Electrochemical reaction analysis using density functional calculation + implicit solvation model 2

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The rechargeable Li-ion battery (LIB) is a successful energy storage device due to its high energy density and long cycle life. In order to improve its performance, quantitative understanding of elementary reactions in the LIB such as the reaction of Li intercalation from electrolyte solution into graphite and crystal structure change in graphite during the reaction must be a great help. In previous studies, we have studied charge transfer reactions at electrode/solution interfaces in Li-ion batteries (LIB) using density functional theory (DFT) calculations combined with implicit solvation model. [1–4]

Structure change of Li-intercalated graphite (LIG) during the charge/discharge processes was recently observed by operando X-ray diffraction measurements using a synchrotron radiation at SPring-8. [5, 6] The operando XRD data cannot explained by conventional staging model for LIG. To compare and discuss these experimental results, we conduct first-principles calculations for the phase stability of LIG.

Formation free energy ΔF_f is defined as

$$\Delta F_f(\mathrm{Li}_x\mathrm{C}_6) = F(\mathrm{Li}_x\mathrm{C}_6) - xF(\mathrm{Li}) - F(\mathrm{C}_6) \quad (1)$$

$$F = E_{\mathrm{DFT}} + F_{\mathrm{vib}} - TS_{\mathrm{conf}} \quad (2)$$

where F are the free energies of LIG at composition $\mathrm{Li}_x\mathrm{C}_6$, metal Li, and AB stacked graphite C_6. Free energy is represented as the following three terms: DFT total energy E_{DFT}, vibrational free energy F_{vib}, and configurational entropy term TS_{conf}.

Atomic configurations and cell parameters of Li/6C, Li/9C, Li/12C, Li/18C, Li/24C, and Li/36C in-plane structures (see Fig. 1a) were investigated within van-der-Waals (vdW) level DFT calculations. Interlayer configurations were set to AA, AB, and mix stacking (Fig. 1b). Mix stacking is defined that Li-intercalated layers were set to AA stacking and the other layers were AB stacking. We performed spin-unpolarized density functional theory (DFT) calculations with Quantum ESPRESSO (QE) package. [7]

The vibrational free energy was approximated by using independent harmonic oscillators representation. In this representation, phonon density of state (DOS) was obtained from density functional perturbation theory (DFPT) implemented in QE. Lattice gas model of suitable constraint was applied to the

configurational entropy term.

Figure 1c shows the calculated formation free energies. LiC_6, $Li_{1/2}C_6$, and $Li_{1/3}C_6$ stable structures are AA-stack Li/6C stage1, stage2, and AA stack Li/9C stage2, these structures are consistent with experiment. [1] AB stacking is stable at the region of $x < 0.05$ in Li_xC_6. We emphasize that formation energies using only DFT term failed to describe higher stage region (C_6 – $Li_{1/3}C_6$) especially $Li_{1/3}C_6$ and AB stacking cannot become convex hull. The calculation also shows the existence of mix stacking at intermediate region ($0.05 < x < 0.3$). The expected AB–mix phase transition is slightly different from AA–AB phase transition at $x \approx 0.1$ suggested from X-ray diffraction analysis. [1] Finally, the computational AB–mix phase transition well explained the entropy behavior comparing with electrochemically observed entropy. [8, 9]

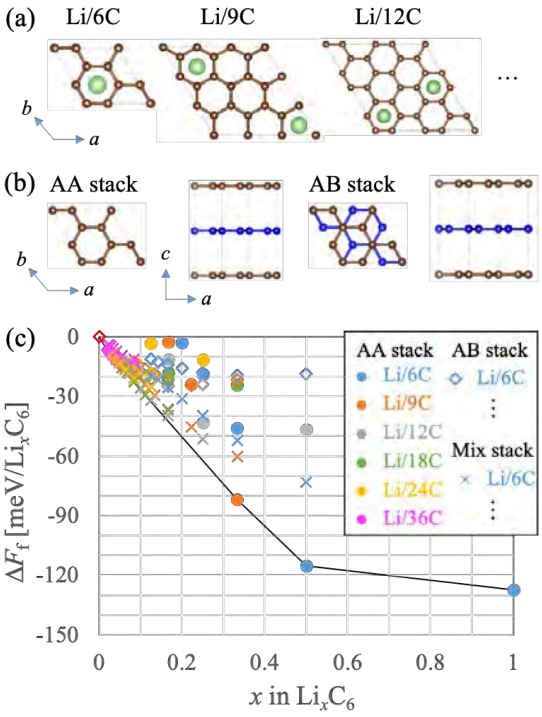

Figure 1: (a) In-plane configurations of Li/6C, Li/9C, Li/12C, … structures. (b) Interlayer configurations of AA and AB stackings. (c) Formation free energies (closed circles, diamonds, and crosses) and convex hull (black solid line) obtained from eq. (1).

References

[1] J. Haruyama, T. Ikeshoji, and M. Otani, J. Phys. Chem. C **122**, 9804 (2018).

[2] J. Haruyama, T. Ikeshoji, and M. Otani, Phys. Rev. Mater. **2**, 095801 (2018).

[3] M. Otani and O. Sugino, Phys. Rev. B **73**, 115407 (2006).

[4] S. Nishihara and M. Otani, Phys. Rev. B **96**, 115429 (2017).

[5] S. Takagi *et al.*, The 60th Battery Symposium, 1B20 (2019).

[6] H. Fujimoto *et al.*, The 59th Battery Symposium, 2E16 (2018).

[7] P. Giannozzi *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009); *ibid* **29**, 465901 (2017).

[8] R. Yazami and Y. Reynier, J. Power Sources **153**, 312 (2006).

[9] J. Haruyama, S. Takagi, K. Shimoda, I. Watanabe, K. Sodeyama, T. Ikeshoji, and M. Otani, in preparation.