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

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ABSTRACT

We report 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 disordered carbon and the graphitic carbon. Both the lithium metal nitrides and the carbonaceous materials exhibit electrochemical activity in the electrodes within a 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, a voltage hysteresis during 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.

1. Introduction

In recent decades, some anode alternatives that show improved capacity density and enhanced thermal safety over commercial graphite have been widely investigated for lithium-ion batteries [1]. Among them, ternary lithium transition-metal nitrides with 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 $[Li_2^+N^{3-}]^-$ layers of Li_3N. The solid solution range of the hexagonal $Li_{3-x}M_xN$ is located at $0<x<0.5$, $0<x<0.6$ and $0<x<0.3$ for M = Co, Ni and Cu, respectively. From an electrochemical standpoint, the most promising and most studied of the compounds is $Li_{2.6}Co_{0.4}N$ [2–7]. The lithium metal nitrides show a structural change from crystalline to amorphous 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, $Li_{2.6}Co_{0.4}N$ does not show a satisfactory capacity retention upon long cycling. 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 $Li_{2.6}Co_{0.4}N$ in terms of capacity retention and cost. A major barrier for lithium transition-metal nitrides as anode candidate is their Li-rich structure. That is, they cannot directly combine with the typically high-potential cathodes such as $LiCoO_2$ and $LiMn_2O_4$. Lithium in the compound can be pre-extracted by a chemical way [10]. Li-rich $Li_{2.6}Co_{0.4}N$ can also be introduced to compensate 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 morphologic instability of such electrodes still is questionable due to the electrochemically Li-alloying reaction. On the other hand, some carbonaceous materials, such as hard carbon or amorphous carbon, generally can storage more lithium than LiC_6. Similar to the ultrafine alloy, these carbonaceous materials show a low efficiency in the first cycle. The lithium transition metal nitrides thus can be introduced to compensate for the high irreversible capacities. The proposed composites, which benefit from the low volume effects of both active hosts, are expected to have a good cycling stability. Furthermore, the 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_3 N and powders of transition metals was homogeneously mixed in an Ar atmosphere. The mixture was pressed into a tablet with 8 mm diameter and 5–8 mm thickness and heated to 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 normal speed.

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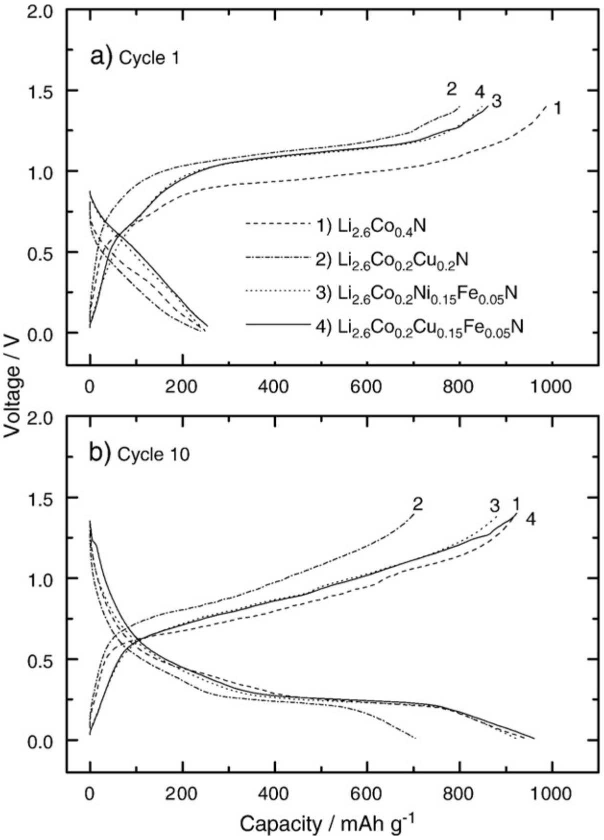

Fig. 1. Charge and discharge profiles of the lithium transition metal nitrides in the first and tenth cycle; electrode composition: 20 wt.% AB, 70 wt.% lithium metal nitrides and 10 wt.% PVDF.

For the compounds containing Fe, the temperature was increased to 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 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 amorphous by X-ray diffraction (XRD, MacScience M18XHF, Japan). The amorphous carbon fiber (ca. 0.010 mm in diameter) 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 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 $LiPF_6$/EC+DMC (ethylene carbonate plus diethyl carbonate as 1:1 in volume) electrolytes was used. Li metal was utilized as both the counter and reference electrode. All 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 discharged stage, and carried out to 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 refers to lithium extraction from, and insertion into the active hosts, respectively.

3. Results and discussion

Fig. 1 shows the charge and discharge profiles of the lithium transition-metal nitrides at the first and the tenth cycle. Due to the vacant sites introduced by the doped metal M, the fully lithiated nitrides can permit a small amount of lithium intercalation in the first cycle [2,8]. The compounds gradually undergo an irreversible transformation from a crystalline to an amorphous phase in the first Li-extraction, resulting in potential plateaus at above 0.9, 1.0, 1.0 and 1.1 V for $Li_{2.6}Co_{0.4}N$, $Li_{2.6}Co_{0.2}Ni_{0.15}Fe_{0.05}N$, $Li_{2.6}Co_{0.2}Cu_{0.15}Fe_{0.05}N$ and $Li_{2.6}Co_{0.2}Cu_{0.2}N$, respectively, as shown in Fig. 1a. Compared with the $Li_{2.6}Co_{0.4}N$, the slight increase in the charge potentials for $Li_{2.6}Co_{0.2}Cu_{0.2}N$, $Li_{2.6}Co_{0.2}Ni_{0.15}Fe_{0.05}N$ and $Li_{2.6}Co_{0.2}Cu_{0.15}Fe_{0.05}N$ indicate that the partial Co substitution by Cu, Ni and Fe may be obstructive for the lithium extraction [8]. In the subsequent cycles shown in Fig. 1b, the charge potential becomes sloped and lithium can be reversibly re-intercalated and extracted, giving high capacities of 700–900 mAh g^{-1}, which are 2–3 times higher than for commercial graphite. As can be seen in Fig. 1b, the discharge potential curves show a hysteresis of *ca.* 0.5 V compared to the charge curves. The cycling stability of the co-doped compounds is much superior to that of $Li_{2.6}Co_{0.4}N$, as shown in Fig. 2. After 60 cycles, $Li_{2.6}Co_{0.2}Cu_{0.2}N$ can retain 98% of the initial extraction capacity of *ca.*700 mAh g^{-1}. The capacity retention for $Li_{2.6}Co_{0.2}Ni_{0.15}Fe_{0.05}N$ and $Li_{2.6}Co_{0.2}Cu_{0.15}Fe_{0.05}N$ electrodes at the 50th cycle are 80% and 84%, respectively, *vs.* 820 mAh g^{-1} and 843 mAh g^{-1} at the first cycle. The significant improvement in the cycling performance for the co-coped compounds over $Li_{2.6}Co_{0.4}N$ can be partly attributed to the improved electrochemical stability associated to the Li extraction degree and the enhanced interfacial compatibility with the electrolyte [8,13].

Lithium transition-metal nitrides having a similar density as the currently used graphite are very attractive with respect to the packing density and volumetric capacity. A major obstruction for these compounds towards the application is their Li-rich structure; therefore they cannot directly be combined with the typical high-potential cathodes such as $LiCoO_2$ and $LiMn_2O_4$. However, such a structure can be introduced to compensate for the high irreversible capacities for disordered carbon in the first cycle. Fig. 3 shows the charge and discharge profiles of several carbonaceous materials. As can be seen, they show a higher insertion capacity but a lower efficiency than

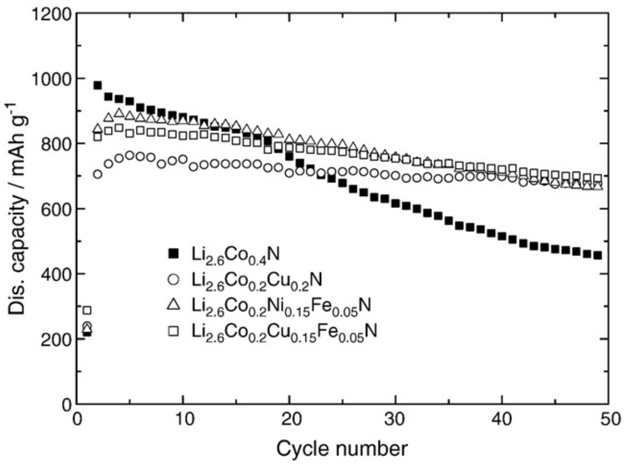

Fig. 2. Cycling performance of the lithium transition metal nitrides.