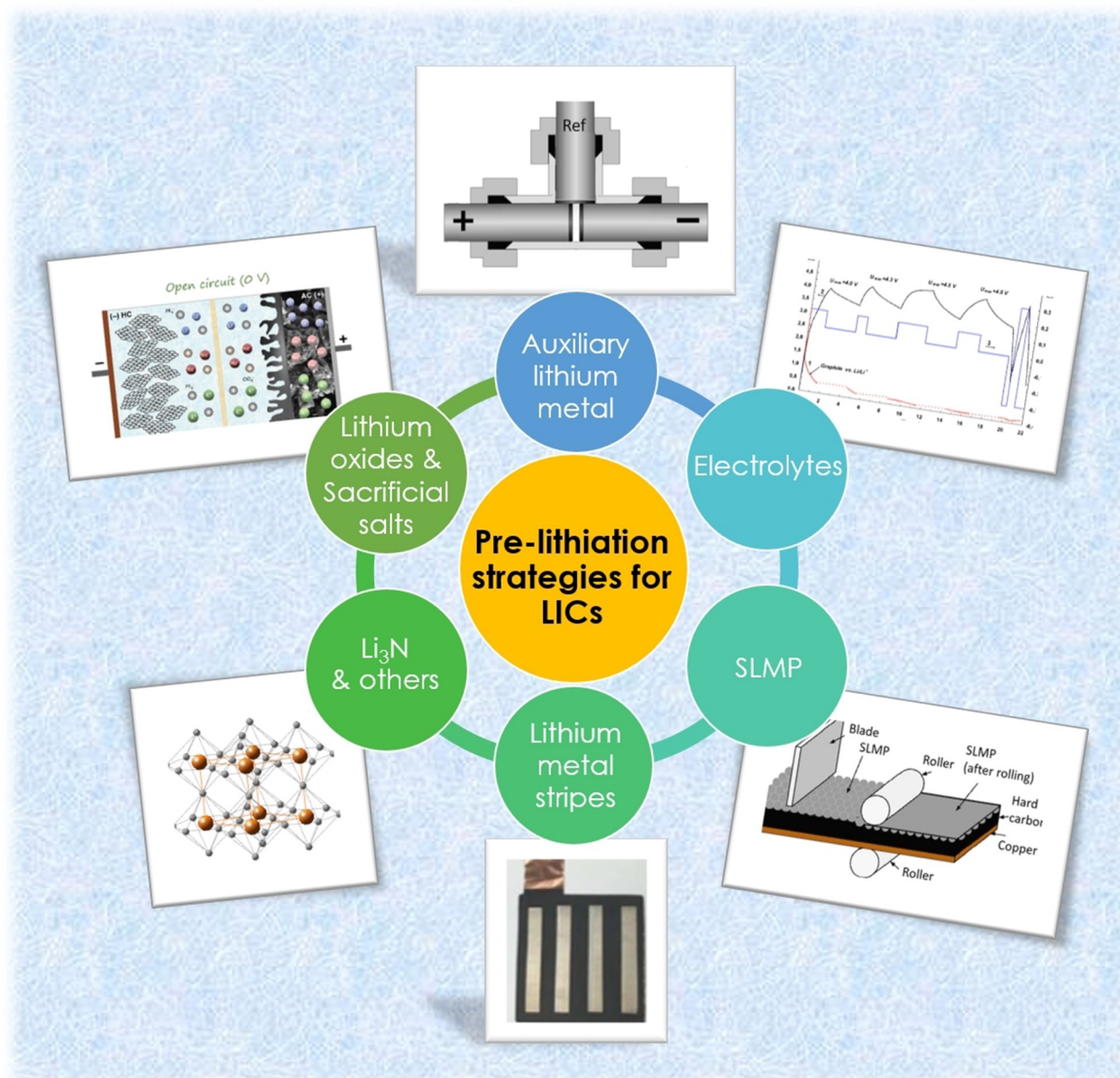Special
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Pre-Lithiation Strategies for Lithium Ion Capacitors: Past, Present, and Future

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Lithium ion capacitor (LIC) is an emerging technology that holds promise to bridge the energy-to-power gap between already market stablished lithium ion battery and electro-chemical double-layer capacitor technologies. Academic research is mainly focused on increasing energy, power and cycle life metrics, but next, pre-lithiation strategy is the key that will open the final door, or not, towards industrialization and commercialization of the technology. Its relevance has only recently been thoroughly considered, but several strategies, all with their own particular set of assets, are already available within the state-of-the-art. It is the right moment to make a retrospective review analysis of the pros and cons of each of the strategies, in order to draw the correct conclusions and look into the future with the best perspective. Despite some reviews newly considered the topic, they were all done in a broader framework, what finally waters down the importance of this critical step. Thus, this review aims to solely focus on the pre-lithiation strategies that have been reported so far for LICs, from the first academic auxiliary lithium metal approach to the latest novel strategies. To conclude, challenges and requierements that the ideal pre-lithiation strategy should fulfil in order to foster market uptake of LIC technology are also discussed.

1. Introduction

The urgent need to reduce CO_2 emissions, main responsible for the climate change, converts decarbonization of worldwide energy sector on a crucial matter of utmost importance. Since the beginning of this century, a slow but progressive transition from fossil fuels to a zero-carbon energy scenario is taking place. In this framework, renewables and e-mobility, both relying on energy storage, are playing an important role towards more competitive, secure and sustainable energy industry, promoting low-carbon technologies.[1] To this end, emergent technologies are focused on the search of more efficient and reliable electrochemical energy storage systems. Among the different technologies developed along the last decades, batteries and electrochemical capacitors succeed to stablish in the market as competitive solutions.[2] Lithium ion batteries (LIBs) are the technology of choice when high energy density is required,[3] while electrochemical double layer capacitors (EDLCs) are the alternative for high power applications.[4] However, a considerable energy-to-power gap yet exists between these two technologies, that needs to be covered in order to give response to new high-energy and high-power demanding applications. Alternative technologies are on the race to reach the 100 Wh kg^{-1}-to-10 kW kg^{-1} energy-to-power threshold while providing a competitive cycle life to capture this emerging market share (Figure 1a).[5] Lithium ion capacitor (LIC) technology is a serious candidate to do so.[6] Being a hybrid technology born from the union of LIBs and EDLCs, it is able to store mid energy values at high power densities while maintaining a cycle life approaching that of EDLCs (Figure 1b).

The concept of asymmetric devices combining a faradaic electrode with a capacitive one was first coined at the end of the 1990s,[7] but it was not until 2001 when the first LIC based on nanostructured $Li_4Ti_5O_{12}$ (negative electrode) and an activated carbon (AC, positive electrode) was reported.[8] Despite $Li_4Ti_5O_{12}$ captured all research attention at the beginning, [9–12] its relatively high potential (i.e., 1.5 V vs. Li$^+$/Li) limiting the output voltage of the cell[13] deviated the attention towards alternative materials able to intercalate Li$^+$ in their structure at lower potentials. The introduction of graphite (~ 0.1 V vs. Li$^+$/Li) moved the technology forward to a new scenario, with attracting energy values able to compete well with other technologies.[14] In addition, its low-cost and good cycle life made graphite the proper candidate to be used as negative electrode, which combined with an AC enabled LIC technology to reach the market and even stablish until the present day.[15] In parallel, academic research has been strongly focused on the development of ultrafast high capacity materials in order to continue increasing the energy outcome of the technology.[16–20] However, the energy, power and cycle life trio needs to be kept well-balanced, assisted by an industrially compatible pre-lithiation technique in order to be competitive and reach the market. Hence, a dual carbon based device based on graphite and AC is still the benchmark product of the technology since its market uptake.[21–23]

Opposite to LIBs, LICs lack of an internal electrode that can act as a lithium source to compensate for the initial irreversible ion consumption geared towards the irreversible electrochemical processes and/or the formation of the solid electrolyte interphase (SEI).[24] This ion consumption takes place during the first charge of the system, where the reduction of electrolyte solvents and their further reaction with lithium ions take place in the negative electrode below 1 V vs. Li$^+$/Li. Thus, the use of a non-lithium containing positive electrode such as an AC-based, requires the use of an external source of lithium. Otherwise, lithium ions involved in SEI formation will starve the electrolyte, reducing cell performance.[25] Moreover, an accurate pre-lithiation will allow to lithiate the anode in its most appropriate degree, enlarge the potential window of the positive electrode and increase the cell voltage. Therefore, a precise pre-lithiation step will result not only in a higher energy density output, but also in improved power performance as well as longer cycle life.

On this basis, pre-lithiation step turns in an unprecedent technological challenge in LICs playground.[26] Indeed, in view of the challenging complexity of the matter, added to the fact that energy, power and cycle life are prior prerequisites for the

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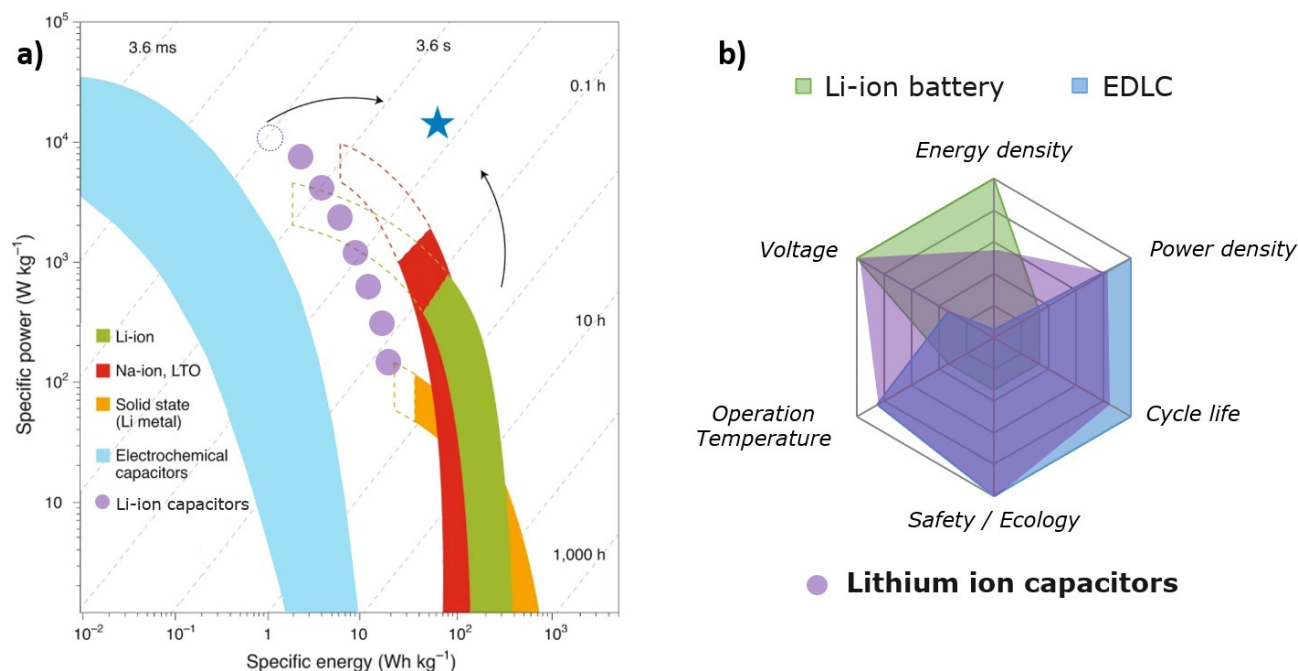
Figure 1. a) Ragone plot of current technologies and future scenario of the electrochemical energy storage field, adapted from Ref. [5] with permission. Copyright (2020) Springer Nature; and b) synergetic features of lithium ion capacitors, born from the union of batteries and EDLCs.

technology, few efforts were dedicated to the pre-lithiation step in the early years of the technology. Currently, once mature and closer to become a widespread reality, pre-lithiation step is gaining momentum, and considerable progress has been achieved in the last years[27] and is yet to come. Furthermore, novel materials that can be the future of the technology are just around the corner,[17,19,20] but will require an efficient, low-cost pre-lithiation strategy to enable the development, industrialization and market entry of novel LICs. To this aim, we gathered the different pre-lithiation strategies followed along the last years in this work, in order to provide a better vision towards the bright future that awaits this technology (Figure 2).

2. Electrochemical Pre-Lithiation

The first and still most commonly used approach in academia for LICs was introduced by Aida *et al.* in 2006.[28] The so called electrochemical pre-lithiation approach consists of an auxiliary lithium metal electrode used to provide the extra lithium ions needed by the system.[19,29] This method can be followed in two different ways. On the one hand, a three-electrode cell can be used where the negative electrode is lithiated from the metallic lithium used as the reference electrode. The advantage of this approach consists of a single assembly of the system, on the contrary, pre-lithiation needs to be carried out very slowly and a gradient in SEI formation might be observed due to the geometrically disfavored approach. On the other hand, in a two-step process, first a two-electrode cell is assembled to pre-lithiate the electrode and is afterwards recovered for further full cell assembly. Despite being more complex and time-consuming approach, the homogeneity of the formed SEI is considerably better. This approach is the main strategy followed in academia when research is focused on studying electrode materials or electrolytes. Nevertheless, this is a lab-scale limited strategy that cannot be transferred to an industrial process.

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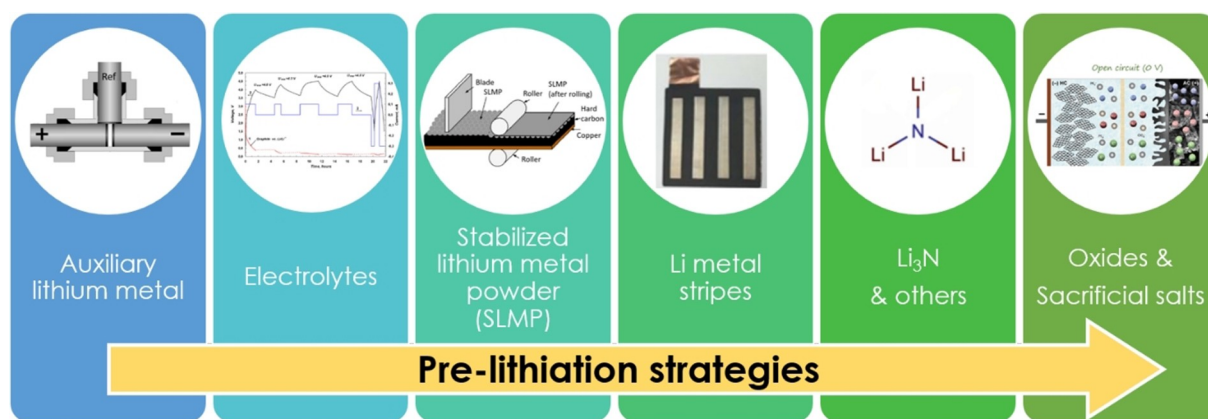
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Figure 2. Different strategies to overcome the pre-lithiation step in lithium ion capacitors.

3. Pre-Lithiation Strategies Towards Industrial Development: An Overview

In parallel to the development of materials and the technology itself, pre-lithiation strategies have significantly evolved among the last years.[30,31] From the initial auxiliary lithium metal electrode used only for laboratory research, to more sophisticated and industrially compatible strategies based on sacrificial salts. This transition attends to the logic evolution of a variety of strategies that started to consider market needs such as processability, safety and cost. In the following overview, all the strategies utilized so far are gathered, their pros and cons considered, and so, future prospects given in order to pave the way towards the final solution that can trigger the market uptake of the technology.

3.1. Electrolytes

Initially, in order to avoid the use of any auxiliary agent in the device, some authors implemented a SEI formation protocol designed *ad-hoc*, consisting on the utilization of lithium ions from the electrolyte to proceed with the pre-lithiation. In order to validate the strategy, a third lithium metal reference electrode was introduced to monitor both positive and negative electrode potentials. The special protocol reported by Khomenko *et al.* in 2008 was based on charging/relaxation periods of a LIC using AC and graphite as the positive and negative electrode, respectively, in 1 M LiPF$_6$ (EC:DMC) electrolyte.[32] In the first charge step, ideally, PF$_6^-$ were adsorbed in the AC, while Li$^+$ were inserted into graphite layers. However, this first step did not allow to provide enough lithium to create the required graphite intermediate compounds (GICs). Therefore, considering that the overall self-discharge of electrochemical capacitors is the sum of the individual self-discharge of each electrode,[33] a relaxation period was applied. In this step, the AC – which is capacitive – showed faster self-discharge than the graphite – which is faradaic. This way, the desired potential of 100 mV *vs.* Li$^+$/Li, corresponding to the second stage GIC (*i.e.*, LiC$_{12}$), was possible

to achieve through few further charge/relaxations cycles (Figure 3a). However, even that the developed LIC showed good energy-to-power values, far better compared to conventional EDLCs, this strategy directly consumes lithium from the electrolyte. As consequence, it reduces the initial concentration of the utilized 1 M LiPF$_6$ (EC:DMC) electrolyte, what later aggravates the overall performance and durability of the device.

As a result, later in 2012, after calculating the exact amount of lithium ions consumed in the pre-lithiation step for a graphite:AC LIC, it was concluded that the concentration of the previous electrolyte was too low to form the expected GICs and at the same time guarantee a good electrical conductivity of
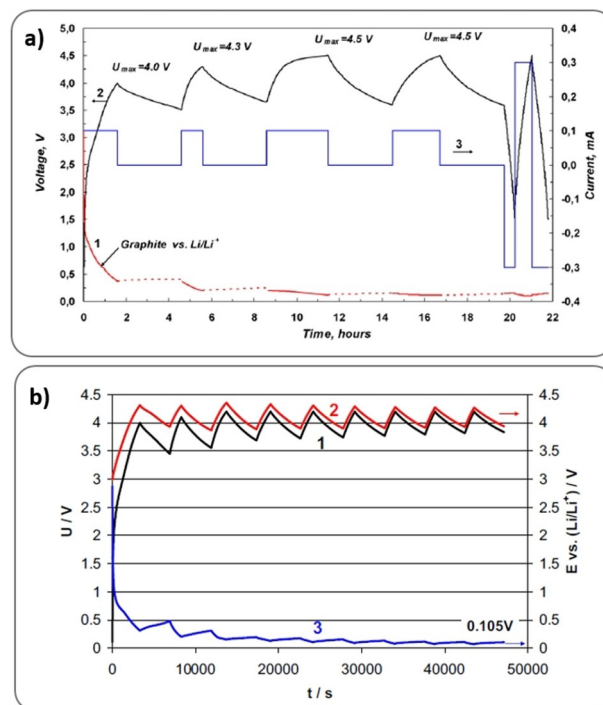

Figure 3. Electrolyte as pre-lithiation agent using: a) 1 M LiPF$_6$ (EC:DMC)[32] and b) 2 M LiTFSI (EC:DMC)[34] and following charge/relaxation formation cycles. Reproduced from Refs. [32] Copyright (2007), Elsevier and [34] with permission Copyright (2012), Elsevier.

the electrolyte. Hence, with the aim of avoiding those undesired issues, Decaux et al. prepared a highly concentrated 2 M LiTFSI (EC:DMC) electrolyte.[34] This way, following the same charge/relaxation periods, the low potential where LiC_{12} GIC is formed (i.e., 100 mV vs. Li^+/Li) was much easier to reach without starving the electrolyte (Figure 3b). Additionally, the upper potential of the formation cycles was limited to 4.2 V vs. Li^+/Li due to the corrosive nature of LiTFSI at higher potentials. Thus, using such electrolyte not only ion starving was avoided but also operating at over-potentials (i.e., 4.5 V vs. Li^+/Li), where electrolyte oxidation occurs, was circumvented. In 2017, the company Taiyo Yuden patented a similar strategy for dual carbon LICs using LiFSI or $LiBF_4$ salts with concentrations ranging between 1.2 and 1.8 M.[23]

Despite the simplicity of the strategy, it is difficult to find a highly concentrated electrolyte able to keep the required viscosity, conductivity, thermal and electrochemical features for a LIC. Thus, different alternatives to follow the pre-lithiation step without affecting the performance of the overall device were kept on investigating.

3.2. Anodes

In the meantime, in 2006 Jarvis et al., in collaboration with FMC-Lithium company, introduced for the first time the use of stabilized lithium metal powder (SLMP) as lithium source in the negative electrode for LIBs development,[35] which was some years later transferred to LIC technology.[36] SLMP consists on lithium metal particles sealed in a thin coating of Li_2CO_3, which avoids the exposure of lithium metal to ambient environment. SLMP is normally in the range of 10–200 nm and owing to its protective layer, it can be handled in dry air. However, some complexities arose in the slurry formulation due to its incompatibility with the most common used organic solvent (i.e., N-methyl pyrrolidone, NMP). Hence, among the different strategies investigated in the field of batteries, SLMP was either dissolved in non-polar solvents such as hexane or toluene to later disperse it in pre-fabricated negative electrodes (Figure 4a)[37] or mixed with an appropriate binder able to be dissolved in previously mentioned non-polar solvents.[38] The latter would allow the incorporation of SLMP in battery slurry formulation (Figure 4b).

In 2012 Cao and Zheng first introduced this strategy in LIC technology. SLMP was added onto the surface of a pre-fabricated hard carbon (HC) negative electrode in order to introduce the lithium ions needed to compensate the first charge irreversibility of a HC-SLMP:AC based LIC and avoid the consumption of the electrolyte during cycling (Figure 4c).[36] The developed LIC showed an energy density output of 82 Wh kg⁻¹ at 100 W kg⁻¹ and 14 Wh kg⁻¹ at 20000 W kg⁻¹ per mass of both electrodes. Nonetheless, still much higher energy-to-power values could be obtained since the HC negative electrode swings in a non-optimal potential window of 0.8–2 V vs. Li^+/Li.[39] Hence, even this work opened a new avenue towards the use of SLMP as a pre-lithiation agent for LICs, it still required some further optimization.

Later in 2014, the same group scale-up and transferred the technology from lab-scale three-electrode cells to first proto-type pouch cells.[40] Within this approach, Cao et al. introduced a roll-to-roll process for a better incorporation of the SLMP dissolution into 80×50 mm HC electrodes (Figure 4d). Optimization and scale-up of the technique allowed developing two different 250 F and 365 F LICs with a maximum energy density output of 22 Wh kg⁻¹ and 31.5 Wh kg⁻¹, and an energy retention of 50% and 36.2%, respectively. Furthermore, both systems were able to keep 80% of their initial energy output after 10000 cycles, showing a low leakage current of only 0.3 μA cm⁻². Thus, when SLMP was roll-to-roll processed onto the surface of a pre-fabricated HC, highly effective lithiated negative electrodes were achieved showing viability towards industrially scalable LICs. However, some safety issues might arise regarding the use of SLMP, as it is very reactive and sensitive to humidity, and it could be scattered in the air making it difficult to handle. Moreover, the purity is limited to 97–98%, what directly alters the self-discharge of LICs. Instead, lithium metal shows a purity grade of 99.9%. Hence, in 2017, Cao et al. reported a new-generation HC:AC 200 F pouch cell LIC which utilized 40×4×0.045 mm lithium metal stripes loaded onto the surface of pre-fabricated HC as lithium source (Figure 4e).[41] The amount of lithium metal, being about 9.6 wt.%, was calculated based on the specific capacity of the HC. Once the lithium metal stripes were loaded, electrodes were soaked and sealed in a package filled with electrolyte. After 18 h, all lithium was diffused through the carbon sheets of the HC, enabling its utilization as pre-lithiated negative electrode in LICs. The developed system reached 14 Wh kg⁻¹ and 28 Wh L⁻¹ energy densities at 6 kW kg⁻¹ and 12 kW L⁻¹ specific powers, respectively, per total mass and volume of the cell. Furthermore, it showed a floating time of 2000 h at 65 °C with 90% capacitance retention and cycle life over 100000 cycles at 50 C (4 A) with 88% capacitance retention.

As it has been demonstrated by the group of Prof. Zheng, the use of lithium metal as pre-lithiation agent has shown to be an effective manner to compensate the lack of lithium ions in the system, suitable for industrialization. Nevertheless, the difficulty of controlling the pre-lithiation degree by SLMP needs for more research on the topic.[42–44] In addition, the use of such an air sensitive agent makes mandatory the utilization of an inert atmosphere for the fabrication of the devices, what remarkably increases the cost of the technology.

3.3. Cathodes

As consequence of the processing difficulties that lithium metal might arise, the most popular strategies adopted in the last years are focused on the integration of lithium-based inorganic or organic compounds in the formulation of the positive electrode. Among others, lithium oxides, lithium nitride, 3,4-dihydroxibenzonitrile dilithium salt, dilithium squarate, lithium sulfide or a combination between pyrene and lithium phosphate have been utilized.
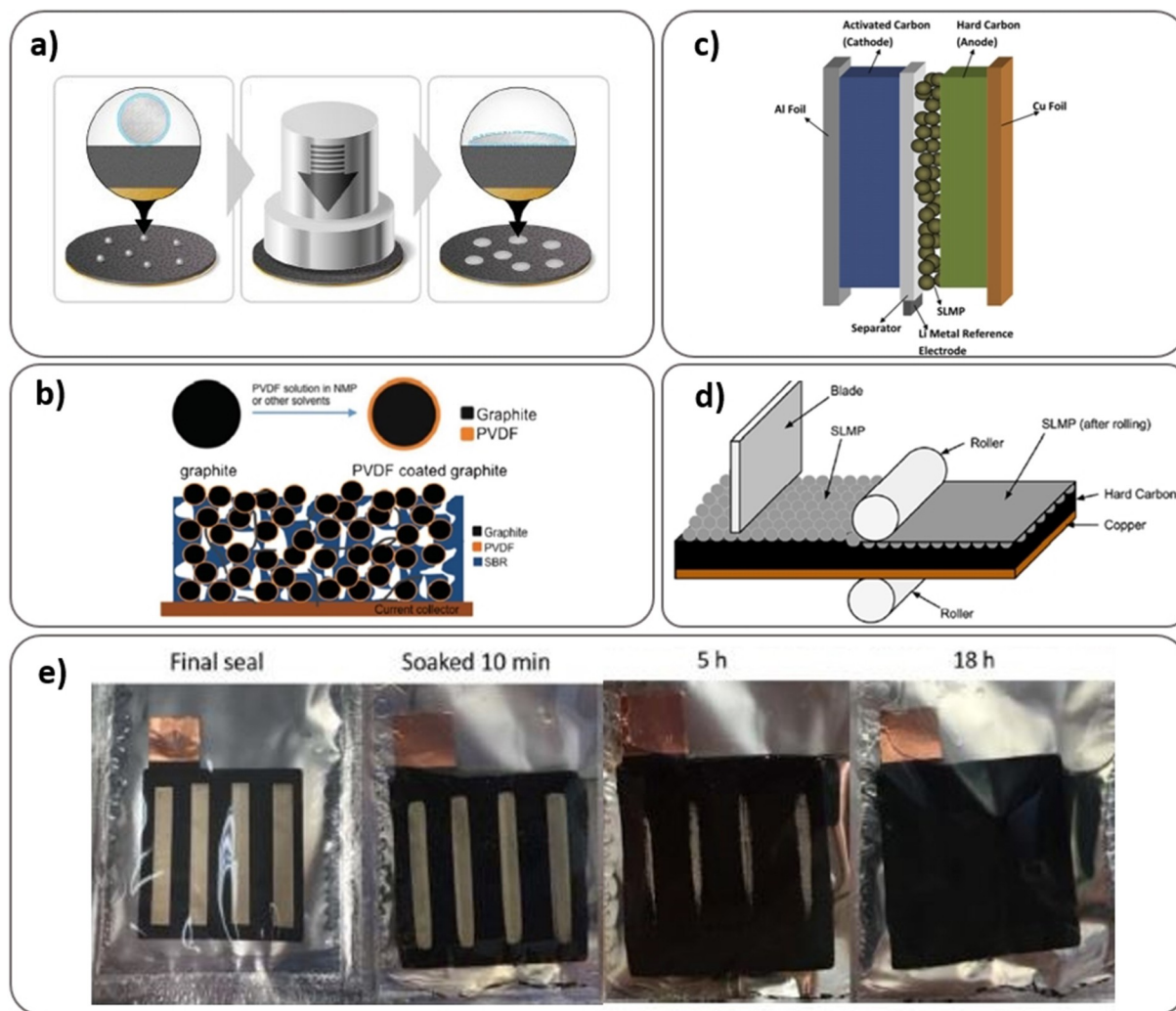
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Figure 4. a) Scheme of the deposition of SLMP into the surface of the negative electrode and its following shape after applying pressure. Reproduced from Ref. [24] with permission. Copyright (2018) The Authors. b) Scheme of the addition of SLMP particles in the slurry preparation. Reproduced from Ref. [38] with permission. Copyright (2013) Royal Society of Chemistry. c) SLMP onto the surface of the negative electrode of a LIC. Reproduced from Ref. [36] with permission. Copyright (2012) Elsevier. d) Roll-to-roll processed SLMP in a negative electrode of a LIC[40] and e) Lithium stripes in a 46×46 mm hard carbon soaked in electrolyte.[41] Reproduced from Refs. [40] Copyright (2014) Elsevier and [41] Copyright (2016) The Electrochemical Society with permission.

3.3.1. Lithium Oxides

Opposite to reactive SLMP and lithium metal, lithium oxides such as Li_2MoO_3,[45] Li_5FeO_4,[46] Li_6CoO_4,[47,48] Li_5ReO_6,[49] $Li_{0.65}Ni_{1.35}O_2$[50] or Li_2CuO_2[51] that can be used to pre-lithiate the negative electrode, when implemented in the formulation of the AC positive electrode, represent a safer alternative. These materials irreversibly oxidize in the same potential range in which the positive electrode operates (*i.e.*, 3–4.2 V *vs.* Li+/Li) in the first charge step of the device. During the oxidation of above-mentioned materials, lithium ions are irreversibly released from the positive electrode and diffused to the negative electrode enabling the formation of the SEI and the graphite intercalation compounds.

In 2011 Park *et al.* first introduced this novel approach by integrating 26.75 wt.% Li_2MoO_3 in the AC positive electrode.[45] The selected material was first individually characterized charging it until 4.7 V *vs.* Li+/Li at C/10. Two plateaus at around

3.6 and 4.4 V *vs.* Li+/Li were observed, where Li+ extraction from lithium layers and transition metal layers occurs, delivering over 250 mAh g^{-1} (Figure 5a). This first irreversible reaction creates a de-lithiated phase, $Li_{2-x}MoO_3$ ($0 < x < 1.7$), which is a metallic conductor, while if full de-lithiation occurs an insulator product -MoO_3- is obtained. Therefore, the operating voltage of the LIC should be well-controlled in order to avoid formation of any insulating product. Moreover, the unappropriated particle size of the reported Li_2MoO_3 penalized rate capability and cycling performance of the LIC. Later, the same group showed that combining the reported AC-Li_2MoO_3 positive electrode together with 5–10 wt.% of additional Li_2RuO_3 could significantly enhance the electrochemical performance of the developed system. Thus, by using Li_2MoO_3 as a lithium source in combination with Li_2RuO_3 as additive a pre-lithiated high energy density LIC was achieved, showing maximum volumetric energy of 25 Wh L^{-1} at a power density of 3 W L^{-1}, per volume of active material.[52]

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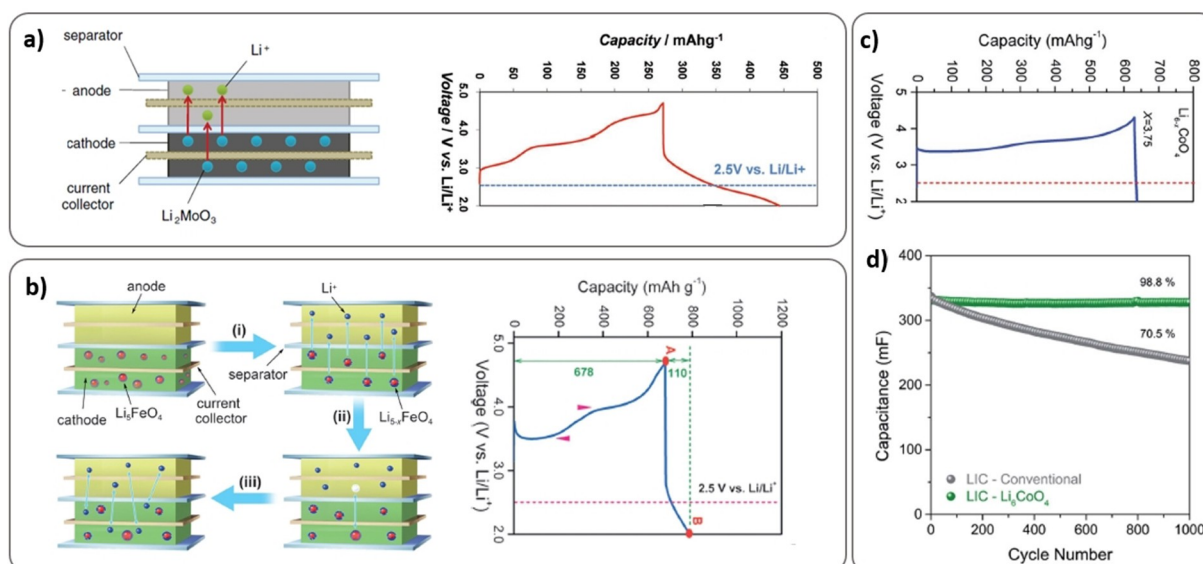European Chemical
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Figure 5. Different lithium oxides integrated in the positive electrode in order to act as pre-lithiation agents: a) scheme of the Li$^+$ diffusion of Li$_2$MoO$_3$ from the cathode to the anode and its electrochemical behavior during the oxidation process. Reproduced from Ref. [45] with permission. Copyright (2011) Wiley-VCH. b) scheme of the Li$^+$ diffusion of Li$_5$FeO$_4$ from the cathode to the anode and its electrochemical behavior during the oxidation process. Reproduced from Ref. [46] with permission. Copyright (2014) Wiley-VCH. c) Oxidation process of Li$_6$CoO$_4$ and d) the comparison of the capacitance retention between a LIC with Li$_6$CoO$_4$ and without it. Reproduced from Ref. [47] with permission. Copyright (2015) Royal Society of Chemistry.

However, the need to reduce the weight percentage of the pre-lithiation agent used in the positive electrode pushed the group towards the synthesis of new materials with higher irreversible capacities. In 2014, a novel single-phase Li$_5$FeO$_4$ with an antifluorite structure was reported providing a high irreversible capacity of 700 mAh g^{-1} after an initial charge up to 4.7 V vs. Li$^+$/Li at C/10 (Figure 5b). A 3-fold increase in capacity output respect to previous Li$_2$MoO$_3$ allowed reducing the lithium oxide content in the electrode from almost 27 wt.% to 10.3 wt.%.[46]

Nevertheless, both Li$_2$MoO$_3$ and Li$_5$FeO$_4$ require to operate at high potentials (i.e., > 4.7 V vs. Li$^+$/Li) in the first charge step. Therefore, even that initially insignificant electrolyte decomposition or O$_2$ release at those high potentials was assumed, a new work in 2015 demonstrated that operating the system at that high potentials inevitably causes some side reactions affecting the cyclability of the system.[47] Hence, on the search of alternative lithium rich materials, Li$_6$CoO$_4$ was identified as a promising candidate. Its large amount of available Li$^+$ (about 600 mAh g^{-1}, being less than 3.5 mol Li$^+$ available for pre-lithiation), poor reversibility due to its unique crystal structure and its lower lithium ion extraction potential compared to other materials (i.e., 4.3 V vs. Li$^+$/Li) (Figure 5c) were highly interesting.[47] Authors compared the performance of their developed LIC with 11 wt.% and 17.2 wt.% Li$_6$CoO$_4$ as well as without it, showing much higher volumetric energy values for the lithium oxide containing LIC. In contrast, slightly lower capacity values were obtained for the LIC-Li$_6$CoO$_4$ due to the microscale particle size of the oxide, responsible of the large overpotential at high currents. Nonetheless, it was shown that the LIC with Li$_6$CoO$_4$ was able to maintain about 98.8% of its initial capacity after 1000 cycles, while the LIC without it

exhibited only 70.5% retention (Figure 5d). Authors attributed this limited cycle life to the possible undesirable lithium deposition from the auxiliary lithium metal onto the surface of the negative electrode.

Recently, Guo et al. reported on the same Li$_6$CoO$_4$ as pre-lithiation agent for LICs, while different amounts of lithium oxide and the influence of the oxidation product were also investigated. Authors verified that even after the oxidation of Li$_6$CoO$_4$, the remaining product of Li$_{6-x}$CoO$_y$ did not undertake any additional Li$^+$ insertion and/or extraction, while extra capacity coming from a surface capacitance mechanism was observed. Thus, it was demonstrated that the incorporation of this lithium oxide as pre-lithiation agent might play an additional and positive role owing to its capacitive charge storage mechanism that further enhanced the energy and power outputs of the developed LIC.[48] However, the use of cobalt should be avoided for the sake of green, sustainable and recyclable energy storage systems.

Despite all the above-mentioned approaches based on lithium metal oxides (Li$_x$MO$_y$) combined with an AC showed some rate capability and performance limitations due to their large particle size, the studied materials show direction towards an industrially viable alternative avoiding the use of metallic lithium to pre-lithiate LICs. Notwithstanding, their use still requires operating at high potentials to ensure lithium extraction, what might cause some undesired parasitic reactions. Therefore, new materials able to oxidize at lower potentials are still highly desired. In pursuit of that goal, in 2016 Jeżowski et al. presented lithium rhenium (VII) oxide (Li$_5$ReO$_6$)[49] and a non-stoichiometric lithium nickel oxide (Li$_{0.65}$Ni$_{1.35}$O$_2$)[50] as alternative lithium sources both combined in a different weight percentage with AC in order to be used as

lithium source and positive electrode. On the one hand, Li_5ReO_6 shows high irreversible capacity (*i.e.*, 410 mAh g^{-1}) delivered below 4.3 V *vs.* Li$^+$/Li (see Figure 6a and 6b). In combination with AC (40:40 wt.% Li_5ReO_6:AC), authors studied different electrochemical protocols for the first pre-lithiation step. It was observed that applying a first C/20 rate (being C the theoretical capacity of graphite, 372 mAh g^{-1}) a thick and cracked SEI was obtained, while when applying a faster initial rate of 1 C the created SEI was much thinner and homogeneous. Thus, an initial charge at 1 C was applied to the LIC in order to create a suitable SEI, and after 2 h relaxation period, the system was charge at C/20 up to 4.2 V for further intercalation of lithium ions into the graphite electrode (see Figure 6c). Once the SEI and GICs were formed, the LIC was characterized at different current densities in the cell voltage of 2.2–4.1 V showing high energy-to-power values of around 40–60 Wh kg^{-1}$_{AM}$ and 20–700 W kg^{-1}$_{AM}$, per active mass (AM) of both electrodes, as well as long cycle life showing stable capacitance after 5000 cycles.[49] On the other hand, an alternative non-stoichiometric lithium nickel oxide, $Li_{0.65}Ni_{1.35}O_2$, was also studied. The extraction of lithium ions in this material take place in the potential range of 4.1–4.3 V *vs.* Li$^+$/Li (Figure 6d), delivering an irreversible capacity close to 120 mAh g^{-1}. As it was calculated that at least 220 mAh g^{-1} were required to form the SEI and GIC compounds, a 55 wt.% of $Li_{0.65}Ni_{1.35}O_2$ was introduced in the formulation of the AC positive electrode. As shown in Figure 6e, an initial charge at C/5 was followed in order to form a suitable SEI, and after a relaxation period of 2 h, lithium ions were intercalated into graphite at C/20. Afterwards, the LIC was

successfully characterized in the cell voltage of 2.2 to 3.8 V. Nonetheless, due to the relatively high amount and low capacity of $Li_{0.65}Ni_{1.35}O_2$, the energy output of the LIC was not as high as expected, limiting its maximum energy output to 15–20 Wh kg^{-1}$_{AM}$, per active mass of both electrodes.[50]

At the same time, Zhang *et al.* demonstrated a LIC based on graphite as the negative electrode and AC together with 50 wt.% Li_2CuO_2 as the positive electrode.[51] As stated from authors, Li_2CuO_2 oxidizes at around 3.6 V *vs.* Li$^+$/Li delivering a specific capacity of 342 mAh g^{-1}. However, it also gives some pseudocapacitance below 2.8 V *vs.* Li$^+$/Li. Thus, as shown in Figure 6f, when the AC-Li_2CuO_2 electrode was cycled in the range of 2–4.2 V *vs.* Li$^+$/Li, the high capacity of the first cycles was representative of the irreversible reaction of Li_2CuO_2. However, from the 18th cycle onwards, the higher capacity/ capacitance values obtained respect to bare AC were a contribution by the additional reported pseudocapacitance. Further cycling in the reduced operating potential range of 2.8–4.2 V *vs.* Li$^+$/Li, have almost no impact on the capacity output, showing both bare AC and AC-Li_2CuO_2 electrodes very similar capacity/capacitance values. Figure 6g shows the first two cycles of LIC-Li_2CuO_2, where a large plateau at 3.6 V *vs.* Li$^+$/ Li can be observed in the first charge where the oxide is de-lithiated, while in the following discharge some pseudocapacitance is given owing to the lower potential of the positive electrode (*i.e.*, 2.8 V *vs.* Li$^+$/Li). Accordingly, when the LIC was operating in the cell voltage of 2.8–4.2 V, 196 Wh kg^{-1}$_{AC}$ energy density at 456 W kg^{-1}$_{AC}$ power density were obtained, while when operating between 2.0–4.2 V the stored/delivered energy
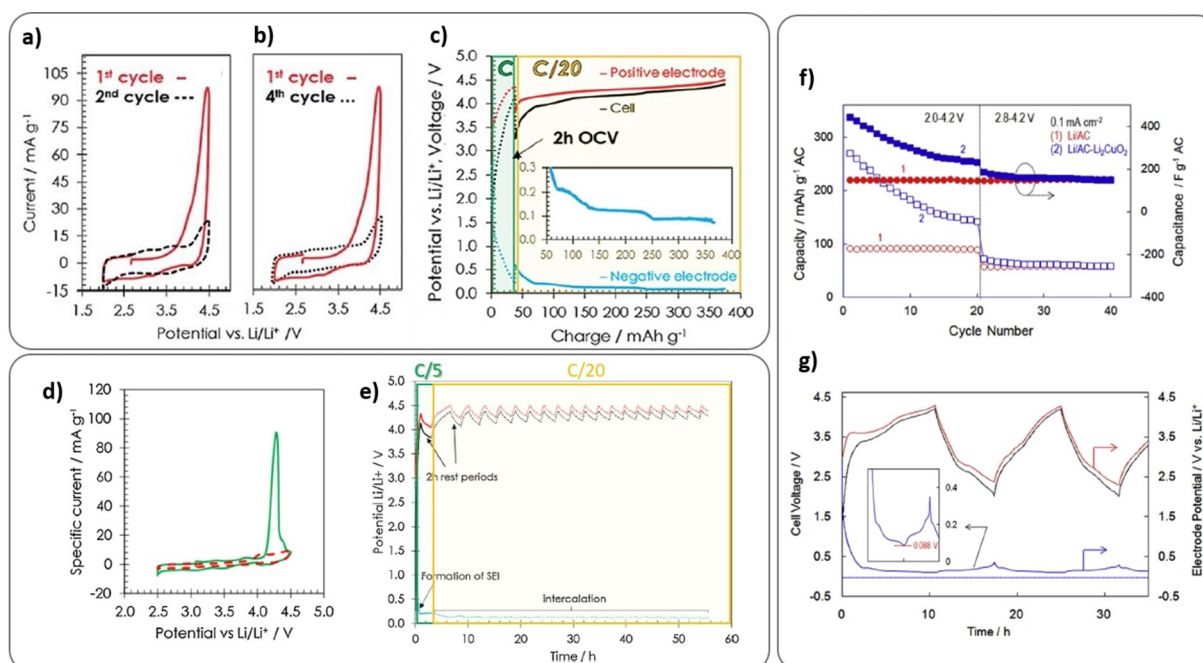

Figure 6. a) and b) Cyclic voltammograms of AC-Li_5ReO_6 electrode and c) Pre-lithiation step using AC-Li_5ReO_6 as positive electrode and lithium source. Reproduced from Ref. [49] with permission. Copyright (2016) Royal Society of Chemistry. d) Cyclic voltammogram of $Li_{0.65}Ni_{1.35}O_2$ electrode and e) pre-lithiation step using AC-$Li_{0.65}Ni_{1.35}O_2$ as positive electrode and lithium source, all in LiPF$_6$ in 1:1 EC:DMC. Reproduced from Ref. [50] with permission. Copyright (2015) Elsevier. f) Comparison of specific capacity values of AC and AC-Li_2CuO_2 and g) pre-lithiation step using AC-Li_2CuO_2 as positive electrode and lithium source. Reproduced from Ref. [51] with permission. Copyright (2017) Elsevier.

density was 315 Wh kg$^{-1}_{AC}$ at a power density of 454 W kg$^{-1}_{AC}$ (all values are given per mass of AC).[51]

From the above-reviewed research works, it seems that the use of different lithium oxides might offer a safer and more realistic and cost-effective alternative to metallic lithium on the search of an industrially compatible strategy for LIC technology. Nonetheless, in general terms, they still show some limitations such as i) large particle size, ii) high oxidation potentials, iii) high cost, iv) low irreversible capacity, and v) the high amount of remaining inactive mass that needs to be addressed towards the final goal.

3.3.2. Lithium Nitride

Despite it was first patented in 2012,[53] Li$_3$N has lately caught attention as a promising alternative owing to its i) high practical specific capacity (*i.e.*, 1379 mAh g^{-1}), ii) decomposition potential around 4 V *vs.* Li$^+$/Li when mixing with AC in a battery slurry process, and iii) the lack of residues after decomposing. Theoretically, Li$_3$N decomposes at around 0.9 V *vs.* Li$^+$/Li, however, it was found that a passivation layer on Li$_3$N formed during material processing could enhance the oxida-

tion potential up to 4–4.3 V *vs.* Li$^+$/Li (Figure 7a),[54] showing its potential use as a pre-lithiation agent when mixed with AC in the positive electrode. Instead, its main limitation is its high reactivity with most commonly used solvents in electrode manufacture procedure, such as N-methyl-2-pyrrolidone (NMP) or dimethyl sulfoxide (DMSO). Thus, in order to avoid the need of using an unsafe solvent as tetrahydrofuran (THF),[55] Liu *et al.* recently demonstrated the stabilization mechanism of Li$_3$N in an alternative solvent by the higher hydrogenation energy of N, N-dimethylformamide (DMF). This way, it was possible to add 12 wt.% of Li$_3$N in the AC electrode manufacturing process.[56] Unfortunately, the profile of the negative electrode operates too close to 0 V *vs.* Li$^+$/Li (Figure 7b) at a discharge time of 200 min, what most probably will infer lithium plating at higher rates. However, energy-to-power values showing up to 50 Wh kg$^{-1}_{AM}$ energy density output at 5000 W kg$^{-1}_{AM}$ power density, per mass on active materials on both cathode and anode, were reported.

Sun *et al.* also reported the use of Li$_3$N as pre-lithiation agent recently, but in this case AC-Li$_3$N was constructed by loading Li$_3$N onto a pre-fabricated AC electrode surface through cold pressing.[57] LICs with different mass ratio of positive to negative electrode to Li$_3$N were designed. It was concluded
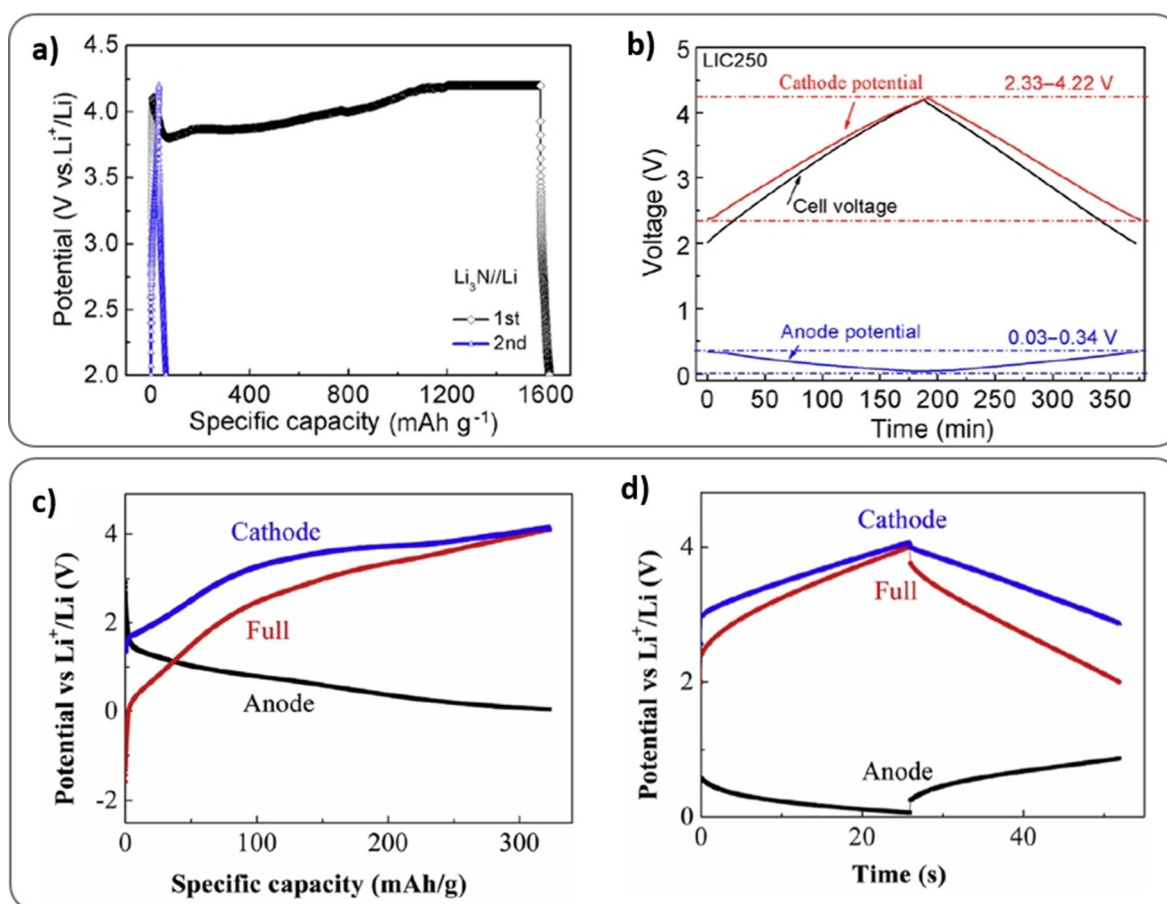

Figure 7. Li$_3$N as pre-lithiation agent introduced in the AC electrode manufacturing process: a) oxidation of surface protected Li$_3$N and b) charge/discharge initial cycle for a LIC using 12 wt.% of Li$_3$N. Reproduced from Ref. [56] with permission. Copyright (2019) Science China Press. LIC with Li$_3$N loaded onto a pre-fabricated AC c) initial charge step for a Li$_3$N pre-lithiated LIC and d) charge/discharge profile at the lower discharge time of the reported LIC. Reproduced from Ref. [57] with permission. Copyright (2019) Elsevier.

that: i) an excess of lithium ions might promote lithium plating, worsening the electrochemical performance mainly at high rates and ii) a lack of lithium ions might elevate the potential of the positive electrode causing electrolyte oxidation. Beyond this conclusion, authors showed an excellent LIC pouch cell within a mass ratio of 8:4:1 AC:HC:Li$_3$N (Figure 7c and 7d) exhibiting a maximum energy and power density of 74.7 Wh kg$^{-1}_{AM}$ and 12.9 kW kg$^{-1}_{AM}$ per mass of both electrode active materials in a cell voltage of 2.0–4.1 V, within a capacitance retention of 91% after 10000 cycles.

Li$_3$N might be a promising pre-lithiation agent, nevertheless, some key issues such as particle size reduction of commercial Li$_3$N and more importantly its difficulties to integrate it in standard slurry processing need to be addressed in order to properly evaluate the real potential of this strategy for its implementation on an industrial fabrication process.

3.3.3. Sacrificial Salts

In view of the necessity to design new materials that show higher irreversible capacity output at lower oxidation potentials, generating zero residue and being more ecologically friendly as well as cost-effective, Jeżowski et al. designed a novel organic 3,4-dihydroxibenzonitrile dilithium salt (Li$_2$DHBN) and reported its performance as a pre-lithiation agent in 2018.[58] Despite organic compounds usually require high amount of conductive carbon due to their poor electronic conductivity, since the organic salt is incorporated within the AC positive electrode, good electronic conductivity was ensured. As shown in Figure 8a and 8b, Li$_2$DHBN irreversibly oxidizes at 3.2 V vs. Li$^+$/Li delivering about 365 mAh g^{-1} specific capacity. Thus, being the specific capacity of graphite 372 mAh g^{-1}, almost equal masses of graphite and Li$_2$DHBN were needed. Hence, a positive electrode with 40 wt.% AC, 40 wt.% Li$_2$DHBN, 15 wt.% carbon black and 5 wt.% polytetrafluoroethylene (PTFE) was utilized. Combined with graphite in the negative electrode, the LIC was galvanostatically charged/discharged within the cell voltage of 2.2–4.0 V, showing 40–60 Wh kg^{-1} energy density per total mass of electrode materials, measured up to 2000 W kg^{-1} power density. Furthermore, cyclability test of the device showed outstanding results within a very low capacitance fade after 25000 cycles. Furthermore, compared to other reported materials, the product originated from the Li$_2$DHBN oxidation (i.e., 3,4-dioxobenxonitrile, DOBN), was soluble in carbonate-based electrolytes, thus, there was not any additional dead mass left in the electrode after the pre-lithiation step. Moreover, it was confirmed by ionic conductivity measurements, that the presence of DOBN in the electrolyte did not show any significant influence as evidenced by the long cyclability, what makes Li$_2$DHBN an attractive alternative as sustainable lithium source. However, Li$_2$DHBN is unstable under air what requires an oxygen free environment for its use, a clear impediment towards a low-cost solution.

Thereby, on the search for more cost-effective solutions, Arnaiz et al. recently reported on the use of dilithium squarate (Li$_2$C$_4$O$_4$) as an easy to synthesize, safe and air-stable compound

that oxidizes in a potential range from 3.9 to 4.2 V vs. Li$^+$/Li, releasing Li$^+$ and gas, with a theoretical capacity of 425 mAh g^{-1}.[59] A positive electrode consisting on 50 wt.% AC, 40 wt.% Li$_2$C$_4$O$_4$, 5 wt.% carbon black and 5 wt.% polyvinylidene fluoride (PVdF) was fabricated. On the one side, the cyclic voltammogram of the composite reveals that the salt is almost fully decomposed in the above-mentioned oxidation potential despite a small amount remains in the subsequent cycles (see Figure 8c). On the other side, the rate capability of only AC compared to the AC-Li$_2$C$_4$O$_4$ electrode shown in Figure 8d reveals that the voids left behind by the decomposition of the salt are able to enhance the capacity output of the positive electrode, similar to what was reported for Li$_6$CoO$_4$[48] and Li$_2$DBHN.[58] As a first approach, a LIC based on graphite as negative electrode and AC-Li$_2$C$_4$O$_4$ as positive electrode was demonstrated. The first charge step at C/10 (being C = 372 mAh g^{-1}) respect the mass of graphite shown in Figure 8e top describes how lithium ions are perfectly inserted into graphite layers, creating their corresponding GICs, described by the plateaus at low potentials below 100 mV vs. Li$^+$/Li, while the dilithium squarate salt of the positive electrode oxidizes. Furthermore, the strategy was also demonstrated for an olive-pits derived HC-based LIC, a great challenge owing to the higher irreversibility of HC respect to graphite (Figure 8e bottom). Further electrochemical characterization of the devices showed good energy-to-power values respect the total active mass of both electrodes in a cell voltage range of 2–4 V, delivering 88 Wh kg$^{-1}_{AM}$ at 952 W kg$^{-1}_{AM}$ for the graphite-based LIC and 68 Wh kg$^{-1}_{AM}$ at 745 W kg$^{-1}_{AM}$ and 45 Wh kg$^{-1}_{AM}$ at 5780 W kg$^{-1}_{AM}$ for the HC-based LIC within discharge times of 6 min and 28 s, respectively. Moreover, the cyclability test run to a scaled up 20.2 cm^2 monolayer HC-based LIC pouch cell showed a capacitance retention of 84.6% after 48000 cycles, what validates the strategy.

One of the major advantages of the last two strategies -lithium oxides or sacrificial salts- over the rest is that the pre-lithiation degree can be easily and safely controlled by the amount of oxide or sacrificial salt incorporated in the positive electrode. Simply, by knowing the theoretical capacity and calculating the experimental one, the right formulation of the composite positive electrode can be easily developed. This way, deficient or excessive pre-lithiation degrees that might form unstable SEIs or foster lithium plating when high currents are applied can be avoided. These later strategies offer an alternative way towards the substitution of metallic lithium by safer and easier-to-handle materials that might be closer to industry in a near future.

3.3.4. Li$_2$S

Other different novel approaches such as using Li$_2$S in combination with an AC in the positive electrode were reported by Zhang et al. in 2017.[60] The main care of this strategy arose from the concerns with sulfur chemistry, mainly by the chemical incompatibility of polysulfide anions with carbonate-based electrolytes. Nonetheless, Li$_2$S can either react with the
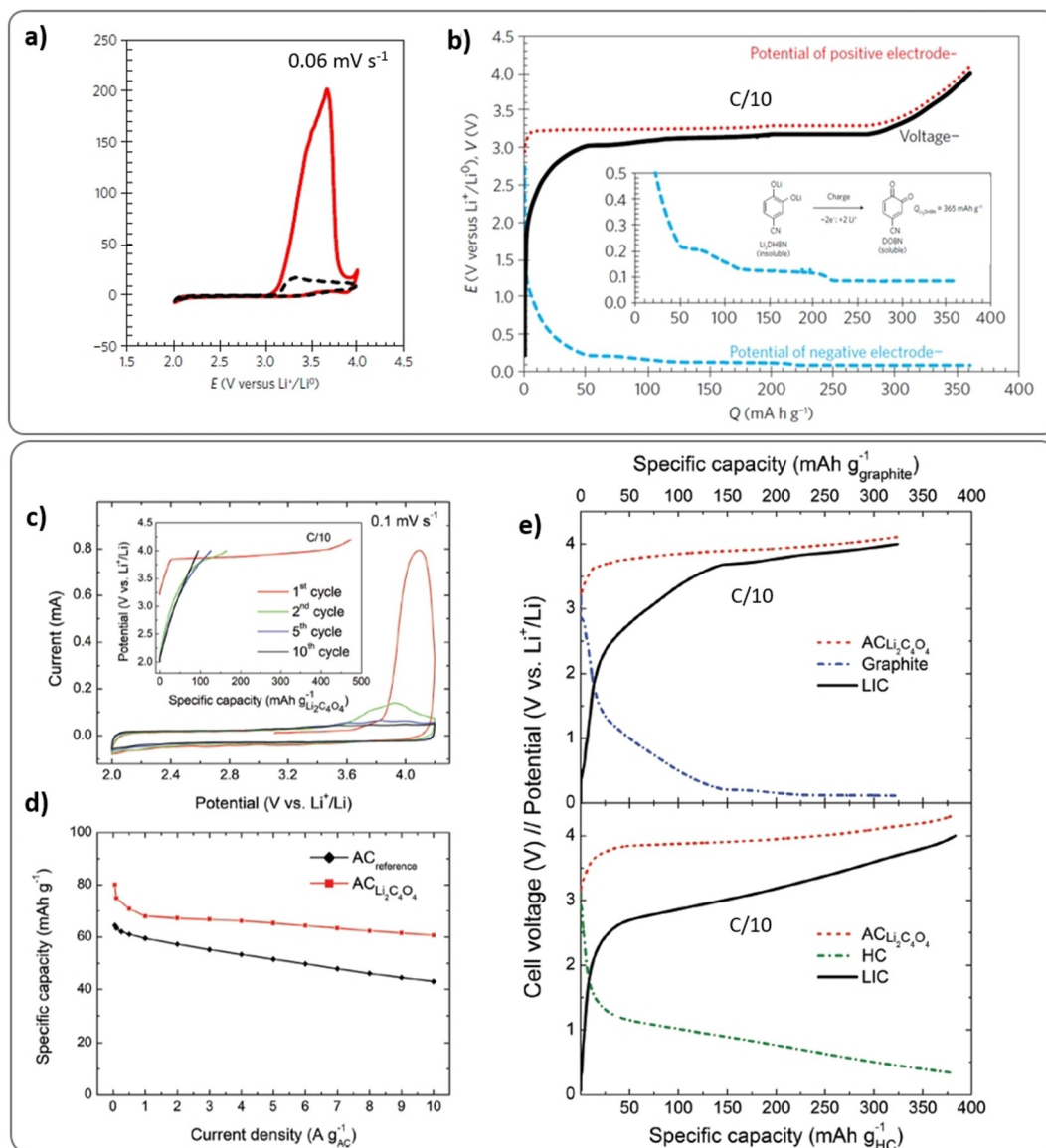
Figure 8. Li_2DHBN sacrificial salt: a) Cyclic voltammogram of the salt electrode and b) the pre-lithiation step of the LIC. Reproduced from Ref. [58] with permission. Copyright (2017) Springer Nature; and $Li_2C_4O_4$ sacrificial salt: c) cyclic voltammogram of the AC-$Li_2C_4O_4$ electrode, inset: charge profiles, d) Rate capability of AC reference and AC-$Li_2C_4O_4$ and e) Pre-lithiation step of graphite-based and HC-based LICs. Reproduced from Ref. [59] with permission. Copyright (2020) Royal Society of Chemistry.

surface oxygen functionalities of the AC -which in this case contains 4.26% of oxygen- to form stable sulfurized carbon or oxidized to Li_2SO_4 in the presence of the formers. This reaction mechanism was confirmed by the authors following X-ray Photoelectron Spectroscopy (XPS) measurements (Figure 9a). Moreover, both, the sulfurized carbon and the Li_2SO_4 have shown to be electrochemically stable in the usual operating potential of positive electrodes. In order to validate the strategy, composites within different amounts of AC (*i.e.*, 85–70%) and Li_2S (*i.e.*, 15–30%) were electrochemically characterized at 0.1 mA cm^{-2} up to 4.5 V *vs.* Li$^+$/Li. The charge profiles of the studied composites show a smooth potential increase revealing the previously mentioned reactions between the AC and Li_2S. However, when the amount of Li_2S was increased up to 30%, an additional plateau at around 2.3 V attributed to the

elemental sulfur by-product is described. Additionally, it dramatically increases the Li$^+$ release during the charging process, which shows not to be necessary for a graphite-based LIC. As consequence, 15 wt.% of Li_2S in combination with the AC shows to be the most adequate formulation. As shown in Figure 9b, along the initial step where the LIC was charged up to 4.5 V, the Li$^+$ from the positive electrode were released and intercalated into the graphite negative electrode reaching 89.4 mV *vs.* Li$^+$/Li. Then, the device was characterized at different cell voltages, showing that the LIC running within the operating voltage of 2.5–4.2 V only stood tens of cycles, while between 2.5–4.0 V stands for 650 cycles, finally surpassing 800 cycles at 2.5–3.8 V. Authors described that this fast capacity fading at wider cell voltages might be attributed to the oxidation product of C=S (and ultimately CS_2) by the release of

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Reviews
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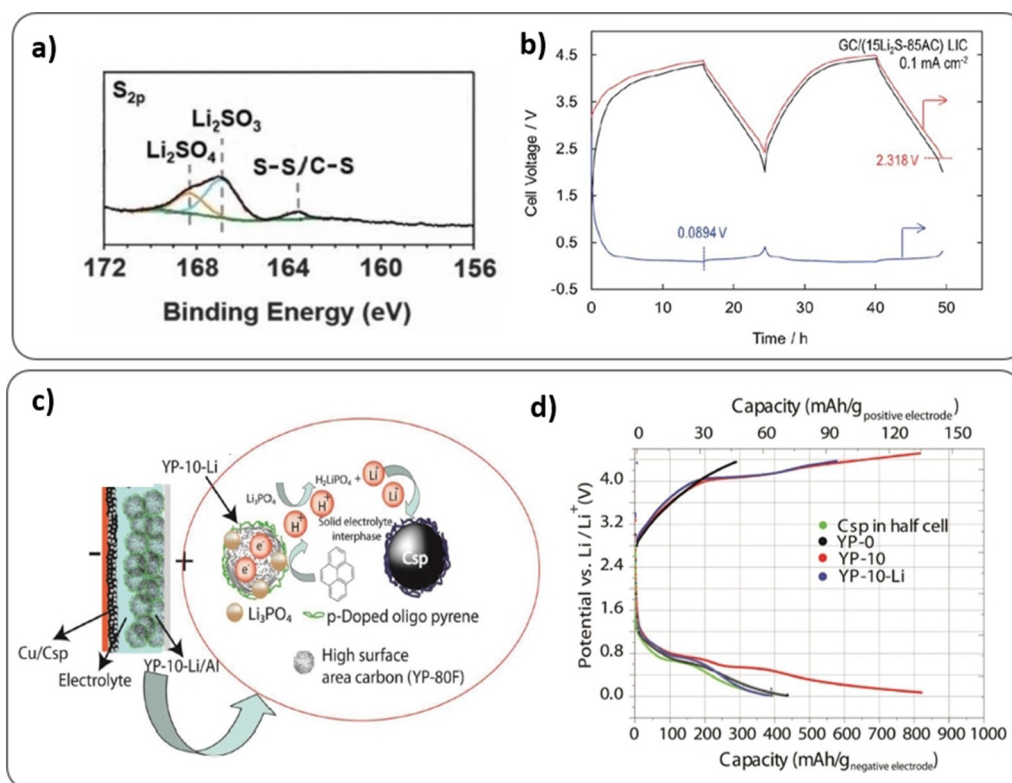European Chemical
Societies Publishing

Figure 9. Li$_2$S as pre-lithiation agent: a) S2p XPS spectrum of an 8 wt.% Li$_2$S loaded AC electrode after initial activation by charging at 0.1 mA cm^{-2} to 4.2 V vs. Li$^+$/Li and b) LIC charge/discharge profiles. Reproduced from Ref. [60] with permission. Copyright (2017) Royal Society of Chemistry; Cascade-type pre-lithation approach: c) Scheme of the pre-lithiation mechanism and b) Initial charge step for the developed LIC. Reproduced from Ref. [61] with permission. Copyright (2019) Wiley-VCH.

elemental sulfur. This could produce highly reactive polysulfide radical cations that react with electrolyte solvents to form a resistive surface on AC particles. Therefore, the upper potential should be limited to 3.8 V in order to keep cycle life rather stable. In any case, the natural abundance and low-cost of elemental sulfur reinforces this strategy as one of the most economic.

3.3.5. Pyrene-Li$_3$PO$_4$ Based Cascade-Type Method

Another novel strategy was reported by Anothumakkool et al. in 2019, based on a cascade-type pre-lithiation approach consisting of two consecutive irreversible reactions taking place in the positive electrode during the first charge step of the LIC.[61] In this case, the positive electrode was formulated by 79.4 wt.% AC, 9.3 wt.% pyrene, 6.6 wt.% Li$_3$PO$_4$ and 4.7 wt.% PVdF. During the initial charge, first, oxidative electropolymerization of pyrene produces oligomers and/or low order small chain polymers that release protons, and second, Li$_3$PO$_4$ captures the protons and releases an equal amount of Li$^+$ ensuring the pre-lithiation of the negative electrode (see Figure 9c). The main advantage of this approach is that the redox potential of the monomer can be tuned between 3.5 and 4.5 V vs. Li$^+$/Li, depending on the nature of the utilized pyrene substituents.[62–64] It was also shown that the Li$^+$ source does

not need to be an electron conductor, hence, a low-cost, air-stable and a non-soluble inorganic base, Li$_3$PO$_4$, which plays a key role on scavenging the protons released by pyrene, was proposed. Thus, the combination of pyrene and Li$_3$PO$_4$ together with the AC in the positive electrode successfully pre-lithiated a carbon black based LIC. In Figure 9d, the initial charge steps of different LICs are described, being YP-0 a LIC with the positive electrode based on the activated carbon itself, YP-10 based on AC together with pyrene and YP-10-Li the full composite with pyrene and Li$_3$PO$_4$. It is shown that in both YP-10 and YP-10-Li an additional capacity arose, firstly from the electropolymerization process occurring above 4.0 vs. Li$^+$/Li and secondly -in this case only for YP-10-Li based LIC- from further proton scavenging and Li$^+$ release. Authors demonstrated that a lithium source such as Li$_3$PO$_4$ was absolutely necessary to provide sufficient lithium to compensate the initial consumption on SEI formation and avoid H$_2$ evolution originated due to the internal H$^+$/H$_2$ shuttle mechanism in YP-10. Further characterization of the developed carbon black:YP-10-Li based LIC shows a capacity retention of almost 100% at 0.3 A g^{-1} current density over 2000 cycles. This cascade-type strategy, first introduced in LIC technology, is undoubtedly a novel strategy that might open a wide avenue towards the investigation on combinations of different-in-nature materials.

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Reviews
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4. A Success Story: LIC ULTIMO®

LICs are still quite a young technology compared to its battery and EDLC counterparts and these days still few products are commercially available in the market. Among others, Taiyo Yuden presents a wide product portfolio of cylindric designs from 20 F to 270 F and laminate pouch cell that reaches 3200 F.[65] Yunasko also developed a laminate pouch cell of 1.3 Ah,[66] but the technology flagship since 2008, is without any doubt the LIC ULTIMO® family from JM Energy.[67]

JM Energy -now Musashi Energy Solutions Co., Ltd- was the first corporation commercializing the technology in 2008 with their brand name product ULTIMO®. Among these last years the company has remarkably evolved and they are currently offering a wide product portfolio of LICs: from laminate and prismatic cells to modules comprising 4 to 12 cells (from 8.8 to 45.6 V) and also large voltage modules (up to 1000 V) of 24 to 48 cells, that can cover a wide range of power demanding applications, such as energy regeneration and assistance in an electric vehicle or leveling electric power in renewables. The pre-lithiation strategy that enabled the successful implementation of LIC ULTIMO® in the market is based on a sacrificial lithium metal electrode what combined with porous current collectors in the positive and the negative electrodes is utilized to pre-lithiate graphite. This way, in the first charge lithium ions are extracted from the sacrificial electrode and diffuse through all the electrodes in order to form the SEI and GICs during the pre-lithiation process (see Figure 10). Then, as published in the company's website, all LICs operate in a cell voltage of 2.2–3.8 V. The prismatic 3300 F device shows maximum gravimetric and volumetric energy density of 14 Wh kg^{-1} and 20 Wh L^{-1} and maximum gravimetric and volumetric power of 8 kW kg^{-1} and 12 W L^{-1}, per total mass and volume of the device. Furthermore, the commercial LIC does not show neither noticeable deterioration after 10000 h at 70 °C floating test, nor a capacitance retention lower than 85 % after 1000000 cycles at 200 A. Additionally, it describes a low self-discharge of only 10 % after
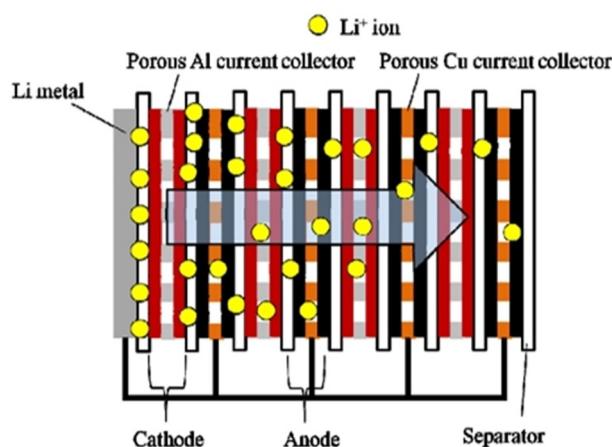

Figure 10. Schematic illustration of industrially used pre-lithiation method, ULTIMO®. Reproduced from Ref. [69] with permission. Copyright (2017) The Electrochemical Society.

10000 hours, demonstrating the outstanding features of this promising technology.[68]

5. Outlook and Perspective

Since LICs were first reported in the beginning of the 2000s, academic research has been mainly focused on the increase of the energy density. Sometimes, even sacrificing power and cyclability for the sake of it, reporting only faulty batteries. However, especially in the last years, several LICs based on novel materials and configurations, presenting well-balanced energy, power and cyclability features have been reported. Even though, all of them continue sharing a common unresolved question: How can the pre-lithiation barrier be overcome?

During the first decade of the century, research on pre-lithiation was almost negligible and basically limited to the use of lab-scale auxiliary lithium metal strategy. However, the second decade became a turning point, progressively capturing research attention and exploring alternative methods (see Table 1). After first unfruitful trials to pre-lithiate LICs from the electrolyte, the use of metallic lithium in different forms was considered. After several studies, pre-lithiation was well-achieved by using metallic lithium, either on its stabilized powder version or on its foil version. However, the complexity of fabrication processes, the difficulty to adjust the desired lithiation degree, added to some safety concerns, derived the research towards lithium containing oxides. The latter can be solution processed together with the AC in the positive electrode without further slurry processing modification. This approach is the one that has received most attention and effort by the research community in the last years. A wide variety of lithium oxides have been explored, easily adjusting the required lithiation degree of the negative electrode and presenting efficient LICs in terms of energy and power densities. Nevertheless, lithium oxides commonly present oxidation potentials above the safety threshold of standard electrolytes, promoting some undesired side reactions that compromise cyclability. In addition, they are expensive and the large dead mass left being is a penalty for the gravimetric and volumetric performance. To circumvent these limitations, lithium nitride as well as organic and inorganic sacrificial salts have been also explored. The former shows high interest as lithium source, but its incompatibility with standard processing solvents requires further investigation to be resolved. The latter seems to be the best positioned one towards a low-cost, easy-to-process solution. Overall, among these last two decades, pre-lithiation strategies have logically evolved from complex solutions to more simple and cost-effective ones.

However, an all-in-one strategy enabling technology transfer to market is still missing. Future pre-lithiation strategies achieving such accomplishment should fulfil the following requirements in terms of material specifications:

i) To be highly irreversible. New compounds with higher first irreversible capacity are highly desired in order to minimize the presence of the lithium source in the positive electrode

Table 1. Summary of all mentioned pre-lithiation strategies and their characteristics.

Ref.	Year	Strategy	Negative electrode	Positive electrode	Lithiation agent	Pros	Cons
[28]	2006	Electrochemical pre-lithiation	Carbon	AC	Auxiliary lithium metal	Easiest strategy for academia	Lab-scale
[32]	2008	Electrolyte	Graphite	AC	1 M LiPF$_6$ (EC:DMC)	No additional compound is required	Difficult to fulfil high conductivity and low viscosity requirements
[34]	2012		Graphite	AC	2 M LiTFSI (EC:DMC)		
[36]	2012	SLMP	HC	AC	SLMP onto the HC	Not air sensitive	Incompatibility with commonly used NMP
[40]	2014		HC	AC	SLMP onto a 46×46 mm HC		Difficult to handle
[41]	2017	Lithium metal stripes	HC	AC	Lithium metal stripes onto a 46×46 mm HC	–	Air sensitive, unsafe, difficult to control the pre-lithiation degree
[45]	2011	Lithium oxides	Graphite	AC + 26.75% Li$_2$MoO$_3$	Li$_2$MoO$_3$ (4.7 V vs. Li$^+$/Li), 250 mAh g^{-1}	Pre-lithiation degree can be controlled	Might show high oxidation at high potentials; High weight percentage needed; Medium irreversible capacity; Might be air sensitive; High temperature synthesis
[46]	2014		Graphite	AC + 10.3% Li$_5$FeO$_4$	Li$_5$FeO$_4$ (4.7 V vs. Li$^+$/Li), 700 mAh g^{-1}		
[47]	2015		Graphite	AC + 17.2% Li$_6$CoO$_4$	Li$_6$CoO$_4$ (4.3 V vs. Li$^+$/Li), 600 mAh g^{-1}		
[49]	2016		Graphite	AC + 40% Li$_5$ReO$_6$	Li$_5$ReO$_6$ (4.3 V vs. Li$^+$/Li), 410 mAh g^{-1}		
[50]	2016		Graphite	AC + 55% Li$_{0.65}$Ni$_{1.35}$O$_2$	Li$_{0.65}$Ni$_{1.35}$O$_2$ (4.1–4.3 V vs. Li$^+$/Li), 410 mAh g^{-1}		
[51]	2017		Graphite	AC + 50% Li$_2$CuO$_2$	Li$_2$CuO$_2$ (3.6 V vs. Li$^+$/Li), 342 mAh g^{-1}		
[56]	2020	Lithium nitride	HC	AC + 12% Li$_3$N	Li$_3$N (4–4.3 V vs. Li$^+$/Li), 1379 mAh g^{-1}	Very high capacity output	Incompatibility with commonly used NMP solvent
[57]	2020		HC	AC + 10% Li$_3$N	Li$_3$N (4–4.3 V vs. Li$^+$/Li), 1379 mAh g^{-1}		
[58]	2018	Sacrificial salts	Graphite	AC + 40% Li$_2$DBHN	Li$_2$DBHN (3.2 V vs. Li$^+$/Li), 365 mAh g^{-1}	Pre-lithiation degree can be well-controlled; React at lower and safer potentials; By-products do not affect the performance; Easy to synthesize; Low-cost	Air sensitive; Medium irreversible capacity, high amount of sacrificial salt needed
[59]	2020		Graphite and HC	AC + 40% Li$_2$C$_2$O$_4$	Li$_2$C$_2$O$_4$ (3.9–4.2 V vs. Li$^+$/Li), 425 mAh g^{-1}		Medium irreversible capacity, high amount of sacrificial salt needed
[60]	2017	Others	Graphite	AC + 15% Li$_2$S	Li$_2$S	Natural abundance	Undesired by-products
[61]	2019		Carbon black	AC + 9.3% pyrene + 6.6% Li$_3$PO$_4$	Li$_3$PO$_4$	A non-faradaic material realizing lithium ions can be utilized; Different nature materials can be combined	Major difficulties to match between appropriate materials
[69]	2008	Lithium metal	Graphite	AC	Holed Cu foil within lithium metal	Efficient technique	Air sensitive, expensive

and diminish its mechanical impact on the electrode architecture.

ii) To present an oxidation potential between 3–4 V *vs.* Li$^+$/Li. As the pre-lithiation agent is desired to be introduced in the formulation of the positive electrode and to be oxidized in the first charge of LICs, its oxidation potential should lie in the same operating potential range of the positive electrode. Moreover, oxidation potentials above 4 V *vs.* Li$^+$/Li should preferably be circumvented in order to avoid further electrolyte oxidation.

iii) Eliminating lithium metal as lithiation agent for LICs. The use of lithium metal requires an oxygen-free processing environment. Thus, its abolition enables atmospheric conditions, substantially reducing technology cost in terms of fabrication process.

iv) To be air-stable and solution processable in atmospheric conditions. As for the above-mentioned reason, pre-lithiation agents able to safely handle in atmospheric conditions are required. As well as materials processable in air-stable solvents. This way, safety would be improved and cost reduced.

v) To avoid leaving any dead mass behind. The material selected as pre-lithiation agent should reduce to zero the dead mass left in the system after its oxidation. Generated side-products should even turn into removable gas, become active material or dissolve in the electrolyte in order to avoid any negative impact on LICs performance.

vi) To be cost-effective. Cost is one of the major drawbacks for LIC technology when compared to other technologies. Thus, any solution needs to be addressed from a cost-effective perspective, adding no substantial increase to the final price. Thus, the synthesis procedure of these materials should rely on low-cost precursors and soft synthesis conditions.

Attainment of such a pre-lithiation strategy might once and for all trigger the lithium ion capacitor technology.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: pre-lithiation · Li-ion capacitor · lithium ion capacitor · hybrid supercapacitor · metal-ion capacitor · energy storage

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