

Lithium-Ion Storage Mechanism in Metal-N-C Systems: A First-Principles Study

Zhiping Lin,* Yongqi Chen, Qi Zhang, Lingling Bai, and Fugen Wu

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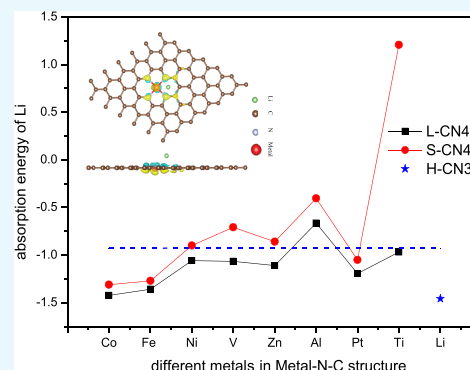
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ABSTRACT: In metal-N-C systems, doped metals have an obvious valence change in the process of Li-ion deintercalation, which is in agreement with the operational principle of traditional anode materials. Doped metals will transfer some electrons to the neighboring N atoms to improve the valence state. Along with Li adsorption, the charge transferred to the nearest N or C from Li is less compared to that transferred to the doped metal. Hence, doped metals have an obvious valence change in the process of Li-ion deintercalation, and doped N just serves as a container for holding electrons. The local states of C and N p electrons in the Co-N-C structure can be fully destroyed, which can effectively improve the electronic properties of graphene.



1. INTRODUCTION

In the recent years, graphene has received attention as an anode for Li-ion batteries (LIBs) because of its high intrinsic electrical conductivity, excellent mechanical flexibility, and large theoretical surface area.^{1,2} Along with restacking or agglomeration of graphene sheets by strong van der Waals interactions among the sheets, the decrease in the surface area and the increase in impediment will lead to low energy density and poor rate capability.³ Heteroatomic doping is the most popular and effective method to improve graphene's performance. Various heteroatom dopants have been investigated in carbon materials, such as phosphorus, boron, sulfur, and nitrogen.^{4–6} The doped heteroatom is able to enhance electronic and ionic conductivities, to add active sites for Li⁺ storage, and to improve wettability between electrolytes and electrodes. Many investigations have also shown that transition metal (*i.e.*, M = Fe, Ni, and Co)^{7–9} single atoms or atom clusters embedded in nitrogen-doped carbon frameworks (N-C) can lead to promising electrochemical properties in catalytic applications. Metal single atoms not only could possess amazing electronic and reactive properties but also exhibit a theoretical 100% atom utilization efficiency.^{10,11} The interaction between metal and N is energetically favorable for the adsorption and reduction of charge/mass at the metal site. Based on their remarkable oxygen reduction reaction activities, metal-N-C systems as cathodes for various metal (for example, Zn, Al, and Li)-air batteries have been intensively reported.^{12,13} Moreover, the M-N-C systems as cathodes for lithium sulfur batteries have also been found to deliver high capacity and cycling stability.^{14–20} It is because the electrical conductivity can be improved by the hybrid and the

adsorption ability of lithium polysulfides between metal-N-C and sulfur can be enhanced along with significantly reducing the “shuttle effect” of polysulfides during the cycles.²¹

In order to understand the role of heteroatoms in improving the performance of carbon anodes in lithium batteries, we investigate the adsorption of Li ions in metal-N-C structures by first-principles calculation. With our results, it can be understood which doped metals can improve lithium storage properties and why are they good for the performance improvement of LIBs.

2. CALCULATION DETAILS

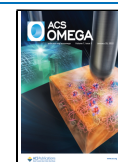
First-principles calculation was performed based on density functional theory implemented in the VASP.²² PBE pseudopotentials were used to describe the electron–ion interactions.^{23,24} The E_{cut} is set to 350 eV, and the allowed error in total energy is 10^{-4} . The single-layer graphene with 66 atoms is adopted as a calculation model, as shown in Figure 1. The vacuum region of 20 Å along with the Z-axis direction is adopted to avoid interaction between images caused by periodic boundary conditions. We use Bader's theory to analyze the charge change.^{25–27}

The formation energy of metal dopants and the adsorption energy of Li ions can be obtained by the following formula:

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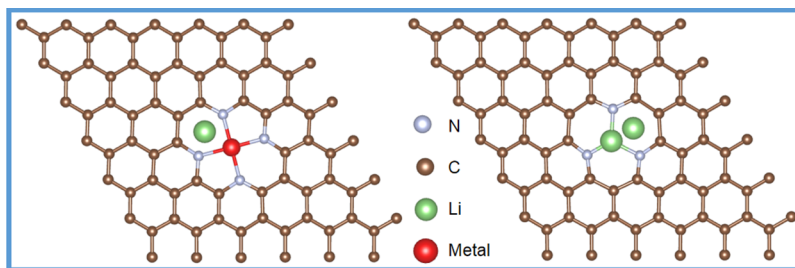


Figure 1. Adopted calculation model for Li-ion adsorption: metal-N4-C and Li-N3-C.

$$E_{\text{adsorption energy}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{adsorbents}}$$

where E_{total} , E_{slab} , and $E_{\text{adsorbents}}$ are the total energies of different adsorption sites, the energies of the clean slab, and the energies of the adsorbent (metal or Li), respectively.

3. RESULTS AND DISCUSSION

3.1. Formation of Metal-N-C Structures. In experiments, heteroatom doping can be prepared by an ionic liquid impregnation silica templated method followed by an annealing process.^{15–18} From a theoretical perspective, building a model and calculating the formation energy of a structure can obtain the stable structure of heteroatom doping. We build two models to discuss metal atom doping, as shown in Figure 1. One is a metal-N4-C model that has four pyridinic N, which was reported in an experimental paper.¹⁴ The other model is used to discuss the Li metal doping structure, which has three pyridinic N and forms a Li-N3-C interlink. Also, the formation enthalpy of the Li-N3-C structure (−6.598 eV) is lower than that of Li-N4-C (−6.237 eV), in which the formation enthalpy is calculated as follows:

$$\Delta H(\text{metal-N-C}) = E_{\text{total}}(\text{metal-N-C}) - E_{\text{total}}(\text{metal}) - nE_{\text{total}}(\text{N}) - mE_{\text{total}}(\text{C})$$

where E_{total} is the density-functional total energy of every element and n and m are the numbers of atoms N and C. Hence, the adsorption of Li ions in the N-C structure may be derived from Li-ion doping, and its formation energy is controlled by the N amount.

The possible doping metals that we have considered consist of nontransition metals, transition metals, and noble metals. Some metal dopings have been reported, such as Zn, Al, and Li-air batteries.^{13–18} The formation energies of metal-N4-C structures are shown in Figure 2. It can be seen that the formation energies of all metal dopings are negative. This means that metal-N4-C structures are relatively accessible, which is in agreement with lots of experimental reports. From the results, we can also find that the formation energies for transition metals Fe, Co, and Ni are lower than those for other metals. There is about 2–5 eV difference from Zn to Co doping. Then, Fe/Co/Ni-N4-C compounds have been synthesized for electrocatalytic hydrogen evolution^{9,10} and oxygen electrocatalysts in Zn-air batteries.^{11–13} Based on the loss of the electrochemical surface area and TEM images, Pt/CNx have exhibited a better stability than Pt/CNTs.²⁸ Comparing the Li-ion doping formation energy for Li-N3-C with the Li-N4-C structure, it can be seen that the formation energy of the Li-N4-C structure is lower, and then the N4-C structure more easily traps Li than N3-C. Hence, the improvement of intercalation potential vs Li/Li⁺ may arise

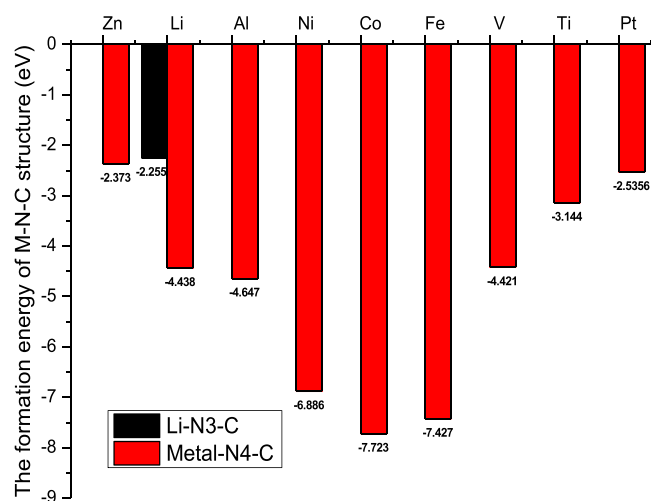


Figure 2. Formation energies of metal doping for different metals located in M-N4-C structures and the Li-N3-C structure.

from the adsorption of Li-ion vacancy defect in N-C compounds without metal doping.¹⁴

In metal atom-doped N-C systems, the length of C–N bonds and the number of electrons of N atoms will change. Figure 3 show the difference charge state of densities for different metal-N4-C structures and Li-N3-C structure. Table 1 lists the lengths of metal-N bonds and C–N bonds in the formed M-C-N structures as well as the number of transferred electrons (NTE) from the metal to N atoms. The bond length for Li doping N3-C

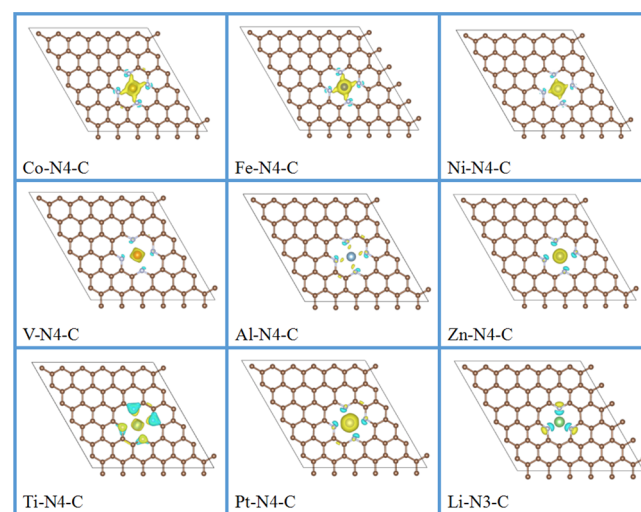


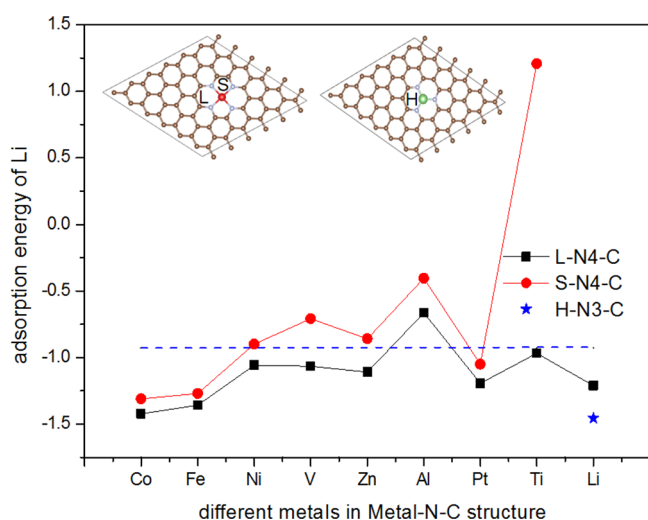
Figure 3. Difference charge state of densities for different metal-N4-C structures and the Li-N3-C structure.

Table 1. Lengths of Metal-N Bonds and C-N Bonds in the Formed M-C-N Structures and the Number of Transferred Electrons (NTE) from the Metal to per N Atom

	metal-N bond length (Å)	C-N bond length (Å)		NTE from the M atom to per N atom
C-N4		1.3617 × 4; 1.3246 × 4		
Co-N4-C	1.8660 × 4	1.3942 × 4; 1.3679 × 4	↑	0.0525e
Fe-N4-C	1.8682 × 4	1.4038 × 4; 1.3708 × 4	↑	0.0451e
Ni-N4-C	1.8781 × 4	1.3815 × 4; 1.3683 × 4	↑	0.0868e
V-N4-C	1.9201 × 4	1.3931 × 4; 1.3832 × 4	↑	0.1421e
Al-N4-C	1.8893 × 4	1.3972 × 4; 1.3746 × 4	↑	0.3424e
Zn-N4-C	1.9552 × 4	1.3646 × 4; 1.3523 × 4	↑	0.1691e
Pt-N4-C	1.9510 × 4	1.3707 × 4; 1.3657 × 4	↑	0.0367e
Ti-N4-C	1.8660 × 4	1.4013 × 4; 1.3776 × 4	↑	0.2435e
C-N3		1.3517 × 4; 1.3266 × 2		
Li-C-N3	1.6272 × 3	1.3453 × 4; 1.3241 × 2	↓	0.1643e

decreases and those for other metal-N4-C increase. This is because the interaction of Li and N is weaker than those of other metals and N. Along with metal doping, electrons will transfer from the doped metal to N atoms. The NTE from the metals to N atoms is from 0.0367e (Pt) to 0.3424e (Al), in which the number of transferred electrons from Al to N atoms is the highest and Pt is the least. The number of transferred electrons from Li to N is 0.1643e. The numbers of net electrons transferred from the metals are 0.1468e to 1.3696e. Thereinto, metal Co is 0.21e, Fe is 0.1804e, Ni is 0.3472e, and Pt is 0.1468e.

3.2. Adsorption of Li Ions in M-N-C Structures. As is known to all, it is very important for the capacity to accommodate Li ions as carbon anode materials. To illuminate the capacity change for accommodating Li ions, we have calculated the adsorption of Li ions on the surface of M-N4-C structures. The results are shown in Figure 4. The blue dotted

**Figure 4.** Adsorption energies of Li ions in different sites for metal-N-C structures. The dotted line is the adsorption energy of Li for graphene.

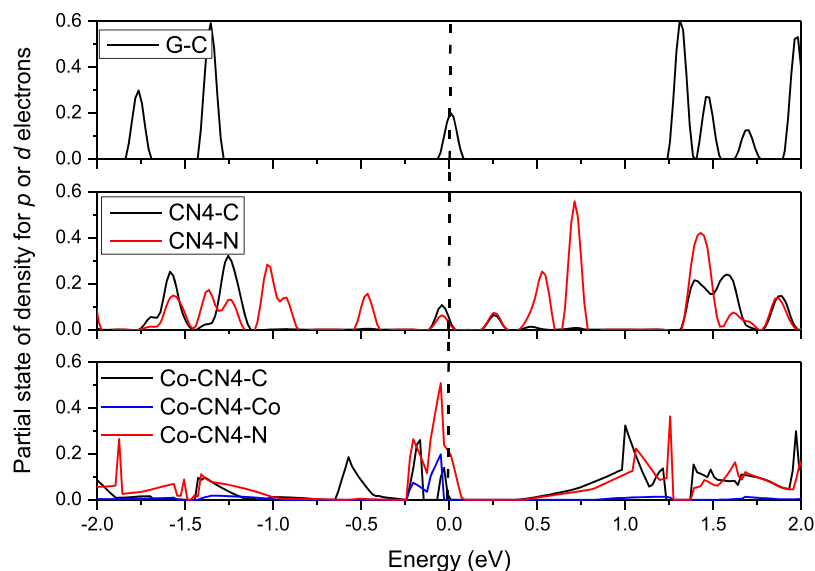
line is the adsorption energy of Li ions on the surface of graphene. There are two different adsorption sites with the nearest metal in metal-N4-C structures, which are represented by S and L. There are three equivalent sites in the Li-N3-C structure, which are represented by H. It can be seen from Figure 4 that the adsorption energy of Li ions on the S site is higher than that of the L site. Except for Al doping, other metal dopings are able to improve the adsorption of Li ions on the L site. Only Fe, Co, and Pt dopings are clearly better on the S site, and others are even worse than graphene. For the Li-N3-C structure, the adsorption energy of the H site (−1.4583 eV) is better and is even better than Li-N4-C (the adsorption energy is −1.21 eV on the L site¹⁴). Then, for Li doping, the N3-C structure has a more obvious advantage than N4-C on Li-ion adsorption.

The lower NTE from metal to per N atom, the more Li-ion adsorption for doped structure. In order to obtain the role of doped metals, we collected together the charge change of metal (Fe, Co, Pt, and Li) atoms along with Li-ion adsorption, shown in Table 2. When the Li atom is adsorbed in the M-N-C structure or graphene, the charge will transfer to the neighboring metal, N, or C. The charge transferred to the nearest N or C from Li is less compared to that transferred to the doped metal. Compared with that transferred to C for pure graphene, doped N has a stronger ability to accept charges from Li. Hence, N doping can improve graphene electrochemical properties.^{29,30} Comparing the NET of metal atoms both in Table 1 and Table 2, it can be found that the number of electrons transferred by metal atoms (for example, Co: 0.21e) during doping is basically the same as that transferred by lithium ion absorption (Co: 0.2133e). That is to say, the valence of doped metals will increase accompanying the doping process and will decrease along with Li absorption. Therefore, doped metals have an obvious valence change in the process of Li-ion deintercalation, which is in agreement with the operational principle of other anode materials (for example Li_3VO_4 ³¹ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ³²). Comparing the doped N and metal of the receptive elements, we also find that N does not have the rise and fall of the valence state and just serves as a container for holding electrons, which has the ability to better accommodate electrons than graphene C. Therefore, a reasonable selection of doped metals can available improve the electrochemical properties of C anodes.

3.3. Electronic Properties of M-C-N. It is well known that in graphene, the p hybridization of the $2p_x$ and $2p_y$ orbitals of carbon atoms creates lateral σ bonds, and the remaining $2p_z$ orbitals form the π bonds.³³ A single graphene sheet shows a metallic behavior due to topological singularities at the K points in the Brillouin zone,³⁴ in which the conduction and valence bands touch in the so-called conical or Dirac points and the dispersion is essentially linear within ± 1 eV of the Fermi level. The interactions of transition metals and graphite or a graphene sheet have shown that carbon p_z orbitals hybridize strongly with the d orbitals of transition metal atoms.³⁵ Figure 5 shows the partial state of density of p or d electrons for C, N, and Co atoms. The p electronic states of C in graphene are localized near the Fermi level, which consist of the hybridization of $2p_x$, $2p_y$, and $2p_z$ orbitals. In the N4-C structure without doped metals, the p electrons of the nearest neighbor C hybridized with the p electrons of the N atom, and the local states localized near the Fermi level shift to low energy and unfold into several local energy levels due to the p electrons of the neighboring N atom. Along with Co doping, the local states of C and N p electrons are fully destroyed, which can improve graphene's electronic

Table 2. NET to the Nearest N Atoms or C Atoms and NET to the Doped Metal along with Li Adsorbed in M-C-N Porous Carbon or Graphene¹⁴

site of Li-ion insertion	NET to the nearest N atom			NET to the nearest C atom		NET to the metal atom	
	S	L	H			S	L
Co-C-N4-Li	0.0366e	0.0404e			0.015e	0.2133e	0.1771e
Fe-C-N4-Li	0.0081e	0.0146e			0.013e	0.1860e	0.1617e
Pt-C-N4-Li	0.0420e	0.0530e			0.015e	0.1211e	0.1128e
Li-C-N3-Li graphene-Li			0.0885e		0.013e 0.01e	0.0887e (H site)	

**Figure 5.** Partial states of density of p electrons for C and N and d electrons for Co atoms during graphene heteroatom doping.

properties and electrochemical performance as an anode material.¹⁴

4. CONCLUSIONS

The formation of metal-N-C structures is relatively accessible, which is in agreement with lots of experimental reports. The formation energies for transition metals Fe, Co, and Ni are lower than those for other metals. Along with metal doping, the length of the C–N bond will increase and electrons will transfer from the doped metal to N atoms. The adsorption energy of Li ions on the S site is higher than that of the L site. Except for Al doping, other metal dopings are able to improve the adsorption of Li ions on the L site. Only Fe, Co, and Pt dopings are clearly better on the S site; others are even worse than graphene. When Li is adsorbed in the M-N-C structure or graphene, the charge transferred to the nearest N or C from Li is less compared to that transferred to the doped metal. Hence, the introduced N does not have the rise and fall of the valence state and just serves as a container for holding electrons, which is better than C of graphene. Also, doped metals have an obvious valence change in the process of Li-ion deintercalation, which is in agreement with the operational principle of traditional anode materials. Transition metal doping can clearly destroy the local states of C and N p electrons. Therefore, transition metal doping (M-N-C) is propitious to improve the electronic and electrochemical characteristics of carbon anode materials.

AUTHOR INFORMATION

Corresponding Author

Zhiping Lin – School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou 510006, China; orcid.org/0000-0002-3179-0784; Email: zhipinglphy@gdut.edu.cn

Authors

Yongqi Chen – School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou 510006, China

Qi Zhang – School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou 510006, China

Lingling Bai – School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou 510006, China

Fugen Wu – School of Materials and Energies, Guangdong University of Technology, Guangzhou 510006, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.1c04673>

Notes

The authors declare no competing financial interest.

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