Stabilized Li$_3$N for efficient battery cathode prelithiation

Yongming Sun$^{a,1}$, Yanbin Li$^a$, Jie Sun$^a$, Yuzhang Li$^a$, Allen Pei$^a$, Yi Cui$^{a,b,*}$

$^a$ Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, United States
$^b$ Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, United States

**A R T I C L E   I N F O**

Keywords: Li$_3$N  
Cathode prelithiation  
Surface passivation  
Stability  
High capacity

**A B S T R A C T**

Li$_3$N can deliver more than 10 times the theoretical capacity of existing cathode materials and can serve as an excellent cathode prelithiation additive to offset the initial lithium loss in lithium-ion batteries. However, Li$_3$N has intrinsic problems of poor environmental and chemical stability in battery electrode processing environments due to its reactivity with moisture in ambient conditions and incompatibility with solvents used for battery slurry mixing. Herein, we report a facile route to prepare a surface-passivated Li$_3$N material by the reaction of lithium metal with nitrogen followed by an annealing process. A dense surface passivation layer consisting of crystalline Li$_2$O and Li$_2$CO$_3$ isolates the active composition of materials from air and thus enables good stability of Li$_3$N particles in ambient conditions. The as-prepared Li$_3$N powder is processable by slurry coating for electrode fabrication using a low-polarity solvent. The Li$_3$N is verified to work as a secondary lithium source to offset the initial capacity loss at the anode using a Li$_3$N/graphite cell configuration. A high “donor” lithium-ion specific capacity of 1761 mAh/g is achieved for a pristine Li$_3$N electrode. When Li$_3$N is included into cathodes, including LiCoO$_2$ (LCO), LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (NCM) and LiFePO$_4$ (LFP), the hybrid electrodes can be baked and calendared in ambient conditions, and, as expected, high prelithiation efficiency is achieved. As a typical example, with a 2.5% Li$_3$N additive, a LCO electrode delivers a 51 mAh/g higher capacity than that of the pristine LCO electrode in the first charge process and shows stable cycling behavior. The good stability and high prelithiation efficiency of the Li$_3$N powder enable its potential application in high-performance lithium-ion batteries.

1. Introduction

There is unrelenting demand for rechargeable lithium-ion batteries (LIBs) with higher energy density to address the ever-increasing energy needs of modern society for wide applications such as extended-range electric vehicles and grid-scale storage [1–4]. The electrodes of batteries largely decide their lithium storage capacity and energy density [5,6]. In existing lithium-ion technology, lithium is provided by lithium-intercalated cathode materials, such as LiCoO$_2$ (LCO), LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (NCM) and LiFePO$_4$ (LFP). Graphite has been as the most commonly used commercial anode material for LIBs since 1991 due to its high reversibility and low cost [7]. On the other hand, various alternative high-capacity anode materials such as silicon, with a theoretical capacity more than ten times that of graphite [8,9], have been well studied and have already shown promise in potential applications. The formation of a solid electrolyte interphase (SEI) layer on the anode surfaces is a critical process that occurs prior to regular battery operations and consumes a significant amount of lithium, irreversibly reducing the overall capacity of batteries. Graphite anodes exhibit an irreversible capacity loss of 5–10% from the initial battery charging process [10–14], while for high-capacity anode materials, the first-cycle lithium loss is even higher (e.g., 15–35% for Si) [15]. Such lithium loss in the so-called “formation process” appreciably reduces the energy density of LIBs.

Electrochemical prelithiation is an effective route to solve the issue of initial lithium loss in LIBs; however, it needs an extra process of electrochemical cell building [16]. To improve the overall energy density of LIBs, it is vitally important to pre-store lithium into electrodes to compensate the initial lithium loss by using high-capacity, low-cost, environment/dry air stable prelithiation materials. Currently, a wide range of prelithiation materials have been investigated, including anode and cathode prelithiation additives. Typical anode prelithiation materials are stabilized lithium metal [17,18] and lithium silicide powder [19–21]. Due to the high specific capacities of these anode additives (> 2000 mAh/g), the initial lithium loss of LIBs can be offset with just a small amount of additives. However, due to their low potential and high chemical reactivity, these high-capacity anode prelithiation additives have compatibility issues with common solvents,
ambient environments and thermal processing procedures involved in existing battery fabrication conditions. On the other hand, cathode pretreatment materials possess higher potentials and better chemical stability. In some early work, Li-rich compounds have been explored, such as Li4CoO4, Li2NiO2, and Li2MoO4 [22–25]. However, their lithium-ion donating capacities are limited (~300 mAh/g). Recently, we demonstrated that conversion reaction based nanocomposites (e.g., Li2O/metal, LiF/metal and Li2S/metal composites) could be attractive cathode pretreatment materials with high lithium-ion donating capacities in the range of 500~700 mAh/g, good stability and compatibility with existing battery processing conditions [26–28].

Binary lithium compounds (e.g., Li2O, LiF and Li3N) have much higher theoretical capacities than that of Li-rich compounds and other sacrificial lithium salts [29]. Among them, Li3N is an attractive cathode pretreatment material for LIBs, considering its high theoretical specific capacity (2309 mAh/g based on the reaction formula: 2Li3N → 6Li+ + 6e− + N2) and low theoretical decomposition potential (~0.44 V vs. Li+/Li) [30]. A large amount of Li can be extracted from Li3N during the “formation process” of batteries to offset the initial lithium loss. Very recently, the potential application of Li3N as a cathode additive for LiCoO2 (LCO) cathodes was investigated by blending LCO powder with ground commercial Li3N powder (Alfa Aesar) and coating ground commercial Li3N powder on top of pre-prepared LCO electrodes without using any solvent in an argon-filled glovebox [31]. In order to take advantage of the high pretreatment capacity of Li3N, two challenges must be overcome: (i) Pure Li3N has high chemical reactivity with moisture in ambient atmosphere; (ii) Li3N is not compatible with the widely used N-methyl-2-pyrrolidone (NMP) solvent in conventional slurry casting processes due to its high reactivity [31]. These two challenges make it difficult for Li3N to survive multiple processing steps in battery electrode fabrication, such as exposure to air, slurry mixing and baking, and electrode calendaring in ambient/dry air conditions. Therefore, it is highly desirable to design Li3N with improved stability, and explore suitable slurry manufacturing processes.

We have previously shown that the stability of lithium silicide anode pretreatment reagents can be improved through protection by either a Li2O shell [20] or a passivation layer consisting of LiF and lithium alkylcarbonate [19]. Very recently, we have reported that crystalline Li3O matrix enables excellent stability of Li3O in ambient air with 40% relative humidity [21]. We believe that a similar passivation layer of crystalline Li7O and/or other lithium compounds can help to improve the chemical and environmental stability of Li3N. Herein, we report a surface-passivated Li3N material made through annealing fresh Li3N in a nitrogen-filled glovebox with trace oxygen species. It is found that the reactivity of the Li3N is suppressed under ambient conditions after the surface passivation by a dense layer consisting of crystalline Li2O and Li2CO3. When a small amount of such Li3N powder was included into various cathodes (e.g., LCO, NCM and LFP) using slurry baking and electrode calendaring operations in ambient conditions, lithium was easily extracted from Li3N after the initial charge process and high prelithiation efficiency was achieved.

2. Materials and methods

2.1. Materials synthesis

Lithium metal foil (99.9%, Alfa Aesar, 0.75 mm thick) was used as the starting material for the synthesis of Li3N. During the synthesis, a piece of lithium metal foil (~1 g) was put in a nitrogen-filled glovebox. After 3 days, the lithium metal foil transformed into a Li3N flake, which was further heat-treated at 200 °C for 24 h. Li3N powder was obtained after grinding. To fabricate the Li3N film on a conducting substrate, lithium metal foil was first melted at 200 °C on a Cu foil. After the nitridation in a nitrogen-filled glovebox, the Li3N film was obtained.

2.2. Characterization

The X-ray diffraction (XRD) measurements were carried out on a panalytical Xpert diffractometer with Ni-filtered Cu Ka radiation (λ=1.5406 Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) of the samples were acquired on a FEI XL30 Sirion scanning electron microscope. A PHI Versa Probe 5000 system (Physical Electronics, MN) was employed for X-ray photoelectron spectroscopy (XPS) characterization. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) were performed on a FEI Titan 80–300 environmental TEM. The samples were maintained at a low temperature of ~100 K by a liquid nitrogen cryo-holder during the TEM and EELS measurements.

2.3. Electrochemical measurements

2032-type coin cells were assembled in an argon-filled glove box with concentrations of moisture and oxygen below 1.0 ppm for electrochemical characterizations using 1 M LiPF6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) as the electrolyte, and a Celgard 2300 membrane as the separator. Battery performances were investigated by galvanostatic charge/discharge cycling on an Arbin Battery Cycler instrument. A VMP3 potentiostat (Bio-Logic) was employed for cyclic voltammetry (CV) measurements at a scanning rate of 0.2 mV s−1. Both the Li3N film on a Cu foil and normal Li3N electrode fabricated by a slurry method were subjected to electrochemical measurements. To prepare the pristine Li3N electrode, Li3N powder (60%), carbon black (30%) and polyvinylidene fluoride (PVDF, 10%) were dispersed uniformly in tetrahydrofuran (THF) to form a slurry.

All the cathodes with the addition of Li3N were constructed using a slurry method by mixing the Li3N powder, cathode materials, carbon black and PVDF binder at different weight ratios in THF solvent. The slurry was cast onto an Al foil. The cathodes were baked and calendared in ambient conditions. The contents of carbon black and PVDF are both 5% in weight in LiCoO2 (LCO) cathodes. The as-prepared LiFePO4 (LFP) and LiNi0.4Co0.05Mn0.12O2 (NCM) cathodes contain 10% carbon black and 10% PVDF. The typical mass loading of cathodes is ~4 mg/cm². Graphite electrodes consist of 80% graphite powder (MTI Corporation), 10% carbon black and 10% PVDF.

The lithium metal half cells of Li3N film electrode on Cu foils were charged to 3.5 V at a current density of 0.1 ma/cm². Li3N/Li and Li3N/graphite cells were charged to 4.8/4.5 V at a current density of 30 ma/g. The galvanostatic charge/discharge measurement of LCO and NCM/ Li metal half cells was carried out with the cut-off potential range of 3.2~4.5 V for the first cycle at 0.1 C and 3.2~4.3 V upon the following cycles at 0.2 C. The cut-off potential range for LiFePO4/Li half metal cells is 2.5~4.5 V for the first cycle at 0.1 C and 2.5~4.2 V for the subsequent cycles at 0.2 C. The specific capacities here are calculated based on the mass of the cathode active materials. To protect samples from moisture and other reactive gases in ambient air, samples for XPS, SEM and TEM characterizations were loaded onto the sample holders, sealed in the Argon-filled glove box, and then quickly transferred into the chambers of the equipments.

3. Results and discussion

We present a simple and easily scalable synthetic route for the preparation of surface-passivated Li3N (Fig. 1a). During the synthesis, pristine lithium metal foil was left in a nitrogen-filled glovebox with trace oxygen. The reaction between lithium metal and nitrogen gas to form Li3N occurred spontaneously. After 3 days of exposure, the color of the lithium foil changed from white to black. As verified by XRD, the starting lithium metal was completely converted to a pure phase of alpha-Li3N after the reaction with nitrogen (Fig. S1). The black Li3N
Y. Sun et al.  

Fig. 1. Fabrication of Li₃N and XRD characterizations. (a) Synthesis of Li₃N material via nitridation of lithium metal in N₂ atmosphere and annealing processes (200 °C, 24 h). (b, c) XRD results of the as-prepared Li₃N flake (b) and powder after grinding (c). The XRD result shows that the as-formed Li₃N flake is pure alpha-phase Li₃N. After grinding, the product contains a small portion of beta-phase Li₃N. The XRD peaks at 21° arise from the Kapton tape.

Electrochemical investigations were carried out on Li₃N electrodes to test the performance of the as-fabricated Li₃N powder alone. A slurry casting process was employed to fabricate the Li₃N electrodes using the surface-passivated Li₃N powder and a low-polarity tetrahydrofuran (THF) solvent. The as-prepared Li₃N electrodes exhibit a decomposition potential above 4 V. Impressively, a high specific capacity of 1761 mAh/g is achieved with a charge cut-off potential of 4.8 V, which is ~10 times that of current cathode materials. When the charge cut-off potential is limited to 4.5 V, the specific capacity still reaches 1163 mAh/g (Fig. 3a). This extremely high “donor” capacity demonstrates that although a small amount of capacity is sacrificed to form a passivation layer on the surface of Li₃N, the final capacity of the surface-passivated Li₃N can be improved relative to the pristine Li₃N.
and its unannealed counterpart (Fig. S4) due to its better stability. Meanwhile, cyclic voltammetry (CV) measurements were also performed for Li₃N electrodes. Consistent with the potential profile, a strong oxidation peak starting from 4.30 V is clearly observed (Fig. 3b), suggesting the high decomposition potential of Li₃N electrodes. This high decomposition potential of Li₃N electrodes compared to 0.9 V in the literature study[31] may be caused by the insulating nature of the surface passivation layer on Li₃N formed during the material processing.

To investigate the effects of the passivation layer formed during the material annealing, grinding and/or slurry manufacturing processes on the decomposition potential of Li₃N, Li₃N film electrodes on a metal current collector were prepared by the nitridation of lithium metal films on Cu foils. The Li₃N particles formed on Cu foils are interconnected with each other and have sizes similar to that of the annealed and passivated Li₃N powder (200–300 nm, Fig. 3c).

Without the annealing processes and other operations involved in the slurry casting processes which lead to form a passivation layer, the Li₃N film on Cu electrodes show a much lower decomposition potential (~1.15 V) than that of Li₃N electrodes fabricated using Li₃N powder with a slurry manufacturing process (Fig. 3d). Thus, surface passivation of Li₃N increases the decomposition potential, likely due to the slow kinetics of the passivation layer. A cathode prelithiation material is normally mixed with cathode active materials, binder and carbon black to fabricate cathodes. The working principle involves extracting the stored lithium from the additive on the cathode side and transferring it to the anode side to compensate the initial lithium loss. To confirm the lithium compensation effect of the as-synthesized Li₃N powder, an electrochemical cell was constructed with a Li₃N cathode and a graphite anode. Fig. 3e displays the charge potential profile of a Li₃N/graphite cell. A potential slope between 2.5 and 3 V is observed, corresponding to the formation of SEI on the graphite surface. After further charging to a higher potential, the graphite electrode is lithiated by the lithium from Li₃N, and an lithium intercalation product (LiC₁₂) is confirmed by the XRD pattern (Fig. 3f). This result indicates that during the battery charging process, the as-prepared Li₃N can be an...
effective cathode prelithiation material to offset the lithium loss at the anode surface caused by the formation of SEI and/or other side reactions.

After confirming the lithium compensation effect of the as-synthesized Li$_3$N material, we investigated the electrochemical performance of LCO cathodes with the addition of various amounts of Li$_3$N powder. A slurry casting process was used to prepare the hybrid cathodes so that Li$_3$N powder could be uniformly distributed throughout the electrodes. The electrode baking and calendaring processes were carried out in ambient atmosphere before battery assembly. The galvanostatic charge/discharge measurement of LCO cells was carried out with the cut-off potential range of 3.2–4.5 V for the first cycle (formation process) at 0.1 C to maximize the amount of lithium extracted from Li$_3$N, and 3.2–4.3 V upon the following cycles at 0.2 C to achieve good cycling performance. Compared with the pristine LCO electrode, the potential profile of the LCO cathode with Li$_3$N additive extends above 3.8 V in the charge process, arising from the decomposition of Li$_3$N during charging (Fig. 4a). With the addition of 2.5% Li$_3$N, the initial charge capacity of the LCO cathode reaches 246 mAh/g, 51 mAh/g higher than the pristine LCO electrode. This increased capacity corresponds to 1782 mAh/g from Li$_3$N, indicating that high utilization of Li$_3$N is achieved in LCO cathodes. When 5% Li$_3$N is included into a LCO electrode, the cathode delivers a even higher initial charge capacity of 291 mAh/g with an extra Li-ion capacity supply of 96 mAh/g from Li$_3$N. Furthermore, after the initial cycle, both the LCO electrodes with and without Li$_3$N display similar discharge capacities (based on the mass of LCO, ~150 mAh/g) and stable cycling (Figs. 4b and S6). This good cycling performance confirms that the Li$_3$N additive does not have obvious negative effects on the stability of cathodes, although the decomposition of micrometer-size Li$_3$N produces a small amount of “holes” in the electrodes due to the evolution of nitrogen. The nitrogen gas caused by the Li$_3$N additive during the first cycle can be easily removed before the battery is sealed, which is accepted in a real battery system. To show the generality of using Li$_3$N as a prelithiation additive for various cathodes, we also prepared NCM and LFP cathodes with Li$_3$N additives using the same electrode fabrication procedures. As expected, their initial charge capacities increase significantly. The initial charge capacity of a NCM electrode with 2.5% Li$_3$N is 273 mAh/g, while a pristine NCM electrode delivers an initial charge capacity of 229 mAh/g (Fig. 4e). After adding 2.5% Li$_3$N in a LFP electrode, the first charge profile shows two obvious plateaus. The first plateau is around 3.48 V with a capacity of ~170 mAh/g, while the second plateau is around 4.1 V, delivering a capacity of 62 mAh/g, corresponding to the extraction of Li from Li$_3$N (Fig. 4d).

4. Conclusions

In summary, surface-passivated Li$_3$N powder was prepared through a spontaneous chemical reaction between lithium metal and nitrogen, followed by an annealing process in a nitrogen filled glovebox with trace oxygen species. The surface passivation layer of Li$_3$N particles consists of dense and highly crystalline Li$_2$O and Li$_2$CO$_3$, which imparts good environmental stability and an increased electrochemical decomposition potential. Electrochemical extraction of lithium from a Li$_3$N electrode was confirmed by characterizing a cell with a Li$_3$N cathode and a graphite anode. The as-synthesized Li$_3$N exhibits a high OCV (1.16 V vs. Li$^+/Li$) and a high lithium-ion donating specific capacity of 1761 mAh/g. Electrodes using typical cathode active materials and Li$_3$N additives were prepared through a slurry casting process. LCO cathodes with 2.5% and 5% Li$_3$N additive show increased first-cycle charge capacities, 51 mAh/g and 96 mAh/g higher than that of the pristine LCO counterpart (with an initial charge capacity of 195 mAh/g), supporting the high prelithiation effectiveness of Li$_3$N. The stable cycling of the LCO cathodes with Li$_3$N additives indicate that the synthesized Li$_3$N has negligible effects on the cycling stability of the cathode material. Additionally, our Li$_3$N powder can serve as a...
universal prelithiation material for various cathode materials. High prelithiation efficiency of the Li3N powder is also achieved for NCM and LFP electrodes. The facile synthesis, high “donor” Li-ion specific capacity, and good stability in battery electrode fabrication processes make the as-prepared Li3N suitable for potential application in LIBs to offset the first-cycle lithium loss and thus improve the overall battery energy density.

Acknowledgements

Y.C. acknowledges the support from the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under the Battery Materials Research (BMR) Program. A.P. acknowledges the support from the U.S. Department of Defense through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program and from Stanford University through the Stanford Graduate Fellowship (SGF) Program.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ensm.2016.10.004.

References

[17] C.R. Jarvis, M.J. Lain, M.V. Yakovleva, Y. Gao, A prelithiated carbon anode for...