Artificial protective coatings for lithium metal anode to improve its stability

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The use of lithium metal as an anode in lithium-metal batteries is desired due to its high capacity and highly negative potential but is still not achieved due to the high activity and consequent chemical and electrochemical instability of this metal. On contact with the electrolyte, a film (SEI) is formed on the lithium surface consisting of the electrolyte decomposition products. Typically, this film has a heterogeneous structure, making it unstable and it cracks during cycling, which leads to lithium local deposition in the form of outgrowths – dendrites. A short circuit can occur when the dendrites grow to the cathode, followed by a possible battery fire. To solve this problem, it was proposed to coat lithium anodes with artificial SEI with the desired properties: homogeneous structure, high ionic and low electronic conductivity, and mechanical and chemical stability. The main methods for applying such coatings are dipping, dripping, doctor blade smearing, chemical or electrochemical reaction with lithium, and techniques such as magnetron sputtering, atomic and molecular layer deposition, and plasma activation. In this review examples of artificial protective coatings of different nature on lithium, their structure and functional features are considered. The reasons for their enhancement of lithium-metal anode operation stability and the characteristics obtained as a result of anode protection by these films are also indicated. At comparison of various approaches to creation of artificial SEI the methodological problem on an estimation of their efficiency is revealed and the decision variant is offered.

Keywords: lithium metal anode; solid electrolyte interphase; artificial protective coating; lithium metal batteries.

Литий металл анодының тұрақтылығын жақсарту үшін жасанды қорғаныс жабындары

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Литий металын литий-металл батареяларында анод ретінде пайдалану оның жоғары сыйымдылығы мен жоғары теріс потенциалына байланысты өте тартымды, бірақ бұл металдың жоғары белсенділігі мен соның салдарынан химиялық және электрохимиялық тұрақсыздығына байланысты әлі толық қол жеткізілген жоқ. Электролитпен жанасқанда литий бетінде электролиттің ыдырау өнімдерінен тұратын қабықша (SEI) түзіледі. Әдетте, бұл пленка гетерогенді құрылымға ие, бұл оны тұрақсыз етеді және цикл кезінде ол жарылып кетеді, бұл процестер литийдің жергілікті тұнуына әкеледі – дендриттер түзіледі. Дендриттер катодқа дейін өскен кезде қысқа тұйықталу орын алуы мүмкін, содан кейін батареяның өртенуі мүмкін. Бұл мәселені шешу үшін литий анодтарын қажетті қасиеттері бар жасанды SEI-мен қаптау ұсынылды: біркелкі құрылым, жоғары иондық және төмен электронды өткізгіштік, механикалық және химиялық тұрақтылық. Мұндай жабындарды қолданудың негізгі әдістері батыру, тамшылату, пышақпен жағу арқылы қаптау, литиймен химиялық немесе электрохимиялық реакция, сондай-ақ магнетронды шашырату, атомдық және молекулалық қабаттарды тұндыру және плазманы белсендіру сияқты әдістер болып табылады. Бұл шолуда литийге әртүрлі сипаттағы жасанды қорғаныс жабындарының мысалдары, олардың құрылымы мен функционалдық ерекшеліктері қарастырылады. Сондай-ақ литий металды анодтың тұрақтылығын арттыру себептері көрсетілген және анодты осы қабықшалармен қорғау нәтижесінде алынған сипаттамалар келтірілген. Жасанды SEI құрудың әртүрлі тәсілдерін салыстыру кезінде олардың тиімділігін бағалаудағы әдістемелік мәселе анықталды және оны шешу жолы ұсынылды.

Түйін сөздер: литий металды анод; қатты электролит интерфазасы; жасанды қорғаныс жабыны; литий металл батареялары.

Искусственные защитные покрытия для литий-металлического анода для повышения его стабильности

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Использование металлического лития в качестве анода в литий-металлических батареях очень привлекательно ввиду его высокой емкости и высоко отрицательного потенциала, однако все еще не достигнуто из-за высокой активности и, как следствие, химической и электрохимической нестабильности данного металла. При контакте с электролитом на поверхности лития образуется пленка (SEI), состоящая из продуктов разложения электролита. Как правило, данная пленка имеет неоднородную структуру, что делает ее нестабильной и в ходе циклирования она растрескивается, что приводит к локальному осаждению лития в виде отростков – дендритов. Когда дендриты дорастают до катода, может произойти короткое замыкание с последующим возможным возгоранием аккумулятора. Для решения данной проблемы было предложено покрывать литиевые аноды искусственными SEI с желаемыми свойствами: однородной структурой, высокой ионной и низкой электронной проводимостью, механической и химической стабильностью. Основными способами нанесения таких покрытий являются погружение, капание, намазка с помощью ракельного ножа, химическая или электрохимическая реакция с литием, а также такие методы, как магнетронное напыление, атомно- и молекулярно-слоевое осаждение и плазменная активация. В данном обзоре рассмотрены примеры искусственных защитных покрытий различной природы на литии, их структура и функциональные особенности. Также указаны причины повышения ими стабильности работы литий-металлического анода и приведены характеристики, полученные в результате защиты анода данными пленками. При сравнении различных подходов к созданию искусственных SEI выявлена методологическая проблема по оценке их эффективности и предложен вариант решения.

Ключевые слова: литий-металлический анод; межфаза твердого электролита; искусственное защитное покрытие; литий-металлические батареи.

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Review

Artificial protective coatings for lithium metal anode to improve its stability

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1. Introduction

The most desirable but still unrealised achievement in the field of chemical current sources is the use of lithium metal as an anode in lithium-ion batteries. The main reason for the attractiveness of this metal is its exceptionally high capacity, dozens of times higher than the commonly used graphite, as well as the lithium RedOx potential (-3.04 V vs SHE), the most negative among metals.

One of the main obstacles to the commercialisation of lithium metal batteries (LMB) is the chemical and electrochemical instability of the electrolyte in the presence of metallic lithium. Chemical instability refers to the chemical interaction of lithium with the electrolyte (dissolved salt and solvent), while electrochemical instability refers to the chemical interaction under the influence of an electric field. As a result of chemical interaction between lithium and electrolyte, a film consisting of insoluble products of interaction (the so-called Solid Electrolyte Interphase (SEI)) is formed on the surface of the lithium, which slows down the rate of chemical process, reducing it to almost zero. After assembling the cell with metallic lithium, injection of electrolyte into the cell and electrochemical polarisation of the anode (metallic lithium), electrochemical reduction of electrolyte takes place with formation of additional interphase layer to the already existing (chemically obtained) one. The structure, conductivity, stability and elasticity of this layer strongly depend on the electrolyte composition, temperature and on the anode polarisation rate. Ideally, the resulting film should block the access of fresh electrolyte portions to the electrode surface, be electron non-conductive (dielectric) to prevent electrolyte decomposition on the surface of the film, but allow lithium ions to pass through and be reduced/oxidised. In the real system, due to inhomogeneity and stretching-compression during repeated oxidation/reduction of Li (cycling), the film structure is distorted and the process of metal deposition occurs on the cracks, which leads to the formation of protrusions of metal nuclei that can grow perpendicularly to the electrode surface and form so-called dendrites, which can lead to short circuits and related consequences.

Due to the ongoing interest in this problem, many studies have been conducted and many approaches have been applied in attempts to modify the inevitable SEI film in order to give it the properties necessary to obtain a reliable and durable anode for a lithium-metal battery. One of the most effective is the creation of an artificial SEI film with optimal parameters on the lithium metal surface (Figure 1).

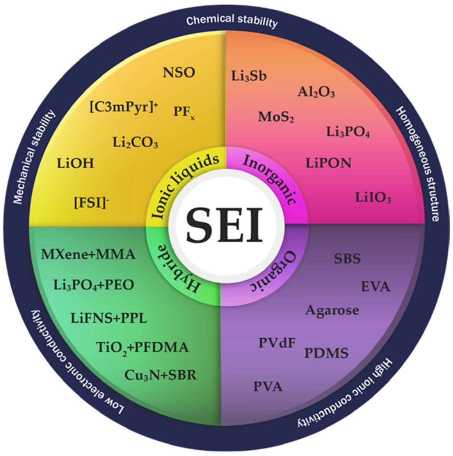

Figure 1 – Artificial protective SEIs for the lithium metal anode

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A set of these parameters required for the interfacial film has been identified by numerous and long-term studies [1-4]: 1) mechanical, chemical and electrochemical stability; 2) moderate thickness (too thin film will not provide sufficient surface protection, while too thick film will create excessive resistance and deteriorate the electrode characteristics [2]); 3) high ionic conductivity by lithium ions (for their supply to the anode surface for Li reduction/oxidation processes); 4) electronic insulation - dielectric (to avoid lithium recovery on the SEI film surface); 5) hydrophobicity (prevention of water contact with the electrode to enable its use in aqueous systems and protection against trace amounts of water in organic electrolytes); 6) elasticity and flexibility (for fast and qualitative adaptation of the protective layer to changes in the volume of the anode material during Li deposition/dissolution); 7) ability to self-healing in case of damage (this property is more often exhibited by artificially formed SEI in electrolytes with certain additives); 8) homogeneity of the structure, which also contributes to the enhancement of all types of stability due to the uniformity of properties over the entire area of the coating; 9) simplicity and relatively low cost of obtaining (this refers both to the cost of reagents and the method used for obtaining and applying).

To create SEI films possessing a number of the above properties, there are many approaches based on their artificial formation by chemical reactions of lithium metal with certain reagents (before immersion to the electrolyte solution or during reaction in the electrolyte) or by physical methods of application (atomic layer deposition (ALD), sputtering, smearing). In this review, the most novel methods for obtaining artificial films at the time of this article are considered, structured into groups and their applicability and prospects are critically evaluated.

2. Basic concepts of SEI

2.1 Formation, composition and structure of SEI: standard and artificial

Standard SEI is formed naturally on the anode surface due to reactions between metallic lithium and electrolyte components [5]. It plays a key role in the stabilisation of the anode surface and the protection against further electrolyte decomposition and anode damage. The structure of the standard SEI consists of electrolyte decomposition products with different chemical nature, physical properties and functional value. In this case, the structure can be either mosaic, with chaotic arrangement of sections of different composition, or layered. In the structure of the second type two layers can be distinguished: internal inorganic and external organic layers. The inner layer contains mainly inorganic compounds - oxides, hydroxides and carbonates of lithium, formed as a result of direct interaction of metallic lithium with the components of the electrolyte. The outer layer is represented by organic compounds obtained as a result of electrochemical decomposition of organic solvents [6].

The nature of the electrolyte has a significant influence on the chemical composition of the SEI film. For example, when the fresh lithium surface was treated with different solvent vapours, it was found that esters such as tetrahydrofuran and 1,3-dioxolane react with lithium to form the corresponding polyester film, whereas in carbonate solvents such as dimethyl carbonate, diethyl carbonate and propylene carbonate, the composition of the SEI film includes $LiOCO_2R$ and LiR (where R is an alkyl radical) [7].

The naturally formed SEI layer can be porous and unstable, resulting in the formation of cracks and defects that can degrade battery performance [5]. Dendrites grow through such cracks leading to short circuits. In addition, part of the dendrites can break off from the anode surface, which leads to the formation of ‘dead’, i.e. electrochemically inactive, lithium (Figure 2) [6].

Therefore, the scientific world is extremely interested in artificially creating SEI films that have a set of characteristics, both chemical and physical, that would provide the lithium metal anode with stable protection. Artificial SEI is created intentionally using a variety of materials and methods. This can be achieved through the pre-coating of a protective coating on the anode or by adding special additives to the electrolyte that form a stable SEI [8]. Artificial SEI usually has a more homogeneous and controlled structure compared to standard SEI. It consists of one or more layers with carefully selected properties to maximise stability and efficiency [9]. This layer is less porous and has higher mechanical strength, which reduces the risk of cracks and defects.

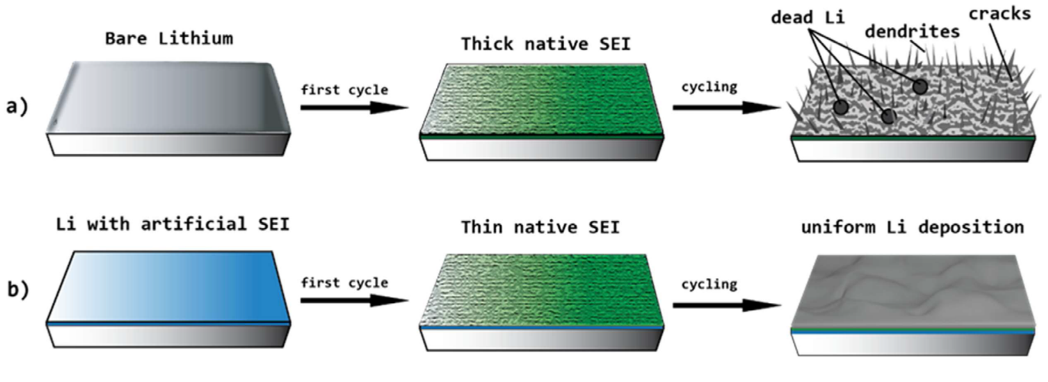

Figure 2 – Schematic diagram of the cycling of bare (a) and artificial protective film-covered (b) lithium metal anode

2.2 Methods of artificial SEI formation on lithium

The development of an artificial SEI layer with high ionic conductivity, electrical insulation and good mechanical strength is crucial to improve the stability of lithium metal anodes, as this layer is able to prevent the formation of dendrites, ensuring the long-term operation of a lithium metal battery.

At present, there are various methods of producing and/or application of artificial films of interfacial electrolyte. The simplest and least expensive method is coating by drying a solution or suspension on the lithium surface in a glove box with an inert atmosphere. In this case, the main methods of application of the required material are three: dripping [10,11], immersion [12-21] and smearing [22-27]. In this case, the least uniform coatings are obtained by dripping, because a drop can dry unevenly over the area. A more uniform coating is achieved by immersing the lithium in the solution, but it is necessary to ensure that the entire working surface is wetted. The most uniformity can be achieved by applying the slurry with a doctor blade, which is also one of the main methods for applying electrode materials for batteries as it is one of the most reliable. It is also worth mentioning the possibility of improving uniformity in drip coating by rotating the electrode (Spin coating) on a special machine, which is installed in a glove box with an inert atmosphere, at a certain (optimal for each material) speed until complete drying. The choice of method is also significantly influenced by the consistency of the material to be applied: viscous polymer materials are preferably applied by smearing, whereas liquid materials are optimally applied by dripping or dipping.

Due to the high activity of metallic lithium, the creation of protective coatings by direct reaction of lithium with the corresponding reagent, liquid or gaseous, deserves attention [28-37]. The resulting film is thin and homogeneous, which is an undoubted advantage, considering the rather low costs of this approach. Chemical vapour deposition also belongs to this method of coating production [38-46]. Another variation of this approach is the polymerisation of the film on the surface from a monomer solution [47-51].

The electrochemical deposition method also allows very thin coatings to be obtained, and by varying the electrolyte composition and deposition conditions, the resulting film can be optimised to provide the required properties [52,53].

More expensive methods of protective coatings include magnetron sputtering [54-58], atomic and molecular layer deposition [59-63] and plasma activation [64]. They require special equipment as well as a deep vacuum system. On the other hand, the coatings obtained by these methods are perfectly uniform and their thickness is clearly controlled by the duration or number of cycles depending on the method.

3. Types of protective artificial coatings on lithium

3.1 Inorganic coatings

3.1.1 Alloys

The use of alloys of the surface layer of lithium with various metals is a rather effective method of anode protection. Basically, such alloys are obtained either by the exchange reaction of metallic lithium with halides of the desired metals followed by mixing of the resulting pure metal with the underlying lithium layer [12,13], by immersion of the lithium substrate in liquid metal [14], or by magnetron sputtering of the desired metal [54] on the lithium surface.

For example, the alloy of antimony with lithium in various ratios was obtained by soaking the pure surface of metallic lithium in antimony fluoride solution [12]. In this case, the SEI protective layer consisted of a mixture of lithium fluoride and lithium-antimony alloy. Due to the low diffusion energy and strong adsorption of lithium to the obtained Li_3Sb alloy, Li^+ ions are rapidly transported to the lithium surface through the SEI layer and concentrated there. The obtained electrode demonstrated high cycling stability in a symmetric (Li vs Li) cell, 1100 h at a current density of 2 mA/cm^2, as well as operation in a lithium-sulfur battery for 60 cycles with an initial capacity of 325 W h/kg (1034.2 mAh/g).

A similar approach, but with chlorides, has been applied to alloys of lithium simultaneously with a number of metals including indium, zinc, bismuth and arsenic [13]. It was determined that lithium deposition occurs through the electron isolating surface layer of LiCl that forms over the alloy, with further diffusion into the alloy layer with high ionic conductivity, allowing rapid ionic transport of lithium and suppressing dendrite growth. Batteries based on the alloy-modified lithium anode and $Li_4Ti_5O_{12}$ cathode exhibited a substantial stability of 1500 cycles at a current density of 2 mA/cm^2 with an initial capacity of about 160 mAh/g and showed approximately the same operating stability in a symmetrical lithium cell of more than 1000 hours [13].

By immersing metallic lithium in an alloy of gallium and zinc followed by exposure to air, a 10-nm layer of gallium oxide was obtained, successfully protecting the lithium anode from oxygen and moisture, which is able to inhibit the growth of Li dendrites during cycling, as proved by the authors [14]. The electrode exhibited excellent stability in the Li-S cell with more than 500 cycles at currents of 0.5 and 1C with initial capacitances of 750 and 650 mAh/g, respectively, and Coulomb efficiency (CE) of 99.1%. The good electrochemical performance can be attributed to the additional enhancement of gallium oxide at the first cycles – the surface of the $GaO_x/Li_xLM/LiM$ film is lithiated to become Li_xGaO_y, which may contribute to the ionic conductivity of the coating.

A surface alloy of lithium with zinc was obtained by magnetron sputtering, and such parameters as the current applied to the Zn target, the distance between the substrate and the target, and the tilt of the substrate were varied [54]. Since low current (deposition rate) and relatively small distance to the substrate allow to obtain a more uniform and high-quality coating, a combination of current, distance and tilt parameters equal to 20 mA, 45 mm and 25°, respectively, was found to be optimal. The obtained anode in a $LiFePO_4$ cathode (LFP) cell showed a capacity of 92 mAh/g over 26 cycles at 1C current.

3.1.2 Aluminium oxide-based coatings

The use of aluminium oxide (Al_2O_3) as a protective coating on lithium metal is motivated by several important factors that make this material especially attractive for use in lithium-metal batteries: chemical stability, film hardness, possible ionic conductivity, stability over a wide temperature range, and compatibility with various application methods. In [22], the coating was applied as a suspension of Al_2O_3 nanoparticles in polyvinylidene fluoride (PVdF) solution in dimethylformamide with spin drying. In this case, a porous layer of optimal thickness was formed, simultaneously preventing side reactions of lithium with electrolyte components and not blocking the diffusion of lithium ions.In a lithium-sulfur battery, the protected anode showed a capacity of 800 mAh/g from the original 1200 mAh/g after 50 cycles, whereas the capacity of the battery with unmodified anode dropped to 600 mAh/g under identical conditions.

In another case, aluminium oxide nanopowder was mixed with polyimide as a binder and carbon black as a conductive additive, then applied to the surface of lithium foil with a doctor blade [23]. The resulting porous ceramic layer both protects the lithium from corrosion and provides space for its deposition. However, even in combination with the addition of fluoroethylene carbonate to the electrolyte, the capacity of the cell with the $LiFePO_4$ cathode decreased by cycle 50 to 34 mAh/g from the initial 112, although at the same time the unprotected anode showed a capacity of only 4.1 mAh/g after only 3 cycles.

An alternative method of Al_2O_3 film deposition was magnetron sputtering – the 20 nm thick coating provided layer-by-layer uniform deposition of lithium on the film, which allowed the symmetrical cell with solid electrolyte to operate stably for 660 hours at a current of 0.1 mA/cm^2 [55]. An even thinner coating layer of the same composition, only 2 nm, was deposited by atomic layer deposition (ALD) using trimethylaluminium and water as precursors [59]. The main advantages of this method of anode protection were the possibility of coating at temperatures below the melting point of lithium and the ability of aluminium oxide to create a stable film of $LiAlO_x$ composition with lithium ionic conductivity. The protected electrode worked stably at a current of 1 mA/cm^2 for more than 1200 cycles.

In another example, a thicker coating of 14 nm was deposited using this method, with plasma oxygen as the precursor instead of water [60]. The composition of the forming compound is slightly different – $Li_xAl_2O_3$, probably due to the use of a different precursor, but the film parameters remained generally unchanged: a lithium-sulfur cell with a protected anode after 100 cycles retained 87.5% of the capacity from the original 1200 mAh/g, whereas with unprotected – only 50%.

The authors of [61] studied the surface wettability of pure lithium and coated 4 nm aluminium oxide using the ALD method, and found that the coating increased the wettability for ether and carbonate electrolytes. This resulted in a more uniform SEI film during cycling, which enabled the Li-Cu system to operate for 180 cycles at a current density of 1 mA/cm^2 and a Coulombic efficiency close to 100%.

3.1.3 Coatings based on silicon compounds

Silicon is also used as an anode for lithium-ion batteries instead of graphite because it has a capacity comparable to lithium metal. However, its significant disadvantage is the dramatic increase in volume when lithium is intercalated, which leads to destruction of the silicon anode and deterioration of battery performance. At the same time, protective coatings for lithium anode based on this element are actively used and show good results. Thus, as a result of reaction of tetraethoxysilane with metallic lithium in the presence of trace amounts of water, a coating of Li_xSiO_y composition was formed, which contributed to the increase in the operating life of lithium-metal battery with LFP cathode – the capacity after 500 cycles remained at the level of 103 mAh/g, while the capacity of the cell with pure lithium decreased to this value after 300 cycles [28]. The increase in stability is explained by the presence of polar functional groups in the coating, which adsorb and redistribute lithium, preventing it from accumulating on the protrusions, thus preventing the growth of dendrites.

The solid-state batteries used a silicon and sulphur-based protective layer, also produced on lithium by a two-step reaction with lithium polysulphide and silicon tetrachloride:

$$Li + Li_2S_8 = Li@Li_2S_x \tag{1}$$

$$Li@Li_2S_x + SiCl_4 = Li@Li_xSiS_y \tag{2}$$

The protected anode showed stable operation for more than 2000 h at a current density of 0.5 mAh/cm^2 in a symmetric cell and more than 100 cycles in a cell with a $LiCoO_2$ cathode with a discharge capacity of 110 mAh/g, due to the combination of excellent ion transport through the protective layer to the anode and isolation of the anode itself from interaction with the electrolyte.

A combined protective film with a predominance of silicon constituents was obtained by soaking lithium in a 3-mercaptopropylmethyldimethoxysilane solution for 10 min, leading to the formation of reaction products such as LiF, Li_2S, Li_2CO_3, and Li_xSiO_y, which proved capable of providing stable cycling with the $LiFePO_4$ cathode at a rate of 0.5C for 150 cycles with a capacity of 100 mAh/g [15], which is attributed to the lithiophilicity of the mercapto groups and the mechanical strength of Li_xSiO_y.

An alternative, metallurgical method was used to create a lithiated anode consisting of a Li_2O matrix with Li_xSi nanoparticles [65], and 90 cycles of stable operation of a cell with an LFP cathode at a current of C/5 and a discharge capacity of 120 mAh/g were achieved. An important advantage of this structure is the presence of individual protection of each Li_xSi nanoparticle, which eliminates the risk of mass corrosion of the anode in case of local damage of the protective layer of lithium oxide and increases the lifetime of the anode.

The chemical vapour deposition method has also been used for this type of coatings. In this case, the protective coating itself consists mainly of silicates [38,39]. For example, the hybrid organic-inorganic silicate coating was able to simultaneously suppress the growth of dendrites and ensure the strength and flexibility of the interfacial film, due to which the sulfur cathode cell retained a capacity of 693 mAh/g with a Coulomb efficiency of 96.6% after 300 cycles [38]. It is also worth noting the good ionic conductivity of Li_xSiO_y, providing lithium transport through the coating.

In a more complicated way, using electron cyclotron resonance-chemical vapour deposition technique, a protective interfacial film with a hierarchical layer-by-layer structure was obtained: amorphous α-SiO_2, lithiated silicon oxide and lithium silicide [39]. In this case, during the cycling process, a partial transformation of α-SiO_2, which has no lithium ion conductivity, into Li_4SiO_4, which is an ionic conductor, takes place, with the amount of lithium silicate depending on the thickness of the initial material. Moreover, the strength of silicon oxide also increases after lithiation, from 118.3 GPa to 141.1 GPa, which provides an additional barrier for dendrite growth. A 92.5 nm-thick α-SiO_2 lithium-sulfur cell with α-SiO_2 showed the best performance with 655.7 mAh/g after 100 cycles and the highest lithium diffusion coefficient (7.06×10^{-14} cm^2/s).

3.1.4 Nitride-based coatings

Nitride (Li_3N) coatings represent a promising solution for protecting metallic lithium in lithium metal batteries due to their high chemical and thermal stability, ionic conductivity, ability to resist dendrite growth and mechanical strength. These coatings can significantly improve the performance and safety of lithium batteries. The simplest way to produce such film is the direct reaction of metallic lithium with nitrogen [40]. The resulting lithium nitride layer is dense and consists of large grains bonded together, which makes it mechanically stable even under severe bending, and its high ionic conductivity (5.2×10^{-4} S/cm) allows maintaining a capacity of 160 mAh/g at 1C with a sufficiently large electrode thickness of 20 μm for 500 cycles paired with a $Li_4Ti_5O_{12}$ cathode [40]. In addition, the composition and properties of films obtained by a similar method in the atmosphere of four gas mixtures: Ar, CO_2-O_2 (2:1), N_2, and CO_2-O_2-N_2 (2:1:3) were studied [41]. By different techniques (X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS), and scanning probe spectroscopy), the coatings were found to consist of Li_2CO_3 (when reacted with CO_2-O_2), Li_3N (when reacted with N_2), and their mixture (when reacted with CO_2-O_2-N_2). Lithium carbonate forms a denser and more uniform film than nitride, but is highly resistive and unstable in the presence of polysulfides, unlike Li_3N, which is able to block their movement to lithium, so the best properties were shown by the coating obtained by reaction with a mixture of CO_2-O_2-N_2 (2:1:3): the symmetric cell showed good (compared to the one precured in argon) stability for 280 cycles at 1 mA/cm^2, and the lithium-sulfur cell showed 100 cycles at 65 $\mu A/cm^2$.

The authors of [42] studied the effect of water vapour impurities (~1 mol%) in nitrogen during coating by this method and found that a porous film is formed and qualitative passivation of lithium is not achieved, whereas in dry gas the film is dense and uniform.

A more complicated approach to the reaction of the lithium and nitrogen surface using plasma activation for two minutes was not justified: the ionic conductivity of the obtained coating was 5.02×10^{-4} S/cm, as in the case of a simple chemical reaction [40], and the discharge capacity of the Li/$LiCoO_2$ cell was 135 mAh/g at 1C after 100 cycles [64].

3.1.5 Application of phosphorus compounds as coatings

Phosphorus compound-based coatings also attract significant attention for the protection of metallic lithium in lithium-metal batteries. These materials have unique properties that make them promising for improving battery efficiency and safety. The main component in phosphorus-containing protective films on lithium is most commonly Li_3PS_4 [30,31], LiPON [66,67] or Li_3PO_4 [56]. Depending on the composition of the coatings, different methods are used to form them. For example, a 60 nm thick lithium phosphosulfide film was obtained by chemical reaction between metallic lithium and P_4S_{16} in N-methyl-2-pyrrolidone [30]. The electrochemical stability and high ionic conductivity allowed the protected anode to be cycled in a lithium-sulfur cell for 400 cycles at a high rate of 5 A/g with a capacity of 800 mAh/g.

A similar coating was obtained using other precursors, P_2S_5 and S in tetrahydrofuran, but the stability of the coated anode in a lithium-sulfur battery was lower, only 20 cycles at a capacity of 803 mAh/g [31]. The possible reason is the presence of impurity phases other than Li_3PS_4 in this example, as explained by the authors of the paper.

The method of deposition from nitrogen plasma is more labor-consuming, since it requires the creation of a nitrogen atmosphere and electron bombardment, but at the same time the formed coatings are characterized by greater uniformity and density. Thus, lithium phosphorus oxynitride film (LiPON) obtained on lithium allowed to cycle symmetric cells at a current of 3 mA/cm^2 for 900 cycles, and Li-S battery configuration "pouch cell" with a specific energy density of 300 Wh/kg – more than 120 cycles with preservation of capacity of 1 Ah from the initial 1.5 Ah, with the maximum value held to 60 cycles [66]. Such high performance is due to the fact that this coating meets one of the most important requirements for SEI films: its ionic conductivity (1.79×10^{-6} S/cm) is significantly – by 6 orders of magnitude - higher than the electronic conductivity (1.04×10^{-12} S/cm).

A coating of the same composition was obtained by radiofrequency reactive evaporation using lithium phosphate as a target [67]. The protected electrode was tested at different energy densities, and the stability limit of 350 Wh/kg was established, above which a large mass of deposited lithium leads to the appearance of cracks, causing non-uniform current density and shortening the lifetime of the tested elements. A 30 nm thick Li_3PO_4 composition coating with low electronic and ionic conductivity (1.4×10^{-10} S/cm and 2.8×10^{-8} S/cm, respectively) and amorphous nature was obtained by magnetron sputtering [56]. The stability performance of the coated anode in a lithium-sulfur cell was 200 cycles at 0.5 C with only 52% capacity retention from the original 900 mAh/g, which is significantly lower than that of the LiPON coating [66].

3.1.6 Application of sulphur compounds as coatings

Coatings based on sulphur compounds are also considered promising for protecting lithium metal in lithium metal batteries due to their unique characteristics that can significantly improve the performance and safety of lithium anodes. Concerning sulfide-based protective coatings on lithium, it is worth noting that the applied thickness is very small, probably to reduce the resistance of the resulting layer. Accordingly, methods such as atomic layer deposition [62] and sputtering [57] are used to deposit extremely thin films. By the first method, a 50 nm thick aluminium-lithium sulphide (Li_xAl_yS) coating was obtained [62], which allowed the cycling of a Li/Cu cell with a protected anode for 700 cycles at a current density of 0.5 mA/cm^2 and a CE of 97%, due to a sufficiently high ionic conductivity (2.5×10^{-7} S/cm) and effective suppression of dendrite growth.

An even thinner layer, only about 10 nm, was obtained by sputtering MoS_2 layered material on lithium metal [57]. Paired with a carbon nanotube and sulphur cathode, the protected anode showed excellent stability with a high specific energy density of 589 Wh/kg – 1200 cycles with a Coulomb efficiency of 98%. The energy density obtained is 40% higher than the ultimate energy density found for the LiPON-coated anode [67], indicating the greater efficiency of the molybdenum disulfide protective film. This is explained by its layered structure, in which lithium ions intercalate, improving lithium transport through the film and reducing the interfacial resistance.

3.1.7 Application of fluorine compounds as coatings

One of the most popular types of protective coatings on lithium is lithium fluoride, since it not only provides good anode performance, but is also capable of spontaneously forming on the lithium surface in fluorine-containing electrolytes. At the same time, the rate of SEI film formation in solution during cycling is almost impossible to control, so artificial coatings based on this compound are considered as a more practical option. Nevertheless, it is still quite effective to obtain LiF coating by chemical reaction in solution [32-34] under controlled conditions. For example, the reaction of lithium metal with a solution of polyvinylidene fluoride in dimethylformamide produced a LiF-rich film that allowed stable cycling for 300 cycles at 3 mA/cm^2 in a symmetric cell [32], due to the suppression of side reactions with the electrolyte and dendrite growth.

To obtain an uniform and monophasic LiF protective film, it is necessary to use solvents of high purity, without water impurities, because an undesirable by-product, lithium hydroxide, may be formed in addition to the target product [33]. Using NH_4HF_2 in high purity dimethyl sulfoxide (DMSO) as a precursor ($>$99.9%), a lithium anode with LiF protective coating was obtained and was cycled for 400 h at a high current density of 5 mA/cm^2 in a symmetrical cell. This coating possessed a cuboidal structure that reduced its interfacial resistance, and its high pore content allowed lithium to first fill the pits in the anode with lithium and then deposit the metal in a flat layer, which provided a more efficient utilisation of the space in the cell.

An original approach was used in [34]: an exchange reaction between lithium and copper fluoride produced a lithium fluoride film of mosaic structure with copper atoms on the grain faces, which created additional channels for lithium diffusion and increased ionic conductivity. The anode with this coating was cycled in a symmetric cell for 830 h (2000 cycles) at a current of 2.5 mA/cm^2, which is noticeably better than with previously described LiF films.

The production of fluorinated protective films is also achieved by reaction in the gas phase by methods such as chemical vapour deposition (CVD) [43,44] and atomic layer deposition (ALD) [63]. In a homemade reactor, metallic lithium reacted with gaseous fluorine generated by heating the CYTOP fluoropolymer to 350°C to produce a sufficiently thin (380 nm) and pure lithium fluoride layer without direct manipulation with the highly toxic fluorine, which facilitated the cycling of a symmetric lithium cell for 300 cycles at 5 mA/cm^2 [43]. The ability to cycle at such a high current density was ensured by the structure of the obtained film: ion transport was carried out along the grain faces of microcrystals with dimensions of 5-10 nm.

A LiF coating was obtained by chemical vapour deposition using PVDF as a precursor: when heated to 400°C, HF was released and reacted with metallic lithium [44]. The application of high temperature was not justified by the performance of the protected anode compared to that obtained in solution: only 200 h in a symmetric cell at a current density of 0.5 mA/cm^2; moreover, the charge-discharge profiles for bare lithium and the coated one practically overlapped.

Much better cycling performance was demonstrated by lithium also coated with lithium fluoride, but by the ALD method: 260 hours at twice the current density of 1 mA/cm^2 [63]. It is worth noting that the thickness of the protective layer was only 8 nm and the coating process took place at 150°C, which confirms the greater efficiency of this coating method compared to CVD. Also, the lithium fluoride in this film was characterised by high purity (>99%), shear modulus (58 GPa) and excellent isolation for lithium from the electrolyte.

3.1.8 Lithium surface iodisation

Lithium iodide is also used as a protective coating, for the same reasons as LiF – high ionic conductivity, uniformity of the coating and its flexibility, and it is applied mainly by chemical method in various environments. In the gas phase, an artificial film was obtained by the reaction of lithium with iodine vapour and promoted stable cycling of a Li-Li cell for 700 h at a current density of 1 mA/cm^2 [35]. The coating obtained by the reaction in the gas phase is significantly cleaner and thinner than that obtained by immersion in solution, which allows to increase the uniformity of the layer and, consequently, its stability, and to reduce the resistance of lithium ion transport to the anode.

The coating obtained from the reaction of lithium with iodic acid consisted of LiI and $LiIO_3$ and with it the stability performance was worse: at 1 mA/cm^2 the symmetric cell worked only for 100 hours [36]. The reason for this could be less homogeneity of the film and thus less uniform deposition/ dissolution of lithium on the anode.

The composition of the protective film based on the AlI_3 precursor is more complex: formed LiI salt at the interface between lithium and the reagent solution and formed Li-Al alloy in the upper metal layer with aluminium reduced as a result of the reaction, as well as organic inclusions of dioxolane oligomerisation products. It allowed the protected anode to operate in a lithium-sulfur cell for 100 cycles at 0.5C and 950 mAh/g, and in a symmetric cell for 100 cycles at 2 mA/cm^2 with a CE of about 90% [37].

3.2 Organic coatings

3.2.1 Polymers

Compared to inorganic compounds, organic compounds have the advantages of diversity of molecular design and flexible mechanical properties and are therefore widely used to create artificial SEIs with different products both in electrochemical reduction and in the chemical reaction of metallic lithium with organic electrolytes (salt, solvent, additives). The main difference of organic polymer protective films is their elasticity, which allows them to adapt to changes in the volume of lithium during deposition, as well as to prevent the penetration of dendrites to the cathode. The main methods of deposition of this type of coatings are immersion (soaking) in the polymer solution and spreading the suspension by means of a doctor blade. Thus, by immersing lithium wafers for only a few seconds in a solution of a mixture of polyethylene oxide and wax in toluene, followed by drying at a relatively low temperature of 60°C, a coating stable both in air and when immersed in water was obtained [18]. Meanwhile, the wax perfectly insulated the surface of the lithium anode, protecting it from corrosion, and the polyethylene oxide provided ionic conductivity, while slowing down the flow of lithium ions due to their electrostatic interaction with the polar groups of polyethylene oxide (PEO), resulting in a more uniform layer of deposited lithium. The protected lithium also showed good electrochemical performance, with 500 hours of cycling at a current density of 1 mA/cm^2 in a symmetric cell and retention of 776 mAh/g capacity after 300 cycles at 0.5 C in a lithium-sulfur cell.

Significantly longer immersion – 1.5 hours – was required to create a protective film of polydimethylsiloxane (PDMS), but the result did not justify the time consumption: with the same number of cycles, the lithium-sulfur cell showed a lower capacity at a lower rate of 0.2C – 737 mAh/g [19]. The exact composition of this protective film has not been determined due to the complexity of the polymer composition and the difficulty in dealing with lithium in the physicochemical study, but it is claimed that a compound of PDMS-Li composition is formed which has lithium ionic conductivity, unlike the original polymer.

A polyvinyl alcohol (PVA) coating was applied to the anode surfaces using different methods: doctor blade on copper foil and dripping on lithium foil [24]. In both cases, the foil turned out to be quite uniform and allowed stable cycling: more than 630 cycles at a current density of 2 mA/cm^2 with a CE of 98.3% in Li||Cu cells and maintaining after 800 cycles at 1C the capacity at 600 mAh/g (80% of 750 mAh/g initial) in Li-S cells. Here it is worth noting that the contact of PVA, possessing polar hydroxyl groups, with lithium salts in the electrolyte forms a solid polymer electrolyte with good lithium conductivity, that is, this artificial layer participates in the process of formation of the natural SEI film, giving it the desired properties - the ability to suppress dendrites and ensure uniform deposition of lithium.

A coating of polyvinylidene fluoride (PVdF), which has excellent mechanical stability, was applied as a suspension to the lithium surface and dried for 5 days in a box. The low ionic conductivity combined with a rather large thickness of 28 µm could completely block the transport of lithium ions to the anode, but the porous structure of this polymer may have been the reason for the good capacity retention during cycling at high 4C rate – 80% capacity (92 mAh/g) after 500 cycles paired with a $LiFePO_4$ cathode [25].

The agarose protective film was even more effective under similar conditions, with a high stiffness of 65 MPa, allowing it to easily suppress dendrite growth [26]. The cell with $LiFePO_4$ after 500 cycles retained 87.1% of capacity (102 mAh/g from 117.1 initial ones) also at 4C.

3.2.2 Copolymers

Good results have been achieved by using protective coatings made of copolymers of different nature. Their main advantage is the complementarity of the properties of their constituent monomers, for example, one can provide high mechanical strength and elasticity, while the second - responsible for the diffusion of lithium ions to the surface of the anode under the film. One such coating was the thinnest, only 70 nm, film on lithium, which consisted of a copolymer of poly(ethylene oxide) (PEO) and ureido-pyrimidinone (UPy) [47]. UPy was responsible for the mechanical properties – self-healing and elasticity – while PEO promoted excellent lithium ion diffusion, which allowed the symmetric cell to cycle for 1000 h at 5 mA/cm^2 and the cell with $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM) cathode to retain 84.2% capacity (124.8 mAh/g) after 200 cycles at 1C. It is also interesting that despite the solubility of the PEO-UPy copolymer separately in the mixture of solvents used to prepare the electrolyte (1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), v/v – 1:1), it is stable as a coating on lithium in the same mixture, which can be explained by the strong bonds formed with metallic lithium. Another film, obtained by dripping on copper, consisted of a poly(styrene-butadiene-b-styrene) block copolymer, with an optimum monomer ratio of 40:60 (styrene:butadiene), which provided stability over 100 cycles with 147 mAh/g (89%) capacity retention at 0.5C [48]. Here, both components provided mechanical stability: the more rigid styrene provided strength and the softer butadiene provided elasticity and adhesion on the anode surface. Polyvinylidene fluoride (PVdF), which is widely used as a binder, showed good performance in a copolymer with hexafluoropropylene (HFP) cross-linked at 150°C – symmetrical cells were stably cycled for more than 500 h at a current density of 0.5 mA/cm^2 [49]. In this case, PVdF exhibited mechanical and electrochemical stability, whereas HFP promoted hydrophobicity and ionic conductivity due to the increased fluorine content in the film.

An ethylene-vinyl acetate copolymer applied by immersing lithium in an appropriate solution was also proposed as a protective coating [50]. A significant improvement of anode performance was expected due to a large number of ether polar groups increasing ionic conductivity, and hydrophobic methyl and methylene groups, were supposed to protect lithium from interaction with water and air. However, its efficiency appeared to be insufficient: in a cell with NCM cathode at a rather low rate of 0.1C, the capacity decreased from 150 mAh/g to 121 mAh/g after 100 cycles, which is significantly inferior to the values obtained with the same cathode and anode with PEO-UPy film [47].

The unusual structure of the protective coating, formed by interconnected poly(styrene/divinylbenzene) copolymer microspheres capable of suppressing the growth of dendrites due to the pressure on them, which is further enhanced by the bonds between the microspheres, and controlling the distribution of deposited lithium, demonstrated good cycling stability [51]. The capacity of modified lithium paired with a $LiNiCoAlO_2$ (NCA) cathode decreased to 90% only after 190 cycles at 1.45 mA/cm^2, while for pure lithium this limit was reached already after 140 cycles.

3.3 Hybrid organic/inorganic coating

In addition to organic coatings, insoluble inorganic additives are also used to pre-modify the surface of the lithium anode, thus precisely adjusting SEI parameters such as flexibility, ionic conductivity, mechanical properties and SEI distribution. Double and even triple hybrid coatings are also used to protect lithium anodes. In this case, they are composed of both inorganic and organic substances that fulfil different complementary functions. Most often, the harder inorganic component provides mechanical strength and suppresses dendrite growth, while the softer organic component maintains film integrity through elasticity and flexibility. In addition, depending on the properties of the individual components, hybrid films can have high ionic conductivity, hydrophobicity and good compatibility with lithium electrolytes.

The peculiarity of using oxides as an inorganic part of hybrid films is high mechanical strength of the film under the condition of uniform distribution. This is the contribution made, for example, by titanium oxide representing the top layer, while the bottom layer consists of polyperfluorodecylmethacrylate (PFDMA) and provides a qualitative interaction between the anode and the penetrating lithium ions [68]. Due to this protection, the symmetric cell operates for 800 hours and the full $LiFePO_4$||Li cell for 300 cycles with a capacity of 136.7 mAh/g at 1C rate. A more complex composition including zirconium oxide and a dielectric polymer, PVdF-HFP, with the addition of an electrolyte to enhance ionic conductivity is not separated by layers and is a homogeneous film [69]. In this case, PVdF-HFP provides ionic conductivity, while the rigid zirconium oxide ceramic structure provides mechanical protection to the anode. The lithium anode modified with this film was tested with a $LiMn_2O_4$ cathode at a current density of 0.5C, giving a capacity of just under 90 mAh/g after 400 cycles. This was 87.2% of the initial capacity, only slightly higher than the result of unprotected lithium - about 81% was retained under the same conditions.

In another example, a protective layer of lithiated Nafion and aluminium oxide was developed for a lithium-air battery, and it was experimentally found that without the inorganic component, the film performance is only slightly superior to that obtained on pure lithium [70]. This is clearly confirmed by scanning electron microscopy (SEM) images after cycling, where a dendrite-covered surface is observed on pure and Li-Nafion-only coated lithium, while on the Li-Nafion+Al_2O_3 coated anode the surface is smooth. The positive effect is attributed to the combination of a rigid inorganic framework blocking the growth of dendrites and a chemically stable polymer with respect to oxygen. Regarding electrochemical stability, the hybrid film allowed the symmetric cell to operate for 1000 h at 0.5 mA/cm^2, and the lifetime of the uncoated and Li-Nafion anodes was 150 and 190 h, respectively. The protected lithium was also tested in a Li-O_2 cell at a current density of 0.2 mA/cm^2, where it showed a high capacity of 2000 mAh/g over 40 cycles with cathode replacement after 32 cycle.

Unlike the Li-Nafion+Al_2O_3 coating, in which the oxide acted as a framework, the coating with the same organic part and an inorganic one made of garnet, $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$, is bilayer [71]. The top layer of Li-Nafion provided elasticity, while the bottom layer provided stiffness and fast ion transport. However, the symmetric cell test showed the lower efficiency of this coating: at a current of 1 mA/cm^2, the lifetime of the protected anode was only 210 hours, while on pure lithium this value reached 120 hours, i.e. the improvement is noticeably less than with the Li-Nafion+Al_2O_3 film.

Artificial protective film of copper nitride nanoparticles and styrene-butadiene rubber (Cu_3N+SBR), was applied to the surface of lithium by the method of “doctor blade” in the form of colloidal solution in tetrahydrofuran and incubated for 2 days [27]. Upon contact with lithium, Cu_3N nanoparticles were transformed into Li_3N, so that the protective layer had good lithium ion conductivity and mechanical strength, while the polymer component provided flexibility. The porous lithium anode obtained by embedding molten lithium into zinc oxide-coated polyimide nanofibres exhibited stable operation at 0.5 C for at least 90 cycles with a Coulombic efficiency of 97.4%.

The inorganic part could also be represented by a lithium-metal alloy formed by the reaction of the salt of this metal with the lithium surface. The Li/Sn alloy promoted excellent diffusion of lithium ions, and poly(tetramethylene glycol ether) obtained by polymerisation of tetrahydrofuran gave the coating hydrophobicity [72]. Due to this protection, the anode operated stably for 1000 h in a symmetric cell at a current density of 1 mA/cm^2 and 300 cycles in a lithium-sulfur battery with a capacity of 766.3 mAh/g at 0.5C. An alloy of the same composition was prepared by a similar method, but tin fluoride rather than tin chloride was used as a precursor, due to which the composite film also included LiF [73]. The organic outer layer was also different and consisted of PVdF-HFP, but performed similar functions as in the previous example. Despite lithium fluoride, known to have a positive effect in similar films, the Li-Li cell operated for only 350 h at the same rate and the capacity of the Li-Li battery also at 0.5C decreased after 100 cycles to 870 mAh/g (in [72] the capacity after 100 cycles was 1050 mAh/g). On the other hand, it is possible that there is a difference in the efficiency of the organic part of these coatings, but there are no clear arguments either in favour or against this.

LiF was also included in the complex inorganic part of the LiFNS-PPL film, which consisted of LiF, Li_3N, Li_2S and a porous polymer layer (PPL) [74]. This prevented direct contact of lithium with the electrolyte, but kept the possibility of ion diffusion through the pores, thus achieving uniform lithium deposition. The initial capacity of the Li||NCM cell with the protected anode was 4.7 mAh/cm^2 (214 mAh/g) at 0.2C, but after 200 cycles it almost halved to 2.5 mAh/cm^2.

The coating with an inorganic component based on lithium phosphate and an organic component based on PEO also showed excellent results: 1638 hours in a symmetric cell at a current density of 1 mA/cm^2 and 300 cycles paired with an LFP cathode at 0.5C with 93.1% capacity retention (135 mAh/g from an initial 145 mAh/g) [20]. The organic PEO polyester layer showed useful properties such as flexibility (to adapt the anode to volume changes), chemical inertness, and tight film adhesion to the lithium, which could also contribute to the stability of the anode performance.

In the work [75], where the protective layer consisted of the organic component $-COPO_3-$, $-(CO)_2PO_2-$ and $-(CO)_3PO-$, obtained by immersing the lithium in a polyphosphoric ester solution, while at the same time an inorganic layer, of lithium phosphate, was formed. The stability of the symmetric cell at a current density of 1 mA/cm^2 was 2000 hours, and the complete Li||$LiFePO_4$ cell showed an initial capacity of 150 mAh/g at a rate of 1C and retained 115 mAh/g after 300 cycles.

The layered MXene material has already shown its efficiency when used as a matrix for lithium deposition [17], but in [76] it is already used as a protective coating within a hybrid film where the organic component is represented by methyl methacrylate (MMA). Due to its high ionic conductivity ($1.65×10^{-3}$ S/cm) and MXene's ability to inhibit electrolyte decomposition side reactions, the protected anode in a Li||$LiFePO_4$ cell retained a capacity of 106.6 mAh/g even after 1000 cycles at 1C rate (after 300 cycles, 130 mAh/g from 135 initial cycles).

A complex three-layer film on lithium was obtained by a three-stage method, and each layer was applied differently: first, the lithium disc was immersed in a polyethylene oxide (PEO) solution for a few seconds, then a lithium-aluminium-titanium-phosphate (LATP) film was pressed into the first layer, and the third stage was the filling of microcracks in the middle layer with melted wax [11]. The main advantage of wax over other variants of the outer layer composition is the absence of pores, which allows the anode to be completely isolated from air and electrolyte components, which is extremely important for lithium-air batteries. The protected anode in this type of cell operated in a wet (5% water) electrolyte for 200 cycles with a constant capacity of 1.5 mAh/cm^2. The paper also states that symmetrical cells with pure and coated lithium were cycled at different current densities (0.015 mA for coated and 0.15 mA for uncoated), but does not state the basis for this. It makes sense that when cycled at 10 times less current, the coated anode is stable for a greater number of cycles and one might assume that it should also perform better than the uncoated anode at 0.15 mA current. However, this cannot be stated due to the lack of results obtained under equal conditions.

3.4 Ionic liquid based coatings

An alternative approach to creating artificial SEI protective films on lithium is to pretreat the metal surface with an ionic liquid-based electrolyte to form a coating of the desired composition. Ionic liquids are salts capable of being in a dissociated liquid state at a low (ideally, room temperature) without the addition of solvent. In this case, the principle of SEI films production is the same as that of natural formation in a battery: chemical decomposition of the electrolyte with deposition of products on the surface [21] or electrochemical decomposition [52,53] occurs. The difference is that after pretreatment, an electrolyte of a different composition is used for anode tests.

By simple immersion in ionic liquids of different compositions, LiFSI/[C_3mPyr$^+$][FSI$^-$], $LiPF_6$/[C_3mPyr$^+$][FSI$^-$] and $LiAsF_6$/[C_3mPyr$^+$][FSI$^-$], protective coatings on lithium were obtained by allowing Li|$LiFePO_4$ cells to cycle for 1000 cycles with a Coulombic efficiency of >99.5% at 1C with an average capacity of 60 mAh/g [21]. Compounds such as LiF, Li_2CO_3, NSO , [C_3mPyr]$^+$, [FSI]$^-$ were present in the composition of all the protective films, the film obtained in the electrolyte with LiFSI salt addition also contained LiOH, $LiSO_2F$, Li_2S and propyl pyrrolidine, with $LiPF_6$ addition - PF_x, LiOH and methyl pyrrolidine , with $LiAsF_6$ addition – propyl pyrrolidine and Li_2SO_2F. However, the anode incubation time in solution to form an effective film is 12 days, and in addition, salt additives such as LiFSI, $LiPF_6$ or $LiAsF_6$ are used, which may increase the cost of this approach.

In another example, 10 charge/discharge cycles with a current of 1 mA/cm^2 (both charge and discharge time was one hour) were carried out in an electrolyte of composition 1:1

P_{1222}FSI:LiFSI, after which the protected electrode was removed, washed with dimethyl carbonate and dried in a box atmosphere without heating. As a result, an interfacial film was created that blocked the effect of not only water but also air in the organic electrolyte [52]. The authors also compared the quality of the coating obtained in dry and wet electrolytes and found that it was better in the absence of water: after 50 cycles at 0.5C, the cycling overvoltages were 0.6 V and 6.24 V, respectively, in a symmetrical lithium cell. An artificial protective film, also obtained by electrochemical method in an ionic liquid diluted with 1,3-dioxolane (LiFSI-2G4-50 vol% DOL), allowed the protected lithium to cycle stably at a current density of 5 mA/cm^2 and a Coulomb efficiency above 99.98% for almost 650 h [53]. This high stability was observed due to the strong interaction between the protective coating and lithium, resulting in uniform lithium deposition without dendrites.

4. Comparison of artificial SEI films of different compositions in terms of efficiency based on their electrochemical performance

During the review of various protective coatings, the advantage of lithium anodes with artificial SEI films over unmodified lithium in terms of electrochemical performance has been observed, even in cases where the difference was minimal.However, by comparing the efficiencies of artificial films obtained in different works, conclusions can be drawn about the quality of lithium anode protection in each case. Such a comparison was made among the 70 papers presented in this review, and among them, for each type of coating, the papers with the most outstanding performance are present. The comparison took into account the currents, capacitance and stability of anodes in different cell types: Li-Li, Li-S, Li-O_2, Li-LFP and others.

As a result, the 20 papers with the best combination of characteristics were identified and are presented as a table in the order of mention in this review for clarity (Table 1). For Li-Li and Li-Cu cells, data for current densities of 1 mA/cm^2 were given when available.

The most promising deposition methods are dipping and casting, due to the lack of need for expensive equipment and high temperatures, as well as the ability to work with almost any substance, both inorganic and organic. Methods such as ALD, MLD, CVD and magnetron sputtering, on the one hand, allow the deposition of nano-scale films, but on the other hand, they are performed with expensive equipment, not available in every laboratory or production facility, and their applicability is limited to compounds with specific properties (individual for each method).

As can be seen from Table 1, the conditions of the cycling stability tests vary noticeably between papers, so it is extremely difficult to rank the effectiveness of protective coatings. Despite this, the protective coatings obtained for the different types of full cells (Li-S, Li-air and Li-metal-oxide) were compared and the best variants for each type in terms of capacity and stability values were selected as accurately as possible due to the different cycling rates. For the Li-S battery, the best combination of capacity and stability can be achieved with Li_3PS_4 (400 cycles with a capacity of 800 mAh/g at a high rate of 5 A/g (3C)) and MoS_2 (highest capacity and cyclability at 0.5C, 940 mAh/g and 1200 cycles, respectively) protective films. The lithium-air battery exhibits the highest efficiency when the lithium anode is protected by a graphene film – 230 cycles with a capacity of 1000 mAh/g at a cycling rate of 200 mA/g. In the case of batteries with lithium metal-oxide cathodes, two different approaches to anode protection proved to be the most promising: a protective film of Li-In, Li-Zn, Li-Bi and Li-As alloys (at 5C current, almost theoretical capacity of 160 mAh/g and 1500 operating cycles) and a lithium deposition matrix of $Ti_3C_2T_x$/Cu (3500 cycles at a very high cycling rate of 10C while maintaining a capacity of 85.5 mAh/g).

In addition, the cycling results can also be influenced by many parameters, ranging from the electrolyte composition to the temperature of the experiments. All this raises the question of the critical necessity of creating a rigorous standard for testing various kinds of battery material improvements, not only for the area chosen in this review but for others as well. We recommend implementing this standard condition for battery performance evaluation at the first stage and adding other parameters afterwards.

Based on the reviewed papers, we propose a number of the most optimal test parameters, and either average or most common values have been chosen. Standard values have been established for the following parameters, and both options (for both milder and more severe test conditions) are recommended:

— current density (for symmetrical cells) - 1 and 10 mA/cm^2;

— current (for full cells) - 0.1 C and 1 C;

— potential scan rate - 0.1 and 1 mV/s;

— number of cycles in the stability test - 500 and 2000;

— electrolyte composition - 1 M $LiPF_6$ in EC/DMC (1:1);

— cell (or system) type - symmetric (Li||Li) and the most suitable type of full cell (Li-S, Li-LFP or Li-O_2).

5. Conclusion

In this review, various artificial protective films on lithium, their structure, nature, and the mechanisms that enable them to improve the stability of lithium metal batteries have been discussed. It was found that the most common beneficial functions among most films are chemical and mechanical stability, high ionic and low electronic conductivity, and the ability to inhibit dendrite growth, both through mechanical pressure and by enabling lithium to be deposited in a uniform layer.

Despite the general similarities, each type of coating has its own characteristics:

— alloy-based films inhibit dendrite formation due to the rapid diffusion of lithium ions and the ability to concentrate under the alloy;

Table 1 – Electrochemical characteristics of cells with Li anodes coated with artificial SEI films

Coating composition or main component	Coating method	Li-Li and Li-Cu(*)			Full cell				Reference
		Current density, mA/cm^2	Capacity, mAh/cm^2	Stability, hours	Cell type (cathode)	Cycling rate	Capacity, mAh/g	Stability, cycles	
LiF/Li_3Sb	Immersion	2	2	1100	Li-S	231 mA/g	946,3	60	[12]
Alloys Li-In, Li-Zn, Li-Bi and Li-As	Immersion	2	2	1000	Li-LTO	5C	160	1500	[13]
GaO_x	Immersion	1	1	1500	Li-S	1C	650	600	[14]
Li_3PS_4	Reaction between Li and P_4S_{16}	0,5	1	2000	Li-S	5 A/g	800	400	[30]
LiPON	Deposition from nitrogen plasma	3	1	600	Li-S	0,2C	700	200	[66]
MoS_2	Magnetron sputtering	10	5	300	Li-S	0,5C	940	1200	[57]
LiF	Reaction between Li and NH_4HF	1	1	520	Li-LFP	2C	94	100	[33]
Graphene	Immersion	1	1	2000	Li-LFP	1C	129	300	[16]
C_{60}/Mg	Immersion	1	1	550	Li-LFP	1C	141	200	[77]
Graphene	CVD	1	1	1200	Li-O_2	200 mA/g	1000	230	[45]
Graphene oxide	Matrix for lithium	0,5	1,5	900	Li-LFP	1 mA/cm^2	125	700	[78]
$Ti_3C_2T_x$/Cu	Matrix for lithium	1	1	1800	Li-LFP	10C	85,5	3500	[17]
PVA	Immersion	2*	1*	630*	Li-S	1C	600	800	[24]
					Li-LFP	0,5C	125	400	
					Li-NMC	0,3C	130	120	
PVDF	Casting	1	1	620	Li-LFP	4C	92	500	[25]
Agarose	Casting	1*	1*	550*	Li-LFP	4C	102	500	[26]
Copolymer PEO/UPy	Dripping	5	10	1000	Li-NMC	1C	124,8	200	[47]
TiO_2/PFDMA	Dripping	1	1	800	Li-LFP	1C	136,7	300	[68]
Li-Sn/PTMEG	Immersion	1	1	1000	Li-S	0,5C	766,3	300	[72]
					Li-LFP	0,5C	138	300	
Li_3PO_4/copolymer PEGDA–Co–VC	Casting and UV polymerisation	1	1	1638	Li-LFP	0,5C	135	300	[20]
					Li-NMC	0,5C	126	200	
Li_3PO_4/-$COPO_3$-, -$(CO)_2PO_2$- and -$(CO)_3PO$-	Immersion	1	1	2000	Li-S	1C	700	100	[75]
					Li-LFP	1C	115	300	
					Li-LCO	1C	152	100	

— aluminum oxide coatings are porous and very rigid, creating an ideal combination of anode protection and lithium ion diffusion to the anode;

— an important feature of silicon coatings, in particular Li_xSiO_y, is the ability of its polar functional groups to adsorb and rearrange lithium, which ensures uniform deposition, as well as its high strength (141.1 GPa);

— nitride-based coatings, represented mainly by lithium nitride, are dense and have high ionic conductivity (5.2×10^{-4} S/cm). In addition, they are stable in the presence of polysulfides, which gives them an additional advantage when used in lithium-sulfur batteries;

— phosphorus-containing protective films are characterized by very low electronic conductivity of 10^{-10} - 10^{-12} S/cm and a rather dense uniform structure, which makes them excellent insulators of lithium from the electrolyte;

— molybdenum disulphide is worth mentioning among sulphur-based coating compositions: its layered structure is capable of intercalating lithium, which reduces the interfacial resistance and improves the diffusion of Li^+ ions;

— the granular microcrystalline structure of lithium fluoride, the main representative of fluoride-containing films, allows for a significant increase in lithium ionic conductivity due to additional transport channels located on the grain faces;

— regarding the application of iodine compounds for lithium protection, it can be noted that significantly better stability and uniformity parameters are obtained when the film is formed chemically in the gas phase than in the liquid phase;

— carbon nanostructures are highly hydrophobic, which allows them to easily protect lithium from moisture and thus improve its stability, and due to their rigidity, they can inhibit dendrite formation;

— also layered nanomaterials such as graphene oxide and MXene show excellent results as a three-dimensional matrix for lithium precipitation, which not only improves the performance of protected anodes, but also optimizes cell space;

— polymer protective coatings are flexible, allowing them to maintain their integrity even when the anode volume changes significantly during charge/discharge. Ion transport can be ensured either by good ionic conductivity (PEO or PVA-based films) or by porous structure (PVdF);

— to increase the efficiency of polymer coatings, the use of copolymers was effective, where the components contributed their useful properties complementing each other, among which strength (ureido-pyrimidinone, styrene, PVdF), elasticity (butadiene), hydrophobicity (hexafluoropropylene, methyl and methylene groups) and ionic conductivity (polyethylene oxide, ether groups);

— hybrid protective films, which include both organic and mineral components, also have complementary characteristics, but unlike copolymers, the separation of properties is clearer: the inorganic part most often provides rigidity and ion diffusion, while the organic part provides mechanical stability and hydrophobicity. It is also worth noting an additional increase in the mechanical stability of films of this type due to the ability of interpenetration of layers of different nature in their composition;

— another precursor for obtaining protective coatings are ionic liquids, but the increase of lithium anode characteristics is accompanied by the high price of salts and long coating time by immersion method.

The analysis of the considered coatings in terms of efficiency on the basis of their electrochemical characteristics (capacity, cyclability) has shown the absence of a standard test methodology (current density, electrolyte composition, cathode and others), which makes such a comparison not only difficult, but also insufficiently objective, since in many works the stability test is carried out not until the loss of anode functionality, but only a certain number of cycles. Consequently, in the future it is necessary to establish clear test standards for protective coatings on lithium, which will help to analyze their performance relative to each other and not only to pure lithium.

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Conflict of Interest

The authors declare no conflict of interest

CRediT authorship contribution statement

Lepikhin Maksim: Conceptualization, Supervision, Validation; Ryabicheva Margarita: Conceptualization, Writing – original draft, Writing – review & editing; Zhigalyonok Yaroslav: Investigation, Writing – original draft; Kiyatova Marzhan: Writing – review & editing; Abdimomyn Saken: Writing – review & editing; Fyodor Malchik: Supervision, Validation, Writing – review & editing; All authors have discussed the results, read the manuscript and agreed with its content.

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