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Review Article

An Overview of Nanostructured Li-based Thin Film Micro-batteries

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Li-ion batteries have ushered the portable electronics revolution empowering myriads of consumer electronic devices. The bulk Li-ion batteries using liquid organic electrolytes have gone through unprecedented commercial success. In parallel, all-solid-state thin film micro-batteries, employing solid electrolytes, have attracted much interest due to their potential applicationin microelectronic devices. Replacing the liquid electrolytes via solid electrolytes, operational safety can be enhanced while preserving the electrochemical performance. In this spirit, thin films of cathodes, anodes and solid electrolytes can be assembled to fabricate multilayered all-solid-state micro-batteries. The success of this niche sector largely depends on the development and assembly of key electrode and solid electrolyte components. The current review explores a gamut of cathodes, anodes and solid electrolytes for their potential application in all-solid-state thin filmmicro-batteries.

Keywords: All-solid-state Micro-batteries; Thin Films; Cathodes; Anodes; Solid Electrolytes

Introduction

'Energy' has emerged as the principal concern in the 21st century with predicted global energy consumption crossing over 30 Terawatt by 2050. Energy shortage and environmental pollution have become a global concern facing the world today. There is an urgent need to develop sustainable renewable energy generation to reduce fossil fuel consumption and efficient round-the-clock energy storage. Energy storage can be most practically realized by electrochemical storage technologies using reversible conversion of chemical to electrical energy. In this sector, lithium-ion batteries (LIBs) rule the roost owing to their light weight, high gravimetric/volumetric energy density, high power densityalong with long cycle life (Kuwata, 2006; Takada, 2013).No doubt, they are ubiquitous these days,propelling variety of consumer electronic devices and (hybrid) electric vehicles. On the other hand, recent developments in redox flow batteries have become prominent for large scale storage applications as they offer the high-power rate, long energy storage time and excellent response time with the ability to get full power in few seconds. These unique characteristics are really helpful to replace the LIBs, especially for large scale application (Ravikumar, 2017). However, the usage of flammable organic electrolytes in these LIBs can lead to thermal runaway and explosion during overcharging or short circuiting thereby leading to safety concerns (Kuwata, 2006; Takada, 2013; Mrgudich, 1960). One approach to circumvent the safety issue is to replace the liquid electrolytes by solid electrolytes to fabricate all-solid-state batteries (ASSBs), which can deliver an ideal combination of energy density along with operational safety. Hence, ASSBs have attracted significant attention over the years from both fundamental science and technological application point-of-view. The schematic diagrams of battery with liquid electrolyte, solid-state electrolyte and thin film solid-state electrolyte are shown in the Fig. 1A-C.

An all-solid-state battery consists of cathode and anode along with solid electrolyte instead of liquid electrolyte. The working principle of solid-state battery is the same as the conventional liquid

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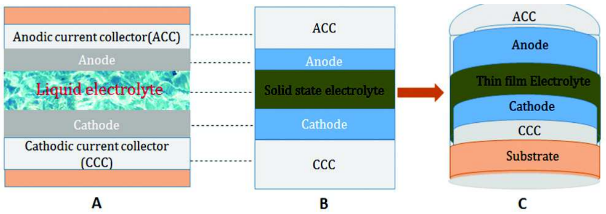

Fig. 1: Schematic diagram of battery with (A) liquid electrolyte (B) solid-state electrolyte and (C) thin film electrolyte

electrolyte based batteries (Bruce, 1997; Yoon, 2013). These batteries can overcome the potential problems of liquid electrolyte based batteries, such aschemical decomposition, safety hazards and flammability. In the quest to realize next generation batteries, all-solid-state batteries form a niche sector encompassing robust energy density and excellent safety (Kotobuki, 2013). In addition, various complicated design/architecture can be realized in these solid-state batteries. Moving over from organic liquid electrolytes, safe and environmentally compatible solid-state electrolytes have received intense research focus (Li, 1994; Ueda, 2013; Liu, 2014; Bates, 2000; Nishio, 2009). Solid-state electrolytes are mainly classified into two types based on their configurations and electrode/electrolyte materials setups: bulk solid-state electrolytes and thin film solid-state electrolytes. There are two main differences between the bulk and thin film electrolytes: (i) thickness and (ii) fabrication method. While the thickness of bulk solid-state electrolytes is usually in the range of several hundred micrometers; the thin film solid-state electrolytes have thickness in the range of hundreds of nanometers to several micrometers. Bulk solid-state electrolytes are usually manufactured by conventional techniques such as mechanical milling, compaction and high temperature sintering. In contrast, thin film solid-state electrolytes are fabricated by a variety of sophisticated methods like pulsed laser deposition (PLD), spark plasma sintering (SPS), radio frequency sputtering (RF sputtering) and chemical vapor deposition (CVD). The solid-state batteries have slowly but steadily emerged over last three decades. In this review, we have attempted to provide a sneak peek on brief historical journey, various fabrication methods,some state-of-the-art electrode/electrolytes and current status of all-solid-state thin film micro-batteries.

A Brief History of All-Solid-State Thin Film Batteries

All-solid-state thin film batteries were first reported by Hitachi Co. Ltd. (Japan) in 1982. The full cell battery assembly of TiS_2 (cathode)/$Li_{12}Si_3P_2O_{20}$ (electrolyte)/Li (anode) was prepared by vapor deposition techniques (Miyauchi, 1983; Kanehori, 1986). However, it was far from commercialization as it was not sufficient for practical applications. NTT Co. Ltd. (Japan) developed a $Li_{3.4}V_{0.6}Si_{0.4}O_4$ glassy electrolyte based solid-state battery by RF sputtering technique (Ohtsuka, 1989; Ohtsuka, 1990). EvereadyBattery Co. Ltd. (USA) later developed solid-state batteries using sulfide glasses ($Li_4P_2S_7$ and Li_3PO_4-P_2S_5) as electrolytes (James, 1988). They improved the battery performance in 1990s to reach over 1000 cycle performance between 1.5-2.8V with capacity of 10-135μAh.cm^{-2}. At the same time, Bellcore Co. Ltd. (USA) also developed a thin film battery using $LiMnO_2$ cathode, lithium metal anode and lithium borophosphate (LiBP) or lithium phosphorous oxynitride (LiPON) as solid electrolyte (Shokoohi, 1991). The cell showed over 150 cycles operated in the voltage window of 3.5-4.3V giving the capacity around 70 μAh.cm^{-2}. Bates and Dudney *et al*. at Oak Ridge National Laboratory (ORNL) reported significant progress on LiPON-based thin film batteries, which were produced by RF sputtering technique (Bates, 1993; Bates, 2000; Dudney, 1999). In order to fabricate LiPON thin film batteries, the metallic anode was produced by vacuum evaporation and anodes/cathodes were fabricated by RF sputtering method. LiPON thin films are very stable in air compared to lithium oxide or sulfide based batteries, albeit having low ionic conductivity of ~10^{-6} S.cm^{-1}. LiPON thin films reported by ORNL showed very good performance between 2-5V with stability over 10,000 cycles. Baba *et al.* and Park *et al.*, developed the rocking chair type solid-state batteries using $LiMn_2O_4$ cathode | LiPON electrolyte | $Li_xV_2O_5$ anode configuration by RF sputtering technique. They developed solid-state batteries without using Li metallic anode and were successful in obtaining capacity of ~10 μAh.cm^{-2} (Baba *et al.*, 1999; Baba *et al.*, 2001; Park *et al.*, 1999; Baba *et al.*, 2003). Inspired by these early successes, there have been numerous reports on potential electrodes, solid-state electrolyte materials and design/architecture of superior thin film Li-ion micro-batteries.

It is known that the battery performance strongly depends on quality of electrode materials and its interfaces (Machida, 2004). While selecting the electrode materials, some key parameters should be taken into account, such as their capacity for energy storage, uniform electrode-electrolyte contact surface area and ability to facilitate reversible lithiation/ delithiation. Although, many different electrode materials have been developed for conventional lithium-ion battery using organic liquid electrolytes, many of these cathodes and anodes developed so far are not yet suitable for solid-state thin film lithium-ion batteries. We have attempted to review promising electrodes (cathodes and anodes) and solid electrolyte materials, suitable for realization of solid-state thin film Li-ion micro-batteries.Some key all-solid-state thin film batteries, reported overthe last 25 years, are enlisted in Table 1. Some salient features of different cathodes, anodes and electrolyte materials are tabulated in Table 2.

Thin film Deposition Techniques

One key hurdle in realizing efficient thin film micro-batteries is to deposit uniform layers of thin films with adequate interfacial contacts with neighboring electrode/electrolytes. There are few vapor deposition techniques that can be employed in order to produce good quality thin film materials. These include simple heating of a source material, laser-induced vaporization, and bombarding the material with energetic ions. All of these techniques are performed under vacuum and primarily rely on the kinetic theory of gases in order to understand their behavior. Some major thin film deposition methods are briefly described below. The schematic diagram of thin film growth mechanism from physical vapor deposition (PVD) techniques is illustrated in Fig. 2. The schematic diagrams of the pulsed laser deposition, RF sputtering and chemical vapor deposition technique are shown in Fig. 3(A-C).

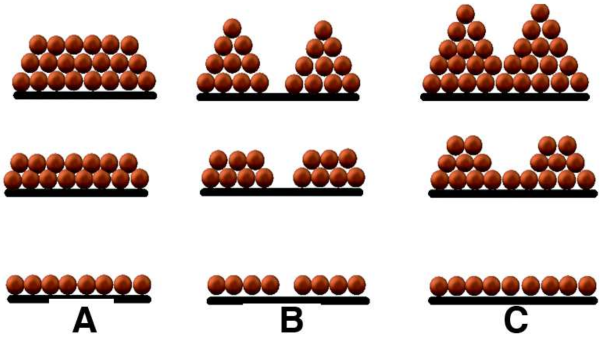

Fig. 2: Schematic diagram of thin film growth models (A) layer by layer (B) Island (C) Layer by layer + Island

Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is a growth technique in which the photon energy of a laser characterized by pulse duration and laser frequency interacts with a bulk material (Chrisey, 1994; Willmott, 2000; Yang, 2000). As a result, material is removed from the surface of target depending on the absorption properties of target materials. Pulsed laser deposition (PLD) involves using a laser beam to vaporize the surface of a target material. In general; the PLD process can be divided into four stages. First, the laser beam is focused onto the target material. The elements in the target are rapidly heated to their evaporation temperature, where there are sufficiently high flux densities over a short pulse duration. Second, the ablated target elements move towards the substrate according to the laws of gas-dynamics. In the third stage, the high energy atoms bombard the substrate surface where a collision region is formed between the incident flow and the sputtered atoms. A film begins to grow after a thermalized region develops and when the condensation rate is higher than the rate of sputtered atoms. Finally, nucleation and growth of a thin-film occurs on the substrate. This step can be controlled by several factors such as laser density, energy, deposition duration, vacuum level and the temperature of the substrate. PLD has some advantages over the other techniques in that, the stoichiometry of the target can be retained in the deposition film, irrespective of composition complexity. Further, many different materials can be deposited with easy handling when compared to other techniques such as CVD and ion implantation techniques (Kaczmarek, 1996; Bao, 2005). On the other hand, it has some disadvantages; such as the deposition of droplets, the splashing or the particulates deposition on the thin-film and lower energy density and slower deposition rate compared to other thin film deposition techniques (Willmott, 2000; Yoshitake, 2001).

Radio Frequency Magnetron Sputtering (RFMS)

A high-voltage radio frequency (RF) source at a typical frequency of 13.56 MHz is used to ionize a sputtering gas, which produces the plasma (Yamashita, 1999). The ionized gas then bombards the target,

Table 1: All-solid-state lithium-based thin film batteries reported in the past 25 years

Cathode	Anode	Electrolyte	Capacity	Voltage	Year	Ref.
$LiMn_2O_4$	Li	$Li_{6.1}V_{0.66}Si_{0.39}O_{5.36}$	33.3ìAh/cm^2	3.5-5.0	1990	(Ohtsuka, 1990)
TiS_2	Li/LiI	LiI-Li_2S-P_2S_5-P_2O_5	70mAh/cm^3	1.8-2.8	1992	(Jones, 1992)
$LiMn_2O_4$	Li	LiPON	10-30 ìAh/cm^2	4.0-5.3	1995	(Bates, 1995)
Li-V_2O_5	Li	LiPON	10-20 ìAh/cm^2	1.5-3.0	1996	(Wang, 1996)
$LiCoO_2$	Li	LiPON	35 ìAh/cm^2	2.0-4.2	1997	(Wang, 1996)
$Li_x(Mn_yNi_{1-y})_{2-x}O_2$	Li	LiPON	100mAh/g	3.5-4.0	1998	(Neudecker, 1998)
$LiMn_2O_4$	Li	LiPON	45 ìAh/cm^2-ìm	3.7-4.3	1999	(Park, 1999)
$LiCoO_2$	Li	LiPON	130 ìAh/cm^2	3.5-4.5	2000	(Bates, 2000)
$LiMn_2O_4$	V_2O_5	LiPON	18 ìAh/cm^2	1.0-3.5	2001	(Baba, 2001)
$LiCoO_2$	Li	LiPON	170mAh/g	3.0-4.4	2002	(Jang, 2002)
$LiNiO_2$	Li	$Li_{2.94}PO_{2.37}N_{0.75}$	37 ìAh/cm^2-ìm	2.0-4.2	2002	(Kim, 2002)
$Li_yMn_xNi_{2-x}O_4$	Li	LiPON	52 ìAh/cm^2-ìm	3.0-5.5	2003	(Whitacre, 2003)
FeS_{1+x}	Li	CPE	40 mAh/g	1.0-2.5	2004	(Yufit, 2004)
$LiMn_2O_4$	V_2O_5	LiPON	13.7 ìAh/cm^2	0.3-3.5	2005	(Nakazawa, 2005)
$LiMn_2O_4$	SnO	LVSO	9 ìAh/cm^2	1.0-2.5	2006	(Kuwata, 2006)
TiO_2	Li	LiPON	19 ìAh/cm^2-ìm	1.0-3.5	2007	(Wen, 2007)
$CuWO_4$	Li	LiPON	145ìAh/cm^2-ìm	1.0-4.0	2008	(Ma, 2008)
$LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$	Li	LATSP	150mAh/g	2.5-4.5	2010	(Xiea, 2010)
$LiCoO_2$	In	Li_2S-P_2S_5	46mAh/g	0.0-3.5	2011	(Sakurai, 2011)
$LiCoO_2$	Li	LiBPON	9 ìAh/cm^2	3.4-4.2	2013	(Yoon, 2013)
$LiCoO_2$	Sn_xN_y	LiPON	163 ìAh	2.0-4.0	2014	(Li, 2014)
$LiCoO_2$	Li	$Li_3PO_{4-x}N_x$	103mAh/g	3.5-4.5	2015	(Nakazawa, 2015)
$LiCoO_2$	Al	LiPON	48 ìAh/cm^2	3.0-4.2	2015	(Gong, 2015)
$LiCoO_2$	Si	LiPON	2100 mAh/g	2.0-4.0	2016	(Wang, 2016)
MoO_3	Li	LiPON	180 ìAh/cm^2-ìm	1.0-3.5	2016	(Glenneberg,2016)
$Li_4Ti_5O_{12}$	Li	LiPON	34 ìAh/cm^2	1.0-2.0	2017	(Schichtel, 2017)

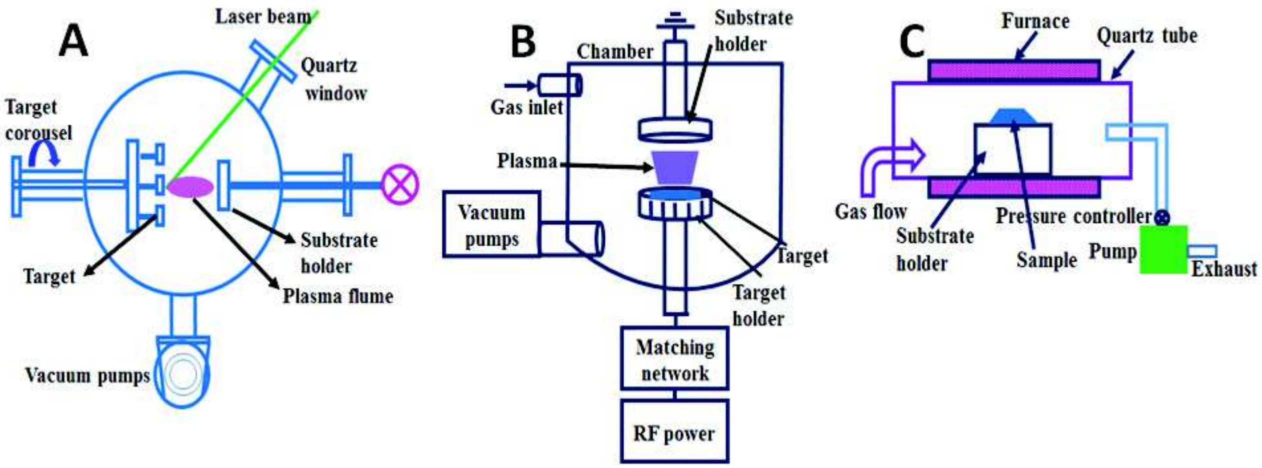

Fig. 3: Schematic diagram of (A) Pulsed laser deposition (B) RF sputtering (C) Chemical vapor deposition

Table 2: Salient features of difference anode, cathode and electrolyte materials

Material	Advantages	Disadvantages	References
Anode materials			
Li	● High theoretical capacity ~ 3860 $mAh.g^{-1}$ ● Low electrochemical potential (–3.04 V)	● Uncontrollable dendritic Li growth ● Low Coulombic efficiency	(Ohtsuka, 1990) (Ohtsuka, 1989)
V_2O_5	● Theoretical capacity of V_2O_5 is as high as ~ 290 $mA{\cdot}h.g^{-1}$ ● Feasibility of reversible insertion and extraction of lithium ions ● Low cost	● Poor stability ● Low ionic and electronic conductivity	(Nakazawa, 2005) (Nakazawa, 2007) (Baba, 2003)
Al	● Theoretical capacity of ~ 2235 $mAh.g^{-1}$	● Short cycle life& large volume ● High irreversible capacity loss	(Gong, 2015)
Si	● Highest theoretical capacity ~4200 $mAh.g^{-1}$	● Large volumetric changes ● Large electrochemically related stress ● Early capacity fading	(Tong, 2014) (Polat, 2015) (Polat, 2016)
Cathode materials			
$LiCoO_2$	● High theoretical capacity ~ 274 $mAh.g^{-1}$ ● Theoretical capacity ~ 170 $mAh.g^{-1}$ ● Long cycle life ● Easy operation at high temperature ● Low self-discharge	● Expensive ● Low thermal stability	(Wang, 1995) (Whitacre, 2001) (Hayashi, 2007) (Kuwata, 2010) (Jacke, 2010)
$LiNiO_2$	● High theoretical capacity ~ 275 $mAh.g^{-1}$ ● High energy density	● Thermally unstable ● Blocking of Li^+ ion pathways during process	(Kim, 2002)
$LiNi_xCo_yMn_zO_2$	● High theoretical capacity ~ 280 $mAh.g^{-1}$ ● Good cycle stability and low cost		(Kim, 2002) (Wang, 2017) (Kun, 2017)
$LiFePO_4$	● Theoretical capacity ~ 170 $mAh.g^{-1}$ ● Thermal stability ● High power capabilities	● Low operating voltage ~ 3.2V. Low ionic and electronic conductivity	(Xie, 2009) (Bajars, 2011) (Alexis, 2016)
$LiMnPO_4$	● Theoretical capacity ~ 170 $mAh.g^{-1}$ ● Operational voltage ~ 4V ● High specific energy	● Low ionic and electronic conductivity	(Baba, 2001) (Park, 1999)
$LiCoPO_4$	● Theoretical capacity ~ 165 ● High operational voltage ~ 4.2V	● Expensive ● Low ionic and electronic conductivity	(Li, 2006) (Li, 2008)
Electrolyte materials			
LiPON	● High ionic conductivity ~ 3.3 x 10^{-6} S/cm ● Excellent electrochemical stability.· ● High operational potential ~ 5.5V		(Bates, 1992) (Yu, 1997) (Vereda, 2002) (Kim, 2008)
$Li_{10}GeP_2S_{12}$	● Highest ionic conductivity ~ 12 m $S\text{-}cm^{-1}$		Noriaki (2011)
$Li_2S\text{-}P_2S_5$	● High ionic conductivity ~ 2 x 10^{-6} S/cm	● Electrolyte instability ● Large increase in cell resistance	(Kbala, 1984) (Yamashita, 1996)
LVSO	● Ionic conductivity ~ 2.5 x 10^{-7} S/cm ● Low voltage window around 3.5 V	Electronic conductivity ~ 10^{-10} S/cm	(Yamashita, 2001) (Kawamura, 2004)
LLTO	● Highest ionic conductivity of 10^{-3} S/cm	● Highly unstable ● Choice of electrodes are limited. Cathodic potential > 2.4V will react with electrolyte	(Kitaoka, 1997) (Stramare, 2003) (Lee, 2006) (Maqueda, 2008)

where multiple collisions take place, releasing atoms of the target material into the plasma. These atoms condense upon the substrate, which is placed in front of the target. A permanent magnet is added to the sputtering gun in order to enhance the deposition rate and minimize the secondary electron bombardment of the film. There are several important reasons for selecting radio-frequency magnetron sputtering (RFMS) as the technique of choice. First, there is no need to produce thick films. To produce a protective barrier for lithium metal anodes, a layer is needed and it only needs to be thick enough so that it does not have large numbers of pin holes that will lead to failure of the anode. A layer of 50 to 5000 Å is considered to be thick enough and can easily be produced by RFMS. In addition, sputtering can be done within the confines of a sealed glovebox. It can be used with multiple targets and film chemistries to produce very uniform films of high compositional integrity and it consequently produces films with excellent adherence to the substrate. Finally, it is possible to deposit insulator films through RF reactive sputtering at rates higher than those of direct current methods (Dudney, 1999; Souquet, 2002).

Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) process is related to transforming gaseous molecules and precursors by chemical reaction occurring on the heated substrate surface. CVD can be capable of making material, is in the form of a thin-film, powder or single crystal (Mount, 2003). By optimizing the experimental conditions, including composition of reaction gas mixture, substrate temperature, and substrate material etc., materials with wide range of physical and chemical properties can be grown. The characteristic feature of the CVD is its excellent throwing power, deposition of uniform thickness over large surfaces and selective deposition on patterned substrates. CVD processing is widely used in various fields such as integrated circuits, optoelectronic devices, sensors, micro-machines and fine metal and ceramic powders. CVD has many advantages compared to physical vapor deposition (PVD) techniques such as sputtering and molecular beam evaporation. While PVD processes may not give complete conformal coverage due to a shadowing effect, CVD can be allowed to coat thin-films of three dimensional structures with large aspect ratios. The deposition rates of the CVD process are several times higher than those of PVD routes. In addition, ultra-high vacuum is not needed and high purity films can be produced by CVD process. However, there are some disadvantages of the CVD process. It employs high deposition temperature(over 600^{o}C), which is not suitable for already grown thin films on substrates. CVD precursors are at time dangerous and toxic, which calls for strict safety measures. Further, metal organic chemical vapor deposition (MOCVD) needs very expensive precursors.

Thin Film Cathodes: Metal Oxides and Chalcogenides

Cathode materials play an important role in supporting the lithium ion(de) intercalation process in secondary Li-ion thin film batteries. A good cathode material is expected to have light weight, superior energy/power density, limited self-discharge and robust cycling stability (Whittingham, 2004). The first ever thin-film cathode (TiS_2 chalcogenide) was deposited by CVD and was incorporated into thin film lithium battery by Hitachi Central Research Laboratory (Kanehori, 1983; Kanehori, 1986). These films were composed of small plate-like crystals randomly intersecting each other. They exhibited very promising electrochemical activity involving efficient Li^+ diffusion delivering about 55% of its theoretical capacity at a current density of 16 mA.cm^{-2}. Later, Meunier *et al.*, fabricated TiO_xS_y amorphous thin films via sputtering (Meunier, 1989). These micro-batteries were constructed using amorphous thin-film cathode with the composition $TiO_{1.5}S_{0.7}$ with an open circuit voltage (OCV) of 2.6 V. These cells were expected to support relatively high current densities, upto 62 mA.cm^{-2}, but the corresponding capacity obtained was 23% of the first discharge capacity at current density of 1 mA.cm^{-2} due to the low diffusion co-efficient of the cathode material. However, Eveready Battery Company could commercialize a thin-film lithium battery with TiS_2 cathode deposited by radio-frequency sputtering (Steven, 1995). The deposited film had good stoichiometry ($TiS_{2.09}$) with small crystallites that resulted in very large active surface area favoring easy Li^+intercalation into the cathode thin film. Thin film batteries constructed with TiS_2 cathode film had an OCV around 2.5 V and exhibitedover 1000 cycles between 1.4 and 2.8 V, retaining over 90% cathode utilization at current densities up to 300 mA.cm^{-2}.

Following, metal sulfide (nickel sulfide) thin films were developed by Matsumura *et al.*, as cathode for thin film batteries(Matsumura, 2007; Yufit, 2004). The Ni_3S_2 | LISICON | Al-Li all-solid-state cell delivered a large reversible capacity of 300 $mAh.g^{-1}$ even after 300 cycles (Matsumura, 2007). The wt. % of Ni_3S_2 plays an important role to exhibit stable reversible capacities. As the depth of the first discharge capacity also influences the cycling properties, Ni_3S_2 consumed during the discharge reaction may affect the nickel reduction mechanism. Following, iron sulfide thin film incorporated into a Li | CPE | FeS_x cell showed good electrochemical performance over 650 cycles with 0.06% capacity fade per cycle and near 100% Coulombic efficiency at a current density of 50 $mA.cm^{-2}$ at 125°C (Yufit, 2004). Apart from metal sulfides, metal oxides and selenides were also successfully incorporated into thin-film lithium batteries. However, the fabricated selenide thin-films with the structure of Li | Li^+-borate glass | InSe delivered very poorcapacity. NTT Co. Ltd. (Japan) fabricated several thin-film lithium batteries with different metal oxides such as WO_{3-x}, MnO_{2-x} and MoO_{3-x} cathodes using RF sputtering method (Yamaki, 1996; Ohtsuka, 2001). Among them, MoO_{3-x} thin film with a thickness of ~ 4.66 μm showed an initial discharge capacity of 398 $mAh.cm^{-2}$ per unit area up to 40 cycles. The charge-discharge curves and discharge curves at different cycles of Li/MoO_{3-x} thin films are shown in Fig. 4(A-B). The polarization between charge and discharge curves at 20th cycle was only about 0.3 V. It was observed that increasing the cathode film thickness slightly reduced the cathode utilization at a high discharge current density, but the discharge capacity increased. Some other oxide based thin films such as V_2O_5 (Bates, 1993; Eun, 2001; Danmei, 2014), TiO_2 (Wen-Yen, 2007), Fe_2O_3 (Kitaura, 2007), V_2O_5-WO_3 (Kirino, 1986), V_2O_5-TeO_2 (Jourdaine, 1988), V_2O_5-P_2O_5 (Jourdaine, 1988), $NiCo_2O_4$-$NiFe_2O_4$ and MoO_3 (West, 2005; Zheng, 2015; Choi, 2017) were also successfully integrated into thin film lithium batteries by several groups. While metal chalcogenides are electrochemically active, they have several practical issues including low operational voltage. Thus, battery scientists moved over to explore Li-based transition metal oxides as efficient thin-film battery components.

Lithium Transition Metal Oxides

Layer structured lithium transition metal oxides are the most popular cathode materials for commercial lithium-ion thin film batteries. Researchers at Oak Ridge National Laboratory first introduced $LiCoO_2$ as cathode for thin film batteries, which is a well-known member in the layer oxide family (Wang, 1996). These $LiCoO_2$ thin films were deposited by planar RF sputtering and were subjected to various post-annealing temperatures. By optimizing several processing conditions, films annealed at 700°C was found to exhibit superior capacity retention with minimal lossofaround 0.0001-0.002%/cycle for over 100 cycles for microbatteries with cathode film thickness 0.05-0.5 μm. Later, the same group successfully fabricated thin film Li-ion batteries based

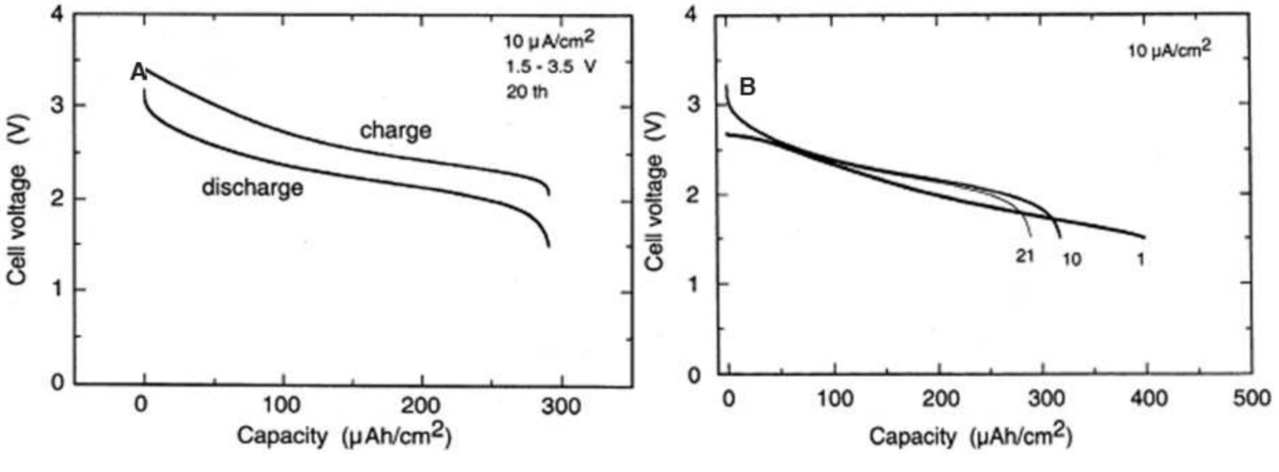

Fig. 4: (A) Charge-discharge curvesof Li/MoO_{3-x} thin film battery (B) discharge curves at different cycles. Reproduced from reference (Ohtsuka, 2001)

on $LiCoO_2$ cathodes (Neudecker, 1999). These exciting results attracted the attention of several research groups towards $LiCoO_2$-based thin film lithium/lithium-ion batteries (Whitacre, 2001; Hayashi, 2007; Kuwata, 2010; Kuwata, 2004; Jacke, 2010). The Jet Propulsion Laboratory (JPL at California Institute of Technology) deposited $LiCoO_2$ thin films at low temperature (ca. 300°C) using RF sputtering delivering good electrochemical properties suitable for micro-batteries. Later, NTT Corporation (Japan) employed electron cyclotron resonance (ECR) sputtering method to prepare $LiCoO_2$ thin films (Hayashi, 2007). These films were well crystallized without any post heating by controlling the O_2 to Ar ratio. A full cell battery using $LiCoO_2$ thin film (thickness: 6.2 μm) delivered relatively large discharge capacity around 250 $mAh.cm^{-2}$ with steady cyclability. Moreover, this battery exhibited high discharge capacities over 100 $mAh.cm^{-2}$ along with excellent rate performance. The feasibility of preparing thin film batteries on flexible polymer substrate was demonstrated successfully. Kuwata *et al.*, used PLD route to fabricate $LiCoO_2$ thin films (Kuwata, 2010; Kuwata, 2004) to construct lithium/lithium-ionthin film batteries. *In-situ* photoelectron spectroscopy was utilized to investigate $LiCoO_2$| LiPON interface at different temperatures during the deposition of LiPON solid electrolyte (Jacke, 2010). It was observed that an intermediate layer composed of some new nitrogen-containing species affects the interface dipole modifying the electronic structure at the heterogeneous $LiCoO_2$ | LiPON interface. Liu *et al.* tested the electrical performance of Li | LiPON | $LiCoO_2$ all-solid-state thin film lithium battery (Li, 2008). The results showed that $LiCoO_2$ thin film annealed at 700°C exhibited best performance with a clear discharge plateau observed between 3.8-4.2 V. The specific capacity reached 55.4 $mAh.cm^{-2}.\mu m^{-1}$ with a good cyclic performance. Sivaji *et al.* studied Zr/Ti doped $LiCoO_2$ thin films prepared by RF sputtering, which revealed the enhancement of discharge capacity upon Zr/Ti doping *vis-a-vis* pristine $LiCoO_2$ thin films. Similarly, Zr-doped $LiCoO_2$ films were found to exhibit stable electrochemical performance (Sivaji, 2016).

Besides lithium cobalt oxides, other layer structure lithium transition metal oxide thin films, such as $Li_x(Mn_yNi_{1-y})_{2-x}O_2$ (Neudecker, 1998), $LiNiO_2$ (Kim, 2002), $LiNi_{1-x}Co_xO_2$ (Kim, 2002; Wang, 2017; Kun, 2017), $LiCo_{0.8}M_{0.2}O_2$ (M = Ni, Zr) (Li, 2006), $LiNi_{0.8}$-$Co_{0.2}O_2$ (Baskaran, 2009) and $Li(Ni_{1/4}Mn_{1/2}Co_{1/4})O_2$ (Ding, 2010) were successfully explored for thin film lithium/lithium-ion batteries. Ding *et al.* fabricated $Li(Ni_{1/4}Mn_{1/2}Co_{1/4})O_2$ |LiPON | Li thin film batteries with capacity increasing upon longer cycling due to the gradual improvement of the interface between cathode and electrolyte (Ding, 2010). A reversible capacity of30 $mAh.cm^{-2}.\mu m^{-1}$ was achieved between 3-5 V. Exploring spinel oxide materials, Bellcore and Eveready Battery Co. (USA) fabricated thin film battery with crystalline $LiMn_2O_4$ as cathode and LIPONas electrolyte (Jones, 1994). It showed approximately 75% Li intercalation into cathode materials when cycled between 3.5 and 4.3 V at current densityof 30 $mA.cm^{-2}$. Park *et al.* fabricated a full cell thin film battery using $LiMn_2O_4$ | LiPON | Li architecture (Park, 1999). It exhibited reversible discharge capacity of approximately 48 $mAh.cm^{-2}$ corresponding to 0.8 Li per mole of Mn_2O_4 involving a sharp plateau around 4V. The capacity loss was less than 4% after 100 cycles at a current density of 100 $mA.cm^{-2}$. By interconnecting 8 unit cells in series, they also achieved a high voltage of approximately 32V.A thin film battery with nanocrystalline $Li_xMn_{2-y}O_4$ cathode film was fabricated at Oak Ridge National Laboratory (Dudney, 1999). In nanocrystalline films, it was observed that the Li^+ diffusivity was greatly reduced, thereby limiting its power density. The advantage of this cathode wasthe ability to fabricate thin-film batteries on substrates maintained at low temperature or temperature-sensitive devices. Furthermore, these batteries also proved to be very stable with long cycle life even when operated at high temperature up to 100°C. Baba *et al.* incorporated $LiMn_2O_4$ spinel films into a thin-film lithium-ion battery (Baba, 2001). Several other transition metal oxides were developed by Whitacre *et al.* They successfully demonstrated a new method to fabricate hundreds of cells with slightly different cathode compositions in less than 10 h and subsequently analyzed them using traditional electrochemical techniques (Whitacre, 2003). Zhou fabricated ZrO_2-doped $LiMn_2O_4$ thin film by RF magnetron sputtering (Li, 2007). It was found that ZrO_2 doping lowered the particle size of as deposited thin films. The electrochemical testing of $LiMn_2O_4$-ZrO_2 | LiPON | Li solid-state thin film batteries exhibited a gradually sloping discharge plateau between 4.0 to 2.0 V, while the undoped one showed two flat discharge plateaus at 4.0 V and 2.8 V. It was predicted that adding ZrO_2 substantially enfeebled the free energy in annealed $LiMn_2O_4$-ZrO_2 thin film, which led to smaller particle size affecting their electrochemical kinetics. The films with sloping voltage plateau can more suitable for certain practical applications than the films having distinct plateaus.

Polyanionic Compounds

Moving from oxides to polyanionic cathode systems, lithium transition metal phosphate thin films were studied by several groups (Sauvage, 2004; Iriyama, 2004; Ma, 2005). $LiCoPO_4$ and $LiMnPO_4$ were the first systems to be implemented in thin-film lithium batteries (West, 2003; Ma, 2005; Fujimoto, 2015). Unfortunately, these thin films exhibited poor discharge capacity of 11 mAh.cm^{-2} for $LiCoPO_4$ (at a rate of C/15) and 5-20 mAh.g^{-1} for $LiMnPO_4$ (at current density of 20mV.min^{-1}) in comparison to previously discussed layered oxide and spinel oxide cathodes. At this nascent stage, various other polyanionic systems must be investigated to find suitable candidates for thin film lithium/lithium-ion batteries. In this spirit, $LiFePO_4$ thin films have been extensively studied by varying deposition techniques, substrates, and deposition temperature etc. (Sauvage, 2007; Xie, 2009; Alexis, 2016; Bajars, 2011; Pana, 2018). Notably, Pana *et al.* introduced a new way of hydrothermal process to fabricate homogeneous and continuous carbon coated nitrogenated $LiFePO_4$/N-C films. The $LiFePO_4$/N-C films deposited on carbon clothed substrate exhibited a near theoretical high capacity of 169 mAh.g^{-1} at 1C. It was observed that nanopores and N-C coating favored fast Li^+diffusion and electronic conductivity, thereby leading to superior electrochemical properties (Pana, 2018). In parallel, Fu group investigated a series of polyanion compounds to fabricate thin film lithium batteries. Initially, nitrogen doped-$FePO_4$ (FePON) as implemented as cathode to form FePON | LiPON | Li full cell. Interestingly, the FePON thin film micro-batteries showed a higher capacity and better cycling performance than pristine $FePO_4$ micro-batteriesdue to improved electronic conductivity with nitrogenation (Li, 2006). Later, same group worked on other polyanionic materials likeLiFe $(WO_4)_2$ (Li, 2008; Li, 2009; Li, 2008). An all-solid-state thin film battery $LiFe(WO_4)_2$ | LiPON | Li with a new amorphous cathode of LiFe $(WO_4)_2$ was constructed. It delivered a reversible capacity of 220 μAh.cm^{-2} involving two redox centers (Fe^{3+}/Fe^{2+} and W^{6+}/W^{x+}, where, x = 4 or 5) with excellent capacity retention over 1000 cycles. It exhibited much better rate capacity in comparison to $LiCoO_2$ and $LiMn_2O_4$ thin films due to its favorable electrode-electrolyte interface. LiFe $(WO_4)_2$ thin film was proposed to be a suitable electrode material for application in all-solid-state thin film lithium batteries. Polyanionic systems offer virtually infinite number of cathode materials, which should be systematically explored to unravel efficient thin film cathode materials.

Thin Film Anodes

Anode (or the negative insertion) materials act as host to reversibly accommodate Li^+ coming from cathodes during battery operation. Broadly speaking, all-solid-state thin film batteries widely use Li metal as anode. However, the low melting point and its strong reactivity with moisture restricted the use of Li metal in real-life thin film batteries. In addition, the choice of electrolytes that are stable enough for use with metallic lithium is also limited. Therefore, it is mandatory to find suitable anode candidates to realizethin film lithium-ion full cell. Nevertheless, when compared with the volume of work on cathode films, the research on anode films is quite sparse with only limited numbers of known compounds tested in thin film lithium-ion batteries. Bates *et al.* tested several nitrides as anodes such as silicon-tin oxynitrides (SiTON), Zn_3N_2 and Sn_3N_4 (Neudecker, 1999; Bates, 2000). Among them, a $LiCoO_2$ | LiPON | SiTON cell delivered a reversible discharge capacity around 340 mAh.g^{-1}. This full cell exhibited robust cycling stability between 3.93-2.7 V with capacity fading of only 0.001% per cycle. Baba *et al.* fabricated several thin-film lithium-ion batteries based on V_2O_5, Nb_2O_5 as anode and $LiMn_2O_4$ spinel as cathode (Dudney,1999; Nakazawa, 2005; Nakazawa, 2007; Baba, 2003). They examined the electrochemical properties by varying the thickness of Nb_2O_5. The results revealed that the batteries with a negative electrode thickness of ~200 nm showed an unstable cycling behavior consisting of a two-step curve, while the batteries with a negative electrode thinner than 100 nm showed a stable cycling curve up to 500 cycles. Lee *et al.* developed a Si-V anode film with the stoichiometry of $Si_{0.7}V_{0.3}$ and constructed a $LiCoO_2$ | LiPON | $Si_{0.7}V_{0.3}$ cell (Lee, 2003). It exhibited an excellent cycling stability between 2-3.9 V delivering a reversible discharge capacity of ~50 $mAh.cm^{-1}.mm^{-1}$ Kuwata *et al.* obtained SnO anode thin film by PLD and constructed several thin-film lithium-ion batteries with $LiCoO_2$, $LiNi_{0.8}Co_{0.2}O_2$ and $LiMn_2O_4$ (Kuwata, 2006). To match the Li free cathode, Baba *et al.* fabricated $Li_xV_2O_5$ anode films (Baba, 1999; Lee, 1999) by electrochemical lithiation of as-deposited V_2O_5 thin film to a potential of 0.1 V (vs. Li) before cell operation. Lee *et al.* fabricated the same compound by thermally evaporating pure Li metal on to the V_2O_5 layer at room temperature to form $Li_8V_2O_5$ anode (Lee, 1999). Both kinds of cells showed a very stable cycling performance. An *in-situ* SPM study was made on a TiO_2 anode within an all-solid-state thin film lithium battery ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ | LiPON | TiO_2) (Zhu, 2012). Revealing cyclic expansion/contraction during Li-ion insertion/extraction processes. On another note, Si can in principle, work as a high capacity anode material for Li-ion batteries. However, it does not present pragmatic candidate for anode materials due to its extreme volume changes (over 300 %) that leads to poor cycling stability and material degradation. Recently, many researchers observed that nanoscale Si materials can decrease the volume stress resulting in promoting superior cyclability than bulk Si (Tong, 2014; Polat, 2015; Polat, 2016). The charge-discharge curves and rate capability of Si/C thin films are shown in Fig. 5(A-B). Recently, we fabricated Ti-based $SrLi_2Ti_6O_{14}$ anode thin-films on SS substrates by pulsed laser deposition.Results indicate that the preferentially oriented thin films exhibited a reversible capacity over 160 $mAh.g^{-1}$ without any carbon or conducting additives (Rambabu, 2018).

Solid-State Electrolytes

In the commercial realization of all-solid-state Li-ion micro-batteries, the holygrail lies in development and implementation of solid-state electrolytes. Electrolytes work as a media for ionic mobility, allowing the chemical reactions to be completed at separate terminals to deliver energy to the external circuit. In case of liquid electrolytes, overcharging or short-circuiting can lead to high temperature resulting in fire or explosion (Robertson, 1997; Xu, 2006), creating chances of safety hazards. Numerous such accidents arising from liquid electrolytes have been reported worldwide involving portable electronics toairplanes. The safety limitations of liquid electrolytes restrict the development of electric vehicles (EVs) and large-scale grid-storage devices. To circumvent this safety issue, all-solid-state lithium batteries (ASSLiBs) have emerged as viable solution. ASSLiBs consist of cathode, anode and solid electrolyte obviating the need for liquid electrolyte. The solid electrolyte is the most critical component in all-solid-state thin film batteries. Efficient solid electrolyte materials should exhibit the following specifications.

1. It should have ionic conductivity higher than 10^{-7} $S.cm^{-1}$ at room temperature.
2. It should be chemically stable against metallic lithium and cathode materials.
3. It should have a high electrochemical decomposition voltage (higher than 5.5 V vs. Li)
4. It must have low toxicity.
5. It can be easily synthesized and fabricated (Thangadurai, 2005; Thangadurai, 2006).
6. It must carry as low cost, materials and productions as possible.

Some of the fundamental issues need to be cautioned for all-solid state thin film batteries

1. Volume and stress changes in materials during charge-discharge process, which effect the cycle life and safety.
2. Ion and electron migration between electrodes and electrolyte, which effects the specific capacity, specific power and cycle life.
3. Solid electrode/electrolyte interface, affecting the specific capacity and self-discharge.

From structural point-of-view, solid electrolytes are mainly classified into glassy and crystalline systems. Inthe last two decades, glassy lithium-ion conductors have been extensively studied as electrolytes for solid-state lithium-ion batteries due to several advantages such as: wide range selection of compositions, isotropic ion conduction and ease of fabrication as dense thin films along with minimal grain boundaries. These glassy lithium-ion conductors are further classified into two types based on the host materials: oxide glass and sulfide glass. Some principal solid electrolytes systems and their current status are briefly described below.

Oxide Glass Electrolytes

The oxide glass electrolytes are extensively studied due to their chemical/structural stability owing to less hygroscopic nature in comparison to sulfide glass electrolytes. In addition, oxide electrolytes do not react with electrode materials during (de)intercalation process, which is favorable to long cycling performance (Cho, 2006; Cho, 2007). Recently, Braga (2017) attempted a novel method of fabrication to make Li-S cell with glass electrolyte $A_{2.99}Ba_{0.005}O_{1+x}Cl_{1-2x}$ (A= La or Na) having ionic conductivity > 10^{-2} S cm^{1}. Cathode consists of plating the anode alkali-metal on a copper-carbon with Na or Li glassy electrolyte exhibited excellent properties, such as huge capacity giving a large energy density, long cycle life, low cost and especially safety which are suitable for friendly environmental large scale applications. This new approach of making solid-state battery made the researchers attention towards solid state batteries. Moreover, these electrolytes can be easily fabricated by physical vapor deposition methods especially in thin film form, which is beneficial for micro-battery application. The main disadvantage of these oxide glass electrolytes is low ionic conductivity. Extensive research has been focused to improve the ionic conductivity by selecting different compositions from binary systems such as Li_2O-B_2O_3 to ternary systems such as Li_2O-SiO_2-P_2O_5. Among these thin film electrolytes, high Li^+ ionic conductivity has been obtained in twospecific material systems, namely Li_2O-SiO_2-V_2O_5 (LVSO) and Li_2O-P_2O_5-N_2 (LiPON), leading to their successful commercial application in micro-batteries.

Li_2O-SiO_2-V_2O_5 (LVSO) Thin Film Electrolytes

The LVSO thin film electrolyte was deposited by Ohtsuka and Yamaki (Ohtsuka, 1989a; Ohtsuka, 1989b; Ohtsuka, 2001) using RF sputtering technique. The room temperature deposited amorphous film exhibited low ionic conductivity (10^{-11}S.cm^{-1}) compared to the crystalline film (10^{-10}S.cm^{-1}). This might be due to the amorphous Li_2O in the film that reacts with ambient H_2O or CO_2 forming LiOH or Li_2CO_3, thereby reducing the conductivity of the film. Ohtsuka *et al.* (Ohtsuka, 2001) fabricated micro-batteries using LVSO as electrolyte with MoO_3 thin film cathode and Li metal anode. The battery worked between 1.5-3.5V, delivering a discharge capacity of 60 μAh.cm^{-2} with 1-μm thickness cathode. Kawamura *et al.* (Kawamura, 2004) fabricated amorphous LVSO film by PLD with an ionic conductivity of about 10^{-7} S.cm^{-1} and an electronic conductivity of about 10^{-13} S.cm^{-1}. The ionic conductivity of the LVSO amorphous films was lower than that of crystalline LVSO, probably due to the different degree of crystallinity and different compositions between the films and bulk material. Later, Kuwata *et al.* were the first to successfully demonstrate the fabrication of LVSO-based full cell micro-batteries ($LiCoO_2$ | LVSO | SnO) and ($LiMn_2O_4$ | LVSO | SnO) by PLD technique (Kuwata, 2006).

Li_2O-P_2O_5-N_2 (LIPON) Thin Film Electrolytes

The lithium phosphorous oxynitride thin film (LIPON) was first developed by Bates *et al.* (Bates, 1992) using RF sputtering with help of high purity Li_3PO_4 target in nitrogen atmosphere. Later, Yu *et al.* (Yu. 1997) observed that small amount of N incorporation can effectively stabilize the films with enhanced ionic conductivity. In the LIPON family, maximum ionic conductivity of 3.3×10^{-6} S.cm^{-1} was observed for $Li_{2.9}PO_{3.3}N_{0.46}$ composition with activation energy of 0.55eV with negligible electronic conductivity. From above studies, it can be concluded that the high quality LIPON film can be prepared by RF sputtering. However, the rate of deposition is very low because of low pressure and low power required to avoid cracks of the target during deposition. Therefore, alternative techniques have been used to improve rate of deposition. Vereda *et al.* (Vereda, 2002) used an ion beam assisted technique to evaporate the Li_3PO_4 compound in N_2 atmosphere to obtain LIPON films with faster growth rate, but the films appeared to creak due to large tensile stresses. PLD is another technique yielding high rate of deposition, but surface of the films was very rough, limiting its applications (Zhao, 2002). Kim *et al.* used Plasma-Assisted Directed Vapor Deposition (PA-DVD) to prepare LIPON thin films (Kim, 2008). The rate of deposition was extremely high compared to other techniques and the observed ionic conductivity was about 10^{-7} S.cm^{-1}. They conclude that controlling the plasma conditions can improve the deposition rate and ionic conductivity without compromisingwith other electrolyte properties. Overall, LIPON thin filmswere found to be good electrolyte because of its high ionic conductivity, electronic resistivity and electrochemical stability with both metallic and metal oxide electrodes at cell potential up to 5.5 V (vs. Li). Subsequently, many all-solid-state micro-batteries have been developed implementing LIPON electrolytes delivering excellent electrochemical performance (Bates, 1996).

Sulfide and Oxysulfide Glass Electrolytes

The higher ionic conductivity of sulfide electrolytes has attracted significant attention to sulfide based systems. The thinfilm research on glassy sulfide was first studied by Kbala *et al.* (Kbala, 1984) focusing on B_2S_3-Li_2S and B_2S_3-Li_2S-LiI sulfide systems. Interestingly, superior ionic conductivity (10^{-3}-10^{-4} $S.cm^{-1}$) was observed in sulfide systemsin comparison to the oxide glassy electrolytes. This may be due to the presence of LiI in the ternary system. Later, Creus *et al.* (Creus, 1989) used vacuum evaporation technique to prepare thin film of Li_2S-SiS_2 binary glass and its ternary derivative Li_2S-SiS_2-P_2S_5. They found that cell resistance is very large due to the electrolyte reactivity with lithium metal and forming a resistance layer. This resistance layer can be avoided by using a LiI protective layer as proposed by Creus *et al.* (Creus, 1989). With this idea, Eveready Battery Company (USA) developed Li-TiS_2 thin film batteries with outstanding performance. These micro-batteries were cycled more than 1000 cycles between 1.4-2.8 V with over 90% of cathode utilization. The thin films of Li_2S-GeS_2-Ga_2S_3 glass system prepared by RF-sputtering were reported by Yamashita *et al.* (Yamashita, 1996; 2003). The ionic conductivity was almost identical to that of bulk glasses with similar compositions, which increases with higher Li_2S content. The film had an ionic conductivity of about 1.4×10^{-4} $S.cm^{-1}$ at room temperature with the highest lithium content. Despite having high ionic conductivity, unfortunately glassy sulfides have not been used widely in micro-batteries due to the chemical corrosion and hygroscopic nature.

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 with crystalline lithium ionic conductors whose ionic conductivities and electrochemical decomposition potentials are usually lower than glassy materials (Xia, 2009). The sole 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 enhancement of electrode/electrolyte interfacial quality. There is a constant search for new crystalline lithium-ion conductors. Some compounds have been found with promising Li^+ ionic conductivity at room temperature and possible use as thin film electrolyte for micro-batteries.

NASICON-type Electrolytes

The schematic crystal structure of NASICON-type compound is shown in Fig. 5. Various NASICON type compounds with general formula $LiM^{IV}_2(PO_4)_3$ (M^{IV} = Ti, Zr, Hf, Ge, Sn and etc.) or $LiM^{V}M^{III}(PO_4)_3$ (M^{V} = Nb, Ta, Sb, and V and M^{III} = Al, Cr and Fe) have been reported (Goodenough, 1976; Bates, 2000). The main advantages of these compounds are their high ionic conductivity, high temperature stability, low thermal expansion behavior and large surface area. Brike *et al.* successfully fabricated the first all-solid-state thin film battery ($LiMn_2O_4$ | $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$| $Li_4Ti_5O_{12}$) (Birke, 1999). $Li_4Ti_5O_{12}$ anode was used to overcome the instability between lithium metal and Ti^{4+} containing NASICON electrolyte and $LiBO_2$.LiF was added to block undesired reactions between electrodes and electrolyte. The thin films of $Li_4Ti_5O_{12}$ and $LiMn_2O_4$ spinels were prepared on $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ (LTP) electrolyte by sol-gel method (Hoshina, 2005; Dokko, 2007).The interface between electrodes and electrolyte was studied by fabricating the all-solid-state battery $Li_4Ti_5O_{12}$ (or $LiMn_2O_4$) | LTP | PMMA | Li, where PMMA is poly (methylmethacrylate) to avoid direct contact between LTP and lithium metal. It was found that the battery performance was mainly controlled by the electrode/electrolyte contact and the sol-gel coated thin films led to porous morphology with rough surface that induced poor electrode-electrolyte contact. Wu *et al.* (Wu, 2003) investigated $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ NASICON thin films prepared by the sol-gel spinning method with post annealing between 750-900°C. Films annealed at 800°C exhibited an ionic conductivity of $1.5\times10^{-5}$$S.cm^{-1}$ and electronic conductivity of

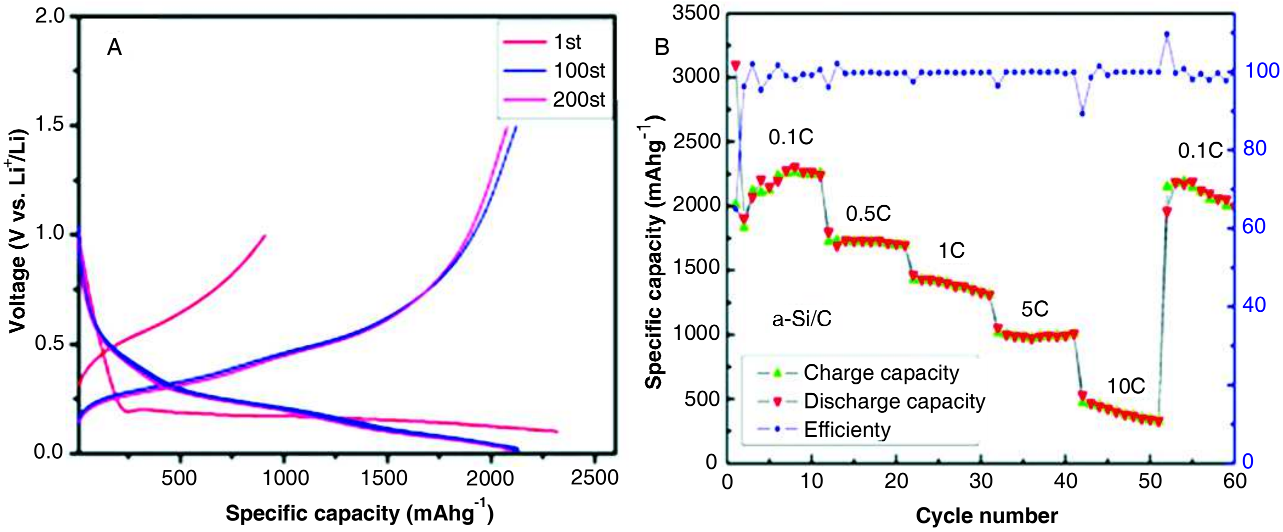

Fig. 5: (A) Charge- discharge curves of Si/C multilayer thin films (B) rate capability and coulombic efficiency of Si/C films. Reproduced from reference (Tong, 2014)

5×10^{-11} S.cm^{-1}. Overall, NASICON systems form a robust family to design highly conducting solid-electrolyte for thin film batteries.

LISICON-type Electrolytes

The LISICON (lithium super ionic conductor) type $Li_{4\pm x}Si_{1-x}X_xO_4$ (X = P, Al, or Ge) compounds are attracted much as a solid-state electrolytes for all solid-state batteries because of its high lithium ionic conductivity. The first material given the name LISICON was $Li_{3.5}Zn_{0.25}GeO_4$ (Robertson, 1997). Whitacre (2004) fabricated the all solid-state thin film battery by depositing Li film and $LiCoO_2$ films on each side of the of a crystalline Li_3PO_4/Li_4SiO_4 electrolyte chip. Cathode crystallization was done by annealing at 700°C. Results revealed that annealing at high temperature is not affecting on full cell performance. Solid-state full cell works well without induce any interfacial defects between electrode and electrolyte. Therefore, fabrication all-solid-state thin films batteries with crystalline LISICON thin film is recommended for further developments in battery technology.

Apart from oxide compounds, sulphide compounds with LISICON type structure have been developed and are named as thio-LISICON. The compounds of Li_2S-GeS_2, Li_2S-GeS_2-ZnS, Li_2S-GeS_2-Ga_2S_3, and Li_2S-GeS_2-P_2S_5 systems have the structures related to the γ-Li_3PO_4 type (Kanno, 2001). The new bulk compound of $Li_{10}GeP_2S_{12}$ exhibited extremely high ionic conductivity of 1.2×10^{-2} S.cm^{-1} (Kamaya, 2011). Ohta (2005) fabricated the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ thin films on the sapphire substrates using pulsed laser deposition. The observed lithium ionic conductivity is about 1.7×10^{-4} S.cm^{-1} that was one-fifth of the bulk material. The decrease in ionic conductivity in thin film was related to the increased lithium content leading to reduction in the number of lithium vacancies in the LISICON structure. However, the thio-LISICON material exhibited promising ionic conductivity at room temperature along with good electronic conductivity and electrochemical stability. All-solid-state thin film battery of these compounds warrants elaborate study.

Perovskite Electrolytes

Perovskite family of compounds form a potential family to design polycrystalline solid electrolyte because of their high ionic conductivity. The crystal structure of perovskite with general formula ABO_3 is shown in Fig. 6. Stramare *et al.* (Stramare, 2003) observed that the ABO_3-type lithium lanthanum titanates (LLTO) $La_{2/3-x}Li_{3x}TiO_3$ (La, Li at A site, and Ti at B site) exhibited high ionic conductivity with its three-dimensional framework built from corner-sharing TiO_6 octahedra with alternative stacks of La-rich and La-deficit sites along c-axis. Although, having high ionic conductivity, it was not used as electrolyte due to its lack of stability when in contact with the electrodes. The first thin film work on perovskite-type materials was reported by Kitaoka *et al.*

(Kitaoka, 1997). They measured the ionic conductivity of LLTO thin films prepared by sol-gel process around 10^{-7} S.cm^{-1} that is less than the conductivity of bulk materials. Lee *et al.* prepared LLTO thin films by RF-sputtering, but they failed to fabricate high quality thin films (Lee, 2006). Later, LLTO thin film was successfully prepared by pulsed laser deposition exhibiting high ionic conductivity value of 8.2×10^{-4} S.cm^{-1}similar to the bulk material (Maqueda, 2008). Further, Ahnand Yoon found that amorphous LLTO thin films exhibited better electrochemical properties than crystalline LLTO films (Ahn, 2005). Various perovskite structured compounds can be unveiled for practical application/s in all-solid-state micro-batteries.

Garnet Type Electrolytes

Recently, oxides with garnet related structures have received great attention as a potential solid-state electrolyte for LIBs. The typical structure of garnets is $A_3B_2C_3O_{12}$ with CO_4 tetrahedra and BO_6 octahedra that are connected via edge sharing fashion (Murugan, 2007). Although this is the general formula, it has been reported that increasing the number of lithium per formula unit from 5-7 results in increase of ionic conductivity 3-5 orders of magnitude. For example, $Li_7La_3Zr_2O_{12}$ (LLZO) exhibited a highest ionic conductivity approximately 2×10^{-4} S.cm^{-1} at room temperature with good thermal stability against lithium metal, air, and moisture (Masashi, 2010). The unique properties of garnet type structures are attracted wide research interest for further developments in sold-state electrolytes. Thin film research on this material is encouraged to explore the possibility of their use in thin film electrolyte for micro-batteries. The amorphous LLZO thin films are successfully deposited using RF magnetron sputtering. It was observed that films deposited at low RF power (40 W) exhibited the highest ionic conductivity (4×10^{-7} Scm^{-1}) due higher concentration of Li_2O (Kalita, 2012). Epitaxial growth of Al- doped LLZO thin films was realized by using pulsed laser deposition. The ionic conductivities in the grains of (001) and (111) films were 2.5×10^{-6} and 1.0×10^{-5} S.cm^{-1}. It revealed that the decrease in conductivity due to (a) Al^{3+} substitution in the LLZO lattice decreases the number of movable lithium ions and blocks the three-dimensional lithium migration pathway (b) lattice mismatch between substrate and film which led to lattice distortion of LLZO film (Sangryun, 2013). Later, Al-doped LLZO thin films were prepared using sol-gel method. Polycrystalline cubic structured LLZO films were obtained during the heat treatment at 900°C having an ionic conductivity of 2.4×10^{-6} S.cm^{-1} at 25°C (Kiyoharu, 2015). The typical crystal structure of NASICION, LiPON, Perovskite and Garnet are shown in Fig. 6.

Summary and Perspectives

In summary, there has been great interest in research and understanding of all-solid-state thin film micro-batteries because of their potential applications, ranging from micro-electronics to (plug-in) hybrid electric vehicles. The all-solid-state-batteries have an ideal combination of high electrochemical energy/ power density, cycling stability along with robust operational safety. Nanostructured thin film materials offer tunable features based on the particle size, morphology and chemical composition. The advantages of thin film batteries such as high purity, perfect composition and free from conductive additives or carbon coating have driven the researchers to explore the intrinsic properties of thin film electrodes and electrolytes. Thin-film technology provides (a) clean surface of the compound and improve the electrode-electrolyte interface contact reducing the interface resistance and permitting a high reversibility, (b) deposition in vacuum avoids possible moisture problems, (c) generally gives very good adhesion between layers and large areas can also be obtained which leads to minimize the self-discharge rate in thin films and improve the overall battery performance. In the current article, various well-known family of cathodes, anodes and solid electrolytes were reviewed with special focus on solid-electrolytes. Over the last three decades, there has been significant improvement in solid-state battery research with performance inching close to that of conventional batteries.

The future demand for cost effective and miniaturized electronic devices can be served with implementation of all-solid-state thin film micro-batteries.In this sector, various processing techniques such as pulsed laser deposition (PLD) and RF Sputtering can be employed to fabricate thin films with desired shape/size, light weight, multilayer formation having corrosion resistance and thermal stability. The design and architecture of all-solid-state thin film batteries is quite different from traditional

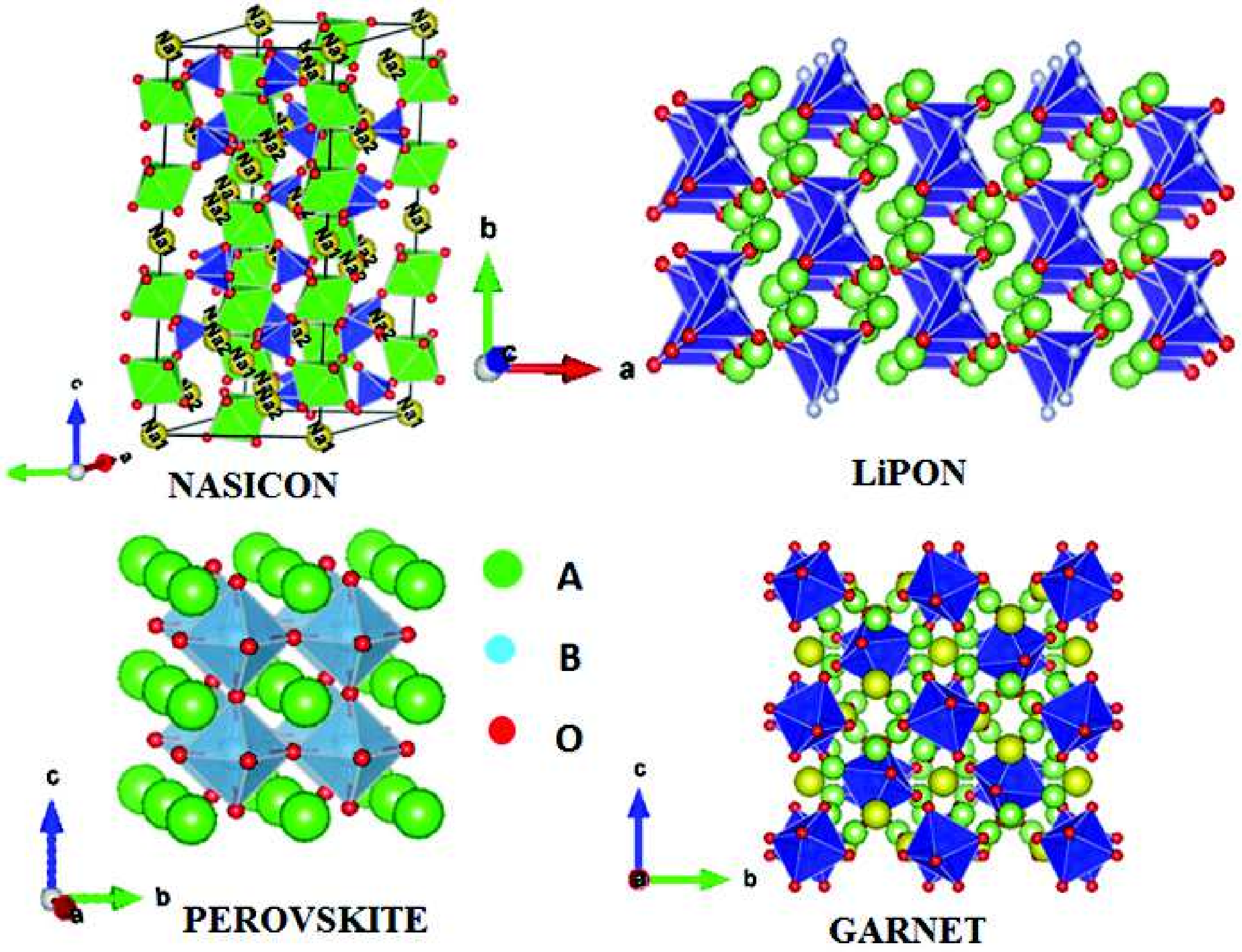

Fig. 6: Schematic crystal structures of NASICON, LiPON, Perovskite and Garnet type electrolytes

batteries using liquid (organic) electrolytes. The most difficult challenge in fabricating all-solid-state batteries is to assure intimate and uniform contact between electrode and solid electrolyte interface. Additionally, it is an uphill task to match the Li^+ ionic conductivity of solid-electrolyte to that of currently used liquid electrolytes.It calls for multi-disciplinary material and process innovation targeting (i) novel low cost and energy-dense electrode materials and (ii) unraveling novel solid electrolyte materials having an ideal combination of superior ionic conductivity along with material/ thermal stability. Future research efforts also need to be geared toward addressing some fundamental challenges such as electrode-electrolyte degradation owing to microstructural change, low cost processing enabling uniform electrode/electrolyte interfacial contactand upscaling of micro-batteries fabrication for commercial viability. With these research pursuits, the world is on the verge of yet another battery revolution with large-scale dissemination of all-solid-state batteries. Propelling suites of small-scale micro-electronics/gadgets to large-scale (hybrid) electric vehicles.

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