



# Mesoporous molybdenum nitride nanobelts as an anode with improved electrochemical properties in lithium ion batteries



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## HIGHLIGHTS

- Mesoporous Mo<sub>2</sub>N nanobelts (NBs) are prepared via a template-free synthesis.
- The Mo<sub>2</sub>N NBs exhibit a well-defined mesoporous structure.
- The Mo<sub>2</sub>N NBs show a one-dimensional nanostructure.
- The meso-Mo<sub>2</sub>N NBs exhibit improved intercalation properties of lithium ions.

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## ABSTRACT

The well-defined mesoporous nanostructure electrodes have been known to have improved lithium ion reaction properties such as the lithium ion insertion/desertion reaction, cyclability, and high rate performance. We prepared mesoporous molybdenum nitride nanobelts via a template-free synthesis as an anode for lithium-ion batteries. The as-prepared molybdenum nitride nanobelts (meso-Mo<sub>2</sub>N NBs) exhibited face-centered cubic Mo<sub>2</sub>N phase, well-defined mesoporous structure, and growth of [100] direction with 1-dimensional structure. The meso-Mo<sub>2</sub>N NBs showed the improved electrochemical reaction properties of lithium ions such as high specific capacity and high rate cycling performance due to low transport resistance and high lithium ion diffusion coefficient.

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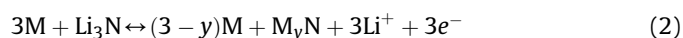
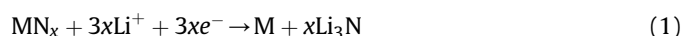
## 1. Introduction

Lithium-ion batteries (LIBs) have been intensively attractive as energy storage devices because of their relatively high energy density and voltage than other energy storage devices, and room temperature operation. The LIBs consist of cathode materials including feature such as transition metal oxide containing lithium sources, anode materials including feature such as carbon, transition metal oxides and nitride, separator such as polyethylene, and electrolyte [1–4].

In particular, the electrode materials for LIBs are required high electrical conductivity and specific surface area, low cost, and long-term electrochemical stability [2–4]. Typically, for an anode in LIBs, the carbon-based materials have been used as promising electrode

materials, but show lower theoretical capacity in LIBs [5,6]. As an alternation electrode material, the ceramic materials such as transition metal oxide, nitride, and sulfide have been reported for electrode materials in LIBs. Among, the transition metal nitrides are well known as lithium ion insertion/desertion material with low production cost, non-toxicity, very low volume change during lithium ion insertion/desertion, good structural stability, high electrical conductivity, and long cycle life in LIBs [7–10].

In the LIBs, transition metal nitride is very intriguing anode materials. Generally, the well-known conversion reaction on transition metal nitrides is as follows:



During first discharge reaction (Eq. (1)), the lithium ion is bonded with nitrogen of transition metal nitride (Li<sub>3</sub>N) and the

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separated transition metal atoms from transition metal nitride are transformed to metallic structure (M). On the other hands, the formed lithium nitride and metal during first discharge reaction regenerates transition metal nitride, which partially maintains lithium nitride in first charge reaction (Eq. (2)). In the subsequent cycles (Eq. (2)), the conversion reactions between lithium nitride and transition metal nitride have reversible reaction [11–17]. Thus, this can explain that the lithium ion insertion reaction of transition metal nitride is irreversible during first charge/discharge cycle, however, the second and subsequent cycles is reversible reaction and more stable.

However, the bulk structure of almost transition metal nitrides appears low specific capacity and electrochemical properties in LIBs because of a low specific surface area and an unfavorable diffusion distance of lithium in comparison with the structure-controlled nanoparticles [18]. To increase the lithium ion reaction properties, there have been many reports in the literature by structure and/or shape control of active materials, and mixed phase in active materials [19–21]. In particular, among them, the mesoporous nanostructures have major advantages such as many lithium ion reaction site and short diffusion distance of lithium ion for LIBs due to their highly specific surface area and controlled pore and channel in the nanometer range [22–24]. Unfortunately, the conventional template methods for synthesis of mesoporous materials are not simple because it is synthesized by template such as zeolite, mesoporous silica, and polymer [24,25].

In this work, the mesoporous molybdenum nitrides nanobelts with 1-dimensional structure were investigated as an anodic material for LIBs. Mesoporous nanostructure can be a candidate of high specific surface area with highly active site for LIBs electrodes. Furthermore, the belt-shaped nanostructures are expected to induce particular properties such as rapid electron collection of carriers and charge transport assisted by its 1-dimensional structure in LIBs electrodes. Accordingly, the main objective of this study is to investigate the lithium ion insertion/desorption reaction, cyclability, and high rate performance of the well-defined mesoporous molybdenum nitride nanobelts compared to that of irregular molybdenum nitride electrode in LIBs. Herein, we suggest the well-defined mesoporous molybdenum nitrides nanobelts with 1-dimensional structure as anode materials for LIBs. The well-defined mesoporous molybdenum nitrides nanobelts were synthesized by nitridation process using the molybdenum oxide nanobelts. The structural analysis of the as-prepared nanostructures was characterized using field-emission transmission electron microscopy (FE-TEM), field-emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD). The specific surface area and pore size of the as-prepared electrodes were analyzed by a nitrogen sorption measurement. To evaluate the performance for LIBs, the charge–discharge and high rate curves, cyclic voltammograms (CVs), and electrochemical impedance spectroscopy of the electrodes were measured using lithium coin cells.

## 2. Experimental

### 2.1. Synthesis of mesoporous molybdenum nitride electrodes

For molybdenum oxide nanobelts ( $\text{MoO}_3$ ) as a precursor, ammonium molybdate tetrahydrate (Sigma–Aldrich) was dissolved in 5 M  $\text{HNO}_3$  with constant stirring at 25 °C for 1 h and then reacted in autoclave at 160 °C for 4 h. The resulting precipitate was washed several times with distilled water and dried in oven at 50 °C. The molybdenum oxide powder was heated at 700 °C for 6 h under the  $\text{NH}_3$  flow of 100 mL  $\text{min}^{-1}$ . The product was cooled down to 25 °C in flowing  $\text{NH}_3$ , followed by passivation for 2 h in 100% air (denoted as meso- $\text{Mo}_2\text{N-NBs}$ ) [26]. For comparison, typical

molybdenum nitride nanoparticles (denoted as com- $\text{Mo}_2\text{N-NPs}$ ) were prepared by a nitrification process of commercial  $\text{MoO}_3$  (Sigma–Aldrich) by means of heat treatment at 700 °C for 6 h under  $\text{NH}_3$  atmosphere.

### 2.2. Structural characterization of as-prepared electrodes

The as-prepared samples were characterized by field-emission TEM using a Tecnai G2 F30 system operating at 300 kV. The TEM samples were prepared by placing a drop of the nanoparticle suspension in ethanol on a carbon-coated copper grid. SEM images were obtained on a JEOL JSM-6360A microscope operated 20 kV. Structural analysis of the samples was carried out by XRD method using a Bruker AXS D2 Phaser X-Ray Diffractometer with a  $\text{Cu K}_\alpha$  radiation source of  $\lambda = 0.15418$  nm with a Ni filter. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020. Before the adsorption measurements, all samples were outgassed at 473 K for 360 min in the port of the adsorption analyzer. The starting relative pressure was 0.995 P/P<sub>0</sub> and ending relative pressure was 0.01 P/P<sub>0</sub>.

### 2.3. Electrochemical characterization of as-prepared electrodes

The electrodes were prepared by mixing 80 wt%  $\text{Mo}_2\text{N}$  nanostructure electrode as an active material, 10 wt% ketjen black as a conducting agent, and 10 wt% polyvinylidene fluoride (PVDF) as a binder. To obtain the slurry, several drops of N-methyl pyrrolidone were added into the mixture of  $\text{Mo}_2\text{N}$  powder with Ketjen black and PVDF. The mixed slurries were cast onto a Cu foil current collector and dried in air at 110 °C for 12 h. The electrode with an area of 1.32 cm<sup>2</sup> was dried at 70 °C vacuum oven. The electrodes were evaluated with respect to a lithium foil (FMC Corporation) counter electrode. The coin cells were assembled inside an Ar-filled glove box (<5 ppm,  $\text{H}_2\text{O}$  and  $\text{O}_2$ ). The positive and negative electrodes of the cells were separated from one another by a porous polypropylene membrane (Wellcos) and an electrolyte solution consisting of 1.1 M  $\text{LiPF}_6$  in ethylene carbonate:diethylcarbonate (1:1) solvent mixture (Techono Semichem). The electrochemical properties of the assembled cells were recorded with charge–discharge curves in a voltage window between 3.0 and 0.01 V vs.  $\text{Li/Li}^+$ . The charge–discharge tests were galvanostatically performed between 3.0 and 0.01 V vs.  $\text{Li/Li}^+$  for 20 cycles at a current density of 100 mA  $\text{g}^{-1}$ . The charge–discharge tests were also performed at various current density from 100 to 4000 mA  $\text{g}^{-1}$  in order to evaluate the C-rate capability. For electrochemical impedance spectroscopic measurements, the excitation potential applied to the cells was 5 mV and the frequency ranged from 100 kHz to 10 mHz. All the electrochemical measurements were carried out at 25 °C. Furthermore, The CVs of the electrodes were obtained at 0.5 mV  $\text{s}^{-1}$  between 0 and 3 V vs.  $\text{Li/Li}^+$  using a potentiostat (Eco Chemie, AUTOLAB).

## 3. Results and discussion

The meso- $\text{Mo}_2\text{N-NBs}$  were prepared via template-free synthesis process, i.e. nitrification process of as-prepared molybdenum oxide nanobelts as a precursor at 700 °C under  $\text{NH}_3$  atmosphere. Fig. 1(a) and (b) shows SEM image of  $\text{MoO}_3$  nanoparticles as a precursor synthesized by hydrothermal method. The  $\text{MoO}_3$  nanoparticles exhibit a belt type and single-crystalline orthorhombic structure grown into [110] direction (Fig. 1(c)–(f)). In particular, the FE-SEM and TEM images of the sample prepared using  $\text{MoO}_3$  nanobelts are shown in Fig. 2. The as-prepared sample is a uniform mesoporous nanostructure with belt-type shape and pore diameter of ~4 nm (inset of Fig. 2(c)). The average length and width of the

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