Chemical stability of layered lithium cobalt nitrides in air

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1. Introduction
In the frame of the intense research focused on new negative electrode materials for Li-ion batteries, the use of layered ternary nitridocobaltates has been proposed to substitute carbonaceous composites [1–7]. In the 1.4 V/0 V vs Li/Li⁺ potential window, one set of electrochemical data reports that Li₂ₓCo₀.₄ₓN acts as a conversion electrode material with contradictory high capacity values in the range 760–400 mA h g⁻¹ (211–111 mC g⁻¹) and a remarkable stability up to 50 cycles [1–5]. Recently, lithium cobalt nitrides Liₓ₋₂ₓCoₓN (0.1 ≤ x ≤ 0.44) have been proposed as genuine Li intercalation materials instead of conversion electrode material in the narrower 1 V/0.02 V vs Li/Li⁺ potential window [6,7]. Whatever the Co content all these nitrides are electroactive with a single step around 0.6 V/0.7 V vs Li/Li⁺ for the discharge and charge processes respectively. Their electrochemical behaviour observed is typical of a Li intercalation compound and involves the Co²⁺/Co⁺ redox couple in the interlayer plane combined with the reversible accommodation of Li⁺ ions in the cation vacancies located in Li₂N layers. This intercalation process explains the excellent capacity retention found after 50 cycles at high and low rates. A specific capacity of 180 mA h g⁻¹ (50 mC g⁻¹) at C/20 rate (i.e. insertion of 1 Li by chemical formula in 20 h) and 130 mA h g⁻¹ (36 mC g⁻¹) at C/5 rate has been achieved for Li₂₋₂ₓCoₓN. As for most of lithiated anode and cathode active materials for Li-ion batteries, handling of lithiated metallic nitrides requires the use of inert atmosphere. The high reactivity in air of a cubic metallic nitride Li₂MnN₄ has been briefly reported as being decreased with the use of the corresponding oxinitride Li₁₋₂ₓMn₂N₂O₁₋ₓ [8]. However no detailed data on the chemical stability in air of the layered lithiated ternary nitrides in the Li–Co–N system are available in spite of their potential interest as rechargeable negative electrode. This has prompted us to investigate the reactivity of the lithiated nitridocobaltate Liₓ₋₂ₓCo₀.₄ₓN towards air at room temperature. The corrosion process of the compound is followed by in situ X-ray diffraction as a function of exposure time in air. Influence of the corrosion process on the anode performance is observed from the evolution of discharge–charge properties as a function of exposure time.

2. Experimental

2.1. Chemical synthesis and structural analysis
The lithium cobalt nitride Li₂₋₂ₓCo₀.₄ₓN was prepared using a solid state route from the reagent grade Li₂N (Alfa-Aesar 99.5%, 10 μm) and Co metal (Alfa-Aesar 99.8%, 1.6 μm). A mixture of Li₂N and Co in a ratio R (R = Co/Li₂N) of 0.5 was first mixed and ground in agate mortar and then pressed into pellet (13 mm diameter and thickness of 6–8 mm). The pellet of about 1 g is then transferred in an alumina crucible enclosed in a silica reactor. The furnace temperature reaches 650 °C with a heating rate of 300 °C/h then 700 °C using a heating rate of 50 °C/h and remained at this temperature for 7 h under a nitrogen gas stream. During the synthesis procedure, handling of reactive species and products was carried out in an argon glove box. A sample was also aged for 3 weeks in a dessicator filled with a large amount of silicagel to evaluate the role played by moisture.

X-ray Diffraction (XRD) experiments were performed using a panalytical XPert pro apparatus equipped with a X'Celerator...
detector and using Co Kα radiation (λ = 1.789 Å). Prior the study of the ageing process, a pattern was recorded for 1 h in air-tight sample-holder between 20 < 2θ < 100° and analysed by a Rietveld refinement using GSAS package with EXPGUI interface [9,10]. During air exposure, XRD patterns were recorded every hour until 26 h with an acquisition time of 5 min in the 20–60° 2θ angular range. Additional diagrams collected after 32 h and 3 weeks were performed with an acquisition time of 1 h each.

Scanning Electron Microscopy (SEM) experiments were carried out using a LEO 1530 instrument.

2.2. Electrochemical measurements

The electrolyte used was 1 Mol.L⁻¹ LiPF₆ in Ethylene Carbonate (EC), DiEthyl Carbonate (DEC) and DiMethyl Carbonate (DMC) solution (1:1:1, v/v, EQ-Be-LiPF₆, MTI Corp.). Electrochemical studies were carried out in two-electrode cells (Swagelok® type) where the lithium disc acts as a reference and auxiliary electrode. The working electrode consisted of a stainless steel grid (6 mm diam., 0.2 mm thickness) with a geometric area of ~25 mm² on which the cathode material was pressed (5000 kg cm⁻²). The cathode was made of a mixture of active material (70% wt), acetylene black (22% wt) and Teflon as binder agent (8%). Electrochemical measurements were made with a Solartron 1470 apparatus.

Fig. 1. Crystal structure of Li₂₋ₓCoₓN compound (P6/mmm space group). Nitrogen ions are in site, lithium ions in 1b and 2c sites, cobalt ions in 1b site.

Fig. 2. XRD pattern and Rietveld refinement of Li₂.13Co₀.43N. Lower and upper marks indicate Lithiated transition metal nitride and Li₂O reflexions respectively. Inset: 36–48° expanded view.

Fig. 3. SEM pictures of the lithiated nitridocobaltate Li₂₁Co₀.₄₃N (a) before, (b) after 60 h and (c) 3 weeks of air exposure.
Galvanostatic discharge–charge tests between 1 and 0.02 V vs Li/Li+ were carried out at C/10 rate (i.e. variation of 1 Li+ by chemical formula in 10 h).

3. Results and discussion

Layered ternary lithiated nitridocobaltates crystallise in the α-Li3N hexagonal type structure (space group P6/mmm). This structure is well described by a pure Li+ layer surrounded by Li2N/C0 planes (Fig. 1). According to the chemical analysis, structural and electrochemical data reported elsewhere on Li3-2xCo2xN (0.1 ≤ x ≤ 0.44) [6,7], Co2+ ions substitute a part of the Li+ ions layered (1b site) with the simultaneous emergence of an equivalent amount of Li vacancies in the 2c sites of the Li2N plane.

X-ray powder diffraction pattern of Li2.13Co0.43N is shown in Fig. 2. Rietveld refinement in the hexagonal space group P6/mmm leads to satisfactory results. The refined cell parameters are a = 3.7245(2) Å and c = 3.6748(2) Å and the agreement factors are Rwp = 2.18% and Rp = 1.62% with goodness of fit $\chi^2 = 1.158$. In addition as can be seen from the expanded view of the 36–48 20 range in the inset of Fig. 2, a low intensity peak located at 39.2° indicates the presence of a small amount of Li2O in the sample (ICSD pattern 00–012-0254). The chemical composition of the lithiated metallic nitride was refined with a constraint on the site occupancies according to the developed formula [Li1-xCo]1-b[Li2-x/xCo]2cN1a (where / represent the lithium vacancies). The corresponding chemical formula, Li2.13(1)Co0.43(1)N (x = 0.43) is found, associated with the cell parameters reported above, in excellent agreement with the evolution of lattice parameters as a function of the Co content in Li3-2xCoxN [6]. The Li2O amount was estimated close to 2.8 wt% (i.e. Li2.13Co0.43N, 0.05Li2O) from the Rietveld refinement.

The morphology observed by SEM indicates the powder is made of large aggregates (size ≈10 μm) made of smaller particles (≈0.5–3 μm) (Fig. 3).

In Fig. 4a are compared selected XRD patterns in the 20–60° 20 range recorded after exposure in air for 0, 2, 5, 10, 15 and 26 h. The intensity of XRD peaks of Li2.13Co0.43N significantly decreases during the first five hours. This intensity loss for 100, 101, 110 peaks is accompanied by a slight shift showing a small change in the unit
cell parameters. Indeed, \( a \) decreases from 3.725 to 3.686 Å after 2 h and remains stable thereafter. At the same time, the interlayer \( c \) parameter increases slightly from 3.675 to 3.716 Å. These variations cannot be only explained by the variation of the cobalt content and probably reflect the nitrogen loss.

The first degradation product observed is LiOH with the main diffraction peaks at 23.8, 38.0 and 41.8° (ICSD pattern 01–085-1064), even after 2 h. LiOH formation is a clear indication of the moisture affinity of the nitride. Moreover, the \( \text{Li}_2\text{O} \) reflexion identified at 39.2° on the starting material doesn't grow up during all the experiment, according to its relative stability in air. Hence, \( \text{Li}_2\text{O} \) is not involved in the degradation mechanism of the ternary nitride. The LiOH amount rapidly increases to reach a maximum after 5 h and then decreases with time to the benefit of lithium carbonate. Indeed, \( \text{Li}_2\text{CO}_3 \) can be clearly identified after 5 h of degradation (reflexions at 24.8, 35.7, 37.1 39.8, 43.2 and 46.3°, ICSD pattern 00–022-1141).

Fig. 4b illustrates the XRD pattern evolution in the 35–45° 2θ range up to 26 h and provides an overall view of all the main changes occurring with time. It illustrates the continuous augmentation of the \( \text{Li}_2\text{CO}_3 \) amount at the expense of LiOH which slightly decreases and the correlative sharp decrease with time for the 101 reflexion of \( \text{Li}_{2.13}\text{Co}_{0.43}\text{N} \).

After 26 h, no cobalt species has been identified. For longer time, drastic changes take place as can be seen in XRD patterns after 32 h and after 3 weeks (Fig. 5). Indeed, after 32 h, cobalt hydroxide peaks located at 21.9, 44.3°, (ICSD pattern 00–030-0443) are observed for the first time. These two small and broad peaks are indicative of a poor structural organisation of \( \text{Co(OH)}_2 \). A significant increase in the \( \text{Co(OH)}_2 \) amount and its crystallinity is observed after 3 weeks (Fig. 5). After 3 weeks, the lithiated metallic nitride is deeply affected with the quasi disappearance of the 100 and 101 reflexions to the benefit of \( \text{Co(OH)}_2 \) and \( \text{Li}_2\text{CO}_3 \) peaks. A mixture of LiOH, \( \text{Li}_2\text{CO}_3 \), \( \text{Co(OH)}_2 \) and metallic nitride with a strongly modified chemical composition is then observed.
SEM micrographs reported in Fig. 3a show the grain morphology prior air exposure and after 60 h and 3 weeks in air (Fig. 3b and c respectively). After 60 h, the surface morphology significantly changes from dense particles to a porous material made of small platelets ≈0.5 μm long with sharp edges, probably related to the release of ammonia. The appearance of this porosity promotes the further degradation process. After 3 weeks, the same kind of morphology is obtained but with smooth edges, which could be an indication of the complete degradation of the material.

The present XRD study clearly indicates the high reactivity of the lithiated metallic nitride $\text{Li}_{1.25}\text{Co}_x\text{N}$ towards moisture rapidly leading to the formation of $\text{LiOH}$ and $\text{Co(OH)}_2$. The reaction could be written:

$$\text{Li}_{1.25}\text{Co}_x\text{N} + 3\text{H}_2\text{O} \rightarrow (3 - 2x)\text{LiOH} + x\text{Co(OH)}_2 + \text{NH}_3 \uparrow$$

The ageing mechanism is supported by the XRD experiments and by the characteristic pungent odour of ammonia emitted by the sample during air exposure. The second step, leading to the formation of $\text{Li}_2\text{CO}_3$, is ascribed to the affinity of $\text{LiOH}$ for carbon dioxide.

One can notice that this step is favourable to the propagation of the degradation since some water is produced and can then react with the metallic nitride. It must be outlined that the lithiated transition metal nitride is still present after one day of exposure (Fig. 4b and a). This can be explained by the large particles, inducing a slow diffusion of water from the surface to the core. The reactivity toward air moisture of a binary metallic nitride such as $\text{AlN}$ in specific conditions has been reported owing a similar reaction with LiOH and $\text{Co(OH)}_2$ formation as well as $\text{NH}_3$ release. This kind of morphology is obtained but with smooth edges, which motivates the further degradation process. After 3 weeks, the same morphology is obtained but with smooth edges, which could be an indication of the complete degradation of the material.

4. Conclusions

We have reported here the ageing process in air of a lithium nitridocobaltate which is a promising anode material for Li-ion batteries. To our knowledge, this topic has never been addressed in spite of the reactive character expected for such materials in air and their potential interest as electrode material. In situ XRD experiments vs. exposure time combined with the electrochemical behaviour observed for aged compounds show the discharge–charge properties are little affected after few hours, significantly after 15 h and dramatically at longer times. The decrease both in the lithium uptake and discharge potential is due to the reaction of the nitride with air moisture leading to its significant destruction with $\text{LiOH}$ and $\text{Co(OH)}_2$ formation as well as $\text{NH}_3$ release. This study clearly indicates that lithiated nitridocobaltates present a greater affinity for moisture than oxygen. These results suggest handling of these anodic materials in dry air would be possible with satisfactory electrochemical properties.

References