Energy &
Environmental
Science

Progress and Perspectives on Pre-lithiation Technologies for Lithium Ion Capacitors

Journal:	*Energy & Environmental Science*
Manuscript ID	EE-REV-03-2020-000807.R1
Article Type:	Review Article
Date Submitted by the Author:	10-Jun-2020
Complete List of Authors:	Jin, Liming; Tongji University, Clean Energy Automotive Engineering Center and School of Automotive Studies Shen, Chao; Florida State University, Shellikeri, Annadanesh; Florida A&M University-Florida State University College of Engineering, Electrical &Computer Engineering Wu, Qiang; Florida A&M University-Florida State University College of Engineering, Electrical &Computer Engineering Zheng, Junsheng; Tongji Unviersity, Clean Energy Automotive Engineering Center ; Florida State University , Department of Electrical and Computer Engineering Andrei, Petru ; FAMU-FSU College of Engineering, Department of Electrical and Computer Engineering Zhang, Ji-Guang; Pacific Northwest National Laboratory, Zheng, Jim; Florida State University, Electrical and Computer Engineering

Progress and Perspectives on Pre-lithiation Technologies for Lithium Ion Capacitors

Liming Jin, [a,b,c,#] Chao Shen [b,c,#,*] Annadanesh Shellikeri,[b,c] Qinag Wu, [b,c] Junsheng Zheng,[a]
Petru Andrei,[b,c] Ji-Guang Zhang,[d] and Jim P. Zheng,[b,c,e,f,*]

[a] Clean Energy Automotive Engineering Center and School of Automotive Studies, Tongji University, Shanghai 201804, China
[b] Department of Electrical and Computer Engineering, Florida A&M University-Florida State University College of Engineering, FL 32310, USA
[c] Aero-Propulsion, Mechatronics and Energy Center, Florida State University, Tallahassee, FL 32310, USA
[d] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA
[e] Center for Advanced Power Systems, Florida State University, Tallahassee, FL 32310, USA
[f] Department of Electrical Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA

Email: cs14t@my.fsu.edu (Chao Shen); jzheng@buffalo.edu (Jim P. Zheng)

Abstract

Lithium ion capacitors (LICs) can generally deliver higher energy density than supercapacitors (SCs) and have much larger power density and longer cycle life than lithium ion batteries (LIBs). Due to their great potential to bridge the gap between SCs and LIBs, LICs are becoming important electrochemical energy storage systems in the field of energy storage and conversion. Although it is generally accepted that pre-lithiation technologies are indispensable for the operation of LICs, no comprehensive overview of the existing pre-lithiation technologies has been conducted. In this progress report, we first classify LICs according to their energy storage mechanisms and discuss the multiple roles that the pre-lithiation technologies play for improving the performance of LICs. Then, we present the existing pre-lithiation methods used in LICs in detail and the current research progress is summarized. Finally, we provide a comprehensive comparison of the current pre-lithiation methods and propose the prospects and challenges of these methods from both a fundamental and a practical point of view. The broader impact of pre-lithiation technologies on next-generation LIBs is also discussed. This progress report aims at providing the fundamental knowledge necessary to researchers who are new to study LICs and

also serving as a guideline to senior researchers in the fields of LICs and LIBs for future research directions.

1. Introduction

The wide utilization of conventional energy resources such as coal and oil have negative effects on climate change and can result in global warming. In this context, the development of new renewable and clean energy systems has emerged as a world-wide important research topic and, during the last several decades, the renewable energy systems such as wind and solar energy have become increasingly competitive with fossil fuels systems. However, these types of renewable energy systems are affected and limited by uncertainties given by the external conditions and therefore require energy storage devices to stabilize their output characteristics. To address these problems, a number of energy storage technologies such as flow and other electrochemical batteries, flywheels, compressed air energy storage, thermal and pumped hydro-power energy storage, have been proposed in recent years. Among these technologies, electrochemical energy storage systems, which already have a large number of applications in consumer electronics, automotive, aerospace, and stationary markets, are increasingly attractive. [1–8]

Secondary batteries and electrochemical supercapacitors are two primary types of devices for reversible electrochemical energy storage systems that offer high energy density, high power, and stable cyclability. Among these devices, commercial lithium ion batteries (LIBs), which are generally made of a lithium metal oxide cathode, a carbon-based anode, and a Li-salt-containing electrolyte, represent the dominant battery technologies. Commercial LIBs have already achieved energy densities of 200~250 Wh kg^{-1} in cell level. However, the power density (< 1,000 W kg^{-1}) and lifespan (< 1,000 cycles) are somewhat unsatisfactory.[9–11] In contrast, the power density and the lifespan of current electrochemical supercapacitors (ECs), which are composed of two symmetrical porous carbon electrodes with high specific surface areas, such as activated carbon (AC), can reach over 5,000 W kg^{-1} and over 100,000 cycles, respectively. Unfortunately, the energy density of ECs is lower than 10 Wh kg^{-1} in organic electrolyte and even lower in aqueous electrolyte.[12,13] The main differences between LIBs and ECs in terms of energy density, power density, and lifespan are due to their distinct energy storage mechanisms. The LIBs store and release energy electrochemically by Faradic processes, i.e. by the intercalation/deintercalation or conversion processes where lithium ions are injected/extracted into/from electrode materials (anode and cathode). The Faradaic processes are capable to accommodate abundant charges but exhibit poor reaction kinetics and durability due to the low lithium ion diffusion efficiency and internal strain in the electrode materials. On the contrary, ECs store and release charges through non-Faradic processes, in particular by adsorption and desorption of ions on the surface of porous materials, which are a much faster and more reversible processes than in the case of Faradaic processes. However, the charge storage capacity is directly limited by the available surface of porous materials. Therefore, neither the LIBs or the ECs can meet all the demands for high energy density, high power density, and excellent cyclability required in many applications.

Recently, hybrid lithium ion supercapacitors, also called lithium ion capacitors (LICs), have emerged as an advanced type of hybrid electrochemical energy storage system to meet the above requirements in the same time.[3,12,14–26] These capacitors consist of a LIB-type electrode and an EC-type electrode in a Li-salt-containing electrolyte and include many of the features of LIBs and ECs. During charge and discharge, the cathode and the anode undergo physical (adsorption/desorption) and chemical (intercalation/de-intercalation or conversion) processes respectively that store and release the energy. Due to the combination of the two energy storage mechanisms into single configuration, LICs exhibit several advantages, including: i) higher cell capacity and energy density than ECs, ii) higher power density than LIBs, iii) large operating temperatures ranging from -20 to 70 °C, and iv) lower self-discharge characteristics than ECs.[18] For these reasons, LICs provide a trade-off between LIBs and ECs, and have attracted a great interest as promising candidates for high energy and power applications in recent years.

In the past several years, there have been tremendous efforts to improve the energy density, power density, and lifespan of LICs by modifying the cathode materials, anode materials, the electrolytes, and using pre-lithiation or other technologies. However, the LICs still face several bottlenecks to achieve wide commercialization: i) the reaction kinetics and stability of anode are still not comparable to the cathode due to the different reaction mechanisms, which results in unsatisfactory power density and lifespan when assembling full cells; ii) there is no significant research progress on modifying the properties of electrolyte and the energy density of LICs still suffers from limitation (lower than 30 Wh kg^{-1}) due to the low ion concentration in electrolyte; iii) the demanding requirements (including the lithium sources and/or environmental condition) for pre-lithiation treatment disables the large-scale processing of LIC electrode, which impedes the successful commercialization of LIC devices.

To summarize the research progress of LICs and outlook the future directions to address the bottlenecks, to date, several reviews with different research focuses have been reported, including cathode materials, anode materials, and the electrode matching principles in LICs.[3,12,14–25] Aravindan and co-works summarized the insertion-type electrodes for nonaqueous LICs.[16] Wang and co-workers reviewed the progress of pseudocapacitive anodes in nonaqueous LICs.[18] Han and co-workers analyzed scientific problems, material development, and key technologies for nonaqueous LIC.[27] Our group also reviewed the electrode materials, the electrolyte, and the current challenges in nonaqueous LIC.[23] These reviews have summarized different components of LIC such as electrode and electrolyte. However, the pre-lithiation technologies for LICs, which is a crucial technology to bridge fundamental research to industry application, were merely briefly mentioned in these reviews.[26] So far, there does not exist a detailed review of the progress and an analysis of the future perspectives of pre-lithiation technologies in LICs.

In this article, we systemically review the progress of pre-lithiation technologies involving the fundamental research and practical application for LICs. First, we classify the definition of LICs according to their energy storage mechanisms, which is seldom discussed in detail in previous reviews, and then discuss the multiple roles the pre-lithiation technologies play for improving the performance of LICs. Next, we summarize the progress of pre-lithiation technologies currently used in LICs, as well as analyze the advantages and drawbacks of various pre-lithiation technologies. Finally, we provide an outlook on the potential pre-lithiation technologies applicable to LICs from the fundamental point of view and the future research direction of practical pre-lithiation technologies for LICs. Moreover, the broader impact of pre-lithiation technologies on next-generation LIBs and different requirements of pre-lithiation for LICs and LIBs are also discussed. This progress report aims at providing the fundamental knowledge necessary to researchers who are new to LICs and also serving as a guideline to senior researchers in the fields of LICs and LIBs for future research directions.

2. Lithium ion capacitors

2.1 The basic classifications of LICs

As introduced above, an LIC is a hybrid device with multiple energy storage mechanisms, composed of a LIB-type electrode (electrochemical intercalation or conversion) and an EC-type electrode (physical adsorption), operating in a Li-salt-containing organic electrolyte. In the literatures, the concept of LIC is somewhat ambiguous due to the fact that various devices were termed as “lithium ion capacitors” regardless of their cathode and anode with different mechanism combinations.[15,19,23,25,26] Herein, the concept of LIC is defined to describe the four types of hybrid configurations presented in Figure 1, which are specifically based on the different structures and energy storage mechanisms of cathode and anode.

a. Electrochemical intercalation (+) || physical adsorption (-). This hybrid configuration consists of a LIB-type cathode and an EC-type anode, such as $LiFePO_4$ (+) || AC (-), Li_2MnO_4(+) || AC (-), etc.,[28–36] in which the cathode and anode undergo chemical intercalation and physical adsorption processes respectively. The voltage profile of this system exhibits approximately linear relationship with the capacity as shown in Figure 1a, similar to the characteristics of ECs. During the charge process, the lithium ions are extracted from cathode into electrolyte and, in the same time, the lithium ions in the electrolyte are adsorbed onto the anode, keeping the ions concentration in the electrolyte constant, i.e. the electrolyte plays the role of lithium ion carrier instead of an active material in this system. Therefore, the key limiting the capacity of this type of LICs is the relatively low voltage output and poor cycling stability that results from the high working potential lower limit of anode caused by the high specific surface area of the porous carbon. Once the porous carbon potential exceeds the lower voltage limit, the severe solid electrolyte interphase (SEI) associated with the high specific surface area will grow rapidly resulting in poor cycling stability. For example, the working potential of AC as anode should be generally higher than 2.0 V and, therefore, the output working voltage (<2.0 V) and thus the energy density of this type of LICs are much lower compared to other types of LICs.

b. Physical adsorption (+) || Electrochemical intercalation or pseudocapacitive mechanism (-). This hybrid configuration is generally composed of an EC-type cathode and a LIB-type anode, for instance, AC (+) || $Li_4Ti_5O_{12}$ (-) or AC (+) || Nb_2O_5 (-),[37–50] in which the cathode undergoes physical adsorption process and the anode undergoes chemical intercalation or pseudocapacitive process. The voltage profile of these systems is also approximately linear, as shown in Figure 1b. The most promising anode materials for this system are $Li_4Ti_5O_{12}$ and pseudocapacitive anode materials (i.e. Nb_2O_5, VN, V_2O_5, TiC, etc.), which always deliver relatively high discharge plateau (>1.0 V) but much better high-rate performance and cyclability than commercial carbon materials (i.e. graphite, hard carbon, soft carbon, etc.) to ensure high power density and long lifespan when pairing with AC cathode. However, the evolutions of the anion and cation concentrations in the electrolyte are significantly different with the continuously changed voltages. During the charge process, the anions in the electrolyte adsorb onto the cathode and the lithium ions are injected into the anode simultaneously. In this process, the electrolyte is the charge carrier and simultaneously an important active material, and therefore the electrolyte concentration decreases gradually with increasing voltage, which indicates that the capacity of this type of LICs is not determined only by the natures of the electrodes (including the potential and capacity) but also by the initial ion concentration of the electrolyte. During the discharge process, the ions transport mechanism is reversed and the ions concentration in the electrolyte recovers gradually. Therefore, similar to the case of EC devices, the energy density of this type of LIC devices has a theoretical maximum limitation as demonstrated in our previous reports,[52] i.e. the energy density based on the weight of the electrode materials and electrolyte cannot exceed approximately 30 Wh kg^{-1}, for ion concentration of the electrolyte of 1 M.

c. Physical adsorption (+) || pre-lithiated electrochemical intercalation or conversion (-). The electrode structure of this type of LICs is identical with type b LIC devices, the only difference being that the anode is pre-lithiated before cycling. Examples of such cells are AC (+) || pre-lithiated hard carbon (-), biomass derived AC (+) || pre-lithiated Li_2TiSiO_5 (-), etc. [51–62]. The ions transport mechanism is more complex in this type of cells because there are two types of transport phenomena that take place during charge and discharge, as shown in Figure 1c. For instance, during the charge process, when the LIC operates from the open circuit voltage (OCV) to the maximum voltage, the anions in electrolyte are adsorbed onto the cathode surface and the lithium ions are injected into the anode, in the same way as in the case of type b LIC devices. During this process the concentration of the electrolyte is also decreasing continuously. When cell voltage increases from the lowest voltage to OCV, the lithium ions desorb from cathode and diffuse into electrolyte, while the lithium ions continue to be injected from electrolyte into the anode, therefore keeping the overall electrolyte concentration constant. In comparison with type b LICs, the anode pre-lithiation treatment results into an additional charge and discharge process, which enables the LIC devices to have higher voltage output then higher energy density and larger power density, thus making this type of LICs the most promising systems.[63]

d. Physical adsorption + electrochemical intercalation (+) || electrochemical intercalation or conversion (-). This hybrid configuration is a combination of the type c LIC devices and LIBs, and is made of a hybrid cathode composed of both an LIB-type and an EC-type cathode material, and a pre-lithiated LIB-type anode, such as AC+$LiFePO_4$ (+) || pre-lithiated hard carbon (-), AC+NMC (+) || pre-lithiated hard carbon (-), etc.[32–36,64–74] The introduction of battery-type materials into the cathode will increase the energy density of the system exactly, but inevitably will sacrifice the power density and cycling lifespan to some extent. The voltage profile of this type of hybrid configuration is no longer linear with respect to the capacity, as shown in Figure 1d, so that it cannot be strictly ascribed into a capacitor type. Therefore, this type of hybrid configuration will not be discussed in this progress report.

In this section, we have clearly defined four types of LIC systems and their working corresponding mechanisms, which is seldom discussed in detail in previous LIC reviews, to clarify the concept of "Lithium ion capacitors" for future researchers. In relation to their different working mechanisms, the dominant characteristics for these LIC systems available as products including the voltage range, energy density, power density as well as cycling lifespan have also been summarized in Table 1. Note that there are not any products parameters for the Type a LIC devices available, which should be resulted from unstable electrochemical stability of AC for anode due to the large specific surface area for severe SEI formation. Among all products, type c LIC devices deliver a higher voltage than type b due to the decreased potential of anode by pre-lithiation treatment, and consequently the corresponding energy density ($E=1/2\ CV^2$) as well as power density ($P=E/t$) of type c LIC devices are also higher than type b. Type d LIC devices exhibit higher energy than type c LIC devices by sacrificing the power density and cycling lifespan, which should be the most important parameters for the power-based electrochemical energy storage devices. Therefore, type c LIC devices represent the most typical and dominating devices and achieve the trade-off between power density, energy density, and lifespan, mainly benefiting from the pre-lithiation treatment in this system. In this progress report, we will therefore focus our discussion on type c LIC devices (all the LICs we mention below refer to the type c LIC devices without special definition), in particular on the roles and research progress of the pre-lithiation technologies in this type of LICs.

2.2 The energy storage principles of LICs

As discussed above, LICs undergo a two-step ion transport mechanism, the first of which below OCV and the second over OCV. During these steps, both the anions and the cations play important roles simultaneously, but the diffusion process of the anions is ignored in most literatures, which impedes the full understanding of the energy storage mechanism. In this report, in order to illustrate the energy storage principles of LICs clearly, the various electrochemical processes occurring inside the different components of the cell (such as cathode, electrolyte, anode, and lithium source) at various stages during cycling will be carefully discussed and coupled with in-situ NMR results reported by our group.[75]

Figure 2a-2b are schematic graphs of typical charge-discharge voltage profiles and in-situ NMR results of an AC (+) // pre-lithiated hard carbon (HC) (-) system, respectively. During the first charge process from OCV to the maximum voltage (I-II), the PF_6^- ions diffuse from the electrolyte towards the cathode and the Li^+ ions intercalate into the anode simultaneously. During this time, the Li^+ ion concentration in the anode increases, while the ions concentration in the electrolyte slightly decreases. When the cell is discharged from the maximum voltage to OCV (II-III), the PF_6^- ions desorb from cathode and the Li^+ ions de-intercalate from the anode into the electrolyte, during which the Li^+ ion concentration in the anode decreases, while the ions concentration of the electrolyte recovers to original state. When the voltage decreases from OCV to the minimum voltage (III-IV), the Li^+ ions concentration in the anode continues to decrease due to the pre-lithiation treatment for the anode, while the Li^+ ion concentration in cathode increases rapidly. The final charge process from the minimum voltage to OCV (IV-V) is simply a reverse of the discharge process from the OCV to lowest voltage. In general, the charge and discharge processes can be generally divided into two parts: the electrolyte consumption part (above OCV) and the Li^+ ion diffusion part (below OCV), in which the capacities are supplied from the electrolyte and from the pre-lithiated Li^+ ions, respectively. This entire theoretical analysis is illustrated using in-situ NMR, the results of which agree well with the analysis. The changes rules of intercalation peaks (2.5~5.5 ppm) and the double layer peaks (~0.6 ppm and ~-2.75 ppm) with the continuously changed voltage are consistent with the analysis, as shown in Figure 2b. The intercalation and double layer peaks are further deconvoluted from the pristine NMR spectra graphs in order to evaluate the Li^+ ion concentration semi-quantitatively, as shown in Figure 2c-2d. As expected, the intercalation peak area decreases when the voltage is varying from the maximum value to the minimum value, indicating that the Li^+ ions de-intercalate from the anode. In the same time, the double layer peak area is relatively small and constant at voltages over OCV, indicating that there are no Li^+ ions adsorbing on the cathode, and then increases when the voltage is reduced from OCV to the minimum value showing that the Li^+ ions are adsorbing onto the cathode gradually. The charge-discharge curve coupled with the in-situ NMR measurements unambiguously demonstrate the ion transport in LIC systems.

In this section, we have combined the theoretical analysis and experimental results to illustrate the entire ions diffusion principles in the LIC systems. From the energy storage mechanisms point of view, there are two important aspects that should be pointed out: (1) the anions (PF_6^-, etc.) originated from the electrolyte are the crucial charge carrier in the whole charge and discharge process when the voltages are above OCV, which is ignored in most literatures; (2) Moreover, the pre-lithiation technologies are essential to enable charge and discharge at the voltage lower than OCV, at which pre-lithiation anode continues to supply the Li^+ ions for the system.

3. The multiple roles of the pre-lithiation process

In section 2, we have demonstrated that pre-lithiation technologies inevitably result in additional charge and discharge processes at the voltage lower than OCV as seen in Figure 2a. These additional processes are beneficial for enhancing the energy density of LIC devices. Besides this important contribution, in this section, all the major roles pre-lithiation plays in LIC systems will be explicated.

3.1 Mitigate the initial lithium loss

The anodes of LICs are typical LIB-type anode materials, which always exhibit a lithium loss during the first cycle due to irreversible electrochemical processes and/or SEI formation, in particular when the anode potential is lower than 1 V. During the recent years, in order to improve the energy density, power density, and lifespan of LIC systems, a variety of novel anode materials with low discharge potential, high capacity, and excellent high-rate and cycling performance were proposed. A summary of these materials, including Si, SnO_2, Li_2TiSiO_5, and various carbon-based compounds is shown in Table 2.[41,42,77-100] These advanced materials were selected due to their one or several desirable electrochemical characteristics for LICs but they often deliver relatively low first cycle coulombic efficiency (CE) as shown in Figure 3a, in which the scattered points are the calculated CEs of typical anode materials presented in Table 2. In LIC systems, the irreversible capacity loss of the anode consumes the Li^+ ions, directly resulting in poor energy density and lifespan theoretically. Pre-lithiation technologies are usually conducted before cycling to mitigate the initial lithium loss and result in stable charge and discharge during the following cycles. For instance, the AC // HC systems after pre-lithiation process exhibit much better cycling stability as shown in Figure 4a. The pre-lithiation process enables formation of stable SEI with complex chemical process on the surface of HC (Figure $5a_1$). More detailed results in Figure $4a_2$-$4a_3$ reveals the AC // HC system without pre-lithiation treatment displays low coulombic efficiency (< 80%) indicating some Li ions are consumed with cycling, and thus poor cycling stability lower than 30 cycles. This example gives strong evidence that the pre-lithiation treatment has a positive effect on the coulombic efficiency and lifespan for the LIC systems.

3.2 Provide a lithium source for a large potential variation window of the cathode

Figure 3b displays the ideal potential profiles of the cathode and anode, showing the increase of the capacity resulting from the pre-lithiation treatment. As discussed above, the LICs without pre-lithiation follow a single step mechanism during charge and discharge; for instance, during charge, the anions adsorb onto the cathode and the Li ions intercalate into the anode simultaneously. The pre-lithiation treatment introduces an additional charge and discharge mechanism so that the available potential window and, consequently, the energy density are increased considerably. In our previous studies, we estimated that the LIC systems without pre-lithiation have a theoretical energy density of at most 30 Wh kg^{-1} when the ion concentration in the electrolyte is 1 M.[52] It is remarkable that, the additional charge and discharge processes that result from pre-lithiation increase the theoretical energy density up to 94.5 Wh kg^{-1} for the same ion concentration, which is a big breakthrough for the LIC systems. As an experimental case in Figure 4b, these systems composed of AC as cathode and mesocarbon microbeads (LMCMB) with different pre-lithiated degrees as anode exhibit distinct voltage profiles. In consistence with our analysis, the cathode in the system without pre-lithiation exhibits a potential profile of 3.5~4.2 V (Figure $4b_1$), and the potential ranges are widened to 2.6~4.2 V and even 2.1~4.2 V as shown in Figure $4b_2$-$4b_3$. Correspondingly, the capacities for the systems with pre-lithiation treatment are also enlarged exhibited by the time scale. [51,57,59,63] These examples strongly demonstrate that pre-lithiation is capable of providing lithium sources for a large potential variation window of the cathode, resulting in wider operating voltages and then higher energy densities for the LIC systems.

3.3 Lower the anode potential to increase the terminal voltage

Figure 3c shows the potential profile of the anode and the voltage profile of the LIC systems as a function of capacity. In general, the anode materials display an initial high operating potential at 2.0-3.0 V in a Li-depleted state. When combining the cathode with the anode, the output voltage of LIC is relatively low. After pre-lithiation, the potential of the anode can be adjusted to a relatively low value by controlling the pre-lithiation degree. As a result, the LIC system is capable to deliver a high voltage output, which results in a high energy density, as shown in Figure 3c. A series of experiments have been carried out in the literatures using an AC (+) // pre-lithiated HC (-) in order to illustrate the effects of the pre-lithiation on the voltage output. Figure 5a shows the effect of pre-lithiation treatment for the anode potential published by our group. As analysed above, the potential of anode can be adjusted by controlling the pre-lithiation degree as shown in Figure 5a$_1$. After assembling LIC full cell, the anode after pre-lithiation exhibits much lower potential profiles, which would result in high voltage and then energy density output (Figure 5a$_2$-5a$_3$). These results are also partially illustrated in Figure 4b. [51,69,101,102]

3.4 Adjust the optimal operating potential of the anode

The last role of the pre-lithiation process is important during electrode matching (Figure 3d). In general, due to the imbalanced energy storage mechanisms of the cathode and anode, the anode always exhibits lower reaction kinetics and cycling stability in comparison with the cathode, which inevitably leads to poor power density and lifespan for the LIC. To address this issue, our group has recently proposed a general electrode matching approach for the fabrication of the LICs, first by analysing the discharge process and the kinetics of the anode at different potentials using in-situ electrochemical impedance spectroscopy (EIS). [54,103,104] After that, the anode is coupled with the cathode by selecting the anode with the optimal window of operating potentials in order to maximize the power density and cycling lifespan. For example, taking the AC (+) || pre-lithiated HC (-) as a case study, the HC exhibits distinct electrochemical performance in four stages from 3.0 V to 0.01 V as shown in Figure 5b$_1$. After analysing the electrochemical performance at various potentials using in-situ EIS, it was concluded that it was optimum that the pre-lithiation results in an anode potential range of 0.1~0.7 V to match with the AC (Figure 5b$_2$). In this example, the final LIC had an energy density of 30 Wh kg^{-1}, a power density of 1,500 W kg^{-1}, and a cycling lifespan of 5,000 times.

In this section, we have carefully reviewed the contributions of pre-lithiation technologies for anode, cathode, and system configurations, which reflects the important roles and essentiality of pre-lithiation for LIC systems. Moreover, the original mechanism in each specific case is analysed and demonstrated by several examples in literatures to provide a comprehensive understanding.

4. Pre-lithiation methods

We have systemically introduced the definition of LIC and the importance of pre-lithiation technologies for LIC systems in the above sections. In section 4, we will focus on the review on the current proposed pre-lithiation technologies and the analysis on the advantages and disadvantages of each pre-lithiation technology. Until now, other than several attempts to use lithium ions from a highly concentrated electrolyte [153,154], most of the pre-lithiation methods are applied to either anode or cathode of the LIC. Based on the various characterizations of proposed pre-lithiation technologies, including position, lithium source, functional mechanism, these pre-lithiation technologies are clarified into four categories in this section.

4.1 Ex-situ Electrochemical (EEC) method

In the case of the EEC method, the pre-lithiation is usually conducted by pre-assembling a half cell with a lithium metal as counter electrode, as shown in Figure 6a. The cell is cycled for several times to reach a required lithiation level by a given pre-defined cycle number, cycle time, or potential. After that, the pre-lithiated electrode is re-utilized to assemble LIC with a fresh cathode. In general, two requirements need to be met: (i) the entire pre-lithiation process should be conducted at a relatively low rate (e.g. 0.05 C) to ensure the complete electrochemical reaction and the accurate control of the pre-lithiation level; (ii) sufficient cycles are necessary to stabilize the cell and eliminate the side reactions including formation of the SEI and other irreversible electrochemical processes. The first application of this method in LIC is reported by Aida et al [105], as shown in Figure 7a. The specific capacity per total volume of the cathode and anode was improved by a factor of about two by pre-cycling the anode. Since then, the EEC method remains the most widely used method for research purposes, especially in laboratory studies. Various anode materials such as graphite [106–108], MCMB [101,102,109], hard carbon [55,59,110], soft carbon [111], LTO [106,112], graphene [21,113,114], and metal oxide [115,116] have been reported in the fabrication of high-performance LICs using this method. Note that instead of assembling a half cell with a lithium metal counter electrode, Kumagai et al [117] used the EEC method with a LIB cathode (e.g. $LiFePO_4$) as the lithium source. However, the lithiation level in this approach is not as precisely defined as that obtained using a lithium metal. Therefore, we believe that it is preferably to use lithium metal as demonstrated by most other research studies in the literature.

Primarily, the EEC method has several typical advantages, which enables its extensive application into laboratory studies. First, the method is capable to pre-lithiate the anode in a well-controlled manner, i.e. the lithiation level can be controlled easily and accurately by setting either the cut-off voltage of the anode material with no voltage plateau or capacity for those with stable plateau. Secondly, the SEI layer formed while applying the EEC method is relatively uniform and stable. However, most importantly, the main drawback of this method is that an additional step to re-assemble the pre-lithiated negative electrode into the LIC cell is required, which inevitably increases the complexity and the cost of this method. In addition, the anodes can be slightly damaged during the re-assembling process resulting in degraded performance [118]. These drawbacks considerably affect the feasibility of this method in large-scale production settings.

4.2 In-situ Electrochemical (IEC) method

In order to avoid the re-assembling process, an alternative method, denoted as the IEC method, was proposed by JM Energy Corp. (Japan) and applied to LICs. In this method, the auxiliary lithium is pre-set in the system when fabricating the LIC devices, as shown in Figure 4b. The pre-lithiation process is done by short-circuiting the anode and lithium electrodes in external circuit. After the complete consumption of the auxiliary lithium, the LIC formed by the graphite intercalation compound and the AC cathode can be cycled. The desired pre-lithiation level is controlled by the amount of lithium metal preset in the cell, while the pre-lithiation rate and duration can be varied by adjusting the external load resistance. During the pre-lithiation process, the lithium metal loses electrons to dissolve and form lithium ions in the electrolyte, and the lithium ions in the electrolyte diffuse from the first electrode close to the Li electrode to more distant electrodes [119]. Therefore, this method requires porous current collectors that are essential to enable the lithium ion transport. In addition, this pre-lithiation method is time-consuming.

The design of the porous current collector and the lithiation time are the key parameters for efficiently pre-lithiating the anode. As seen in Figure 7b, Tsuda et al optimized the above process by introducing porous graphite anodes with an open area of 1%, yielding to a much higher rate of lithiation compared with electrodes that were prepared by simply coating a graphite layer on porous current collectors [119]. Later, they applied additional through-holed on both anodes and cathodes, which further enhanced the ion diffusion efficiency [120]. A similar approach for anode lithiation was used by Sun et al who constructed an LIC pouch cell, in which the single layer structure enables the use of common current collectors.[69]

As mentioned above, the IEC method eliminates the re-assembling process, which increases the expenditure and possibly degrades the mechanical stability of the cell. The IEC method maintains a uniform and stable SEI layer due to similar electrochemical process. In addition, the pre-lithiation level and pre-lithiation rate are readily adjustable, which is beneficial to develop high performance anodes. However, the major disadvantages of this method are the high cost due to the usage of expensive porous current collectors and low efficiency associated with the long lithiation time, which severely hinders its usage in practical applications.

4.3 In-situ Short Circuit (ISC) method

In recent years, our group has developed another approach for pre-lithiation by placing the anode in direct contact with the lithium sources in the presence of electrolyte, and by applying an appropriate amount of mechanical pressure as shown in Figure 4c, in which the lithium no longer exists as a third electrode and the usage of porous current collector is eliminated. Due to the direct contact between the lithium source and the anode, the electrons are able to pass from the lithium metal to the carbon anode and initiate a continuous pre-lithiation process upon soaking with electrolyte. The different electrochemical processes that take place during pre-lithiation are illustrated in Figure 8a. First, the lithium source starts to ionize and releases electrons at the surface of the lithium metal (Process A). Then the produced lithium ions undergo solvation into electrolyte due to the presence of solvent molecules (Process B). The reduction of the electrolyte salt and solvent occurs once the anode attains the onset potential necessary to deposit the reduction products on the carbon surface and form the SEI layer. This SEI layer is insulating electronically and interrupts the reduction of the electrolyte but is highly ionically conductive to provide lithium ion pathways for further intercalation into the bulk of anode. The generated solvated Li^+ ions diffuse through the electrolyte migrating toward the surface of the SEI, where are de-solvated (Process C). This process is followed by an intercalation reaction that consumes one electron from the anode electrode (Process D).

The above pre-lithiation mechanism has also been demonstrated by solid state NMR technologies.[121] As shown in Figure 8b-c, when using either coated lithium metal powder or lithium metal foil as the pre-lithiation agent for graphite, two signals centered at 240-250 ppm (metallic lithium species) and within the region of 25-45 ppm representing intercalated lithium atoms in LiC_x can be detected in the corresponding ^7Li NMR spectra. The lithium metal signal decreases over time but it is compensated by an increase of the signal due to the LiC_x species. The use of coated lithium metal powder can further facilitate the pre-lithiation process and the reaction kinetics.

The ISC method does not require the use of porous current collectors by performing the in-situ pre-lithiation of each electrode. By taking advantage of the low standard redox potential of the lithium metal (-3.04 V vs. SHE), the strong driving force of the pre-lithiation process (i.e. the potential difference between lithium source and anode) results in a high efficiency. However, the whole or at least parts of the electrode manufacturing process must be carried out under dry room conditions and the processing of Li sources brings potential safety concerns. In addition, the ISC method involves a short circuit process followed by severe heat overflow, which could possibly result in thick SEI layer formation and thermal runaway. The applied mechanical pressure between the lithium source and the anode could also possibly damage the electrodes at the beginning of the pre-lithiation process.

So far, the ISC method has been utilized by industrial companies such as General Capacitors [72,122]. Meanwhile, our group has conducted extensive pre-lithiation studies using the ISC method using various lithium sources [51,57,58,64,65,73–75,123–132]. In the following sections, several possible lithium sources that can be used in the ISC method are summarized and compared, which is illustrated in Figure 9.

4.3.1 The stabilized lithium metal powder

The stabilized lithium metal powder (SLMP), a commercial product from the FMC Corporation (USA), is a special lithium source that can be safely handled in dry-air atmosphere. The improved dry-air stability of SLMP is attributed to a protective layer of Li_2CO_3 around the Li particles. [133] When used as the lithium source, the SLMP was first spread on the electrode surface followed by applying mechanical pressure to break the protective layer, as shown in Figure 9a. The concept of using SLMP to either compensate the irreversible capacity or to produce a fully lithiated anode has been proposed by Jarvis et al as early as in 2005 [134]. Our group utilized SLMP as a lithium source for pre-lithiation of AC||HC LIC [51] starting in 2012. The LIC devices built using SLMP had a specific energy of 25 Wh kg^{-1} based on the total weight of active material, electrolyte, separator, and current collectors, and were able to deliver over 60% of the maximum energy at a discharge C-rate of 44 C. Alternatively, Marinaro et al proposed to create suspensions of SLMP in toluene to enable the homogeneous distribution of lithium on the electrode surface with help of an airbrush in a glove box environment [135].

The loading effect of SLMP was later extensively studied by our group, showing that sufficient SLMP loadings on anode can reduce the IR drop during cell operation and extra SLMP loading can improve the cyclability by preventing the SEI layer from HF etching [124,131,132]. The excellent benefit of using SLMP to overcome the initial capacity loss has been demonstrated by many other groups as well [133,135–137].

Using SLMP has the following benefits: (i) using SLMP with a large specific surface area, homogeneous distribution, and high Li utilization rate can significantly magnify the ionization rate in Process A in Figure 6a for high-efficiency pre-lithiation; (ii) using SLMP with small particle size of 10-30 μm can control the pre-lithiation degree more accurately and enable a smooth integration into the electrode; (iii) SLMP has a better chemical stability than other lithium products and can be safely handled for long periods of time and in a wide temperature range from 25 to 55 °C, in dry-air atmosphere (e.g., in the dry room), which displays a strong potential for industrial applications. In the same time, SLMP suffers from several drawbacks: (i) SLMP itself is considerably more expensive than the lithium metal foil; (ii) SLMP has a relative low purity (~98%), which can result in severe self-discharge of the device; (iii) during the first charging process, the non-Li materials in SLMP and the thermal runaway could induce severe side reactions, generating innocuous gaseous products such as N_2, CO, and CO_2 that have a potential working range of 3-4 V vs Li/Li^+ [138].

4.3.2 Lithium stripe/foil

Inspired by the earlier work of Kulova et al who proposed a method to pre-lithiate graphite anodes [139] and Konno et al that pre-lithiated a Si-C-O glass-like compound and exfoliated graphite[140], our group proposed to utilize more cost-friendly thick lithium strips and thin lithium foils as alternatives lithium sources to address some of the issues with SLMP. The lithium stripe and foil with higher purity over 99.9% are capable of suppressing the self-discharge effects, effectively lowering the manufacturing cost and improving the safety of LICs due to the relatively slow pre-lithiation rates.

When fabricated using lithium stripes as the lithium source, the LICs had a specific energy of 14 Wh kg^{-1}, an energy density of 28 Wh L^{-1}, a maximum specific power of 6 kW kg^{-1}, and a power density of 12 kW L^{-1} [126]. As a drawback, the thick lithium stripes require extremely long pre-lithiation times in comparison with SLMP, which largely decreases the efficiency of pre-lithiation, as shown in Figure 9b. In addition, it is rather difficult to keep a continuously electronic conductive pathway and stable lithium source/electrolyte interface, which requires a relatively high mechanical pressure to keep a good contact between the lithium stripes and the anode, which might lead to mechanical damage of the electrode.

Thin lithium foils exhibit medium pre-lithiation rates compared to the other types of lithium sources, as shown in Figure 9c-9d. Our group has analyzed the pre-lithiation process using five different lithium foils as Li sources: a continuous 20 μm Li film, a continuous15 μm Li film, a 15 μm Li film with 25 tiny holes per 25 cm^2, and a 15 μm Li film with 9 holes per 25 cm^2 [122]. A 200 F LIC device was made to illustrate the power and energy output characteristics obtained using the different films. We found that the LIC with the 20 μm Li film exhibited the best electrochemical performance and had the highest capacitance (26.9 F) and energy and power densities (41.65 Wh/L and 16.2 kW/L, respectively, based on the active layers). A similar procedure was used to pre-lithiate MWCNTs/graphite [141], graphite electrode [142], and carbon onion electrode [143] with positive results. On a downside, the ultra-thin lithium metal foil is relatively soft and sticky for readily manufacturing handling and also more expensive than thick lithium foil, which drastically increases the production costs.

The effect of different Li sources has been studied by Shellikeri et al, who thoroughly investigated the efficiency of the ISC method for pre-lithiating graphite and hard carbon anodes using the four Li-source structures, as seen in Figure 9 [123]. The results show that the type of Li-source structure can potentially affect the SEI properties, cycle life, and the electrode processing cost. The pre-lithiation using the foil strips resulted in the lowest anode potential vs. Li/Li^+ among the other four Li-source structures tested over 24 hours of electrolyte soaking period. In the first 10 minutes of electrolyte soaking, the pre-lithiation using SLMP was the fastest to reach a low lithiation potential among the four loaded sources, however, the lithiation rate slowed down over the next 24 hours. Somewhat surprisingly, the introduction of small holes in the Li foil sheet did not have a significant influence in enhancing the lithiation rate.

4.4 Cathode pre-lithiation method

Besides anode pre-lithiation, it is also desirable to pre-lithiate the cathode by mixing cathode additive with the AC-based cathode. In this configuration, during the first charge, the lithium sources release lithium ions into the LIC systems and the lithium ions in the electrolyte intercalate into the anode to achieve pre-lithiation, as shown in Figure 6d. The lithium sources that remain after charging constitute "dead" materials in the cathode in the following cycles, so that the released lithium ions can stay stable in LIC systems during cell operation. Ideally, the lithium sources should meet several requirements: (i) they should align with the working potential range of the LIC system; (ii) they should be compatible with the industrial standard processing techniques and allow for handling in ambient atmosphere; (iii) they should exhibit a high volumetric and gravimetric capacity to enable an effective pre-lithiation; and (iv) they should work only during the first charge process to promote the insertion of lithium cations into the anode, which do not converse back in the following discharge process. Note that to meet requirement (iv), the pre-lithiation of additives can be divided into two types as shown in Figure 10.[144]: for type 1 the additives will only be re-lithiated at potentials lower than AC's lower operation limit; for type 2 the re-lithiation process of additives is substantially irreversible.

Since this concept was firstly proposed using the lithium molybdate (Li_2MoO_3) with a high total capacity of 270 mAh g^{-1} as lithium source [145], a variety of materials were proposed afterwards, as shown in Table 3. Unfortunately, none of these materials can meet all the requirements of ideal lithium sources for cathode pre-lithiation simultaneously. For example, the Li_5FeO_4 has a large irreversible specific capacity of 578 mAh g^{-1} but the extremely high charge potential (>4.7 V), which is over the stable voltage window of LICs and results in severe performance degradation [146]. Recently, Jezowski et al synthesized a sacrificial organic lithium salt, namely 3,4-dihydroxybenzonitrile dilithium salt (Li_2DHBN), which is mixed with AC in cathode[147]. During the first charge process, the Li_2DHBN changes to soluble 3,4-dioxobenzonitrile (DOBN) in electrolyte, irreversibly providing Li cations to the graphite anode to achieve pre-lithiation. This novel organic sacrificial material brings no dead mass in cathode, while the dissolved

DOBN production into electrolyte would bring extra weight the in electrolyte. Its operation voltage is relatively high (close to 3.5 V), however, the irreversible capacity is still low. Therefore, developing an ideal lithium source meeting all the requirements for this concept remains vital but challenging.

In general, the cathode pre-lithiation is even more desirable than the anode pre-lithiation because (i) the lithium metal sources are replaced by the lithium compounds sources, which alleviates the safety concern for pre-lithiation; (ii) the lithium sources are added into cathode directly when preparing electrode, which is technologically feasible and needs minimum modification of the processing line; (iii) the pre-lithiation is conducted based on a moderate electrochemical process, which can form a stable SEI. However, a bottleneck of this method is that the dead materials remaining in the cathode increase the total weight of LICs and thus decrease the energy density of the LICs.

In order to illustrate the last statement, one can estimate the influence of the dead materials in the cathode on the energy density of LICs analytically. For this purpose, let us consider a practical LIC pouch cell AC (+) || pre-lithiated HC (-), in which the weight of cell consists of 15.0 % AC, 18.0 % HC, 2.0 % Li source, 35.0 % electrolyte, and 30.0% extra dead materials. The capacity of the anode was selected about six times higher than that of the cathode to achieve a better power density and cycle life. The energy density of this configuration can be calculated as:

$$\mathbf{E} = \frac{\frac{1}{2}\mathbf{C}\,(\mathbf{V}_{\mathbf{max}}^{2} - \mathbf{V}_{\mathbf{min}}^{2})}{\mathbf{m}_{\mathbf{total}}} = \frac{\frac{1}{2}\mathbf{C}\,(\mathbf{V}_{\mathbf{max}}^{2} - \mathbf{V}_{\mathbf{min}}^{2})}{\mathbf{m}_{\mathbf{extra}} + \mathbf{m}_{\mathbf{electrodes}} + \mathbf{m}_{\mathbf{lithium\ metal}}}$$

If we change the Li foil to Li compounds, the weight of Li sources should be several times higher than the weight of the lithium metal sources due to their low specific capacity in comparison with Li foil (3860 mAh g^{-1}). By assuming that the weight of the other components in this configuration do not change from the previous case, the energy density after changing the Li source can be estimated as:

$$\mathbf{E}' = \frac{\frac{1}{2}\mathbf{C}\,(\mathbf{V}_{\mathbf{max}}^{2} - \mathbf{V}_{\mathbf{min}}^{2})}{\mathbf{m}_{\mathbf{total}}'} = \frac{\mathbf{m}_{\mathbf{total}}}{\mathbf{m}_{\mathbf{total}}'}\mathbf{E} = \frac{\mathbf{m}_{\mathbf{total}}}{\mathbf{m}_{\mathbf{total}} + \mathbf{m}_{\mathbf{lithium\ compounds}} - \mathbf{m}_{\mathbf{lithium\ metal}}}\mathbf{E}$$

Based on the above formula, the energy density retention of LIC systems using the Li compounds instead of the lithium metal can be calculated as shown in the Table 3.[145-151] For instance, when the irreversible capacity of the Li compound is 100 mAh g^{-1} for $Li_{0.65}Ni_{1.35}O_2$ or 568 mAh g^{-1} for Li_5FeO_4, the energy density retention is 57.47 % and 89.78 % can be obtained, respectively. Once the specific capacity of Li compound reaches 1000 mAh g^{-1}, the energy density retention is equal to 94.70 %, which could be acceptable for LIC systems. In other words, since that in practical LIC designs the capacity of the anode should be sufficiently higher than that of the cathode, the utilization of Li compounds will inevitably decrease the energy densities of LIC systems. The energy density loss will be acceptable only if the capacity of the Li compounds is sufficiently high. Therefore, it is still desirable to develop new advanced Li compounds with high specific capacity.

4.5 Comparison of different pre-lithiation methods

The above different pre-lithiation methods have been compared directly in several papers [152–156]. The self-discharge behavior associated with the pre-lithiated anode, which is reflected as a positive drift of the anode potential during cell operation, was studied by Sivakkumare et al who investigated three different pre-lithiation methods: (i) short circuiting the Li and graphite electrodes externally, (ii) using an appropriate resistor to short circuit the electrodes externally, and (iii) by galvanostatic charging at C/20 [152]. They found that methods (i) or (iii) cannot efficiently prevent the self-discharge of pre-lithiated graphite anodes, probably because of the failure to form a uniform SEI. The pre-lithiated graphite electrode by method (ii) exhibited a slower self-discharge rate and a prolonged cycle performance compared with the electrodes obtained using the other two methods, but the lithiation took nearly 11 days, which is much longer than in the case of the other two methods. From their study, it can be concluded that the pre-lithiation technology and the formation of the SEI layer had a great influence on the quality of the pre-lithiated graphite anode, which, in turn, influences the cyclability and self-discharge of the LIC.

Kim et al systematically compared the efficiency of internal short (IS), electrochemical (EC) and external short circuit (ESC) methods for pre-lithiation [155]. It was found that due to the difference potential between graphite and Li (almost zero for the case of IS), IS method exhibits a remarkably larger capacitance, higher CE, and longer cyclability. However, the comparison was conducted during only 30 mins of pre-lithiation. Similarly, Park et al used in situ synchrotron wide-angle X-ray scattering to examine three different pre-lithiation methods, i.e., direct contact (DC), electronic charger (EC), and external short circuit (ESC), up to 60 mins of pre-lithiation, while an extreme excess of lithium metal was used in the experimental setup. A similar conclusion was drawn that the DC method provides much faster phase transformation than the other two methods for the same lithiation time. However, the full lithiation by direct contact of Li can take up to days and the pre-lithiation shows a rather non-linear variation with time [123,126]. Therefore, the conclusion derived from the above studies does not necessarily reflect the pre-lithiation kinetics in the entire process. These studies shed light upon the correlation between the electrochemical performance and the type of the pre-lithiation method to some extent, however, a more thorough analysis is still needed to comprehensively investigate the effect of this pre-lithiation method on the electrode physical properties, pre-lithiation times, and the pre-lithiation anode potentials of LIC.

Here in Figure 11 and Table 4, we have summarized the main characteristics of the above mentioned pre-lithiation methods for LICs including scalability, cost, safety, controllability, environmental requirements and efficiency. The EEC method has poor scalability but high controllability and is relatively safe, which makes this method unsuitable for practical applications but appropriate for laboratory studies. The IEC and ISC methods are utilized often in LICs and have practical advantages over the other two methods when used in commercial applications. The main disadvantages of IEC are the low efficiency and high cost. The most promising lithium source for ISC method seems to be the thin lithium film.

5. Perspectives

In this article, we systemically review the progress of pre-lithiation technologies involving the fundamental research and practical application for LICs. The definition of LICs was firstly clarified based on different energy storage mechanisms, which is seldom discussed in detail in previous reviews. The multiple roles the pre-lithiation technologies play for improving the performance of LICs were also analyzed and discussed. The progress of pre-lithiation technologies currently used in LICs as well as the advantages and drawbacks of various pre-lithiation technologies was reviewed and summarized. Considering the abovementioned progress of pre-lithiation technologies, we expect that the possible future research and development of pre-lithiation technologies needs to focus on multiple aspects. From a fundamental point of view:

- The correlation of the electrochemical performance and energy storage mechanism with different pre-lithiation technologies needs to be carefully studied. Combined experimental characterization and theoretical modeling work is needed to shed light upon the structure integrity, SEI formation, and Li^+ ion distribution in pre-lithiated electrodes with different pre-lithiation methods.
- Special attention should be given to the characterization and control of the SEI after the pre-lithiation process. This interphase plays a pivotal role in the electrochemical stability of LIC device over long-term cycles.
- The Li^+ ion diffusion mechanism and limiting factors for pre-lithiation kinetics need to be better understood in order to optimize the pre-lithiation conditions.
- The pre-lithiation methods that have been used for the pre-lithiation of LIBs but not LICs, such as chemical lithiation [157-160], lithiated anode additive [161,162], and sacrificial salts [163], need to be further explored and their potential in the pre-lithiation of LIC systems needs to be analyzed.
- Finally, more effort on new material development is needed to explore potential candidates for cathode and electrolyte additives.

From a practical point of view, seeking for a better Li source for pre-lithiation is critical for the large-scale development of current practical pre-lithiation technologies. In the industry, there have been extensive efforts to pursue the commercialization of pre-lithiation techniques: besides JM Energy Corporation (Japan), companies like Asahi Kasei Corporation (Japan) or Subaru (Japan), FDK Lithium Ion Capacitor Co., Ltd (Japan), Taiyo Yuden Co., Ltd (Japan), Ling Rong New Energy Technology Co., Ltd. (China) have vigorously researched the pre-lithiation of LICs [27,164–166], in which SLMP and Li foil are exclusively used as Li sources. Li powders with reduced reactivity, higher purity, and lower cost remains in urgent need. The ultra-thin Li foil as an alternative Li source for pre-lithiation can address many issues with SLMP, while its current high price limits its industrial application. In the future, the ultra-thin Li foil technique may replace SLMP in providing the optimum Li source for pre-lithiation if the large-scale manufacturing of ultra-thin Li foils becomes possible at low-cost.

Finally, we need to emphasize that the importance of pre-lithiation is by no means limited to the LIC application. Indeed, the pre-lithiation technologies presented in this progressive report will find its extensive applications in various energy storage devices, particularly, in the next-generation LIBs with advanced electrode active materials. It is well-known that the active lithium loss in LIBs is attributed to lithium consuming parasitic reactions such as the formation of the SEI on the anode and other irreversible reactions. Because of the large volume variation of alloy and conversion type materials (e.g. Si and Sn) during lithiation and delithiation, the loss of the active material becomes even more serious and limits the wide usage of these materials in high capacity and high-power applications. Therefore, the use of pre-lithiation for compensating the lithium loss is becoming increasingly critical for developing high energy density LIBs.

The research effort for pre-lithiation technologies for LICs and LIBs can be undoubtfully synergetic. The fruitful research and development of pre-lithiation technologies in LIC field will certainly encourage the broad application and enable the potential commercialization breakthrough of the advanced electrode active materials for LIBs. However, there are some differences which should be pointed out:

- The objectives to utilize pre-lithiation technologies for LICs and LIBs are not always identical. The roles of pre-lithiation for LIBs mainly focus on the mitigation of irreversible Li^+ loss for stable cyclability, such as SEI formation, irreversible electrochemical process during first several cycles, which means pre-lithiation technologies only plays partial roles in comparison with the roles proposed in LIC field.

- Based on these considerations, all the pre-lithiation methods proposed in LICs should be possibly useful in the fields of next generation of LIBs. However, the lithiation degree for LIBs should be much lower and the conditions to achieve pre-lithiations should be systemically optimized.

- Moreover, different from current pre-lithiation method in practical level (i.e. IEC, ISC), the most promising method for next generation LIBs could be cathode pre-lithiation due to the low lithium source requirement, which would simplify operational procedures with lower costs.

- More high-efficiency and reliable pre-lithiation technologies from the fundamental or practical points of view should be developed in allusion to different LIB systems, which should be of great significance for the practical progress of next generation LIBs.

In conclusion, the LICs attract much attention recent years and are gradually approaching large-scale commercialization. In this progress report, we clarify the definition and reaction principles of LICs for future studies and review the progress of pre-lithiation technologies, which should be one of most challenging bottlenecks for practical applications. We believe this progress report can provide the fundamental knowledge necessary to researchers who are new to LICs and also serving as a guideline to senior researchers in the field of LICs for future research directions. Moreover, we hope this progress report can provide insights for the development of pre-lithiation technologies for next generation LIBs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

L.M. Jin and C. Shen contribute equally to this work. The work is supported by Office of Naval Research under contact No. N00014-17-1-2650, Army Research Laboratory under contract No. W911NF-15-2-0103, National Science Foundation of China, Grant Nos. 511777140, and Pacific Northwest National Laboratory under contract No. 212964.

References

[1] M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P. L. Taberna, C. P. Grey, B. Dunn, P. Simon, Nat. Energy 2016, 1, DOI 10.1038/nenergy.2016.70.

[2] D. Larcher, J. M. Tarascon, Nat. Chem. 2015, 7, 19.

[3] P. Albertus, S. Babinec, S. Litzelman, A. Newman, Nat. Energy 2018, 3, 16.

[4] G. Li, S. Wang, Y. Zhang, M. Li, Z. Chen, J. Lu, Adv. Mater. 2018, 30, 1.

[5] A. Jagadale, X. Zhou, R. Xiong, D. P. Dubal, J. Xu, S. Yang, Energy Storage Mater. 2019, 19, 314.

[6] Y. Wang, Y. Song, Y. Xia, Chem. Soc. Rev. 2016, DOI 10.1039/c5cs00580a.

[7] D. P. Dubal, O. Ayyad, V. Ruiz, P. Gómez-Romero, Chem. Soc. Rev. 2015, 44, 1777.

[8] G. Li, Z. Chen, J. Lu, Chem 2018, DOI 10.1016/j.chempr.2017.12.012.

[9] J. W. Choi, D. Aurbach, Nat. Rev. Mater. 2016, 1, 16013.

[10] V. Ruiz, A. Pfrang, A. Kriston, N. Omar, P. Van den Bossche, L. Boon-Brett, Renew. Sustain. Energy Rev. 2018, DOI 10.1016/j.rser.2017.05.195.

[11] F. Schipper, D. Aurbach, Russ. J. Electrochem. 2016, DOI 10.1134/S1023193516120120.

[12] A. Muzaffar, M. B. Ahamed, K. Deshmukh, J. Thirumalai, Renew. Sustain. Energy Rev. 2019, DOI 10.1016/j.rser.2018.10.026.

[13] A. González, E. Goikolea, J. A. Barrena, R. Mysyk, Renew. Sustain. Energy Rev. 2016, 58, 1189.

[14] K. Naoi, Fuel Cells 2010, 10, 825.

[15] K. Naoi, S. Ishimoto, J. I. Miyamoto, W. Naoi, Energy Environ. Sci. 2012, DOI 10.1039/c2ee21675b.

[16] V. Aravindan, J. Gnanaraj, Y. S. Lee, S. Madhavi, Chem. Rev. 2014, 114, 11619.

[17] J. Ding, W. Hu, E. Paek, D. Mitlin, Chem. Rev. 2018, DOI 10.1021/acs.chemrev.8b00116.

[18] H. Wang, C. Zhu, D. Chao, Q. Yan, H. J. Fan, Adv. Mater. 2017, DOI 10.1002/adma.201702093.

[19] C. Han, H. Li, R. Shi, L. Xu, J. Li, F. Kang, B. Li, Energy Environ. Mater. 2018, DOI 10.1002/eem2.12009.

[20] H. Gu, Y. E. Zhu, J. Yang, J. Wei, Z. Zhou, ChemNanoMat 2016, 2, 578.

[21] Y. Ma, H. Chang, M. Zhang, Y. Chen, Adv. Mater. 2015, 27, 5296.

[22] K. Naoi, W. Naoi, S. Aoyagi, J. I. Miyamoto, T. Kamino, Acc. Chem. Res. 2013, DOI 10.1021/ar200308h.

[23] B. Li, J. Zheng, H. Zhang, L. Jin, D. Yang, H. Lv, C. Shen, A. Shellikeri, Y. Zheng, R. Gong, J. P. Zheng, C. Zhang, Adv. Mater. 2018, 1705670, 1705670.

[24] M. R. Lukatskaya, B. Dunn, Y. Gogotsi, Nat. Commun. 2016, 7, 1.

[25] W. Zuo, R. Li, C. Zhou, Y. Li, J. Xia, J. Liu, Adv. Sci. 2017, DOI 10.1002/advs.201600539.

[26] X. Yao, Y. Zhao, F. A. Castro, L. Mai, 2019, 4, 771-778.

[27] P. Han, G. Xu, X. Han, J. Zhao, X. Zhou, G. Cui, Adv. Energy Mater. 2018, 8, 1.

[28] J. Li, X. Zhang, R. Peng, Y. Huang, L. Guo, Y. Qi, RSC Adv. 2016, DOI 10.1039/c6ra09103b.

[29] K. Karthikeyan, S. Amaresh, V. Aravindan, H. Kim, K. S. Kang, Y. S. Lee, J. Mater. Chem. A 2013, 1, 707.

[30] K. Karthikeyan, V. Aravindan, S. B. Lee, I. C. Jang, H. H. Lim, G. J. Park, M. Yoshio, Y. S. Lee, J. Power Sources 2010, DOI 10.1016/j.jpowsour.2009.11.138.

[31] A. Krause, P. Kossyrev, M. Oljaca, S. Passerini, M. Winter, A. Balducci, J. Power Sources 2011, DOI 10.1016/j.jpowsour.2011.06.019.

[32] J. H. Yoon, H. J. Bang, J. Prakash, Y. K. Sun, Mater. Chem. Phys. 2008, DOI 10.1016/j.matchemphys.2008.01.032.

[33] N. Arun, A. Jain, V. Aravindan, S. Jayaraman, W. Chui Ling, M. P. Srinivasan, S. Madhavi, Nano Energy 2015, DOI 10.1016/j.nanoen.2014.12.006.

[34] A. Brandt, A. Balducci, U. Rodehorst, S. Menne, M. Winter, A. Bhaskar, J. Electrochem. Soc. 2014, DOI 10.1149/2.105406jes.

[35] H. Wu, C. V. Rao, B. Rambabu, Mater. Chem. Phys. 2009, DOI 10.1016/j.matchemphys.2009.04.028.

[36] H. Li, L. Cheng, Y. Xia, Electrochem. Solid-State Lett. 2005, DOI 10.1149/1.1960007.

[37] L. Ye, Q. Liang, Y. Lei, X. Yu, C. Han, W. Shen, Z. H. Huang, F. Kang, Q. H. Yang, J. Power Sources 2015, DOI 10.1016/j.jpowsour.2015.02.028.

[38] S. Dsoke, B. Fuchs, E. Gucciardi, M. Wohlfahrt-Mehrens, J. Power Sources 2015, DOI 10.1016/j.jpowsour.2015.02.079.

[39] S. Hemmati, G. Li, X. Wang, Y. Ding, Y. Pei, A. Yu, Z. Chen, Nano Energy 2019, 56, 118.

[40] B. H. Deng, T. Y. Lei, W. H. Zhu, L. Xiao, J. P. Liu, Adv. Funct. Mater. 2018, DOI 10.1002/adfm.201704330.

[41] L. Shen, H. Lv, S. Chen, P. Kopold, P. A. van Aken, X. Wu, J. Maier, Y. Yu, Adv. Mater. 2017, DOI 10.1002/adma.201700142.

[42] R. Wang, J. Lang, P. Zhang, Z. Lin, X. Yan, Adv. Funct. Mater. 2015, DOI 10.1002/adfm.201404472.

[43] G. Wang, C. Lu, X. Zhang, B. Wan, H. Liu, M. Xia, H. Gou, G. Xin, J. Lian, Y. Zhang, Nano Energy 2017, DOI 10.1016/j.nanoen.2017.04.020.

[44] K. Naoi, S. Ishimoto, Y. Isobe, S. Aoyagi, J. Power Sources 2010, DOI 10.1016/j.jpowsour.2009.12.104.

[45] H. Kim, K. Y. Park, M. Y. Cho, M. H. Kim, J. Hong, S. K. Jung, K. C. Roh, K. Kang, ChemElectroChem 2014, DOI 10.1002/celc.201300186.

[46] C. Jiang, J. Zhao, H. Wu, Z. Zou, R. Huang, J. Power Sources 2018, DOI 10.1016/j.jpowsour.2018.08.103.

[47] S. Dong, X. Wang, L. Shen, H. Li, J. Wang, P. Nie, J. Wang, X. Zhang, J. Electroanal. Chem. 2015, DOI 10.1016/j.jelechem.2015.09.002.

[48] B. G. Lee, S. H. Lee, J. R. Yoon, H. J. Ahn, Electrochim. Acta 2018, DOI 10.1016/j.electacta.2017.11.042.

[49] J. Zhang, H. Chen, X. Sun, X. Kang, Y. Zhang, C. Xu, Y. Zhang, J. Electrochem. Soc. 2017, DOI 10.1149/2.1351704jes.

[50] Z. Chen, H. Li, X. Lu, L. Wu, J. Jiang, S. Jiang, J. Wang, H. Dou, X. Zhang, ChemElectroChem 2018, DOI 10.1002/celc.201701390.

[51] W. J. Cao, J. P. Zheng, J. Power Sources 2012, 213, 180.

[52] F. Sun, J. Gao, X. Liu, L. Wang, Y. Yang, X. Pi, S. Wu, Y. Qin, Electrochim. Acta 2016, 213, 626.

[53] S. R. Sivakkumar, J. Y. Nerkar, A. G. Pandolfo, Electrochim. Acta 2010, 55, 3330.

[54] L. Jin, R. Gong, W. Zhang, Y. Xiang, J. Zheng, Z. Xiang, C. Zhang, Y. Xia, J. P. Zheng, J. Mater. Chem. A 2019, 7, 8234.

[55] O. Bolufawi, A. Shellikeri, J. P. Zheng. Batteries, 2019, 5, 74.

[56] W. Cao, Y. Li, B. Fitch, J. Shih, T. Doung, J. Zheng, J. Power Sources 2014, DOI 10.1016/j.jpowsour.2014.06.090.

[57] W. J. Cao, J. P. Zheng, J. Electrochem. Soc. 2013, 160, A1572.

[58] W. Cao, J. Zheng, D. Adams, T. Doung, J. P. Zheng, J. Electrochem. Soc. 2014, 161, A2087.

[59] X. Sun, X. Zhang, W. Liu, K. Wang, C. Li, Z. Li, Y. Ma, Electrochim. Acta 2017, 235, 158.

[60] Z. Yang, H. Guo, X. Li, Z. Wang, Z. Yan, Y. Wang, J. Power Sources 2016, DOI 10.1016/j.jpowsour.2016.08.088.

[61] X. Han, P. Han, J. Yao, S. Zhang, X. Cao, J. Xiong, J. Zhang, G. Cui, Electrochim. Acta 2016, DOI 10.1016/j.electacta.2016.02.185.

[62] S. R. Sivakkumar, A. S. Milev, A. G. Pandolfo, Electrochim. Acta 2011, DOI 10.1016/j.electacta.2011.06.060.

[63] J. P. Zheng, J. Electrochem. Soc. 2009, DOI 10.1149/1.3121564.

[64] J. S. Zheng, L. Zhang, A. Shellikeri, W. Cao, Q. Wu, J. P. Zheng, Sci. Rep. 2017, 7, 1.

[65] M. Hagen, W. J. Cao, A. Shellikeri, D. Adams, X. J. Chen, W. Brandt, S. R. Yturriaga, Q. Wu, J. A. Read, T. R. Jow, J. P. Zheng, J. Power Sources 2018, 379, 212.

[66] X. Sun, X. Zhang, B. Huang, H. Zhang, D. Zhang, Y. Ma, J. Power Sources 2013, DOI 10.1016/j.jpowsour.2013.06.038.

[67] X. Hu, Y. Huai, Z. Lin, J. Suo, Z. Deng, J. Electrochem. Soc. 2007, DOI 10.1149/1.2779947.

[68] X. Hu, Z. Deng, J. Suo, Z. Pan, J. Power Sources 2009, DOI 10.1016/j.jpowsour.2008.11.033.

[69] X. Sun, X. Zhang, H. Zhang, N. Xu, K. Wang, Y. Ma, J. Power Sources 2014, 270, 318.

[70] A. Shellikeri, S. Yturriaga, J. S. Zheng, W. Cao, J. A. Read, T. R. Jow, J. P. Zheng, in ECS Trans., 2017.

[71] X. Guo, R. Gong, N. Qin, L. Jin, J. Zheng, Q. Wu, J. P. Zheng, J. Electroanal. Chem. 2019, DOI 10.1016/j.jelechem.2019.05.046.

[72] J. Yan, X. J. Chen, A. Shellikeri, T. Du, M. Hagen, J. P. Zheng, W. J. Cao, J. Electrochem. Soc. 2018, 165, A2774.

[73] L. Jin, J. Zheng, Q. Wu, A. Shellikeri, S. Yturriaga, R. Gong, J. Huang, J. P. Zheng, Mater. Today Energy 2018, 7, 51.

[74] A. Shellikeri, S. Yturriaga, J. S. Zheng, W. Cao, M. Hagen, J. A. Read, T. R. Jow, J. P. Zheng, J. Power Sources 2018, 392, 285.

[75] A. Shellikeri, I. Hung, Z. Gan, J. Zheng, J. Phys. Chem. C 2016, 120, 6314.

[76] E. Lim, C. Jo, H. Kim, M. H. Kim, Y. Mun, J. Chun, Y. Ye, J. Hwang, K. S. Ha, K. C. Roh, S. Yoon, J. Lee, ACS Nano 2015, DOI 10.1021/acsnano.5b02601.

[77] P. Yu, G. Cao, S. Yi, X. Zhang, C. Li, X. Sun, K. Wang, Y. Ma, Nanoscale 2018, DOI 10.1039/c8nr00380g.

[78] S. Li, T. Wang, Y. Huang, Z. Wei, G. Li, D. H. L. Ng, J. Lian, J. Qiu, Y. Zhao, X. Zhang, J. Ma, H. Li, ACS Appl. Mater. Interfaces 2019, 11, 24114.

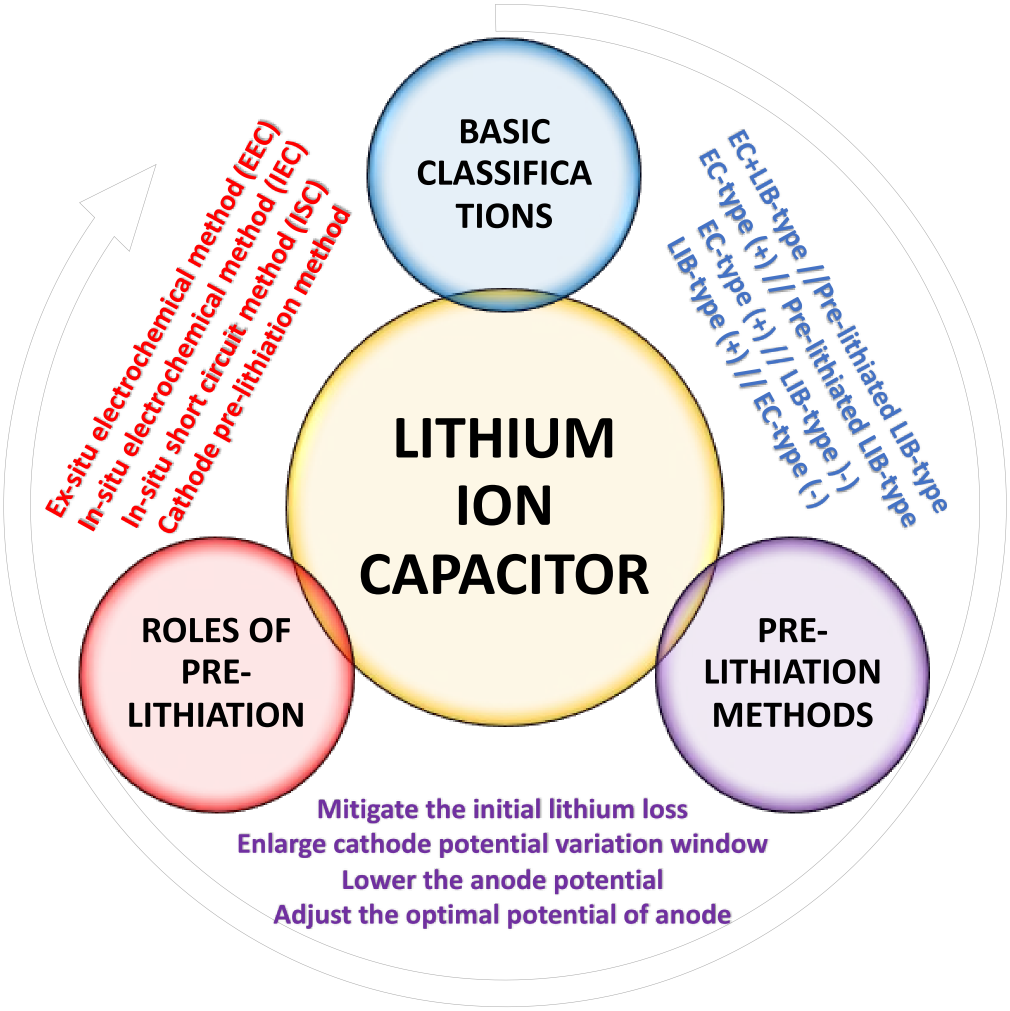
[79] S. Li, J. Chen, X. Gong, J. Wang, P. S. Lee, NPG Asia Mater. 2018, DOI 10.1038/s41427-018-0042-5.

[80] H. Wang, Y. Zhang, H. Ang, Y. Zhang, H. T. Tan, Y. Zhang, Y. Guo, J. B. Franklin, X. L. Wu, M. Srinivasan, H. J. Fan, Q. Yan, Adv. Funct. Mater. 2016, DOI 10.1002/adfm.201505240.
[81] S. Li, J. Chen, M. Cui, G. Cai, J. Wang, P. Cui, X. Gong, P. S. Lee, Small 2017, DOI 10.1002/smll.201602893.
[82] W. S. V. Lee, E. Peng, M. Li, X. Huang, J. M. Xue, Nano Energy 2016, 27, 202.
[83] C. Liu, Q. Q. Ren, S. W. Zhang, B. S. Yin, L. F. Que, L. Zhao, X. L. Sui, F. Da Yu, X. Li, D. M. Gu, Z. B. Wang, Chem. Eng. J. 2019, DOI 10.1016/j.cej.2019.04.044.
[84] J. Ajuria, M. Arnaiz, C. Botas, D. Carriazo, R. Mysyk, T. Rojo, A. V. Talyzin, E. Goikolea, J. Power Sources 2017, DOI 10.1016/j.jpowsour.2017.07.096.
[85] A. Jagadale, X. Zhou, D. Blaisdell, S. Yang, Sci. Rep. 2018, DOI 10.1038/s41598-018-19787-z.
[86] S. Fleischmann, M. Zeiger, A. Quade, A. Kruth, V. Presser, ACS Appl. Mater. Interfaces 2018, DOI 10.1021/acsami.8b03233.
[87] W. S. V. Lee, X. Huang, T. L. Tan, J. M. Xue, ACS Appl. Mater. Interfaces 2018, DOI 10.1021/acsami.7b15473.
[88] X. Zhao, H. E. Wang, J. Cao, W. Cai, J. Sui, Chem. Commun. 2017, DOI 10.1039/c7cc06851d.
[89] S. Zhang, C. Li, X. Zhang, X. Sun, K. Wang, Y. Ma, ACS Appl. Mater. Interfaces 2017, DOI 10.1021/acsami.7b03452.
[90] M. Arnaiz, J. L. Gómez-Cámer, F. Mijangos, T. Rojo, E. Goikolea, J. Ajuria, Batter. Supercaps 2019, DOI 10.1002/batt.201800099.
[91] X. Zhao, X. Zhang, C. Li, X. Sun, J. Liu, K. Wang, Y. Ma, ACS Sustain. Chem. Eng. 2019, DOI 10.1021/acssuschemeng.9b00641.
[92] C. M. Lai, T. L. Kao, H. Y. Tuan, J. Power Sources 2018, DOI 10.1016/j.jpowsour.2018.01.046.
[93] F. Sun, J. Gao, Y. Zhu, X. Pi, L. Wang, X. Liu, Y. Qin, Sci. Rep. 2017, 7, 1.
[94] F. Sun, X. Liu, H. Bin Wu, L. Wang, J. Gao, H. Li, Y. Lu, Nano Lett. 2018, DOI 10.1021/acs.nanolett.8b00134.
[95] G. Zhu, T. Chen, L. Wang, L. Ma, Y. Hu, R. Chen, Y. Wang, C. Wang, W. Yan, Z. Tie, J. Liu, Z. Jin, Energy Storage Mater. 2018, DOI 10.1016/j.ensm.2018.04.009.
[96] R. Wang, Q. Zhao, W. Zheng, Z. Ren, X. Hu, J. Li, L. Lu, N. Hu, J. Molenda, X. Liu, C. Xu, J. Mater. Chem. A 2019, DOI 10.1039/c9ta06316a.
[97] S. Wang, R. Wang, Y. Bian, D. Jin, Y. Zhang, L. Zhang, Nano Energy 2019, 55, 173.
[98] A. Byeon, A. M. Glushenkov, B. Anasori, P. Urbankowski, J. Li, B. W. Byles, B. Blake, K. L. Van Aken, S. Kota, E. Pomerantseva, J. W. Lee, Y. Chen, Y. Gogotsi, J. Power Sources 2016, 326, 686.
[99] Q. Xia, H. Yang, M. Wang, M. Yang, Q. Guo, L. Wan, H. Xia, Y. Yu, Adv. Energy Mater. 2017, DOI 10.1002/aenm.201701336.
[100] D. P. Dubal, K. Jayaramulu, R. Zboril, R. A. Fischer, P. Gomez-Romero, J. Mater. Chem. A 2018, DOI 10.1039/c8ta00549d.
[101] J. Zhang, H. Wu, J. Wang, J. Shi, Z. Shi, Electrochim. Acta 2015, 182, 156.
[102] J. Zhang, Z. Shi, C. Wang, Electrochim. Acta 2014, 125, 22.
[103] L. Jin, X. Guo, R. Gong, J. Zheng, Z. Xiang, C. Zhang, J. P. Zheng, Energy Storage Mater. 2019, DOI 10.1016/j.ensm.2019.04.027.

[104] L. Jin, X. Guo, C. Shen, N. Qin, J. Zheng, Q. Wu, C. Zhang, J. P. Zheng, J. Power Sources 2019, 441, 227211.
[105] T. Aida, K. Yamada, M. Morita, Electrochem. Solid-State Lett. 2006, 9, 534.
[106] T. Rauhala, J. Leis, T. Kallio, K. Vuorilehto, J. Power Sources 2016, 331, 156.
[107] S. Li, X. Wang, J. Power Sources 2015, 282, 394.
[108] J. M. Jiang, P. Nie, S. Y. Dong, Y. T. Wu, X. G. Zhang, Wuli Huaxue Xuebao/ Acta Phys. - Chim. Sin. 2017, 33, 780.
[109] Z. Shi, J. Zhang, J. Wang, J. Shi, C. Wang, Electrochim. Acta 2015, 153, 476.
[110] X. Sun, X. Zhang, K. Wang, N. Xu, Y. Ma, J. Solid State Electrochem. 2015, 19, 2501.
[111] M. Schroeder, M. Winter, S. Passerini, A. Balducci, J. Electrochem. Soc. 2012, 159, A1240.
[112] N. Xu, X. Sun, F. Zhao, X. Jin, X. Zhang, K. Wang, K. Huang, Y. Ma, Electrochim. Acta 2017, 236, 443.
[113] Y. Sun, J. Tang, F. Qin, J. Yuan, K. Zhang, J. Li, D. Zhu, L. Qin, J. Mater. Chem. A 2017, 5, 13601.
[114] J. J. Ren, L. W. Su, X. Qin, M. Yang, J. P. Wei, Z. Zhou, P. W. Shen, J. Power Sources 2014, 264, 108.
[115] X. Yu, J. Deng, C. Zhan, R. Lv, Z. Huang, F. Kang, Electrochim. Acta 2017, 228, 76.
[116] P. Sennu, V. Aravindan, Y. S. Lee, Chem. Eng. J. 2017, 324, 26.
[117] S. Kumagai, T. Ishikawa, N. Sawa, J. Energy Storage 2015, 2, 1.
[118] M. Li, Z. Chen, T. Wu, J. Lu, Adv. Mater. 2018, 30, 1.
[119] T. Tsuda, N. Ando, N. Mitsuhashi, T. Tanabe, K. Itagaki, N. Soma, S. Nakamura, N. Hayashi, F. Matsumoto, ECS Trans. 2017, 77, 1897.
[120] T. Tsuda, N. Ando, Y. Haruki, T. Tanabe, T. Gunji, K. Itagaki, N. Soma, S. Nakamura, N. Hayashi, F. Matsumoto, ECS Trans. 2018, 85, 1507.
[121] F. Holtstiege, R. Schmuch, M. Winter, G. Brunklaus, T. Placke, J. Power Sources 2018, 378, 522.
[122] J. Yan, W. J. Cao, J. P. Zheng, J. Electrochem. Soc. 2017, 164, A2164.
[123] A. Shellikeri, V. Watson, D. Adams, E. E. Kalu, J. A. Read, T. R. Jow, J. S. P. S. Zheng, J. S. P. S. Zheng, J. S. P. S. Zheng, J. Electrochem. Soc. 2017, 164, A3914.
[124] W. Cao, Y. Li, B. Fitch, J. Shih, T. Doung, J. P. Zheng, ECS Trans. 2015, 64, 67.
[125] A. Shellikeri, V. G. Watson, D. L. Adams, E. E. Kalu, J. A. Read, T. R. Jow, J. P. Zheng, ECS Trans. 2017, 77, 293.
[126] W. J. Cao, J. F. Luo, J. Yan, X. J. Chen, W. Brandt, M. Warfield, D. Lewis, S. R. Yturriaga, D. G. Moye, J. P. Zheng, J. Electrochem. Soc. 2017, 164, A93.
[127] W. J. Cao, J. Shih, J. P. Zheng, T. Doung, J. Power Sources 2014, 257, 388.
[128] A. Cappetto, W. J. Cao, J. F. Luo, M. Hagen, D. Adams, A. Shelikeri, K. Xu, J. P. Zheng, J. Power Sources 2017, 359, 205.
[129] J. Boltersdorf, S. A. Delp, J. Yan, B. Cao, J. P. Zheng, T. R. Jow, J. A. Read, J. Power Sources 2018, 373, 20.
[130] M. Hagen, J. Yan, W. J. Cao, X. J. Chen, A. Shellikeri, T. Du, J. A. Read, T. R. Jow, J. P. Zheng, J. Power Sources 2019, 433, 126689.
[131] K. Yao, W. J. Cao, R. Liang, J. P. Zheng, J. Electrochem. Soc. 2017, 164, A1480.
[132] W. J. Cao, M. Greenleaf, Y. X. Li, D. Adams, M. Hagen, T. Doung, J. P. Zheng, J. Power Sources 2015, 280, 600.
[133] B. Xiang, L. Wang, G. Liu, A. M. Minor, J. Electrochem. Soc. 2013, 160, A415.

[134] C. R. Jarvis, M. J. Lain, Y. Gao, M. Yakovleva, J. Power Sources 2005, 146, 331.
[135] M. Marinaro, M. Weinberger, M. Wohlfahrt-mehrens, Electrochim. Acta 2016, 206, 99.
[136] X. Sun, W. Chen, X. Li, J. Wang, H. Hu, G. Liang, Y. Huang, C. Wei, in Sci. Technol. Adv. Appl. Supercapacitors, IntechOpen, 2019, p. 13.
[137] K. W. Nam, S. B. Ma, W. S. Yoon, X. Q. Yang, K. B. Kim, Electrochem. commun. 2009, 11, 1166.
[138] V. Aravindan, Y. S. Lee, S. Madhavi, Adv. Energy Mater. 2017, 7, 1.
[139] T. L. Kulova, A. M. Skundin, J. Solid State Electrochem. 2003, 8, 59.
[140] H. Konno, T. Morishita, C. Wan, T. Kasashima, H. Habazaki, M. Inagaki, Carbon N. Y. 2007, 45, 477.
[141] M. Cai, X. Sun, W. Chen, Z. Qiu, L. Chen, X. Li, J. Wang, Z. Liu, Y. Nie, J. Mater. Sci. 2018, 53, 749.
[142] J. Libich, J. Vondrak, M. Sedlarikova, J. Maca, O. Cech, Surf. Eng. Appl. Electrochem. 2017, 53, 597.
[143] A. Reza, S. W. Chen, R. Rajagopalan, C. Randall, A. R. Aref, S. W. Chen, R. Rajagopalan, C. Randall, Carbon N. Y. 2019, 152, 89.
[144] S. S. Zhang, J. Power Sources 2017, 343, 322.
[145] M.-S. Park, Y. Lim, J.-H. J. J.-H. Kim, Y.-J. Kim, J. Cho, J.-H. J. J.-H. Kim, Adv. Energy Mater. 2011, 1, 1002.
[146] M.-S. Park, Y.-G. Lim, S. M. Hwang, J. H. Kim, J.-S. Kim, S. X. Dou, J. Cho, Y.-J. Kim, ChemSusChem 2014, 7, 3138.
[147] P. Jeżowski, O. Crosnier, E. Deunf, P. Poizot, F. Béguin, T. Brousse, Nat. Mater. 2018, 17, 167.
[148] M.-S. Park, Y.-G. Lim, J.-W. Park, J.-S. Kim, J.-W. Lee, J. H. Kim, S. X. Dou, Y.-J. Kim, J. Phys. Chem. C 2013, 117, 11471.
[149] P. Jeżowski, K. Fic, O. Crosnier, T. Brousse, F. Béguin, Electrochim. Acta 2016, 206, 440.
[150] Y.-G. Lim, D. Kim, J.-M. Lim, J.-S. Kim, J. Yu, Y.-J. Kim, D. Byun, M. Cho, K. Cho, M. Park, J. Mater. Chem. A 2015, 3, 12377.
[151] Y. Zhan, H. Yu, L. Ben, Y. Chen, X. Huang, Electrochim. Acta 2017, 255, 212.
[152] S. R. R. Sivakkumar, A. G. G. Pandolfo, Electrochim. Acta 2012, 65, 280.
[153] G. Gourdin, P. H. Smith, T. Jiang, T. N. Tran, D. Qu, J. Electroanal. Chem. 2013, 688, 103.
[154] M. Yuan, W. Liu, Y. Zhu, Y. Xu, Russ. J. Electrochem. 2014, 50, 1050.
[155] M. Kim, F. Xu, J. H. Lee, C. Jung, S. M. Hong, Q. M. Zhang, C. M. Koo, J. Mater. Chem. A 2014, 2, 10029.
[156] H. Park, M. Kim, F. Xu, C. Jung, S. Man, C. Min, J. Power Sources 2015, 283, 68.
[157] M. G. Scott, J. Electrochem. Soc. 1998, 145, 1506.
[158] T. Tabuchi, H. Yasuda, M. Yamachi, J. Power Sources 2005, 146, 507.
[159] J. Zhao,J. Sun, A. Pei, G. Zhou, K. Yan, Y. Liu, D. Lin, Y. Cui, 2018, 10, 275-281.
[160] Y. Shen, J. Zhang, Y. Pu, H. Wang, B. Wang, J. Qian, Y. Cao, F. Zhong, X. Ai, H. Yang, ACS Energy Lett. 2019, 4, 1717.
[161] D. Liu, F. Du, W. Pan, G. Chen, C. Wang, Y. Wei, Mater. Lett. 2009, 63, 504.
[162] Y. Takeda, J. Yang, N. Imanishi, Solid State Ionics 2002, 152–153, 35.
[163] D. Shanmukaraj, S. Grugeon, S. Laruelle, G. Douglade, J. M. Tarascon, M. Armand, Electrochem. commun. 2010, 12, 1344.

[164] S. Tasaki, N. Ando, M. Nagai, A. Shirakami, K. Matsui, Y. Hato, Lithium Ion Capacitor, 2006, US7733629B2.
[165] S. Tasaki, M. Nagai, N. Ando, Lithium Metal Foil for Battery or Capacitor, 2014, US8685117B2.
[166] M. Mizukami, K. Nansaka, N. Ando, Method for Producing Electric Storage Device, and Electric Storage Device, 2015, US9093228B2.


BASIC CLASSIFICATIONS
LITHIUM ION CAPACITOR
ROLES OF PRE-LITHIATION
PRE-LITHIATION METHODS
Ex-situ electrochemical method (EEC)
In-situ electrochemical method (IEC)
In-situ short circuit method (ISC)
Cathode pre-lithiation method
EC+LIB-type //Pre-lithiated LIB-type
EC-type (+) // Pre-lithiated LIB-type
EC-type (+) // LIB-type)-)
LIB-type (+) // EC-type (-)
Mitigate the initial lithium loss
Enlarge cathode potential variation window
Lower the anode potential
Adjust the optimal potential of anode

TOC

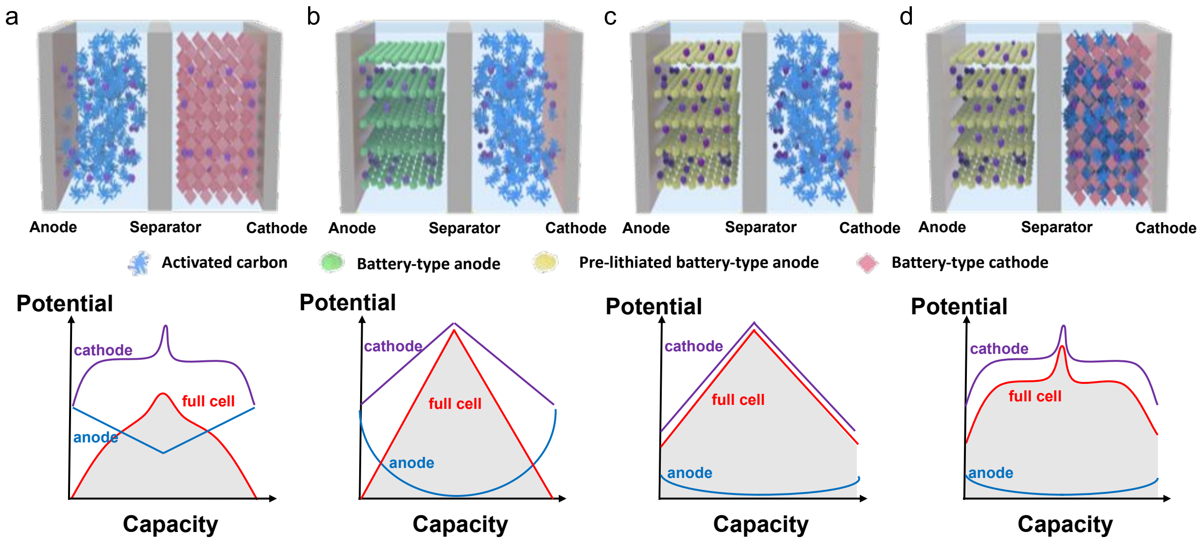


Figure 1. The structures and corresponding potential profiles of four typical energy storage systems commonly termed as “lithium ion capacitors”: (a) Battery-type cathode and capacitive anode; (b) capacitive cathode and battery-type anode; (c)capacitive cathode and pre-lithiated battery-type anode; and (d) hybrid cathode (capacitive and battery-type cathode) and pre-lithiated anode.

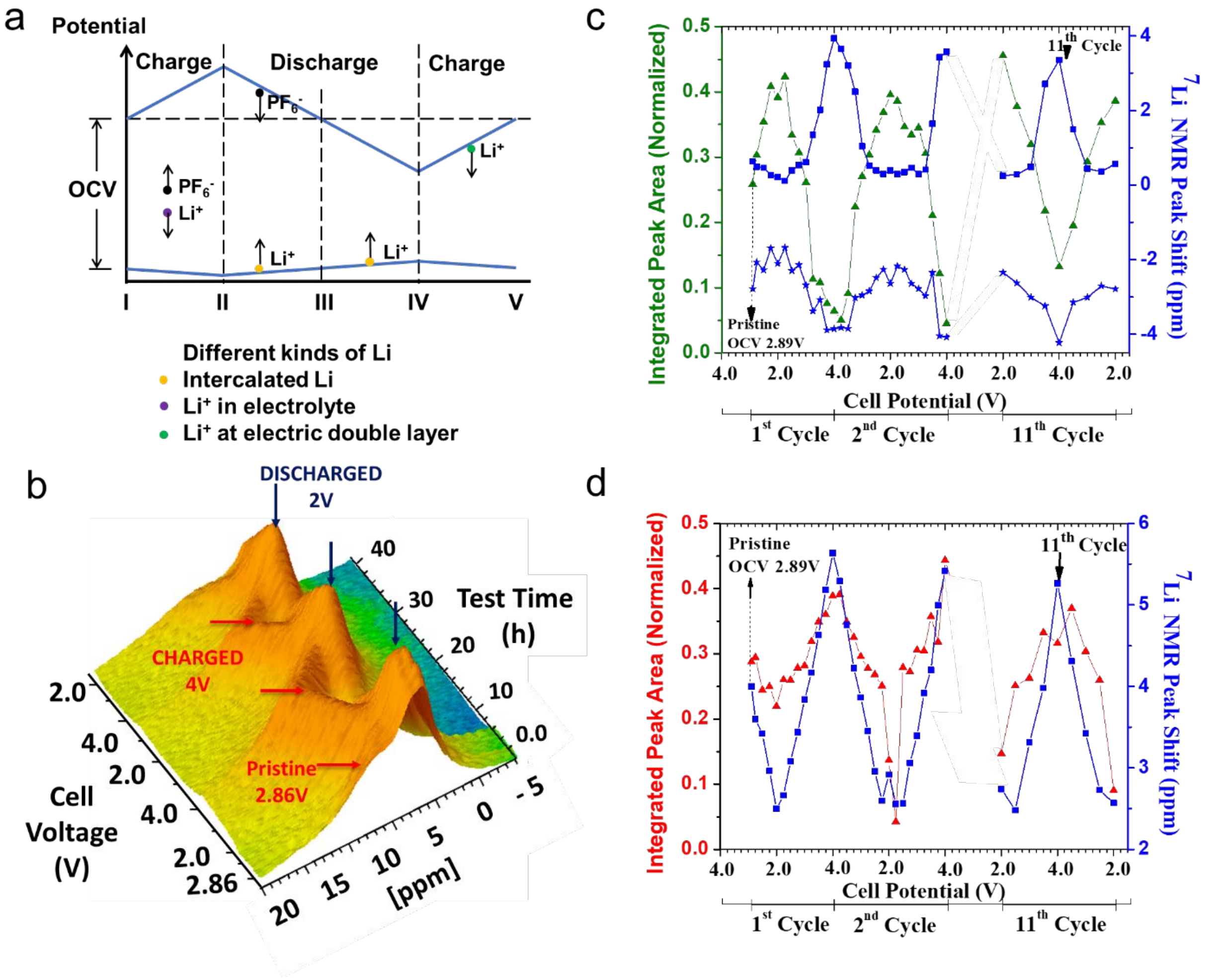


Figure 2. Energy storage mechanisms in lithium ion capacitors. (a) The charge and discharge profiles of the cathode and anode of LICs and the corresponding ion diffusion processes; (b) in-situ NMR spectra of the AC//HC system for several cycles; (c-d) 7Li peak shifts and the integrated shift areas (which are proportional to the local concentration of Li ions) for the double layer and intercalation regions as a function of the depth of charge and discharge during cycle 1,2, and 11. Reproduced with permission from ref. 75. Copyright (2016) American Chemical Society.

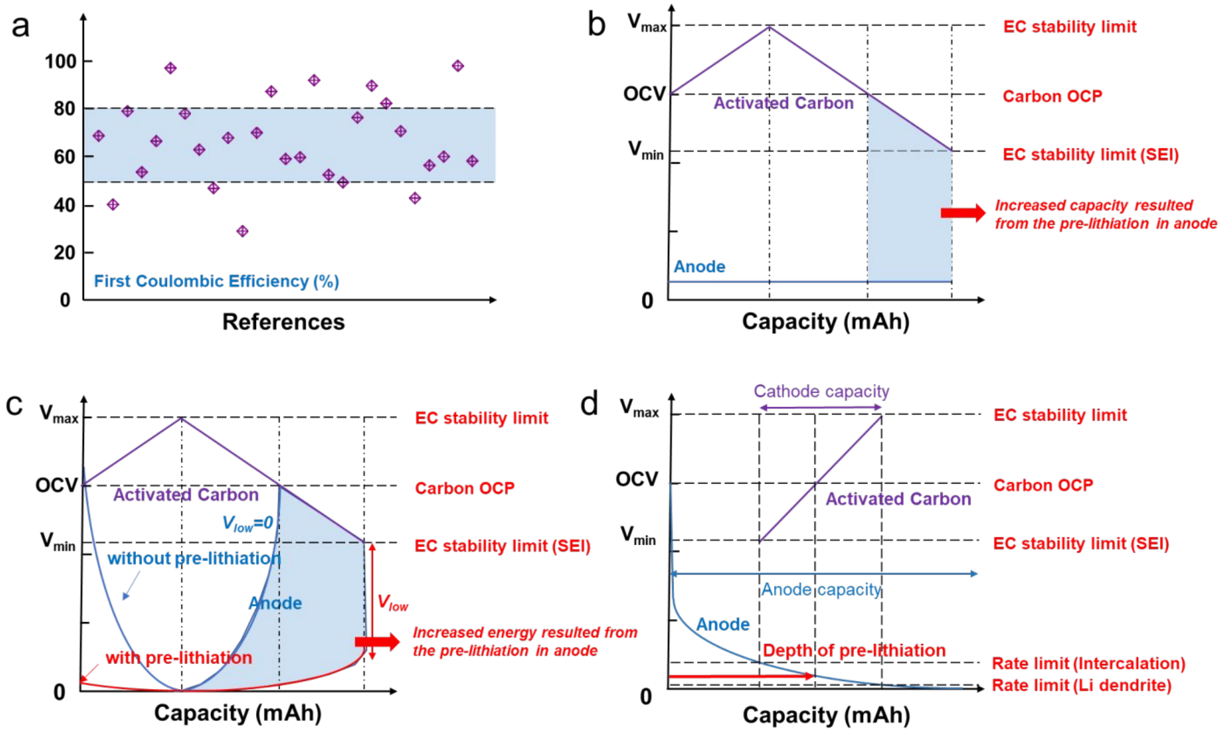


Figure 3. The role of pre-lithiation technologies in LICs. (a) The summary of first coulombic efficiency of typical anode materials with different energy storage mechanism in LICs; (b) the enlarged potential swings of the cathode achieved by pre-lithiation technologies; (c) the decreased potential of the anode achieved by pre-lithiation technologies; (d) the optimal potential range selection for matching the anode and cathode electrodes.

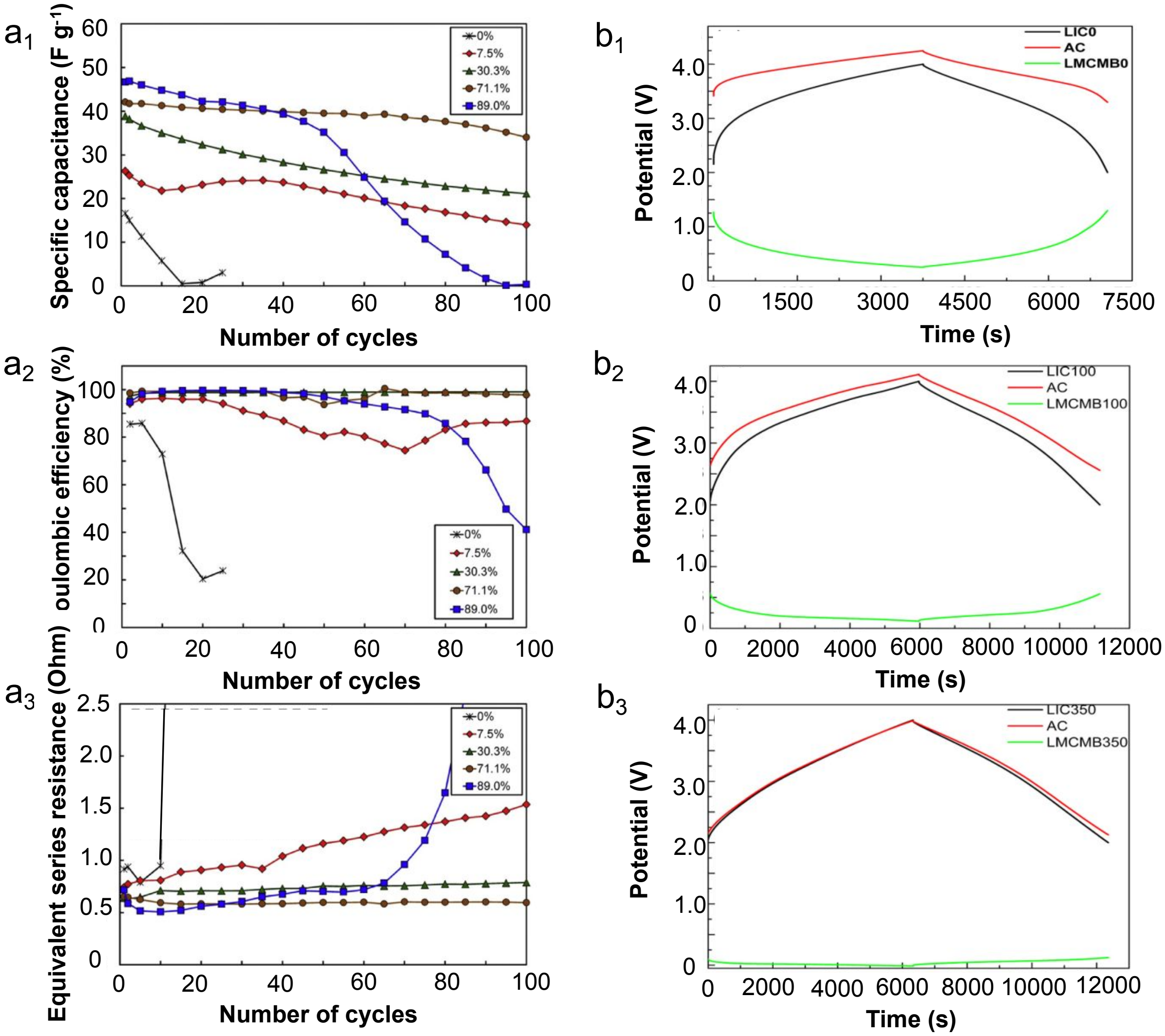


Figure 4. (a) The example of AC//HC system with or without pre-lithiation treatment: (a_1) the effect of pre-lithiation degree to the coulombic efficiency of the system; (a_2) the effect of the pre-lithiation degree to the cycling stability; (a_3) the effect of pre-lithiation degree to the internal resistance. Reproduced from Ref. 117 with permission from Elsevier Ltd. (b) The charge and discharge profiles of AC//LMCMB system with or without pre-lithiation treatment: (b_1) system without pre-lithiation process; (b_2) system with low pre-lithiation degree; (b_3) system with high pre-lithiation degree. Reproduced from Ref. 102 with permission from Elsevier Ltd.

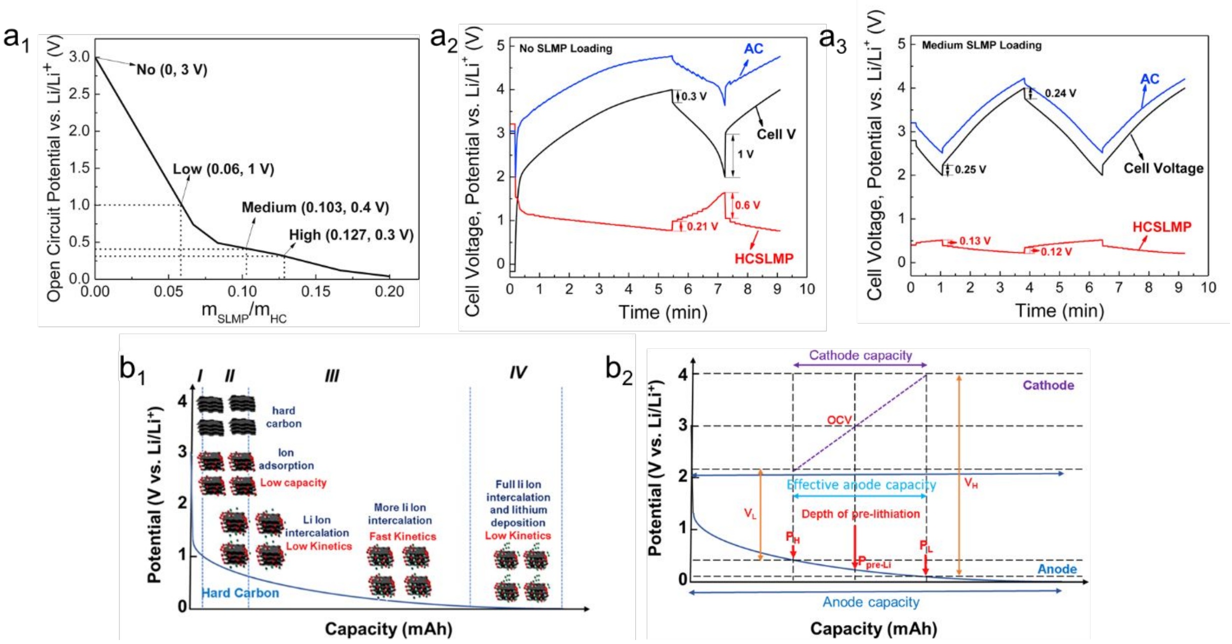


Figure 5. (a) The effect of the pre-lithiation process to the anode potentials in AC//HC system: (a_1) the relationship between the anode potential to the pre-lithiation degree; (a_2) the cathode and anode potential profiles in LIC without pre-lithiation process; (a_3) the cathode and anode potential profiles in LIC with pre-lithiation process. Reproduced from Ref. 117 with permission from Elsevier Ltd. (b) The electrodes matching approach for AC//HC system: (b_1) the reaction mechanisms of HC at different potentials; (b_2) the electrodes matching parameters determination. Reproduced from Ref. 104 with permission from Elsevier Ltd.

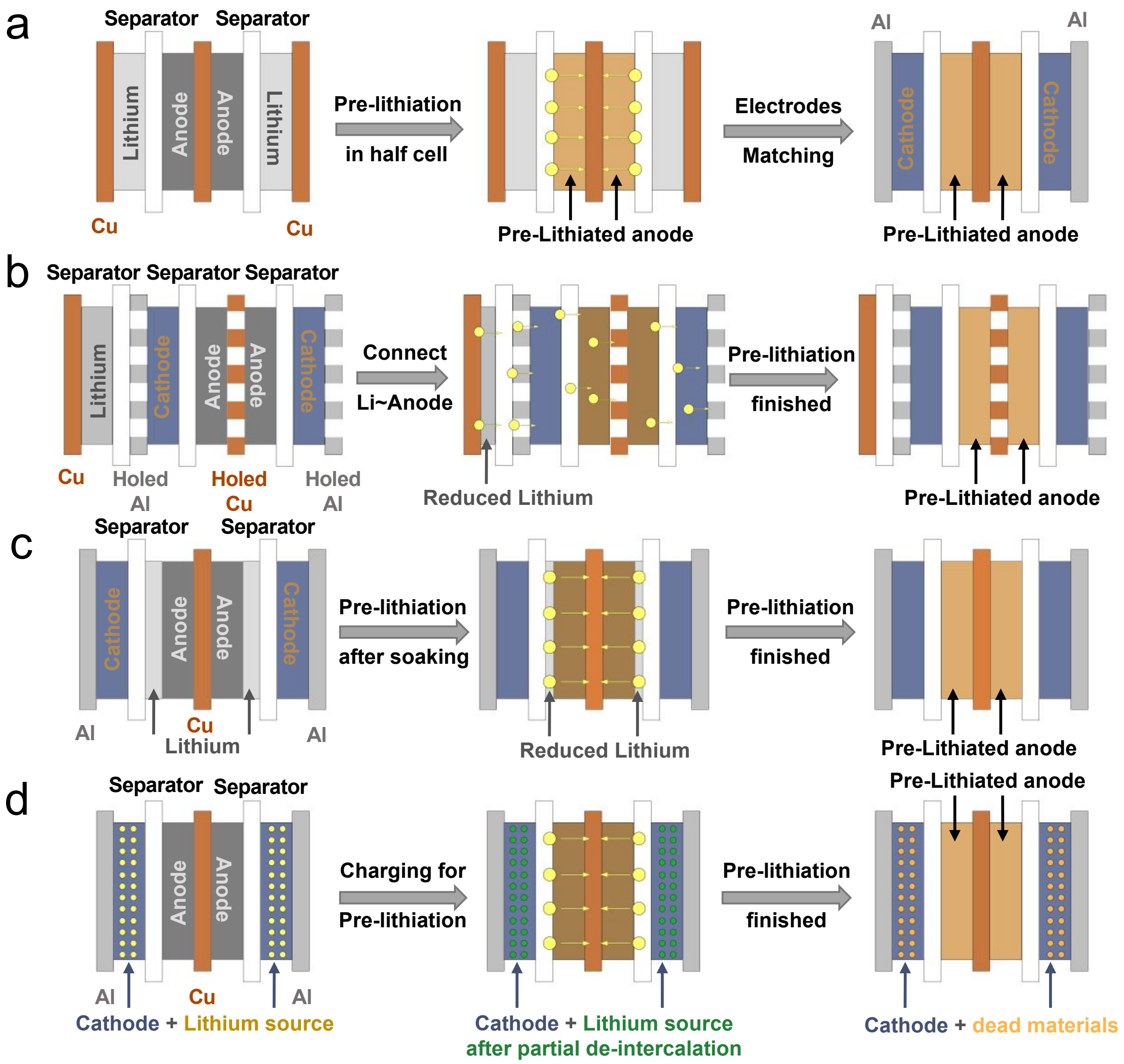


Figure 6. Schematic graphs of four types of typical pre-lithiation methods: (a) ex-situ electrochemical method (EEC); (b) in-situ electrochemical method (IEC); (c) in-situ short circuit method (ISC); and (d) cathode pre-lithiation method.

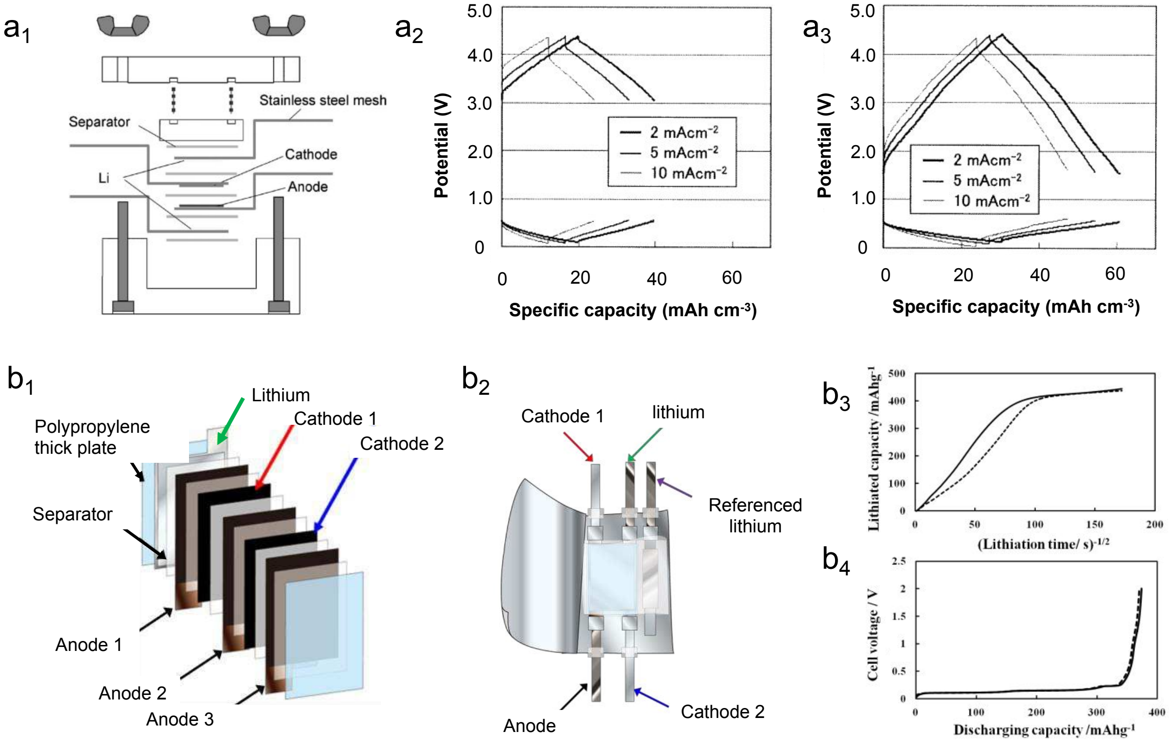


Figure 7. The experimental examples of EEC and IEC method. (a_1) The battery structure for EEC method with four electrodes; the charge and discharge potential profiles (a_2) without pre-lithiation and (a_3) after pre-lithiation. Reproduced from Ref. 105 with permission from IOP Publishing. (b_1) The detailed pouch cell structure and (b_2) assembled pouch cell of IEC; the relationship of capacity (b_3) and (b_4) voltage change with the pre-lithiation capacity. Reproduced from Ref. 120 with permission from IOP Publishing.

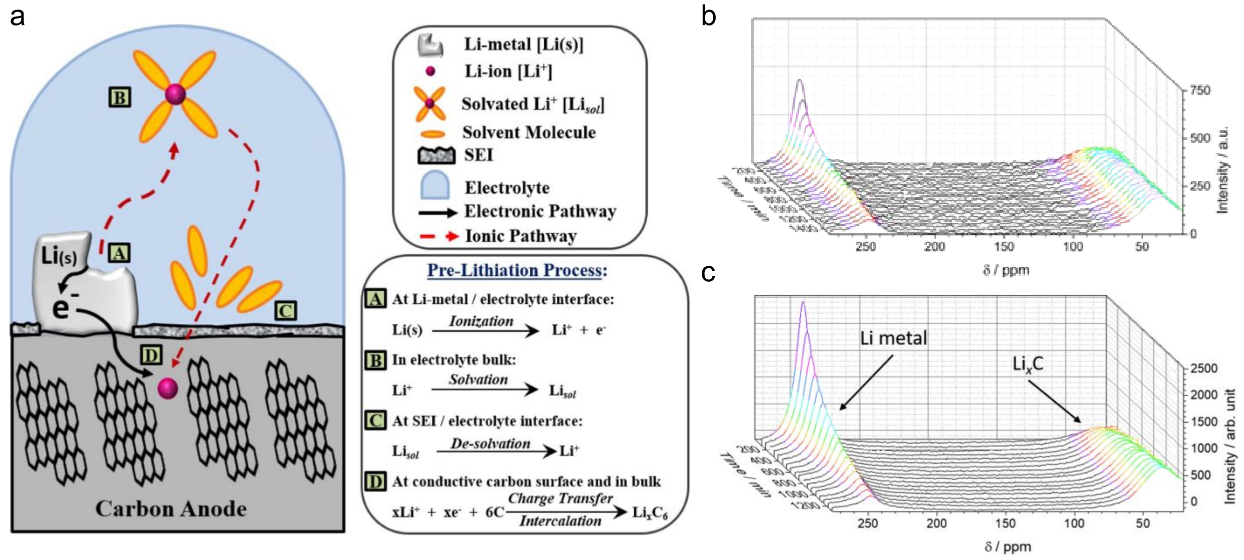


Figure 8. (a) Schematic diagram of the in-situ short circuit (ISC) method. Reproduced from Ref. 123 with permission from IOP Publishing; The NMR spectra of the pre-lithiation of graphite using coated (b) lithium metal powder and (c) lithium metal foil. Reproduced from Ref. 121 with permission from Elsevier Ltd.

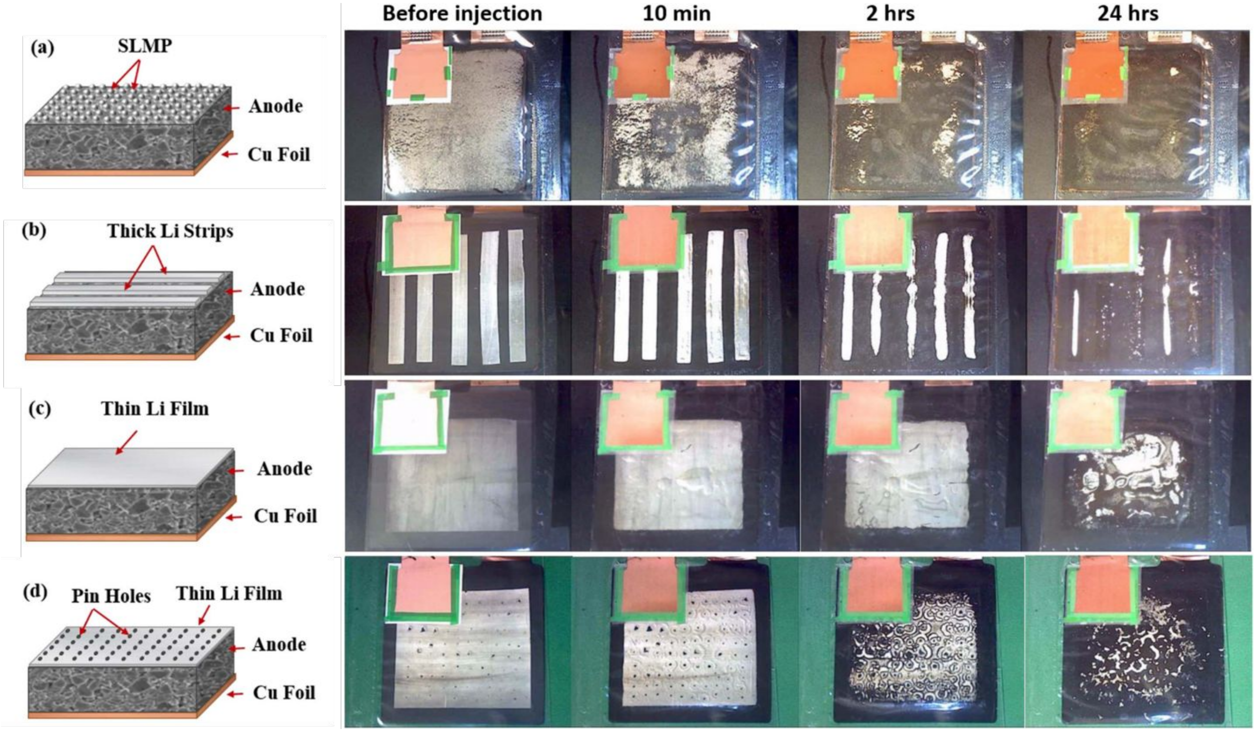


Figure 9. Photos of various lithium sources used in-situ short circuit (ISC) method: (a) SLMP; (b) thick lithium strips; (c) thin lithium film, and (d) thin lithium film with holes. Reproduced from Ref. 123 with permission from IOP Publishing

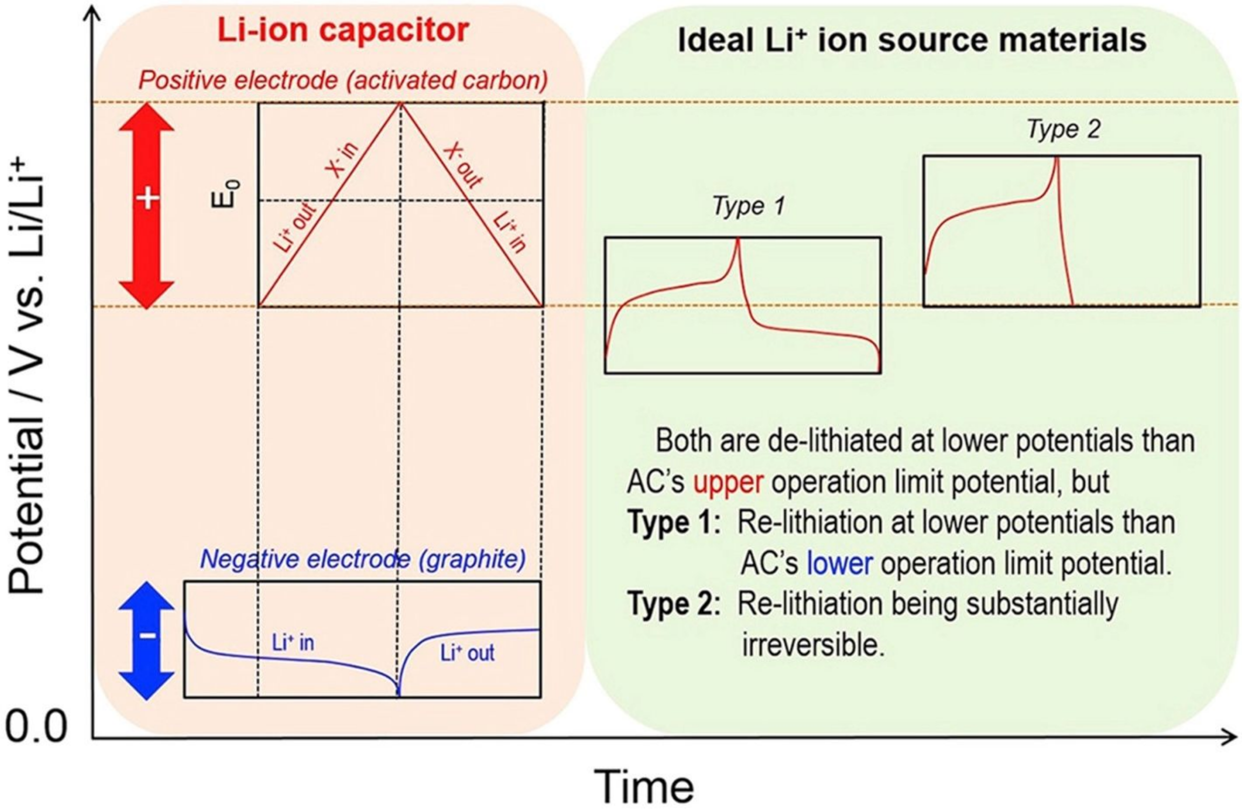


Figure 10. The theoretical requirements of cathode additives for pre-lithiation. Based on the charge and discharge profiles of cathode and anode, the additive in cathode as lithium sources can be divided into two types. Type 1: re-lithiation at lower potentials than AC's lower operation limit potential; type 2: re-lithiation being substantially irreversible. Reproduced from Ref. 144 with permission from Elsevier Ltd.

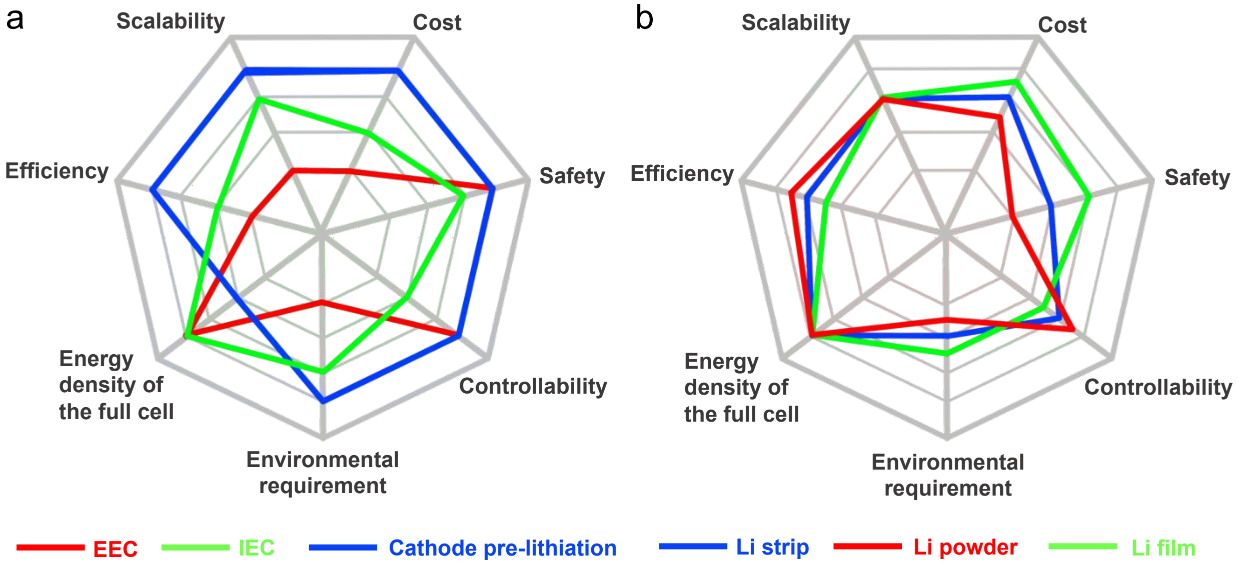


Figure 11. Comparison of the scalability, efficiency, cost, safety, controllability, environmental requirement, and the resulted energy density of the full cell for different types of pre-lithiation methods: (a) IEC and cathode pre-lithiation technologies; (b) comparison of using various lithium sources in the ISC pre-lithiation method.

Table 1. The dominant characteristics for type b,c,d LIC systems including the voltage range, energy density, power density as well as cycling lifespan

Company	Type	Voltage	Energy density	Power density	Cycle life
Nippon Chemi-con Corp.	b	1.4-2.8 V	9.1 Wh L^{-1}	4,700 W L^{-1}	-
Nippon Chemi-con Corp.	b	1.4-2.8 V	13 Wh L^{-1}	3,400 W L^{-1}	-
JM Energy Cooperation	c	2.2-3.8 V	10 Wh kg^{-1} (20 Wh L^{-1})	14,000 W kg^{-1} (27,000 W L^{-1})	1,000,000
TAIYO YUDEN	c	2.2-3.8 V	15 Wh kg^{-1}	-	100,000
Advanced Capacitor Technologies, Inc.	c	2.0-4.0 V	15 Wh kg^{-1}	-	-
NEC Tokin	c	2.2-3.8 V	8 Wh kg^{-1}		
General Capacitor	c	2.2-3.8 V	18 Wh kg^{-1} (32 Wh L^{-1})	8,000 W kg^{-1} (15,000 W L^{-1})	200,000
General Capacitor	d	2.2-3.8 V	45 Wh kg^{-1} (90 Wh L^{-1})	5,000 W kg^{-1} (9,000 W L^{-1})	50,000
JM Energy Cooperation	d	2.2-3.8 V	24 Wh kg^{-1} (40 Wh L^{-1})	4,000 W kg^{-1} (6,000 W L^{-1})	300,000

Table 2. The summary of typical anode materials with different energy storage mechanisms for lithium ion capacitor

Anode Materials	Voltage range (V)	Energy storage mechanism	First discharge capacity (mAh g^{-1})	First charge capacity (mAh g^{-1})	First coulombic efficiency (%)	ref
Nb_2O_5@C	1.0~3.0	intercalation	253	174	68.8	76
Amorphous carbon	0.01~3.0	intercalation	1438	579	40.3	87
3D VN–RGO	0.01~3.0	intercalation	~810	640	79.1	42
ANCS	0.02~3.0	intercalation	2032	1091	53.7	94
Co3ZnC	0.01~3.0	intercalation	1200	800	66.7	95
A-N-GS	0.01~3.0	intercalation	407	395	97.1	96
Li_3VO_4/N-doped Carbon	0.2~3.0	intercalation	529	413	78.1	41
Nb_2CT_x	0.01~3.0	intercalation	650	410	63.1	98
0.1-BNC	0.02~3.0	intercalation	~2400	1130	47.1	99
$BiVO_4$ Nanorods	0.01~3.0	intercalation	1730	1177	68.0	100
Ti_3C_2Tx/CNTs	0.05～3.0	intercalation	1673	489	29.2	77
Nb_4N_5/rGO	0.01~3.0	intercalation	812.5	569.9	70.1	78
HG-TNO-3	0.8~3.0	intercalation	370	323	87.3	79

3D porous TiC	0.005~3.0	intercalation	851	505	59.3	80
$ZnMn_2O_4$-G	0.01~3.0	conversion	1750	1049.5	59.9	81
$MnFe_2O_4$	0.01~3.0	conversion	1237	1138	92.0	82
Mn_3O_4/3D-Graphene	0.01~3.0	conversion	718.4	377.8	52.6	83
SnO_2-rGO	0.002~2.0	conversion	1920	950	49.5	84
CNF@CoNi2S4	0.005~3.0	conversion	~720	~550	76.4	85
MoO_2-CNT	1.1~2.8	conversion	145	130	89.7	86
MoO_2 Nanosheets	1.0~3.0	conversion	243	200	82.3	88
Fe_3O_4–G	0.03~3.0	conversion	1200	850	70.8	89
$TiSb_2$	0.05~1.5	conversion	1140.8	490.5	43.0	90
LTSO/C	0.1~3.0	conversion	470	265.9	56.6	97
CoO-rGO	0.05~3.0	conversion	2780	1674	60.2	91
Si/Cu bilayer fabric	0.01~1.5	alloy	2800	2744	98	92
Sn-C	0.01~3.0	alloy	1850	1081	58.4	93

Table 3. The summary of lithium sources extracted from sacrificial cathode material for lithium ion capacitors

	First charge capacity (mAh g^{-1})	First discharge capacity (mAh g^{-1})	Irreversible capacity (mAh g^{-1})	Charge potential vs Li/Li$^+$	Requirement not met *	Estimated capacity retention based on a practical system	ref
Li_2MoO_3	267	85	182	4.7	(i), (iii)	71.43%	[145]
Li_2RuO_3	231	220	11	4.7	(i), (iii), (iv)	12.67%	[148]
Li_5FeO_4	678	110	568	4.7	(i), (ii)	89.78%	[146]
$Li_{0.65}Ni_{1.35}O_2$	120	20	100	4.2	(iii)	57.47%	[149]
Li_6CoO_4	~500	~100	400	4.3	(iii)	85.47%	[150]
Li_2CuO_2	342	31	331	4	(iii)	82.67%	[144]
Li_2S	~600	~200	400	4	(ii), (iii)	85.47%	[151]
Li_2DHBN	365	~0	365	<3.5	(iii)	84.16	[147]

* (i) the lithium metal sources are replaced by the lithium compounds sources, which alleviates the safety concern for pre-lithiation; (ii) the lithium sources are added into cathode directly when preparing electrode, which is technologically feasible and needs minimum modification of the processing line; (iii) the pre-lithiation is conducted based on a moderate electrochemical process, which can form a stable SEI.

Table 4. The detailed characterizations comparisons of typical pre-lithiation method for lithium ion capacitors

Characteristics	**EEC**	**IEC**	**ISC**			**Cathode pre-lithiation method**
			SLMP	**Lithium film**	**Lithium strip**	
Scalability	-The complex two-step process enables no potential for up-scaling	-This method is easy for practical application by pre-set the lithium when fabricating the cell	-The SLMP is easy to be coated onto the anode for practical application.	-The lithium film is capable to coat onto the anode directly	-The lithium strip is still possible scalable by coating lithium stripe onto the anode	-It is quite easy to achieve scalability by add the lithium source into cathode
Cost	-Two-step process inevitably brings extra expenditure	-The usage of holed current collector is of extremely high price for practical production	-The SLMP is of extremely high price for practical application	-The price of lithium film is between the SLMP and lithium strip, but it goes to be extremely high ultrathin lithium foam	-The price of lithium strip is low for practical application	-The cost is determined by the price of lithium source. There is still no ideal lithium sources candidate for evaluation
Safety	-All the procedures must be finished in glove box with excellent safety	-Only one piece of lithium foil is used when fabricating the cell with good safety	-The SLMP will bring severe safety issue due to its small particle size and high specific surface area	-The stability of lithium film is between the SLMP and lithium strip	-The stability of lithium strip is pretty good when operating dry room	-The safety is better than EES, IEC and ISC, because there is no metal lithium exist
Controllability	-The pre-lithiation level is well controlled by potential or capacity for the anode with or without discharge plateau respectively	-It is not accurate the control the weight of pre-set lithium into the cell, because the lithium distributions are not uniform due to the various distance between the anode and lithium source	-Due to the small particle size, it is convenient to control the pre-lithiation level by adjusting the usage of SLMP.	The pre-lithiation is easy to control by adjusting area of the lithium film and the process can be also controlled by punching the holes on the lithium film	-The lithium strip is relatively difficult to control accurately due to its thickness	-The controllability is pretty good by adjusting the weight of lithium source into the cathode when preparing the cathode electrodes
Condition requirements	-The glove box is necessary due to the re-assembling process	-The dry room is necessary for cell fabrication due to the usage of metal lithium	-The dry room is necessary for coating the SLMP onto the anode and cell fabrications	-The dry room is necessary for coating the lithium film onto the anode and cell fabrications	-The dry room is necessary for coating the lithium strip onto the anode and cell fabrications	-There are no additional condition requirements.
Efficiency	-The efficiency is extremely low due to the re-assembling process	-The efficiency is relatively low due to the long time for ion diffusion	-The efficiency is pretty good because the coating of SLMP can be controlled automotive and the pre-lithiation kinetics is very fast	-The efficiency is still good and the reaction kinetics between anode and lithium strip is fast due to large contact surface area	-The efficiency is relatively low due to the thickness of lithium strip, but it is still higher than IEC due to the short ion diffusion distance	-The efficiency is pretty good because it can be controlled by out circuit by adjusting the current density

Energy density of the full cell	-Metal lithium as lithium sources with no extra weight	-Metal lithium as lithium sources with no extra weight	-Metal lithium as lithium sources with no extra weight	-Metal lithium as lithium sources with no extra weight	-Metal lithium as lithium sources with no extra weight	-The energy density will be sacrificed inevitably due to the dead material after pre-lithiation