

Cathode pre-lithiation/sodiation for next-generation batteries

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Keywords: Pre-lithiation, pre-sodiation, irreversible capacity, solid electrolyte interphase, lithium-ion batteries, sodium-ion batteries, electrochemical energy storage

Abstract

Electrochemical energy storage (EES) is playing a pivotal role in the global pursuit of a clean and sustainable energy future. Lithium-ion batteries (LIBs) are the state-of-the-art technology but future energy requirements demand higher energy densities and a more diverse battery landscape to meet a wide variety of applications. Unfortunately, many next-generation LIB chemistries and beyond-LIB technologies suffer from large first cycle irreversible capacity caused by active ion loss (AIL). The field of pre-lithiation/sodiation have recently emerged as researchers attempt to mitigate AIL and boost the energy density of next-generation LIBs and sodium-ion batteries (SIBs). In this short review, we highlight recent advances in cathode pre-lithiation/sodiation using sacrificial additives and pre-lithiation/sodiation of cathode active materials (CAMs).

Introduction

Lithium-ion batteries (LIBs) are ubiquitous in daily life and provide electrochemical energy storage (EES) for an ever growing list of applications including electric vehicles, portable electronics, and utility-scale energy storage. The worldwide effort to reach zero-carbon emissions and mitigate global warming continues to drive growth of the battery market. While LIBs will continue to improve and pervade new devices,[1] concerns over cost, sustainability, and mineral resource availability is creating market opportunities for alternative battery chemistries.[2] One such system, sodium-ion batteries (SIBs), are on the cusp of commercialization and are especially promising for large-scale energy storage applications.[2,3]

Given the similar operational principles of “rocking-chair” LIBs and SIBs, it is perhaps unsurprising that certain failure mechanisms are common to both. For example, a large first cycle irreversible capacity (IC) due to active ion loss (AIL) plagues both LIBs and SIBs.[4–6] This is primarily due to parasitic side reactions at the anode resulting in the formation of the solid electrolyte interphase (SEI).[7] Since the Li^+/Na^+ content of the cathode defines the

maximum energy density of the full cell, AIL immediately lowers the reversible capacity and energy density. In LIBs, active lithium loss (ALL) is particularly troublesome for next-generation high-energy anodes, of which Si is the frontrunner.[8] The large volume changes of Si upon lithiation/delithiation result in ongoing SEI breakage and re-formation, leading to an unacceptably large first cycle IC of 20-35 % and rapid capacity fading thereafter.[8,9] Similarly, in SIBs, SEI formation at the anode results in active sodium loss (ASL). Hard carbon anodes, which are extensively investigated and show considerable promise, suffer from low first cycle IC of ~75 %.[5,6] Compounding the issue in SIBs is the initial sodium deficiency of P2-type sodium layered oxide cathodes, which otherwise show promising performance.[2,3]

In the last decade, research into pre-lithiation/sodiation technologies has emerged, and grown exponentially in the last 2-3 years, as a promising avenue to mitigate AIL in LIBs and SIBs. It is worth noting that pre-lithiation/sodiation research has widespread impact in the EES field, also addressing key issues in Li/Na-free cathodes for LIBs/SIBs,[10] Li/Na-ion capacitors (LIC/NIC),[6,11] Li/Na-sulfur batteries, and Li/Na-air batteries.[12] In this short review we will introduce the principles of pre-lithiation/sodiation in the context of LIBs and SIBs, critically review recent reports of cathode pre-lithiation/sodiation for LIBs and SIBs, and provide a perspective on future directions in the field.

Principles of pre-lithiation/sodiation

Pre-lithiation/sodiation is the term used to describe the addition of active Li^+/Na^+ to the battery prior to operation. In most reported cases, its purpose is to compensate the AIL in the first cycle, thus increasing the reversible capacity. Some recent reports add more Li^+/Na^+ , thereby creating a reserve of ions that can compensate for AIL beyond the first cycle.[13,14] The additional Li^+/Na^+ can be stored at either the anode or the cathode by a variety of pre-lithiation/sodiation strategies, each with associated advantages and disadvantages.[12,15] Once cycling begins, the extra Li^+/Na^+ are shuttled between the electrodes, along with that starting on the cathode active material (CAM), as illustrated in Figure 1a-c. We have established a methodology employing a high capacity LiFePO_4 (LFP) cathode to determine the impact that pre-lithiation/sodiation has on cycling performance, using a Si-graphite composite anode as an example.[16] While practical levels of pre-lithiation can compensate for the IC in early cycles and delay capacity fade, it does not fundamentally alter the underlying IC (i.e. rate of AIL) of the system.

Pre-lithiation/sodiation of the CAM is attractive to avoid the poor atmospheric stability of pre-lithiated/sodiated anodes and the incompatibility with current processing solvents.[12,15,17] Cathode pre-lithiation/sodiation can be achieved by addition of sacrificial salts and compounds or direct pre-lithiation/sodiation of the CAM, which are discussed below.

Sacrificial additives

Li^+/Na^+ -containing salts and compounds can be added directly to the cathode to sacrificially (i.e. irreversibly) release Li^+/Na^+ to the battery – see Figure 1d. They should have the following attributes. (1) Electrochemically oxidized (releasing Li^+/Na^+ , “activated”) in the potential window of the CAM, preferably during the first charge cycle. (2) High volumetric and gravimetric capacity so that their inclusion outweighs any penalty introduced by residues left after activation. (3) After activation, the additive must be stable electrochemically, chemically, thermally, and mechanically. (4) Be compatible with current manufacturing processes.

Sacrificial lithium-containing additives for IC compensation were first proposed in the early 2000s.[18] Since then a large number of pre-lithiation agents have been reported, which include additives based on: Li_3N ,[19] LiN_3 ,[20] Li_2O ,[21] Li_2O_2 ,[22] LiF ,[23] Li_3P ,[24] Li_2S ,[25] $\text{Li}_2\text{C}_2\text{O}_4$,[20,26] Li_2NiO_2 ,[27] Li_2CuO_2 ,[28] Li_2MoO_3 ,[29] Li_5FeO_4 ,[13,30] and Li_6CoO_4 . [31] For visual comparison, the gravimetric and volumetric capacity of these additives are plotted in Figure 2a. A number of critical reviews of pre-lithiation additives have been published recently,[12,15,17] so the anticipated advantages/disadvantages of each are not discussed in detail here. It is interesting to note, however, that while many of the proposed additives initially presented challenges (e.g. poor conductivity and high over-potential for Li^+ release), novel solutions have been forthcoming. For example, Cui and coworkers[21,23,25,32,33] synthesized LiX/M nanocomposites (where $\text{X} = \text{O}, \text{F}, \text{S}$, and $\text{M} =$ transition metal, such as $\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$, etc.) that reduce the over-potential and greatly enhance the pre-lithiation efficacy (Figure 3a-c), although inactive M_aX_b (e.g. Co_3O_4) is left on the cathode as dead-weight/volume. Other additives, like Li_5FeO_4 , have recently been reported to have synergistic effects, simultaneously releasing Li^+ to the battery and suppressing CAM degradation.[13] Also of note are reports where the irreversible electrochemical activation of CAMs on the first cycle have been exploited for pre-lithiation, which has been demonstrated for Li-rich $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ (or $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$)[34] and $x\text{Li}_2\text{O} \cdot (1-x)\text{Li}_{2/3}\text{Mn}_{1/3}\text{O}_{5/6}$ non-stoichiometric disordered rock-salt oxides, wherein the structural Li_2O is electrochemically activated.[35]

Reported sodium additives include: NaN_3 ,[36] Na_2O (with Ru-graphene catalyst),[37] Na_2O_2 ,[38] Na_3P ,[39] NaNO_2 ,[40] Na_2CO_3 ,[41] $\text{Na}_2\text{C}_2\text{O}_4$ (oxalate),[42] $\text{Na}_2\text{C}_4\text{O}_4$ (squarate),[43] $\text{Na}_2\text{C}_3\text{O}_5$ (mesoxalate),[44] $\text{Na}_2\text{C}_6\text{O}_6$ (disodium rhodizonate),[45] $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (citrate),[46] $4\text{Na} \cdot \text{EDTA}$ (ethylenediamine-tetraacetic acid tetrasodium),[47] $5\text{Na} \cdot \text{DTPA}$ (diethylenetriamine-pentaacetic acid pentasodium),[48] NaCrO_2 ,[49] and Na_2NiO_2 . [50] The number of additives proposed is growing rapidly, with two-thirds of these reported since 2019. The gravimetric and volumetric capacity of these additives are plotted in Figure 2b (note that the axis scales are half that in Figure 2a). Several of the proposed additives will likely face problems due to toxicity (e.g. NaN_3 , Na_3P), release of water that can adversely react with cell components (e.g. $4\text{Na} \cdot \text{EDTA}$, $5\text{Na} \cdot \text{DTPA}$, $\text{Na}_2\text{C}_6\text{O}_6$), or form products that can undergo further parasitic reactions (e.g. $\text{Na}_2\text{C}_6\text{O}_6$, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$). Conversely, there are some reports of synergistic effects that improve the cathode performance (e.g. $\text{Na}_2\text{C}_3\text{O}_5$ and $\text{Na}_2\text{C}_4\text{O}_4$ – Figure 3d-f).[43,44] Despite these considerations, in all cases the additive in the cathode increased the SIB full cell energy density compared to the CAM alone (e.g. Figure 3e). At this stage, however, cycle life testing is limited (generally 50-100 cycles) and any side reactions, beneficial or adverse, initiated by the gasses or solid residues are largely unexplored.

Pre-lithiation/sodiation of cathode active materials

Pre-lithiation/sodiation of CAMs typically involves an additional processing step that adds Li^+/Na^+ directly to the CAM structure – see Figure 1e. The Li^+/Na^+ added is generally lower than with sacrificial additives, since it requires corresponding TM redox changes in the CAM. Most reports for LIBs take advantage of $\text{Mn}^{3+/4+}$ redox in the $[\text{M}_2]\text{O}_4$ spinel framework of LiMn_2O_4 (LMO) and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO). Electrochemical insertion of lithium into LMO was established soon after its discovery.[51] Owing to the current manufacturing challenges associated with electrochemical pre-lithiation, we do not herein review literature using this approach. Chemical lithiation approaches to reduce LMO and LMNO reported in the literature

employ: LiI,[52] n-butyl Li,[53] and more recently, microwave assisted chemical over-lithiation using tetraethylene glycol (TEG) as the reducing agent and hydrated LiOH as the lithium source,[54] solid-state synthesis with a “reductive lithium-containing compound”,[55] Li metal in liquid ammonia,[56] and Li metal in boiling pentanol (Figure 4a-c).[57] The amount of pre-lithiation in each of these methods can be tuned by the ratio of the Li source to CAM. The solid-state synthesis[55] and boiling pentanol-based approach[57] seem most promising in terms of practicality and scalability. However, efforts to commercialize LMNO are still ongoing, and based on energy density LMO does not compete with layered Co- and Ni-rich LIB CAMs such as LiCoO_2 (LCO), $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), and $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC).[51] As such, methods to pre-lithiate these CAMs for best-in-class LIBs are highly desirable. Therefore, we recently reported that $\text{Li}_{1+x}\text{NMCO}_2$ (with $x \leq 1$, Figure 4d) can be synthesized chemically via a reaction between NMC and lithium naphthalide,[14] with Liu et al.[58] simultaneously reporting a similar approach. In each of the above cases, the extra Li^+ is released from the CAM on the first charge (Figure 4b), whereupon it is shuttled to the anode (graphite and Si-graphite are commonly studied) and used to mitigate the AIL in the first cycle and in ongoing cycles.

There are far fewer reports of pre-sodiation of CAMs for SIBs. Tarascon and coworkers[39] reported that layered oxides and polyanionic cathodes could be pre-sodiated by ball milling with Na metal or NaP_3 , which was exemplified with $\text{P2-Na}_{0.67}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ yielding $\text{P2-Na}_1\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (Figure 4e-f), and with $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ yielding $\text{Na}_4\text{V}_2(\text{PO}_4)_2\text{F}_3$. Pre-sodiation of $\text{P2-Na}_{0.67}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has also been reported via direct contact with Na metal for 5 min.[59] The pre-sodiated cathodes from both approaches were tested in full cells versus a hard carbon anode, and as expected, showed improved energy density compared to untreated cathodes (Figure 4f).

Concluding remarks

This short review highlights the recent advances made in the rapidly growing field of cathode pre-lithiation/sodiation in LIBs and SIBs. Sacrificial additives offer the advantage of a significantly higher pre-lithiation/sodiation capacity compared to direct pre-lithiation/sodiation of CAMs, and so will likely find application in battery chemistries with larger AIL. Further, in principle they can be added to any cathode material making them more versatile, whereas only a few over-lithiated/sodiated cathode materials have been reported to date. Conversely, direct pre-lithiation/sodiation of cathode materials have the advantage of not adding dead-weight/volume (only Li^+/Na^+ are added), unlike many sacrificial additives that leave a dead-weight/volume residue, which adversely impacts the energy density. The best choice of pre-lithiation/sodiation material will therefore depend on the cell chemistry and the particular EES application requirements.

Several challenges remain that should be the focus of future research in this field. First, the long-term effects of the residues and/or gas release from sacrificial additives are currently poorly understood. For example, careful investigation of any interactions with the electrolyte and other electrode components, as well as changes in the electrode porosity as a result of gas release, are needed. **The latter may result in disruption to the 3D network of active material and conductive carbon, and the effect this may have on the long-term electrochemical performance is not currently understood.** Second, more synthesis approaches for pre-lithiation/sodiation of the most commercially relevant cathode materials should be explored, in conjunction with in-

depth studies of the long-term physicochemical properties and electrochemical performance. Third, while both fields are young, the field of pre-sodiation is in its infancy compared to pre-lithiation. Therefore, there is considerable scope for rapid advancement; specifically, exploring new sodium-containing sacrificial additives, developing approaches for pre-sodiated cathode materials, and understanding the underlying reaction mechanisms leading to performance enhancement.

In conclusion, in the near-term pre-lithiation/sodiation is predicted to play an important role in developing advanced LIBs and bringing more SIB cell chemistries to market-readiness. In the longer-term, the field of pre-lithiation/sodiation will continue to hold an important position in EES research and development, and will likely play a key role in addressing critical issues in beyond-LIB chemistries such as Li/Na-sulfur and Li/Na-air batteries.

Declaration of interest

None

Acknowledgements

W.D. acknowledges support from the Faraday Institution degradation project (FIRG001) and EPSRC (EP/S003053/1). C.J. acknowledges support from the Vehicle Technologies Program, Hybrid and Electric Systems, of the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy. Argonne National Laboratory is operated under Contract No. DE-AC02-06CH11357.

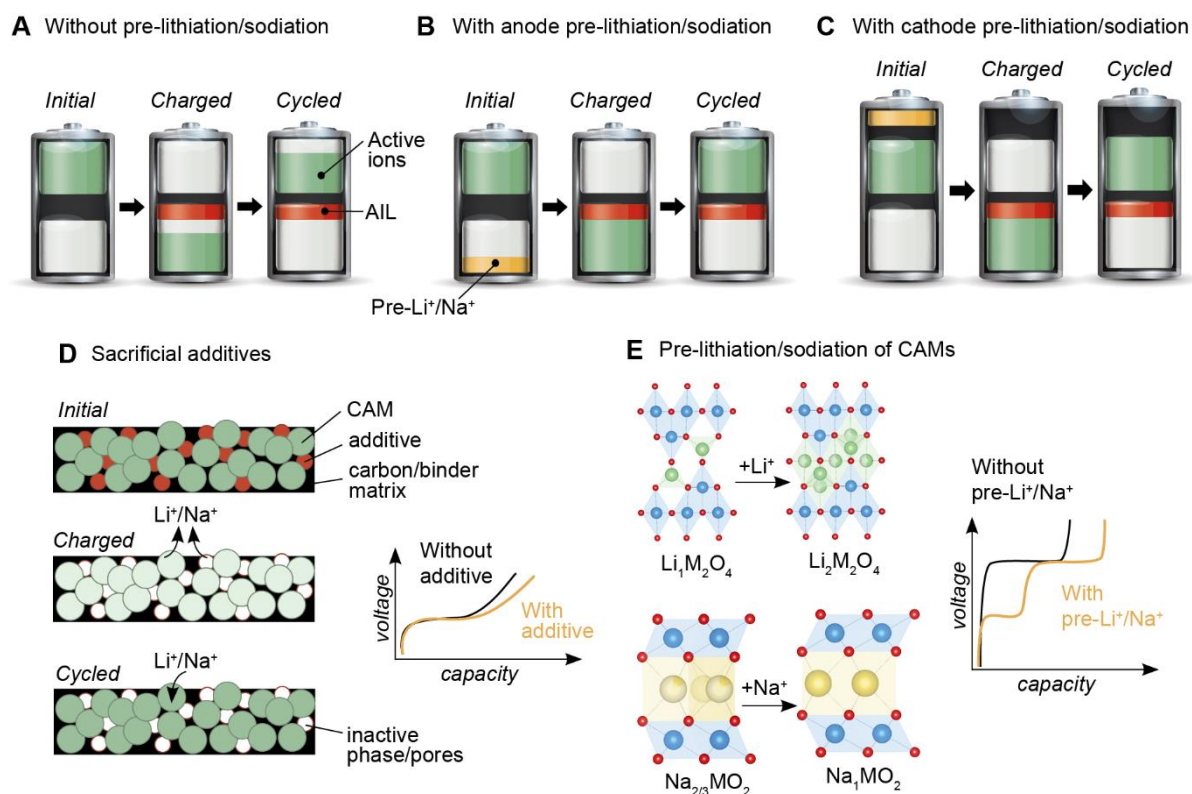


Figure 1. Schematic illustration of active ion loss (AIL) during the first cycle of a battery without pre-lithiation/sodiation (A) and concepts to compensate for AIL with anode (B) and cathode (C) pre-lithiation/sodiation. (D) Schematic of the irreversible release of Li^+/Na^+ from a sacrificial additive in a cathode composite electrode. (E) Schematic for pre-lithiation/sodiation of cathode active materials (CAMs) exemplified for spinel LiM_2O_4 and layered $\text{Na}_{2/3}\text{MO}_2$, where M represents transition metals.

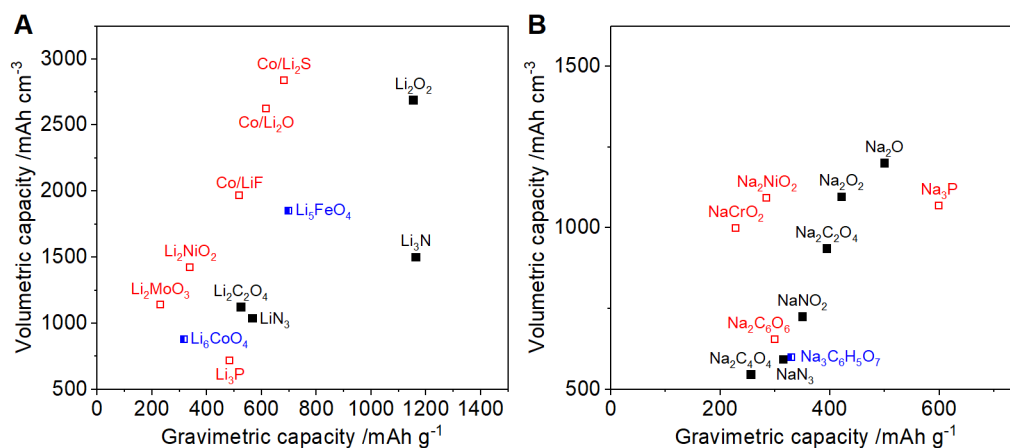


Figure 2. Volumetric versus gravimetric capacity for various cathode sacrificial additives proposed for (A) lithium-ion batteries[13,19,29–31,20–27] and (B) sodium-ion batteries[36,37,39,40,42,43,45,46,49,50]. Data points for the additives are colored based on whether they release gas (black), leave a solid residue (red), or both (blue). The gravimetric capacity values were taken from the respective literature reports – note that these vary in terms of electrode composition (e.g. carbon and binder content), upper cutoff potential, and current rate. The volumetric capacity values were calculated using the crystallographic density of the material.

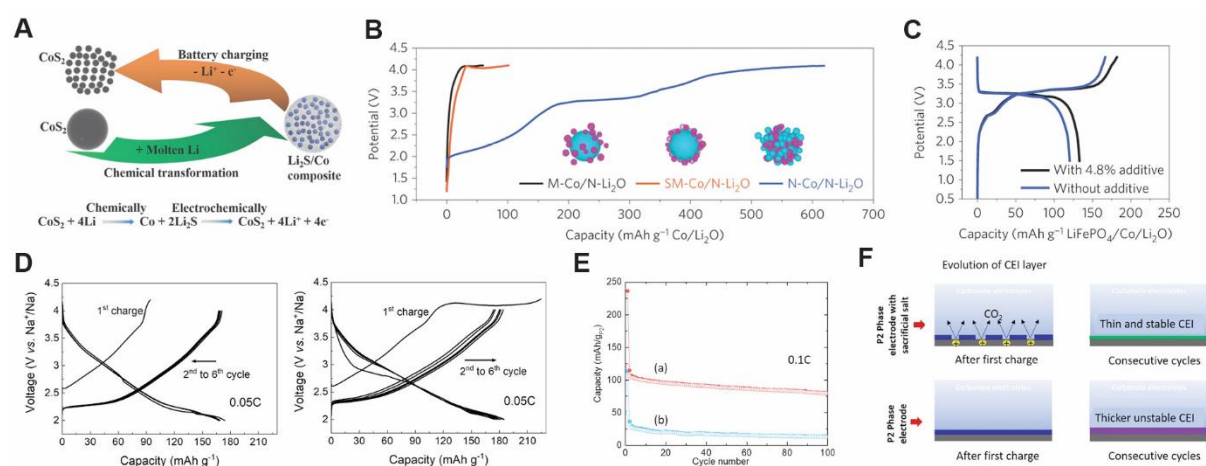


Figure 3. Sacrificial additives. (A) Schematic for the synthesis of LiX/M nanocomposites and their subsequent electrochemical release of Li^+ . Reproduced with permission from [25] Copyright 2016, Wiley-VCH. (B) First charge potential profile of a $\text{Li}_2\text{O}/\text{Co}$ nanocomposite in a half-cell and (C) first cycle voltage profile of a $\text{LiFePO}_4/\text{graphite}$ full cell with and without

the $\text{Li}_2\text{O}/\text{Co}$ additive. Reproduced with permission from [21] Copyright 2017, Springer Nature. (D) First charge potential profile of P2- $\text{Na}_{2/3}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Ti}_{0.1}\text{O}_2$ without (left) and with (right) a $\text{Na}_2\text{C}_3\text{O}_5$ additive in half-cells, (E) discharge capacities of P2-cathode/hard carbon anode full cells without (blue) and with (red) a $\text{Na}_2\text{C}_3\text{O}_5$ additive, and (F) schematic of proposed synergistic effect of the $\text{Na}_2\text{C}_3\text{O}_5$ additive on controlling the SEI formation on the P2-cathode. Reprinted with permission from [44] Copyright 2021 American Chemical Society.

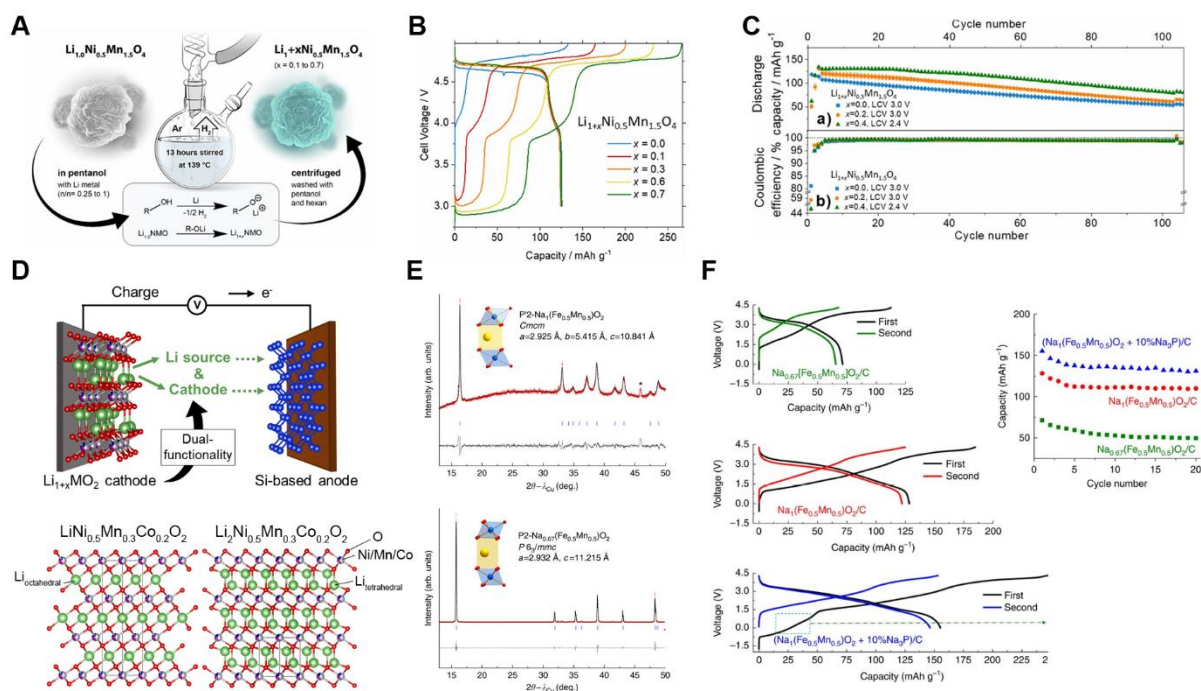


Figure 4. Pre-lithiation/sodiation of cathode active materials. (a) Schematic of the reaction scheme for chemical pre-lithiation with lithium metal in 1-pentanol, (b) first cycle potential profiles of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ without ($x=0$) and with ($x>0$) pre-lithiation in half-cells, and (c) discharge capacities (top) and coulombic efficiencies (bottom) of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Si-C}$ full cells without (blue) and with (orange and green) pre-lithiation. Reproduced from [57] under the terms of the Creative Commons Attribution 4.0 License (CC BY 4.0). (d) Schematic of a chemically lithiated NMC cathode paired with a Si-based anode in a full cell (top) and structures of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ and lithiated $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (bottom). Reproduced from [14] with permission from The Royal Society of Chemistry. (e) X-ray diffraction patterns and structure (insets) of P'2- $\text{Na}_1[\text{Fe}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ obtained using ball milling with Na (top) and P2- $\text{Na}_{0.67}[\text{Fe}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ (bottom) and (f) voltage profiles (left) and discharge capacities (right) of $\text{Na}_x[\text{Fe}_{0.5}\text{Mn}_{0.5}]\text{O}_2/\text{hard carbon}$ full cells without pre-sodiation (green), with pre-sodiation (red), and with pre-sodiation and a Na_3P sacrificial additive (blue). Reproduced from [39] under the terms of the Creative Commons Attribution 4.0 License (CC BY 4.0).

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Reference annotations

6. Dewar et al. (*)

A pertinent review of the literature on pre-sodiation strategies for sodium-based energy storage cells, including sodium-ion batteries (SIBs).

13. Dose et al. (*)

This pioneering work introduces a chemical lithiation method for commercially relevant $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) cathodes using lithium naphthalene ($\text{C}_{10}\text{H}_8\text{Li}$) in tetrahydrofuran (THF) as the reducing reagent and lithium source.

14. Dose et al. (**)

Li_5FeO_4 (LFO) is demonstrated to be a highly effective sacrificial lithium-containing additive in $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC)/Si-graphite full cells, and shown to have synergistic effect towards NMC leading to less secondary particle cracking and surface reconstruction.

17. Jin et al. (*)

A pertinent review of the literature on pre-lithiation strategies for next-generation lithium-ion batteries (LIBs).

32. Du et al. (**)

This work builds on the innovative discovery of LiX/M nanocomposites (where $X = \text{O}, \text{F}, \text{S}$, and $M =$ transition metal, such as Mn, Fe, Co, Ni, etc.) as sacrificial lithium-containing additives first reported by Cui et al. – see refs.[21,23,25].

34. Han et al. (*)

The principal finding in this work is the stabilization of silicon anodes using $\text{M}(\text{TFSI})_x$ ($M = \text{Mg}, \text{Zn}, \text{Al}$, and Ca) electrolyte additives. Also of significance is the report of Li-rich layered oxide cathodes (e.g. $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$) as a dual-purpose lithium source and cathode material, where the irreversible electrochemical activation on the first cycle compensates for the lithium consumption at the Si anode.

38. Guo et al. (*)

Sodium peroxide, Na_2O_2 , is demonstrated to be an effective sacrificial sodium additive with high gravimetric and volumetric capacity. Na^+ release is accompanied by the release of O_2 gas without leaving deadweight/volume on the cathode.

44. Fernández-Ropero et al. (**)

Sodium mesoxalate, $\text{Na}_2\text{C}_3\text{O}_5$, is introduced as a sacrificial sodium additive leading to an impressive 4 times increase in the specific capacity of P2- $\text{Na}_{2/3}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Ti}_{0.1}\text{O}_2$ /hard carbon full cells, and synergistically promotes formation of a more effective cathode electrolyte interphase (CEI).

57. Betz et al. (**)

An innovative chemical lithiation synthesis approach using lithium metal in boiling pentanol is introduced for the pre-lithiation of the high voltage spinel cathode, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO). The method is simple, scalable, and the pre-lithiation amount is easily controllable.

58. Liu et al. (**)

This pioneering work independently introduces lithium naphthalene ($\text{C}_{10}\text{H}_8\text{Li}$) in tetrahydrofuran (THF) as a chemical lithiation synthesis approach for $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) cathodes.

59. Moez et al. (*)

These authors report an electrode-sodium metal direct contact method to pre-sodiate the sodium-deficient P2- $\text{Na}_{0.67}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode. This work builds on the seminal work of Tarascon and coworkers,[39] who reported an approach based on ball milling the cathode active material (CAM) with sodium metal to pre-sodiate Na-ion battery cathodes.