1P09

アルカリ金属-黒鉛層間化合物の理論的研究: Li, Na, K イオン電池負極への応用

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Li_xC_6 ($0 \leq x \leq 1$) is a widely used anode material in Li-ion batteries in which Li is intercalated into graphite during charge and the reverse occurs during discharge. We use VASP to perform *ab initio* calculations. Because the conventional DFT calculations fail to describe van der Waals interactions, we test the reliability of van der Waals correction methods, DFT-D3 method and vdW-DF functional. As a result, vdW-optPBE functional which gives the reasonable results especially with respect to the formation energy of LiC_6 and LiC_{12} is used in our calculations.

The formation energies of Li_xC_6 defined as

$$E_{form} = E(Li_xC_6) - xE(LiC_6) - (1-x)E(C_6)$$

are plotted with respect to x in Li_xC_6 (Fig.1.(a)). The structures which lie on a convex line appear as stable phases during charge and discharge. The average voltage between x_1 and x_2, where x_1 and x_2 are concentrations of Li in stable Li_xC_6, is calculated as

$$\overline{V} = -\frac{E(Li_{x_2}C_6) - E(Li_{x_1}C_6) - (x_2 - x_1)E(Li)}{x_2 - x_1}$$

and plotted (Fig.1.(b)).

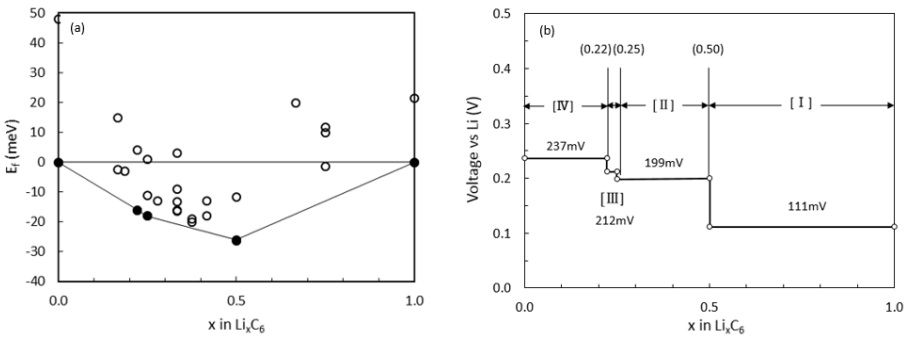

Fig.1. (a) The formation energy E_{form} and (b) voltage profile of Li_xC_6.

Na and K-ion batteries have been proposed as alternatives to Li-ion batteries due to the limited availability of Li resources. Graphite is used as an anode material in K-ion batteries. We perform similar calculations to Li_xC_6 for K_xC_8 to obtain voltage profile of K-ion batteries.

Although graphite is a standard anode material for Li and K-ion batteries, it cannot be used for Na-ion batteries as few Na can be intercalated into graphite. To confirm the low capacity of Na-graphite intercalation compounds (GICs), we calculate the formation energy (E_f) of alkali metal-GICs, which shows a peculiar non-monotonic dependence on alkali metal (Fig.2.(a)). For simpler analysis, we have shown that a similar trend of E_f is observed for diatomic alkali metal fluoride molecules (Fig.2.(b)). The analogy between alkali metal-GICs and alkali metal fluoride molecules is discussed.

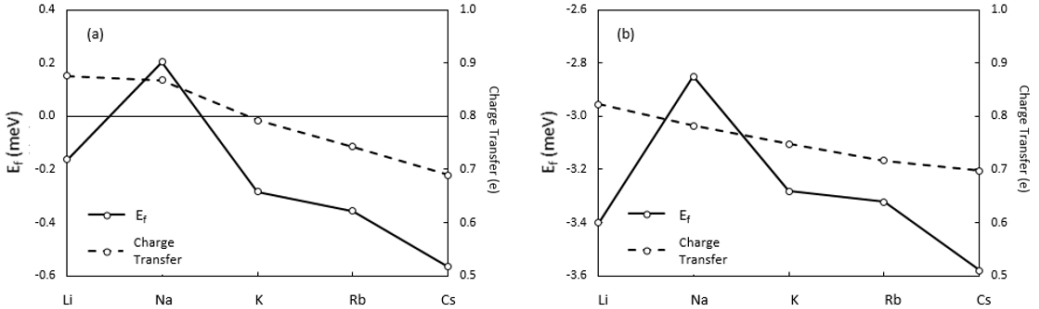

Fig.2. The formation energy E_f and charge transfer of (a) alkali metal-graphite intercalation compounds and (b) alkali metal fluoride molecule.