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Structural and electronic properties of lithium ion battery anode material LiMN (M = Ni, Co, Cu)

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ABSTRACT

The structural and electronic properties of anode materials LiMN (M = Ni, Co, Cu) for lithium ion batteries have been studied by the first-principles method. The calculations reveal different bonding characteristics for LiMN (M = Ni, Co, Cu). The Li–N bond on the LiN planes shows covalent mixed with ionic characters, with the covalent interaction strengthened and ionic one weakened gradually from LiNiN to LiCoN and then to LiCuN. In the direction of N–M chains, the bonding characteristics are analogous on the whole. The N–M bonding shows both ionic and covalent characters again, while the covalent interaction slightly weakened in sequence. Electronic structure calculations suggest that LiMN (M = Ni, Co, Cu) are all metallic, where the LiNiN is of anisotropic conductivity along the directions of N–Ni chains, while for LiCoN and LiCuN, electrons can also be feebly conductive on the LiN planes besides along the linear N–Co and N–Cu chains.

1. Introduction

Lithium ion batteries are state-of-the-art power sources for portable electronic devices and electric vehicles. Aiming at improving the performance of lithium ion batteries, a great deal of efforts has been devoted to improve the performance of electrode materials. It still, however, requires ever-greater scientific efforts to search for new materials, specially those exhibiting excellent properties and superior security capacities. Because the heat of reaction between electrode materials and electrolytes depends on the anode potential, one possible avenue to increase safety would be using negative electrode materials with higher potential [1]. Since the reaction mechanism of Li_3N with the first low transition element has been studied [2], Li–M–N (M denotes transition metal) has been explored as promising anode materials for lithium ion battery, especially in recent years, many significant electrochemical results for the lithium ternary nitrides have been obtained. Nishijima et al. [3] showed that the solid solutions of $Li_{3-x}M_xN$ could be formed in the range of $0 \le x \le 0.5$, $0 \le x \le 0.6$ and $0 \le x \le 0.3$ for M = Ni, Co, Cu, respectively. They also presented the charge–discharge capacities of these lithium layered ternary nitrides. By adopting a different technique, Weller et al. [4] successfully synthesized the $Li_{2.4}Cu_{0.6}N$ ($x = 0.6$) which is in the analogous hexagonal structure with Li_3N. In 2002, Niewa et al. [5] made a big progress in their successful synthesis of the $Li_{3-x}Ni_xN$ ($0 < x \le 0.85$) by applying the temperature in the range of 773–873 K. In their experiments, Stoeva et al. [6] showed that the limitation of x were below 0.4 for $Li_{3-x}M_xN$ (M = Co and Cu), but for M = Ni, they synthesized the layered ternary nitrides LiNiN (with $x = 1$), i.e., each LiNiN primitive cell contained one Li vacancy. They also showed that LiNiN was of isotropic conductivity, displaying an interesting combination of fast Li^+ ion diffusion and metallic property. Therefore, LiNiN can be a promising anode material for lithium ion battery [7]. Within the crystal structure of LiNiN (space group $P\overline{6}m2$), alternate Li–N and Ni planes stack perpendicular to the Ni–N chains [8], and the Li–N planes are linked via infinite, straight Ni–N chains, as shown in Fig. 1.

It is well known that the structure of $Li_{3-x-y}M_x\square_yN$ ($\square$ denotes the vacancy) is either an anti-fluorite structure or the one which is slightly modified on the basis of the hexagonal structure of lithium nitride Li_3N. Late first row transition nitridometallates such as those formed with Ni, Co and Cu favour this latter structure type [2]. With the amount of transition metal in these structures increasing, the inter-atomic interaction as well as the structures of the materials will be changed. Besides, the increase of the lithium vacancies in the materials will also lead to the change of the electrochemical properties of the lithium ternary nitrides. Since all the three materials $Li_{3-x}M_xN$ (with M = Ni, Co, Cu) are in the analogical hexagonal structure [9], whether or not the LiCoN and LiCuN will behave analogous to LiNiN and what similarities and differences are

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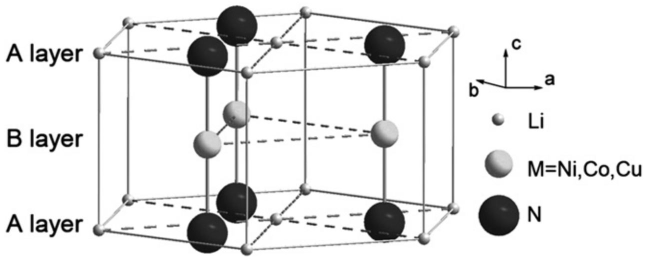

Fig. 1. Primitive cell of LiMN (M = Ni, Co, Cu).

in electrochemical properties among them are the key issues of the present paper. We have been, therefore, prompted to carry out first-principles calculations on the structural and electronic properties of LiMN (M = Ni, Co, Cu), including the structure parameters, charge density differences, band structures and electronic density of states.

2. Calculational methods

The present calculations have been performed using the Vienna ab initio simulation package (VASP) which is based on the density functional theory, the plane-wave basis and the projector augmented wave (PAW) representation [10,11]. The exchange-correlation potentials are approximated by the generalized gradient-corrected function (GGA) given by Perdew and Wang [12,13]. LiMN (M = Ni, Co, Cu) are all studied in a hexagonal lattice (see Fig. 1), where LiN planes are chosen as the X–Y plane and the direction of N–M chains are chosen as *Z* axis. In all the calculations, the wave functions were expanded by plane-waves with a cutoff of plane-wave kinetic energy up to 450 eV. The integration over the Brillouin zone (BZ) was replaced by discrete summation over a special set of **k**-points, using Monkhorst–Pack scheme [14]. The 13 × 13 × 15, 15 × 15 × 17 and 15 × 15 × 17 **k**-points meshes were employed for LiMN (with M = Ni, Co, Cu), respectively. Both the kinetic energy cutoff and the Monkhorst–Pack **k**-points mesh had been optimized, so that accuracy of the total energy could be at the level of 0.001 eV. Tetrahedral method with Blöchl corrections [15] was introduced to determine the electronic partial occupancies f_{nk}. Optimization of the crystal structures was done with the conjugate-gradient technique, taking the calculated Hellmann–Feynman forces as a guide. All the crystal geometries were fully relaxed until the forces on all the atoms were less than 0.001 eV/Å. So, the obtained structures were all stable or meta-stable phase. Since the spin-states of transition metals may have significant effects on the properties of LiMN (M = Ni, Co, Cu), we have also performed the spin-polarized calculations. However, no magnetization was found for all the three materials. Thus, the rest of our calculations are the non-spin-polarized ones.

3. Results and discussions

LiMN (M = Ni, Co, Cu) are isostructural with Li_3N and exhibit hexagonal layered structure, with alternating A layers (LiN planes) and B layers (M atomic planes) linked via infinite, linear N–M (M = Ni, Co, Cu) chains (see Fig. 1). Firstly, the crystal structures of LiMN (M = Ni, Co, Cu) are fully optimized, and the corresponding calculated lattice constants and cohesive energies (per molecular formula) are listed in Table 1. The theoretical results for LiNiN here are in good agreement with the experimental results [7], and the difference between theoretical and experimental data is less than 3%.

In order to see the nature of interaction in LiMN (M = Ni, Co, Cu), the contour plots of the differences of electronic charge densities on the LiN plane, the transition metal M plane and the $(11\bar{2}0)$ plane where one dimensional (1-D) linear N–M chains locate are presented in Fig. 2. The charge density differences, which help to visualize the bonding characteristics, are defined as the differences between the LiMN (M = Ni, Co, Cu) systems and the superposition of atomic charge densities, i.e., $\Delta\rho(\vec{r}) = \rho(\vec{r}) - \sum \rho_{\text{atom}}(\vec{r} - \vec{R}_\mu)$, where $\rho(\vec{r})$ is the total charge density of the system, $\rho_{\text{atom}}(\vec{r} - \vec{R}_\mu)$ is the charge density of every single atom and $\vec{R}_\mu$ is the atomic coordinates. The charge accumulation (solid lines) and depletion (dashed lines) regions related to the interacting atoms are clearly shown. For the sake of seeing the differences among these lithium ternary nitrides, the maximum and minimum values of contour lines are both set to be equal, and the interval values are Δ = 0.015, 0.06 and 0.075 eV/Å^3 in Fig. 2(a)–(c), respectively. Nitrogen is five-coordinated, which is made by two Ni atoms and three Li atoms. The bonding between Li and N in LiMN (M = Ni, Co, Cu), as can be seen from Fig. 2(a), shows covalent mixed with ionic characters, with the covalent interaction strengthened while the ionic one weakened gradually from LiNiN to LiCoN and then to LiCuN. Within the M (M = Ni, Co, Cu) atomic planes which are perpendicular to the *c*-axis, weak interaction between M–M atoms is apparently seen from the plots of charge density differences as shown in Fig. 2(b). This is due to the large M–M inter-atomic distances, which are as big as 3.64 Å, 3.46 Å and 3.60 Å, respectively. The calculated Ni–Ni inter-atomic distance is in reasonably good agreement with experimental value of 3.74 Å [7]. As a result, the interaction between transition metal and other atoms is mostly concentrated in the direction of linear N–M chains perpendicular to the M planes. From Fig. 2(c), it suggests that the bonding between N and transition metal M (M = Ni, Co, Cu) is of a strong covalent interaction combined with ionic one. The covalent interaction between N and Ni atoms in LiNiN is the strongest, while the covalent interaction is slightly weakened from LiNiN to LiCoN and then to LiCuN. The calculated N–M (M = Ni, Co, Cu) inter-atomic bond lengths are 1.71, 1.72 and 1.76 Å, respectively.

Table 1
The optimized lattice constants and cohesive energies, E_{coh}, of LiMN (M = Ni, Co, Cu).

		Lattice constants			E_{coh} (eV)
		a (Å)	*b* (Å)	*c* (Å)	
LiNiN	This work	3.64	3.64	3.42	11.96
	Exp. [7]	3.74	3.74	3.52	–
LiCoN	This work	3.46	3.46	3.43	10.09
LiCuN	This work	3.60	3.60	3.52	10.03

The calculated band structures, the total electronic density of states (TDOS) and the partial density of states (PDOS) are presented in Figs. 3 and 4, respectively, where the Fermi level is set to be at 0 eV. From Fig. 3, common grounds of lithium ternary nitrides LiMN (M = Ni, Co, Cu) are clearly visible. On the one hand, they are all metallic since they all have bands crossing the Fermi level. On the other hand, the “3d–2p” band dispersion (approximately ranging from −7.5 eV to 2.5 eV) among transition metal M (M = Ni, Co, Cu) and N atoms, as well as the “3d–2p” bandwidth are all analogous. The calculated “3d–2p” bandwidths are about 8.21 eV, 8.77 eV and 7.56 eV for LiMN (M = Ni, Co, Cu), respectively. A similar band dispersion of CaNiN had also been presented by Mattheiss [16]. Furthermore, in the band structure of LiNiN, the bands cutting the Fermi level are all in the directions paralleling to the *z*-axis of the BZ, i.e., along the Γ–A, K–H and M–L lines, which indicate that LiNiN is of an anisotropic electronic conductivity along the linear Ni–N chains. Stoeva et al. [7] have already demonstrated such a peculiar electronic conductivity for LiNiN from both the experimental and theoretical studies. Structurally, there are many other kinds of compounds reported containing linear Ni–N chains, such as CaNiN [16] and $Li_3Sr_3Ni_4N_4$ [17] as representatives, and they may have