

Electrochemical behavior of the composite anodes consisting of carbonaceous materials and lithium transition-metal nitrides for lithium–ion batteries

K. Hanai^a, Y. Liu^{b,*}, T. Matsumura^a, N. Imanishi^a, A. Hirano^a, Y. Takeda^a

^a Department of Chemistry, Faculty of Engineering, Mie University, Kamihama-cho, Tsu, Mie 514-8507, Japan

^b Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, China

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Abstract

We report the composite anodes that show a high first cycle efficiency of *ca.* 100% and a large capacity of *ca.* 400–450 mAh g⁻¹ for Li–ion batteries. The composites are prepared by mixing or ball-milling the hexagonal lithium transition-metal nitrides with different carbonaceous materials, such as the disordered carbon and the graphitic carbon. Both the lithium metal nitrides and the carbonaceous materials are electrochemically active in the electrodes within the potential window of 0–1.4 V vs. Li/Li⁺. Additionally, a high cycling stability is feasible due to the low volumetric effects of the composite electrodes upon Li intercalation and extraction. However, the voltage hysteresis during the charge and discharge is obvious because the two active hosts react with lithium at different potentials in the electrode. Some factors influencing the electrochemical behavior of the composite anodes are discussed.

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1. Introduction

In recent decades, some anode alternatives that show the improved capacity density and the enhanced thermal safety over the commercial graphite have been widely investigated for lithium ion batteries [1]. Among them, ternary lithium transition-metal nitrides with the hexagonal symmetry, P6/*mmm*, such as Li_{2.6}M_{0.4}N (M = Co, Cu, Ni), show some attractive points [2–6]. Li_{2.6}M_{0.4}N is composed of M (M = Co, Cu, Ni) substituting lithium between the Li₂N³⁻ layers of Li₃N. The solid solution range of the hexagonal Li_{3-x}M_xN is located in 0 < x < 0.5, 0 < x < 0.6 and 0 < x < 0.3 for M = Co, Ni and Cu, respectively. From an electrochemical standpoint, the most promising and most studied of the compound is Li_{2.6}Co_{0.4}N [2–7]. The lithium metal nitrides possess a structure change from a crystal to an amorphous phase in the first Li extraction. Such an irreversible transformation indicates an atom rearrangement and lithium in the

compound can be electrochemically extracted and re-intercalation with a high reversibility. However, the Li_{2.6}Co_{0.4}N does not show a satisfactory capacity retention upon long cycles. Additionally, the high cost and toxicity of the cobalt compound suggests that a better material would be based on Fe, Cu or Ni. Recently, we prepared a co-doped lithium transition-metal nitride by means of solid-state reaction and high-energy mechanical milling (HEMM) [8,9]. These compounds are obviously superior to the Li_{2.6}Co_{0.4}N in terms of the capacity retention and the cost. A major barrier to the lithium transition-metal nitrides as the anode candidate is their Li-rich structure. That is, they cannot directly combine with the typically high-potential cathodes such as LiCoO₂ and LiMn₂O₄. Lithium in the compound can be pre-extracted by a chemical way [10]. The Li-rich Li_{2.6}Co_{0.4}N also can be introduced to make a compensation for the high irreversible capacities for the ultrafine alloy powders, such as SnSb_x, SnO and SiO_x, in the first cycle [11,12]. The resulting composites demonstrated a high first cycle efficiency of *ca.* 100% and a large capacity. However, the morphological instability of such electrodes still is questionable due to the electrochemically Li-alloying reaction. On the other hand,

* Corresponding author. Tel.: +86 21 52412272; fax: +86 21 52413903.

E-mail address: yuliu@mail.sic.ac.cn (Y. Liu).

some carbonaceous materials, such as hard carbon or amorphous carbon, generally can storage more lithium over the LiC_6 compound. Similar with the ultrafine alloy, these carbonaceous materials show a low efficiency in the first cycle. The lithium transition metal nitrides thus can be introduced to make the compensation for the high irreversible capacities. The proposed composites, which are benefited from the low volume effects of both active hosts, are expected to have a good cycling stability. Furthermore, high first cycle efficiency of *ca.* 100% and large capacity of *ca.* 400–450 mAh g^{-1} are also feasible.

2. Experimental

2.1. Material preparations

To produce the hexagonal lithium transition metal nitrides, a given ratio of Li_3N and powders of transition metals was homogeneously mixed in an Ar atmosphere. The mixture was pressed into a tablet with 8 mm in diameter and 5–8 mm in thickness and heated at 700 °C for 12 h under N_2 stream at a heating rate of 35 °C min^{-1} . The reactions were allowed to cool down to room temperature under a normal speed. For the compounds containing Fe, heating temperature was increased to be 800 °C. The resulting products were ground in a glove box and further treated by high-energy mechanical milling (HEMM) with a rotational speed of 500 rpm for 20 h. The disordered carbon was simply prepared from the thermal pyrolysis of different carbon sources, such as phenol resin and coffee bean, at a high temperature of 900 °C for 18 h under an Ar atmosphere. The resulting products were ground and confirmed

to be of amorphous structure by means of X-ray diffraction (XRD, MacScience M18XHF, Japan). The amorphous carbon fiber was commercially obtained and further dried under vacuum over night. The composites consisting of Mesocarbon Microbead (MCMB, graphitic carbon, typical particle size: 25 μm) and lithium metal nitrides were prepared by ball-milling the MCMB (70 wt.%) powders with the lithium metal nitrides (30 wt.%) at a rotational speed of 500 rpm for 10 h in an Ar atmosphere.

2.2. Electrode fabrications and electrochemical measurements

A given weight of the electrode components, including acetylene black (AB), active materials and poly (vinylidene fluoride) (PVDF), was homogeneously mixed in an agate mortar in a glove box and further pressed onto a 300-mesh stainless steel grid, which served as a current collector. The geometric area of the electrodes was 0.55 cm^2 , and the typical thickness was 100–160 μm . Electrode capacity was calculated according to the weight of the active materials. To evaluate the electrochemical properties of the electrodes, a half-cell containing $\text{LiPF}_6 / \text{EC} + \text{DMC}$ (ethylene carbonate plus diethyl carbonate as 1:1 in volume) electrolytes was used. Li metal was utilized as both the counter and reference electrodes. All the three layers, including the test electrode, the separator and the Li metal, were stacked in a 2025 coin type cell in a glove box. Unless stated elsewhere, cycling was started from a discharge stage, and carried out at a potential cutoff of 0–1.4 V vs. Li/Li^+ with a constant current density of 0.15 mA cm^{-2} . The rest time between the charge and discharge was 1 min. Charge and discharge of the cells refer,

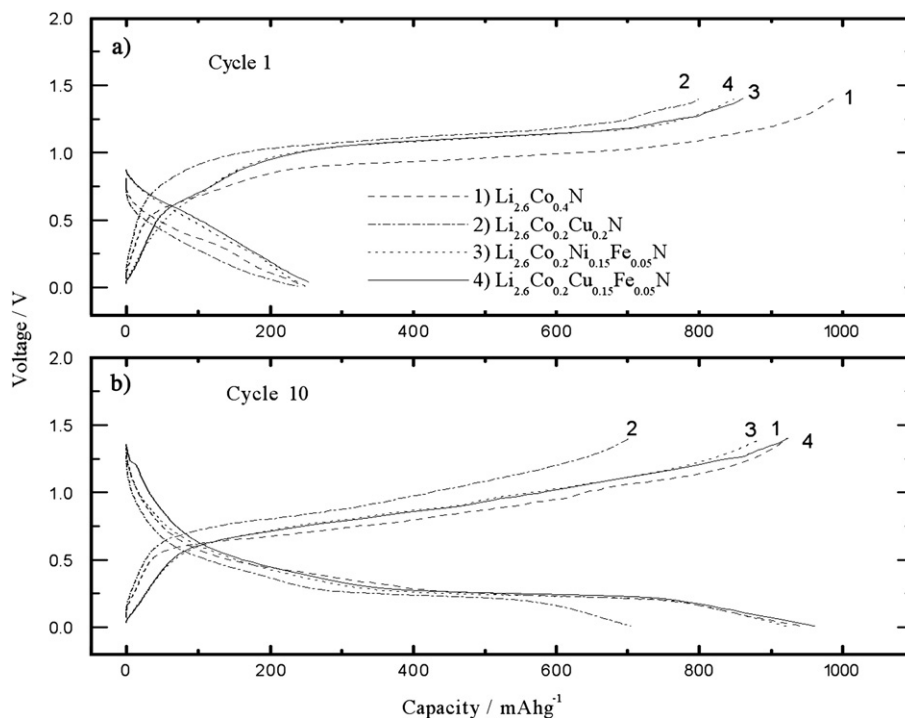


Fig. 1. Charge and discharge profiles of the lithium transition metal nitrides at the first and tenth cycle; the electrode composition: 20 wt.% AB, 70 wt.% lithium metal nitrides and 10 wt.% PVDF.

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