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Pre-Lithiation Strategies and Energy Density Theory of Lithium-Ion and Beyond Lithium-Ion Batteries

Jim P. Zheng,[1,z] Petru Andrei,[2] Liming Jin,[3] Junsheng Zheng,[3] and Cunman Zhang[3]

[1] *Department of Electrical Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States of America*
[2] *Department of Electrical and Computer Engineering and Aero-Propulsion, Mechatronics and Energy Center, Florida A&M University and Florida State University, Tallahassee FL 32310, United States of America*
[3] *Clean Energy Automotive Engineering Center and School of Automotive Studies, Tongji University, Shanghai 201804, People’s Republic of China*

Pre-lithiation is the most effective method to overcome the initial capacity loss of high-capacity electrodes and has the potential to be used in beyond-conventional lithium-ion batteries. In this article we focus on two types of pre-lithiation: the first type can be applied to batteries in which the cathode has been fully lithiated but the anode has a large initial capacity loss, such as batteries made with lithium metal oxide cathode and silicon-carbon anode. The second type can be applied to batteries in which both electrodes are initially lithium-free and suffer a loss of lithium during the initial cycles, such as batteries made with sulfurized-polyacrylonitrile cathode and silicon-carbon anode. We describe the pre-lithiation procedures and electrode potential profiles during pre-lithiation corresponding to different pre-lithiation sources for both types of pre-lithiation. We also derive formulas for the theoretical specific energy and energy density that are based entirely on measurable parameters such as specific capacities, porosities, mass densities of two electrodes and extra lithium source, Coulombic efficiencies of electrodes, and the voltage of the cell. These formulas can be applied to different pre-lithiation sources to predict the specific energy of conventional and beyond-conventional lithium-ion batteries as a function of the type of pre-lithiation.
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List of symbols

c_a	Specific capacity of anode, mAh/g
c_c	Specific capacity of cathode, mAh/g
c_{Li}	Specific capacity of Li metal, 3,860 mAh g^{-1}
c_{ls}	Specific capacity of pre-lithiation source, mAh g^{-1}
c_{ls-eff}	Effective specific capacity of pre-lithiation source, mAh g^{-1}
E	Specific energy or energy density, Wh/kg or Wh/L
L_a	Thickness of anode, cm
L_c	Thickness of cathode, cm
L_{ls}	Thickness of pre-lithiation source, cm
M_1	Total mass of electrodes, extra Li source, and electrolyte in electrodes, g
M_2	Total mass of current collectors, separator paper, electrolyte in separator, and package materials, g
m_a	Mass of anode, g
m_c	Mass of cathode, g
m_e	Mass of electrolyte, g
m_{e-a}	Mass of electrolyte in anode, g
m_{e-c}	Mass of electrolyte in cathode, g
m_{e-ls}	Mass of electrolyte in pre-lithiation source, g
m_{Li}	Weight of Li in pre-lithiation source, g
m_{ls}	Weight of pre-lithiation source, g
m_{mls}	Weight of extra Li source that left in battery cell after pre-lithiation, g
q_0	Reversible capacity, mAh
q_{ira}	Irreversible capacity of anode, mAh
q_{irc}	Irreversible capacity of cathode, mAh
U_1	Total volume of cathode, anode, and extra Li source, cm^3
U_2	Total volume of current collectors, separator paper, and package materials, cm^3
V	Average cell voltage, V

Greek Symbols

α	Weight ratio of the vaporized part to the pre-lithiation source
β_a	Porosity of anode, %
β_c	Porosity of cathode, %
β_{ls}	Porosity of pre-lithiation source, %
ε	Coulombic efficiency, %
ε_a	Coulombic efficiency of anode, %
ε_c	Coulombic efficiency of cathode, %
ρ_a	Mass density of anode, g/cm^3
ρ_c	Mass density of cathode, g/cm^3
ρ_e	Mass density of electrolyte, g/cm^3
ρ_{ls}	Mass density of pre-lithiation source, g/cm^3
σ	Gravimetric package efficiency, %
σ'	Volumetric package efficiency, %

Since SONY’s commercialized the first lithium (Li)-ion battery (LIB) in 1990, people have made great efforts to improve the batteries and their number of applications has increased significantly. As of today, commercial LIBs are mainly made using oxide-type (layered, spinel, and polyanion families)[1] crystal structure cathodes and graphite anodes. By improving the electrode material structure, the electrolyte, the electrode fabrication process, and the packaging technology, the average annual growth rate of gravimetric energy density (also called specific energy) and volumetric energy density of LIBs was between 3%−5%.[2] Despite this growth, current LIBs are still unable to meet the growing demands in electric vehicles and portable electronic devices. Ambitious targets have been set by governments of several industrial countries to reach specific energies of 500 Wh kg^{-1} in the near future.[3,4] One way to reach such specific energies is to use metallic Li and silicon-carbon (Si–C) as the main material for the anode electrode. Unfortunately, the use of Li metal anodes has negative effects on performance and safety, such as dendrite formation and surface passivation.[5,6] In addition, Si–C anodes have large irreversible capacity loss and low Coulombic efficiency during the initial cycles, and large volume variation during charge and discharge.[7–9] These negative effects need to be addressed to make batteries with Si–C anodes commercially available. The pre-lithiation of Si–C anodes using extra Li sources with high specific capacity is the most effective way to

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[z] E-mail: jzheng@buffalo.edu

compensate the irreversible capacity loss and increase the energy density of LIBs. In addition, pre-lithiation opens the door for making a wider range of cathodes, that are not fully lithiated or even Li-free (for instance, cathodes that use sulfur or sulfur components).[10–12]

Pre-lithiation is a technique that introduces extra Li-ions into a battery, prior to the first use of the battery. Different pre-lithiation methods, Li-source materials, and their respective advantages and disadvantages have been already discussed in the literature, and the effectiveness, scalability, controllability, and safety of these methods have been evaluated.[13–18] We have derived formulas for the specific energy and energy density for simple LIB systems,[19] in which the cathode is fully lithiated, the anode has a large initial capacity loss (ICL) and needs to be pre-lithiated, and by assuming that the weight of the battery does not change during pre-lithiation. In this paper we derive specific energy and energy density formulas that can be applied to a wider range of LIB systems and present different strategies that can be used for pre-lithiation.

According to whether the electrodes of the battery contain Li-ion or not (before pre-lithiation), we divide pre-lithiation in two categories: 1) pre-lithiation for batteries in which the cathode has been pre-doped with Li (such as Li metal oxides) and the main function of pre-lithiation is to compensate for the ICL of the anode (called *compensatory pre-lithiation*); and 2) pre-lithiation for beyond-conventional LIBs, in which the electrode material does not contain Li or does not have enough Li to match the electrode capacity (called *source-based pre-lithiation*). These two cases are analyzed separately in the next two sections. In each case, we will describe the method of pre-lithiation, compute the specific energy and energy density, and present practical examples in which these two methods can be used.

Method of Compensatory Pre-Lithiation

Generally, the cathodes of commercial LIBs are made of layered transition metal oxides (e.g., $LiCoO_2$, $Li(NiMnCo)O_2$, etc.) or olivine type (e.g., $LiFePO_4$) materials, which are coupled with high specific capacity anodes, such as Si–C composites in a Li-containing organic electrolyte. Different ways of placing the extra Li sources, have been discussed comparatively previously.[17,18] In general, the extra Li source can be placed at the anode and/or at the cathode as a Li salt, or using a third Li metal electrode. Figure 1 illustrates the potentials of the cathode and anode as a function of the capacity during pre-lithiation and the first cycle, for different types of extra Li sources placed at different locations inside the battery. In this figure, it is assumed that the ICL of the cathode is negligible, so the extra Li source is introduced to compensate only for the ICL of the anode. Therefore, there is no Li-ion exchange between the cathode material and the extra Li source.

Figure 1a shows the electrode potentials when the extra Li source is Li metal. Depending on the way in which the extra Li source is introduced in the anode, we distinguish two cases. The first case is to place the Li metal in direct contact to the anode. When the electrolyte is introduced in the cell, the pre-lithiation occurs through a closed loop of extra Li source–anode–electrolyte.[19] After the pre-lithiation is completed, the battery cell can be cycled normally, as shown in Fig. 1a. The second case to introduce the Li source in the anode is to use a third electrode made of Li metal, which counts as the extra Li source; in this case the Li-ions will be transferred to anode through an external discharge process between the extra Li source and the anode. The advantage using a third electrode is that the pre-lithiation rate and the degree of pre-lithiation can be controlled externally; however, the disadvantage is that all current collectors must be made with densely packed pinholes to allow the Li-ions to pass through during pre-lithiation.

Figures 1b and 1c show the potential-capacity characteristics when the Li salt is placed on the cathode. Depending on whether the potential of the extra Li sources is smaller or larger than the potential of the cathode, we distinguish again two cases. In both cases, the pre-lithiation will be completed during the 1st charge process. The capacity of extra Li source equals the capacity of ICL of the anode (q_{ira}) regardless of whether the extra Li source is placed at the anode or the cathode.

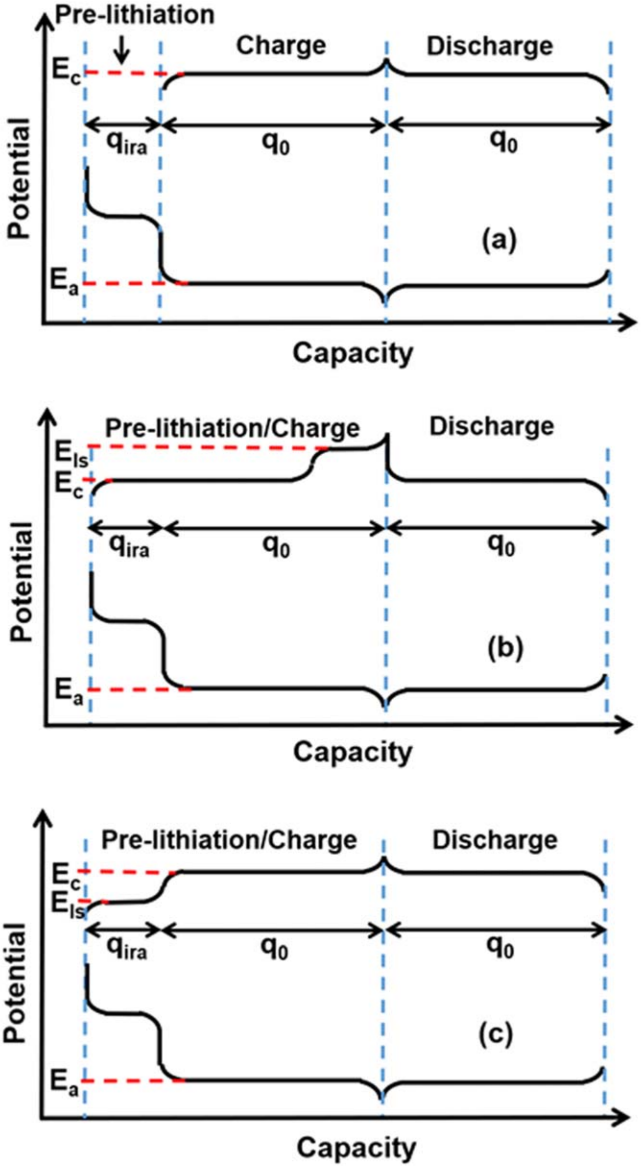

Figure 1. Cathode and anode potentials during pre-lithiation and initial charge-discharge cycle when the extra Li source is (a) Li metal at anode, (b) Li salt at cathode, in which the salt potential is higher than that of the cathode, and (c) Li salt at cathode, in which the salt potential is lower than that of the cathode. E_c, E_a, and E_{ls} are the potentials of cathode, anode, and extra Li source; q_0 and q_{ira} are reversible capacity of electrodes and irreversible capacity of anode, respectively.

Specific energy without pre-lithiation.—To maximize the theoretical specific energy in batteries that do not use extra Li sources, the capacity of the cathode should equal the total capacity of the anode including reversible and irreversible capacities. Some Li-ions from the cathode will be consumed to compensate the ICL of the anode. Therefore, by taking into consideration the ICL of the anode, the capacity ratio between anode and cathode, also called the Coulombic efficiency of the anode, should be:

$$\varepsilon = \frac{q_0}{q_0 + q_{ira}} = \frac{m_a c_a}{m_c c_c} \qquad [1]$$

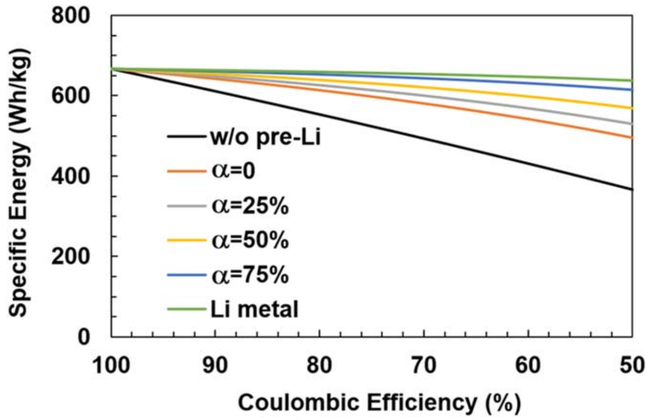

Figure 2. Specific energy as a function of the Coulombic efficiency of the anode with different weight loss from extra Li source after pre-lithiation, calculated using Eq. 7. w/o Pre-Li is the base line for a LIB without pre-lithiation. The battery has an NMC cathode (220 mAh g^{-1}) and a Si-C anode (1,000 mAh g^{-1}) with an imperfect Coulombic efficiency. The average cell voltage is 3.7 V. The specific capacity of the extra Li salt is 516 mAh g^{-1} (which is equivalent to the maximum possible specific capacity of Li formate, $LiHCO_2$).

where, q_0 and q_{ira} are the reversible and irreversible capacities of the anode, respectively; m_c and m_a are masses of the cathode and anode active materials, respectively; and c_c and c_a are the reversible specific capacities of the cathode and anode active materials, respectively. The specific energy is:

$$E_1 = \frac{m_a c_a V}{m_a + m_c} = \frac{V}{\frac{1}{c_a} + \frac{1}{\varepsilon c_c}} \qquad [2]$$

where V is the average voltage of the battery cell, which is determined by the potential difference between the cathode and anode. As an example, let's take the case of a LIB made with a Si–C anode ($c_a = 1{,}000$ mAh g^{-1}) and a $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC) cathode ($c_c = 220$ mAh g^{-1}),[20] which has an average cell voltage of 3.7 V. If we assume that the Coulombic efficiency of the anode is $\varepsilon = 70\%$ then, according to the Eq. 2, the specific energy based on the weight of two electrodes is $E_1 = 494$ Wh kg^{-1}.

Specific energy with pre-lithiation and no mass loss.—Previously,[21] we have developed a formula for the specific energy of LIBs with pre-lithiation, in which we assumed that the weight of the LIB does not change during pre-lithiation. The cathode and anode have the same capacity and the extra Li source is used to provide the Li-ions for ICL, such that:

$$q_0 = m_c c_c = m_a c_a \qquad [3]$$

The theoretical maximum specific energy is:[21]

$$E_2 = \frac{V}{\frac{1}{c_a} + \frac{1}{c_c} + \frac{1}{\frac{1-\varepsilon}{\varepsilon c_{ls}}}} \qquad [4]$$

where c_{ls} is the specific capacity of the extra Li source. By using the same electrodes and Coulombic efficiently (hence, the same ICL) as in the previous example, the specific energy becomes equal to $E_2 = 654$ Wh kg^{-1} when the extra Li source is Li metal ($c_{ls} = 3{,}860$ mAh g^{-1}). One can see that the specific energy was significantly improved by using the pre-lithiation.

Specific energy with pre-lithiation and mass change.—In deriving Eq. 4, we assumed that the mass of the battery remains unchanged during pre-lithiation, which is true for some of the existing extra Li source materials, including Li metal. However, the molecular structure of many Li-rich salts that can be used as extra Li sources decomposes during pre-lithiation and results in gas release (the advantages of using Li salts have been described by a number of authors).[22–30] When such Li salts are used as extra Li sources, the consumption of the salts can be divided into three components: 1) some Li-ions in the Li salt lithiate the anode or cathode during the pre-lithiation process; 2) part of the Li salt becomes gas after decomposition and is released from the battery; and 3) the rest of the Li salt becomes dead material. If the weight ratio of the vaporized part of the salt to the initial Li salt is α, then the weight of the Li salt left in the battery cell after the completion of pre-lithiation is:

$$m_{mls} = (1 - \alpha) m_{ls} \qquad [5]$$

where m_{ls} is the weight of Li salt before pre-lithiation. It can be shown that the maximum weight ratio $\alpha_{\max} \leqslant 1 - c_{ls}/c_{Li}$ for any given extra Li source, where $c_{Li} = 3{,}860$ mAh g^{-1} is the specific capacity of Li metal. The actual weight ratio can be determined by measuring the battery weight change before and after pre-lithiation.

Since the extra Li source is used to compensate for the ICL of the anode, we can write:

$$m_{ls} c_{ls} = q_{ira} = \frac{1-\varepsilon}{\varepsilon} m_a c_a \qquad [6]$$

The specific energy is:

$$\begin{aligned} E_3 &= \frac{m_a c_a V}{m_a + m_c + m_{mls}} = \frac{V}{\frac{1}{c_a} + \frac{1}{c_c} + (1-\alpha)\frac{1-\varepsilon}{\varepsilon c_{ls}}} \\ &= \frac{V}{\frac{1}{c_a} + \frac{1}{c_c} + \frac{1-\varepsilon}{\varepsilon c_{ls-eff}}} \end{aligned} \qquad [7]$$

where $c_{ls-eff} = c_{ls}/(1-\alpha)$ is the effective specific capacity of the extra Li source. Equation 7 is similar with Eq. 4, however the specific capacity of the extra Li source is replaced with the effective specific capacity of extra Li source. If there is no gas evolution during pre-lithiation ($\alpha = 0$), then the Eq. 7 will be identical to Eq. 4. In the same time, if all the substances other than the Li-ions in the extra Li source are released from the battery after pre-lithiation in the form of gas, then $c_{ls-eff} = c_{Li}$ and the maximum specific energy can be obtained as:

$$E_{3-\max} = \frac{V}{\frac{1}{c_a} + \frac{1}{c_c} + \frac{1-\varepsilon}{\varepsilon c_{Li}}} \qquad [8]$$

To maximize the energy density, the extra Li source (Li salt) used in the cathode should result in minimal or no dead residue products during pre-lithiation. In addition to maximizing the specific energy, considering battery manufacturing and other battery characteristics, the ideal Li salts should satisfy following conditions: 1) they should be stable in the air; 2) the potential for de-lithiation at cathode should be lower than the potential of the decomposition of the electrolyte; 3) the decomposition products from the Li salt should not be corrosive to the materials in LIBs; and 4) the Li salt should be soluble in solvents. In addition, it is preferred that no conductive additives be added in the extra Li source once the Li salt is dissolved in the electrolyte and is desired to be able to place the Li salts either at the anode or at the cathode. Some potential Li salts that can be used as extra Li sources are listed in the Appendix (Table A·I).

Figure 2 shows the specific energy of LIBs as a function of the Coulombic efficiency of the anode for different weight ratios α. In these calculations, we used $c_a = 1{,}000$ mAh g^{-1}, $c_c = 220$ mAh g^{-1}, $V = 3.7$ V, and $c_{ls} = 516$ mAh g^{-1} (which is equivalent to the maximum possible specific capacity of Li formate ($LiHCO_2$), see Table A·I in the Appendix). It can be seen that the specific energy can be increased significantly by using pre-lithiation. This increase is

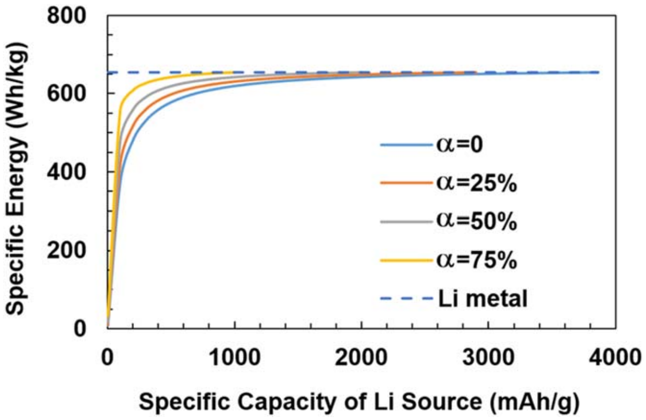

Figure 3. Specific energy as a function of specific capacity of extra Li sources for different weight losses (α) from the extra Li source after pre-lithiation, calculated using Eq. 7.

higher when the weight proportion of the extra Li source that is gasified is larger. In these simulations, we used the theoretical specific capacity of $LiHCO_2$, however, the practical capacity of the lithium salt can be slightly different because it depends on other factors such as the decomposition potential of the Li salt, the process of pre-lithiation, the conductive network surrounding the Li salt, and others.

Figure 3 shows the specific energy as a function of the specific capacity of the extra Li source in cells having the same anode, cathode, cell voltage, and a Coulombic efficiency of $\varepsilon = 70\%$, for different weight losses α ranging from 0 to 75%. The maximum specific capacity is limited by $c_{ls} = (1 - \alpha)c_{Li}$. It can be seen that the specific energy does not dependent only on the specific capacity of the extra Li source but also on the weight ratio factor (α), especially when Li salts with low specific capacity are used. Using the same parameters as in Fig. 2, the maximum specific energy is $E_{3-\max} = 654$ Wh kg^{-1} at $\varepsilon = 70\%$.

Specific energy considering the electrode porosity and cell packaging.—The above estimations of the specific energy are based on the total mass of solid electrodes and extra Li sources, but exclude other materials like electrolyte, separator, current collector, and package materials. The obvious advantage for considering only the mass of the solid electrodes is that the equations for specific energy are simple and one can easily observe the impact of pre-lithiation on the specific energy. However, since practical LIBs include additional materials that are necessary for the assembling of the battery, in this section we reevaluate the specific energy by including all these materials in the calculations.

Assuming that the entire pore volume of the cathode, anode, and extra Li source materials is filled with electrolyte, the total mass of the electrolyte (m_e) per unit area of the cell can be expressed as:

$$m_e = m_{e-c} + m_{e-a} + m_{e-ls} = L_c\beta_c\rho_e + L_a\beta_a\rho_e + L_{ls}\beta_{ls}\rho_e \qquad [9]$$

where m_{e-c}, m_{e-a} and m_{e-ls} are the mass of the electrolyte in the cathode, anode, and extra Li source, respectively; L_c, L_a, and L_{ls} are the thicknesses of the cathode, anode, and extra Li source, respectively; β_c, β_a, and β_{ls} are porosities of the cathode, anode, and extra Li source respectively, which are equal to the volume fraction of the pores in the electrodes and extra Li source; ρ_e is the mass density of the electrolyte. The masses of the solid cathode, anode, and extra Li source layer per unit area can be expressed as:

$$m_a = L_a(1 - \beta_a)\rho_a \qquad [10]$$

$$m_c = L_c(1 - \beta)\rho_c \qquad [11]$$

$$m_{mls} = L_{ls}(1 - \alpha)(1 - \beta_{ls})\rho_{ls} \qquad [12]$$

where ρ_a, ρ_c, and ρ_{ls} are mass densities of the anode, cathode, and extra Li source, respectively, which are determined by the intrinsic properties of active materials, binder, and conductive additives.

Combining Eqs. 9–12, the specific energy (E_4) based on the total mass of cathode, anode, extra Li source and electrolyte, can be obtained as:

$$\begin{aligned} E_4 &= \frac{m_a c_a V}{m_a + m_c + m_{mls} + m_e} \\ &= \frac{V}{\left(1 + \frac{\beta_a\rho_e}{(1 - \beta_a)\rho_a}\right)\frac{1}{c_a} + \left(1 + \frac{\beta_c\rho_e}{(1 - \beta_c)\rho_c}\right)\frac{1}{c_c} + \left(1 + \frac{\beta_{ls}\rho_e}{(1 - \beta_{ls})\rho_{ls}}\right)\frac{1 - \varepsilon}{\varepsilon}\frac{1 - \alpha}{c_{ls}}} \\ &= \frac{V}{(1 + P_a)\frac{1}{c_a} + (1 + P_c)\frac{1}{c_c} + (1 + P_{ls})\frac{1 - \varepsilon}{\varepsilon c_{ls-eff}}} \end{aligned} \qquad [13]$$

where $P_i = \beta_i\rho_i/[(1 - \beta_i)\rho_i]$ ($i = a,\ c,\ ls$) are unitless parameters that depend on the porosity and mass densities of the anode, cathode, and extra Li source. Notice that Eq. 13 is identical with Eq. 7 if the specific capacities c_i are replaced by $c_i/(1 + P_i)$. When porosities $\beta_i = 0$, parameters $P_i = 0$ and no electrolyte is present in the electrodes Eq. 13 is identical to Eq. 7. There are two special cases worth mentioning, namely: (1) when the over-weight cathode is used as the extra Li source, then $\beta_{ls} = \beta_c$, $\rho_{ls} = \rho_c$, $c_{ls} = c_c$, and $\alpha = 0$; and (2) when a Li metal is used as the extra Li source, then $P_{ls} = 0$ and $\alpha = 0$.

As a completely packaged LIB cell, in addition to the electrodes and electrolyte, the weights of other materials must also be accounted for. These weights come from separators soaked with electrolyte, current collectors, conducting additives and binders in electrodes, and package materials. Due to the uncertainty of the relative ratio of the weight of the above individual materials to the electrode materials, which further depends on the shape of the cells and electrode production processes, etc., it is common to introduce the gravimetric package efficiency (σ), which is defined as the ratio between the combined weight of the electrodes and electrolyte to the weight of the entire cell. Therefore, the specific energy based on the weight of the entire cell can be expressed as:

$$E_{4-cell} = \sigma E_4 \qquad [14]$$

The typical value of σ for commercial pouch LIBs is around 65%.[31] The value of σ can be estimated as:

$$\sigma = \frac{M_1}{M_1 + M_2} \qquad [15]$$

where M_1 is the total mass of the solid cathode, anode, extra Li source and electrolyte in the cathode and anode, and M_2 is the total mass of current collectors for cathode and anode, separator paper, electrolyte in separator and package materials.

Energy density.—In addition to specific energy, the energy density based on cell volume is another important parameter of LIBs. Previously,[19] we have derived the following equations for the volumetric energy density based only on the volume of the electrodes and Li-source:

$$\begin{aligned} E_v &= \frac{V}{\frac{1}{c_a\rho_a(1 - \beta_a)} + \frac{1}{c_c\rho_c(1 - \beta_c)} + \frac{1 - \varepsilon}{\varepsilon}\frac{1}{c_{ls}\rho_{ls}(1 - \beta_{ls})}} \\ &= \frac{V}{D_a\frac{1}{c_a} + D_c\frac{1}{c_c} + D_{ls}\frac{1 - \varepsilon}{\varepsilon c_{ls}}} \end{aligned} \qquad [16]$$

where $D_i = 1/[\rho_i(1-\beta_i)]$ $(i = a,\ c,\ ls)$ are parameters that depend on porosities β_i and mass densities ρ_i and have the units of inverse mass density.

It should be pointed out that the energy density given by Eq. 16 is based on the battery volume before pre-lithiation; however, taking into account the amount of gas escaping from the battery and the changes in the volumes of the anode, cathode, and extra Li sources during pre-lithiation, the energy density of the final cell will be slightly higher than the value calculated using Eq. 16.

Similarly to the case of specific capacity, one can also define the volumetric package efficiency (σ') as the ratio between the combined volume of the electrodes and extra Li sources and the volume of the entire cell. With this notation, the energy density of an entire cell is:

$$E_{v-cell} = \sigma' E_v \tag{17}$$

The typical value of σ' for commercial pouch LIBs is about 60%.[31] The value of σ' can be estimated as:

$$\sigma' = \frac{U_1}{U_1 + U_2} \tag{18}$$

where U_1 is the total volume of the cathode, anode and extra Li source, and U_2 is the total volume of current collectors for cathode and anode, separator paper and package materials.

Method of Source-Based Pre-Lithiation

For (beyond) LIBs in which the anode and cathode are initially free of Li-ions (i.e. undoped) such as sulfurized-polyacrylonitrile (S-PAN) cathode and Si–C anode, pre-lithiation becomes mandatory, and the theoretical specific energy will dependent not only on the anode and cathode electrode materials, but also on the type and amount of extra Li sources used for pre-lithiation. Assuming again that the reversible capacities of the anode and cathode are equal to each other, we can write:

$$q_0 = m_a c_a = m_c c_c \tag{19}$$

The extra Li source provides both the amount of Li-ions that shuttle between anode and cathode during cycling and the Li-ions that compensate for the ICL in the cathode and anode electrodes during the initial cycles. In this case, the capacity of the extra Li sources can be written as:

$$q_{ls} = m_{ls} c_{ls} = q_0 + q_{ira} + \ q_{irc} \tag{20}$$

where q_{ira} and q_{irc} are the irreversible capacities of the anode and cathode, respectively.

Figure 4 illustrates the potentials of the cathode and anode as a function of the capacity during pre-lithiation and the first cycle, for different types of extra Li sources that are placed at various different locations inside the battery. Figure 4a shows the electrodes potentials when the extra Li source is Li metal. Similarly to the case of compensatory pre-lithiation, there are two cases that depend on the way in which the Li source is introduced in the anode. In the first case, the Li metal is in contact with the anode and the anode will lithiate spontaneously when the electrolyte is filled into the battery cell. The number of Li-ion transfers from extra Li source to the anode is equivalent to a capacity of $q_0 + q_{ira}$. The cathode ICL compensation (with capacity q_{irc}) will be completed during the following discharging process, as shown in Fig. 4a. In the second case, the extra Li source is a third electrode made of Li metal and the lithiation of the anode and cathode is controlled by an external circuit designed to discharge the electrodes using this third electrode.

Figure 4b shows the potential-capacity characteristics in the case when the Li salt is placed in the cathode and the potential of the extra Li source is lower than the potential of the cathode. The cathode will be fully lithiated during the spontaneous redox reaction between the cathode and extra Li source after the electrolyte is filled into the battery cell. The total capacity that is transferred from the extra Li source to the cathode is $q_0 + q_{irc}$; the excess Li-ions (with capacity q_{ira}) will be transferred from the Li source to the anode during the following charge process between the extra Li source/cathode and anode, as shown in Fig. 4b.

Figure 4c shows the potential-capacity characteristics in the case when Li salt is placed on the cathode and the potentials of extra Li source is higher than the potential of cathode. In this case, there is no spontaneous redox reaction between the cathode and extra Li source except for the electric double-layer buildup on the surface of both materials after the electrolyte is filled into the battery cell. However, the Li-ions will be transferred to the anode during the charge process between extra Li source/cathode and anode. Since the capacity of the extra Li source is higher than that of the anode, the excess Li-ions (with a capacity of q_{irc}) will be plated on the surface of the anode as shown in Fig. 4c and subsequently be transferred to the cathode during the following charging process.

Figure 4d shows the case when the Li metal is placed on the anode and the Li salt (or Li metal) is placed on the cathode. The capacity of Li metal on the anode is $q_0 + q_{ira}$ and the capacity of Li salt on the cathode is q_{irc}. If the potential of the Li salt is lower than the potential of the cathode, Li-ions from the Li metal, anode and the Li salt at the cathode will be transferred to the anode and cathode through spontaneous redox reactions, respectively, after the electrolyte is filled into the battery cell. If the potential of the Li salt at the cathode is higher than the potential of the cathode, the pre-lithiation of the cathode will be completed by the process of Li plating onto the surface of the anode, as shown in Fig. 4c.

Theoretical specific energy.—Defining the Coulombic efficiencies of the anode and cathode by:

$$\varepsilon_a = \frac{q_0}{q_0 + q_{ira}} \tag{21}$$

$$\varepsilon_c = \frac{q_0}{q_0 + q_{irc}} \tag{22}$$

the mass of the necessary extra Li source becomes:

$$m_{ls} = \frac{q_0 + q_{ira} + q_{irc}}{c_{ls}} = \frac{q_0}{c_{ls}}\left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_c} - 1\right) \tag{23}$$

Combining Eqs. 19 and 23, the specific energy based on the total mass of anode, cathode, and extra Li sources becomes:

$$\begin{aligned} E_5 &= \frac{q_0 V}{m_a + m_c + (1-\alpha)m_{ls}} \\ &= \frac{V}{\frac{1}{c_a} + \frac{1}{c_c} + \frac{1}{c_{ls-eff}}\left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_c} - 1\right)} \end{aligned} \tag{24}$$

Figure 5 shows the specific energy of the battery cell as a function of the Coulombic efficiency for different values of the weight loss (α). Here is assumed that the Coulombic efficiencies of the anode and cathode are equal to each other, $c_a = 1{,}000$ mAh g^{-1} (Si–C anode), $c_c = 900$ mAh g^{-1} (S-PAN cathode),[12,32] $V = 1.7$ V, and $c_{ls} = 516$ mAh g^{-1}. One can see that the specific energy depends strongly on the effective specific capacity of the extra Li sources. Compared to conventional LIBs, more extra Li sources are required for pre-lithiation not only to compensate the ICL of the electrodes but also to provide enough mobile Li-ions necessary for shutteling between the two electrodes. Assuming that the Coulombic efficiency of the electrodes are $\varepsilon_a = \varepsilon_c = 70\%$, the

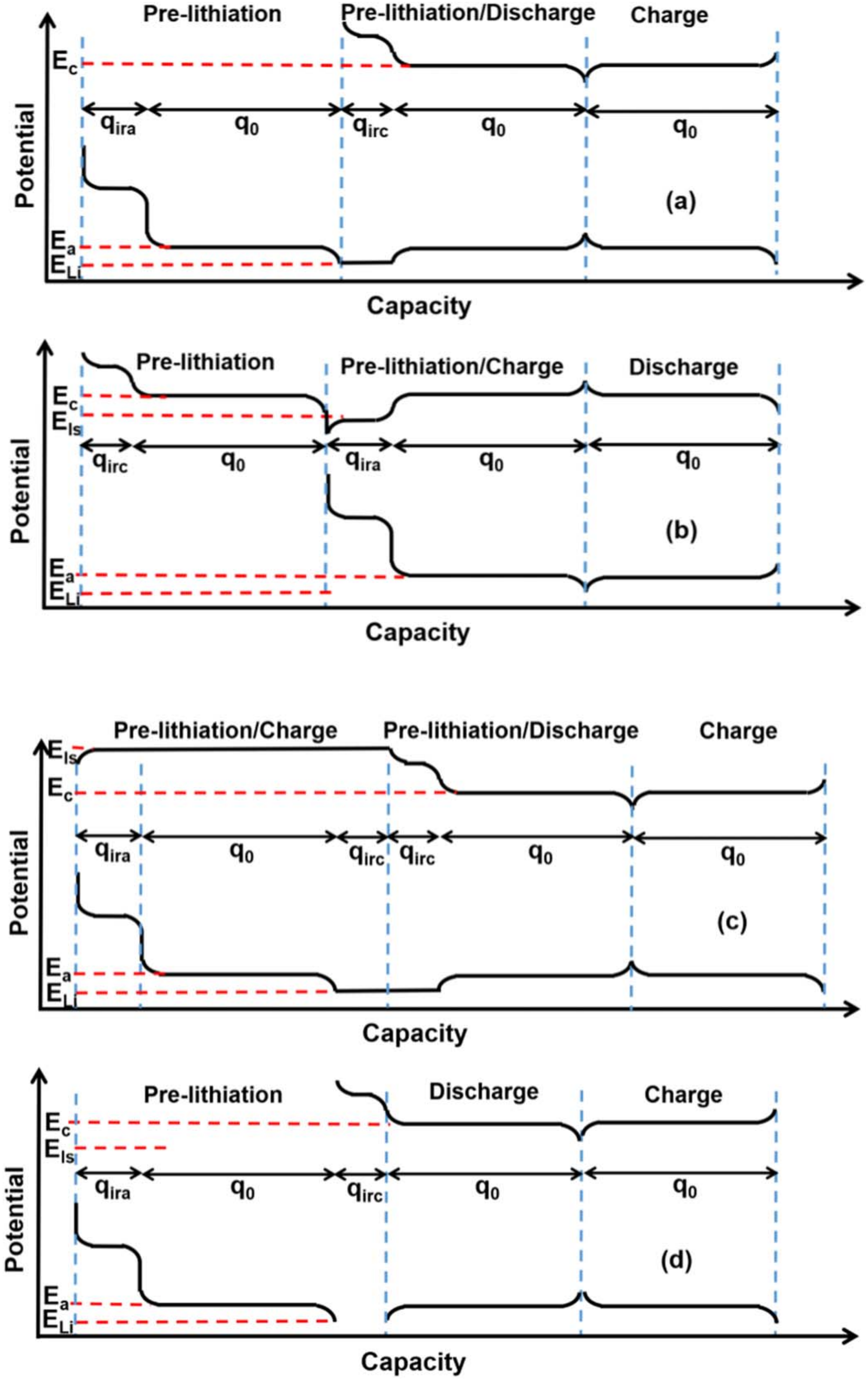

Figure 4. The cathode and anode potentials during pre-lithiation and initial charge-discharge cycle in the cases when: (a) Li metal is placed at the anode, (b) Li salt is placed at the cathode and its potential is lower than that of the cathode, (c) Li salt is placed at the cathode and its potential is higher than that of the cathode, and (d) Li metal is placed at the anode, Li salt is placed at the cathode and its potential is lower than that of the cathode.

maximum specific energy is $E_5 = 656$ Wh kg^{-1}, which higher but closed to the maximum specific energy with pre-lithiation and no mass loss, $E_3 = 654$ Wh kg^{-1}.

Specific energy considering the electrode porosity and cell packaging.—Using the same line of reasoning as in the derivation of Eq. 13, one can show that:

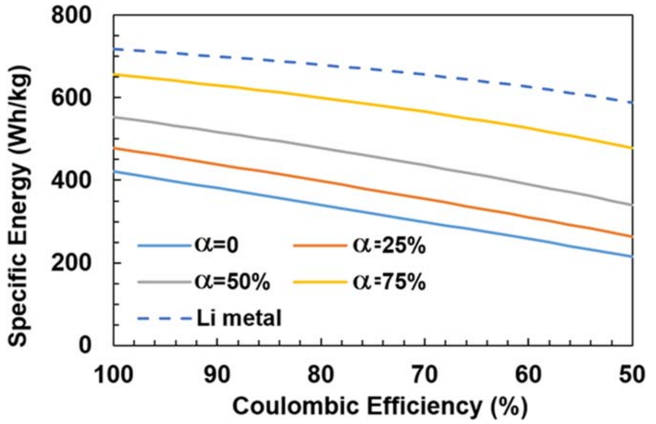

Figure 5. Specific energy as a function of Coulombic efficiency for different weight losses (α) from extra Li source after pre-lithiation, calculated using Eq. 22. It is assumed that the cathode and anode have the same Coulombic efficiency. The battery has a S-PAN cathode (900 mAh g^{-1}) and a Si–C anode (1,000 mAh g^{-1}). The average cell voltages 1.7 V. The specific capacity of the extra Li source is 516 mAh g^{-1}.

$$E_6 \frac{V}{(1+P_a)\frac{1}{c_a} + (1+P_c)\frac{1}{c_c} + (1+P_{ls})\frac{1}{c_{ls-eff}}\left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_c} - 1\right)} \quad [25]$$

where parameters P_a, P_c, and P_{ls} have been defined in Eq. 13. The specific energy of a completely packaged battery cell is:

$$E_{6-cell} = \sigma E_6 \quad [26]$$

The formulas of the specific energy of a completely packaged battery cell (see Eqs. 13 and 23) require the values of many material parameters (i.e. specific capacity, mass density, porosity, potential of electrode, and Coulombic efficiency) that can all be measured experimentally. Table I lists the values of the parameters, which were used to calculate the specific energy of battery cells. In addition, we assume that the porosities of cathode and anode are 20% and the Coulombic efficiencies of NMC, S-PAN, and Si–C are of 100%, 70%, and 70%, respectively. Figure 6 shows the specific energy of a battery with Si–C anode and NMC or S-PAN cathode, calculated using Eqs. 13, 14 and 23, 24, respectively. In these calculations, the package efficiency was assumed to be 65%. It can be seen that in the case of LIBs with NMC cathodes, although the specific energy increases with increasing the specific capacity of the anode, when the specific capacity of the anode is greater than 600 mAh g^{-1}, the rate of increase in specific energy is reduced. This effect appears because the reciprocal of the effective specific capacity of the cell is the sum of the reciprocal of the specific capacity of the anode and cathode electrodes, as described by Eq. 13. Therefore, among the two electrodes, the electrode with the smaller specific capacity will play a dominating role in determining the final specific energy of the cell. In the case of battery cells with S-PAN cathodes, the specific energy is less than that of using NMC if the specific capacity of anode is less than 1,000 mAh g^{-1} because of the low cell voltage (1.7 V). However, the increase rate of the specific energy is larger. When the specific capacity of the anode is larger than 1,000 mAh g^{-1}, the specific energy of battery cells with S-PAN is larger than that of the LIBs with NMC.

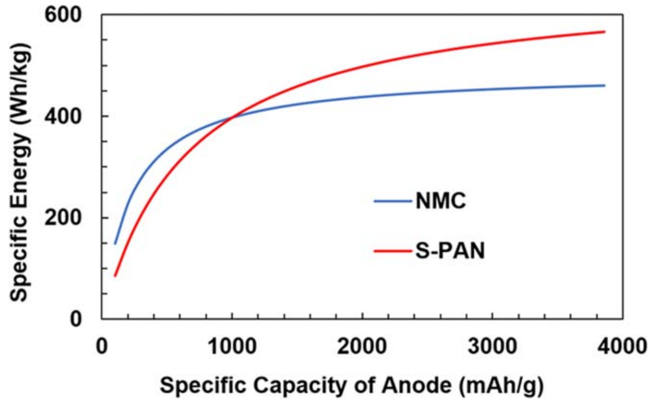

Figure 6. Specific energy of packaged battery cells with Si–C anode and NMC or S-PAN cathodes, calculated using Eqs. 13 and 23. The extra Li source is Li metal. The other parameters are listed in Table I.

Energy density.—Using the same approach as in the derivation of Eq. 15, the volumetric energy density of the batteries with source-based pre-lithiation is:

$$\begin{aligned} E_v &= \frac{V}{\frac{1}{c_a\rho_a(1-\beta_a)} + \frac{1}{c_c\rho_c(1-\beta_c)} + \frac{1}{c_{ls}\rho_{ls}(1-\beta_{ls})}\left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_c} - 1\right)} \\ &= \frac{V}{D_a\frac{1}{c_a} + D_c\frac{1}{c_c} + D_{ls}\frac{1}{c_{ls}}\left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_c} - 1\right)} \end{aligned} \quad [27]$$

where parameters D_a, D_c, and D_{ls} have been defined previously.

Pre-Lithiation Strategies

Various pre-lithiation methods have been proposed and studied in the literature, including the half-cell electrochemical method, the direct contact electrochemical method, the chemical lithiation method, the lithium metal in anode method, and the lithium source in cathode method. In this section, we briefly discuss three pre-lithiation strategies suitable for industrial manufacturing, as shown in Fig. 7, for before and after pre-lithiation. The anode material is Si-C and the cathode materials can be pre-doped with Li such as Li metal oxides, or be Li-free such as S-PAN. If the cathode materials are fully doped with Li and the ICL of the cathode is negligible, the composition of the cathode materials will not change after pre-lithiation. The capacity of the extra Li source is approximately equal to the ICL of the anode. If the cathode materials are fully doped with Li and the ICLs of the anode and cathode are not negligible, both electrodes need to be pre-lithiated. The capacity of the extra Li source is approximately equal to the sum of ICLs of the cathode and anode.

Table I. List of parameters used in the estimation of specific energy of packaged LIB cells.

	Specific capacity (mAh g^{-1})	Mass density (g cm^{-3})	Porosity (%)	Potential (V vs Li/Li^+)	Coulombic Efficiency (%)
Si–C	Variable	2.3	20	0.2	70%
NMC	220	4.4	20	3.9	100%
S-PAN	900	1.63	20	1.9	70%
Extra Li source	3,860	0.534	0	0	N/A
Electrolyte	N/A	1.1	N/A	N/A	N/A

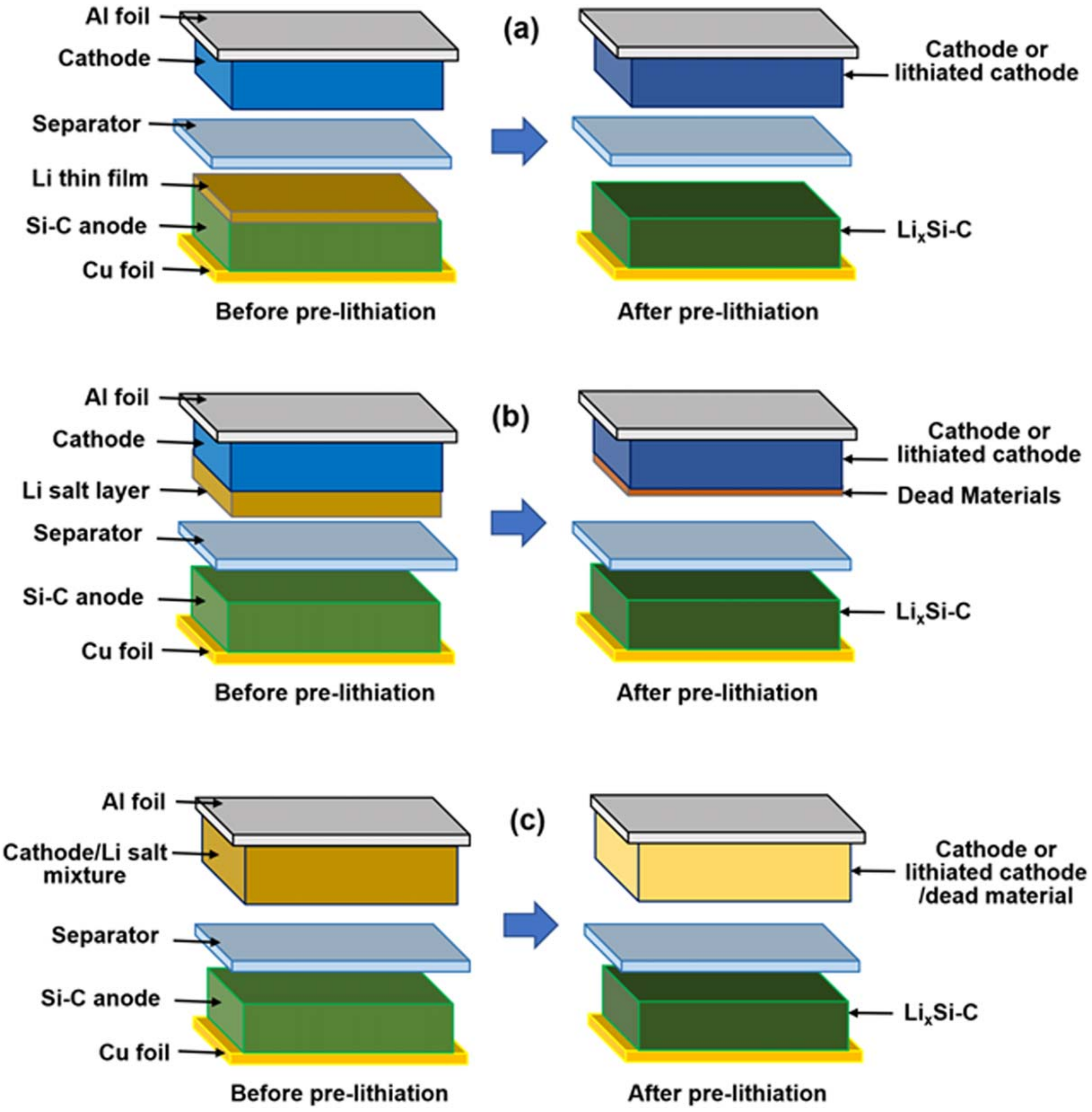

Figure 7. Three pre-lithiation strategies using different pre-lithiation sources: (a) a metal Li film placed on the surface of the anode, (b) a layer of Li salt coated on the surface of the cathode, and (c) Li salt and cathode materials mixed uniformly.

If the cathode materials are Li-free, both the cathode and the anode need to be pre-lithiated. The capacity of the extra Li source is approximately equal to the sum of the reversible capacity of cathode (or anode) and the ICLs of the cathode and anode. Figure 7a shows an example in which the extra Li source is a Li metal film, placed on the surface of the anode. The advantages of using Li metal as the extra Li source are that Li metal has the maximum specific capacity and there are no dead materials after pre-lithiation because the Li metal has a high electrical conductivity and makes good electrical contact with the anode. The disadvantage is that the pre-lithiation rate cannot be controlled. Figure 7b shows the case when a layer of Li salt is coated on the surface of the cathode and used as the extra Li source. The advantage is that the effect of pre-lithiation on the electrode structure and composition is minimized. The disadvantage is that since the lithium salt is non-conductive, conductive additives need to be added to the layer of lithium salt, and the dead materials left on the surface of the positive electrode may have negative effect on the battery rate, lifetime, and leakage current. Finally, Fig. 7c shows the case when Li salt as the extra Li source is uniformly mixed with the cathode materials. The advantage of this strategy is that the manufacturing processes of the electrodes and batteries are simple. The disadvantage is that the electrode structure and composition is changed after pre-lithiation and can have negative effects on battery performance. If the Li salt is soluble in the solvent of the electrolyte, then no conductive additive is needed and the amount of dead material left in the battery is minimal.

Conclusions

Electrodes with high specific capacities are crucial to achieving high energy density in LIBs. Unfortunately, not only the anode and cathode electrodes are often accompanied by significant irreversible charge loss, but many high specific capacity cathode materials such as sulfur-based materials are built without Li pre-doping. Therefore, when such high-capacity electrodes are used in LIBs, pre-lithiation is one of the most efficient, controllable, and practical methods to provide additional extra Li sources, thus maximizing the energy density of the LIBs.

The pre-lithiation procedures and electrode potential profiles during pre-lithiation were discussed in detail for different types of extra Li sources (including Li metals and various Li-rich salts). If the potential of the extra Li source is lower than that of the electrode and the extra Li source and the electrode are electrically connected, pre-lithiation will occur spontaneously when the electrolyte is filled into the LIB. If the potential of the extra Li source is higher than that of the electrode, the pre-lithiation will be achieved by an external charging process between the extra Li source and the electrodes. The estimations of the specific energy show that the specific capacity (or effective specific capacity) of the extra Li source plays an important role in determining of specific energy of the batteries, especially for batteries made with electrodes without pre-doped Li. It is demonstrated that a battery using a sulfur-based cathode could have a specific energy greater than batteries with commercial Li metal oxide based cathodes.

Although the discussion of the pre-lithiation procedure and the formulas of the specific energy and energy density derived in this article are based on Li-ion systems, these results are also applicable to sodium-ion, magnesium-ion, zinc-ion, and other ion battery systems. For instance, in the case of sodium-ion battery systems, the only parameter that needs to be changed is the maximum specific capacity of the extra ion source that is $c_{Na} = 1{,}160$ mAh g^{-1} (instead of $c_{Li} = 3{,}860$ mAh g^{-1}).

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Appendix

To design the cell, one needs to select the Li salt that meets the requirements of the LIB under consideration. A list of possible such salts that are soluble in water is presented in Table A·I. Notice that all these salts are stable in air but insoluble in most of the organic solvents used in electrolytes for LIBs. Theoretically, there are no dead materials for $LiHCO_2$ ($\rightarrow Li^+ + e^- + \frac{1}{2}H_2\uparrow + CO_2\uparrow$), $Li_2C_2O_4$ ($\rightarrow 2Li^+ + 2e^- + 2CO_2\uparrow$), Li_2CO_3 ($\rightarrow 2Li^+ + 2e^- + \frac{1}{2}O_2\uparrow + CO_2\uparrow$), $LiNH_2$ ($\rightarrow Li^+ + e^- + \frac{1}{2}N_2\uparrow + H_2\uparrow$), Li_3N ($\rightarrow 3Li^+ + 3e^- + \frac{1}{2}N_2$), $LiOH$ ($\rightarrow Li^+ + e^- + \frac{1}{2}O_2\uparrow + \frac{1}{2}H_2\uparrow$), and Li_2O_2 ($\rightarrow 2Li^+ + 2e^- + O_2\uparrow$) after decomposition due to de-lithiation; in the case of $Li_2C_4O_4$ ($\rightarrow 2Li^+ + 2e^- + 2C + 2CO_2\uparrow$) there is less than 20% dead material. The salts listed in Table A·I do not have any corrosive products after decomposition such as LiF, LiCl, and LiBr salts.

Also notice that some unstable high-capacity Li salts, such as $LiNH_2$ which is a very reactive compound, LiH which is extremely strong irritant and highly toxic, LiOH which produces H_2O after

Table A·I. Li salts and their theoretical specific capacities.

Li salts	c_{ls} (mAh g^{-1})[a]	Li salts	c_{ls} (mAh g^{-1})	Li salts	c_{ls} (mAh g^{-1})
LiH	3,375	Li_2CuO_2	490	$LiClO_3$	297
Li_2O_2	1,168	Li_2SO_4	488	$LiBF_4$	286
$LiNH_2$	1,168	$Li_2C_4O_4$	426	LiH_2PO_4	258
LiOH	1,120	Li_2CrO_4	413	$LiClO_4$	252
Li_2CO_3	726	LiSCN	413	$LiMnO_4$	213
Li_3PO_4	694	$LiC_2H_3O_2$	406	$LiC_7H_5O_2$	209
LiO_2	688	$LiHCO_3$	394	LiI	200
Li_2Se	577	$LiNO_3$	389	$LiBrO_3$	199
LiN_3	548	Li_2SeO_3	380	$LiSiF_6$	180
$Li_2C_2O_4$	526	$Li_2C_4H_4O_6$	331	$LiPF_6$	176
$LiHCO_2$	516	$LiHPO_3$	308	$LiAsF_6$	170
Li_2NiO_2	513	Li_2MoO_4	308		
$LiNO_2$	506	Li_2CrO7	301		

a) c_{ls} is the theoretical specific capacity of the Li salt.

de-lithiation, and Li_3N which reacts with moisture in the air to release ammonia, are excluded from Table A·I.

ORCID

Jim P. Zheng https://orcid.org/0000-0003-2689-0067
Liming Jin https://orcid.org/0000-0003-4278-0685

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