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The effect of cationic disordering on the electrochemical performances of the layered nitrides $LiWN_2$ and $Li_{0.84}W_{1.16}N_2$

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Abstract

The layered nitrides $LiWN_2$ and $Li_{0.84}W_{1.16}N_2$ are investigated related to their electrochemical performances as possible electrodes for rechargeable lithium batteries. In the case of $LiWN_2$, for which Li and W atoms are ideally ordered in alternating Li and W layers, de-intercalation of lithium proceeds up to 50%. The de-intercalated lithium can be intercalated again subsequently. The reversible reaction is the origin of the high cyclability observed in the corresponding lithium cells. On the other hand, in $Li_{0.84}W_{1.16}N_2$ the Li layers are statistically occupied by tungsten (16%) and lithium (84%). A clear effect of the disordered cationic occupation on the electrochemical behaviour has been found, since for $Li_{0.84}W_{1.16}N_2$ a very low extraction rate is obtained during the first oxidation (0.03 Li per formula unit). In addition, cyclability is rather poor. The very different electrochemical behaviour is explained by the structural differences between both layered nitrides.

Keywords: Powders-solid state reaction; X-ray methods; (Layered) Nitrides; Batteries; Lithium intercalation

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1. Introduction

For many years research on lithium battery materials has been focused on oxides. Nevertheless, other types of materials have been found to be of interest for such application. Nitrides have been subject of research due to the similarity between the oxide and the nitride ions regarding size, polarisability, electronegativity and its structural chemistry. Among them, some $Li_{3-x}M_xN$ derivatives were proposed as high energy density anode materials.[1,2] The case of $LiMoN_2$ is quite interesting in as much as it is a metallic layered nitride containing lithium. It is not surprising that the electrochemical performances were also investigated.[3] However, the electrochemical characterization showed that de-intercalation of lithium was not reversible. Structural reasons may be at the origin of the observed behaviour.

In recent years new ternary nitrides AMN_2 (A = Li, M = Mo, W) have been synthesized.[3–5] The structures of these layered nitrides are built up from alternating layers of AN_6 octahedra and MN_6 trigonal prisms. For lithium metal (M) nitrides (M = Mo, W), two stacking variants are observed, in which the nitrogen atoms form a close-packed array. $Li_{0.84}W_{1.16}N_2$ adopts the anti-titanium phosphide type structure (Fig. 1a) with the space group $P6_3/mmc$ and $a = 2.8809(1)$ Å, $c = 10.3456(4)$ Å. It is described as a stacking AbAγBaBγ of close-packed nitrogen layers (AABB) with cations in octahedral (γ) and trigonal prismatic (a and b) holes. The octahedral holes are statistically occupied by tungsten (16%) and lithium (84%), whereas the tungsten atoms occupy the trigonal prismatic holes, in agreement with its chemical formula.[5] Only edge-sharing M-O_6 polyhedra are found. A second variant is observed for the isostructural $LiMoN_2$[3] and $LiWN_2$[4] (Fig. 1b). The space group is $R3$ with $a = 2.868$ Å, $c = 15.787$ Å and $a = 2.863$ Å, $c = 15.608$ Å, respectively. Both show an AbAγBcBαCaCβ stacking of close-packed nitrogen layers (AABBCC) with edge-and face-sharing metal-centered polyhedra. $LiWN_2$ shows the ideal layered structure, in which the octahedral holes are occupied by lithium and the trigonal prismatic holes by tungsten. A scheme of the stackings observed in the lithium metal nitrides $LiMN_2$ (M = Mo, W) is given also in Fig. 1. The AABBCC stacking in $LiMN_2$ (M = Mo, W) comprises six close-packed nitrogen layers, whereas four analogous nitrogen layers are needed to reproduce the AABB

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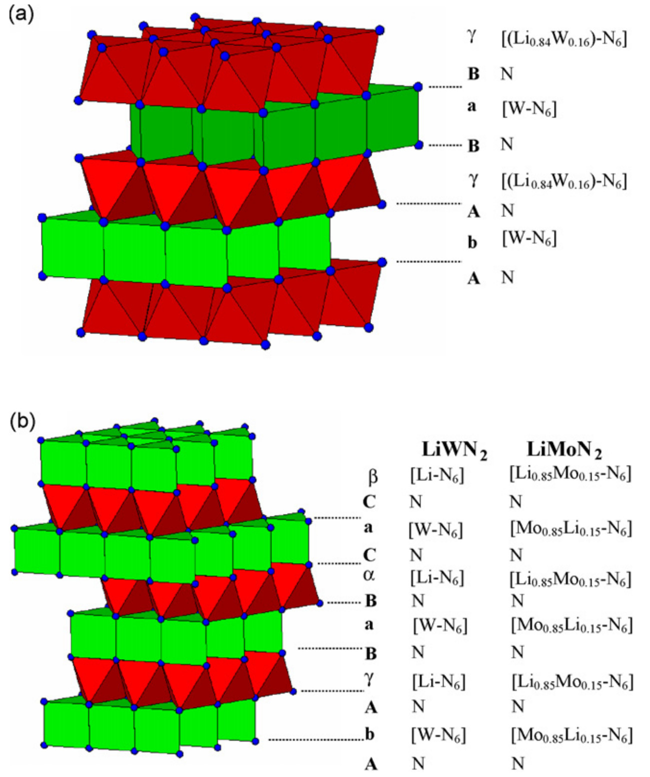

Fig. 1. Structures of $Li_{0.84}W_{1.16}N_2$ (a) and isostructural $LiMoN_2$ and $LiWN_2$ (b). The different stacking of close-packed nitrogen layers is indicated (capital letters).

stacking in $Li_{0.84}W_{1.16}N_2$. As a consequence, with the stacking always along the [0 0 1] direction, the c-axis of the latter (10.3456 Å) is only two third the value of the former (15.608 Å in $LiWN_2$).

$LiMoN_2$, however, presents cation anti-site defects. Both the octahedral and the trigonal prismatic holes are statistically occupied by molybdenum and lithium. The cation distribution in the octahedral layers with molybdenum (15%) and lithium (85%) is very close to that observed in $Li_{0.84}W_{1.16}N_2$. According to its chemical formula, however, the trigonal prismatic holes in lithium molybdenum nitride have also a statistical occupation, in contrast with $Li_{0.84}W_{1.16}N_2$, by molybdenum (85%) and lithium (15%).

The formula, taking this characteristic into account, is $(Li_{0.85}Mo_{0.15})_{oct}$ $(Mo_{0.85}Li_{0.15})_{tp}N_2$. The presence of Mo in the Li layer is indicated as responsible for the poor electrochemical performance of $LiMoN_2$.[3] The effect of cationic disordering in layered material has been investigated extensively in the case of oxides such as $LiNiO_2$. This well known electrode material has to be prepared under controlled conditions in order to avoid even a very small degree of cationic disordering that affects the electrochemical cycling behaviour [6,7] drastically.

We have investigated the possibility of extracting lithium from both $LiWN_2$ and $Li_{0.84}W_{1.16}N_2$ by electrochemical methods. For this purpose, the nitrides have been used as the positive electrodes in lithium batteries and their electrochemical performances are presented. Although materials with such high formula weight have scarce possibilities to be useful as electrode materials, the comparison of the electrochemical behaviour between ordered ($LiWN_2$) and disordered layered phases ($LiMoN_2$ and $Li_{0.84}W_{1.16}N_2$) is interesting.

2. Experimental

The ternary nitride $LiWN_2$ was obtained following the method described by Kaskel et al.[5] consisting in the ammonolysis reaction:

$$Li_2CO_3 + 2WO_3 + 6NH_3 \rightarrow 2LiWN_2 + CO_2 + 7H_2O + N_2 + 2H_2$$

A powdery mixture of Li_2CO_3 and WO_3 in a 0.5/1 ratio was heated at 700 °C for 12 h under flowing ammonia. After slowly cooling down to room temperature the sample was ground and treated under the same conditions once more.

In the case of $Li_{0.84}W_{1.16}N_2$, the same general procedure and ratio of the reagents Li_2CO_3 and WO_3 was used, the difference being the temperature of reaction; a higher temperature, 900 °C, was used.

Structural characterisation of parent nitrides were done by using a *Siemens D5000* diffractometer in transmission mode with Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å). A rotating (15 rpm) air tight sample holder was charged in an argon filled glove box to prevent decomposition.

Electrochemical measurements were performed using two electrode Swagelok cells. A disk of Li metal was used as both the counter and the reference electrodes and a 1 M solution of $LiPF_6$ in EC/DMC (1:1 v/v, Merck LP30) as the electrolyte. The working electrode was fabricated by mixing the corresponding nitride with carbon black (Super S, MMM Carbon, Belgium) and Kynarflex 2801® (Elf-Atochem). A typical ratio of nitride, C and binder was 87:10:3 (w/w). The cells were assembled in an argon filled glove box and afterwards connected to a MacPile battery tester. Galvanostatic experiments were carried out at 0.1 mA/cm^2 current density.

3. Results and discussion

A black powder was obtained after the ammonolysis reaction at 700 °C. The corresponding powder X-ray diffraction pattern was indexed in the rhombohedral system (S.G. *R*3) with lattice constants: $a = 2.874(2)$ Å and $c = 15.62(2)$ Å, in good agreement with the results reported for $LiWN_2$ by Herle et al.[4]

Further, treatment of $LiWN_2$ at 900 °C produced a dark grey powder. The corresponding pattern was indexed in the hexagonal system (S.G. $P6_3/mmc$) with lattice constants $a = 2.859(6)$ Å and $c = 10.33(2)$ Å, in agreement with the lattice constants reported for $Li_{0.84}W_{1.16}N_2$ [5] ($a = 2.8820(4)$ Å, $c = 10.333(2)$ Å).

The electrochemical behaviour of $LiWN_2$ was first investigated by charging a cell from the rest potential (ca. 2.5 V) to 4.8 V. Fig. 2 shows the result as a typical voltage composition curve. On charge and using our experimental conditions, a capacity of ca. 67 mA/g can be reached. The quantity of lithium involved in this reaction is close to 0.55 Li per formula unit. A similar quantity (ca. 0.65 Li/formula) was found in the case of

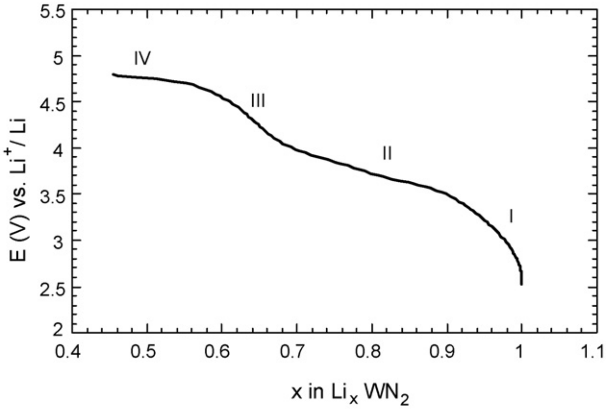

Fig. 2. Voltage-composition curve of a $LiWN_2$/Li cell charged to 4.8 V.

$LiMoN_2$[3] during the first oxidation, although the corresponding capacity values were almost twice due to the much lower formula weight of $LiMoN_2$.In the voltage-composition profile, four regions, labeled as I–IV in Fig. 2, can be distinguished. Each of them is due to different oxidative processes during the deinsertion reaction. As it is well documented, the voltage in an electrochemical cell should be constant in a two-phase region, and the observed plateau is due to a first order transition.[8] In practice, kinetic effects generally cause the voltage to decrease slightly through the two-phase region. On the other hand, a continuous phase transition (without phase coexistence) is characterized by a steadily variation of the cell voltage over the whole compositional range of the solid solution formed.[9] The voltage drop observed in Fig. 2 in regions I and III seems to indicate that a solid solution is formed in each of the corresponding compositional ranges. On the other hand, the flatter profiles observed in regions II and IV are apparently due to the existence of two-phase regions.

After the first charge up to 4.8 V the cell was discharged down to a voltage for which the total capacity was recovered. This was reached at ca. 1 V, as it can be seen in Fig. 3, which shows the variation of capacity upon cycling. However, it can also be seen that on discharge a large drop of potential is followed by a steady decrease. No relevant feature is observed in the discharge curve. Besides, note that the shape of the curve obtained on charge is quite different from that obtained on discharge.

Further cycling of the cell shows that the capacity is well maintained after the first cycle (see Fig. 3). It is interesting to note that a difference between the charging process and the discharging process is still observed. Discharging curves are identical while charging curves are different to that developed during the first charge. However, the high voltage plateau is present in both the first and the rest of charging curves pointing perhaps to a side reaction (i.e., oxidation of the electrolyte). A plateau at high voltage (4.1 V) was also reported by Elder et al.[3] The large difference between the voltage of this plateau and the stability of the $LiClO_4$-based electrolyte (4.6 V) used by Elder et al.[3] allowed the assignment of the 4.1 V-plateau to the irreversible oxidation of $LiMoN_2$. In our case the difference between the plateau observed at ca. 4.8 V, and the stability of the electrolyte, ca. 5.0 V, is smaller and the assignment of the plateau to oxidation of the tungsten nitride cannot be unequivocally made. However, another experimental observation points to this plateau as being related to the active material. The capacity developed in the high voltage plateau is needed to account for the total discharge capacity (see Fig. 3). Besides, if the upper cut off voltage is lowered from 4.8 to 4.4 V (in order to avoid the reaction that takes place during the high voltage plateau), the reversible capacity also decreases and no improvement in cyclability can be observed (see Fig. 4).

The electrochemical behaviour shown in Fig. 4 is significant in comparing to data reported for $LiMoN_2$.[3] For the molybdenum case, the behaviour between the rest potential and 4.2 V indicated that extraction of lithium at 3.8 V produces a delithiated product that is irreversibly oxidized at 4.1 V. Reduction of the delithiated product also showed the irreversibility of the reductive process. For the tungsten case, oxidation also occurs between 3.5 and 4 V (region II in Fig. 2) but it can proceed up to higher voltage without irreversible oxidation. On the other hand, the delithiated product can be reduced reversibly.

The differences found between the electrochemical behaviour of $LiMoN_2$ and $LiWN_2$ are quite significant and

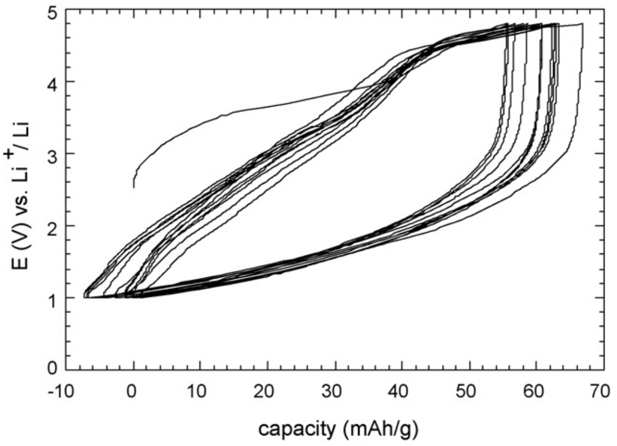

Fig. 3. Cycling of a $LiWN_2$/Li cell as a voltage–capacity curve between 4.8 and 1 V.

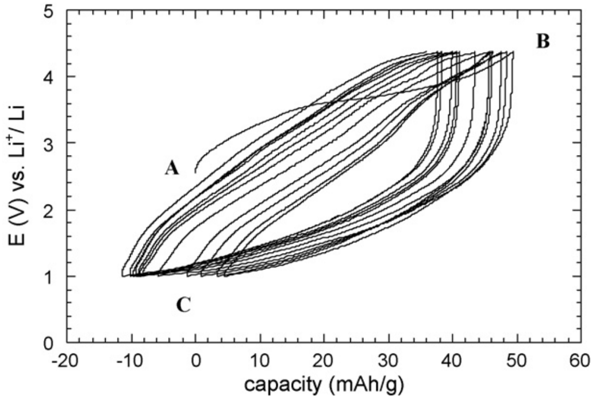

Fig. 4. Cycling of a $LiWN_2$/Li cell as a voltage–capacity curve. The upper cut-off voltage was limited to 4.4 V. For further structural studies cells are stopped on charge at 4.4 V (label B) and on discharge at 1 V (label C) (see also text).

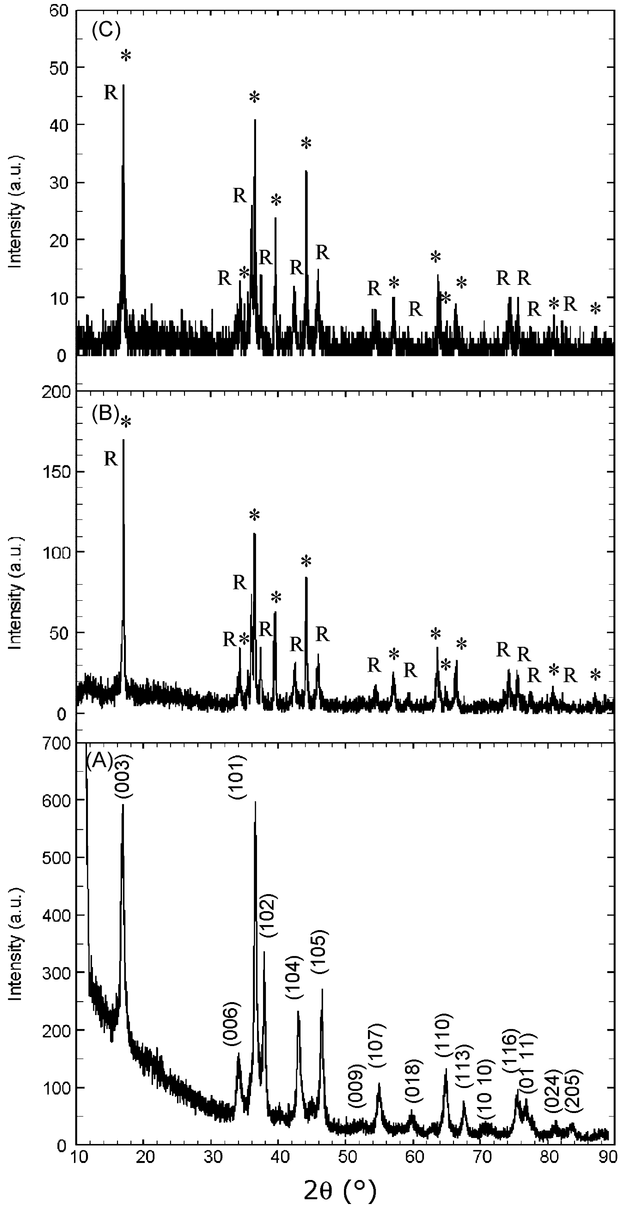

Fig. 5. XRD patterns recorded for pristine $LiWN_2$ (A), $LiWN_2$ charged to 4.4 V (B) and afterwards discharged to 1 V (C) (see also text and Fig. 4). *R*: rhombohedral $LiWN_2$; (*) second phase indexed based on a hexagonal cell: $a = 2.9276(3)$ Å; $c = 10.450(2)$ Å.

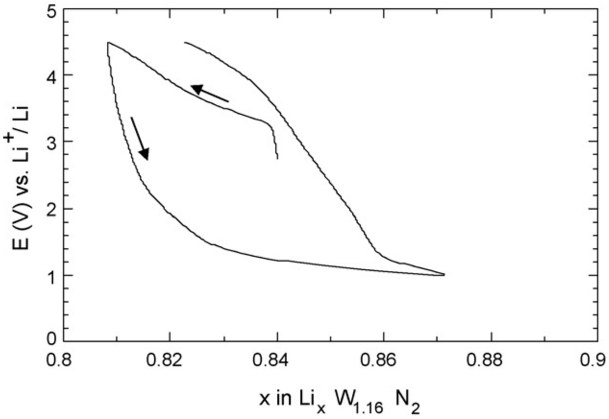

Fig. 6. One charge–discharge cycle and a second charge of a $Li_{0.84}W_{1.16}N_2$/Li cell between 4.8 and 1 V.

are thought to be due to structural effects. While the Li–N_6 layers in $LiMoN_2$ contain 15% of Mo, the same type of disordered layers is not found in $LiWN_2$. Therefore, the Li–N_6 layers in $LiWN_2$ are apparently free of this cationic ordering defect.

In addition, the structural evolution of $LiWN_2$ during deintercalation and intercalation of lithium has been followed by *ex situ* X-ray diffractometry. Fig. 5 shows the X ray patterns of $LiWN_2$ taken at the initial rest potential (point A in Fig. 4), charged then to 4.4 V (point B in Fig. 4) and afterwards discharged to 1 V (point C in Fig. 4).

When the electrochemical cell with $LiWN_2$ is charged to 4.4 V (Fig. 5B), 0.40 Li/formula unit are deintercalated from $LiWN_2$, giving $Li_{0.60}WN_2$. The main reflections of the rhombohedral phase are preserved (marked by *R* in Fig. 5B), and the cell parameters of deintercalated Li_xWN_2: $a = 2.9177(4)$ Å; $c = 15.841(4)$ Å are similar to those of the initial nitride. In addition, several new reflections (marked by asterisks in Fig. 5B), which are not observed in the original pattern of $LiWN_2$ (Fig. 5A), are indicative for a second phase. This finding is in agreement with the electrochemical results, which indicate the existence of a two-phase transformation (labeled as II in Fig. 2) at high potential. The additional main reflections positioned at ∼16.65° (overlapped with the (003) reflection of $LiWN_2$), ∼36.40° and ∼44.12° were incompatible with the rhombohedral cell of $LiWN_2$. However, we have found that all additional reflections emerging upon lithium deintercalation can be indexed with a hexagonal cell with cell parameters $a = 2.9276(3)$ Å; $c = 10.450(2)$ Å. These cell dimensions are similar to those reported for the non-stoichiometric nitride $Li_{0.84}W_{1.16}N_2$. However, a pronounced loss of crystallinity of the nitride material upon lithium deintercalation is evidenced by a dramatic decrease in intensities (Fig. 5B and C). For this reason, we ruled out any further attempt to get more detailed structural information about this second phase. Finally, no significant changes are observed in the X-ray pattern of $LiWN_2$, when the electrochemical cell is discharged to 1 V (Fig. 5C), corresponding to the reintercalation of the 0.40Li, which has been deintercalated previously in the first charge. This indicates that the host structure is maintained during the electrochemical reactions, a fact that can be directly related to the good reversibility of the intercalation process.

At this point it is important to summarize briefly the electrochemical behaviour of $Li_{0.84}W_{1.16}N_2$, which presents a related structure,[5] but that allows the disordering of Li and W in the Li–N_2 layers, while keeping the presence of the same redox-active metal as in $LiWN_2$. The first charge–discharge cycle of a cell that uses $Li_{0.84}W_{1.16}N_2$ as the active material is shown in Fig. 6. Similar galvanostatic set-up conditions to that applied in $LiWN_2$ have been used. The general electrochemical behaviour is comparable to that of $LiMoN_2$: a first irreversible oxidation is followed by an irreversible reduction, with the difference that the extent of both oxidative and reductive reactions is clearly smaller in $Li_{0.84}W_{1.16}N_2$. Only 0.03 Li can be deintercalated after the first charge. This is a strong evidence for the impediment of the deintercalation–intercalation reactions in layered nitrides due to cation disorder.

4. Conclusions

The electrochemical study on the two different layered ternary nitrides, $LiWN_2$ and $Li_{0.84}W_{1.16}N_2$, has proved that the electrochemical behaviour for such layered compounds is strongly influenced by cationic disordering phenomena within the layers. In $LiWN_2$, Li and W are completely ordered in alternating layers. The deintercalation of lithium proceeds easily and in a reversible way. Reversible capacity values of 67 mA/g are well maintained after the first oxidation. On the contrary, lithium and tungsten in $Li_{0.84}W_{1.16}N_2$ statistically occupy the Li layers, impeding thereby lithium diffusion which is needed for the occurrence of a deintercalation reaction. As a consequence of this cation disordering, the deintercalation–intercalation is practically negligible and irreversible.

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