions for improvement of the reducible nature. The Ta-perovskites with a stable +5 oxidation state, Li₂₋ₓSrₓM₀.₅₋ₓTa₀.₅+xO₃ (M = Cr, Fe, Co, A1, Ga, In, Y) have been synthesised by Watanabe and Kuwano (1997) and exhibited a highest bulk conductivity of 1 × 10⁻⁴ S/cm at room temperature. The Nb-perovskites, La₁₋ₓLiₓNbO₃, have been synthesised by Garcia-Martin et al. (1999), and exhibited a highest conductivity of 4.3 × 10⁻⁵ S/cm at room temperature. However, the cyclic voltammetry result in this study showed that Nb-perovskites undergo reduction below 2 V, as compared to lithium metal. Nevertheless, there is too little research on the electrochemical stability and electronic conductivity of these Ti-free perovskites to assess whether they are suitable for being electrolyte for all-solid-state batteries. If a stable composition is identified, a perovskite electrolyte may prove highly conductive and relatively easy to fabricate and handle in air.

Table 5 Properties of LLTO thin films prepared by different methods

<table>
<thead>
<tr>
<th>Composition</th>
<th>Li₀.₅La₀.₅TiO₃</th>
<th>Li₀.₅La₀.₅TiO₃</th>
<th>Li₀.₅La₀.₅TiO₃</th>
<th>Li₀.₂₉La₀.₅7TiO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition method</td>
<td>PLD</td>
<td>RF-Sputtering</td>
<td>E-Beam</td>
<td>PLD</td>
</tr>
<tr>
<td>RT, 400–600°C</td>
<td>RT</td>
<td>100°C</td>
<td>700°C</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>Amorphous</td>
<td>crystalline</td>
</tr>
<tr>
<td>Ionic conductivity</td>
<td>10⁻⁵–10⁻⁴ S/cm</td>
<td>&lt;10⁻⁷ S/cm</td>
<td>1.8 × 10⁻⁷ S/cm</td>
<td>8.2 × 10⁻⁴ S/cm</td>
</tr>
</tbody>
</table>
3.4 Other crystalline electrolytes

Some 2-D layered compounds, such as Li$_3$N and Li-$\beta$-Al$_2$O$_3$, exhibited very high lithium ionic conductivity $\sim 10^{-3}$ S/cm at room temperature. However, these compounds either have very poor electrochemical stability vs. lithium (Li$_3$N low decomposition potential $\sim 0.445$ V) or have high reactivity with air (Li-$\beta$-Al$_2$O$_3$ is extremely hygroscopic) (Thangadurai and Weppner, 2006). Therefore, they are unlikely to have practical applications, especially for thin film batteries. Novel garnet-type lithium containing transition metal oxides with general compositions Li$_5$LaM$_2$O$_12$ (M = Nb, Ta) and Li$_6$Al$_2$M$_2$O$_12$ (A = Ca, Sr, Ba; M = Nb, Ta) have attracted a lot of interest due to their fast lithium ionic conductivity (Thangadurai and Weppner, 2006). Among these materials, Li$_6$BaLa$_2$TaO$_12$ exhibits the highest lithium ionic conductivity of $4 \times 10^{-5}$ S/cm at room temperature, good electrochemical stability up to 6 V against lithium, and good chemical stability with many positive electrodes such as LiCoO$_2$ and LiMn$_2$O$_4$ up to 900ºC (Thangadurai and Weppner, 2005). Thin film research on this material is encouraged to explore the possibility of using this thin film electrolyte for micro-batteries. The integration of thin film batteries onto a chip requires the thin film battery is compatible with silicon Integrated Circuit (IC) technology in terms of fabrication methods, materials, and performance. Based on this consideration, Ariel et al. (2005) chose silicon dioxide thin film as the electrolyte due to the high level of process control for its growth, as well as its insulating properties, and its well-known permeability to light ions. Ultra thin SiO$_2$ layer (7–40 nm) is thermally grown from an amorphous Si layer deposited on highly doped polycrystalline silicon layer and a LiCoO$_2$/SiO$_2$/polycrystalline-silicon all-solid-state thin film battery was successfully fabricated. Although Chemical Mechanical Polishing (CMP) was used to control the surface roughness, it was found the series resistance of SiO$_2$ electrolyte is still high, which limits the discharge capacity (Ariel et al., 2006).

4 Conclusions

Researches on thin film Li electrolytes are still under way to achieve high electric performance. Fabrications of the thin film glassy Li electrolytes have attracted most of the attentions due to the specific advantages of glassy electrolytes over crystalline ones. The real utilisation of thin film electrolytes for successful fabrication of the micro-batteries has not been realised until the development of the LiPON electrolyte. The nitrogen incorporation in glassy thin films not only improves their lithium ionic conductivity but also improves their electrochemical stability. A series of new oxide glass electrolytes have been, or will be, developed with nitrogen incorporation, such as LiSiPON and LiSON thin film electrolytes. These newly developed oxide glass thin films exhibited high lithium ionic conductivity of about $10^{-5}$ S/cm and high electrochemical stability of up to 5.8 V, which makes them promising for next generation of micro-batteries. Although the thin film sulphide glassy electrolytes exhibit higher lithium ionic conductivity compared to thin film oxide glassy electrolytes, the high cost of thin film fabrication and the instability of sulphide glasses with direct contact with lithium will limit their application in micro-batteries. Crystalline electrolytes with NASICON, LISICON or perovskite-related structures could exhibit very high lithium ionic conductivity at room temperature. However, the potential for lithium insertion is
Thin film Li electrolytes for all-solid-state micro-batteries

compensated for by the reduction of transition metal cations in the NASICON and perovskite electrolytes such as LiTi$_2$(PO$_4$)$_3$ and La$_{2/3-x}$Li$_x$TiO$_3$ may prohibit their use with most lithium anodes. Researches on thin film micro-batteries for fast lithium ion conductors are still very limited. Further thin film studies will focus on the materials with less Ti or no Ti, which will improve the reducible nature.

Acknowledgements

This research was supported by National University of Singapore and Agency for Science, Technology and Research.

References


Thin film Li electrolytes for all-solid-state micro-batteries


Thin film Li electrolytes for all-solid-state micro-batteries


Watanabe, H. and Kuwano, J. (1997) ‘Formation of perovskite solid solutions and lithium-ion conductivity in the compositions, Li$_{2x}$Sr$_{1-2x}$M$_{0.5-x}$Ta$_{0.5+x}$O$_3$ (M = Cr, Fe, Co, Al, Ga, Ln, Y)’, *Journal of Power Sources*, Vol. 68, pp.421–426.


Xu, X.X., Wen, Z.Y., Wu, X.W., Yang, X.L. and Gu, Z.H. (2007) ‘Lithium ion-conducting glass-ceramics of Li$_{1.5}$Al$_{5}$Ge$_{1.5}$PO$_{4}$-xLi$_2$O (x = 0.0-0.20) with good electrical and electrochemical properties’, *Journal of American Ceramic Society*, Vol. 90, No. 9, pp.2802–2806.


