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Morphological Investigation of Li Thin Film Deposited on LiPON Solid Electrolyte and the Influence of Interlayers on It

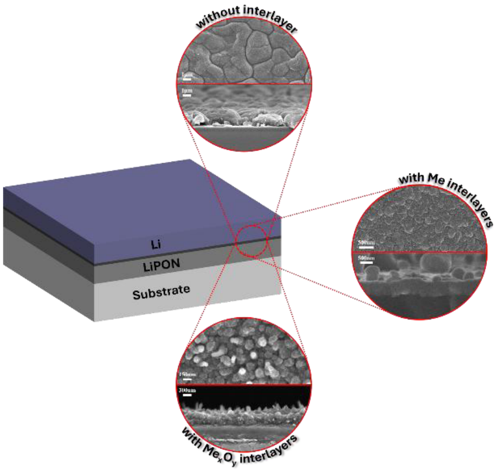
All-solid-state thin-film lithium metal batteries (ASSTFBs) hold great promise for next-generation energy storage due to their long cycle life, stability across a wide temperature range, and low self-discharge, making them ideal for applications in wearable devices, medical implants, and IoT systems. Achieving uniform lithium (Li) deposition on lithium phosphorus oxynitride (LiPON) solid electrolytes is a critical challenge for advancing ASSTFBs. This study evaluates the role of various interlayers in improving film uniformity and adhesion and compares thermal evaporation (TE) and magnetron sputtering (MS) methods for depositing Li films on LiPON. Initial TE trials revealed discontinuous, droplet-like Li particles with poor interconnection and adhesion on the LiPON surface. To address these issues, metallic interlayers (Sn, Al, Ag, Au, Pt) and metal oxides (ZnO, Al_2O_3) were explored. Among these, Pt demonstrated the most promising results, forming a lithophilic alloy that improved particle connectivity and interface uniformity. MS produced more consistent Li films compared to TE, attributed to its better-controlled deposition rate and reduced thermal effects. However, MS requires precautions due to Li's reactivity and potential system contamination. The findings emphasize the importance of interlayer selection and deposition method optimization in achieving dense, uniform Li films. This work contributes to the development of high-performance, reliable microbatteries for advanced energy storage applications. Future studies will focus on refining deposition parameters and evaluating electrochemical performance to further enhance battery efficiency and stability.

Keywords: lithium, LiPON, thin film, solid electrolyte, thermal evaporation, magnetron sputtering, all-solid-state lithium metal microbattery

Introduction

Lithium-ion batteries (LiBs) have become a leading energy storage technology, widely utilized in electric vehicles, power tools, and portable devices due to their high energy and power density. As the demand for microscale devices, such as medical apparatus, grows, advancements in LiBs have extended to energy storage microsystems using thin-film technology. Thin-film electrodes enable the reduction of inactive components, ensuring sufficient electrical conductivity, improved cycling stability, and enhanced power density, making them ideal for miniaturized applications [1–3].

Rechargeable lithium-metal batteries (LMBs), which use metallic lithium (Li) as an anode or operate as anode-free systems, have emerged as promising alternatives to conventional LiBs with graphite anodes. The advantages of LMBs include a high theoretical capacity (3860 mAh g^{-1}), low negative potential (–3.04 V), low density (0.59 g cm^{-3}), and high electrical conductivity, along with the potential to eliminate inactive components in the negative electrode [4–6]. However, challenges such as dendritic Li growth, safety risks due to short circuits, and the formation of dead Li layers resulting from side reactions have hindered their practical application.



The cycling performance of Li-metal anodes is highly dependent on the electrolyte. Solid electrolytes, particularly lithium phosphorus oxynitride (LiPON), offer advantages such as high ionic conductivity, chemical stability, and compatibility with thin-film systems. These properties enable the development of safer, longer-lasting, and more compact Li-ion microbatteries [7]. However, challenges persist at the Li-LiPON interface, including poor adhesion, high interfacial resistance, and the formation of dendrites, all of which need to be addressed to unlock the potential of LMBs for practical applications [8, 9].

Thermal evaporation (TE) is a common method for depositing Li thin films due to its simplicity and applicability in various industries. This process involves heating a source material under high vacuum until it sublimes, condensing onto a substrate as a thin film [10]. Despite its advantages, TE often results in nonuniform Li films with low surface coverage, posing challenges for achieving consistent morphology and adhesion.

A critical issue limiting the performance of solid-state LMBs is the lithiophobic nature of solid electrolytes like LiPON. This results in poor wettability, space charge layer formation, interfacial resistance, and dendritic growth. Enhancing lithiophilicity is essential for improving Li deposition and overall battery performance. Approaches to achieving better lithiophilicity include modifying surface energy, introducing alloying additives (e.g., Sn, In, Mg), or applying coatings like Al_2O_3, ZnO, Au, or Al, which improve physical contact and chemical compatibility between Li and the electrolyte [11–20].

In this study, we aimed to achieve uniform and consistent Li deposition on LiPON solid electrolytes using TE. To address the limitations of TE, we explored various interlayers, including metals (Ag, Au, Al, Sn, Pt) and metal oxides (Al2O3, ZnO), to improve lithiophilicity and adhesion. Additionally, magnetron sputtering (MS) was investigated as an alternative technique, which demonstrated superior uniformity and contact at the Li-LiPON interface without requiring interlayers.

Experimental

The deposition of Li was performed mainly by TE, utilizing a resistive heating technique involving high electric current and low voltage, in a COVAP Physical Vapor Deposition (PVD) chamber (Angstrom Engineering), maintaining a high vacuum of around 10^{-6} mbar, integrated with a glove box filled with argon (Ar) with H_2O concentrations below 0.1 ppm and O_2 levels below 0.1 ppm.

For the process of depositing a thin layer of lithium onto a silicon wafer, Li metal chips (99.9 %, MTI Corp.) were placed in a tantalum evaporation boat. For evaporation of metals, pure pieces of Ag, Au, Sn (Angstrom Engineering, 99.9 %) were placed on Al_2O_3 coated tungsten boat and Al pieces on graphite coated boat (Angstrom Engineering). The system, with a maximum power output of 2000 W, allocated approximately 12 % of this power for the evaporation of the Li metal, and 25–30 % for Al, Ag, Au, Sn metals. The deposition rate for all metals was approximately 1 Å s^{-1}.

The thickness of film was monitored using quartz crystal microbalance (QCM) sensors operating at 6 MHz frequencies and controlled by an SQC-310 controller (Inficon). This setup allowed for adjustments to deposition rate, additional heating settings, and the final film thickness. The substrate, mounted on a holder, rotated at a speed of 50 rpm, and a shutter was employed to protect the substrate until the desired deposition rate of 1Å s^{-1} was achieved. Once the required rate was reached, the shutter opened giving a start to the deposition. For all samples, the optimized thickness of 10 nm was chosen due to the quicker lithium diffusion [21].

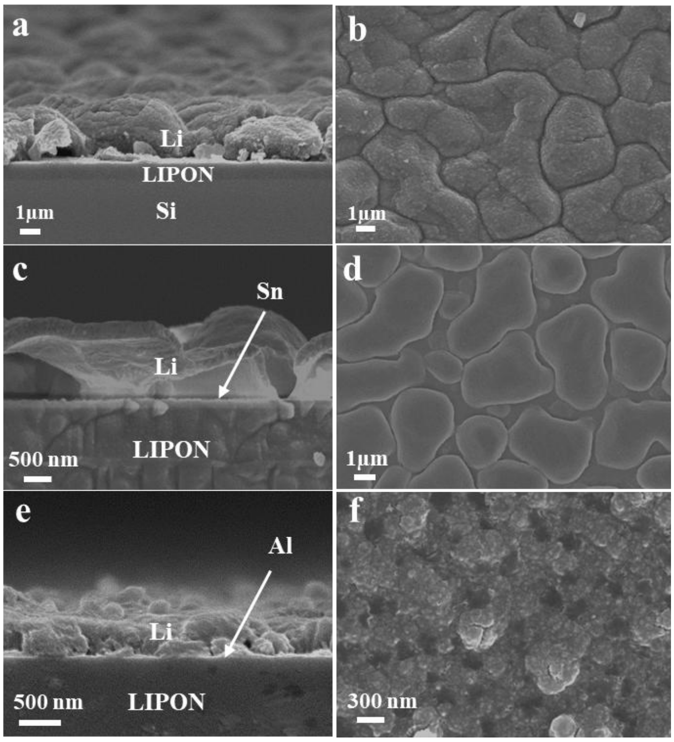
To deposit oxides, targets of Al_2O_3, ZnO (Kurt J. Lesker 99.99 %), Pt (Angstrom Engineering, 99.99 %) and Li (home-made) were used in a magnetron sputtering (MS) system (Nexdep, Angstrom Engineering). To prepare a Li target, 10–15 pieces of Li chips were melted in a 2-inch copper mold at 350 °C for 30–40 minutes, after which it was left to cool and harden. The whole process was carried out inside a glove box. The sputtering chamber was evacuated down to 2×10^{-6} mTorr by a turbo vacuum pump. Argon gas was introduced into the chamber, and pressure was balanced to 5 mTorr. The target was cleaned by a 10 min presputtering before the substrate shutter was opened to eliminate oxide layer and other contaminations on the target surface. The lithium depositing rate was calculated to be 0.39 Å s^{-1} by QCM sensor at a power of 1.78 W cm^{-2}.

To analyze the sample morphology, the ZEISS Crossbeam 540 model Scanning Electron Microscope (SEM) was used. The SEM images were acquired with an accelerating voltage of 3 kV and a variable working distance spanning from 3.5 to 4 mm.

Results and Discussion

Initially, passing all the optimization steps of thin-film electrodes and coming to the point of their integration into microcells, unexpected topological challenges with the formed Li film on LiPON solid were faced and it was decided to explore this phenomenon deeper. In Figure 1 *a*, *b*, the SEM images of the bare Li film thermally evaporated on the surface of LiPON can be seen, which demonstrates non-uniformly distributed, island-shaped lithium droplet-like particles on the electrolyte surface, lacking interconnection, potentially resulting in poor adhesion. The observed configuration may give rise to the formation of space charge layers between lithium and the electrolyte [22, 23]. This spatially discontinuous distribution of Li particles elevates concerns about the overall coherence and effectiveness of the electrode-electrolyte interface, emphasizing the importance of addressing adhesion issues for enhanced electrochemical performance in the studied microsystem.

The poor deposition of evaporated lithium onto LiPON can be attributed to its compositional complexity, morphology and the deposition parameters. LiPON surfaces may have different chemical compositions and surface energies, which can affect the adhesion and nucleation of evaporated lithium atoms. The presence of phosphorus, oxygen, and nitrogen species on the LiPON surface may interact unfavorably with lithium atoms, leading to non-uniform deposition. The surface morphology of LiPON may also not provide suitable sites for the nucleation and growth of lithium atoms. Irregularities or roughness on the LiPON surface can hinder the formation of a continuous and uniform lithium film. However, from all the SEM images (Fig. 1), it can be seen that the sputtered LiPON is well deposited and uniform. Next, the electrochemical properties, such as ion conductivity and stability, may not be compatible with the deposition of evaporated Li. Chemical reactions or diffusion limitations within the LiPON material may inhibit the deposition process. Finally, the temperature and pressure conditions during the deposition process can significantly influence the behavior of evaporated Li and its interaction with LiPON [24]. Here, we should mention that the conditions were optimized to achieve the lowest possible deposition rate since at higher one, the morphology was even worse.



a, b — Li-LiPON; *c, d* — Li-Sn-LiPON; *e, f* — Li-Al-LiPON

Figure 1. The cross-sectional and top-view SEM images of the samples

With the goal to improve the uniformity of the evaporated Li onto LiPON interface, we explored the application of various metals, including Sn, Al, Ag, Pt, and Au, as well as some metal oxides like Al_2O_3 and ZnO as intermediary layers between Li and the LiPON solid electrolyte.

Firstly, as an interlayer, Sn metal was investigated due to the better adhesion, faster Li ions diffusion as well as immediate alloying reaction with Li, which is supposed to result in the dense Li-Sn interlayer formation [25–27]. A 10 nm thick Sn film was evaporated on the LiPON substrate. The obtained results (Fig. 1 *c*, *d*) exhibited a lack of uniformity, showing the surface with an island-shaped structure that lacked proper interconnection between particles, as illustrated in Figure 1 *d*. Furthermore, a detailed examination of the cross-sectional image (Fig. 1 *c*) revealed the presence of noticeable voids within the particles. These observations suggest the existing challenges in achieving a homogeneous structure and effective interparticle contact, emphasizing the complexity involved in optimizing the electrode-electrolyte interface for improved performance in Li-Sn-LiPON system.

Similarly, hoping to get ionically conductive Li-Al alloy that serves as an interfacial layer when Al is added [28], Al was evaporated on LiPON. The resulting structure is prominently illustrated in Figure 1 *e, f*. Notably, the Li-Al-LiPON samples exhibit a denser configuration in contrast to those with above-mentioned Sn. A discernible improvement is observed in the connectivity of particles, indicating a more cohesive arrangement without the presence of large clusters. The enhanced connectivity of particles is indicative of a potentially improved electrode-electrolyte interface. It may promote efficient ion transport and minimize impedance at the interface. However, unevenly distributed bumps and cracks are still visible on the surface of the thin lithium film.

The subsequent metal, Ag, has the lowest electrical contact resistance and the maximum electrical conductivity when compared to other metals. This can prevent the production of lithium dendrites and encourages more uniform plating of lithium ions [29]. From Figure 2 *a, b*, the examination of the images reveals a surface characterized by enhanced smoothness and a more uniform distribution of the deposited layer. Additionally, there is an observable reduction in the size of the particles compared to previous instances with other metals. The distinct improvements in surface smoothness and homogeneity, coupled with the reduction in particle size, highlight the favorable impact of Ag as an intermediary layer in the Li and LiPON interface. These characteristics are indicative of a more controlled and refined deposition process, underscoring the potential of silver to contribute to the development of a highly uniform and well-structured electrode-electrolyte interface.

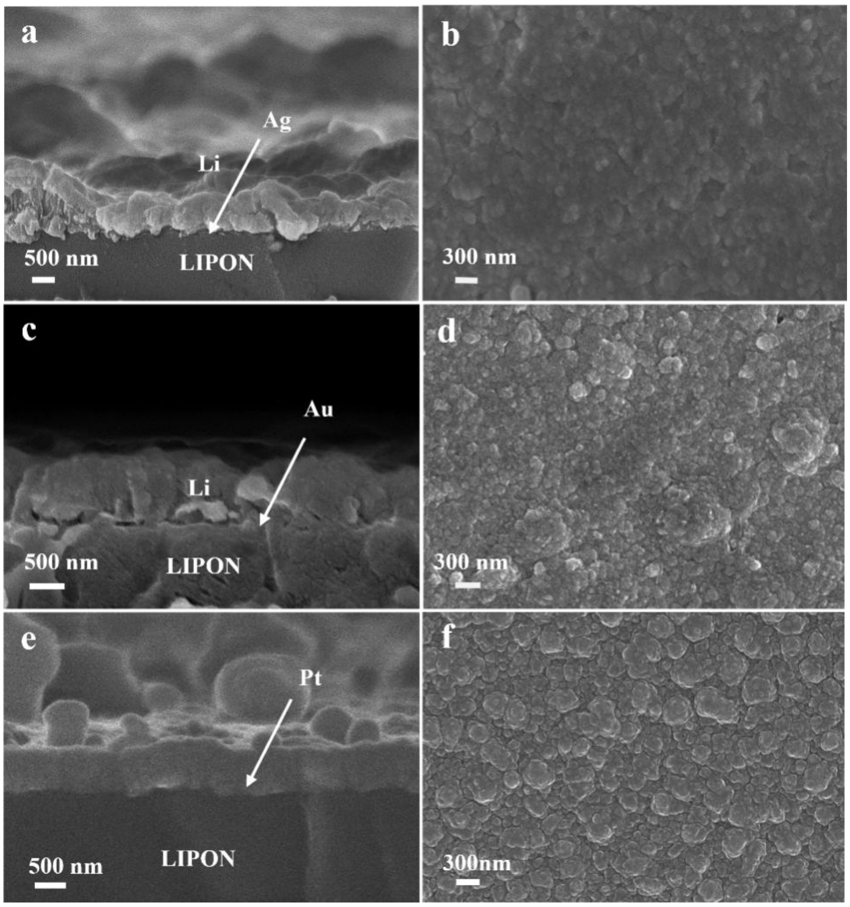


Figure 2. The cross-sectional and top-view SEM images
of the samples with Ag (*a, b*), Au (*c, d*), Pt (*e, f*) interlayers

Next, the Au was tested, as it has been already reported for maintaining a stable Li deposition [30]. The results obtained from this investigation (Fig. 2 *c, d*) indicate that the application of gold as an intermediary layer also yielded notably superior characteristics. A discernible enhancement in the wettability of Li was observed, accompanied by a more even and flattened surface in comparison to preceding samples. The superior characteristics exhibited by the Au-deposited samples suggest a positive influence on the overall homogeneity of the Li layer. The improved wettability is particularly noteworthy, as it underscores the effectiveness of gold as an intermediary material in facilitating a more uniform and well-adhered Li film evaporated on the LiPON solid electrolyte.

Consequently, Pt was incorporated as the interlayer to assess its potential impact (Fig. 2 *e, f*) on morphology of evaporated Li film. The desired uniformity in the deposition process was achieved by this metal since it might alloy with Li metal in electrochemical systems [31]. As it can be seen from the cross-sectional image (Fig. 2 *e*), the interface of the Li on LiPON is more improved, particles are well connected and form dense thin film with the uniform thickness. The additional particles can be noted on the top surface of Li which might be attributed to non-uniformly deposited Li on top of alloy layer.

Pt and Li have Gibbs free energies that are less than zero, which means that they could combine to produce $LiPt_x$ alloy. The creation of a three-dimensional framework also facilitates the plating and stripping of Li ions and keeps the volume of Li metal from expansion. By forming a $LiPt_x$ alloy, the 10 nm thin Pt the surface of electrolyte changes from lithiophobic to lithiophilic. In literature, for the garnet surface, the $LiPt_x$ alloy layer increases the wettability of the Li–electrolyte contact, favorable Li transport across the interface [32].

Further, the impact of incorporating an inorganic metal oxide interlayer was systematically investigated. The ZnO layer can effectively lower the interface impedance and enhance solid electrolyte compatibility with metallic Li [33]. To achieve this, a 10 nm thick ZnO layer was meticulously deposited through RF MS, strategically positioned between the lithium phosphorus oxynitride (LIPON) and lithium (Li) layers. The outcome of this investigation (Fig. 3 *a, b*) revealed notable enhancements, particularly in the uniformity of Li deposition, accompanied by a discernible increase in particle density.

The addition of the ZnO layer yielded a more homogeneous deposition of lithium, evident in the observed uniformity across the substrate. The resultant particles exhibited a denser configuration, which is a favorable characteristic for enhancing the overall performance of the battery system. However, a closer examination of cross-sectional images unveiled the formation of knots on the surface. This observation suggests the possibility of side reactions occurring during the deposition process, impacting the uniformity of the film.

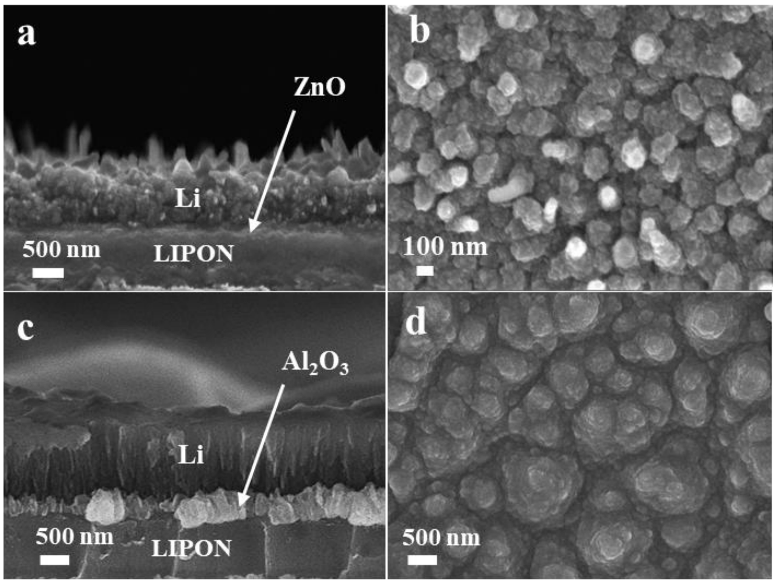


Figure 3. The cross-sectional and top-view SEM images of the samples with ZnO (*a, b*), Al_2O_3 (*c, d*) interlayers

Another metal oxide implemented as an interface layer was Al_2O_3, which was previously applied with ionic liquid electrolyte and was reported for better stability and lithiophilicity [34]. As a result of the investigation (Fig. 3 *c, d*), the homogeneous deposition of Li was achieved. As it can be seen from the SEM image, Li on Al-LiPON formed the dense structure with the interconnected particles. This can be explained by the good adhesive properties and chemical inactivity of alumina towards different materials, including Li. Some roughness on the Li thin film surface can be observed; however, it is within acceptable limits.

The advantage of TE compared to MS is its high deposition rate. But as our above-mentioned experimental results have shown, the evaporated Li films are not always uniform, which are very crucial for mcrobattery. To compare TE and MS, the Li thin films were sputtered on LiPON surface using MS. Figure 4 *a, b* shows the top and cross-sectional SEM image of the obtained Li thin film. As can be seen, the surface of the resulting film is uniform as usual for other MS materials, which is an advantage of the magnetron.

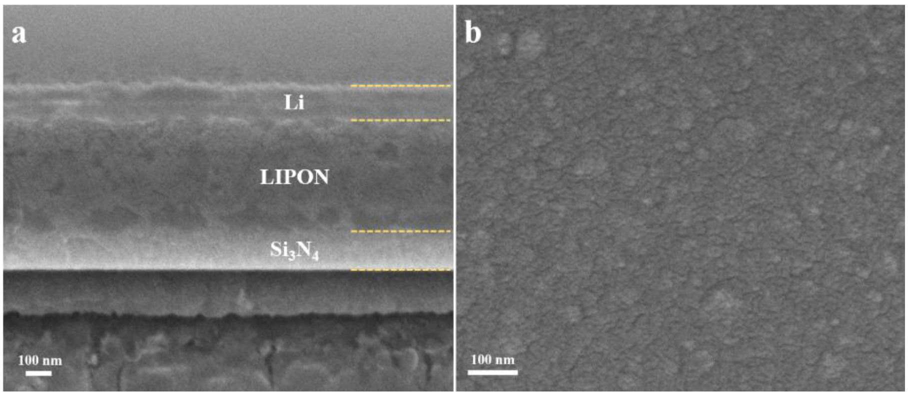


Figure 4. The cross-sectional (*a*) and top-view (*b*) SEM images of Li-LiPON sample

This can be probably explained by the better-controlled deposition rate of MS. The rate fluctuates extensively during TE. Even though the thickness of Li is measured after stabilization, the evaporation rate after several tens of minutes slowly decreases from 1–1.5 Å s^{-1} to 0.45 Å s^{-1} [35]. Among the other possible reasons of uniform morphology by MS are the better directionality of deposition which is controlled using magnetic fields, ensuring that Li atoms or ions are deposited evenly onto the substrate, and reduced heating effects on substrate, minimizing thermal effects and promoting uniformity.

Magnetron sputtering systems are more commonly used equipment, but precautions must be taken when sputtering Li due to its tendency to form deposits within the work chamber and react with other system components such as targets and walls. This can degrade system performance and lifespan, causing electrical shorts, increased electrical resistance, and potential plasma instabilities due to Li's unique properties, including high reactivity and low ionization potential. In contrast, evaporation of Li poses a lower risk of damage because the process occurs in a deep vacuum with negligibly low gas impurities, minimizing the potential for reactions with Li.

The results obtained offer a comprehensive investigation into the challenges faced during the integration of thin-film electrodes into microcells, particularly concerning the deposition of Li onto LiPON solid electrolytes using TE. This study highlights the intricate influence of interlayers on the lithium deposition process, stressing the need for a thorough understanding of both the beneficial and potentially adverse effects of various materials. Addressing the non-uniform distribution of Li particles on the LiPON surface can be achieved by switching to the MS technique with proper handling and equipment maintenance.

Conclusion

This study highlights key challenges and solutions for lithium (Li) deposition on LiPON solid electrolytes in all-solid-state thin-film lithium microbatteries. Initial thermal evaporation (TE) of Li produced discontinuous, droplet-like particles on LiPON, resulting in poor adhesion. Interlayers of Sn, Al, Ag, Au, and Pt were evaluated to improve uniformity, with Pt achieving the best results due to the formation of a lithophilic alloy that enhanced particle connectivity and adhesion. Metal oxides like ZnO and Al_2O_3 also improved Li film density, though minor surface irregularities remained.

Magnetron sputtering (MS) provided a more consistent Li film than TE, benefiting from controlled deposition and reduced thermal effects. These findings underline the importance of selecting interlayers and deposition methods carefully to optimize Li films for microbatteries. Further refinement of these parameters will support the development of high-performance, stable energy storage for applications from portable electronics to electric vehicles.

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LiPON қатты электролитіне тұндырылған жұқа литий пленкасын және оған аралық қабаттардың әсерін морфологиялық зерттеу

Толық қатты күйдегі жұқа пленкалы литий аккумуляторлары (ТҚЖПЛА) ұзақ қызмет ету мерзіміне, әртүрлі температурадағы тұрақтылыққа және өзін-өзі разрядтаудың төмен деңгейіне байланысты энергия сақтау құрылғыларының келесі буыны үшін үлкен әлеуетке ие. Бұл оларды киюге болатын құрылғыларда, имплантацияланатын аспаптарда және интернет заттары жүйелерінде қолдануға өте ыңғайлы етеді. Алайда, металл литий мен LiPON сияқты қатты электролит арасындағы тұрақты интерфейсті құру үлкен қиындық тудырады. Себебі LiPON-ның төмен литийфильділігі қарсылықты арттырып, иондардың тиімді тасымалдануын тежейді. Осы зерттеу барысында литийдің біркелкі түзілуін жақсарту мақсатында LiPON бетінің литийфильділігін оксидтік және металл аралық қабаттар арқылы арттыру қарастырылды. Толық СЭМ-талдау нәтижесінде Pt және Au металдары литийдің біркелкі және жақсы байланысуын қамтамасыз ететін үйлесімділіктің жоғары екенін көрсетті, ал ZnO және Al_2O_3 оксидтері тұндыру консистенциясын жақсартты. Бұл нәтижелер ТҚЖПЛА жүйелерінде фаза аралық кедергілерді төмендету және литийдің біркелкі түзілуін жақсарту мүмкіндігін көрсетіп, қатты денелі микробатареяларды кеңейтілген қолдануға жол ашады.

Кілт сөздер: литий, LiPON, жұқа пленка, қатты электролит, термиялық булану, магнетронды бүрку, толық қатты күйдегі жұқа пленкалы литий аккумуляторлары (ТҚЖПЛА).

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Морфологическое исследование тонкой пленки лития, осажденной на твердый электролит LiPON, и влияние промежуточных слоев

Полностью твердотельные тонкопленочные литиевые аккумуляторы (ПТТЛА) обладают большим потенциалом для следующего поколения накопителей энергии благодаря длительному сроку службы, стабильности при различных температурах и низкому уровню саморазряда, что делает их идеальными для применения в носимых устройствах, имплантируемых приборах и системах интернет-вещей. Однако создание стабильного интерфейса между металлическим литием и твердым электролитом, таким как фосфороксинитрид лития (LiPON), представляет значительные трудности, связанные с его низкой литиефильностью. Это увеличивает сопротивление и препятствует эффективному переносу ионов. В данном исследовании изучено улучшение литиефильности поверхности LiPON с помощью оксидных и металлических промежуточных слоев, направленное на повышение равномерности осаждения лития. Детальный СЭМ-анализ показал, что металлы, такие как Pt и Au, обладают высокой совместимостью, способствуя более равномерному и прочному осаждению лития, в то время как ZnO и Al_2O_3 обеспечивают улучшенную консистентность осаждения. Полученные результаты демонстрируют возможность снижения межфазного сопротивления и повышения равномерности осаждения лития в ПТТЛА, что открывает путь для расширенного применения твердотельных микробатарей.

Ключевые слова: литий, фосфороксинитрид лития (LiPON), тонкая пленка, твердый электролит, термическое испарение, магнетронное распыление, полностью твердотельные тонкопленочные литиевые аккумуляторы (ПТТЛА).

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