

Towards New Negative Electrode Materials for Li-Ion Batteries: Electrochemical Properties of LiNiN

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Since their first commercialization by Sony in 1991,¹ lithium-ion batteries have become the primary power source of choice in applications where high energy densities (i.e., energy provided per mass unit) are required, such as portable devices. However, the fact that their performance, in terms of energy and, especially, power density, requires continuous improvement has encouraged ever-greater scientific efforts toward the search for new materials that could replace the current state-of-the-art materials. Moreover, in view of the recent recall of millions of lithium-ion cells by battery manufacturers, the need for alternative and safer materials has re-emerged. Because of the heat of reaction between electrode materials and electrolytes depending on the negative electrode potential, one possible avenue to increase safety would be the use of higher potential negative electrode materials.²

Lithium transition metal nitrides were first proposed in the 1990s as alternative materials for negative electrodes in lithium-ion batteries. Among them, $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ has received much attention as a result of the very high specific capacity values that can be achieved (typically 700–800 mA·h/g^{3,4}) at somewhat higher voltages than those used for carbonaceous electrodes. This compound is isostructural with Li_3N and exhibits a hexagonal layered structure with alternating $[\text{Li}_2\text{N}]$ and (Li,Co) planes. Other structurally related $\text{Li}_{3-x}\text{M}_x\text{N}$ phases with $\text{M} = \text{Fe},^5 \text{Cu},$ and $\text{Ni},^{3,6}$ have been described and successfully tested in lithium batteries.

Our recent investigations in the $\text{Li}_{3-x-y}\text{M}_x\text{N}$ systems ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$) reveal the possibility of preparing phases with

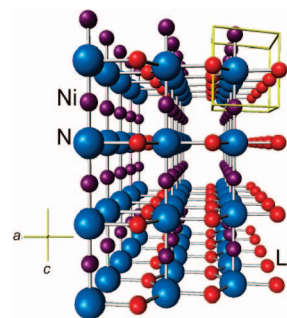


Figure 1. Perspective plot of the layered structure of LiNiN.

significant levels of lithium vacancies (denoted as “y”) in the $[\text{Li}_2\text{N}]$ plane.^{7–11} The highest value of y is found in LiNiN ($x = 1$, Figure 1), for which up to one lithium vacancy per formula unit is present in the planes.^{12–14} Previous studies showed that these vacancies are ordered (leading to a change in hexagonal space group symmetry from $P6mm$, as for Li_3N , to $P\bar{6}m2$ in LiNiN). This defect structure leads to significant Li diffusion within the planes, and in LiNiN is coupled with metallic conductivity as Li is completely substituted by Ni between Li–N layers. These factors invite us to consider questions as to whether the properties of LiNiN as electrode material in lithium-ion batteries could be interesting.

Lustrous green-black powders of LiNiN were synthesized by heat treating Li_3N and nickel foil at 730–750 °C for 7 days following a method described previously.^{13,14} The polycrystalline nitride was characterized by powder X-ray diffraction (XRD) and shown to be single phase with identical diffraction patterns to materials described previously (see Supporting Information).^{13,14}

The electrochemical properties of LiNiN as electrode material in lithium batteries were tested galvanostatically against Li metal, using a rate of C/20. Upon initial discharge of the cell, a capacity equivalent to 0.6 mol Li per mol LiNiN, corresponding to 160 mA·h/g, could be obtained reversibly between 0 and 1 V (Figure 2), mostly and most likely coming from intercalation in the cationic vacancies of the structure, as was previously described by other authors in the $\text{Li}_{3-x-y}\text{M}_x\text{N}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$) system.^{6,15,16} It is worth noting that the amount of lithium exchanged via this process is noticeably larger than that obtained for other very recently

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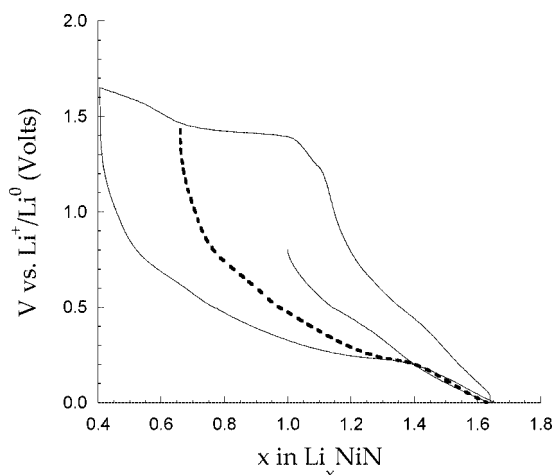


Figure 2. Voltage vs composition plot of the first discharge-charge cycle and the second discharge of an electrochemical cell containing lithium and LiNiN as electrodes, cycled at C/20 between 0 and 1.65 V (continuous line). The broken line depicts the second discharge if the charge cutoff voltage is set at 1.45 V instead of 1.65 V.

reported $\text{Li}_{3-x-y}\text{Ni}_x\text{N}$ phases,¹⁶ in which a maximum of 0.6 cationic vacancies was found.

During this discharge-charge process, the voltage decreases and increases monotonically, suggesting that lithium is intercalated (and deintercalated) following a single-phase mechanism.¹⁷ This hypothesis was confirmed by electrochemical potential spectroscopy (EPS) measurements,¹⁸ a close-to-equilibrium technique that provides information on the reaction mechanism with lithium (see Supporting Information for further details on the technique). The chronoamperometric response of LiNiN (Figure 3a) is consistent, both on reduction and upon oxidation, with that expected from a regime under the Cottrell law of diffusion ($1/t^{1/2}$ dependence). This indicates that the kinetics of the reactions taking place are dominated by the lithium diffusion in the material, implying the existence of a $\text{Li}_{1+x}\text{NiN}$ solid solution and, most probably, the filling of the vacancies.

When the battery is charged beyond the starting voltage, lithium can also be extracted, giving rise to a series of complex processes. First, a plateau at 1.40 V extends up to $x = 0.6$ in Li_xNiN , where a change in the slope takes place and a new process develops up to approximately 1.6 V and $x = 0.4$. After that, there is a sharp increase in voltage up to 3.8 V, followed by a very long plateau-like region. However, given that, at this point, $x < 0$, this capacity must arise from other processes (product decomposition, reaction with the electrolyte) that are not associated with an exchange of lithium in the compound (see Figure S2 in Supporting Information).

The reversibility and effects of the processes around 1.4 and 1.6 V were further evaluated by using 1.45 and 1.65 V as the cutoff voltage in two different electrochemical cycling

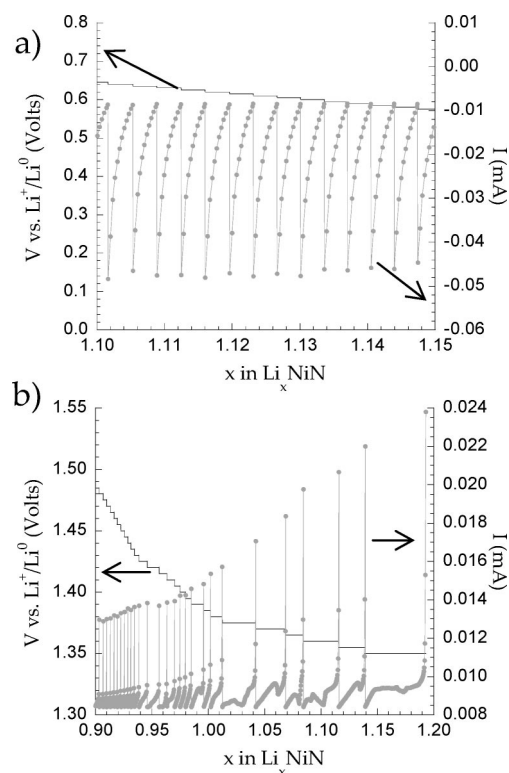


Figure 3. Evolution of lithium content and intensity during potentiometric cycling (see experimental details in text) of an electrode containing LiNiN against lithium metal: (a) close-up of the first discharge of the cell down to 0 V; (b) close-up of the first charge up to 1.50 V.

experiments (Figure 2). The profile upon the second reduction looks, in both cases, drastically different from that of the first oxidation, as the voltage decreases steadily down to 230 mV, when a small pseudo-plateau appears before it finally goes down to 0 V. This behavior is similar in both cases, suggesting that the major changes occur in the 1.4 V plateau. Similar voltage profiles, both on oxidation and on reduction, were reported for $\text{Li}_{3-x-y}\text{M}_x\text{N}$ phases with $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$, and Cu ,^{3-6,15} with a long plateau (at voltages ranging from 1.1 to 1.4 V, depending on the metal) upon the first oxidation, and a process around 200–300 mV upon the subsequent reduction. More specifically, the profile for $\text{M} = \text{Ni}$ is very similar to the one we obtained for LiNiN, suggesting that the redox processes taking place in both phases are very similar. Previous XRD measurements^{3,4,6,19} have shown that, for these phases, the oxidation process leads to an amorphization of the sample, which is thought to be the origin of the drastic differences between the first oxidation and the second reduction profiles. Our EPS experiments provide additional evidence for the formation of, at least, one new phase during this plateau. We observe a stabilization of the potential around 1.35 V and a current response that does not follow a Cottrell-like behavior (Figure 4b), which would be consistent with a two-phase mechanism, and kinetics that are dominated by the processes at the interface between the initial phase and the new one(s) formed. Further studies, in situ and ex situ, to characterize the structure of the different phase(s) formed both on reduction and upon oxidation are currently underway.

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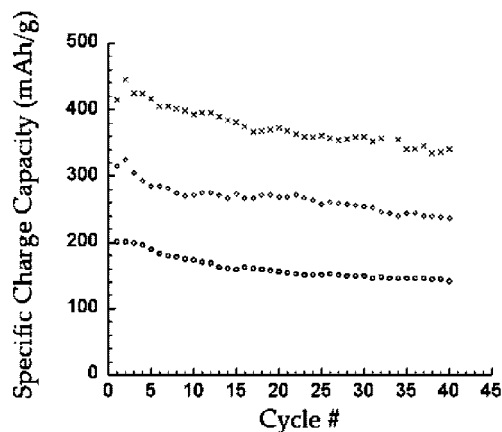


Figure 4. Specific charge capacity vs cycle number of LiNiN when tested galvanostatically as electrode material against lithium, at C/20 rate between 0 and 1.3 V (circles), 1.45 V (diamonds), and 1.65 (crosses).

The amount of lithium recovered after the second discharge is 1.2 (equivalent to 420 mA·h/g or 1260 mA·h/cm³) and 1 mol Li/mol LiNiN (equivalent to 325 mA·h/g or 975 mA·h/cm³), when the cutoff was set at 1.65 and 1.45 V, respectively. In both cases, it is almost the same as that extracted on the first oxidation. These values are similar or higher than the theoretical capacity of a carbonaceous electrode (372 mA·h/g or 837 mA·h/cm³),²⁰ the material that is most commonly used in Li-ion batteries at present. Furthermore, they are, in general, higher than those reported by several authors for Li_{2.5-y}Ni_{0.5}N, the only member of the Li_{3-x-y}Ni_xN that has been studied extensively.^{3,6} Around 200 mA·h/g (0.5 mol Li/mol Li_{2.5-y}Ni_{0.5}N) were reported for a sample prepared using a similar synthetic method when cycled between 0 and 1.4 V. The higher amount of lithium (i.e., specific capacity) that can be deintercalated from LiNiN seems to be associated to the increased Ni content, which can charge-compensate the reactions that take place. Interestingly, the capacity of Li_{2.5}Ni_{0.5}N was increased to approximately 500 mA·h/g when the sample was prepared by high energy mechanical milling (HEMM),²¹ suggesting that this could be a path to improve our results with LiNiN.

The extended cycling properties of LiNiN as an electrode were tested galvanostatically, always starting with a discharge of the cell, between 0 V and 1.3, 1.45, and 1.65 V, to probe the effect of each electrochemical process on the cyclability. The specific gravimetric (volumetric) capacity values after 40 cycles for each window are 142 mA·h/g (426 mA·h/cm³), 237 mA·h/g (711 mA·h/cm³), and 341 mA·h/g (1023

mA·h/cm³), respectively. Despite the existence of a process that implies electrode reorganization, such as that at 1.4 V, the retention when using the larger voltage windows is good, around 80%. Unfortunately, no extended cycling was reported for Li_{2.5-y}Ni_{0.5}N made by solid state synthesis. On the contrary, the retention after 50 cycles reported for the sample made by HEMM, 78% of the capacity in the second cycle, is somewhat lower than ours,²¹ given that the drop between the first and the second cycle is considerable.

When using a more restricted window, the initial drop (after 15 cycles) is higher, but the specific capacity value subsequently stabilizes around 130 mA·h/g, and up to 100 cycles can be made with a remarkably small loss (see Figure S3 in the Supporting Information). The values obtained in this window are comparable with those recently reported for samples in the Li_{3-2x}Ni_xN system (containing substantially less Ni¹⁶) and for Li₄Ti₅O₁₂,^{22,23} a compound with a strong technological interest which, nonetheless, has to be cycled at higher potentials (typically between 1 and 2.5 V). When used in a full battery, this leads to a lower overall voltage of the cell, thus affecting its power output.

Given these results, we can state that the electrochemical performance of LiNiN is very promising, and further improvements can be envisaged by changing the reaction conditions and the processing of the electrode. Additional work is in progress to rationalize the changes undergone by the electrode upon lithium insertion/removal and how such changes might influence the electrochemical performance. The results above also strongly suggest that lithium transition metal nitrides have appreciable potential as negative electrodes in lithium batteries, giving rise to high capacities at low voltages (below 1.7 V).

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Supporting Information Available: Experimental details, experimental and theoretical XRD patterns, and figures showing the electrochemical performance of LiNiN when cycled up to 4 V and the extended cycling of the compound in the 0–1.3 V window (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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