Effect of transition metal (M = Co, Ni, Cu) substitution on electronic structure and vacancy formation of Li_3N

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We carried out first principles calculations to investigate the effect of transition metal (M = Co, Ni, Cu) substitution on electronic structure and vacancy formation of Li_3N in this study. Transition metals are shown to selectively substitute interplanar Li(1) atoms. Both Co and Ni substitution remarkably reduces the energy band gap to 0.55 eV in comparison with 1.13 eV of Li_3N, while Cu substitution insignificantly decreases the energy band gap by 0.07 eV. Covalent bonding between transition metal atom and the coordinated N, which is manifested both visually by the contour plots of valence charge density difference and numerically by bond length variation, results in the formation of $Li_{3-x-y}M_x\square_yN$ with y dependent on the covalency and concentration of transition metal. Ni substitution significantly reduces $V_{Li(2)}$ formation energy, which suggests greatly increased Li vacancy concentration for improved Li ionic mobility and conduction. Therefore, controlling the energy band gap and vacancy concentration by transition metal substitution provides a viable approach to tailor Li_3N for variable applications in rechargeable lithium ion batteries.

Introduction

Transition metal substituted lithium nitrides have emerged as promising candidates for anode materials in rechargeable lithium ion batteries.[1–5] Li_3N can react with transition metals at approximately 600–900 °C under nitrogen-rich conditions to form two groups of ternary nitride compounds, one with the anti-fluorite structure and the other with the layered Li_3N structure.[6–8] The structure of these ternary lithium nitrides follows a predictable trend that the anti-fluorite structure is favored for Ti through Fe and a structure is based on the layered Li_3N structure for Co, Ni and Cu.[9] Transition metals (M = Co, Ni, Cu) are proposed to substitute Li in Li(1) sites of Li_3N as shown in Fig. 1, irrespective of the dopant concentration and the synthesis conditions applied.[10–14] The layered morphology is claimed to be beneficial to fast Li-ion conduction and low transition metal oxidation states.[9] It is claimed that no ternary lithium nitrides could surpass the high capacity of the $Li_{2.6}Co_{0.4}N$ nitride at low potential, yet substitution of Co by Ni or Cu can dramatically improve the cycling performance with a slightly decreased capacity.[1,15]

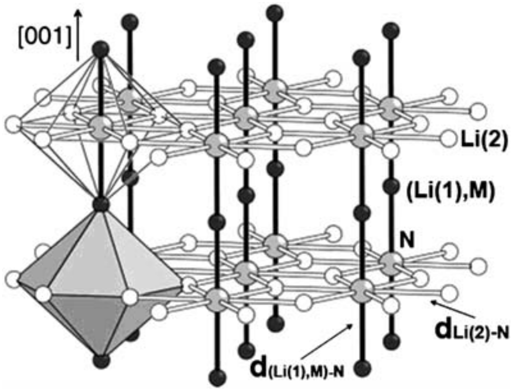

Fig. 1 Schematic illustration of transition metal substituted Li_3N.

Two disputable models have been proposed to account for the substitution of Li by transition metals in Li_3N. Some claimed ostensibly isovalent substitution of Li^+ by M^+, which leads to the formation of $Li_{3-x}M_xN$. Consequently, the Li vacancy concentration would be about 1–2% generally observed in Li_3N. The charge balance of $Li_{2.6}Co_{0.4}N$ was well described with monovalent cobalt.[16,17] Negligible lithium vacancies were determined in $Li_{2.6}Co_{0.4}N$ from chemical composition analysis.[16] $Li_{2.57}Cu_{0.43}N$ showed 1–2% disordered Li vacancies similar to Li_3N,[10] which seemed insensitive to reaction temperature. Niewa *et al.* also claimed that transition metal (M = Ni and Cu) substituted Li_3N contains predominately M^+ species over the whole range of x in $Li_{3-x}M_xN$ based on their X-ray diffraction data, thermal measurements, and chemical analysis.[13]

Since transition metals rarely exist in the +1 oxidation state as M^+ (Cu^+ and few Ni^+, Co^+ oxo-ligands are exceptions[18–22]), others asserted aliovalent substitution of Li^+ by M^{+2}, which gives rise to the formation of $Li_{3-2x}M_x\square_xN$ ($\square$ = Li vacancy). This suggests that high concentration of Li vacancies is required to compensate the charge balance for divalent (or even trivalent) transition metals, and that Li vacancy concentration increases with the concentration of doped transition metal. LiNiN was claimed to serve as an excellent model compound of the stoichiometric $LiNi\square N$ with 50% Li vacancies in the $[Li_2N]$ plane.[23] Ducros *et al.* declared to synthesize a series of stoichiometric $Li_{3-2x}Ni_xN$ ($0.20 \leq x \leq 0.60$) compounds with the existence of Ni^{2+} and correspondingly compensated Li vacancies.[24]

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