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Review

Pre-Lithiation Strategies for Rechargeable Energy Storage Technologies: Concepts, Promises and Challenges

Florian Holtstiege [1], Peer Bärmann [1], Roman Nölle [1], Martin Winter [1,2,*] and Tobias Placke [1,*]

[1] University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstraße 46, 48149 Münster, Germany; florian.holtstiege@uni-muenster.de (F.H.); baermann@uni-muenster.de (P.B.); roman.noelle@uni-muenster.de (R.N.)

[2] Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich, Corrensstraße 46, 48149 Münster, Germany

* Correspondence: martin.winter@uni-muenster.de or m.winter@fz-juelich.de (M.W.); tobias.placke@uni-muenster.de (T.P.); Tel.: +49-251-83-36826 (M.W.); +49-251-83-36031 (T.P.)

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Abstract: In order to meet the sophisticated demands for large-scale applications such as electro-mobility, next generation energy storage technologies require advanced electrode active materials with enhanced gravimetric and volumetric capacities to achieve increased gravimetric energy and volumetric energy densities. However, most of these materials suffer from high 1st cycle active lithium losses, e.g., caused by solid electrolyte interphase (SEI) formation, which in turn hinder their broad commercial use so far. In general, the loss of active lithium permanently decreases the available energy by the consumption of lithium from the positive electrode material. Pre-lithiation is considered as a highly appealing technique to compensate for active lithium losses and, therefore, to increase the practical energy density. Various pre-lithiation techniques have been evaluated so far, including electrochemical and chemical pre-lithiation, pre-lithiation with the help of additives or the pre-lithiation by direct contact to lithium metal. In this review article, we will give a comprehensive overview about the various concepts for pre lithiation and controversially discuss their advantages and challenges. Furthermore, we will critically discuss possible effects on the cell performance and stability and assess the techniques with regard to their possible commercial exploration.

Keywords: pre-lithiation; prelithiation; pre-doping of lithium ions; lithium ion batteries; post-lithium ion batteries; active lithium loss; solid electrolyte interphase; Coulombic efficiency

1. Introduction

A major strategy to tackle the sophisticated challenges associated with the increasing shortages of non-renewable (fossil) resources and the environmental impact of their combustion, i.e. (air-) pollution and global warming, is the integration of clean and highly efficient energy storage technologies based on renewables (wind power, solar energy, etc.) into different energy sectors, particularly for transportation and grid storage. Nowadays, the most feasible concept for these applications clearly points to rechargeable battery technologies. Lithium ion batteries (LIBs) are the state-of-the-art technology for various applications, i.e., they do not only dominate the small format battery market for portable electronics but have also been successfully introduced as the technology of choice for electro-mobility and for grid storage [1–4].

Currently, the development of LIBs is dominated by the run for further performance improvements, most likely by enhancements of the specific energy (gravimetric energy density (Wh kg^{-1})) and volumetric energy density (Wh L^{-1}), e.g., in order to further boost the driving range of electric vehicles [2,3,5,6]. Besides LIBs, there also exists a variety of different promising battery technologies that, depending on their respective characteristics, might be suitable. These alternative battery systems, the so-called "post-lithium ion batteries" (PLIBs), including e.g., metal/sulphur, metal/air or metal/oxygen, or so-called "post-lithium technologies" (battery systems without lithium) that are based on alternative single (Na^+, K^+) or multivalent cations (Mg^{2+}, Ca^{2+}), are recently intensively studied by various academic researchers [7–11].

The useable energy content of LIBs and other types of batteries over a certain number of charge/discharge cycles or over a certain lifetime is typically reduced by sophisticated degradation mechanisms or parasitic reactions, often simply referred to as "aging mechanisms" [12–14]. In general, there are two types aging mechanisms, i.e., those leading to the loss of the active species, e.g., Li^+ for LIBs or Na^+ for sodium ion batteries, etc., capacity fade) and those which do not change the active species content of the cell but change other parameters, such as the internal resistance (power fade). For LIBs, it is well-known that active lithium loss (ALL) is attributed to lithium consuming parasitic reactions such as the formation of the solid electrolyte interphase (SEI) [15–20] at the negative electrode (anode), active material loss or irreversible lithium metal plating [20]. In particular, high surface area carbons and graphites result in more SEI formation and thus higher ALL [21–24]. Moreover. high-capacity LIB anode materials, such as silicon (Si) and tin (Sn), suffer from ongoing active lithium loss due to continuous SEI breakage and re-formation, as a result of their large volume changes upon lithiation/de-lithiation [20,25–27]. This, in turn, leads to rapid capacity fading of the cell, that also do affect the positive electrode performance [28].

In order to compensate the loss of active lithium, various "pre-lithiation" methods have been developed that result in an increased reversible capacity and, consequently, in a higher gravimetric energy or volumetric energy densities [29–32], as schematically illustrated in Figure 1. The term "pre-lithiation," in some publications also named as "prelithiation" or "pre-doping of lithium ions," describes the addition of lithium to the active lithium content (=reversibly transferable lithium ions between positive and negative electrode) of a LIB prior to battery cell operation [20]. In a "standard" lithium ion cell set-up, the active lithium content is stored within the positive electrode (cathode), e.g., $LiNi_xMn_yCo_{1-x-y}O_2$, prior to battery cell operation (Figure 1a). During the 1st charge of the cell (=formation cycle), a certain amount of active lithium is typically lost (ALL), mostly by SEI formation at the negative electrode, depending on the electrode active material [20], so that the remaining active lithium content is reduced after the 1st charge/discharge cycle. One major strategy to overcome this issue is to store a certain amount of active lithium in the negative electrode by pre-lithiation prior to charge/discharge cycling (Figure 1b). This (partially) compensates for the ALL and thus leads to an increased active lithium content after the 1st cycle and, thus, to an enhanced remaining cell energy. However, the pre-lithiation concept is not limited to the negative electrode, it is also possible to use pre-lithiation additives inside the positive electrode (Figure 1c). In the majority of cases and independent from the pre-treatment concept, pre-lithiation is conducted to compensate the 1st cycle active lithium loss, attributed mainly to SEI formation. This increases the remaining amount of active lithium inside the cell during ongoing charge/discharge cycling, leading to an increased reversible capacity (Figure 1b,c) and resulting in an increased energy density . In most studies, this is shown by a drastically increased Coulombic efficiency of the 1st cycle as well as an increased discharge capacity over a few number of cycles (Figure 2) [31,33,34]. However, it is very important to note that the degree of pre-lithiation has to be adjusted with a high accuracy. Otherwise, an over-lithiation could lead to an excess of lithium, thus lithium metal plating on top of the negative electrodes surface, resulting in safety hazards during operation [35–37].

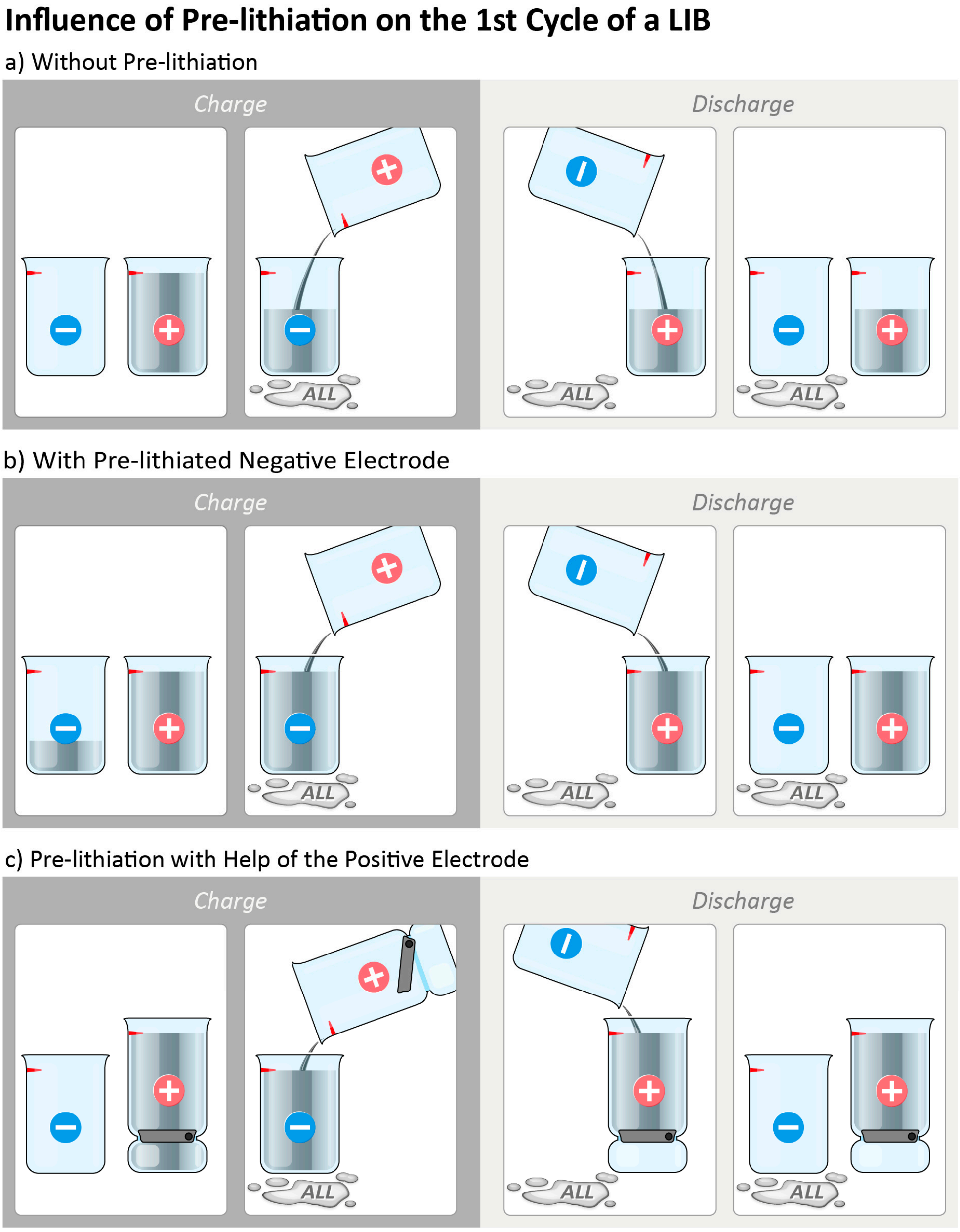

Figure 1. Schematic illustration of (**a**) active lithium loss (ALL) in the 1st charge/discharge cycle in a lithium ion cell and concepts for reducing the active lithium loss by pre-lithiation, i.e., (**b**) by pre-lithiation of the negative electrode (−) or (**c**) by pre-lithiation with help of the positive electrode (+).

Another important issue is the amount of inactive material, which has to be added in order to perform pre-lithiation. In the worst-case scenario, this inactive mass and volume leads to decreased energy densities, which offset the energy density gain attributed to pre-lithiation. In the optimal case, just lithium ions (and electrons) are added during pre-lithiation. In addition, this is also the reason why a "larger" positive electrode, with respect to anode/cathode capacity balancing, is not useful [38]. Moreover, in view of maximizing the energy density of LIBs, the maximum positive electrode capacity is limited by the electrode coating thickness and porosity due to kinetic factors [39]. A decisive factor in the process of battery cell manufacturing is the time required to perform the pre-lithiation and the costs triggered by this extra preparation step. Furthermore, it should be noted that pre-treatment is not only limited to LIBs, e.g., pre-sodiation in sodium ion batteries or other pre-treatment strategies for alternative battery technologies are also possible (Figure 2) [34].

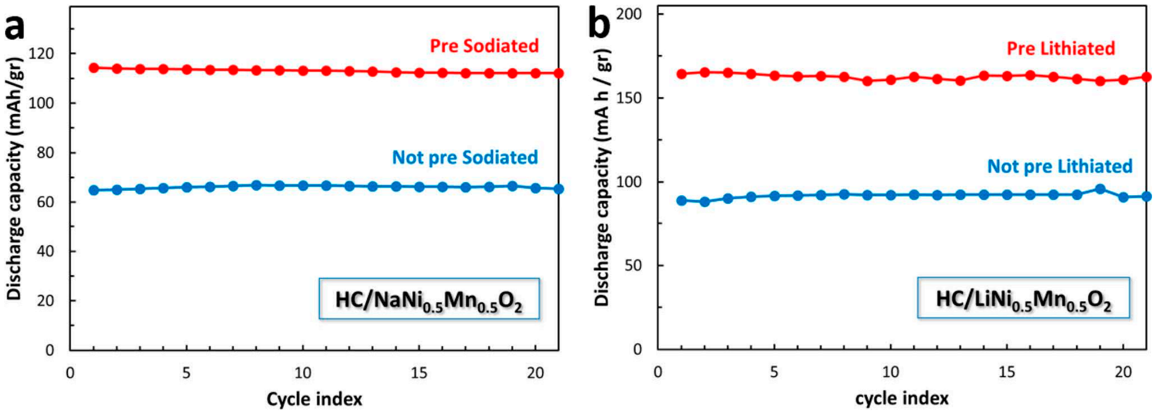

Figure 2. Effect of negative electrode pre-treatment on the discharge capacity of sodium and lithium ion cells. (**a**) Hard carbon(HC)/$NaNi_{0.5}Mn_{0.5}O_2$ (**b**) Hard carbon/$LiNi_{0.5}Mn_{0.5}O_2$. Reproduced with permission from [34] Copyright 2016, American Chemical Society.

Beyond this, pre-lithiation can have some further advantages, which are at first glance not as obvious as the increased remaining reversible capacity after the 1st cycle. For example, pre-lithiated electrodes can show a better rate capability than not pre-lithiated electrodes, attributed to a decreased impedance [40–42]. Furthermore, pre-lithiation of silicon (Si)-based anodes can lead to a pre-volume-expansion, which decreases the relative volume change of Si during cycling, causing a reduced cracking and pulverization of Si and may enhance the mechanical electrode stability [43]. In addition, pre-lithiation of Si causes a decrease in the elastic and shear moduli and an increase of the diffusion coefficient of lithium, reducing the stress in comparison to pristine Si and leading to an improved cycle performance [44]. Finally, it may also be possible that pre-lithiation and the resulting SEI formation triggered by some techniques supersede the formation cycles of LIBs [45]. However, systematic investigations on the SEI layer characteristics and stability, formed by pre-lithiation, are needed to prove this statement. Hypothetically, pre-lithiation in certain electrolyte formulations (e.g., in the presence of electrolyte additives [15,46,47]), which are known to have a beneficial effect on SEI formation and stability but which are not favourable in contact to the positive electrode, may be useful as well.

Overall, there is a variety of techniques and methods known for pre-lithiation, including chemical and electrochemical pre-lithiation, pre-lithiation by direct contact to lithium metal or the pre-lithiation with help of electrode additives. In this review, these techniques and methods for lithium ion batteries are comprehensively explained and compared to each other, with particular focus on possible commercial exploration. Furthermore, the use of pre-lithiation within lithium-ion capacitors (LICs) and post-lithium ion batteries (PLIBs) will be discussed in detail.

2. Pre-Lithiation Concepts for the Negative Electrode in Lithium Ion Batteries

This chapter reports on the different techniques and methods in order to pre-lithiate the negative electrode of LIBs. The reader should note that pre-treatment of the negative electrode is the most utilized method in academic studies so far to perform the pre-lithiation of lithium ion cells.

2.1. Concepts for Chemical Lithiation Using Active Reactants

First investigations with the intent to reduce the active lithium loss (ALL), attributed to SEI formation were conducted by Scott et al. in 1998 [48]. They reported a chemical treatment of carbon black-based negative electrodes with *n*-butyl lithium (*n*-BuLi) prior to cell construction and were able to show that there is a thick film (SEI) formed on top of these model electrodes. As a result of the treatment, the irreversible capacity was reduced by a small amount ($\approx$340 mAh g^{-1} vs. $\approx$265 mAh g^{-1}) and the open circuit voltage of the produced lithium metal/carbon black cell was a bit lower than without the treatment (≈2.70 V vs. ≈2.96 V). However, no lithium ion insertion into carbon black was observed due to the relatively high redox potential of *n*-BuLi (≈1 V vs. Li/Li^+). Nevertheless, chemical treatment with *n*-BuLi created interfacial conditions, similar to the exposure to an electrolyte at a low electrode potential, which eliminated easily reducible surface groups such as oxide or carbonyl groups that would otherwise lead to enhanced irreversible capacity. Furthermore, it was also expected that the strong basic nature of *n*-BuLi causes a replacement of reactive protons at the carbon surface by lithium ions. However, the formed film occurred to be thicker and more brittle than an electrochemically formed SEI, especially with prolonged *n*-BuLi treatment. Thus, the authors found that the emerging damage to the electrodes during cell operation offsets the advantage of a smaller irreversible capacity by far [48].

Some years later, Tabuchi et al. used a Li-organic complex solution consisting of naphthalene and metallic lithium dissolved in butyl methyl ether, in order to pre-lithiate silicon monoxide (SiO)-based negative electrodes [49]. The open circuit potential drastically shifted to less noble values and became stable after 72 h of immersion time (≈0.21 V vs. Li/Li^+). The degree of pre-lithiation could be controlled by the immersion time and a maximal de-lithiation capacity of ≈670 mAh g^{-1} was reached after 72 h [49].

The mechanism of chemical pre-lithiation was proposed to work as follows: The lithium ions are dissolved in butyl methyl ether due to the strong electron affinity of naphthalene, resulting in the formation of a naphthalene radical anion. Thereafter, the electron of the radical anion is transferred to the SiO material, recovering the initial state of naphthalene and resulting in a pre-lithiation (=lithium ion uptake) of the SiO active material (formation of Li_xSiO). Finally, the inserted lithium ions can compensate the active lithium loss, e.g., caused by SEI-formation, which leads to a reduction of the first cycle capacity loss. Naphthalene served as an electron-transfer catalyst in this mechanism [49].

One year later Tabuchi et al. presented the pre-lithiation of lithium titanate (LTO, $Li_4Ti_5O_{12}$) with the same mechanism but different solvents (butyl methyl ether and dimethoxyethane). In summary, they reported that the pre-lithiation of $Li_4Ti_5O_{12}$ (complete pre-lithiation within ≈3 h) is a much faster process than the lithiation of SiO. However, they also found out that the utilized solvent has a strong influence on the actual rate constant of the reaction [50].

Veluchamy et al. used a thermochemical approach in order to reduce the irreversible capacity of a SiO/C composite negative electrode. A mixture of SiO and lithium hydroxide (LiOH) was treated at 550 °C followed by a ball-milling step with graphite. With help of X-ray diffraction analysis, they could confirm the presence of Li_4SiO_4. A quarter of the SiO was reduced to Li_4SiO_4, which resulted in a smaller irreversible capacity (Coulombic efficiency rise of ≈11%) and improved capacity retention after 100 cycles but also in a lower reversible capacity, as Li_4SiO_4 acts as an electrochemically inactive species [51].

Furthermore, it was recently shown that it is also possible to use thermal evaporation of lithium (Li) metal in order to pre-lithiate the negative electrode. With help of this method, high pre-lithiation degrees can be achieved [52].

In conclusion, by using optimized reaction conditions, it is possible to achieve an effective pre-lithiation of the negative electrode with help of chemical methods. Additionally, the amount of pre-lithiation can be adjusted relatively well by the reaction time. However, the utilized chemicals and reaction conditions seem to be problematic in handling due to their rather high reactivity, resulting in safety concerns. Especially, the incorporation into a commercial production process for active material, electrode and/or cell fabrication for LIBs is hampered by these facts.

2.2. Concepts for Electrochemical Pre-Lithiation

The concept of electrochemical pre-lithiation is a relatively simple method in order to produce pre-lithiated negative electrodes. Actually, it does not differ much from the commercially established process of formation of a LIB, except that Li metal is used in most cases as opposite electrode for the lithiation process of the designated insertion negative electrode. The Li metal electrode and the negative electrode are electronically isolated from each other and the negative electrode is charged with a low current or electrical shorting in order to perform lithiation. This process can be repeated for several charge/discharge cycles, for a defined period of time or until the electrode reaches a defined potential [30,34,53,54]. However, the electrochemical pre-lithiation process often requires a re-assembling step of the pre-lithiated negative electrode into the LIB cell, which increases the expenditure and reduces the possibility to use this method in a commercial way. Nevertheless, there are some approaches to circumvent cell re-assembly. One possibility is to use the reference electrode of a three-electrode cell set-up to pre-lithiate the negative electrode [55]. However, for commercial state-of-the-art two-electrode cell designs it is not very practical to add an extra Li metal electrode into the cell. An exception is the pre-lithiation method developed by JM Energy in Japan, which is used in the fabrication of commercially available lithium-ion capacitors (LICs). Further details of the cell design are pointed out in Chapter 4.

Another opportunity to implement the electrochemical pre-lithiation into the commercial battery cell manufacturing process was proposed by Kim et al. (Figure 3) [30].

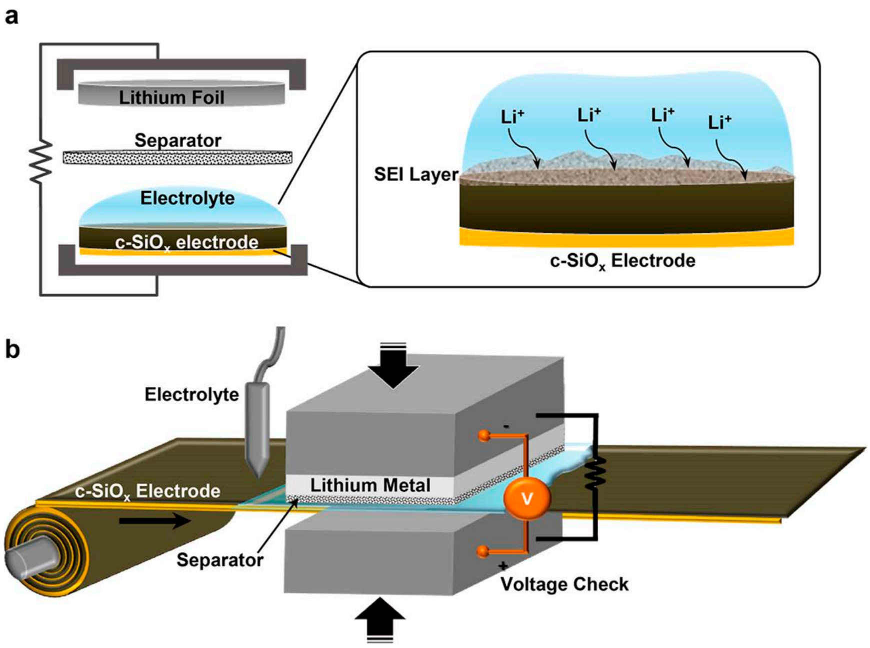

Figure 3. (**a**) Graphical illustration of the pre-lithiation process of a c-SiO$_x$ negative electrode and (**b**) its scalable roll-to-roll process scheme. Reproduced with permission from [30] Copyright 2016, American Chemical Society.

They conceived a scalable roll-to-roll process based on external shorting with Li metal foil for the pre-lithiation of carbon-coated silicon monoxide (c-SiO$_x$; x $\approx$ 1). In this setup, there is no contact between the silicon monoxide electrode and the Li metal electrode and the roll anode is moved through a bath of electrolyte during pre-lithiation. However, it is important to notice that this process has been just proposed as a manufacturing route. To the best of our knowledge, the practical realization of this process has not been realized by Kim et al. until now. Likely, because there are several problems to overcome before it is possible to incorporate this process into a commercial battery cell manufacturing process, for example the evaporation of the electrolyte solvents, the high reactivity of the Li metal foil or the problem of high surface area lithium (HSAL) formation. However, Kim et al. also presented that the external shorting with Li metal enables a delicate control on the degree of pre-lithiation (Figure 4), which is of high importance, especially with a focus on anode/cathode capacity balancing [28,56], SEI formation and the prevention of lithium metal plating at the negative electrode [30].

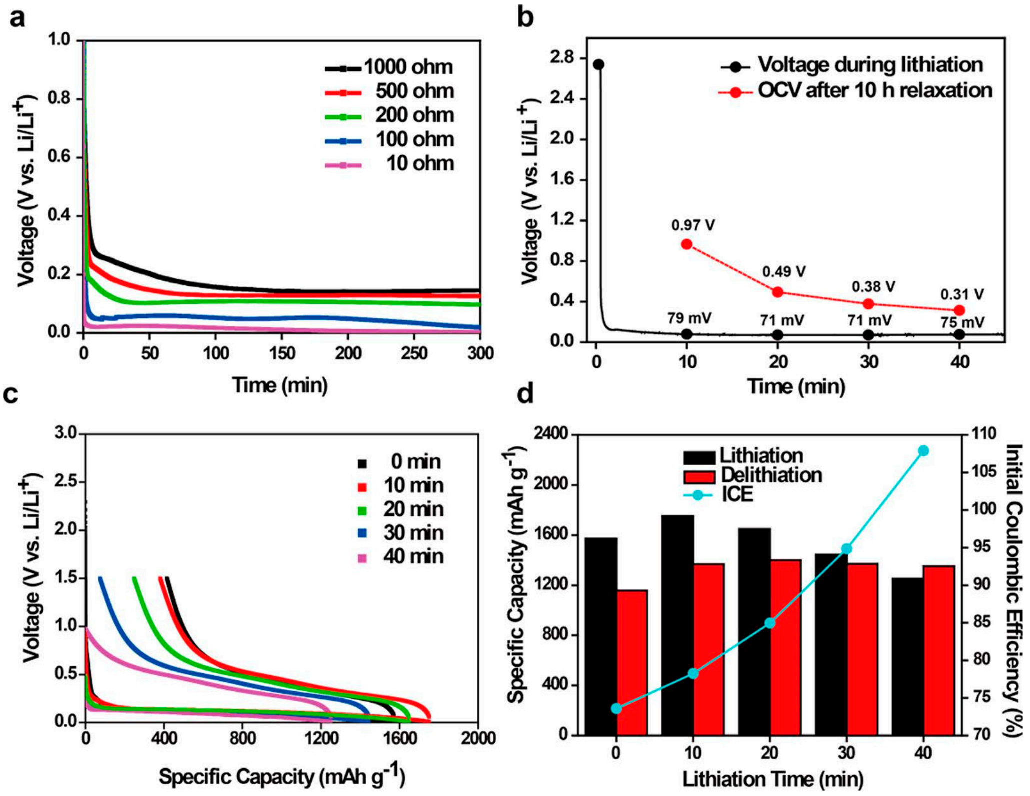

Figure 4. Controlling the degree of pre-lithiation. (**a**) Lithiation potential profiles with different resistances incorporated in the external circuit. (**b**) Potential profile during the external shorting with 100 Ω included in the circuit and open circuit potentials (OCPs) after 10 h of relaxation at different pre-lithiation points. (**c**) The 1st cycle potential profiles of SiO_x with different pre-lithiation durations. (**d**) Comparison of the specific capacity and initial Coulombic efficiency after different pre-lithiation times. Reproduced with permission from [30] Copyright 2016, American Chemical Society.

Figure 4 displays that the degree of pre-lithiation can be controlled by the resistance (Figure 4a) and by the pre-lithiation time (Figure 4c,d). Furthermore, it can be seen that for certain negative electrode materials, the potential cannot be used for an exact determination of the degree of pre-lithiation (Figure 4b), as e.g., SiO_x shows a plateau at ≈0.07 V vs. Li/Li^+ during lithiation. Due to this plateau, the difference in the potentials of different pre-lithiation times becomes only visible after a relaxation time of 10 h. Of course, this is different for other active materials like e.g., hard carbon, which show a sloping potential profile due to the amorphous nature of the material [57]. With the help of electrical shorting, it is possible to increase the first cycle Coulombic efficiency of SiO_x from ≈74% to ≈95% within only 30 min using a resistor of 100 Ω. Finally, the higher Coulombic efficiency results in an increased remaining gravimetric capacity within full cells (165 mAh g^{-1} vs. 106 mAh g^{-1}, based on the mass of the cathode material), leading to an enhanced energy density. Furthermore, the average CE is slightly increased from 98.8% to 99.0%. After 100 cycles, the pre-lithiated full cells still deliver a higher capacity (1.44 mAh cm^{-2}) than the full cells with pristine negative electrodes (1.17 mAh cm^{-2}). However, the capacity fading of the pre-lithiated full cell is slightly enhanced (capacity retention after 100 cycles: pre-lithiated = 61%; pristine = 77%) [30].

In order to overcome the problem of using Li metal for electrochemical pre-lithiation, Zhou et al. presented a novel method, replacing the Li metal with a copper (Cu) pit corrosion electrode (Figure 5) [58].

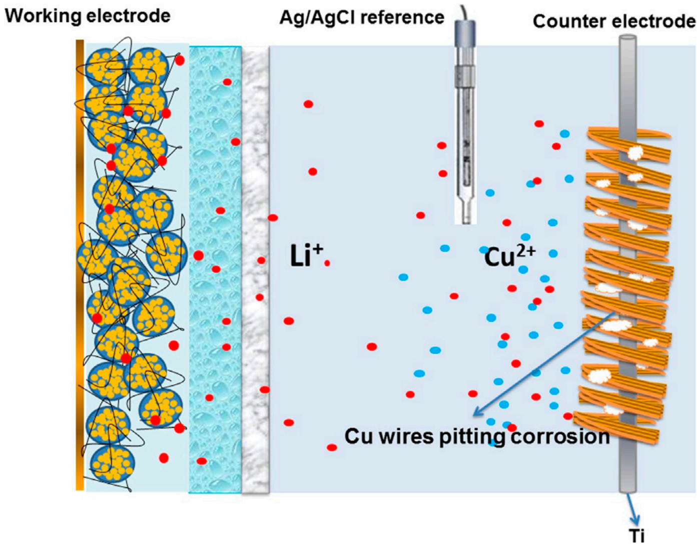

Figure 5. Principle of pre-lithiation of a Si-based working electrode by using an electrolytic cell with a copper pitting corrosion type anodic half-cell in aqueous electrolyte (0.5M Li_2SO_4) and a LIB type cathodic half-cell in gel polymer electrolyte (GPE) soaked in 1M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte (3:7 *v*/*v*). Reproduced with permission from [58] Copyright 2015, Wiley-VCH.

They propose their method as environmentally friendly, well-controlled, safe and potentially cheap. In their study, the cell for pre-lithiation consists of a Cu pitting corrosion type anodic half-cell with 0.5 M Li_2SO_4 aqueous electrolyte and a Si type cathodic half-cell in gel polymer electrolyte. The two half-cells are separated by a LISICON film. Within this set-up, the Cu electrode works as counter electrode instead of a lithium ion donating Li metal electrode. The following reaction takes place during the pre-lithiation process (Equation (1)), whereby Cu is used as electron-donating source and the lithium salt inside the electrolyte as lithium ion source [58].

$$x\mathrm{Li}^+ + (x/2)\,\mathrm{Cu} + \mathrm{Si} \rightleftharpoons \mathrm{Li}_y\mathrm{Si} + (x-y)\mathrm{Li} + (x/2)\,\mathrm{Cu}^{2+} \quad (1)$$

There are several claimed advantages of the method: (1) The usage of a lithium salt instead of Li metal decreases the cost for pre-lithiation; (2) the lithium salt containing solution is environmentally friendly, non-toxic and chemically stable; (3) the only by-product ($CuSO_4$) can be easily recycled. However, there are also some disadvantages: (1) The LISICON film is relatively expensive; (2) there is a high overpotential (≈0.3 V) during pre-lithiation due to the relatively long Li^+ diffusion pathway in this cell set-up, which potentially triggers high surface area lithium (HSAL) formation; (3) the question remains if this technique can be up-scaled [58].

In conclusion, the concept of electrochemical pre-lithiation enables the possibility to perform pre-lithiation in a well-controlled manner, i.e., the degree of pre-lithiation can be easily controlled. This is very important for the usage of pre-lithiated negative electrodes in LIBs with respect to anode/cathode capacity balancing and related safety issues such as Li metal plating at the negative electrode. Furthermore, because of the similarity of the electrochemical pre-lithiation process to the formation cycle(s) of a LIB, it can be assumed that the formed SEI layer shows similar beneficial properties as the SEI layer, which is formed during the first formation cycle(s) in a commercial LIB. However, the main disadvantages, which also inhibit the usage of electrochemical pre-lithiation in the commercial manufacturing of LIB cells, are the required re-assembly of the cell after pre-lithiation and the use of Li metal as lithium ion source. Nevertheless, besides academic studies, also several companies are working on the electrochemical pre-lithiation of the negative electrode, especially on the up-scaling of this technique, like Nanoscale Components Inc. (Hudson, NY, USA) in cooperation with

3M (St. Paul, MN, USA). Nanoscale Components Inc. developed a roll-to-roll pre-lithiation process, comparable to the process proposed by Kim et al. [30,59–61]. Here also an electrochemical bath of non-aqueous electrolyte is utilized in order to perform the pre-lithiation. In contrast to the proposed process by Kim et al. pulsed oxidation and reduction currents are applied to avoid HSAL formation and the setup is suitable for pre-lithiation of double-sided coated roll electrodes. However, to the best of our knowledge there is no information about the fact, if the process is used in the manufacturing process of commercial batteries so far. Nevertheless, this demonstrates the importance of electrochemical pre-lithiation for the possible commercial usage of pre-lithiation. Especially, roll-to-roll processes for electrode pre-treatment might rather simple be implemented into a commercial manufacturing process, thus, facilitating the upscaling of this technique.

2.3. Pre-Lithiation by Direct Contact to Lithium Metal

An alternative possibility to realize the pre-lithiation of negative electrodes is to create a direct (electrical) contact between the negative electrode and Li metal in the presence of electrolyte. Under these conditions, the potential difference between Li metal and the (partly-lithiated) active material of the negative electrode leads to a flow of electrons in precisely this direction. In simultaneous compensation, lithium ions from Li metal are released into the electrolyte. In order to obtain charge neutrality, lithium ions of the electrolyte are intercalated/inserted into the active material of the negative electrode (Figure 6) [62].

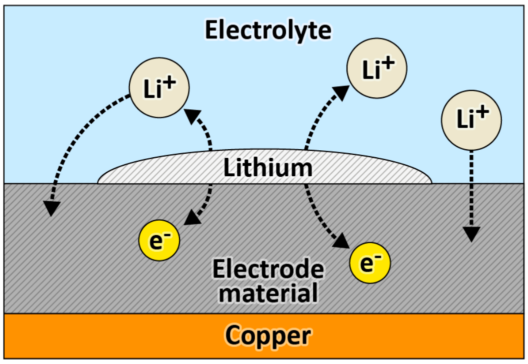

Figure 6. Schematic illustration of the pre-lithiation process by direct contact to Li metal.

One example, where pre-lithiation was carried out via the direct contact with Li metal, was reported by Liu et al. in 2011. They used a Li metal foil to pre-lithiate Si nanowires. Thereby, the Li foil was pressed on top of the Si nanowire-based electrode to create a direct contact (Figure 7). With this relatively easy method, ≈50% of the total capacity of the Si nanowires could be pre-lithiated (charged) within ≈20 min into the electrode [63].

Because of the low standard redox potential of Li metal (−3.04 V vs. SHE) and thus its high reactivity, [8] this method can be easily transmitted to other active materials and has already been reported for e.g., hard carbon [64], Si/graphene oxide composite [65], carbon/MoS_2 [66] negative electrodes, etc. In all cases a drastically increased 1st cycle Coulombic efficiency could be observed. In general, the cost factor can be stated as the major advantage of using rather thick Li metal foil (≈100–200 μm) in comparison to Li metal powder, as pre-lithiation agent. However, in case of Li metal foil, it is more challenging to control the degree of pre-lithiation. Furthermore, the Li metal foil must be removed prior to cell assembly, thus this technique seems to be relatively difficult to be implemented into the commercial battery cell manufacturing process.

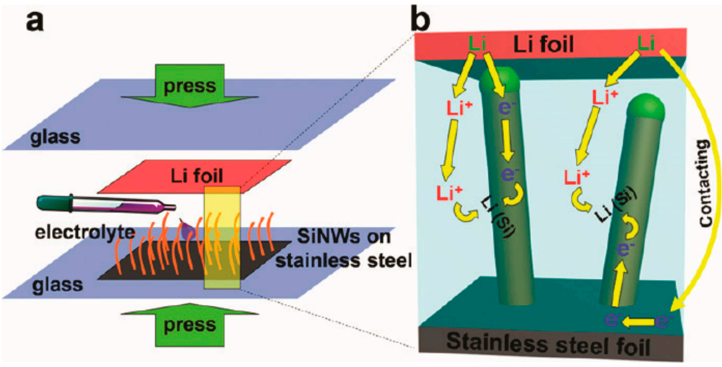

Figure 7. Schematic diagrams showing (**a**) the pre-lithiation of Si nanowires (SiNWs) on stainless steel foil and (**b**) the internal electron and Li^+ pathways during the pre-lithiation. Two possible electron pathways are shown in (b). Electrons can flow directly into the SiNW if the nanowire tip contacts the Li foil, or the electrons can flow across the contacting point of Li foil and stainless-steel foil and enter the SiNW through the bottom. Reproduced with permission from [63] Copyright 2011, American Chemical Society.

In 2005 Jarvis et al. in cooperation with FMC-Lithium Co (Philadelphia, PA, USA). introduced the use of stabilized Li metal powder (SLMP) to pre-lithiate the negative electrode of a LIB, in order to either compensate the irreversible capacity (Coulombic efficiency increase from ≈77.9% to ≈95.4%) or to produce a fully lithiated negative electrode, which in turn can be combined with a non-lithiated positive electrode like V_6O_{13} or LiV_3O_8 [67,68].

Meanwhile, the pre-lithiation with SLMP is one of the most reported pre-lithiation methods in literature. The size of the SLMP particles ranges from ≈10–100 µm. The stabilized Li metal powder (Figure 8) can be handled safely in dry air, in contrast to "normal" (non-treated) Li metal powder which is only stable under inert gas conditions [67]. Other Li products producing companies like Rockwood Lithium (now: Albemarle Corporation, Charlotte, NC, USA) have developed their own Li powder, i.e., coated lithium powder (CLiP) [69,70].

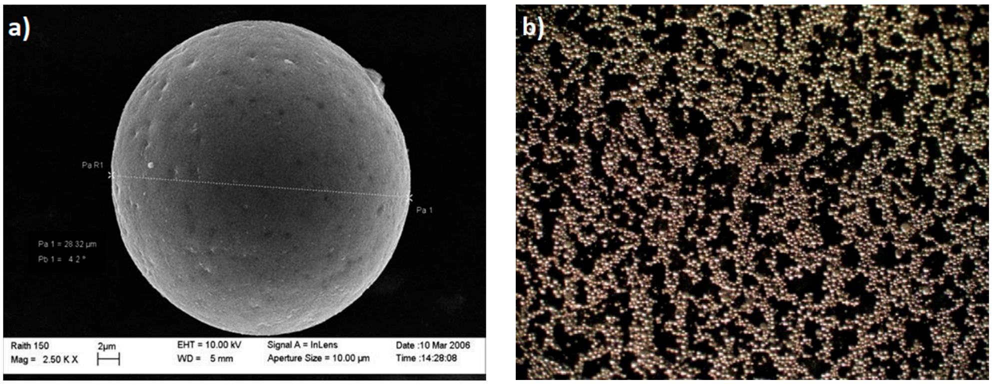

Figure 8. (**a**) SEM image of a single spherical SLMP particle; (**b**) microscopic image of sprayed SLMP on a pre-fabricated negative electrode sheet. Reproduced with permission from [71] Copyright 2011, Elsevier.

The improved dry-air stability of SLMP is attributed to a protective layer of Li_2CO_3 around the Li particles [71,72]. Consequently, the SLMP particles must be activated prior to pre-lithiation by applying pressure (Figure 9) [31,33,71]. This pressure activation cracks the Li_2CO_3 shell and enables the direct contact between Li metal, electrolyte and electrode active material.

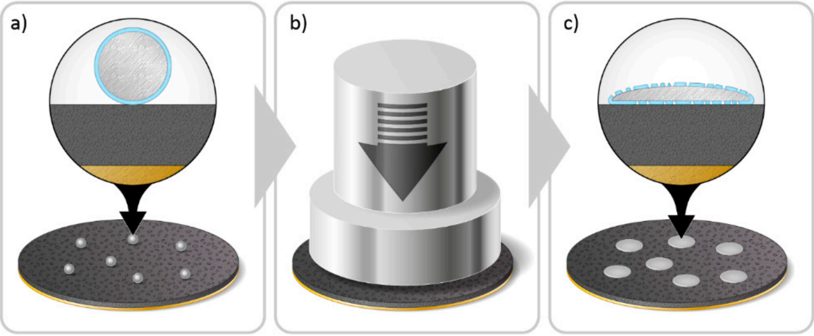

Figure 9. Schematic illustration of the pressure induced activation process of stabilized Li metal powder (SLMP): (**a**) Application of SLMP on electrode surface; (**b**) Pressure induced activation; (**c**) Electrode surface after activation.

There are different methods to perform pre-lithiation with SLMP. One route is to spread out the particles on the electrode surface with a subsequent pressing in order to activate the SLMP as described above [33,45,73]. Another possibility is to prepare a SLMP/solvent (e.g., hexane) suspension, which is then dropped onto the surface of the electrode, again followed by a compression of the electrode after the solvent is evaporated [31,74]. It is also possible to create suspensions of SLMP in toluene or xylene, respectively. These suspensions can be homogeneously distributed onto the electrode surface with help of an airbrush [71,75].

The above-described methods are all conducted by direct application of SLMP on the electrode surface. Another approach would be the addition of SLMP into the electrode paste during processing, which in turn would prevent the above-described extra step during battery cell manufacturing. However, SLMP is not stable in contact with most of the processing solvents used in the industrial electrode preparation, e.g., *N*-methyl-2-pyrrolidone (NMP), etc. [67]. For this reason, other strategies have been developed in order to use SLMP directly within the electrode slurry. The first strategy was based on a styrene butadiene rubber–polyvinylidene difluoride (SBR-PVdF) dual binder approach for graphite anodes developed by Wang et al. [76]. Therefore, in a first step, graphite and PVdF were mixed in NMP to form an electrode slurry. Afterwards, a thick layer was cast onto Cu foil and subsequently scraped off after drying. In the following, the PVdF coated graphite was ground and mixed with SLMP. In the next step, an electrode slurry based on SBR was prepared and cast onto Cu foil again, whereby toluene was used as solvent, which did not react with the SLMP. With this approach, the SBR-PVdF based graphite electrodes (Figure 10) showed comparable mechanical properties to pure SBR binder-based electrodes and a cell performance comparable to pure PVdF binder based electrodes [76].

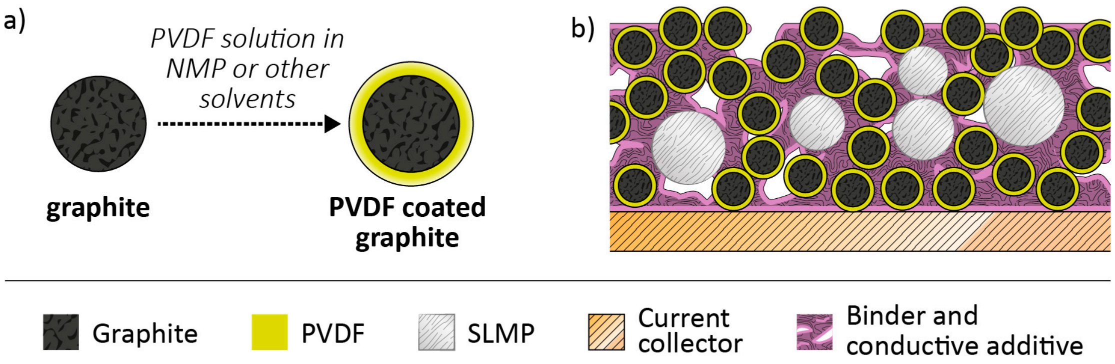

Figure 10. (**a**) Schematic model of PVdF coated graphite particles. (**b**) Schematic model for a SLMP incorporated graphite negative electrode, based on a SBR-PVDF dual binder approach. Adapted with permission from [76] Copyright 2013, Royal Society of Chemistry.

By using toluene or xylene as solvent for the electrode slurry preparation, in combination with SLMP, an additional problem arises: Due to the low density of SLMP, the dispersion is not stable and the particles tend to float to the surface of the solvent, leading to an inhomogeneous distribution of SLMP particles within the electrode. This can be slightly improved by addition of higher percentages of SBR (from 1 to 5 wt %). However, the distribution of SLMP within the electrode is still not homogeneous enough for practical applications. A possible solution is the addition of compounds, which stabilize the dispersion and lead to a good distribution of SLMP particles within the electrode, e.g., the use of polystyrene (PS) (0.5% PS) [77]. Nevertheless, the advantage of adding the SLMP directly into the electrode slurry does not compensate for the fact that the complete electrode fabrication has to take place under dry room conditions, which again increases the cost of manufacturing. In particular, it has to be kept in mind that the commercial preparation of graphite anodes is performed using an aqueous processing route, i.e., using carboxy methylcellulose (CMC)-SBR-based binders. Furthermore, also the state-of-the-art preparation route for Si-containing anodes is based on aqueous processing using mostly polyacrylic acid (PAA)-based binders [78].

In comparison to pre-lithiation with Li metal foil, also by use of SLMP, a wide variety of active materials has already been reported for pre-lithiation, e.g., Fe_2O_3 [79], GeO_x [80], TiO_2 [81], etc. After pre-lithiation, the Coulombic efficiency for these materials is significantly increased, i.e., for GeO_x from ≈66% to ≈85.5% and for Fe_2O_3 from ≈70% to ≈99.5%. Finally, the enhanced Coulombic efficiency results in an increased specific capacity of full cells, e.g., the Coulombic efficiency of SiO electrodes can be increased from ≈48% to ≈90% and, as a result, this full cell shows a remarkably enhanced reversible capacity of ≈110 mAh g^{-1} even after 100 cycles in comparison to a pristine cell which starts at a capacity of ≈80 mAh g^{-1} and drops down to ≈50 mAh g^{-1} after 100 cycles [33]. SLMP can also be used inside all-solid-state LIBs as shown by Yersak et al. [82]. Therefore, they incorporated SLMP into a Si-Ti-Ni composite negative electrode powder prior to cell fabrication and combined this negative electrode with a high capacity FeS+S positive electrode. They could demonstrate a gravimetric energy density of 225 mWh g^{-1} (electrode level), suggesting that an all-solid-state battery can achieve acceptable energy densities, without using Li metal foil as negative electrode.

To conclude, the main advantage by using SLMP is that the degree of pre-lithiation can be controlled with a higher accuracy in comparison to pre-lithiation with Li metal foil. Additionally, it is not necessary to remove the SLMP prior to cell assembly, because in the optimal case the Li metal is dissolved completely prior to real battery cell operation. However, SLMP is considerably more expensive than Li metal foil. Another disadvantage of using SLMP is likely the inhomogeneous distribution on top or within the electrode leading to safety issues, problems with non-uniform SEI formation or unintentional aging behaviour.

A factor of central importance is the time required for the pre-lithiation process in the electrode and cell manufacturing. In this context, Forney et al. estimated the endpoint of pre-lithiation with SLMP by observing the cell voltage and impedance change [31]. The cell voltage appeared to be stable after 15–20 h, whereas the impedance became stable after 40–50 h, suggesting a relatively long pre-lithiation time. However, the measurement of cell voltage or impedance are only indirect methods, which means that the dissolution of Li metal and the formation of the corresponding lithiated active material cannot be monitored. For this reason, Park et al. [83] applied in situ synchrotron wide-angle X-ray scattering in order to monitor the formation of the different lithiated graphite stages with time, during the pre-lithiation in direct contact with Li metal foil. They could demonstrate a rapid speed of pre-lithiation, leading to a fully lithiated negative electrode within less than 60 min. However, they utilized an extreme excess of Li metal (32 mm × 25 mm graphite electrode vs. 40 mm × 30 mm Li metal foil). Zheng et al. [62,84,85] applied different kinds of geometries of the Li metal source and investigated the influence on the speed of pre-lithiation. They could show that apart from the active material, which is pre-lithiated (see Section 2.1), also the amount and the geometry of the applied Li metal source has a strong influence on the kinetics of pre-lithiation. It could be shown that the speed of pre-lithiation is relatively slow when Li metal stripes (≈45 µm) are used as source, leading to a fully lithiated hard carbon electrode within 18–24 h and a fully lithiated graphite electrode within significantly more than 24 h. In comparison to that, a graphite electrode could be fully lithiated within less than 24 h by using SLMP [62,84]. It was reported that the speed of lithiation can be further accelerated when ultra-thin Li metal foil (≈20 µm) is used as pre-lithiation source; i.e., the pre-lithiation of a hard carbon electrode could be accomplished within 2 h, which is remarkably faster than the pre-lithiation with SLMP or lithium stripes. Furthermore, when tiny holes were incorporated into the thin metal foil, which improved the accessibility of electrolyte, the pre-lithiation could be accomplished within 1 h [85]. Overall, one hour seems to be a realistic period of time if pre-lithiation shall be incorporated into a commercial process of battery cell manufacturing without serious problems. However, ultra-thin Li metal foil is not only soft and sticky and, therefore, difficult to handle but also more expensive than thick Li metal foil, which drastically increases the manufacturing costs [86].

In summary, the pre-treatment by direct contact to Li metal seems to be a promising method in order to pre-lithiate the negative electrode. The low redox potential of Li metal (−3.04 V vs. SHE) [8] allows a pre-lithiation of nearly all kinds of negative electrode active materials and no extra mass caused by residues is added to the cell. However, the whole or at least parts of the electrode manufacturing process must be carried out under dry room conditions.

Many different methods were developed in order to use Li metal as pre-lithiation agent. Therefore, it is essential which kind of Li metal is used as pre-lithiation agent, i.e., Li metal foil (with different thicknesses) or SLMP. The choice of the agent has an influence on the cost, the kinetics, the ability to control the degree of pre-lithiation and the implementation of the pre-lithiation process into the manufacturing process of commercial cells. Thick Li metal foil (≈100–200 µm) is typically much cheaper than SLMP and thin Li metal foil (<100 µm). However, with thin Li metal foil, the pre-lithiation process was reported to be much faster. The degree of pre-lithiation can be controlled best with SLMP and worst with relatively thick Li metal foil. The implementation of pre-lithiation into the manufacturing process of commercial battery cells using thick Li metal foil seems to be difficult, because excess Li metal, which is not used for pre-lithiation, must be removed from the surface prior to cell assembly. In contrast, thin Li metal foil or SLMP have the advantage that-in an optimum case-the whole Li metal is consumed during pre-lithiation and, therefore, the cell can be assembled directly.

Regarding all these considerations, SLMP, which can be "dosed" quite precisely, seems to be a good trade-off despite the high costs. Nevertheless, it remains challenging to homogeneously distribute SLMP on top or within the negative electrode and there is a lack of understanding into SEI-formation, safety and aging behaviour asking for further research.

2.4. Pre-Lithiation by Use of Lithiated Active Materials as Negative Electrode Additives

Instead of using Li metal, lithiated active materials, such as $Li_{2.6}Co_{0.4}N$ (capacity: 760 mAh g^{-1}) [87], can also be utilized as additives for the negative electrode in order to perform pre-lithiation. Therefore, these additive particles can be embedded into the composite anode during electrode preparation procedure. For example, $Li_{2.6}Co_{0.4}N$ has been used to compensate the initial capacity loss of a broad variety of active materials like MCMB [88,89], natural graphite [90], hard carbon [91], Si/C composites [92], SiO_x [93,94], SnO [93,95,96], $SnSb_x$ [95,97–99], TiP_2O_7 [100] or $LiTi_2O_4$ [101]. However, for all the above materials, the electrodes had to be fabricated solvent free and in an argon atmosphere, due to the high reactivity of the used pre-lithiation agent.

Zhao et al. [32] introduced the use of dry-air-stable lithium silicide-lithium oxide core-shell nanoparticles (Li_xSi-Li_2O) for the pre-lithiation of Si and graphite electrodes, achieving high first cycle Coulombic efficiencies of 94% to >100%, in Li metal cells. The Li_xSi-Li_2O nanoparticles (NPs) were prepared by mechanical mixing Si NPs and Li metal foil (melting point: ≈180 °C) at 200 °C for 6 h in an argon filled glove box. Thereafter, for pre-lithiation, the Li_xSi-Li_2O particles were added to the electrode slurry during electrode manufacturing. The formation of a Li_2O layer is owing to trace amounts of oxygen in the glove box as well as to SiO_x surface groups of Si. In principle, the Li_xSi-Li_2O particles have several advantages, e.g., a low redox potential of 10 mV vs. Li/Li^+ which allows to pre-lithiate many types of negative electrode materials and a high theoretical gravimetric capacity ($\approx$3500 mAh g^{-1} for the formation of $Li_{15}Si_4$), so only small amounts are required for pre-lithiation. Furthermore, attributed to the nanoscale of the particles, the pre-lithiation can be achieved relatively fast and homogenous, caused by a uniform distribution of particles within the electrode.

However, they also reported that the amount of lithium, which was loaded into the Si NPs, was only corresponding to $\approx$1310 mAh g^{-1}, while the rest of the theoretical capacity of $\approx$3500 mAh g^{-1} was consumed by the formation of the Li_2O layer and during the preparation of the electrode slurry, due to the strong reducing power of Li_xSi in contact to the solvent (1,3-dioxolane) [32]. The Li_xSi-Li_2O particles were capable to retain 91% of their initial capacity after exposure to dry air for 1 day. However, the particles were still sensitive towards moisture (only 5% capacity retention after exposure of 6 h to ambient air) and not compatible with high polar solvents (e.g., NMP) that are normally used for the electrode manufacturing. To sum up, the usage of Li_xSi-Li_2O NPs seem to be a promising method for pre-lithiation of the negative electrode. However, the chemical stability of the NPs has to be further improved for the implementation of this pre-lithiation agent into a commercial process of battery cell manufacturing.

For this reason, Zhao et al. also presented the formation of an artificial SEI upon Li_xSi particles in order to improve their stability [102]. Therefore, they used 1-fluorodecane, which was reduced by Li_xSi and, thereby, formed a homogeneous and dense coating layer around the NPs. These coated Li_xSi NPs delivered a pre-lithiation capacity of $\approx$2100 mAh g^{-1} (processing solvent: tetrahydrofuran), which was remarkably higher than the one of the Li_xSi-Li_2O core-shell NPs. Furthermore, they only showed a negligible capacity decay in dry air after 5 days (8%) and still exhibited a capacity of $\approx$1600 mAh g^{-1} after 6 h in humid air (10% relative humidity (RH)), which was a significant improvement in comparison to the Li_xSi-Li_2O NPs.

Other groups also studied Li_xSi NPs, for example Li et al. [103]. However, in contrast to Zhao et al. they conducted ball-milling to produce the Li_xSi particles with a subsequent exposure to nitrogen in order to form a passivation film. Additionally, they did not use the passivated Li_xSi NPs ($Li_{4.4}Si@Li_xN_ySi_z$) for pre-lithiation but directly as negative electrode active material. The $Li_{4.4}Si@Li_xN_ySi_z$ particles delivered a capacity of $\approx$2808 mAh g^{-1}, which was significantly higher than the one of the Li_xSi core-shell NPs (Table 1) that were protected by an artificial SEI. The reason for the higher gravimetric capacity could be that in this case the electrode preparation was conducted under solvent-free conditions.

Even if a protective layer covering the Li_xSi NPs can improve the stability, there is still a major problem, which cannot be overcome by this core-shell approach: Under the assumption that the protective layer is damaged only at one position (pinhole defect), the complete particle might be de-lithiated (=de-activated for pre-lithiation) as schematically shown in Figure 11a,b. In order to prevent this failure, SiO_x particles instead of Si can be used for synthesis of the pre-lithiation agent [104]. With this approach, the synthesis conditions stay nearly the same but in contrast to Si, the product of the synthesis is a composite with a structure of homogeneously dispersed Li_xSi nanodomains embedded in a robust Li_2O matrix (Figure 11c). Even if few nano-domains are de-activated through a breakdown of the protective matrix, the rest of the nano-domains still stays lithiated and, thus, still active for pre-lithiation. Following this method, pre-lithiation capacities of $\approx$2120 and $\approx$1543 mAh g^{-1} could be obtained based on the masses of SiO and SiO_2, respectively (processing solvent: tetrahydrofuran) [104]. Triggered by this composite design, the Li_xSi/Li_2O particles exhibited a remarkably improved dry air stability, i.e., only 9% of the capacity was lost when the material was exposed to dry air for 5 days. Furthermore, the composite still exhibited a capacity of $\approx$1240 mAh g^{-1} after 6 h of exposure to ambient air ($\approx$40% RH). A disadvantage could be the long reaction time, because the sample, which was used for the stability study, was stirred for 5 days in molten Li metal [104].

Table 1. Comparison of gravimetric capacity and stability of different pre-lithiation additives for the negative electrode. The stability is shown as capacity retention after different exposure times in air with different ratios of relative humidity (RH).

Active Material	**Gravimetric Capacity/mAh g^{-1}**	**Stability (Capacity Retention)**	**Reference**
$Li_{2.6}Co_{0.4}N$	760	-	[87]
Li_xSi-Li_2O (core-shell)	1310	91% (1 day in dry air) 67% (5 days in dry air) 5% (6 h in ≈40% RH)	[32,105]
Li_xSi (core-shell, artificial SEI)	2100	92% (5 days in dry air) 76% (6 h in 10% RH)	[102]
$Li_{4.4}Si@Li_xN_ySi_z$ (core-shell)	2808	-	[103]
Li_xSi/Li_2O (composite, based on SiO)	2120	91% (5 days in dry air) 58% (6 h in ≈40% RH)	[104]
Li_xSi/Li_2O (composite, based on SiO_2)	1543	-	[104]
Li_xSn-Li_2O (core-shell)	910	93% (5 days in dry air) 45% (6 h in ≈40% RH)	[105]
Li_xSn/Li_2O (composite, based on SnO_2)	695	56% (6 h in ≈40% RH)	[105]
Li_xGe-Li_2O (core-shell)	1335	93% (5 days in dry air) 70% (6 h in ≈40% RH)	[105]
Li_xGe/Li_2O (composite, based on GeO_2)	892	85% (6 h in ≈40% RH)	[105]

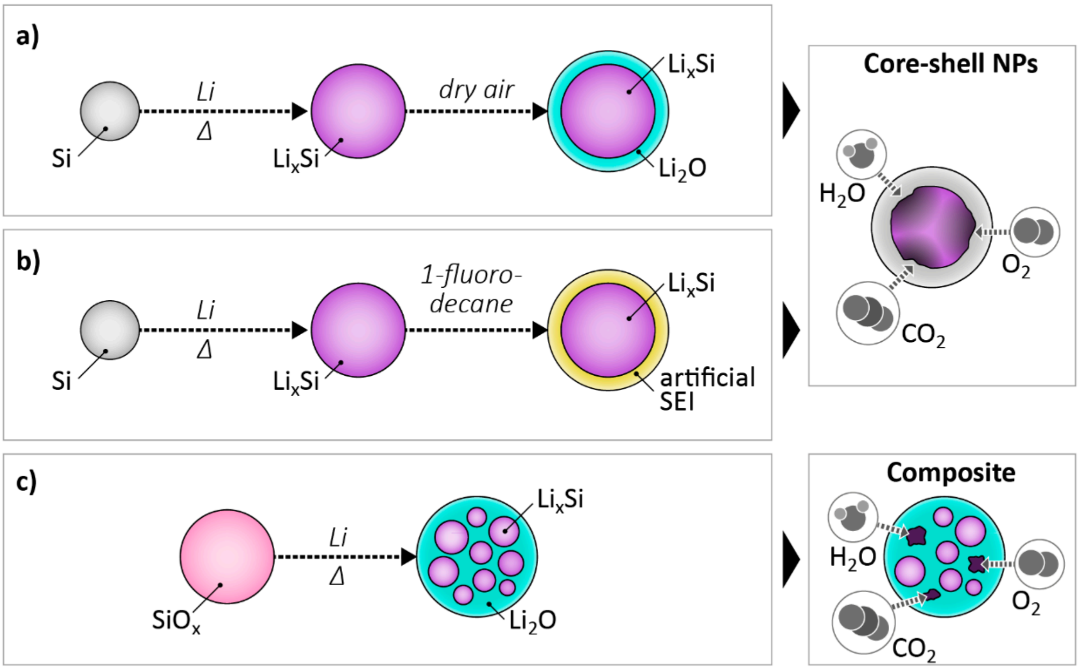

Figure 11. Schematic diagram comparing different approaches in order to produce a pre-lithiation additive for the negative electrode. (**a**) Lithium oxide protected lithium silicide core-shell nanoparticles. (**b**) Artificial SEI protected lithium silicide core-shell nanoparticles. (**c**) Lithium silicide/lithium oxide composite.

Recently, also other group IV elements (Sn, Ge) and their corresponding oxides were used as precursors for the pre-lithiation agent synthesis [105]. DFT calculations showed that the binding energy of Ge-Li (−2.98 eV) and Sn-Li (−2.15 eV) is higher than the binding energy of Si-Li (−0.8 eV), leading to the assumption that the Li_xZ and Li_xZ/Li_2O particles (Z = Sn or Ge) show an enhanced stability than Li_xSi-Li_2O and Li_xSi/Li_2O particles, respectively [105]. This is caused by the fact that the strong bonding between Li and Ge or Sn stabilizes the active Li inside the structure.

Li_xGe-Li_2O and Li_xGe/Li_2O showed gravimetric pre-lithiation capacities (Table 1) of ≈1335 mAh g^{-1} and ≈892 mAh g^{-1}, whereas the values of Li_xSn-Li_2O and Li_xSn/Li_2O were slightly lower, i.e., ≈910 mAh g^{-1} and ≈695 mAh g^{-1}, respectively (processing solvent: tetrahydrofuran). This means that the gravimetric capacities of both compounds are significantly lower than the ones of the Si species. Additionally, when the Li_xGe NPs were exposed to ambient air (≈40% RH) for 6 h, a pre-lithiation capacity of ≈947 mAh g^{-1} was obtained, corresponding to a capacity retention of 70%. When the Li_xGe/Li_2O composite was used, the capacity retention was even higher (85%). In contrast, the Sn species were not as good regarding their capacity retention but comparable or better than the Si species, bearing out the results of the DFT calculation. Even if the accessible capacities of the Ge species are lower in comparison to the Si species, the strongly improved air stability simplifies the requirements for commercial battery cell manufacturing and, therefore, decreases the cost.

In conclusion, pre-lithiation by lithiated active negative electrode materials is a promising approach to prevent the use of Li metal during preparation of the negative electrode and cell assembly. A further advantage is that no inactive materials are added to the cell, as the additives can be lithiated and de-lithiated during battery operation and, hence, the overall energy density is not reduced. Furthermore, some of the agents can be used even under ambient air conditions during electrode processing, which has the potential to further reduce the cost for pre-lithiation in the commercial battery cell manufacturing process. However, due to their high reactivity, lithiated active materials are not compatible with polar processing solvents, in particular with aqueous processing. This is a major problem for Si and other high-capacity anode active materials, where the state-of-the-art binders (CMC/SBR or PAA) are typically processed with water as solvent [78].

In addition, it should be noted that the lithiated negative electrode active materials could also be used as negative electrode in combination with a non-lithiated positive electrode (e.g., V_2O_5) [106], which can have a higher gravimetric capacity than state-of-the-art positive electrode materials.

2.5. Comparison of Different Pre-Lithiation Concepts for the Negative Electrode

It could be shown that there are several concepts, techniques and methods in order to pre-lithiate the negative electrode of LIBs. Thereby, each concept has its own advantages and disadvantages.

Chemical pre-lithiation allows the control of the degree of pre-lithiation by time and can be conducted relatively simple by immersing the electrode into a solution. However, the reaction times are long and the used chemicals or reaction conditions are not suitable for practical applications. Furthermore, the electrodes have to be purified from unwanted reaction species after pre-lithiation, which further increases the expenditure of this technique.

Electrochemical pre-lithiation allows an equally good or even better control of the pre-lithiation degree, which is very beneficial with regard to anode/cathode capacity balancing, SEI formation and the prevention of HSAL formation during operation. However, problems with upscaling are known and often a re-assembly of the cell is needed, resulting in a decreased usability of this technique for commercial battery cell manufacturing. Nevertheless, there exist already some approaches to prevent the reassembly step, e.g., the idea for an industrial roll-to-roll electrochemical bath. Therefore, we believe, that this approach, which still needs to be verified experimentally, is one promising techniques for the commercial battery cell manufacturing in future.

The pre-lithiation by direct contact of the anode to Li metal is another method, which is used very frequently in academic studies. This technique has the advantage that the fundamental principle is very simple, namely to press Li onto the electrode surface or to embed Li within the composite electrode. Furthermore, under optimized conditions, the pre-lithiation can be performed relatively fast. However, it is rather difficult to control the degree of pre-lithiation, especially when Li metal foil is used as pre-lithiation agent. In addition, excess foil has to be removed prior to cell assembly. Stabilized Li metal powder (SLMP) features some advantages, i.e., it is not necessary to remove the Li prior to cell assembly, because in an optimum case, the Li metal amount is precisely dosed and thus completely used prior to battery cell operation. Furthermore, the application of SLMP can be easily performed by spray coating. Therefore, the upscaling of pre-lithiation by using SLMP seems to be more suitable than by using Li metal foil. However, SLMP is most likely more expensive than Li metal foil and the effect of the inhomogeneous distribution of SLMP on top or within the electrode has not been systematically analysed yet. In general, another disadvantage of using highly reactive Li metal for pre-lithiation processes is that the whole process of electrode manufacturing or at least parts of the process must be carried out under dry atmosphere conditions, which further increases the cost of LIB cell production. All above techniques have the major advantage that during pre-lithiation only Li ions are added to the mass of the cell and no inactive material is added for pre-lithiation.

Another approach, the pre-lithiation by use of lithiated active negative electrode materials does also not decrease the energy density of the cell as the corresponding compounds can be reversibly lithiated/de-lithiated. Furthermore, they have the advantage that at least some of them, especially the Sn and Ge species, possess a relatively good ambient air stability, which has the potential to reduce the cost for pre-lithiation in the battery cell manufacturing process. However, they are still too reactive in order to use processing solvents with a high polarity, like NMP or water. This is a major disadvantage, because the state-of-the-art binder systems for the negative electrode rely on aqueous processing.

3. Pre-Lithiation with Help of the Positive Electrode

Electrochemical pre-lithiation of the negative electrode can also be achieved in the LIB cell with the help of lithium excess in the positive electrode, representing an alternative method for the "prior" pre-lithiation of the negative electrode, which is carried out before LIB cell assembly as described in the previous chapter. Two methods are presented in this chapter: (1) the pre-lithiation by using positive electrode additives (2) over-lithiated positive active materials. Generally, additives and over-lithiated cathode materials can create a stoichiometric surplus of lithium in the LIB, which is used in the 1st cycle(s) to pre-lithiate the negative electrode in order to overcome the active lithium loss caused mainly by SEI formation at the negative electrode, as described in Figure 1c.

Firstly, pre-lithiation agents have to be added to the positive electrode, ideally using state-of-the-art industrial standard techniques. Pre-lithiation electrode additives are typically lithium excess positive electrode materials, which do irreversibly de-lithiate in the working potential range of the positive electrode. Secondly, over-lithiation of the positive electrode, as like the pre-lithiation of the negative electrode, can be achieved chemically, electrochemically and physically. Finally, lithiation of the positive electrode can also be used to introduce lithium into Li-free active materials like MnO_2, V_2O_5 or V_3O_8 [107–113].

3.1. Pre-Lithiation by Using Positive Electrode Additives

Most recently, positive electrode additives have gathered great attention because of the rather simple implementation into state-of-the-art industrial cell manufacturing procedures and their enhanced capacities (=pre-lithiation ability) in comparison to over-lithiated positive electrode materials. In general, positive electrode additives should possess four different key features to be regarded as a beneficial pre-lithiation agent.

Firstly, the additive material should exhibit a high volumetric and gravimetric capacity to enable an effective pre-lithiation. Secondly, the additive should be compatible with industrial standard processing, which includes compatibility with current positive electrode active materials, solvents, binders, conductive agents, electrolytes and also handling in ambient atmosphere. As described later, especially the congruity with NMP and ambient air is a problem of some additives.

Thirdly, the pre-lithiation agent has to align with the working potential range of the negative and positive active materials. To ensure de-lithiation of the additive, the de-lithiation potentials of the positive electrode and the additive have to align, as depicted in Figure 12a. This potential window varies in dependence of the used active materials for the positive and negative electrode, as well as of the used electrolyte.

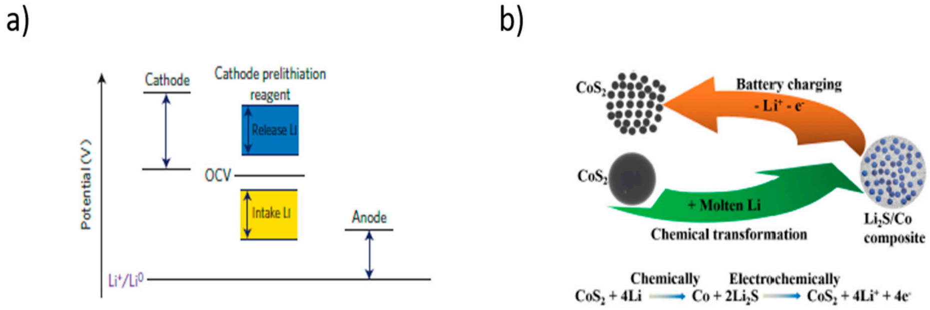

Figure 12. (**a**) Schematic drawing of the required working potential of the pre-lithiation additive. Reproduced with permission from [114] Copyright 2017, Springer Nature. (**b**) Synthesis of the Li_2S/Co. additive and the release of the Li^+ during the initial cycle. Reproduced with permission from [115] Copyright 2017, Wiley-VCH.

Fourthly, the pre-lithiation agent has to be not only electrochemically stable but also thermally, chemically and mechanically stable after de-lithiation. The investigated additives range from binary compounds, such as Li_2S [115,116], Li_3N [117,118], LiN_3 [119], Li_2O [114,120], Li_2O_2 [121] or LiF [122], to ternary compounds, such as Li_5FeO_4 [123], Li_2NiO_2 [124,125], Li_6CoO_4 [126] or Li_2MoO_3 [127].

Focusing on the binary additives, lithium nitride (Li_3N) exhibits the highest theoretical gravimetric capacity ($\approx$1400 mAh g^{-1}; Figure 13) of the investigated positive electrode additives [117]. Moreover, no residues are left after de-lithiation, as the occurring nitrogen gas from decomposition of the additive can be released after the formation cycle [128]. However, Li_3N exhibits a poor electronic conductivity, reacts with NMP and has to be handled in argon atmosphere. To overcome those problems, Sun et al. [118] coated the additive with a passivating layer, comparable to the protection mechanisms used for SLMP. The coated additive allowed handling of the additive in ambient air and ensured a high stability.

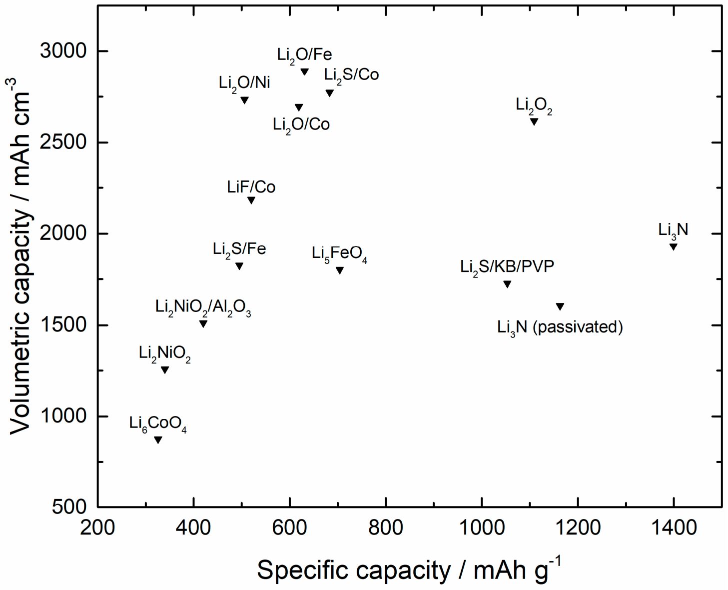

Figure 13. Comparison of different positive electrode additives in regard to gravimetric and volumetric capacity. The gravimetric capacities are determined in a Li metal cell. The volumetric capacities are calculated with the crystallographic density of the material, if the volumetric capacity was not mentioned in the paper. The gravimetric and volumetric capacities for Li_2O_2 and $Li_2S/KB/PVP$ are determined for the pristine material, without taking the additional NMC_{111} and KB/PVP into consideration [114–118,121–123,126].

Li_2S exhibits similar limitations as Li_3N, e.g., instability in ambient atmosphere and poor ionic and electronic conductivity. Furthermore, Li_2S is incompatible with carbonate-based electrolytes. Zhan et al. [116] investigated this issue by mixing Li_2S with Ketjenblack (KB) and poly(vinylpyrrolidone) (PVP) but this mixture was not used with NMP in the positive electrode preparation process. Another approach to solve the compatibility problems of Li_2S is to introduce transition metals (e.g., Fe or Co) [115]. For example, a precursor like CoS_2 was mixed with molten Li metal in argon atmosphere and afterwards stirred at 185 °C for 20 min and at 220 °C for 2 h, which leads to the formation of Li_2S/Co [115]. The chemical transformation and later de-lithiation of the pre-lithiation agent are depicted in Figure 12b. This approach is also applicable for other binary pre-lithiation agents, e.g., Li_2O and LiF [114,122]. It is important to point out that the trace of oxygen existing in the argon atmosphere was reported to be sufficient to passivate the pre-lithiation agent for handling in ambient air [114,115,122].

Unfortunately, the above additive/transition metal (e.g., Li_2O/Co) approach and the later described ternary compounds cause residues (Co_3O_4) after de-lithiation of the additive, which not only add weight but also the possibility of unwanted side reactions. However, the amount of the unreacted additives is rather small in comparison to the amount of added pre-lithiation agent.

Another strategy to solve this problem is the use of lithium peroxide (Li_2O_2) mixed into the positive electrode, e.g., as reported by Bie et al. for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111)-based cathodes [121]. Transition metals, like Ni, Co or Mn, which are available in various positive LIB electrode materials, are also known as decomposition catalysts for Li_2O_2. However, they proposed that the incongruent particle size between Li_2O_2 and the NMC111 prohibited any decomposition of the Li_2O_2 in the desired potential range. Because of this, they added ball-milled NMC111 with a decreased particle size but the ball-milled material showed a poor reversibility and therefore acts as residue after few cycles [121]. Overall, additional research is still necessary to avoid inactive residues. In comparison to Li_3N, Li_2O_2 also releases oxygen, which can be removed easily by opening the cell after the formation cycle.

Other binary pre-lithiation agents are pristine lithium oxide (Li_2O) and lithium azide (LiN_3). The later one releases nitrogen gas like lithium nitride upon de-lithiation, however, LiN_3 is toxic and exhibits safety issues [119]. Li_2O, on the other hand, is safe to use but de-lithiation of the additive depends on the current rate, electrolyte salt and negative electrode active material [120].

As mentioned above, ternary $Li_xM_yO_z$ (M = Ni, Co, etc.) materials can also be used as pre-lithiation additives for LIBs. Li_2NiO_2 was proposed as one of those materials and exhibited a lithiation and de-lithiation capacity of 340 mAh g^{-1} and 83 mAh g^{-1}, respectively, in a Li metal cell cycled between 3.5 V to 4.4 V vs. Li/Li^+ [125]. After the first cycle, the additive exhibited a Coulombic efficiency of 97% with a de-lithiation capacity of 76 mAh g^{-1}. Therefore, the additive did not only serve as a simple pre-lithiation agent but also as additional active material allowed for reversible lithiation and de-lithiation to some extent. Furthermore, 5 wt % additional Li_2NiO_2 were reported to be enough to compensate the active lithium loss of a graphitic negative electrode paired with a $LiCoO_2$ positive electrode [129]. Nevertheless, handling Li_2NiO_2 in ambient atmosphere is problematic. Therefore, a strategy to overcome this instability was presented by Kim and Cho [124], i.e., by coating the additive with Al_2O_3. Another ternary compound that can be used as pre-lithiation agent is Li_6CoO_4. This pre-lithiation agent exhibits a lithiation and de-lithiation capacity of 318 mAh g^{-1} and 13 mAh g^{-1} in a Li metal cell (4.4 V to 1 V vs. Li/Li^+), respectively. Li_6CoO_4 was shown to compensate the active lithium loss of SiO_x-based anodes, where 14 wt % of the pre-lithiation agent was added to a $LiCoO_2$ positive electrode. In comparison, Li_5FeO_4 is a similar pre-lithiation agent with an theoretical capacity of 867 mAh g^{-1} [123]. Su et al. reported that 7 wt % of Li_5FeO_4 added to $LiCoO_2$ were sufficient to compensate for the active lithium loss of a hard carbon-based anode in the 1st cycle. However, Li_5FeO_4 reacts with CO_2 and moisture in ambient air [130].

Another class of positive electrode additives are the also called "sacrificial" salts, which include the ternary compounds of squarate ($Li_2C_4O_4$), oxalate ($Li_2C_2O_4$), ketomalonate ($Li_2C_3O_5$) and di-ketosuccinate ($Li_2C_4O_6$) [119]. They all possess theoretical capacities between 300 mAh g^{-1} and 600 mAh g^{-1} and a working potential between 3 to 4 V vs. Li/Li^+. Moreover, like LiN_3, the lithium salts convert into the gaseous products of N_2 and CO_2, which produce no residues and, thus, could be removed after cell formation cycles. Unfortunately, those salts have not been investigated in LIBs until now.

Figure 13 compares the volumetric and gravimetric capacities of different positive electrode additives in a Li metal cell, which have been described above in terms of their advantages and disadvantages. The figure does not take into consideration the amount of added conducting agent or binder as well as the type of binder. Moreover, the cut off voltages also differ; therefore, the figure serves only as general overview and has to be taken with precaution. The binary additives are superior to the ternary ones with respect to their capacities, with the exception of Li_5FeO_4, showing a gravimetric capacity similar to the binary transition metal additives. Additionally, the binary pre-lithiation agents exhibit the highest volumetric capacities, almost 3000 mAh cm^{-3} (LiO_2/TM and Li_2S/Co.), of the presented pre-lithiation materials. The highest gravimetric capacity is achieved for the passivated LiN_3 additive (≈1163 mAh g^{-1}), which can even be further increased to ≈1761 mAh g^{-1} when the cut-off potential is increased from 4.5 to 4.8 V vs. Li/Li^+. A trade-off between gravimetric and volumetric capacity is achieved by Li_2O_2 (Figure 13). Nevertheless, the large variety in terms of gravimetric and volumetric capacity is an advantage for the different additives, because the desired property of the cell can be tailored by choosing between the materials.

Overall, positive electrode additives are able to compensate the ALL of negative electrode materials and are a good alternative in regard to the "direct" pre-lithiation of the negative electrode. Comparing the main advantages of both pre-lithiation methods, on the one hand, additives are versatile as they can be theoretically added to any positive electrode material. Nevertheless, more research has to focus onto the effect of residues and gas development during decomposition of the pre-lithiation agent. A major drawback of pre-lithiation agents is the additional weight added to the positive electrode, if the additive does not fully decompose upon de-lithiation. On the other hand, after de-lithiation of the over-lithiated positive electrodes there will be no inactive residues in the positive electrode.

3.2. Over-Lithiated Positive Electrode Materials

The general idea of using over-lithiated positive electrode materials providing additional lithium in LIBs is appealing because no positive electrode additive is necessary.

The over-lithiated positive electrodes release their "lithium reservoir" in the 1st cycle in order to compensate the active lithium loss (ALL) of conversion or intercalation type negative electrodes, e.g., α-Fe_2O_3 or graphite [131–133].

It should be noted, that even regular, i.e., not pre-lithiated, $LiNiCoMnO_2$ (NCM) and $LiNiCoAlO_2$ (NCA) materials with various Ni, Co, Mn and Al ratios show a kind of over-lithiation, as a significant part of the charge capacity cannot be recovered during subsequent discharge due to a kinetic limitation of the re-lithiation process. This "kinetically lost" capacity can be used to compensate for ALL [134,135].

The design of over-lithiated of LIB positive electrode materials is usually achieved chemically or electrochemically. The electrochemical lithiation can be performed in a Li metal cell whereas for chemical lithiation, e.g., *n*-butyl lithium (*n*-BuLi) [133] or lithium iodide (LiI) [132] can be used. However, the reduction of the positive electrode compound with *n*-BuLi has to be carried out in inert gas atmosphere, in contrast to the process with LiI. For the latter approach, the over-lithiation of cathode materials is achieved by mixing and heating the pristine material with LiI. Afterwards, any traces of residue LiI are removed with acetonitrile.

The over-lithiated spinels $Li_{1+x}Mn_2O_4$ and $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ have been investigated with regard to their potential as pre-lithiation cathode materials [131,136]. $LiMn_2O_4$ (LMO) and $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) store/extract lithium ions from/into the 8a tetrahedral sites. This insertion/extraction of lithium ions occurs at ≈4.1 V vs. Li/Li^+ and ≈4.7 V vs. Li/Li^+, respectively. A further lithium ion can be inserted in the empty, octahedral sites of LMO and LNMO at ≈2.7 V vs. Li/Li^+, leading theoretically to the tetragonal phases of $Li_2Mn_2O_4$ (*o*-LMO) and $Li_2Ni_{0.5}Mn_{1.5}O_4$ (*o*-LNMO), as depicted in Figure 14. The working potential of 2.7 V vs. Li/Li^+ is not favourable for the overall energy density of the LIB cell and additionally the *o*-LMO and *o*-LNMO materials experience severe capacity fading when cycling at these low potentials. However, the additional lithium ions stored at the octahedral sites are usable in the 1st cycle to pre-lithiate the negative electrode and compensate the ALL. Afterwards, the LIB can be cycled in the "standard" potential range, that only the lithium in the tetrahedral sites is reversibly used [137].

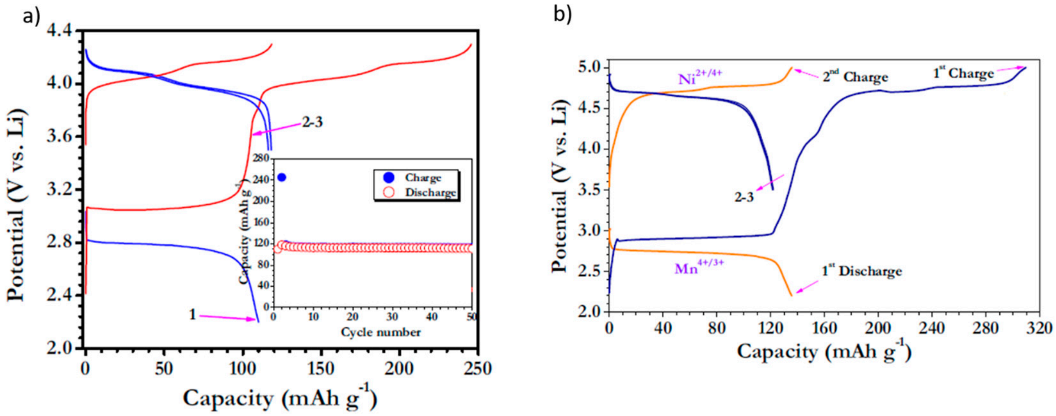

Figure 14. De-lithiation and lithiation of o-LMO (**a**) and *o*-LNMO (**b**) in a Li metal cell. Firstly, pristine LMO and LNMO are over-lithiated by controlling the cut-off potentials. Subsequently the *o*-LMO and *o*-LNMO are cycled in the potential range the tetrahedral site. Reproduced with permission from (**a**) [131] Copyright 2017, Elsevier. (**b**) [136] Copyright 2017, Elsevier.

LNMO is a high voltage positive electrode material, which needs charging up to 5 V vs. Li/Li^+, in comparison to LMO, where an upper charge potential of only 4.3 V vs. Li/Li^+ applies [137,138]. This property makes LNMO an interesting candidate for high voltage applications [139]. Gabrielle et al. and Mancini et al. investigated different degrees of over-lithiated LNMO materials against graphite and Si/C composite anodes [140,141]. The over-lithiated $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ was synthesized by mixing the pristine compound with a reductive lithium-containing compound at 600 °C. In contrast, Aravindan et al. electrochemically over-lithiated LNMO by using a Li metal cell [136].

As mentioned earlier, electrochemical lithiation shows several disadvantages concerning large-scale battery production. In addition, the aforementioned chemical pre-lithiation with lithium iodide is relatively expensive and time-consuming. Therefore, Rosenberg et al. developed a microwave assisted chemical over-lithiation method using tetraethylene glycol (TEG) as a reducing agent and hydrated LiOH as the lithium source, which are cheaper than the chemicals mentioned above [137]. Furthermore, this lithiation method does not require any inert atmosphere, because both, TEG and hydrated LiOH, contain water.

Over-lithiated LMO was also investigated as a pre-lithiation agent, synthesized by using LiI [132] or *n*-BuLi [133]. In both publications, the capability of *o*-LMO to overcome the ALL of graphite is investigated. Moreover, the possibility of electrochemical over-lithiation of LMO was investigated but against an α-Fe_2O_3 negative electrode [131]. The *o*-LMO exhibited improved kinetics compared to pristine $LiMn_2O_4$, leading to an improved long-term stability of the α-$Fe_2O_3/Li_{1+x}Mn_2O_4$ lithium ion cell.

Putting *o*-LMO and *o*-LNMO into perspective towards their usability as pre-lithiation agents, the controllability of the amount of additional lithium is a major advantage but depends on the used lithiation method. Furthermore, state-of-the-art electrode processing techniques are applicable to o-LMO and *o*-LNMO and the de-lithiation of the lithium reservoir does not result in any inactive residues. Nevertheless, there is always an additional production step necessary to prepare over-lithiated cathode materials. An approach to tackle this problem might be positive electrode pre-lithiation additives.

4. Pre-Lithiation in Lithium-Ion Capacitors

Electric double-layer capacitors (EDLCs), also called "supercapacitors," are promising energy storage technologies because of the remarkably improved power density and long-term performance in comparison to LIBs (Figure 15a). Typically, activated carbon (AC) is utilized as positive and negative electrode and the energy is stored electrostatically in the electric double-layer. However, the energy density of electric double-layer capacitors is still significantly smaller than the one provided by LIBs [142–145].

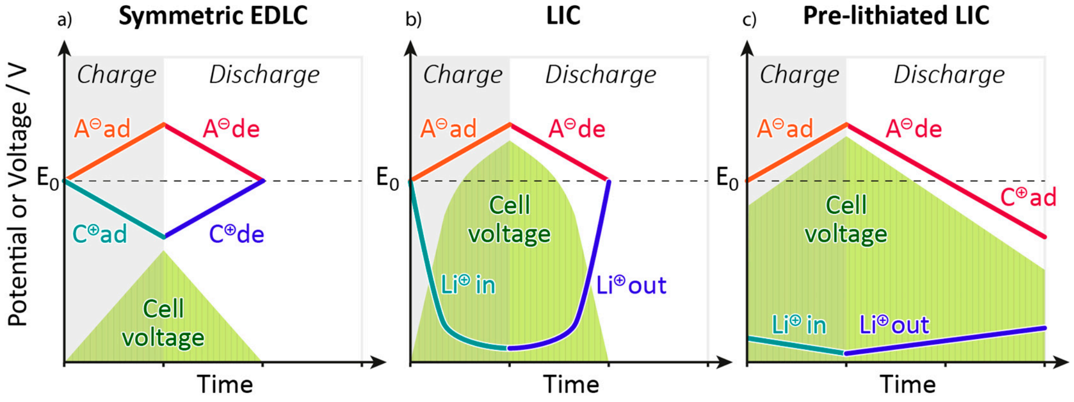

Figure 15. Schematic illustration of the potential and voltage range during galvanostatic cycling inside (**a**) symmetric electrochemical double layer capacitor (EDLC) (**b**) lithium ion capacitor (LIC) and (**c**) pre-lithiated lithium ion capacitor. The shaded area is a measure to compare the energy of the different capacitors when they are cycled at the same current. A^- ad: anion adsorption; A^- de: anion desorption; C^+ ad: cation adsorption; C^+ de: cation desorption; Li^+ in: lithium insertion/intercalation; Li^+ out: lithium de-insertion/de-intercalation.

For this reason, lithium-ion capacitors (LICs) have been developed, exhibiting an improved energy density than EDLCs at comparable power characteristics [146–149]. LICs, are a special form of "hybrid capacitors," i.e., a combination of a supercapacitor electrode and a battery electrode in one device, i.e., both storage mechanisms (Li ion insertion/extraction and adsorption/desorption) occur simultaneously during charge/discharge (Figure 15b). As like in dual ion batteries, which are based on a similar working mechanism [150–153], not only the electrode capacities but also the number of anions and cations in the electrolyte, thus the amount of electrolyte is decisive for the available energy density. Amatucci et al. [154,155] reported in 2001 the use of nanostructured lithium titanate (LTO) as negative electrode in combination with an activated carbon positive electrode. During charge and discharge, insertion and de-insertion of lithium ions occurs at the negative electrode through faradaic processes, whereas adsorption and desorption of anions takes place at the positive electrode. However, the voltage range of this LIC was limited due to the high redox potential of LTO (1.5 V vs. Li/Li^+). If LTO is replaced by graphitic carbon, the voltage window of the cell can be increased, attributed to the low redox potential of graphite ($\approx$0.2 V vs. Li/Li^+), which, in turn, leads to an increased energy density of the LIC [156]. Aida et al. were the first, who used a third auxiliary electrode consisting of Li metal in order to perform the pre-lithiation of a graphitic negative electrode of a LIC. The energy and power density of this pre-lithiated LIC were increased in comparison to the one without pre-lithiation by factors of 1.14 and 2.3, respectively [157]. Thereafter, pre-lithiation soon became a key technology in the production of LICs, triggered by many advantages, which will be described more detailed in the following section. Pre-lithiation of the negative electrode leads to a higher cell voltage, caused by the potential drop which occurs, when lithium ions are intercalated e.g., into graphite (Figure 15c) [57]. A combination of pre-lithiated graphite and activated carbon leads to a cell voltage of up to ≈4 V and, thus, an increased energy density, as shown by Aida et al. [157]. In addition, a pre-lithiation of the negative electrode avoids the cell voltage drop and rise during charge and discharge process as shown by Xu et al. (Figure 15c) [158]. Furthermore, the power density can be increased by pre-lithiation because the resistance of the electrode is reduced, as shown by a decreased impedance of pre-lithiated negative electrodes. However, it was also shown that a very high pre-lithiation degree (>80%) can increase the impedance again, due to the formation of a thicker SEI layer [41,42]. Another important advantage of pre-lithiation is that the possible potential swing of the positive electrode is increased, as illustrated in Figure 15c, besides adsorption and desorption of anions, also cations can be adsorbed/desorbed at the positive electrode, which further increases the energy of LICs. In this case, the difference in capacity between charge and discharge is compensated by pre-lithiation [156,158]. Finally, pre-lithiation is able to compensate the active lithium loss, mainly caused by SEI formation, which occurs in the 1st cycle of operation of a graphitic negative electrode as described above. For LICs, this process prevents a decrease of lithium ions from the electrolyte and, therefore, increases the amount of available remaining free charge carriers.

The pre-lithiation degree has a strong influence on the electrochemical performance of LICs. The Coulombic efficiency, the resistance, the long-term stability and the capacitance are only some of the parameters, which are influenced by the pre-lithiation degree. It could be shown that the optimal degree of pre-lithiation for LICs, using graphite as negative electrode, is between 70–80% [42,159]. However, it was also shown that the mass ratio between positive and negative electrode influences the optimal degree of pre-lithiation. In this context, Xu et al. developed a mathematical model in order to calculate the optimal degree of pre-lithiation [158]. In addition, a suitable pre-lithiation degree allows to avoid the potential drop/increase of the negative electrode during cycling [158].

The pre-lithiation methods and techniques for LICs do not differ from the ones described for LIBs. All techniques and methods described above can be applied for the pre-lithiation of LICs, such as the electrochemical pre-lithiation [54,157,160,161], the pre-lithiation with additives inside the negative or positive electrode [162–164] or the pre-lithiation through direct contact with Li metal [165,166]. In contrast to pre-lithiation of LIBs, pre-lithiated LICs are already commercially available as described in the followings section.

The pre-lithiation set-up shown in Figure 16 was developed by JMEnergy (Minato, Japan) [167]. An auxiliary Li metal electrode is used in order to pre-lithiate the cell stack prior to battery operation. For this technique, porous current collectors are required to enable lithium ion transport. The pre-lithiation method was further improved by using porous electrodes as shown by Tsuda et al. [167]. Besides *JMEnergy*, companies like Asahi Kasei Corporation (Chiyoda, Japan) or Subaru (Shibuya, Japan) have also vigorously researched the pre-lithiation of LICs [42,161,168–170]. In general, higher pre-lithiation degrees are required for LICs in comparison to LIBs, as not only ALL needs to be compensated but also the respective electrode needs to be completely charged. Hence, it is easier to perform pre-lithiation, because the degree has not to be adjusted with so a high accuracy. This could be one reason why pre-lithiation of LICs is already widely commercialized process. Of course, the various advantages related to the pre-lithiation of LICs are also important regarding this point.

In conclusion, pre-lithiation is a key technology in the production of LICs because of the manifold advantages, like an increased voltage window, a higher potential swing of the positive electrode, a lower resistance, an increased capacitance etc. Furthermore, the degree of pre-lithiation has a strong influence on the performance of LICs. The same pre-lithiation techniques, which are used for LIBs, can be applied in order to perform the pre-lithiation of LICs.

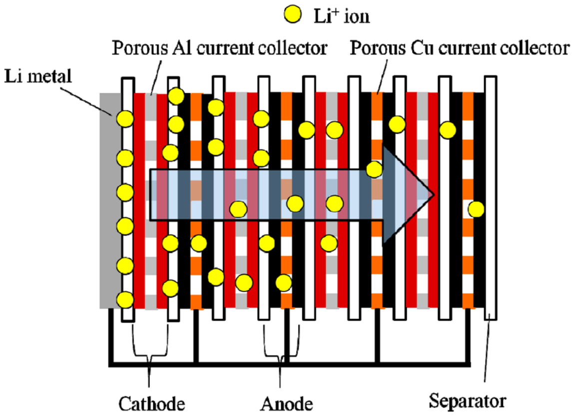

Figure 16. A schematic illustration of the pre-lithiation system, which is commercially used for the fabrication of LICs. Laminated carbon anodes with porous current collectors are pre-lithiated by using an auxiliary Li metal electrode. Reproduced with permission from [167] Copyright 2017, Electrochemical Society, Inc.

5. Pre-Lithiation for Rechargeable Li-Ion/Sulphur Batteries

Rechargeable lithium/sulphur (Li/S) batteries typically consist of a Li metal negative electrode and a sulphur/carbon composite positive electrode, leading to a high theoretical gravimetric energy of ≈2510 Wh kg^{-1} [171,172]. However, the extensive utilization of Li/S batteries in practical applications is still hindered by various severe issues e.g., poor cycle life, low Coulombic efficiency and safety hazards. Most of these issues can be correlated to the use of Li metal, as it forms high surface area lithium (HSAL) deposits often called dendrites during prolonged dissolution/deposition [173,174]. A possible approach to avoid these issues, is the preparation of Li metal-free Li/S batteries, so-called Li-ion/S batteries [175,176], but, consequently, there is a need for an alternative lithium source within the cell. In principle, there are two possible ways to fabricate Li-ion/S batteries. On the one hand, the cells can be prepared in a discharged state, using an already lithiated positive sulphur electrode (Li_2S) in combination with a lithium ion intercalation/insertion negative electrode material like graphite or Si. On the other hand, Li metal-free cells can be realized in a charged state, i.e., by coupling a lithiated negative electrode material with a conventional sulphur positive electrode.

Within both scenarios, one of the electrodes needs to be pre-lithiated prior to cell assembly. Therefore, the technique of pre-lithiation plays a crucial role for the development of prospective Li metal-free Li-ion/S batteries.

5.1. Pre-Lithiation of the Negative Electrode–Charged State

Several lithium ion host materials like carbons [177–181], Ge [182], Si [183–187] or Si/carbon composites [175,188–194], pre-lithiated before cell assembling, are reported as alternative negative electrode materials for the replacement of metallic Li in sulphur cells. Within these reports, mainly two different techniques for the pre-lithiation of the negative electrode were used, namely the electrochemical pre-lithiation and the direct contact to Li metal, as already described above.

Brückner et al. reported the use of hard carbon and Si/C, pre-lithiated by short circuiting vs. metallic lithium, as negative electrode materials in Li-ion/S full cells [190]. They were able to cycle the full cell based on a pre-lithiated Si/C negative electrode for more than 1300 cycles with a low capacity fading of only ≈0.08% per cycle and high Coulombic efficiencies of up to 99.8%. In contrast, when applying metallic Li as negative electrode for Li/S cells, a rapid cell failure after only 46 cycles was observed, indicated by a drastic decrease in capacity and Coulombic efficiency. They attributed this phenomena to the formation of HSAL and a fast electrolyte consumption, especially at high current densities. However, a stable SEI layer seemed to be formed by using pre-lithiated negative electrodes, which prevented electrolyte depletion and enabled a stable long-term cycling [190].

Similar results have been reported by Kang et al. and also by Krause et al. showing that pre-lithiated Si/C composite electrodes, though delivering a lower initial discharge capacity in Li-ion/S full cells compared to Li/S cells, allow a stable and prolonged cycling. These findings have also been assigned to cell failures in Li metal based cells due to HSAL formation, especially in cells with high mass loadings and, therefore, high charge/discharge currents [191,192].

The improved safety of Li-ion/S cells was proven by Zhou et al. They performed external short-circuit experiments with charged Li metal and Si-based full cells, leading to the formation of a Li-Al alloy with the current collector of the positive electrode in Li metal-based cells. During the subsequent re-charge this alloy was de-lithiated, resulting in a degraded current collector. These reactions prevented the recovery of the cell after those abusive conditions, whereas this was possible for the Si-based cells, as no Al current collector degradation took place (Figure 17) [193].

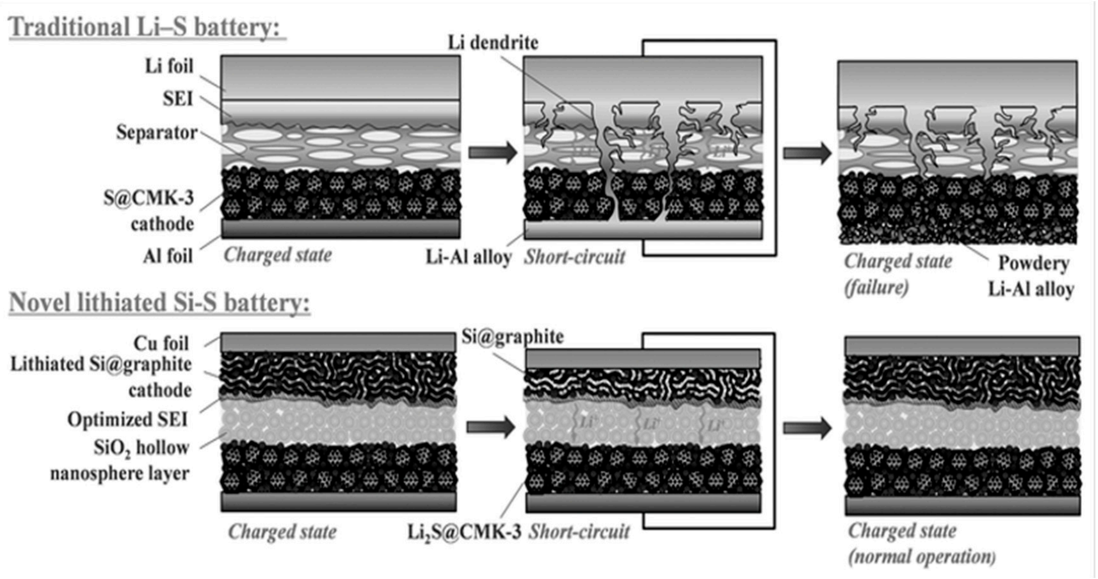

Figure 17. Improved safety of Li-ion/S cells compared to Li/S cells. External short-circuit leading to degradation of the Al current collector in Li/S cells and, therefore, a cell failure. In Li-ion/S cells, no Al current collector degradation took place, enabling the recovery of the cells after abusive conditions. Reproduced with permission from [193] Copyright 2016, Wiley-VCH.

These reports reveal that the replacement of Li metal by pre-lithiated materials is a feasible way to enhance the safety and long-term stability of rechargeable sulphur cells by preventing HSAL formation and associated continuous electrolyte decomposition. However, it has to be taken into account, that the pre-lithiation step needs to be incorporated within the battery cell assembly process, involving the issues of feasibility of different methods mentioned in the chapters before. Another issue arising by using pre-lithiated lithium ion host materials, is a lowered overall energy density, as the cell voltage and the volumetric capacity are reduced in comparison to Li metal based Li/S cells.

5.2. Pre-Lithiation of the Positive Electrode–Discharged State

In the discharged state, a lithium ion host material like graphite or Si is coupled with an already lithiated sulphur composite positive electrode and, therefore, the positive electrode works as lithium source within the cell, comparable to state-of-the-art LIBs. The pre-lithiation of the sulphur cathode can be achieved by several methods like chemical [195,196] and electrochemical lithiation [179] or lithiation by direct contact to Li metal, as explained above [197–199]. Another possibility to prepare a lithiated sulphur composite cathodes, is to perform ball milling of Li_2S and carbons to fabricate the positive electrode composite material [176,200–202]. However, the latter represents not a pre-lithiation method in its original sense but rather a direct use of a reversible lithiated positive electrode material, similar to conventional LIBs.

The process of chemical lithiation was reported by Wu et al. to prepare lithiated sulphur/carbon (Ketjenblack, KB) composite electrodes. They simply dropped a Li-organic complex solution (Li^+Naph^-) on the prepared sulphur composite electrode at room temperature and confirmed the successful pre-lithiation process via XPS analysis (Figure 18).

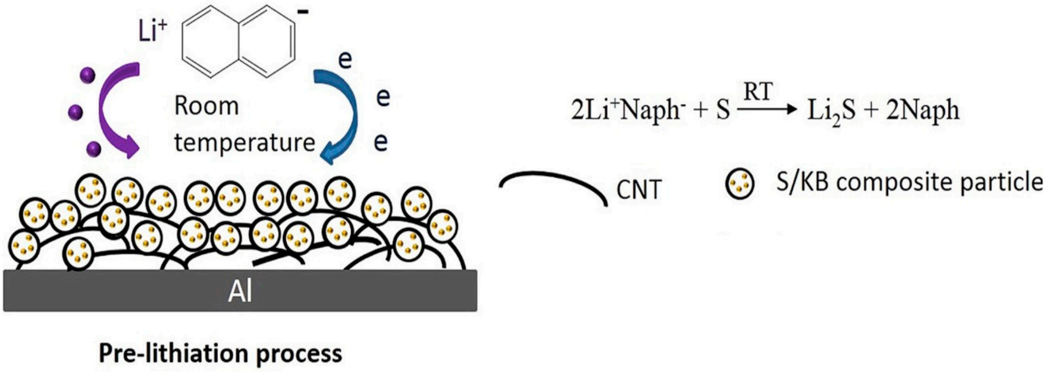

Figure 18. Chemical pre-lithiation process of a sulphur composite positive electrode. The Li-organic complex solution served as lithium source for this pre-lithiation technique. Reproduced with permission from [196] Copyright 2017, Elsevier.

These pre-lithiated positive electrodes achieved a high initial discharge capacity of 1416 mAh g^{-1} in cells using Li metal negative electrodes, maintaining roughly 40% of this initial capacity in the 100th cycle. It was also demonstrated that this technique can be applied when residues of the Li-organic complex solution are not removed by a washing procedure, emphasizing the possibility to integrate this pre-lithiation method in an fabrication process of the sulphur composite electrode [196].

Zheng et al. utilized SLMP as pre-lithiation agent for sulphur/microporous carbon composite electrodes [197]. A well-defined quantity of SLMP, based on the sulphur loading, was sprinkled on top of the electrode and activation of SLMP was achieved by an electrode compressing step. This pre-lithiated sulphur electrode was coupled with a graphite anode to form a Li-ion/S full cell. These cells showed a good cycling stability, reaching a reversible capacity of ≈600 mAh g^{-1} after 150 cycles and Coulombic efficiency close to 100% [197].

An investigation about the influence on which electrode, either positive or negative electrode, is more suitable to be pre-lithiated prior to assembly of Li-ion/S full cells was performed by Xu et al. They pre-lithiated either the sulphur cathode or a graphite anode by electrochemical pre-cycling in half cells vs. Li metal. The pre-lithiated electrodes were then coupled with the associated counter electrode to full cells and the different cells were cycled at the same conditions. The cell comprising the pre-lithiated graphite negative electrode was able to retain a reversible capacity of ≈757 mAh g^{-1} after 50 cycles, whereas the cell containing the pre-lithiated sulphur cathode only delivered ≈515 mAh g^{-1} after the same number of cycles [179]. They attributed this phenomena to capacity loss during the first cycle because of SEI formation on the graphite anode.

This finding revealed that the fabrication of Li metal-free Li-ion/S cells is possible either in charged or discharged state but will not result in similar cell performance. Furthermore, Li_2S is thermodynamically not stable in presence of moisture or ambient air, therefore, all fabrication steps up to cell assembly need to be done in a dry atmosphere, increasing the complexity and costs of manufacturing.

6. Pre-Lithiation for Rechargeable Oxygen Batteries

The lithium/oxygen or lithium/air (Li/O_2) battery is another type of rechargeable energy storage system, often considered as next-generation battery to replace the state-of-the-art LIBs in the future, due to the promising, high theoretical gravimetric energy of 11,420 Wh kg^{-1} for Li/O_2 batteries [203]. Similar to Li/S batteries, Li metal serves as negative electrode in commonly known Li/O_2 batteries, associated with the same issues concerning safety and battery performance as discussed above. These issues can again be addressed by replacing the Li metal negative electrode by a pre-lithiated lithium ion host materials to achieve Li-ion/O_2 batteries. Indeed, there are several reports using pre-lithiated negative electrode materials like Si [203–206], Sn [207], carbon [208] and also Al [209,210] for Li-ion/O_2 batteries. The pre-lithiation of the negative electrode materials was mainly obtained by direct contact to Li metal or electrochemical pre-cycling of the lithium ion host materials in cells vs. metallic Li.

Hassoun et al. were the first to report a Li metal-free Li-ion/O_2 battery comprising a pre-lithiated Si/C composite negative electrode in 2012. They were able to cycle these cells up to 15 cycles at 1000 mAh g^{-1} but also observed a severe voltage decay upon cycling. They speculated an oxygen crossover reaction to be responsible for this phenomenon, i.e., the permeation of oxygen from the positive electrode through the electrolyte, attacking the negative electrode material, leading to self-discharge, side reactions and, therefore, capacity fading [203]. In subsequent publications, this theory was confirmed by Elia et al. and Kwak et al. by proving the formation of lithium oxygen species at the negative electrode due to side reactions of the lithiated material with oxygen. It was also pointed out that this issue is more severe for Li-ion/O_2 batteries, as only a limited amount of lithium is provided by the pre-lithiated negative electrode in contrast to the almost unlimited amount, when using metallic Li foils. Therefore, the effect on the cell performance of side reactions at the negative electrode, consuming active lithium will be more pronounced for Li-ion/O_2 batteries [204,207].

This issue was addressed by Wu et al. by using fluoroethylene carbonate (FEC) as electrolyte additive during electrochemical pre-lithiation of Si-based anodes, to form an optimized SEI layer, which can prevent side reactions consuming active lithium related to oxygen crossover processes. The addition of FEC during pre-lithiation resulted in an SEI mainly containing organic species and polyfluorocarbons, which effectively protected the Si-based negative electrodes from reaction with oxygen [205].

Similar results were reported recently by Qin et al. applying the lithium ion conducting Nafion membrane as oxygen crossover protection in Li-ion/O_2 cells using pre-lithiated Al foil as anode active material and current collector simultaneously [210].

Within all these reports, it was revealed that the replacement of metallic Li in Li/O_2 cells can be achieved using pre-lithiated negative electrodes, therefore, enabling Li metal-free Li-ion/O_2 batteries. However, besides the already mentioned challenges concerning the practical realization of different pre-lithiation methods, common Li/O_2 or Li-ion/O_2 batteries require a huge excess of lithium for effective long-term performance, due to several lithium-consuming side reactions during operation. Hence, the need for additional lithium will lower the energy density of Li-ion/O_2 cell drastically, especially when pre-lithiated lithium ion host materials are used as negative electrodes. Up to now, it is still questionable whether Li-ion/O_2 cells can be a feasible alternative battery system in the near future, due to various unsolved issues preventing efficient long-term operation with satisfying volumetric/gravimetric energies of those cells.

7. Concluding Remarks and Perspectives

Current research on rechargeable electrochemical energy storage technologies, such as lithium ion batteries (LIBs), is strongly driven by the run for high gravimetric and volumetric densities, e.g., to increase the driving range of electric vehicles. However, the implementation of novel, high-capacity active materials is often hindered by introducing parasitic side reactions to the cell, like enhanced electrolyte decomposition and the loss of active lithium, which in turn decrease not only the energy density but also the lifetime.

Pre-lithiation, which refers to the addition of active lithium to the cell before operation, is considered as a highly attractive strategy to compensate the active lithium losses, e.g., caused by formation of the solid electrolyte interphase (SEI) at the negative electrode in the first charge/discharge cycle(s) or by irreversible lithium trapping. Pre-lithiation is shown to significantly improve the Coulombic efficiency and to decrease the capacity loss of the first cycle, resulting in an increased energy density of the LIB. However, there are several further advantages that might be achieved by pre-lithiation, e.g., a better rate capability, a pre-volume expansion effect (for Si-based anodes) or the possibility to tailor the SEI formation by certain pre-lithiation techniques. Furthermore, pre-lithiation is established as a key technology for the fabrication of lithium-ion capacitors (LICs) and can be used to prevent the use of Li metal negative electrodes in post-lithium ion battery technologies (PLIBs) such as sulphur or oxygen (air) batteries by replacement of intercalation/insertion-based anode materials.

There is a broad variety of techniques and methods in order to perform pre-lithiation. These can be divided into (1) chemical pre-lithiation by active reactants, (2) ex situ (before cell assembly) or in situ electrochemical pre-lithiation, (3) pre-lithiation by direct contact to Li metal and (4) the pre-lithiation with help of electrode additives such as lithiated active species or sacrificial salts. In addition, it is possible to either directly pre-lithiate the negative electrode or to use additives within the positive electrode or over-lithiated positive electrode active materials, in order to pre-lithiate the negative electrode of LIBs within the 1st charge/discharge cycle of operation.

With regard to safety and the aging behaviour, it is very important to control the degree of pre-lithiation, because a too high degree might lead to HSAL formation, due to a fully charged and to over-charge tending negative electrode. Beyond that, further important points need to be considered for commercial exploration of pre-lithiation within the battery cell manufacturing process. Additional mass and volume might be added due to inactive residues (for some pre-lithiation strategies), which reduces the gain in energy density. The reactivity, toxicity and hazardousness of some of the utilized chemicals and methods will demand special preparation and security measures, e.g., the use of dry air during processing, which in turn results in increased costs. In addition, the time needed for a certain pre-lithiation technique is of high importance as it also leads to enhanced costs in cell production.

Taking into account all these aspects, the different pre-lithiation techniques have been described and compared within this review article. Each pre-treatment technique has its own advantages and disadvantages. For this reason, currently, the right choice of the ideal pre-lithiation method depends on the manufacturing requirements, i.e., most likely one has to find the optimum balance between the performance gain by pre-lithiation and the additional costs. For example, if the process should be carried out in ambient air, the best choice would be to use air-stable positive electrode additives or a pre-lithiated germanium oxide additive within the negative electrode. In contrast to that, if a maximal energy density and a well-defined SEI layer are of major importance, the electrochemical pre-lithiation would most likely be the best choice. It will be interesting to see which method will be the technique of choice for potential commercial battery cell manufacturing in future, some promising candidates have been shown within this review.

As described before, pre-lithiation is also a key technology in the fabrication of LICs. Numerous advantages result from pre-lithiation of LICs, particularly with respect to the energy density. Due to these advantages, pre-lithiation is recently performed for nearly all publications reporting on LICs. Furthermore, the fact that a higher degree of pre-lithiation is needed in comparison to the pre-lithiation of LIBs, further promoted the use of pre-lithiation for the commercial fabrication of LICs. Hence, pre-lithiated LICs are already commercially available (e.g., from JMEnergy).

Finally, yet important, it is also possible to use pre-lithiation for the fabrication of PLIB chemistries. The main motivation to apply pre-lithiation for PLIBs is the replacement of metallic lithium by lithium ion intercalation/insertion host materials, preventing the severe safety issues related to operation of Li metal negative electrodes. The successful fabrication of Li-ion/S and Li-ion/O_2 cells, utilizing pre-lithiated negative electrode materials, was emphasized within this review. However, the relevance towards commercial application of such cells is still arguable, due to the lowered energy density of Li-ion/S and Li-ion/O_2 cells compared to the metallic Li based analogues.

In summary, we have the opinion that pre-lithiation has the potential to be used in a commercial process of battery cell manufacturing. In particular, for the broad commercial breakthrough of high-capacity anode active materials like Si or SiO_x, which are currently only used in small amounts (2–3 wt %) in few commercial cells, pre-lithiation will be mandatory to compensate the high active lithium losses in the first charge discharge cycle(s).

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