An insight into the electro-chemical properties of halogen (F, Cl and Br) doped BP and BN nanocages as anodes in metal-ion batteries

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Here, electro-chemical properties of BN and BP nanocages as anodes in metal-ion batteries are examined. The effect of halogens adoption of BN and BP-NCs on electro-chemical properties of M-IBs are investigated. Results showed that the BP nanocages as anode electrode in M-IBs has higher efficiency than BN nanocages and the K-IB has higher cell voltage than N-IBs. Results indicated that the halogens adoption of BN and BP-NCs are improved the cell voltage of M-IBs. Results proved that the F-doped M-IBs have higher cell voltage than M-IBs. Finally, F-B17P18 as anodes in K-IB is proposed as suitable electrodes.

In previous studies, the chemical and physical properties of boron nitride nanocages (BN-NC) and boron phosphide nanocages (BP-NC) have been investigated1–3. The results of previous studies confirmed that nanocages have acceptable properties as anodes and cathode materials in batteries due to low band gap energies and high potential to transfer the electrons and ions4–7.

Results of previous studies indicated that the formation heat and formation heat of per atom of B18N18, B24N24 and B36N36 are decreased when the number of atoms are increased. Results of previous studies confirmed that the formation heat and formation heat of per atom of B18P18 is higher than those of B24P24 and B36P36, significantly8–11. Results of previous studies showed that the formation heat of B18N18, B24N24 and B36N36 are –1275, –1197 and –1034 kcal/mol and the formation heat of per atom of B18N18, B24N24 and B36N36 are 15, 13 and 12 kcal/mol8–11.

Results of previous studies indicated that the halogen (F, Cl and Br) adoption of nanocages are decreased the band gap energies of nanocages and halogen (F, Cl and Br) adoption are improved the electro-chemical properties (cell voltage) of nanocages as anodes and cathode materials in batteries12–15. The potential of graphite, nanotubes and nanocages as anodes of metal-ion batteries (M-IBs) have been studied and results showed that nanocages have higher potential rather graphite and nanotubes16–18.

In previous studies, the electro-chemical properties (cell voltage) of B12N12 as anodes in L-IBs and Na-IBs are examined and results confirmed that the F and Br are improved the properties of L-IBs and Na-IBs19–21. In previous studies, the metal adsorption on BN-NCs are investigated and results indicated that the lithium and potassium atoms are increased the properties of NC in M-IBs. The electronic properties of B18N18, B18P18 and B12C24P are examined and results indicated that the electro-chemical properties (cell voltage) of BN nanocages are improved by increasing the size of rings22,23.

Razavi et al.24 studied the roles of halogen on potential of B18N18 and B18P18 in MIBs by theoretical methods. They demonstrated that storage capacities of B18N18 and B18P18 in L-IBs are 893 and 795 mAh/g and they showed that Vcell of F-doped B18N18 and F-doped B18P18 are higher than Br-doped MIBs by theoretical calculation.

Tahvili et al.25 studied the potential of various nanocages as anodes in MIBs by theoretical methods. They indicated that Al13P22 is the suitable candidate as anode in MIBs and they showed that adsorbed halogen nanocages have higher Vcell than nanocages in MIBs. They proposed the F-Al13P22 nanocage as suitable material in anodes of MIBs by theoretical calculation.

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In this study, electro-chemical properties of BN and BP-NCs as anodes in L-IBs, N-IBs and K-IBs are examined. The effects of F, Cl and Br doping of BN and BP-NCs on their electro-chemical properties (cell voltage) as anode electrodes in M-IBs are examined. The main goals of this study are to (1) find the cell voltages of LIBs made of BP and BN nanocages as anodes; (2) compare the cell voltages of LIBs and NIBs made of BP and BN nanocages as anodes; (3) find the effects of halogen adoption on cell voltages of LIBs made of BP and BN nanocages as anodes; (4) propose the metal-ion batteries with high cell voltage values.

Computational details

The geometries of B_{18}N_{18}, B_{18}P_{18}, X-B_{18}N_{18} and X-B_{18}P_{18} (X = F, Cl, Br) were optimized through DFT method, M06-2X and HSE06 functional and 6-31G (d, p) basis set in GAMESS. The DFT is described energies of inorganic–organic nanocages with acceptable accuracy and M06-2X and HSE06 functional have high accurate to estimate the energies of nano-structures. The DFT/M06-2X is predicted the energies and frequencies of nanocages with suitable accuracy and the M06 is the best functional to estimate the vibrational frequencies of nanocages.

The adsorption of halogens (X = F, Cl, Br) on nanocages and adsorption of M and M’ on studied nanocages. The structures of X-nanocages and M-nanocages are optimized by DFT method, M06-2X and HSE06 functional and 6-31G (d, p) basis set. The vibrational frequencies of studied complexes are investigated by DFT method, M06-2X and HSE06 functional and 6-311+G (2d, 2p) basis set.

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The reaction in anode and cathode of metal ion batteries are: Anode: M-nanocage $\rightarrow$ M’-nanocage $+$ e$^-$. The final reaction in metal-ion battery is: M’ $+$ M-nanocage $\rightarrow$ M’-nanocage $+$ M. The cell voltage ($V_{cell}$) is calculated by via Nernst equation: $V_{cell} = - \Delta G_{cell}/zF$. The F is the Faraday constant, z is the charge of M’ and $\Delta G_{cell} = \Delta E_{cell} + P\Delta V - T\Delta S$.

Results and discussion

BN and BP as anodes in M-IBs. In this section, the structures of nanocages and complexes with halogens and metals are shown in Fig. 1. The electro-chemical properties of BN and BP-NCs as anodes in M-IBs are investigated. The structures and bond lengths (in Å) of BN and BP-NCs with metal are showed in Fig. 1. The geometries of B_{18}N_{18}, B_{18}P_{18}, X-B_{18}N_{18} and X-B_{18}P_{18} (X = F, Cl, Br) were optimized through DFT method, M06-2X and HSE06 functional and 6-31G (d, p) basis set. The geometries of X-nanocages and M-nanocages are optimized by DFT method, M06-2X and HSE06 functional and 6-31G (d, p) basis set. The vibrational frequencies of studied complexes are investigated by DFT method, M06-2X and HSE06 functional and 6-311+G (2d, 2p) basis set.

The Gibbs free energy of structures are calculated as follow: $G = E_0 + ZPE + \Delta H_{trans} + \Delta H_{rot} + \Delta H_{vib} + RT-\Delta S$. The Gibbs free energy of adsorption of halogens on nanocages are calculated as follow: $G_{ad} = G_{(X-nanocage)} - G_{(nanocage)} - 0.5 G(X)$. The Gibbs free energy of adsorption of M and M’ on nanocages are calculated as follow: $G_{ad} = G_{(M-nanocage)} - G_{(nanocage)} - G_{(M)}$.

The reactions in anode and cathode of metal ion batteries are: Anode: M-nanocage $\rightarrow$ M’-nanocage $+$ e$^-$. The final reaction in metal-ion battery is: M’ $+$ M-nanocage $\rightarrow$ M’-nanocage $+$ M. The cell voltage ($V_{cell}$) is calculated by via Nernst equation: $V_{cell} = - \Delta G_{cell}/zF$. The F is the Faraday constant, z is the charge of M’ and $\Delta G_{cell} = \Delta E_{cell} + P\Delta V - T\Delta S$.

F, Cl and Br doped BN and BP nano-structures as anodes in MIBs. The calculated $G_{ad}$ of F-, Cl- and Br-doped BN-NCs and BP-NCs by M06-2X and HSE06 functional are summarized in Supplementary Table 1S in supplementary data. The geometries of B_{18}N_{18}, B_{18}P_{18}, X-B_{18}N_{18} and X-B_{18}P_{18} (X = F, Cl, Br) were optimized through DFT method, M06-2X and HSE06 functional and 6-31G (d, p) basis set. The geometries of X-nanocages and M-nanocages are optimized by DFT method, M06-2X and HSE06 functional and 6-311+G (2d, 2p) basis set.

In this study, electro-chemical properties of BN and BP-NCs as anodes in L-IBs, N-IBs and K-IBs are examined. The effects of F, Cl and Br doping of BN and BP-NCs on their electro-chemical properties (cell voltage) as anode electrodes in M-IBs are examined. The main goals of this study are to (1) find the cell voltages of LIBs made of BP and BN nanocages as anodes; (2) compare the cell voltages of LIBs and NIBs made of BP and BN nanocages as anodes; (3) find the effects of halogen adoption on cell voltages of LIBs made of BP and BN nanocages as anodes; (4) propose the metal-ion batteries with high cell voltage values.
Figure 1. Structures of B$_{18}$N$_{18}$, B$_{18}$P$_{18}$, X-B$_{17}$N$_{18}$ and X-B$_{17}$P$_{18}$ with metal atoms and their bond lengths (Å) and calculated $G_{ad}$ of adsorption of halogens on studied nanocages.
The $G_{ad}$ of K-halogen-B$_{17}$P$_{18}$ are higher than Na-halogen-B$_{17}$P$_{18}$ and Li-halogen-B$_{17}$P$_{18}$. The $|G_{ad}|$ of adsorption of metals on halogen-B$_{17}$P$_{18}$ are higher than halogen-B$_{17}$N$_{18}$. The $|G_{ad}|$ of F-NCs are higher than Cl-NCs and Br-NCs. The orbital energies of metals halogen doped nanocages are reported in Supplementary Table 2S in supplementary data. The $|E_{HOMO}|$ of metals with halogen-B$_{17}$P$_{18}$ are smaller than halogen-B$_{17}$N$_{18}$ significantly.

The calculated $V_{cell}$ of metals with halogen doped nanocages by M06-2X and HSE06 functional are reported in Table 1. The $V_{cell}$ of K-B$_{17}$N$_{18}$ are higher than Li-B$_{17}$N$_{18}$ and Na-B$_{17}$N$_{18}$. The $V_{cell}$ of K-B$_{17}$P$_{18}$ are higher than
Li-B_{17}P_{18} and Na-B_{17}P_{18}. The $V_{\text{cell}}$ of metals with halogen-B_{17}P_{18} are higher than metals with halogen-B_{17}N_{18}. Results show that the trends of calculated $V_{\text{cell}}$ by M06-2X and HSE06 functional are same for studied nanocages.

In present paper, F doping of BN and BP-NCs is increased the $V_{\text{cell}}$ of them in M-IBs. The $V_{\text{cell}}$ of F-B_{17}N_{18} and F-B_{17}P_{18} in N-IB are higher than $V_{\text{cell}}$ of F-B_{17}N_{18} and F-B_{17}P_{18} in L-IB. The halogens doping of NCs are increased the $V_{\text{cell}}$ of M-IBs. The K-ion batteries have higher $V_{\text{cell}}$ than M-IBs and the K-F-B_{17}P_{18} in M-IBs has the highest $V_{\text{cell}}$.

**Conclusion**

In this study, the electro-chemical properties of BN and BP-NCs as anodes in M-IBs are examined. The roles of halogens adoption on electro-chemical properties of BN-NCs and BP-NCs as anodes of metal-IB are investigated. The obtained results of this study are: (1) the B_{18}P_{18} as anode electrode of M-IBs has higher efficiency than B_{18}N_{18}; (2) the KIB has higher $V_{\text{cell}}$ than NIB and KIB; (3) halogens are increased $V_{\text{cell}}$ in M-IBs; (4) the F doped NCs have higher $V_{\text{cell}}$ than Cl and Br doped NCs in M-IBs; (5) F-B_{17}P_{18} has the highest $V_{\text{cell}}$ as anode electrodes in K-IB and F-B_{17}P_{18} is proposed as novel anodes in M-IBs.

**Data availability**

The calculated $G_{\text{ad}}$ of nano-structures by M06-2X and HSE06 functional are presented in Table 1S and calculated energies of orbitals and $q$ of nano-structures by M06-2X and HSE06 functional are presented in Table 2S.

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| Position | Complex | $V_{\text{cell}}$ by M06-2X | $V_{\text{cell}}$ by HSE06 | Position | Structure | $V_{\text{cell}}$ by M06-2X | $V_{\text{cell}}$ by HSE06 |
|----------|---------|-----------------------------|-----------------------------|----------|-----------|-----------------------------|-----------------------------|
| B site   | K-B$_{18}$N$_{18}$ | 1.39                         | 1.43                         | B site   | K-B$_{18}$P$_{18}$ | 1.60                         | 1.64                         |
| B site   | Na-B$_{18}$N$_{18}$ | 1.24                         | 1.26                         | B site   | Na-B$_{18}$P$_{18}$ | 1.43                         | 1.45                         |
| B site   | Li-B$_{18}$N$_{18}$ | 1.11                         | 1.14                         | B site   | Li-B$_{18}$P$_{18}$ | 1.28                         | 1.32                         |
| N site   | K-B$_{18}$N$_{18}$ | 1.41                         | 1.44                         | P site   | K-B$_{18}$P$_{18}$ | 1.63                         | 1.67                         |
| N site   | Na-B$_{18}$N$_{18}$ | 1.27                         | 1.30                         | P site   | Na-B$_{18}$P$_{18}$ | 1.45                         | 1.48                         |
| N site   | Li-B$_{18}$N$_{18}$ | 1.13                         | 1.17                         | P site   | Li-B$_{18}$P$_{18}$ | 1.31                         | 1.35                         |
| Bridge B-N | K-B$_{18}$N$_{18}$ | 1.37                         | 1.41                         | Bridge B-P | K-B$_{18}$P$_{18}$ | 1.57                         | 1.62                         |
| Bridge B-N | Na-B$_{18}$N$_{18}$ | 1.22                         | 1.26                         | Bridge B-P | Na-B$_{18}$P$_{18}$ | 1.41                         | 1.45                         |
| Bridge B-N | Li-B$_{18}$N$_{18}$ | 1.08                         | 1.11                         | Bridge B-P | Li-B$_{18}$P$_{18}$ | 1.25                         | 1.29                         |
| K-F-B$_{17}$N$_{18}$ | 3.12                         | 3.22                         | K-F-B$_{17}$P$_{18}$ | 3.59                         | 3.70                         |
| Na-F-B$_{17}$N$_{18}$ | 2.78                         | 2.87                         | Na-F-B$_{17}$P$_{18}$ | 3.20                         | 3.30                         |
| Li-F-B$_{17}$N$_{18}$ | 2.49                         | 2.57                         | Li-F-B$_{17}$P$_{18}$ | 2.86                         | 2.96                         |
| K-Cl-B$_{17}$N$_{18}$ | 2.95                         | 3.04                         | K-Cl-B$_{17}$P$_{18}$ | 3.39                         | 3.50                         |
| Na-Cl-B$_{17}$N$_{18}$ | 2.64                         | 2.70                         | Na-Cl-B$_{17}$P$_{18}$ | 3.03                         | 3.11                         |
| Li-Cl-B$_{17}$N$_{18}$ | 2.35                         | 2.45                         | Li-Cl-B$_{17}$P$_{18}$ | 2.71                         | 2.82                         |
| K-Br B$_{17}$N$_{18}$ | 2.78                         | 2.89                         | K-Br B$_{17}$P$_{18}$ | 3.20                         | 3.33                         |
| Na-Br B$_{17}$N$_{18}$ | 2.49                         | 2.58                         | Na-Br B$_{17}$P$_{18}$ | 2.86                         | 2.96                         |
| Li-Br B$_{17}$N$_{18}$ | 2.22                         | 2.29                         | Li-Br B$_{17}$P$_{18}$ | 2.55                         | 2.64                         |

Table 1. The calculated $V_{\text{cell}}$ of BN and BP nanostructures.
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S.M. wrote the first version of paper. M.A., M.E., and M.G. collaborated in revision.

**Competing interests**
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