Molecular Engineering Approaches to Fabricate Artificial Solid-Electrolyte Interphases on Anodes for Li-Ion Batteries: A Critical Review

Roman G. Fedorov, Sebastian Maletti, Christian Heubner, Alexander Michaelis,* and Yair Ein-Eli*

An intrinsic challenge of Li-ion batteries is the instability of electrolytes against anode materials. For anodes with a favorably low operating potential, a solid-electrolyte interphase (SEI) formed during initial cycles provides stability, traded off for capacity consumption. The SEI is mainly determined by the anode material, electrolyte composition, and formation conditions. Its properties are typically adjusted by changing the liquid electrolyte's composition. Artificial SEIs (Art-SEIs) offer much more freedom to address and tune specific properties, such as chemical composition, impedance, thickness, and elasticity. Art-SEIs for intercalation, alloying, conversion and Li metal anodes have to fulfill varying requirements. In all cases, sufficient transport properties for Li-ions and (electro-)chemical stability must be guaranteed. Several approaches for Art-SEIs preparation have been reported: from simple casting and coating techniques to elaborated Phys-Chem modifications and deposition processes. This review critically reports on the promising approaches for Art-SEIs formation on different type of anode materials, focusing on methodological aspects. The specific requirements for each approach and material class, as well as the most effective strategies for Art-SEI coating, are discussed and a roadmap for further developments towards next-generation stable anodes are provided.

1. Introduction

Lithium-ion batteries (LIBs) were introduced to the market more than three decades ago as rechargeable energy storage devices. Originally used in portable electronic devices, their use expanded to consumer electronics, followed by an unprecedented triumph in further markets, such as electromobility and large-scale grid storage. Although LIBs offer high energy density and have reached a high level of maturity, there are still many technological challenges to meet established user habits and increasing demands.[1]

Among the remaining challenges of LIBs, one of the most crucial issues is the electrochemical instability of anodes toward electrolytes. When using anode materials with favorably low electrode potentials close to Li/Li⁺, common liquid electrolytes are decomposed. Ideally, this leads to the formation of a stable so-called solid-electrolyte interphase (SEI), preventing further electrolyte decomposition and leading to stable cycling performance. Furthermore, the SEI has decisive influence on the charge/discharge kinetics of the battery, as this is where the Li-ions overcome the interface between the electrolyte and the electrode. Accordingly, the SEI is a key component that determines the performance of LIBs. The “natural SEI” that forms at the anode/electrolyte interface during initial cycling represents a thin layer made of salts, oxides, polymers.[2] The conceptual model of SEI was introduced by Peled in 1979[3] and further developed by other groups.[4–12] According to this model, natural SEIs possess only ionic conductivity, while serving as a barrier to electron transfer. In this regard, the thickness and conformity of SEI...
play a crucial role for two particular reasons. First, tunneling of electrons through the SEI and resulting occurrence of side reactions is highly dependent on the distance between the electrolyte and the anode material.[13] Second, a thick SEI consumes more Li during formation and hinders ion transfer, decreasing the capacity and deteriorating rate capability. Furthermore, the composition of the SEI affects the ionic and electronic conductivity and thus the battery performance and the occurrence of side reactions.[14] Therefore, actively influencing and controlling these properties is of particular importance for the development of advanced batteries. This possibility has been acknowledged as an emerging research trend, investigating the formation and manipulation of so-called artificial SEIs. An artificial SEI is an intentionally applied layer, which replaces its natural counterpart, acting as an interphase between the active material and the electrolyte. However, the specific manipulation of SEI properties is not trivial and depends on the specific requirements of the targeted anode material.[15]

SEIs on Li metal anodes usually suffer from the growth of dendrites and continuous side reactions with the electrolyte.[16] The former implies internal short circuits as the dendrites are able to penetrate the separator, establishing direct electron conduction between the electrodes. Moreover, such dendrites consume Li-ions from the electrolyte building so-called "dead lithium."[17] Side reactions significantly contribute to the degradation of both the Li-metal anode and the electrolyte, which leads to drying of the cell and associated capacity fading. SEIs on intercalation-type materials are generally hampered by insufficient adhesion and volume changes during Li-ion (de-)intercalation.[18] These factors frequently lead to inhomogeneity and mechanical degradation of the SEI. Moreover, the inorganic components of the natural SEI, i.e., Li$_2$CO$_3$, LiF, and Li$_2$O cause inflexibility and brittleness, which lead to damage during operation. SEIs on alloying-type and conversion-type anodes usually demonstrate improved adhesion, however, strongly suffer from dramatic volume changes during cycling that can reach up to 400% (e.g., Si).[19] Thus, considerable internal stresses induced by repetitive stretches and contractions can lead to the formation of cracks in the SEI.[20,21]

Leading strategies for advancing LIBs recognize precise control over SEI parameters as one of the most effective measures.[22,23] The approaches realizing such a control include: i) in situ formation of the SEI during cycling of the LIB, e.g., by electrolyte optimization and ii) ex situ formation by engineering Art-SEIs prior to cell assembly.[24] The interphase properties in case i) are mainly determined by the anode material, the electrolyte composition, and the formation conditions and thus are somewhat restricted. Contrarily, the application of Art-SEIs offers much more freedom to address material-specific requirements. Furthermore, the Art-SEI approach has some distinctive advantages, i.e., wide range of routes and techniques, not suffering from side reactions with the electrolyte components, applicability for all types of the anode materials, enabling of improved homogeneity and durability. These promising advantages have recently led to extensive developments of Art-SEIs for different types of anode materials and the emergence of new methods.[25] Chemical, electrochemical and polymer grafting, electrodeposition and electropolymerization, magnetic sputtering, wet chemistry, imprinting, chemical and physical vapor deposition (CVD and PVD), atomic and molecular layer deposition (ALD and MLD), mechanical blending, ball milling, blade coating, drop casting, etc. are applied to form Art-SEIs on anode materials.

Obviously, the effectiveness of these methods for different anode types (intercalation, alloying, conversion, and Li metal) as well as the properties and failure mechanisms for the resulting SEIs vary dramatically due to the unique material properties and lithiation/delithiation characteristics.

Herein, we critically review the approaches for the fabrication of Art-SEIs. We take a systematic approach to reveal the most promising routes for Art-SEI engineering on the different types of anode materials. First, a brief outline of SEI studies since 1979 is provided followed by a summary of general design principles for Art-SEIs. Specific characteristics and material type-related requirements of various anode materials with respect to Art-SEI fabrication are derived and corresponding general and methodological aspects are briefly highlighted. Afterward, Art-SEI engineering approaches are reviewed from a practical perspective, divided into top-down and bottom-up methods. Besides methodological and mechanistic aspects and the resulting electrochemical performance, the different fabrication methods are discussed from decisive points of view, including costs, time consumption, environmental issues, robustness, and scalability. This provides a holistic view on the different approaches, allowing science and industry to assess their suitability. While most of the existing Art-SEI concepts as well as recent reviews[26–29] on the topic are focusing on scientific novelty, we understand this section as a reality check toward real-world applications.

Consequently, the most promising approaches can be identified and pursued further to enable the introduction of Art-SEIs in the mass production of advanced LIB.

2. Fundamentals

2.1. Short Outline on SEI Study Since 1979

Following the observation that the deposition-dissolution behavior in nonaqueous battery systems is different and indeed more complex than in aqueous ones, the concept of the SEI was introduced by Peled in 1979.[3] It was postulated that a surface layer is instantly formed on alkali and alkaline earth metals in nonaqueous media. The possibility of tuning this interphase to maximize the cation transfer kinetics and to minimize parasitic reactions was acknowledged. The same applies for other anode materials, with the peculiarity that the SEI starts to form during the first reduction rather than immediately after immersion in the electrolyte.[30] In general terms, the SEI is the product of multiple solvent and salt reduction processes, forming a complex mixture of organic and inorganic compounds and leading to stability against further electrolyte reduction.[3] While the inorganic components originate from decomposition of the salt (case of alkyl carbonate-based solvents) or the decomposition of Li cations and their solvation shell (case of ether-based solvents), organic ones stem from the reduction of electrolyte solvent, forming an SEI with a thickness usually estimated between a few angstroms up to tens of nanometers.[31] The onset potential of SEI formation depends on electrolyte solvents, salts, and impurities as well as anode material properties, such as the basal-to-edge plane ratio of graphite.[32] The initial SEI growth proceeds as a corrosion process of the
anode: electrons reaching the solid/electrolyte interface reduce solvent molecules and conducting salts, leading to a precipitation of corresponding corrosion products on the anode surface. As the SEI becomes thicker, its growth rate slows down, following a square-root time behavior.[13]

Regarding the composition of SEIs, there is a consensus that a dense layer of inorganic products at the graphite surface is neighboring a more porous organic layer in contact to the electrolyte. While components such as (CH\textsubscript{2}OCO\textsubscript{2}Li\textsubscript{2}, ROCO\textsubscript{2}Li, ROLi, LiF, and polycarbonates are confirmed throughout all investigations, the presence of Li\textsubscript{2}CO\textsubscript{3}, Li\textsubscript{2}O, or LiOH is debated controversially and either assigned to particular electrolyte ingredients or to measurement artifacts, e.g., Li\textsubscript{2}O could be a degradation product of Li\textsubscript{2}CO\textsubscript{3} by sputtering with Ar\textsuperscript{+} during XPS measurements.[34] A comprehensive overview and comparison of possible SEI ingredients is provided in the literature.[2]

Although making up only a minute fraction of the whole electrochemical cell, the SEI strongly affects key parameters, such as safety, rate capability, cycle and shelf life.[32] Its formation leads to a significant initial capacity loss, which is tried to solve not only by material modifications but also by adjusting cycling protocols. Usually, a slow SEI formation is carried out by initial low-rate cycles, since a fast SEI formation might result in nonuniform layers which in turn decrease efficiency and safety. Moreover, a complete wetting of the anode with electrolyte is required to ensure uniform SEI thickness distribution.

At low current densities, the ionic migration through the SEI can become the rate-determining step, therefore an ever-growing layer is not desirable as it would slow down the charge-discharge processes in a battery.[3] While in some systems, as for example Li-S batteries, almost no further SEI growth is observed,[33] other ones, such as Si anodes, suffer from a continuous growth.[36] At high temperatures, the SEI was found to decompose, leading to a reduced thermal stability of batteries.[37] In fact, SEI growth is frequently named the major source of capacity fade and degradation in batteries,[18,19] supported for instance by actual observations of immensely increased SEI thickness and rising charge-transfer resistance.[40]

Throughout the last decades, a large number of studies has sought to improve the solid electrolyte interphase by functionalization of anode materials, an adjusted choice of electrolyte solvents, salts, and additives or the alteration of formation protocols. These approaches attempt to influence the natural SEI forming during initial cycling of the assembled LIB. Another emerging and possibly much more promising route is the targeted application of artificial SEIs on anode materials, adjusted to the very special requirements of the particular anode material.

2.2. General Design Principles for ArtSEIs

In contrast to the natural SEIs formed by electrolyte decomposition during initial cycling, the application of Art-SEIs allows targeted tailoring of properties and adapting specific issues of the anodes in LIBs (Figure 1). The choice of potential materials and methods for Art-SEI fabrication on a certain type of anode material addresses three main properties that are decisive for LIB performance: i) mechanical stability, ii) fast Li transport, and iii) chemical stability. The improvement of these properties ensures that the Art-SEI does not suffer from the typical problems of natural SEI, e.g., brittleness, cracking, hindrance of Li-ion transfer, poor performance at high charge/discharge rates, inability to stop electrolyte decomposition.

Mechanically stable SEIs can be obtained in different ways depending on the anode type. On Li-metal anodes, where dendrite formation is the major problem, either extremely hard or relatively soft SEIs are effective. Hard SEIs enable flat Li deposition serving as a template,[43] soft SEIs favor the uniform lithiation over the entire surface.[42] Quantitative explanations of such effects have been derived using linear elasticity theory[43] and 3D coarse-grained molecular modeling.[44] Such Art-SEIs become more stable in the presence of polymer additives in liquid electrolyte. Polymer additives suppress the dendrite growth making the morphology of the Li anode more smooth and flat during plating and stripping processes.[45]

For carbonaceous anodes, mechanically stable SEIs must sustain the nonuniform lithiation process - Li-ions intercalate into the carbon layers mainly through the edge planes rather than through the basal planes. This leads to anisotropic volume expansion in an individual particle of the powdered anode material and therefore to significant local mechanical stresses in it.[46]

Corresponding stresses must be compensated or released by the flexibility (restoring forces) and elasticity of the SEI layer, respectively.[47] These properties of the SEI are of particular significance given the very small particle size of typical carbonaceous powders, where strains at sharp edges and corners can become very strong.[48]

In alloying/conversion anodes, the adhesion and elasticity characteristics of SEI is of critical importance to achieve mechanically stable performance and to overcome numerous challenges, namely cracking, fracture, electrical disconnection and physical delamination, occurring upon extreme volume changes during battery cycling.[49] In this regard, preferential choice should be given to 1D and 2D nanomaterials, as they are capable to accommodate strains via quantum confinement phenomenon.[50,51] In order to improve the adhesion between the composite anodes and the SEI layer, robust polymeric binders, such as alginate binder,[52] a highly cross-linked polymer binder,[53] and catechol-conjugated polymer adhesive binder[54] should be applied.

Fast Li transport from a bulk electrolyte across the SEI into the anode material necessitates a low interfacial impedance. The overall impedance of the SEI stems from and is dependent on the rate of two processes: i) desolvation—releasing of Li-ions from the solvate shell and ii) Li-ion diffusion through the SEI.[55] While the latter is mainly determined by the crystallinity of SEI layer, the former may be accelerated by appropriately selecting of organic components in the electrolyte solution.[56–59] Both processes typically exhibit similar activation energies.[60] Accordingly, either of the two processes may serve as the rate-limiting step that eventually dictates how fast Li-ions cross the SEI in a certain electrolyte-anode material system.

The main parameters characterizing the Li-ion transport across the SEI are the ionic mobility, diffusion coefficient, residence time, and energy of desolvation. The dynamic simulation, and experimental verification of these parameters have been recently elaborated and clearly show the influence of both crystal lattice (amorphous—disordered; crystalline—well ordered), molecular structure (chain length of organic compounds in the electrolyte) and cosolvents.[61–63] In this regard, a compromise in the permeability of SEI layer has to be reached simultaneously...
provide fast diffusion of Li-ions and also prevent the solvated species from entering the SEI layer and bulk anode material.

Since LIBs usually function beyond the thermodynamic stability window of the organic electrolytes, chemical stability of the Art-SEI is necessary to prevent continuous electrolyte decomposition. Chemical stability includes conformality of the SEI layer and negligible solubility in the electrolyte. Accordingly, nonconformal and/or reactive SEIs inevitably lead to enhanced irreversible capacity losses.

Furthermore, in carbonaceous anodes, the nonuniform current distribution along the SEI causes cointercalation of ion aggregates and probably protons, resulting in local degradation/exfoliation of carbon layers.[64,65] This effect is stronger at higher temperature and at slower cycling rate.

In addition, it is worth mentioning that reductive electrolyte decomposition may proceed even without establishing the direct contact with the anode material, but via the electron tunneling through the SEI.[66] If the interfacial layer is too thin or made of a material with narrow bandgap, electron tunneling can significantly contribute to the overall capacity fading. Therefore, materials with wide bandgap, serving as a strong barrier against electron tunneling, should be applied when designing the Art-SEIs. In addition, the SEI thickness should be carefully balanced to ensure sufficient ionic conductivity on the one hand and to prevent electron tunneling on the other.

2.3. The Requirements of Different Anode Materials

While the existence of an SEI is indispensable for almost every known anode material, its properties have to meet quite different requirements depending on type of anode material,
namely i) intercalation type, ii) alloying and conversion type, and iii) Li metal. A generic overview of the requirements for the different types of anode materials is shown in Figure 2.

2.3.1. Intercalation Type Anode Materials

As intercalation anodes with favorably low electrode potential, such as graphite, suffer from an intrinsic instability against organic carbonate electrolytes, the SEI must provide a protective layer against continuous electrolyte decomposition. Furthermore, in the case of graphite, the SEI ideally forms on the edge planes, allowing ionic conductivity along the insertion paths for Li-ions. In conventional electrolytes, LiF-dominated inorganic layers, covered by solvent-polymerization products, are typically found to fulfill these criteria. Additionally, the SEI should prevent graphite from exfoliating during cycling. Early work by Aurbach et al. remarkably shaped our understanding of SEIs on graphite and how their characteristics can be adjusted. Therein, the influence of different solvents, cosolvents, additives, and temperature was examined. It was shown that the irreversible solvent cointercalation is mainly responsible for the deterioration of cycle life of carbon anodes, however efficient SEIs can dramatically improve their stability. Besides positive effects of low temperature and the presence of CO₂, forming Li₂CO₃, it was recognized that ethylene carbonate (EC) as cosolvent plays an important role as it effectively passivates the anode surface before the intercalation potential is reached. Moreover, the relatively small volume change of graphite was identified as a reason for the effective passivation beneath stable surface films. The behavior of graphite was divided into three categories: i) an unstable situation due to cointercalation of solvent molecules, as observed in ethereal solutions. ii) an unstable situation where capacity fading occurs because of surface films that electrically isolate graphite particles from the current collector, depending on the particle morphology and gas formation caused by the solution, as for example propylene carbonate (PC). iii) a stable situation, featuring highly passivating and cohesive surface films, forming before destructive processes such as solvent cointercalation or gas formation can take place. This applies to EC-containing electrolytes as well as to solutions containing reactive additives. It was emphasized that even in the latter case, continuous surface reactions lead to an increase of electrode impedance during cycling, hence not allowing an “infinite” operation of graphite anodes. A popular misconception about the SEI is the assumption of a complete SEI formation within the first cycle. Dahn and coworkers demonstrated that in fact a continuous growth of the SEI occurs, however decelerated, following a parabolic growth law. This leads to a continuous consumption of active Li not only during cycling but also during storage. The evolution of SEI on graphite during progressive cycling is typically assumed to be as follows: While the inner, inorganic-dominated layer remains stable, the outer organic layer shows morphological changes leading to an irreversible loss of capacity. However, these are much smaller than the first cycle losses due to SEI formation. Furthermore, due to the relatively low volume expansion of maximum 13%, graphite anodes are not associated with cracking and healing cycles, such as Si anodes and Li metal.

Note that Li₄Ti₅O₁₂ (LTO) represents a special case of intercalation-type anodes, since its high operating potential of ≈1.5 V versus Li⁺/Li and the stable crystal structure mostly prevent it from electrolyte decomposition and structural collapse. It is often considered an “SEI-free” material, when operated in a range of 1–3 V versus Li⁺/Li, which is discussed controversial, since various studies found SEI films formed on LTO.

Art-SEIs for intercalation type anodes should ideally mimic the behavior of the stable case described by Aurbach et al., an electron blocking and Li-ion conducting layer must be formed, suppressing solvent cointercalation, decomposition and gas formation. Additionally, an ideal Art-SEI will stop to grow after it
2.3.2. Alloying and Conversion Type Anode Materials

Alloying and conversion anodes pose a greatly different challenge to the SEI. While intercalation materials act as a host, confining the inserted Li, these anodes form different compounds upon lithiation, resulting in dramatic volume changes. Si is probably the most studied material of this family. It offers a theoretical capacity of 4200 mAh g\(^{-1}\), however, accompanied by a volume expansion of 400\%. The volume change during cycling results in stress and fracture phenomena from subparticle to electrode scale and is the central element of research on Si anodes. Regarding applicable SEIs, two main strategies exist: i) suppression of large volume changes by stiff SEIs and ii) the softening of mechanical strains by flexible SEIs. Stiff SEIs, rich in LiF, were shown to be beneficial as they raised the energy barrier for crack formation and propagation. It was shown that microscale Si, covered with an SEI having a Young’s modulus of a few hundred MPa, exhibited a higher vulnerability to crack propagation than nanoscale Si, where parts of the SEI exceeded a strength of 1 GPa. Contrarily, flexible structures react to volume changes by bending, also avoiding the formation of cracks and preserving not only the electrode but also the initially formed SEI.

Groundbreaking work in the field of SEIs on Si has been done by the research group of B. L. Lucht. Therein, a strong influence of electrolyte additives such as fluoroethylene carbonate (FEC), vinylene carbonate (VC) and lithium difluoro-oxalatoborate (LiFECO) was acknowledged in comparison to conventional solutions of LiPF\(_6\) in alkyl carbonates. Moreover, FEC degrades at a higher reduction potential than alkyl carbonates and facilitates the formation of a conformal SEI. While FEC-free electrolytes result in an SEI mainly composed of LDEC, LiF, and Li\(_2\)SiO\(_3\), FEC-containing electrolytes yield LiF, polymeric components and Li\(_2\)SiO\(_3\) with a strongly increased LiF-concentration, provided by the fluorine from FEC. The resulting LiF-rich SEI is more stable and hence provides improved cycling behavior.

The beneficial influence of FEC was also confirmed for siloxane-based solvents. Vinylene carbonate (VC) is also able to improve the capacity retention, especially at elevated temperatures. In fact, it could be shown that, while FEC is mostly responsible for guaranteeing a high rate capability by forming an SEI with high ionic conductivity, VC provides a flexible surface film accommodating volume changes and yielding improved cycling stability. In situ analysis of the SEI formation revealed the mechanisms on a very accurate level. i) while solvent decomposition leads to the formation of lithium alkyl carbonates, salt decomposition forms alkyl phosphates. ii) Li\(_2\)CO\(_3\) is formed by CO\(_2\), that originates from a reaction between lithium alkyl carbonates and HF. iii) During delithiation, the SEI shell is peeling off and iv) the delithiation process is the step mostly associated with the formation of decomposition products. For a prolonged cycling, this leads to a continuous destruction and re-forming of SEI, irreversibly losing Li cycle by cycle. Based on these insights, an Art-SEI for alloying and conversion anodes should ideally provide a flexible matrix which accommodates large volume changes (as provided by reaction products of VC) or a high strength with a Young’s modulus in the GPa range while providing high ionic conductivity of at least 10\(^{-6}\) S cm\(^{-1}\).

2.3.3. Li Metal Anode

Among all anode materials, metallic Li provides the highest theoretical energy density since it delivers 3860 mAh g\(^{-1}\) at a potential of –3.04 V versus SHE. Unfortunately, Li deposits tend to form noneven, mossy or dendritic structures which are detrimental for battery operation. The dissolution and deposition of Li leads to a repetitive cracking and recovery of the SEI, enlarging the surface area, which continuously consumes electrolyte and favors dendritic growth. These dendrites might grow through the separator, causing short circuits or they can detach from the anode, forming “dead lithium”: Li metal, encapsulated in SEI, which is no longer electrochemically active. Therefore, repeated cycling of Li metal anodes results not only in accumulated Li losses due to SEI cracking and recovery, but also bears the risk of short circuits and thermal runaway.

The fundamentals in understanding Li metal anodes have been mainly developed by the works of Peled and Aurbach. Early work stated low cycling efficiency of LiClO\(_4\)-containing electrolytes with PC, BL, and THF as solvents, which was already associated with dendritic Li deposits. Moreover, the unfavorable SEI was identified to be composed of organic species and insoluble lithium-chlorine salts. Consequently, the authors encouraged the community to look for additives, which alter the surface films and therefore enable improved cycling efficiency. Detailed SEI investigations by FTIR, IR and XPS showed that lithium alkyl carbonates were formed as decomposition of the electrolyte solvents while the salt reduction resulted in halides. The presence of Li\(_2\)CO\(_3\) was attributed to water contents in the electrolyte. While these fundamental studies covered solvents and salts that have not reached a wide application, more recent work yielded comparable results for practical electrolytes, such as solutions of LiPF\(_6\) in EC-containing solvent mixtures. In their bare state, LiPF\(_6\) in EC/DEC, LiPF\(_6\) in EC/DMC, LiPF\(_6\) in TEGDME and LiPF\(_6\) in DMSO all showed dendrite formation and electrolyte decomposition, resulting in a poor cyclability. Applying LiBF\(_4\), LiBOB, and LiDFOB revealed similar performance decay of Li metal, accompanied by the production of lithium alkyl carbonate, Li\(_2\)CO\(_3\), lithium oxide, and LiF. While in case of LiBF\(_4\) and LiBOB the surface films were inhomogeneous, containing large LiF particles, the LiDFOB electrolyte generates a stable SEI containing nanostructured LiF, which is assumed to be beneficial for cycling stability. Just as for the other anode classes, additives appear as promising ways to stabilize SEIs on Li-metal anodes. Vinylene ethylene carbonate (VEC) has shown to increase cycling stability by providing a higher amount of polycarbonate and LiPF\(_6\) decomposition products compared to VEC-free electrolytes. The positive effects of...
FEC known from Si anodes were also approved for Li metal and the obtained high coulombic efficiency was attributed to a uniform Li growth, facilitated by a LiF-rich SEI.\[96\] Using cryogenic TEM, the relation between SEI and the morphology of the electrodeposited Li was investigated, confirming the presence of organic species and crystalline LiF. At the same time, the beneficial effect of LiF was questioned and metal ions such as Cs\(^+\) and Zn\(^{2+}\) were proposed to be used as additives to enhance a conformal Li deposition.\[97\]

Originating from research on Li–S batteries, ether-based solvents have demonstrated satisfactory stability toward Li metal anodes. It was shown, that in typical DME:DOL mixtures, DOL is mainly responsible for the interphase chemistry, forming oligo-ethoxides and inorganic oxides, such as Li\(_2\)O.\[98\]

While all above-mentioned concepts rely on the modification of electrolytes by either changing solvents or salts and using additives, there is no doubt that a direct modification of the Li metal surface by an Art-SEI will be just as promising or might even open completely new perspectives. An ideal SEI would suppress dendritic growth, favoring a uniform deposition, providing stability and fast Li\(^+\) conduction. Particularly, a substrate with low roughness, hence covered with a smooth SEI, has been shown beneficial as it limits the nucleation overpotential for Li deposits.\[99\]

On the other hand, 3D structures provide void spaces, acting as a host for Li plating. It seems that, maybe for Li even more than for the other types of anode materials, a complex interplay between the chemical composition of the SEI and its morphological features might lead to enhanced stability during cycling.

Based on the state of knowledge in the field of natural SEI layers, important basic principles for artificial SEI layers can be concluded. In general, the advantageous properties of natural SEI layers should be transferred to artificial SEI layers, whereas disadvantageous properties must be eliminated or optimized. In typical electrolyte formulations, the necessary ionic conductivity for Li ions as well as the electron-blocking behavior to suppress electrolyte decomposition are provided. Hence, the naturally formed SEI, consisting of a rigid inorganic inner layer and a more flexible organic outer layer provides a good role model for artificial layers. At the same time, its mechanical properties are far the most vulnerable point, and Art-SEIs must be developed either in a direction of more rigidity, suppressing volume changes or toward more flexibility, accommodating the volume changes without SEI fracture. Moreover, to minimize continuous Li losses, the once-formed SEI should itself be stable toward the electrolyte and electron-blocking in an early stage, hence not causing further electrolyte decomposition and SEI growth.

### 2.4. General Aspects of Art-SEIs Manufacturing

Obviously, the methodological gap between various approaches for Art-SEI manufacturing is huge. This involves numerous strategic and technological differences, i.e., design principles (top-down and bottom-up), media (solid/liquid/gaseous phase), processing types (serial and parallel), driving forces (molecular interaction, external field), extrinsic and intrinsic conditions, etc. Yet, some general aspects apply to all approaches as they derive from specific features of LIBs and the requirements for Art-SEIs (see Sections 2.2 and 2.3). In this regard, the most important aspects of the Art-SEI fabrication are summarized in this chapter.

#### 2.4.1. Prelithiation

Several anode materials having a huge specific surface area, i.e., graphite powders, carbon nanotubes, Si powder, and many others, consume irreversibly a large amount of Li-ions from the electrolyte during the first lithiation (intercalation or alloying) act, and therefore causing significant capacity loss. In order to overcome this problem, three principle strategies have been suggested: sacrificial electrode, electrolyte additives, and electrode (anode and/or cathode) prelithiation.\[100\] The latter strategy seems to be preferable because it does not suffer from the drawbacks of the two former, namely safety issues and low effectiveness, respectively.\[101\] In particular, the anode prelithiation is required to partially load the active anode material with Li-ions right prior to battery assembling, thereby preventing irreversible accumulation of Li-ions within the crystal lattice of the anode material during the first charging.

In LIBs with Art-SEI, anode prelithiation can be accomplished at different stages of the production process, i.e., during Art-SEI manufacturing as well as before and after it— as an independent stage. In this regard, Art-SEI takes on new significance in LIBs, providing a reliable protection for the lithiation reagents, such as stabilized Li metal powder (SLMP, FMC Lithium), Li\(_x\)M (M = Si, Ge, Sn) nanoparticles and others.\[102\] Indeed, such protection has been demonstrated to provide a superior prelithiation capacity and stable battery performance with a number of various anode materials.\[102,103\]

#### 2.4.2. Distribution of Active Sites

Obviously, one of the key parameters characterizing the quality of Art-SEI is a uniform thickness over the entire substrate. Conformal and thin Art-SEIs enable more elastic and flexible mechanical protection as well as much higher conductivity. In this regard, the distribution of the active sites\[104,105\] i.e., structural defects of the surface (dislocations, vacancies), inclusions of foreign atoms, and oxygen containing functional groups, over the electrode surface plays a crucial role regulating the initial stages of Art-SEI growth process. While the distribution of structural defects and inclusions of foreign atoms are mainly determined by the nature and purity of the active electrode material, tailoring the distribution of surface oxides can be a versatile tool for controlling the uniformity and conformity of thin Art-SEIs.\[106\] In particular, dense and uniformly spread oxygen groups along the electrode surface serve as the active sites for Art-SEI nucleation in heterogeneous process (liquid-solid, vapor–solid) allowing fabrication of conformal and thin Art-SEI. Therefore, novel materials and methods providing the same level of reactivity over the entire surface area are of special interest.\[107\]
2.4.3. Monitoring the Art-SEI Growth

The existing methods for monitoring the Art-SEI growth can be divided into two: in situ and ex situ techniques. Obviously, the in situ methods are of significant privilege over the ex situ ones because they examine/visualize various parameters of Art-SEI (morphology, structure, thickness, composition, impedance, capacity, etc.) at all stages of manufacturing process, therefore allowing studying the mechanism and various aspects of the latter. Nevertheless, the ex situ approaches including XPS, SEM, AES, SIMS, solid state NMR, etc. are indispensable for some cases, where the necessary information is gathered from the depth or cross-section of the sample.[22] Disadvantages of the ex situ methods are the lack of electrical potential control after disassembly of the electrochemical cell and possible changes of the SEI layers in contact with air/moisture, e.g., oxidation or swelling. Among the most popular in situ approaches are the electrochemical methods (electrochemical impedance, cyclic voltammetry, galvanostatic charge–discharge), scanning electron microscopy (SEM), scanning probe microscopy (AFM, STM), various spectroscopic techniques (FTIR, Raman, UV–vis, X-ray, NMR), gravimetric measurements (quartz crystal microbalance), etc. Taking into account a probability of some changes that can be caused by the in situ analysis itself, such as in the cases of conductive AFM, destructive X-ray or laser beams, or local charging by electron beam (in situ SEM), the adequate precautions and tool set-up must be elaborated for each particular system. In addition, the in-detail study of Art-SEI formation mechanism requires complex investigation involving both the qualitative (surface species, crystallinity, morphology) and quantitative (ratio between components, grain size) data at all stages of nucleation and growth processes, especially during first cycle of battery charging.

3. Production Methods—Advantages, Challenges, and Effectiveness

Some excellent recent reviews summarize the current development, design and improvement of Art-SEIs.[26,27,28,99,108–114] In contrast, our present review mainly focuses on the reality check of Art-SEI materials and methods toward real-world applications. Specifically, in this chapter, Art-SEI engineering approaches are reviewed from a practical perspective, divided into top-down and bottom-up methods. Their general and specific advantages and drawbacks are discussed and the overall applicability of different strategies is evaluated.

3.1. Top-Down methods

In general, top-down approaches cover any kind of processes, which involve the formation of a structure, originating from a bigger entity, i.e., by subtracting material. These stand opposed to bottom-up techniques, which feature the formation of structures from smaller building blocks, as in the most drastic case, from atoms or molecules. Although top-down processes are often considered disadvantageous, due to, e.g., a lower degree of material utilization, the majority of industrial manufacturing processes works top-down, providing excellent control over various parameters of the process. Regarding Art-SEI, top-down methods originating from microelectronics, solar cells etc. might be adapted, possibly providing fast and effective scale-up solutions. In the following paragraphs, important top-down approaches of Art-SEIs are reviewed and assessed in terms of their cost, time consumption, environmental issues, robustness, scalability, material and design freedom, atmosphere sensitivity and their electrochemical success.

3.1.1. Magnetron Sputtering

Over a wide range of applications, magnetron sputtering has become a popular technique for producing high-quality functional coatings.[215] In the basic sputtering process, a glow discharge plasma is formed in front of a target, firing ions toward it. The bombardment with ions leads to a removal of target atoms, which condense on the surface of a substrate. The peculiarity of magnetron sputtering is the involvement of magnetic fields in a way to guide secondary electrons emitted from the target close to the target surface, increasing the probability of further electron-atom collisions and therefore densification of the plasma in this region. This leads to a higher rate of sputtering at the target and, consequently, increased deposition at the substrate.

In 2014, Li et al. used a Li3PO4 target under reactive N2 atmosphere and a sputtering power of 90 W to produce lithium phosphorous oxynitride (LIPON) films as Art-SEI on thin-film Si electrodes.[116] The main objective was the formation of an electronically insulating layer between electrolyte and anode, blocking the flux of electrons toward the electrolyte and therefore lowering the chance of electrolyte decomposition. It turned out that thin LIPON coatings of 10 and 20 nm did not prevent the formation of a natural SEI. In contrast, coatings exceeding 50 nm led to the complete absence of an electrochemical SEI formation, suggesting that the Art-SEI is sufficiently preventing electrolyte decomposition. EIS and DC polarization experiments showed that, while the ionic conductivity remains constant as the LIPON thickness is varied, electronic conductivity exhibits a jump over seven orders or magnitude from 10−13 to 10−6 S cm−1 as the thickness decreased from 50 to 40 nm, see Figure 3a. This dramatical increase in conductivity in thin LIPON coatings, resembling an electron tunneling behavior, allows the transport of electrons from the anode toward the electrolyte, thus not being able to prevent electrolyte decomposition. At the same time, thicker Art-SEIs increase the resistance and limit gravimetric capacities, allowing to conclude that the interphase should be as thick as necessary and as thin as possible. In contrast to thinner coatings, both 50 and 100 nm LIPON layers enabled a stable cycling at close to 100% CE over 100 cycles (Figure 3b,c). Nevertheless, the authors emphasize that their approach utilizing a ceramic material is not likely to withstand large volume changes of practical porous electrodes and motivate further research toward more mechanically robust Art-SEIs.

Likewise, the group of Winter and Placke prepared LIPON with various layer thicknesses on thin film Si electrodes by magnetron sputter deposition.[117] All films exhibit a better long
term stability than the pure Si thin-film reference, although the capacity retention at 100 nm and 200 nm coating thickness is improved versus a 300 nm coating (Figure 3d). The rate capability is reduced by LiPON coating as it represents an additional barrier for the transfer of the Li-ions and the ionic conductivity is relatively low (2–3 µS cm⁻¹).[118] Most importantly, the coulombic inefficiency is greatly diminished by applying the LiPON layers, as side reactions between Li metal and the electrolyte are significantly less pronounced (Figure 3e). While pure Si thin films exhibit cracks and a general loss of integrity after 150 cycles (Figure 3f), LiPON/Si with 200 nm Art-SEI appears still homogeneous at similar conditions (Figure 3g). The authors attribute this behavior to increased structural stability and the depression of parasitic side reactions.

Archer’s group investigated magnetron sputtered LiF Art-SEIs on bare copper and Li foil.[119] Therefore a LiF target was used and the process was carried out at ambient temperature, a sputtering power of 80 W, utilizing Ar as sputter gas at a pressure of 10 mTorr. A patterned deposition of LiF was employed by using a Cu mesh as template during the process, resulting in LiF-covered and LiF-free areas. An optimal thickness of the Art-SEI of 150 nm was recognized as, similar to previous work, thicker layers result in increased resistances. SEM investigations after Li plating revealed that, on LiF-covered areas, deposition results in much smoother morphologies as in noncovered regions, where irregular dendritic structures tend to form. Cycling tests in symmetrical cells, “anode free” cells and half cells with Li₄Ti₅O₁₂ confirmed this observation, enabling a longer lifetime of LiF-coated foil. The authors emphasize the transferability of their approach to other types of anode materials. An immense advantage of inorganic-only SEIs consisting of stable compounds such as LiF is their low atmosphere sensitivity, which is a key requirement for practical Art-SEIs. From a practical point of view however, we may preliminarily conclude that magnetron sputtering of ceramic interphases, representing a relatively cheap and well-known process, is limited to thin-film and planar electrodes, but unlikely to succeed for powder-based composites.

3.1.2. Drop Coating, Blade Coating, and Dip Coating

Simple coating approaches, involving the formation of a layer from the liquid phase operate on comparatively simple equipment, can be performed fast and offer large design freedom.[120] Typically, a solution or suspension of the material of interest is prepared. In case of drop coating, it is applied and spread onto the surface of the sample. In case of dip coating, the sample itself is dipped into the liquid and moved out at a defined speed, causing the appropriately designed solution to remain

Figure 3. Magnetron-sputtered Art-SEIs. a) Electronic and ionic conductivity of ultrathin LiPON. b) Reversible (delithiation) capacity and c) Coulombic efficiency as a function of the cycle number for Si coated with LiPON Art-SEI. Data were obtained using half-cells. Reproduced with permission.[116] Copyright 2014, American Chemical Society. d) Capacity and e) accumulated Coulombic inefficiency versus cycle number of the investigated Si and LiPON/Si thin film electrodes. Measurements were conducted in three-electrode Li half cells in a potential range of 1.50–0.04 V versus Li/Li⁺. The calculation of the capacity retention is based on the 10th cycle discharge capacity. C-rate study: from 0.5C to 1C, 2C, 5C, 10C, 20C, 50C, and back to 1C (every 5 cycles; without constant potential step). Only every second cycle is displayed. f) FIB cross-sectional micrograph of a pure Si (140 nm) layer after 150 cycles. g) FIB cross-sectional micrograph of a LiPON/Si (200 nm/140 nm) bilayer after 150 cycles. Reproduced with permission.[117] Copyright 2018, Royal Society of Chemistry.
on the samples surface. In a subsequent drying procedure, the solvent is evaporated and a solid coating remains.

Cui’s group pursued an approach of generating an Art-SEI of ion-conducting Cu₃N nanoparticles in a styrene butadiene rubber (SBR) polymer matrix. Therefore, the inorganic nanoparticles are synthesized from Cu(OMe)₂ and benzylamine and subsequently dispersed in THF. This precursor is then blade-casted over the surface of a Li metal foil, resulting in the formation of Li₃N, which is postulated to not only provide mechanical stability and dendrite suppression, but also to guarantee a uniform Li flux upon plating and stripping. CV analysis confirmed the partially reversible conversion from Cu₃N to Li₃N and Cu, along with Cu oxidation to Cu₂O. After galvanostatic plating and stripping for five cycles, the Art-SEI-covered Li displayed a much smoother planar morphology than a bare Cu foil, on which wire-shaped Li deposits had formed. This was attributed to the ionic conductivity of the inorganic nanoparticles, providing a uniform Li flux and avoiding the formation of local current hot spots. Nanoindentation measurements revealed high robustness of the layer. Besides Li foil, the Art-SEI was applied to a porous Li substrate and a flat cycling profile over 100 cycles in half-cells using Li₂Ti₃O₇ as demonstrated. The authors emphasize the advantage of the facile solution processing and its tunability, allowing not to only treat flat electrodes but also porous samples. Recently, using a similar straightforward blade-casting technique, the possibility of depositing dual-phase Art-SEIs and polymer matrices with incorporated LiF particles was demonstrated. In addition, experimental simplifications were achieved by coating the separator rather than the anode. Subsequently, the Art-SEI is transferred to the anode when the cell is assembled.

Li et al. applied a dip-coating procedure to obtain a Li₃PO₄ layer as Art-SEI for Li metal anodes. Therefore, polished Li samples were dipped into a solution of polyphosphoric acid (PPA) in dimethylsulfoxide (DMSO). Postmortem XPS analysis revealed, that almost no changes in the surface composition of coated samples took place, while untreated Li foil exhibited typical surface films containing inorganic and organic electrolyte decomposition products. Additionally, SEM cross-section micrographs showed a mossy, bloted surface for the bare Li anode, while the electrode with Art-SEI kept its morphology. The authors concluded that the applied Li₃PO₄ film does not undergo repeated break-and-repair cycles and maintains its structural integrity, which is supported by a significantly improved capacity retention after 200 cycles. Apart from the chemical stability and ionic conductivity, the importance of a high Young's modulus, restraining the growth of Li dendrites, is underlined. The entire preparation needs to be performed under inert atmosphere and the presence of slightest amounts of moisture is detrimental. Therefore, a large scale application of this approach appears inconceivable.

A further, comparatively facile coating strategy is the approach of drop coating. Feng et al. prepared a Li-infiltrated Cu matrix, equipped with an Art-SEI by drop coating polyacrylic acid (PAA). Again, a smoother morphology as well as smaller fractions of electrolyte decomposition products are found after 100 plating/stripping cycles and a durable cycling over 1000 cycles was demonstrated. The ionic conductivity and the high elasticity of the coating are emphasized as the most important properties for beneficial Li transport and suppression of dendrite growth.

Another successful application of drop coating was reported by Wang et al., using a copolymer of poly(ethylene oxide) (PEO) and ureido-pyrimidinone (UPy), prepared by reversible addition-fragmentation chain-transfer (RAFT) polymerization and dissolved in tetrahydrofuran (THF). In contact with Li, this polymer layer spontaneously forms an Art-SEI and prevents the typical SEI-forming reactions at the Li surface, see Figure 4a. Moreover, an electrostatic interaction between Li ions and polar PEO segments is postulated to homogenize the charge flow. Convincing cycling properties were obtained not only by using this layer on Li metal, but also on bare Cu, allowing “anode-free” in situ plating and stripping of Li. Interestingly, this layer also provides increased atmospheric stability. Exposed to air with a relative humidity of approximately 30%, untreated Li foil immediately faded to a black color, while LiPEO-UPy@Li showed negligible changes in appearance for 30 min, as depicted in Figure 4b. This finding might be of immense importance to make atmospheric processing of Li metal anodes viable. Application in a half-cell using a NCM positive electrode led to an almost identical voltage profile of bare Li and LiPEO-UPy@Li (Figure 4c). The cycle life however is clearly superior in case of the latter, delivering 84% capacity retention after 200 cycles in contrast to only 50% for bare Li (Figure 4d).

Chen et al. prepared a covalent organic framework (COF) film on Li metal using an in situ Schiff-base reaction between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and terephthaldehyde (PDA) (Figure 4f). The reagents were dropped directly on the Li metal surface. Apart from the high Young's modulus of 6.8 GPa, the hexagonal microcellular structures of the COF are proposed to guide the flux of Li ions, both leading to homogeneous and dendrite-free plating and stripping as illustrated in Figure 4g–h. Electrochemical measurements support this hypothesis, showing very steady overpotentials (Figure 4i) and excellent cycling stability in a Li–S full cell over 300 cycles, while untreated Li exhibits fluctuating overpotentials and cell failure after 111 cycles. Subjected to a constant current of 2 mA cm⁻², COF-Li withstands Li stripping for more than 40 h, while bare Li fails due to short circuits after 17 h (Figure 4j). Top and cross-sectional views of electrodes after 20 cycles confirm uniform and dense morphology for the COF-capped samples, whereas bare Li foil adopts mossy and porous shapes. Despite the electrochemical success of this approach, the excessive use of benzene-containing chemicals should be scrutinized, as the environmental sustainability is doubtful in such a case.

The available literature demonstrates that rather simple coating strategies of Art-SEIs were so far limited to Li metal anodes. This is mainly because of the fact that polymeric layers with good Li conduction and high Young’s modulus are ideally suited for suppressing dendritic Li growth. Future work on transferring this knowledge to other types of anodes appears to be expedient. Although the tensile stiffness of such layers might be unsuitable for alloying and conversion anodes, the investigation of blends with flexible components might be effective. Intercalation-type anodes, not in need of a protection layer with outstanding mechanical strength, could still profit from them since initial Li losses due to SEI formation could be avoided.
3.1.3. Sintering

Sintering processes involve the joining of material, usually at elevated temperature and/or pressure, but below their melting point. Since sintering of powders without absolute densification easily allows to obtain porous materials, these processes are of particular importance for solid state batteries, especially solid state electrolytes.[132]

Li et al. transferred the idea of employing ion-conducting Li₄La₃Zr₂O₁₂ (LLZTO) not as an electrolyte, but as Art-SEI on Li anodes.[133] Therefore, LLZTO particles attached to the Cu current collector were heated to 900 °C under Ar atmosphere. Interestingly, this Art-SEI is not located above the anode active material, but directly on the current collector and its porosity provides space for Li deposits. During the sintering process, the interdiffusion of Cu and Ta₂O₅ was observed, providing a durable mechanical contact, see Figure 5a–d. The Art-SEI was applied to Cu foil as well as to Cu foam and proved better electrochemical properties in both cases. In symmetric plating/stripping tests, shown in Figure 5e, bare Cu foil failed after a few hundred hours of cycling, whereas LLZTO-coated Cu foil survived for more than 4000 h. Similarly, Li@Cu foam-LLZTO demonstrated clearly superior cycle life in full cells with a LFP positive electrode, as compared to Li foil (Figure 5f).

The sintering approach, although still in its infancy, might soon be of growing interest. Since the demand for all-solid-state batteries rises, production capacities for sintered ceramic electrolytes will increase in the near future, also allowing efficient large-scale production of ceramic Art-SEIs, despite drawbacks in its high energy demand and limitations to a continuous operation. Also for sulfidic electrolytes, recent computational work provides a systematic selection scheme for Art-SEIs,[134] Additionally, compared to wet chemical methods, sintering gets along without substantial use of toxic substances and can be considered a zero-waste technology.

3.1.4. Pressing

Perhaps the most straightforward top-down approach of engineering an Art-SEI is the application of a powder layer and subsequent fixation by mechanical pressure.[136–138] This is especially viable for Li metal since its softness favors the embedding of particles. Goodenough’s group loaded Li₃N as well as Al₂O₃ particles on Li foil and subjected to a roll-pressing procedure, see Figure 6a,b.[137] In case of Al₂O₃, an increased dendrite growth was observed, which was attributed to surface defects introduced to the Li foil upon pressing,
acting as favored deposition hot spots. Li$_3$N however exhibits an interesting effect: it does not suppress the growth of dendrites, instead, through its chemical affinity toward Li, it bonds with them (Figure 6c–e), thereby redirecting the dendrite growth and ultimately forming an interconnected network of Li. Low Li deposition overpotentials (Figure 6f) and lower impedances for Li$_3$N than for Al$_2$O$_3$ and bare Li were observed (Figure 6g) and a stable plating and stripping in half cells for more than 300 cycles was shown (Figure 6h). However, the electrochemical success, evaluated from full cell investigations, has not yet been demonstrated. It is therefore questionable if the formed 3D interconnected Li structure does have practical advantages over typical Li deposits, as it very much resembles the unfavored “mossy” growth pattern, which often is sought to circumvent.

Sun et al. prepared a LiF–polymer composite layer (LiF@Po) by roll-pressing polytetrafluoroethylene (PTFE) onto Li metal\[138\]. The interphase between PTFE and Li is proposed to form a LiF layer, while further inside the PTFE a polymeric layer is built. Both these layers remain on the Li surface as the PTFE film is detached. These assumptions are based on TEM imaging, diffraction and EDXS. Li plating and stripping was investigated by post mortem SEM, revealing a more dense and flat plating as well as a clearly more uniform stripping for LiF@Po compared to bare Li. Plating and stripping in symmetric cells revealed cell failure in case of bare Li after approximately 100 h, while LiF-covered Li survived up to 450 h and LiF@Po clearly exceeded both by cycling more than 1000 h. Finally, half-cell tests using LCO and NCM, revealed a longer cycle life compared to bare Li, which suffers from Li depletion in less than 200 cycles. Both its mechanical softness as well as its reactivity render Li metal as very promising for simple mechanical approaches such as the discussed roll-pressing method since it is likely to cause superficial reactions already by providing a sufficiently close contact. Regarding less reactive (and therefore more or less any other) anode types, pressing might not yield similar effects and should at least be assisted, as for example by heat treatment to promote surface film forming reactions.

3.1.5. Methods under Development

A pioneering approach for generating an Art-SEI was proposed by Peled’s group\[139\]. Therein, an aqueous solution of sodium carboxymethylcellulose (Na-CMC) was introduced into the pore structure of tin-copper alloy anodes using a simple vacuum insertion technique. Clearly, the initial capacity loss could be reduced, and the cycle life could be extended. Moreover, the possibility to easily fabricate similar layers using a comparatively quickly electrophoresis technique was demonstrated.

Additive manufacturing and 3D-printing techniques have become a fixture for the manufacturing of all kinds of devices, including batteries\[140,141\]. A major advantage of this technology is the ability to manufacture complicated three-dimensional structures which are not accessible to other preparation methods. During recent years, numerous studies demonstrated the capability of this technique to print electrodes and electrolytes by either lithography-based 3D printing (e.g., LiTiO$_2$/LFP\[142\]), template-assisted electrodeposition (e.g., NiSn/LMO\[143\]), inkjet printing (e.g., Li/LiMn$_{1-x}$Fe$_x$PO$_4$\[144\]), aerosol jet printing (e.g., Li/LFP\[145\]), direct ink writing (e.g., CNF-Li/CNF-LFP\[146\]), and fused deposition modeling (e.g., graphene\[147\]).

While, in principle, polymers as well as oxides, hydroxides, metals and carbons can be processed by such additive approaches, the currently available range of printable battery materials is very limited due to processing aspects, since, for instance, the complex interplay of active materials with rheology-determining ink components requires intense fine-tuning. This gets emphasized even more when considering Art-SEIs, as these layers usually involve sensitive compounds, often in inorganic-organic mixtures. While we do not expect 3D printing to be able to provide chemically sophisticated Art-SEIs in the near future, we see an immense potential in the ability to generate spatially complex structures, such as highly porous and symmetric scaffolds\[143,148\]. As elucidated in the above sections, such geometrical considerations are very important, e.g., helping to confine Li deposits and preventing dendrite growth.
or providing strong, yet elastic envelopes for Si particles to accommodate their volume changes without repeated fracture. While the need for 3D-printed current collectors was already mentioned by Pang et al.,[140] we especially want to encourage researchers to investigate the possibility of using 3D printing for Art-SEIs.
3.2. Bottom-Up Methods

To a wide extent, the bottom-up approach comprises a variety of methods, where the smallest units of a matter (atoms or molecules) are organized via controlled or spontaneous processes forming large 2D or 3D objects. Accordingly, driving forces in different bottom-up synthetic routes can be divided into two: intermolecular microscale interaction (Van der Waals forces, ionic bonding, hydrogen bonding, etc.) and external macroscale stimuli (electromagnetic fields, acoustic waves, mass-transfer, etc.). Hence, controlling (optimizing) the growing process in bottom-up methods usually realized through a precise choice of the applied precursors, environmental media, intrinsic and extrinsic conditions, and power of the external stimuli. Moreover, in most heterogeneous bottom-up processes, as in the case of Art-SEI manufacturing, the key parameter defining the initial stages of nucleation and growth is a surface state involving the number of active sites (oxides, functional groups, defects, impurities, etc.), crystallinity, and roughness. The key advantage of the bottom-up strategy is the ability performing the material manipulation with maximum possible resolution, which is limited only by the size of applied building blocks and, therefore, theoretically reaches the molecular level. The examples of such molecular resolution are the atomic layer deposition (ALD) and molecular layer deposition (MLD) methods, where composition and thickness of 2D coatings are controlled within the accuracy of one monoatomic or one monomolecular layer, correspondingly.

3.2.1. Chemical, Electrochemical, and Polymer Grafting

Chemical grafting realized at liquid/solid interphase through direct chemical reaction of the grafting agent with the grafted surface, which in turn are usually modified with functional reactive groups. Similarly, the electrochemical grafting also proceeds through direct redox interaction of the adsorbed molecules (precursor) with electrically biased substrate that serves as donor or acceptor of electrons. Due to its simplicity and reliability, these approaches deserved special attention in Art-SEI fabrication, especially for the intercalation-type anode materials, where covalently bind thin organic layers significantly improve Li-ions intercalation and prevent exfoliation. Art-SEI films obtained via grafting showed superior electrochemical performance attributed to a stable and compact structure that is capable of accommodating multiple volume changes in carbonaceous nano-powders. Lately, very similar approach was applied to alloying/conversion anodes (Si nanoparticles), where volume alterations are even more problematic. The resulting robust and flexible Art-SEI demonstrated higher capacity and more stable cycling behavior as compared with uncoated (reference) material. A more recent study showed the additional advantage of this route, i.e., the possibility to use the deposited organic layers as a functional matrix in composite (Sn/graphene) anode materials. Diazonium grafting was applied to modify graphene surface with aminophenyl functional groups that served further as a capturing agent for Sn nanoparticles deposition followed by composite (Sn/graphene) anode fabrication. Reproduced with permission. Diazonium grafting was applied to modify graphene surface with aminophenyl functional groups that served further as a capturing agent.
for Sn nanoparticles deposition. The resulting Art-SEI demonstrated low and stable resistance. It enabled much higher reversible capacities in galvanostatic cycling than the untreated Sn-graphene blend.

Chemical grafting of Art-SEIs has also been shown to improve the performance of Li-metal anodes. For example, a fast and simple approach was realized using the spontaneous process of self-assembly of the reactive organic liquid components on pure Li metal film. The resulting Li-metal/Art-SEI anodes exhibit higher corrosion resistance to solvents and oxygen, reduced dendrite growth, higher capacity and Coulombic efficiency, and lower overvoltage compared to an uncoated Li-metal anode.

Similarly, it was shown that the chemisorption of 1-pentylamine molecules from an organic solvent (n-pentane) on Li metal significantly decreases the electrode impedance and overpotential when compared to the treatment with only n-pentane. Grafting of a thin and porous LiF-rich layer (TPL) on Li metal by in situ chemical reaction with a small amount of ammonium hydrogen difluoride (NH₄HF₂) enabled stable cycling over 100 cycles at high current density of 6 mA cm⁻². A ZnCl₂-based layer on Li metal was formed via chemical grafting from tetrahydrofuran (THF) and ethylmethylcarbonate (EMC) containing organic solvent mixtures. It was shown that such an Art-SEI decreases the interfacial resistance by ≈80% and improves cycling stability as compared to untreated anodes.

Electrochemical grafting (electrografting) also can be effectively employed for both intercalation and alloying/conversion-type anode materials. Moock et al. proposed a versatile strategy allowing electrografting of Si, highly ordered pyrolytic graphite (HOPG), and graphite powder with diazonium salts containing a protected alkyne moiety (Figure 7c–f). Specifically, the process was performed in three-electrode configuration from the organic (acetonitrile) electrolyte solution containing diazonium salt (4-(trimethylsilyl)benzene diazonium tetrafluoroborate) between −1 and 0.2 V versus Ag/AgNO₃ using potentiodynamic (20 mV s⁻¹) or potentiostatic (−0.6 V, vs Ag/AgNO₃) regimes. The deposited organic layer was chemically modified, i.e., the TMS-protecting group was removed by treating with tetrabutylammonium fluoride and subsequent thiol-yne click reaction performed in pure 2,2′-(ethylenedioxy)diethanethiol under UV light. Cyclic voltammetry and galvanostatic measurements proved the formation of protective organic layer made of conducting diazonium salt (4-((trimethylsilyl)benzene diazonium tetrafluoroborate) between −1 and 0.2 V vs Ag/AgNO₃ using potentiodynamic (20 mV s⁻¹) or potentiostatic (−0.6 V, vs Ag/AgNO₃) regimes. The deposited organic layer was chemically modified, i.e., the TMS-protecting group was removed by treating with tetrabutylammonium fluoride and subsequent thiol-yne click reaction performed in pure 2,2′-(ethylenedioxy)diethanethiol under UV light. Cyclic voltammetry and galvanostatic measurements proved the formation of protective organic layer made of conducting diazonium salt as well as subsequent increase in the protective effect, when the surface was chemically modified with thiol-yne click reaction (Figure 7d–f). Electrochemical measurements in half-cell configuration revealed a remarkable reduction of irreversible capacity loss.

Strategies of surface coating using polymer grafting (Figure 8) can be classified according to: i) simultaneous graftingpolymerization of organic monomers and ii) direct grafting (bonding)
of the existing polymer matrix to the substrate of interest. The former involves grafting by means of chemical polymerization, oxidative polymerization, and radiation polymerization. The latter usually realizes in two stages, i.e., surface activation with a base-polymer or self-assembled monolayer containing functional (reactive) groups and subsequent bonding of (co-)polymer molecules from aqueous or organic solution. A typical example of the first strategy for Art-SEI fabrication has been proposed by Assresahegn et al., where Si nanoparticles have been modified with polyacrylic acid (PAA) and used further in various composite anodes (Figure 8a–d). In particular, hydrogenated Si powder was initially coated with a thin layer of polymerizationinitiator, 1-(bromoethyl)benzene (A1), followed by monomer grafting with tert-butyl acrylate and subsequent atom transfer radical polymerization (ATRP) resulting in Si-A1-PAA structure (Figure 8a). Thus, modified with such Art-SEI Si nanoparticles showed the improved electrochemical performance, especially in terms of gravimetric capacitance (Figure 8b–d). [158]

A distinctive advantage of the second strategy for Art-SEI fabrication using polymer grafting is the compatibility with Li-metal anodes. Gao et al. reported a Li-metal surface modified with polymer composed of a cyclic ether group and a polycyclic main chain in two steps via a ring open metathesis polymerization method (Figure 8e–g). As a result, Li-ions deposit on and dissolve from the surface of the Li anode protected with the polymer film without the formation of dendrites (Figure 8h–j). This enabled higher and more stable capacity over 400 cycles in full-cell configuration (Figure 8k,l). Polymer grafting was also used to create Art-SEI made of polymers with abundant micropores on Li-metal anodes, which resulted in improved Li transport, electrochemical performance, and dendrite-free Li deposition. [163]

### 3.2.2. Electrodeposition

Electrodeposition techniques are a well-known tool to produce customized coatings by applying a current through a setup of two electrodes and an electrolyte. The fact that electrical current is used to drive the deposition reaction allows excellent control of reaction kinetics and a high level of fine-tuning options for the deposition process. Consequently, electrodeposition techniques are enjoying great popularity in the field of batteries. [162]

Proceeding from the fact that in most cases both the anode and the Art-SEI possess flat and relatively thin geometry, one can assume two major strategies for Art-SEI fabrication via electrodeposition, namely direct electrochemical deposition of Art-SEI film on the anode surface and, vice versa, electroplating of the anode material on (or through) the previously formed Art-SEI surface, which is usually supported on current collector metal substrate. While the former is realized by means of heterogeneous electroreduction of various molecular organics or inorganic precursors to form continuous film (buffer layer) that further stabilizes the process of SEI formation, the latter is usually realized to achieve smooth dendrite-free morphology during numerous deposition/stripping acts of the Li-metal battery cycling and, therefore, it is applied mostly for Li-metal anodes via electroreduction of corresponding precursors (Li salt) at modified Art-SEI/Cu (or another current collector) electrodes.

One of the advanced approaches involved in the first strategy was suggested by Cheng et al., where the authors used the electroplating method to construct an Art-SEI-containing Li anode which was subsequently implanted in either Li–S cells and Li-ion cells (Figure 9a). Therefore, Li metal was “pre-cycled” in an electrolyte containing LiTFSI, LiNO3, and Li2S5.
In DOL/DME. The SEI formed therein is, strictly seen, the natural SEI of the cell used for the formation, as it consists simply of decomposition products between anode and electrolyte. However, due to stability limitations, such electrolytes are usually not used in full cells, although they form desirable SEIs. The transfer of those into another electrochemical cell however makes it turn into an Art-SEI. The authors highlighted the positive effect of the multicomponent electrolyte mixture and the advantage, that the battery cell itself does not need any additives. By means of XPS and TOF-SIMS, a dual inorganic-organic structure of the SEI was determined and optical microscopy showed, that such an SEI tends to drastically decrease the dendrite formation tendency compared to a reference sample. A proof of concept was established in both, Li–S cells with a sulfur cathode and an ethereal electrolyte as well as in Li-ion cells with an NCM cathode and a carbonate-based electrolyte.

In both cases, cells with implanted Art-SEI performed better than cells with an untreated commercial Li foil as anode. In comparison to the NCM-containing Li-ion battery (45 charge–discharge cycles presented), the Li–S battery performance showed itself much more convincing, cycling 600 times at significantly higher capacity retention and rate performance than the reference (Figure 9b,c). Most probably, this performance difference is related to the fact that the Art-SEI, formed in an ethereal electrolyte using LiTFSI, LiNO3 and Li2S5 bears perfect chemical compatibility with Li–S electrolyte chemistries. In contrast, ex situ electrodeposition and implanting of Art-SEIs from carbonate-based electrolytes might present a lever for improved performance in the Li-ion setup.

A basically similar approach was pursued by Li et al., who prepared Li–Sn alloys, coated with an Art-SEI.[166] Using a LiTFSI/DOL electrolyte, a Sn electrode was polarized at 3.0 V to form a layer of polymerization products on the Sn surface. Subsequently, a galvanostatic discharging to 0 V led to the Li–Sn alloy formation. The polydioxolane oligomers formed during electropolymerization established a flexible SEI layer which proved increased capacities and coulombic efficiencies in a Li–S battery.

The example of applying the first strategy, i.e., direct electrochemical deposition of Art-SEI film on the anode surface, to the intercalation-type material was proposed by Kim et al.[167] In this study the SEI-implanted graphite electrode was made using a lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)-based electrolyte via a simple electrochemical process. The Art-SEI implanting process involved the discharging of graphite electrode in a coin-cell configuration from open-circuit voltage (OCV) to 0.01 V followed by potentiostatic treatment at 0.01 V for 12 h to stabilize the Art-SEI layer. The obtained Art-SEI enabled higher reversible capacity (357 mAh g−1 at 0.5C after 50 cycles than that of commercial LIBs with LiPF6 (312 mAh g−1).

A typical example of the second strategy, i.e., electropolating of the anode material on (or through) the previously formed Art-SEI surface, was proposed by Zhu et al. and comprises Li electroplating on porous poly(dimethylsiloxane) (PDM) supported on Cu electrode (current collector) in coin-cell configuration.[164] Specifically, PDMS film with nanopores was deposited on Cu surface using the spin-coating method from methylbenzene solution in two stages: first, at a low speed (100 rpm) to enable uniform coating; and then at high-speed (9000 rpm) to decrease the coating thickness. Next, the coating was dried under vacuum to volatilize the methylbenzene and solidify the PDMS. Nanopores in PDMS coating was formed by etching with HF in order to provide fast Li-ions transport through it in both directions. The obtained Cu/PDMS sample was further used as a substrate for Li electroplating in two-electrode configuration at various current densities from the electrolyte solution containing LiPF6 as Li precursor. The resulting Cu/Li/PDMS anode showed highly stable electrochemical performance with an averaged coulombic efficiency of 94.5% for more than 200 cycles at 0.5 mA cm−2 using the conventional carbonate electrolyte. Hu et al. studied another variant of Li electrodeposition on the stabilized Art-SEI/Cu surface.[165] Thin LiPON film on Cu surface was achieved using radio frequency (RF) magnetron sputtering. This strategy showed less effectiveness in terms of coating conformity and suppressing Li dendrite growth than other approaches.[165] Yet, it was found that the density of Li deposits is lower on Cu/Li/LiPON electrodes while their average size is larger, which is consistent with LiPON film introducing an additional kinetic barrier to electrodeposition.

3.2.3. CVD, ALD, MLD Methods

By analogy with the bottom-up methods of wet chemistry, where individual nanoscale building blocks (atoms or molecules) initially distributed in the liquid phase, in vapor-based bottom-up methods the molecular precursors uniformly load the gaseous flow phase to form organized 2D or 3D structures at various support materials. An advantageous feature of the vapor-based route is the ability to form conformal thin-films on porous and especially powdered materials. The latter can be achieved by using a dynamic flow system, e.g., fluidized bed reactor with precise control of input and output pressure difference. In a typical process, the gaseous precursor molecules are passed through the powder at a velocity high enough to balance the weight of the solid material so that it behaves like a liquid.[168–71] Such configuration enables uniform distribution of the operating conditions and precursor concentration, which results in uniform coating thickness.

Different types of battery materials were shown to be successfully protected by applying thin layers using various modifications of CVD method, namely metal-organic CVD,[74] laser flash evaporation CVD,[75] electron cyclotron resonance CVD.[76] CVD techniques have particular popularity in the context of all-solid-state LIBs, where the large polarization at the interface between Li metal anode and oxide-based (garnet) solid electrolyte is a main challenge. For example, Luo et al. reported the formation of ultrathin (~10 nm) amorphous Si coating on the surface of garnet electrolyte (Nb and Ca doped Li2Zr2O7, LLZ), which simultaneously produces the lithiated Si Art-SEI while placing it in contact with molten Li (Figure 10a–e).[72] Thus, excellent wettability is achieved, allowing the garnet surface to switch from “super-lithiophobic” to “super-lithiophilic” behavior. Such lithiated Si Art-SEI showed 7-fold smaller interfacial resistance as well as stable plating/stripping
behavior as compared with that of the nonmodified materials. Furthermore, CVD techniques allow designing composite anodes made of different types of active materials including Li metal. For instance, Liang et al. reported fabrication of Li/C composite anode, where a thin layer of Si was deposited onto carbon framework (nanofiber scaffold with an average diameter of 196 nm) by CVD to assist further melt-infusion process of Li (Figure 10f–i).\[173\] Li metal was heated above the melting point in inert atmosphere and then absorbed by the modified C/Si scaffold. It was clearly demonstrated that the thin Si film markedly increase Li wettability via the formation of lithium silicide, which provides some bonding interactions to pure Li. This reaction prompts molten Li to uniformly wet and fill in the porous nanofiber matrix under capillary forces. Due to the large active surface area, stable Li/Si/C interface, and small volume change the resulting composite anodes showed outstanding electrochemical performance, i.e., low interfacial resistance, elevated gravimetric (2000 mAh g\(^{-1}\)) and volumetric 1900 (mAh cm\(^{-3}\)) capacities, stable voltage profile and long cycle life.

Over a long period, CVD has been a main bottom-up technique for the vapor deposition of various thin coatings. However, the limited ability of controlling the coating thickness and homogeneity with high-resolution became a significant challenge in different fields, where nanometer-scale or even angstrom-scale resolution eventually dictates the key property, i.e., balance between protection reliability and electronic/ionic conductivity. Moreover, the additional drawbacks of CVD are as follows: i) the chance of chemical reaction in the bulk (vapor phase) rather than on the solid/vapor interface inevitably results in the formation of solid particles incorporated into the growing film, ii) the dependence of film growth rate on the mobility of precursor molecules iii) the absence of precursors for deposition of promising materials including many transition metals and metal oxides.

In contrast to CVD, ALD is a vapor-based technique enabling deposition of thin coatings with an atomic resolution.\[177\] Based on sequential, self-limiting reactions, ALD overcomes the above listed drawbacks of CVD and, more importantly, is capable of controlling the composition of each individual layer in the deposited film. The advantages of ALD arise from the specific deposition mechanism. Volatile precursors used in each ALD single act (half-reaction) are not thermally decomposed upon contact with the substrate. Instead, film growth is achieved via self-terminating chemical interactions between the precursor and the functionalized surface. Most ALD processes use alternating binary reaction sequences, where two successive reactions on the surface lead to a binary composite layer (sandwich type). Therefore, two reactants are used. One of them (precursor) contains functional atoms/molecules that define the properties of the future coating. Another one (coreactant) is responsible for the formation of functional groups at each branch of a growing molecular film. In this regard, the two coreactant types are used underlying the two ALD mechanisms, namely thermal ALD, where the coreactant is a stable entity (H\(_2\)O, O\(_2\), ozone, etc.); and plasma-enhanced ALD, where the monoatomic coreactant species (unstable radicals)
are generated through UV radiation directly in ALD reactor. Thermal ALD is characterized by less complicated reactor design and allows more uniform coatings without damages caused by UV-radiation. Plasma-enhanced ALD provides deposition at much lower temperature, which is crucial for the materials with low decomposition point.

A recent example of thermal ALD route for Art-SEI manufacturing was reported by Crompton et al. in their article dedicated to ALD-coating of carbonaceous nanomaterials, i.e., commercial multi-walled carbon nanotubes (MW-CNT) sheet with a thin (~3 nm) film of Al₂O₃ using trimethylaluminum (TMA) precursor and deionized H₂O coreactant (Figure 11a–c). The resulting MW-CNT/Al₂O₃ anodes showed a significant (on 55%) decrease in cumulative (for 50 charge/discharge cycles) irreversible loss in half-cell configuration as compared with pristine MW-CNT anodes. Moreover, XRD analysis revealed that the Al₂O₃ coating stabilizes the interlayer structure of MW-CNT preventing irreversible disruption (irreversible intercalation of Li into interior sites accessed through wall defects or tube ends) after 50 charge/discharge cycles. Another type, i.e., alloying/conversion type of the active anode materials also can be modified with Art-SEI by means of thermal ALD. Zhang et al. reported a hafnium oxide (HfO₂) ALD layer on Si thin (100 nm) film supported on Cu current collector using tetrakis(dimethylamido)hafnium (TDMAH) and H₂O as the precursor and coreactant, respectively. Varying the number of the ALD cycles enabled precise control over HfO₂ thickness—5, 10, and 20 ALD cycles corresponded to 0.63 nm, 1.25 nm, and 2.51 nm film thickness, respectively. The modified Si/HfO₂ anodes demonstrated improved cycling stability when compared with uncoated Si surface.

A combination of plasma-enhanced and thermal ALD can be used to coat the third type of active anode material, i.e., Li metal with Art-SEI layer. Alaboina et al. reported zirconia (ZrO₂) ALD encapsulation layer on Li-metal anode surface (Figure 11d–g). Here, the ALD process comprised a combination of initial plasma activation to increase the surface functionalization and the number of chemisorption sites for precursors followed by thermal ALD-subcycle to obtain highly dense, smooth, and conformal deposition. The resulting Li/ZrO₂ surface exhibited excellent tolerance to air exposure for at least 1–5 h as compared with the uncoated Li metal, which oxidizes very fast (5 min) upon air exposure. Moreover, enhanced sustainability to heat (170 – 180 °C) exposure for over 1–5 h was recorded for protected Li/ZrO₂ material, while pristine Li metal melted very fast, losing mechanical shape integrity at the same temperature. Furthermore, optical images proved significant Li-dendrite suppression and the capability of uniform distribution of the Li-ion transport along the entire Li/ZrO₂ anode surface. Finally, no degradation in cycling behavior and high-rate capability were registered for modified Li/ZrO₂ anodes in full-cell configuration. Similarly, self-terminating surface reactions,
where the whole organic molecules or molecular fragments are being deposited in each individual ALD cycle, can be applied for the growth of organic or hybrid (inorganic-organic) thin films. This type of ALD is usually classified as molecular layer deposition (MLD).[181] As in the case of ALD, the MLD also enables manufacturing of uniform coatings with molecular resolution and precise control over the composition at each MLD cycle. By combining the ALD with MLD methods, fundamentally new types of inorganic-organic hybrid polymer thin film structures can be formed.[182]

Recently, MLD was effectively employed to fabricate different inorganic-organic hybrid polymer Art-SEIs on Li-metal and Si anodes. Chen et al.[183] and Zhao et al.[184] reported Li-metal modification with hybrid polymer Art-SEI based on Al and ethylene glycol (EG), known as alucone (Figure 12a,b). In both cases, the process involved direct MLD on Li metal at 120 or 150 °C using alternative exposure to trimethylaluminum (TMA) and EG as the precursors. The resulting Li/alucone anode demonstrated substantially improved plating/stripping performance as well as increased lifetime when compared with uncoated Li metal or modified Li/Al2O3 anodes. In a similar way, zircon and zincene coatings were constituted onto Li-metal and Si anodes via MLD process.[186,187] Zircon-coated Li-metal anodes displayed increased air sustainability, improved electrochemical performance and high rate capability.[186] Optimized Si/zincene anodes showed reduced irreversible capacity, higher cycling stability and improved rate capability when compared to untreated Si anodes.[187] Another promising example of hybrid metal-organic MLD is the polyurea thin film coating on Li-metal anode reported by Sun et al (Figure 12c–e).[185,188] The resulting polyurea MLD coating effectively suppressed the dendritic growth during cycling and tripled the lifetime at a current density of 3 mA cm⁻².

4. Reality Check of Manufacturing Procedures

While improvements in terms of battery performance might easily tempt to consider a method suitable for real-world application, a substantiated evaluation needs to take more aspects into account. With that aim, we evaluated the available literature based on their cost, time consumption, environmental issues, robustness, scalability, material and design freedom, atmospheric sensitivity, and their electrochemical success, all resulting in a grade for the method's overall applicability, as given in Table 1.

Top-down methods, such as magnetron sputtering, drop- and dip-coating, pressing and sintering provide precise control over the processes, typically allowing scale-up possibilities and they can be applied to all anode types. Most promising results were obtained using LIPON coatings on Si to prevent side reactions and natural SEI formation, however more development in
Table 1. Comparison overview of top-down and bottom-up methods for ArtSEI fabrication.

| Procedure                                                                 | Year and reference | Anode type | Cost | Time consumption | Environmental issues | Robustness | Scalability | Material & design freedom | Atmosphere sensitivity | Electrochemical success | Overall applicability |
|---------------------------------------------------------------------------|--------------------|------------|------|------------------|----------------------|------------|-------------|--------------------------|-----------------------|-----------------------|-----------------------|
| **TOP-DOWN Methods**                                                      |                    |            |      |                  |                      |            |             |                          |                       |                      |                       |
| LiF magnetron sputtering                                                  | 2017[119]          | Li         | ++   | 0                | ++                   | +          | +           | –                        | –                     | +                    | +                     |
| Magnetron sputtering of LIPON film                                        | 2014[36]           | Si         | +    | 0                | –                    | –          | –           | 0                        | +                     | +                    | +                     |
| Sb-doped Li$_3$PO$_4$ by magnetron sputtering                            | 2019[149]          | Li         | ++   | 0                | –                    | –          | –           | –                        | +                     | 0                    | 0                     |
| LIPON by magnetron sputtering                                            | 2014[116]          | Si         | 0    | 0                | +                    | –          | –           | –                        | +                     | +                    | +                     |
| LIPEO-Upy drop coating                                                   | 2020[124]          | Li/Cu      | –    | +                | –                    | –          | +           | +                        | –                     | +                    | +                     |
| PAA drop coating on Li-infiltrated Cu matrix                             | 2020[127]          | Li         | ++   | –                | 0                    | +          | +           | –                        | +                     | +                    | +                     |
| Drop coating of covalent organic framework film                          | 2020[129]          | Li         | −    | 0                | –                    | +          | –           | –                        | –                     | +                    | –                     |
| Coating with Cu$_3$N nanoparticles and SBR                                | 2017[121]          | Li         | –    | 0                | ++                   | +          | +           | –                        | –                     | +                    | +                     |
| Dip coating in PPA solution                                              | 2016[125]          | Li         | +    | ++               | 0                    | +          | +           | –                        | –                     | +                    | +                     |
| Sintering Li$_2$ZTO on Cu foam                                            | 2019[131]          | Li         | –    | –                | +                    | +          | ++          | 0                        | +                     | +                    | +                     |
| Roll pressing of Li$_3$N                                                  | 2017[17]           | Li         | +    | ++               | +                    | +          | ++          | +                        | –                     | 0                    | 0                     |
| Electropainting or vacuum insertion of PEAA/Na-CMC                         | 2009[139]          | Sn-Cu      | +    | ++               | 0                    | +          | ++          | 0                        | +                     | +                    | +                     |
| LiF–polymer composite by roll pressing                                    | 2020[138]          | Li         | +    | ++               | +                    | ++         | –           | –                        | +                     | +                    | +                     |
| **BOTTOM-UP Methods**                                                    |                    |            |      |                  |                      |            |             |                          |                       |                      |                       |
| Chemical grafting of the aminophenyl layer                               | 2017[131]          | graphene/Sn| ++   | –                | –                    | –          | +           | –                        | –                     | +                    | +                     |
| Electrochemical grafting with diazonium salts                            | 2018[137]          | Si, HOPG, graphite | +    | –                | –                    | +          | –           | ++                       | +                     | +                    | +                     |
| Polymer grafting with polyacrylic acid                                   | 2017[134]          | Si         | –    | –                | +                    | +          | ++          | +                        | +                     | +                    | +                     |
| Polymer grafting with graphene nanosheets and polyacrylic acid           | 2018[139]          | Si         | –    | –                | +                    | +          | ++          | +                        | +                     | +                    | +                     |
| Polymer grafting with composite “skin”                                    | 2017[160]          | Li         | –    | 0                | –                    | +          | +           | –                        | –                     | +                    | –                     |
| Li electroplating on Art-SEI modified current collector                 | 2017[134]          | Li         | +    | –                | ++                   | +          | 0           | +                        | ++                   | 0                    | 0                     |
| Li electrodeposition on the stabilized Art-SEI/Cu surface                | 2020[151]          | Li         | –    | –                | –                    | –          | –           | +                        | –                     | –                    | –                     |
| Electrodeposition via cycling in 1,3-Dioxolane-based electrolyte         | 2019[136]          | Li–Sn alloys | +    | ++               | –                    | +          | ++          | –                        | –                     | +                    | 0                     |
| Electrodeposition via discharging in LiTFSI-based electrolyte            | 2020[157]          | graphite   | +    | –                | +                    | ++         | –           | +                        | +                     | +                    | +                     |
| Chemical vapor deposition of Si on garnet-type solid electrolyte         | 2016[122]          | Li         | –    | +                | –                    | +          | +           | ++                       | –                     | +                    | +                     |
| Chemical vapor deposition of Si on carbon framework with subsequent Li melt infusion | 2016[137]          | Li-C       | +    | –                | +                    | –          | 0           | –                        | +                     | 0                    | 0                     |
| Thermal atomic layer deposition of Al$_2$O$_3$                            | 2018[134]          | MW-CNT     | +    | +                | +                    | +          | +           | +                        | +                     | +                    | +                     |
| Plasma-thermal atomic layer deposition of Z$_2$O$_3$                     | 2018[134]          | Li         | –    | +                | –                    | +          | +           | 0                        | –                     | +                    | +                     |
| Thermal atomic layer deposition of HfO$_2$                               | 2017[138]          | Si         | –    | +                | 0                    | +          | +           | +                        | +                     | +                    | +                     |
terms of mechanical robustness is required. For Li metal, drop coating polyethylene oxide and ureido-pyrimidonone prevents SEI-forming reactions, homogenizes the charge flow and, most importantly, yielded very promising advances regarding the air stability of Li anodes. A general weakness of processing Li metal anodes is their vulnerability toward ambient atmosphere, so identifying procedures which result in an improved air-stability of Li was a major target. Apart from other concerns, an ambient atmosphere processability of modified Li metal would be a major breakthrough toward Li metal batteries. Moreover, different polymers with good Li conductivity and high Young’s modulus were identified, however their enhancement by flexible components is yet to be done and expected to lead to progress not only for Li metal but also for alloying and conversion anodes. Finally, the importance of simple techniques, such as pressing approaches should not be underestimated since they allow an easy integration into production processes.

On the other hand, some methods have to be considered immature for a large-scale industrial usage in their current state, such as methods involving excessive use of toxic chemicals.

The bottom-up approach for Art-SEI manufacturing involving different methods, i.e., chemical, electrochemical and polymer grafting, electrodeposition, chemical vapor deposition, atomic/molecular layer deposition enables formation of thin-films with precise control over the coating thickness and selectively finds application for all types of anode active materials. Here, a major procedure determining conformity of defect-free plating is the pretreatment of anode material surface aiming at achieving uniform distribution of the surface reactivity especially in the case of porous and/or powdered materials. This involves controlling the number of active sites (oxides, functional groups, defects, impurities, etc.) spread laterally and in depth of the pristine bulk material. Moreover, in each bottom-up method the maximum possible vertical resolution is limited only by the size of applied building blocks (precursor molecules) and, therefore, in some cases (ALD, MLD) achieves the atomic/molecular level. Chemical inertness for the majority of existing liquid media (aqueous/organic solvents), excellent electric conductivity as well as thermal stability of the carbonaceous anode materials lay behind their complete applicability for wet chemistry bottom-up methods, i.e., (electro)chemical and polymer grafting, and electrodeposition. On the other hand, similar to the case of top-down approaches, in bottom-up methods the application of alloying/conversion and particularly Li-metal anode types finds their limitations. In particular, Li metal, whose electric potential is located in extremely negative region (−3.040 V vs SHE), is thermodynamically unstable in aqueous and many organic solvents restricting the application of such wet-chemistry routes for the interfacial engineering. For Si anodes, where the volume alteration induced by lithiation/delithiation process reaches up to 400%, only the methods that guarantee thin, conformal, and elastic Art-SEIs capable of withstanding the numerous deformation acts during repetitive stretches and contractions can be recognized as perspective ones. Furthermore, both the intercalation and alloying/conversion type active materials possessing porous structure dictate strict requirements for all potential Art-SEI fabrication approaches, i.e., uniform distribution of precursor molecules throughout the surface and in depth of the bulk during the whole coating process.

Obviously, the most universally applicable and versatile strategies among all bottom-up techniques are those accomplishing in vapor phase. Indeed, CVD, ALD, MLD methods allow coating of the whole variety of active anode materials. Moreover, by equipping the vapor phase deposition tool with a fluidized bed reactor one can achieve uniform distribution of the operating conditions and precursor concentration throughout the entire reactor volume leading to conformal coating of each individual particle. Furthermore, the deposition of different inorganic-organic hybrid coatings with controlled layer-to-layer composition became possible due to MLD technique. Combining the mentioned above advantages of vapor phase methods with their high-resolution that is in the cases of ALD and MLD reaches the atomic/molecular level, makes these methods the most promising ones.

Different grafting strategies showed selective applicability to different anode materials. Thus, while the alloying/conversion type materials were successfully modified using all grafting approaches, no effective examples of polymer grafting onto intercalation-type materials has been reported. And, vice versa, no successive examples of electrochemical grafting on Li metal was suggested. Moreover, the electrodeposition route was shown to be less effective for alloying/conversion anodes than for carbonaceous and Li-metal materials. In addition, the unique strategy, where the anode material has been electroplated on previously formed and stabilized Art-SEI was elaborated for Li metal. Here, using conventional coin-cell configuration, Li precursor was electro-reduced at the surface of current collector premodified with Art-SEI.

The perspective strategy of Art-SEI on Li metal via ALD method is of special interest as it promises high effectiveness due to precise control over the composition of each individual atomic layer as well as angstrom-scale resolution capability. In this regard, the main challenge is seemed to be in choosing the appropriate coreactant that will be thermodynamically

| Procedure | Year and reference | Anode type | Cost | Time consumption | Environmental issues | Robustness | Scalability | Material & design freedom | Atmosphere sensitivity | Electrochemical success | Overall applicability |
|-----------|-------------------|------------|------|------------------|---------------------|------------|------------|--------------------------|---------------------|----------------------|----------------------|
| Molecular layer deposition of alucone | 2018[183,184] | Li | − | + | − | + | + | + | − | + | + |
| Molecular layer deposition of zircone | 2019[185] | Li | − | + | − | + | + | + | − | + | + |
| Molecular layer deposition of polyurea | 2019[185] | Li | − | + | − | + | + | + | − | + | + |

Table 1. Continued.
stable in the presence of Li surface and at the same time will be sufficiently reactive to interact with ALD precursor. In spite of a few attempts,[190] an obvious lack of examples showing the reliable electrochemical success of Li/[ALD Art-SEI] anodes for LIBs places this research direction among the promising ones.

5. Conclusions and Perspectives

The design of Art-SEIs represents a promising path of solving multiple issues which are currently plaguing the development of next-generation batteries. While the formation of natural SEIs, built up by anode-electrolyte decomposition products, is ceded solely to the electrolyte composition, introducing Art-SEIs opens a wide range of engineering possibilities. This has the potential to immensely facilitate the transition from graphite to the next generations of anodes, such as Si and Li metal. While the natural SEI has demonstrated its positive effect on graphite anodes for decades, its limitations considering the application of alloying and conversion type materials as well as Li metal have also become quite clear. In case of Si, the natural SEI of conventional electrolytes is not capable of withstanding the repeated volume changes and for Li metal, homogeneous nucleation and growth cannot be provided. In both cases, this leads to cycles of SEI formation and destruction, consuming significant electrolyte amounts and severely degrade battery performance. For these classes of anode materials, the fabrication of Art-SEIs provides the opportunity to specifically address the requirements of the certain material. In the case of intercalation-based anodes, such as graphite, these Art-SEIs can provide improved cycling stability and rate performance.

Herein, we have reviewed and compared techniques for the fabrication of such Art-SEIs with the aim to conclude the overall applicability of the different approaches. Art-SEIs are shown to represent an auspicious solution for overcoming problems presently associated with anode materials. In addition to batteries using liquid electrolytes, some examples proved the usefulness of ArtSEIs also for all-solid-state batteries. For a large-scale usage, not only the electrochemical success of the approaches is decisive, but other factors, such as production costs, atmosphere sensitivity and environmental impact have to be taken into account.

The major outcome of our review comprises the systematic multiparameter analysis of various Art-SEI manufacturing approaches in terms of their real-world applicability to different types of the active anode materials. In general, the top-down methods possess excellent scale-up capability and compatibility with most of the anode materials, while the bottom-up routes enable atomic/molecular level resolution with precise control over layer-to-layer composition. For Si anodes, the magnetron sputtering of LIPON thin-film appeared to be the most promising top-down approach. In particular, increased attention must be paid in the future to improving the mechanical reliability, i.e., the flexibility and elasticity of the LIPON layer, to accommodate vigorous volume changes during LIB cycling. The most promising bottom-up methods are polymer grafting with polyacrylic acid, thermal ALD of metal oxides, and MLD of different inorganic-organic hybrid coatings. For Li-metal anodes, various drop-coating routes as well as conventional pressing technique are among the most favorable top-down approaches, while numerous variants of chemical grafting and vapor phase deposition (CVD, ALD, MLD) represent the most effective bottom-up strategies. For carbonaceous intercalation-type anodes typically adopting porous morphologies, only bottom-up methods providing uniform lateral and in-depth coating, i.e., (electro) chemical and polymer grafting, electrodeposition, and thermal ALD are of commercial interest for LIB industry.

In addition, efforts should be made to further develop suitable methods and material combinations to build Art-SEIs that meet specific requirements of high-energy or high-power batteries. In view of energy density, the transition to higher capacity anodes, such as Li and Si, is indispensable. Apart from the desired electron-blocking and ion-conducting behavior, the mechanical properties of the SEI will gain importance to accommodate repetitive volume changes during cycling. The purposeful design of either stiff SEIs that suppress large volume changes, or flexible SEIs that cushion and absorb them, or hybrid composites that simultaneously provide stability and flexibility is required. To reach high power density, other factors will be decisive since the SEI needs to withstand high current densities. The SEI layer must have high intrinsic Li conductivity or a small thickness to avoid large overvoltage under high loads. In addition, there is a need to better understand how high current densities affect degradation and how Art-SEIs must be designed to prevent it. Presently, one of the most promising approaches to deal with high current densities is the development of 3D-structured anodes, breaking down high current densities to lower currents on a large area. In this case, the application of an Art-SEI is not trivial due to the complex geometry and requires further development.

The systematic approach used in this review, aiming at evaluating various Art-SEI manufacturing methods in terms of their real-word applicability, will serve as a practical guide for the further development of advanced battery anodes. The correlation between the specific properties of concrete active anode materials and the most suitable synthesis routes, taking into account fabrication-relevant factors, will be helpful in the identification of promising strategies for the design of the next generation of LIBs.

Acknowledgements

R.G.F. and S.M. contributed equally to this work. This work was supported by the German-Israeli Foundation (GIF) for Scientific Research and Development in the framework of the project “Artificial solid electrolyte interphase developed on a single particle Li-ion anode materials via ALD – formation, modifications and detection” (Grant No. 1-1494-401.10/2019), and by the Planning & Budgeting Committee/Israel Council for Higher Education (CHE), and Fuel Choice Initiative (Prime Minister Office) within the framework of “Israel National Research Center for Electrochemical Propulsion” (INREP 2) and by the Grand Technion Energy Program (GTEP).

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.
Keywords
anode materials, artificial solid-electrolyte interphase, lithium-ion batteries, SEI

Received: April 13, 2021
Revised: May 12, 2021
Published online: June 2, 2021
Roman G. Fedorov finished his Ph.D. in Electrochemistry at The Hebrew University of Jerusalem (Israel) in 2019 under supervision of Professor Daniel Mandler and since that time he has been working at Department of Materials Science and Engineering of Technion-Israel Institute of Technology (Haifa) as electrochemistry scientist. He has a broad range of experimental research expertise: (electro)catalysis, energy storage systems, batteries, capacitors, fuel cells, metal plating, corrosion protection, hydrogen fuel, electrochemical sensors.

Sebastian Maletti received a Diploma degree in Materials Science at TU Dresden (Germany) in 2017 and worked at the Leibniz Institute for Solid State and Materials Research, graduating with a Ph.D. thesis about post-Li battery concepts. In 2020, he started as a postdoctoral fellow at the chair of Inorganic Nonmetallic Materials at TU Dresden, belonging to the working group combinatorial microelectrochemistry. Sebastian’s research interests focus on development of energy storage materials and advanced electrochemical characterization methods.

Christian Heubner graduated from TU Dresden (Germany) as a chemical engineer in 2012 and received his Ph.D. in materials science 2016 under supervision of Professor Alexander Michaelis. He worked as a postdoctoral fellow at the Institute of Materials Science (TU Dresden) and joined the Department of Mobile Energy Storage Systems and Electrochemistry of the Fraunhofer IKTS in 2019. Christian’s research interests are mainly focused on electrochemistry, modeling, and development of materials for energy storage.

Alexander Michaelis received his degree in Physics and Ph.D. in Electrochemistry from the University of Düsseldorf in Germany. Since 2004, he is president of the Fraunhofer Institute for Ceramic Technologies and Systems IKTS and holds the chair of Inorganic Nonmetallic Materials at TU Dresden. He is Fellow of the American and the European Ceramic Society. In 2019 he was elected President of the German Ceramic Society.
Yair Ein-Eli is a professor at the Technion’s Materials Science and Engineering Department. He graduated from Bar-Ilan University (1995) and joined the Department of Materials Engineering at the Technion in 2001, after serving 3 years as the VP of R&D of Electric Fuel Ltd. (Israel). Before that, he was a postdoctoral fellow (1995–1998) at Covalent Assoc. Inc. (MA, USA). Current research projects of Yair in the field of power sources involve advanced materials for Li-ion batteries, alkaline batteries, metal-air cells and fuel cells. He is also engaged in research and development of electroplating methods, and corrosion inhibitors studies.