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Advanced Battery Applications of Thin Films

Fatma Özütok

Çanakkale Onsekiz Mart University, 17020, Çanakkale, Turkey, fatmaozutok@comu.edu.tr

+90 5412071982

Abstract

Increasing demand of the renewable and clean energy sources and the rapid depletion of fossil resources have been increased the interest in different and new alternative energy production and energy storage systems. Among the electrochemical energy storage systems, next-generation thin film batteries are so attractive because of their long cycle life, stability, high capacity, portability and decreasing prices. The integration of solid parts as electrode or electrolyte in Li-based batteries brings to safety that's why causes no leakage or explosion and prevents thermal runaway. The current studies are intended to reduce the difference between theoretical and practical specific energy densities of these batteries. It can be realized that using micron (less than 5 μm) or nano thickness microbatteries in the practical applications with moderating the battery weight. Thin film reduces diffusion length of electrons/Li ions and Li dendrite formation so expected rate performance is obtained.

In this review, thin film batteries (TFBs) were studied in detail. Especially, 3D microbatteries were investigated depending on their flexibility or printable. Additionally, their performance as electro-active components was investigated compared to their traditional counterparts. It is also planned to be a guide for inspired similar studies in the future direction.

Keywords: Li-ion battery, 3D microbattery, electrolyte, electrode, thin film

1. Introduction

Globally, more renewable energy and fewer fossil fuels/environmental pollution requirements have increased the demand for high power requirements and energy storage systems. Rapid development of technological and military applications, is showed in Fig.1., causes to improve efficiencies of supercapacitors or Li-based microbatteries which are commonly used energy storage systems. Li-based batteries can store one to two orders of magnitude more energy than supercapacitors [1]. Li-based batteries are given generally as Li-ion, Li-S, Li-air (Li-O_2 batteries are preferred than no-longer used Li-CO_2 batteries) batteries. An ideal Li-based battery satisfy these requirements such as cheap, high/improving energy density, high-power operation voltage at high-current charge/discharge rates and working a wide temperature range [2].

Fig.1. Common application areas of Li-ion rechargeable batteries (photos were quoting from different websites)

Compared to widely using of heaviest lead acid batteries, Li-ion batteries have been so interesting in energy storage/release systems since last ten years with their high specific energy, high cell voltage, high Columbic efficiency and low self discharge properties. On the other hand, main problems about next generation Li-ion batteries may list as power density, compactness, durability, cost and safety [3]. On the other hand, although Li-S batteries have unresolved shuttle mechanism they are so attractive especially in the last years with their high theoretical specific capacity (1672 $mAhg^{-1}$), low cost and non-poisonous nature of sulfur [4]. Lastly, Li-O_2 batteries have a theoretical energy density (3505 $mAhg^{-1}$) almost twice that of Li-S batteries and no intercalation process therefore Li-O_2 batteries have been used in large area applications such as wind turbines and solar cells [5].

Solid future is so brilliant for Li-ion batteries due to no SEI layer formation, high thermal stability, high working temperature stability, more cycles and enhanced safety with non-flammability. Especially, the primary problem is electrolyte solutions decomposition during discharge-charge process in Li-O_2 batteries [6]. If solid electrolyte is used, activated oxygen could not attack the electrolyte so that no decomposition occurs and oxygen reduction (ORR)/oxygen evolution reactions (OER) at the air electrode might be activated [7].

With increasing effect nanotechnology in our daily life, microelectronic devices and integrated optoelectronic circuits need to small sized and space-consuming nanomaterials. This important property may be given by this situation in the next generation batteries. It has been generally known that nanomaterials such as nanowires, nonorods, nanospheres and thin films may have higher rate capabilities compared to their bulk-materials because of shorter lithium/electron diffusion path, higher surface reactivity and improved mechanical stability [8]. In thin film batteries with <20 μm thickness, reduced surface, high thermal resistance, the support of conductive substrates and essential self standing feature are provided. Multilayer thin film batteries are preferred in potentially smart cards, RFID devices, micro sensors, pacemakers, neural stimulators, implantable medical devices and drug delivery systems. Thin film batteries firstly were offered to market by Hitachi Company in 1982 [9] and thin film Li-ion battery was patented by Wang in 2013 [10]. The first thin-film lithium-ion battery was produced by using lithium cobaltoxide (LCO)/lithium phosphorus oxynitride (LiPON)/lithium (Li) layered structure [11]. A large number of thin film battery studies related to Li-ion batteries compared to Li-S and Li-air batteries, fundamentally including thin film electrolytes.

The production techniques of thin/micro film batteries are generally either simple methods (electrochemical synthesis, spin coating, screen printing and sol-gel method) or complex (physical vapor deposition (PVD), chemical vapor deposition (CVD), RF or DC sputtering systems, which including vacuum chambers and high temperatures [12].

Table 1. Advantages/disadvantages of Li-ion batteries depending on forming structure

Table 2. Advantages/disadvantages of Li-ion batteries depending on material type

The development and improvement of electrochemically active components progress of next generation thin film batteries are urgent for desirable high power and low cost Li-based batteries. In this study, recent advances and constructions in Li-ion thin film batteries are summarized.

2. 3D Microbatteries

A lot of study concerning multi layered rigid (planar or stacked) (2D) microbatteries has been focused on their inexpensive and effective production with using pulsed laser deposition (PLD), chemical vapour deposition (CVD) and sol-gel method. Li ion transport has a severe effect on the rate performance and power density of Li-ion battery [13]. In traditional 2D Li-based microbatteries, Li ions and electrons are transported by liquid electrolytes and they have low areal capacity with limited configurations. 2D film batteries allows either low energy density/high power density or high energy density/low power density due to the capacity is restricted by the battery dimensions [14]. Additionally, randomly distributed slurries and their agglomerative particle components on the current collector may cause an undetermined Li^+ diffusion pathway [15]. Basic problem is ohmic drop in the electrolyte/separator layer this causes the separator thickness increasement [16]. This limitation may cause a mechanical stress and fracture in both anode and cathode.

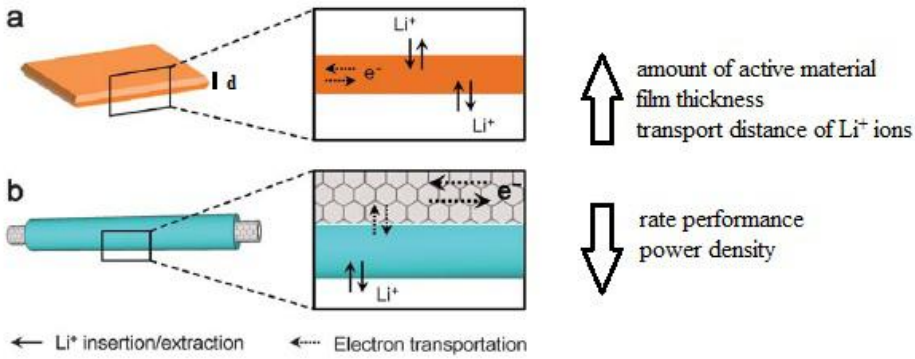

Fig.2. (a) lithiation and delithiation with 2D nanosheet structure (b) electron transport by incorporating agents e.g. CNTs (reprinted from [17] with permission).

To overcome such obstacle, Wu et.al. investigated that lithiation/delithiation 2D nanosheets with/without carbon nanotubes (CNTs) as an incorporating agent for improving carrier diffusion, as showed in Fig.2. Although these relative successful improvements (C-coating, surface modification as showed in Fig.3. etc.), nowadays different cell designs are able to increase energy demand and long cycle life necessity in very small scale microelectronic devices (MEMS). These devices can be listed as micro-drones, wearable devices, smart skins, touch screens, e-textile, radio-frequency identification tags and roll-up displays etc. At this point, next generation 3D thin film batteries as a reliable power supply that have been so attractive especially in the last years without embedded any additive or binder for electrode design. On the contrary of 2D batteries, Li ion transport remains constant with increasing

thickness in 3D microbatteries so power density can be conversely. All components (firstly, columnar current collectors are microfabricated with new architectures) contributes to the capacity and redox electrochemical reactions. Direct fabricated electrodes meanwhile penetrating the electrode with the current collector can be attributed to a facile and shorter pathway for electrons with enhanced electrochemical reactions. This supplies high surface in favor of high capacity. Kang et.al. showed that 3D anode architecture of MWCNTs directly grown on Cu mesh substrate and it exhibited 160% enhancement of specific capacity in the cycling performance [18]. They are generally named as ‘’3D self-supported electrodes’’. 3D trench design is preferred for thin film batteries to increase electrode surface area, as showed in Fig.4. However they can conclude an increased amount of active material on the similar footprint area compared to 2D battery [19]. It is aimed that specific surface area/volume must be obtained. These electrodes need different conductive and flexible substrates, such as metal foil, lithium foil, Kapton and carbon cloth [20]. Blake et.al. proposed a nano-carbon based substrate due to metal foil current collectors remain susceptible to crack formation [21]. Substrate coating is so important and this process must be thickness-controlled, pine-hole free and conformal.

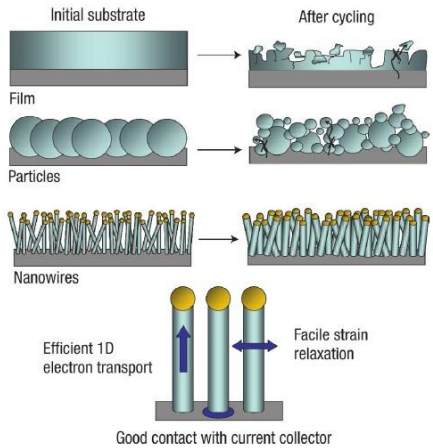

Fig.3. Surface effect with repeated lithiation and delithiation processes (reprinted from [22] with permission).

Micro-fabrication of 3D self-supported electrodes especially in the cathodes that could be categorized as self-growing, wet-etching and template-based growth [23]. As a new model extrusion-based additive manufacturing process for macro-control and an EF for micro-control with combining additive manufacturing and an electric field process were used by Li et.al. so synergistic control of micro/macro structures were able to a high areal capacity (3.1 mAh/cm^2) and double the areal capacity [24]. On the other hand, 3D electrolyte design is

problematic due to pinholes which could act as short circuit paths for electrons. The manufacturing difficulties and its compatibility with the integrated circuit technology are major challenges in 3D microbattery architecture [25]. Progress of 3D half-cell systems nearly was achieved. However, there are a lot of theoretically microbattery battery designs fewer commercial 3D designs are reliable and also they are time consuming and costly. It is not understood how the complex nano-scale architecture of the 3D battery has an effect on electrochemical processes during charge/discharge.

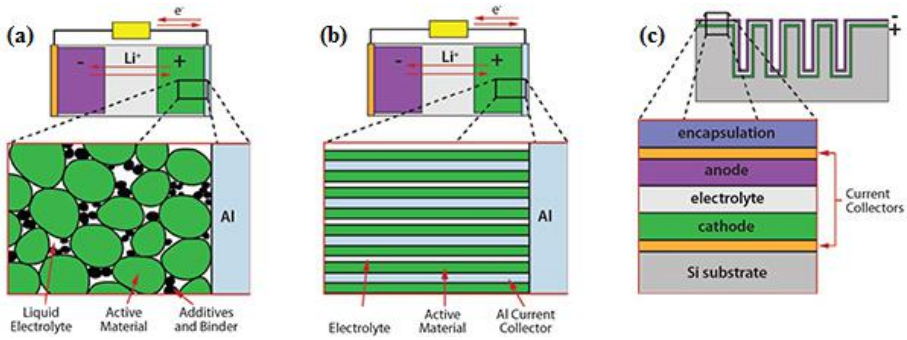

Fig.4. Schematical description of (a) the slurry procedure of commercial electrodes (b) 2D thin film battery and (c) 3D microbattery (reprinted from [58] with permission)

3. Flexible 3D Thin Film Batteries

With increasing development of smart communications and e-skin/wearable devices, the current flexible Li-ion batteries can not afford the need thus resulting in new alternative solutions. Flexible 3D batteries, as showed in Fig.5., are considered a promising battery architecture and miniaturization with their short Li ion transport pathways and thereby improved capacity, lighter and smaller packaging, high surface area and mechanical reinforcement due to internal stresses. However, there are some unresolved issues about 3D flexible batteries in the global battery market. First, direct deposition of crystalline active materials onto substrates is not possible for flexible thin film electrode, indicating soft Si anodes were developed with using Si/Ni/PVDF membrane to obtain high flexibility. Second, multiple stages of fabrication, including multiple processing steps, high cost, time and energy consumption, are limited its widespread commercial using. Therefore alternative simple and cheap techniques are necessary, excluding magnetron sputtering, PVD, photolithography and wet etching to achieve flexibility. Flexible test battery systems may be listed as LED luminescence, 3-point bend, automated mandrel bending test and static folding/bending [26].

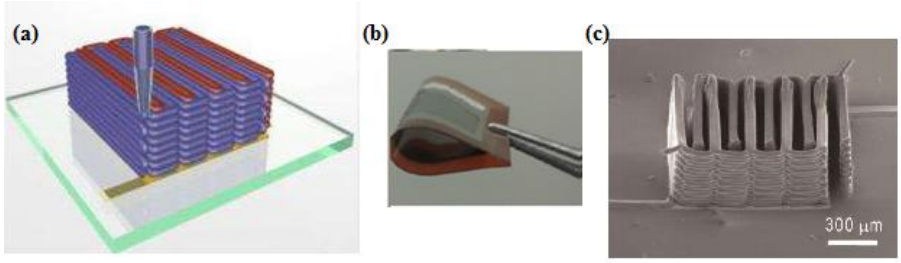

Fig.5. (a)Schematical and (b) real and (c) SEM images flexible 3D thin film battery (reprinted from [27] and [60] with permission)

The most used flexible electrodes are graphene paper, carbon nanofiber and carbon nanotubes, fabricating onto individual cells or multichannel plate substrates. Vieira et.al. proposed Ge-anode (300 nm thick) and LiCoO2/LiPON (cathode/solid-state electrolyte, 1.5 µm) with using PVD techniques (RF and DC sputtering, and e-beam evaporation) that obtained integration in MEMS microelectronics with this architecture but also the absence of battery encapsulation could damage the battery performance [27]. Study of Kang et.al. [28] revealed that 3D MWCNTs-graphene on transparent and flexible polyethylene terephthalate (PET) film with lamination process. These samples showed high reversible specific capacity of 250 mAhg-^{1} and high Coulombic efficiency of over 99%. Electrospinning of molybdenum carbide (MoC) embedded in carbon nanofibers as an anode was studied by Lee et.al [29]. They showed that high charge/discharge rate of 10 A g^{-1} and the specific capacity of MoC/CNF (109 mAh g^{-1}) was significantly higher than that of pure CNF electrode (3 mAh g^{-1}). In 2018, Gong was proposed 3D flexible and porous garnet-based lithium-ion conductive ceramic textiles derived from templates as solid polymer electrolyte [30].

4. Printed 3D Thin Film Batteries

3D printing is so useful and versatile method which has been adapted from structural components to functional materials for a large scale. Microbattery design problems may be solved with using beneficial properties of printing. It is a cheap system compared to other 3D fabrication methods to integrate microdevices, it is printable several layers on top of each other simply, stretchable interconnect points supplies mechanical strength and tunable open channels allows fast transport of Li ions and electrons [31]. Therefore, next generation battery phenemonia is based on 3D flexible printed thin film batteries, as showed in Fig.6., excluding their cylindrical, coin, prismatic and flat Li-ion batteries [32]. With using 3D printed technology that controlled film thickness (known as additive manufacturing), it is

ensured that low-cost electronic devices, uniformity on large-area applications and high-throughput production capabilities especially for wireless sensors and implantable medical devices. However, the main problem is low resolution and high contact resistances in printed battery technology [33]. Stencil printing, screen printing, ink-jet printing, spray printing are generally preferred to fabricate battery components. Printable inks were developed for the active layers, current collectors and electrolyte. Despite the fact that novel 3D printed battery geometry is a big improvement which needs to be further research with their low discharge capacities for future Li-ion batteries.

Fig.6. Flexible Li-ion battery (reprinted from [61] with permission)

5. Electrochemically Active Components of Thin Film Batteries

Electrochemically active components of Li-based batteries are electrode (cathode, anode), converting chemical energy to electrical energy and electrolyte which can allow Li ion and electron transportation. In general, anode was produced by thermal evaporation or pulsed laser deposition (PLD) and also cathode-electrolyte produced by RF sputtering in Li-ion batteries. Thin film electrodes are binder free, they reduce the internal resistance of the cell and charged/discharged time of them less than one minute compared to bulk counterparts. An ideal electrode must be a)low cost, density and atomic weight of components, b) chemically stable, c)fast lithiation/delithiation process, d) high (cathode) and low (anode) standard redox potential), e) permission of crystal structure for lithium inclusion, f) high charge density and g) high degree of reversibility [34]. Although imperfections in crystal structure for amorphous thin films could hinder Li ion diffusion compared their crystalline counterparts. On the other hand, the most interesting and attractive part of battery is solid thin film electrolyte since 1970 [35]. They are electrochemically compatible with thin film electrodes and seperators, prevent possible short circuits and have no inherent risk of safety and compatible with high temperature.

5.1. Thin Film Cathode

Thin film cathodes have a key role with lower discharge potential in response to increase electric-capacity density compared to thin film anodes. Working of cathode materials have been examined under four main groups for almost forty years; i) layered, ii) spinel, iii) olivine and iv) tavorite. Layered structure (general form of LiMxOy, M:Co,Ni or Mn) allows excessively diffusion paths for Li^+ ions due to convenient of its crystal structure [36]. The traditionally used cobalt based layered $LiCoO_2$ (LCO) cathode has been replaced with new and alternative materials because of its toxicity, low diffusion rate and high price of cobalt. However, high delithiation voltage and stability of LCO could not be obtained with other cathode material types. An alternative for toxic and expensive $LiCoO_2$, spinel $LiMn_2O_4$ or spinel $LiNi_{0.5}Mn_{1.5}O$ (high voltage of ~4.7 V and theoretical specific capacity of 147 mA h g^{-1}) provides a 3D network for Li-ion diffusion, low cost, easy produce and environmentally friendliness [37,38]. However, spinel to cubic phase transition and e Jahn-Teller (JT-) distortion causes capacity retention. Another alternative in the battery market, olivine $LiMPO_4$ have been preferred due to low cost and more safety compared LCO cathodes [39]. Pulsed laser deposition (PLD), RF magnetron sputtering and electrostatic spray deposition techniques were used to prepare olivine $LiMPO_4$ (M: Ni, Mn, Fe or Co) and $Li_3M_2(PO_4)_3$ (M:V or Fe) thin films [40]. $Li_3M_2(PO_4)_3$ had higher energy density and 3D channels for Li^+ diffusion so improved rate capability was obtained which was explained by Wang et.al.[41]. According to our knowledge, there is no thin film form of tavorite ($LiFeSO_4F$) cathodes due to its low thermodynamically stable temperature is not proper for thin film growth conditions (500-900 °C) [42].

Although thin film intercalation cathodes come to a certain point in term of good cyclability, low capacity and long-term stability still are a great problem. If high voltage surpasses the voltage window of carbonate based electrolytes, two different situations occurs. Firstly, dissolution of metal (M)-component into the electrolyte causes capacity fading upon cycling. Secondly, side-reactions between the electrolyte and active electrode (especially metal ion compounds) may cause a decrease in the cyclability. Transformation between crystal structures changes stability of cathode material during the charge-discharge of insertion. Additionally, mechanical properties such as elastic modulus and hardness have an effect on the electrode performance because cracking or even fracture of electrode was observed under high tensile stress. In order to solve these problems different perspectives have been presented such as Li-rich materials, surface coating (metal oxides, C-based materials, SiO_2),

cationic doping with Al or Ag, cheap production technique using, derivates of intercalation cathodes, laser structuring processes, electrolyte additive and different stoichiometry choosing etc. [43].

5.2. Thin Film Anode

Anode operating voltage arrangement is so important in battery design after cathode-based studies to obtain high safety cells. Lithiation ability of anodes remarkably depends on their morphology, dimension, microstructure and crystallinity. Thin film anodes have been largely concerned in the last years due to their modified microstructure and suitable morphology regulation. Anode materials are generally categorized intercalation/de-intercalation materials, alloy/de-alloy materials and conversion materials in slurry forms. However, anode types are restricted such as Si, SnO_2, graphitic carbon and graphene in thin film forms due to failed production/battery performances of other thin film anodes and increasing anode-free studies. The basic problems are surface oxidation, Li dendrites growth with decreasing columbic efficiency, particle aggregation and un-stabilization of solid electrolyte interphase (SEI) which emerged with parasitic reactions at the interfaces [44]. Althogh these restrictions

C-based anodes (Li-C systems) acts as a buffer during the cycling and they supplies fast carrier transfer, as explained by Yao et.al. [45]. Graphitic carbon (LiC_6 for graphite) thin films have decreasing cycle performance and increasing relative peak area with increasing annealing temperature up to 700 °C, as explained by Nam et.al. [46]. Although graphene (LiC_3 for graphite) has high gravimetric capacity (960 mAh g^{-1}) still some disadvantages such as low initial Coulombic effciency, the degree of restacking of graphene sheets and synthesis steps are complex and expensive.

On the other hand, non-carbon anode provides volumetric performance due to their high gravimetric capacity and compact densities according to Andre et.al. [47]. Additionally, non-carbon materials have certain Li^+ diffusion pathway compared Li-C systems. The most interested and investigated thin film anode is Si with enormous volumetric capacity of 9744 mAh cm^{-3} and proper potentials for lithiation/delithiation of 0.02–0.6 V vs. Li/Li^+. However their poor electrical conductivity, high volume expansion, low Coulombic efficiency, oxophilic nature of Si and unstable solid-electrolyte interphase are restricted in its practical applications. Higher irreversible consumption of Li ions or expanding passivating layers appears with unstable Si-electrolyte interface. There are several silicides or intermetallic cmopounds ($Li_{12}Si_7$, $Li_{13}Si_4$, $Li_{15}Si_4$, $Li_{21}Si_5$ and etc.) which can be formed with ≥200 % upon

lithiation and this leading to an electrical contact loss between Si particles and current collector [48]. A lot of efforts were achieved by different purposes such as additives (vinylene carbonate (VC), fluoro-ethylene carbonate (FEC), trimethoxy methyl silane (TMMS), and succinic anhydride (SA)) for improving Si thin film cycle life and stabilizing SEI layer. Applying 3D structured current collectors is an effective strategy to overcome Si limitations. n-doped a-Si thin film on graphene coated nickel foam as anode active material was proposed by Mukanova et.al. [49]. Si/C composites, in where C as a buffer, were prevented the agglomeration of silicon particles and obtained a capacity retention of ~ 96% from 100th to 200th cycle, explained by Lee et.al. [50]. Sn-thin film anodes also so attractive especially last years due to its Li storage ability, high theoretical gravimetric capacity of 994 mAh/g and volumetric capacity of 7313 mAh/L. Li et. al. used Cu buffer inserted between the Cu foil and the Sn thin-film so cyclic performance of Sn-thin films was improved [51].

5.3. Thin Film Electrolyte

In the literature, there are a lot of electrolyte types such as aqueous, non-aqueous, fluorinated ethers and solid state materials (ionic liquids, ionogels and thin films) [52]. Dendrite formation is related to plating-out reactions between lithium metal and liquid electrolytes. Additionally, ionic conductivity of liquid electrolytes depends on temperature, generally. Therefore, they have an impact on the tolerance of the cell. Conventional polymer-based and organic carbonate liquid electrolytes enhance the overall volume of battery and they have electrochemical in-stabilization, respectively. Additionally safety, durability, volatility, flammability and limited working temperatures of them are also serious problems. Unwanted and dangerous thermal runaway might be appears while battery was overcharged. Hence, they are not proper for high energy density systems.

On the other hand, solid state electrolytes especially thin film electrolytes are so interesting due to their superior operational safety and elimination of separator. Additionally, they are suited for high temperature condition due to ion movement depending on temperature in the thin film. They are generally categorized as oxides, phosphates and sulfides. However, solid electrolyte materials have low ionic conductivity at room temperature compared to typical liquid electrolytes. Adding a buffer layer is necessary between the cathode and the solid electrolyte to reduce interface problems. Additionally, binder free, durable in highly reductive/oxidative environments and wide electrochemical windows are expected in next generation electrolytes. Cathode or electrolyte doping are preferred to increase grain boundary transport. Physical vapor deposition, RF magnetron sputtering, ALD and sol-gel

synthesis were used to synthesis thin film electrolytes. Crystalline thin film electrolytes have 3-5 orders of magnitude low ionic conductivity and thereby low transport number compared to amorphous counterparts and glassy type electrolytes. Therefore, ionic conductivity enhancement research is continuing.

The most popular and unfortunately vulnerable phosphate-based lithium phosphorous oxynitride (LiPON) thin film has been widely investigated as solid-state thin-film electrolyte with its low ionic conductivity (10^{-6}–10^{-7} S/cm), high cyclability and large electrochemical stability window since discovered in 1990 [53]. It is known that oxide electrolytes have more stability in air and contact with lithium metal anode. Garnet-type cubic or tetragonal ceramic oxide-based $Li_7La_3Zr_2O_{12}$ (LLZO) is thermally and chemically stable against metallic lithium and have high ionic conductivity (>10^{-4} S/cm). Also, it was used as adding in electrolyte to improve ionic conductivity [54]. However, their sintering temperature is up to 1000 °C which has been shown to break thin films and lithium can react irreversibly with oxygen to form lithium oxide, Li_2O. Unlike typical garnet type $Li_7La_3Zr_2O_{12}$ (LLZO), Loho et.al. investigated $Li_5La_3Ta_2O_{12}$ films with their two order magnitude ionic conductivity [55]. According to Seo et.al., sulfide-based GeS_2 thin film electrolytes are so interesting in the last years compared traditional soft sulfide thin film electrolytes. Because their stability are strong in air and they have nearly two orders of magnitude higher than those of commercial LiPON thin-film electrolytes [56].

Low solid electrode/electrolyte interface resistance and optimizing grain boundaries are so important for improve rate capability of thin film Li-ion batteries. One option is coating on active material with solid electrolyte so it suppresses unwanted side reactions via inter-diffusion and lithium deficient layer. Additionally, physical and chemical properties of these interfaces as well as their mechanical properties must be detailed investigated [57].

6. Conclusion

Recently, Li-ion and other Li-based batteries are so attractive due to increasing demand of hybrid vehicles, electrical charge stations, medical devices and smart cards. Therefore, new architectures and alternative material-based Li-ion batteries have been frequently studied. Thin film Li-ion batteries are similar to conventional counterparts. In spite of this, arrangement thin film thickness and thereby particle size, surface morphology, new component/coating/anchoring materials, no leakage risk with solid electrolyte and understand

of interface electrochemistry improves substantially Li-based battery efficiency.

Transition from 2D to 3D thin film microbattery systems and then from 3D thin film microbattery systems to printed 3D thin film batteries represents a phenomena that is the need of high power density and simple production of batteries. In conventional 2D batteries, energy increase is limited by the film thickness and tentative Li pathway whereas 3D Li-ion microbatteries can realize short ion transport pathway, sufficient material storage, increasing rate performance and high mechanical strength with decreasing crack formations. However, volumetrically efficient package design, selection of active materials and electrochemical reactions of interfaces are still unresolved problems in 3D battery design. In addition, optimizing ionic and electronic current paths are so important in 3D electrode architecture with proper electrode locations, using flexible and printed batteries.

The thin film electrode and electrolyte components are the basic factors to limit of energy density of Li-ion batteries. In order to improve cathode performance Li-rich or high voltage cathodes using are so prevalent yet cathode efficiency still can limited by high capacity. The critical issue is risk of Li dendrite growth which reduced by employing thin film battery architecture replacing with Li-metal deposition. In spite of their high volume expansion and thereby pulverization in active materials, there are many thin film anode studies which towards high lithiation/delithiation ability. On the other hand, thin film electrolytes have the potential to replace liquid electrolytes in Li-based batteries. A lot of efforts have been made to solve low ionic conductivity and large interface resistance of thin film electrodes in Li-ion thin film batteries. Interfaces between the layers are so important for long term cell performance due to solid electrolyte-electrode interfacial resistance has a severe effect on capacity losing.

As a result, there are still problems in each battery types (2D planar, 3D microbattery, flexible 3D or printed etc.) that must be addressed urgently. New approaches will bring together energy boost, utility and high rate performance from Li-ion thin film batteries such as advanced 4D batteries and hetero-atom incorporated C-based materials [59].

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