Supporting Information

Mechanism of Li Nucleation at Graphite Anodes and Mitigation Strategies

Chao Peng,*[a,b,d] Arihant Bhandari,[c,d] Jacek Dziedzic,[c,d,e] John R. Owen,[c,d] Chris-Kriton Skylaris[c,d] and Denis Kramer*[b,d,f]

[a] Multiscale Crystal Materials Research Center, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

[b] School of Engineering, University of Southampton, Southampton SO17 1BJ, U.K.

[c] School of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.

[d] The Faraday Institution, Quad One, Becquerel Avenue, Harwell Campus, Didcot, OX11 0RA, U.K.

[e] Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Gdańsk 80-233, Poland

[f] Faculty of Mechanical Engineering, Helmut-Schmidt University, Hamburg, 22043, Germany

Nucleation free energy from the classical nucleation theory (CNT)

The nucleation free energy of big Li particle can be evaluated by the CNT model. The nucleation free energy consists of Li bulk energy ($\Delta G(Bulk)$), the surface energy of Li cluster $\Delta G(Surface)$ and the interface energy ($\Delta G(Interface)$) between the attached Li cluster and the graphite surface. The equation of nucleation free energy can be expressed as:

$$\Delta G = \Delta G(Bulk) + \Delta G(Surface) - \Delta G(Interface) \tag{1}$$

where $\Delta G(Bulk)$ is the free energy change of bulk Li. We chose the chemical potential of a single Li adsorption (μ_{Li}') on the basal plane as the reference state for Li nucleation on the basal plane of graphite. Thus, $\Delta G(Bulk)$ equals to $n(\mu_{Li} - \mu_{Li}')$. n is the number of Li in the cluster and μ_{Li} is the chemical potential of bulk Li.

$\Delta G(surface)$ is the surface energy of deposited Li cluster. The morphology of Li cluster is considered to be equilibrium and computed by the Wulff construction. Three main surfaces of metallic Li, namely (100), (110) and (111) surfaces, are considered with surface tension of 0.041, 0.044 and 0.047 eV/Å^2, respectively. The surface energy can be written as:

$$\Delta G(Surface) = \sum A_i \gamma_i = \eta V^{\frac{2}{3}} \gamma_{ave} \tag{2}$$

η is the shape factor and calculated by $Area / V^{\frac{2}{3}}$. γ_{ave} is the average surface tension which can be expressed as follows:

$$\gamma_{ave} = \frac{\sum A_i \gamma_i}{\sum A_i} \tag{3}$$

$\Delta G(Interface)$ is the interface energy between the Li cluster and the basal plane of graphite. We assume the most stable (100) surface as the adhesive surface of Li cluster on the basal plane of graphite. The interface energy was calculated by constructing the Li(100)@graphite(001) composite system. γ_{int} is 0.026 eV/Å^2.

Therefore, the nucleation free energy can be expressed as:

$$\Delta G = n(\mu_{Li} - \mu'_{Li}) + \eta V^{\frac{2}{3}}\gamma_{ave} - \gamma_{int}A(100) \tag{4}$$

$$\Delta G = n\Delta\mu_{Li} + \eta V^{\frac{2}{3}}\gamma_{ave} - \frac{A(100)}{6A(total)}\eta V^{\frac{2}{3}}\gamma_{int} \tag{5}$$

$$\Delta G = n\Delta\mu_{Li} + \eta(nV_{Li})^{\frac{2}{3}}\gamma_{ave} - \frac{A(100)}{6A(total)}\eta(nV_{Li})^{\frac{2}{3}}\gamma_{int} \tag{6}$$

$$\Delta G = n\Delta\mu_{Li} + \eta V_{Li}^{\frac{2}{3}}\left(\gamma_{ave} - \frac{A(100)}{6A(total)}\gamma_{int}\right)n^{\frac{2}{3}} \tag{7}$$

where:

n: number of Li atoms in the cluster

V: volume of Li cluster ($V = n \times V_{Li}$)

V_{Li}: volume per Li atom

A(total): the total surface area of isolated Li cluster

γ: the surface tensions

η: shape factor ($\eta = \frac{A}{V^{2/3}}$)

Accordingly, the nucleation free energy can be rewritten as:

$$\Delta G = \emptyset \times n + \Psi \times n^{\frac{2}{3}} \tag{8}$$

where,

$$\emptyset = \Delta\mu_{Li} \tag{9}$$

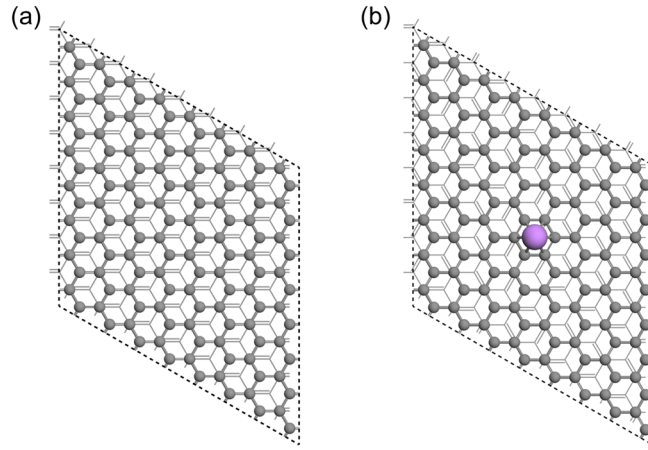$$\Psi = \eta V_{Li}^{\frac{2}{3}}\left(\gamma_{ave} - \frac{A(100)}{6A(total)}\gamma_{int}\right) \tag{10}$$

When $\frac{d(\Delta G)}{dn} = 0$,

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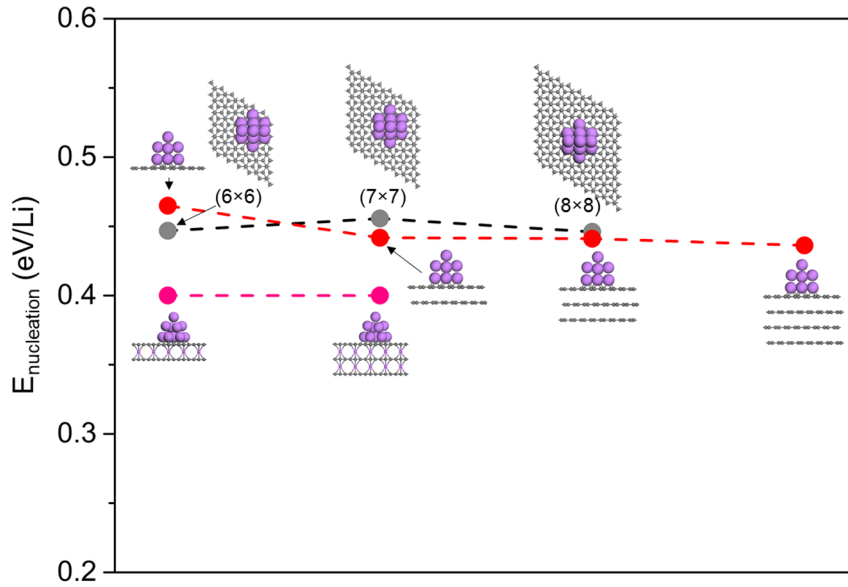$$n^* = \left(-\frac{2\Psi}{3\emptyset}\right)^3 \; ; \Delta G^* = \frac{4}{27}\frac{\Psi^3}{\emptyset^2} \tag{11}$$

For Li nucleation on the basal plane of graphite, $\emptyset = -0.33\ eV, \Psi = 1.47\ eV$. Thus,

$$\Delta G = -0.33n + 1.47n^{\frac{2}{3}} \tag{12}$$

$$n^* = 27; \ \Delta G^* = 4.43\ eV \tag{13}$$

Figure S1. The structures of pristine graphite and a single Li adsorption on the basal plane of graphite. The grey and purple spheres denote carbon and Li atoms, respectively. This notation is adopted throughout the whole work.

Figure S2. The convergence test for the size of the supercell and the number of layers to construct the substrate for Li nucleation.
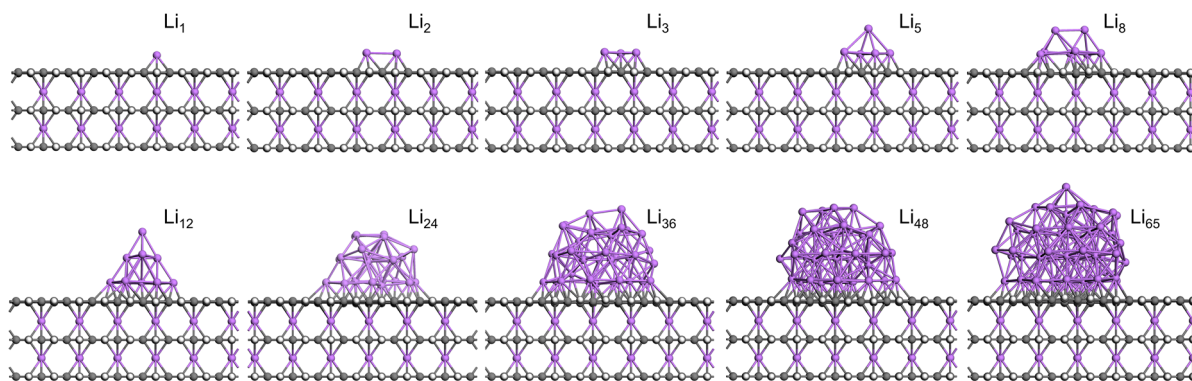
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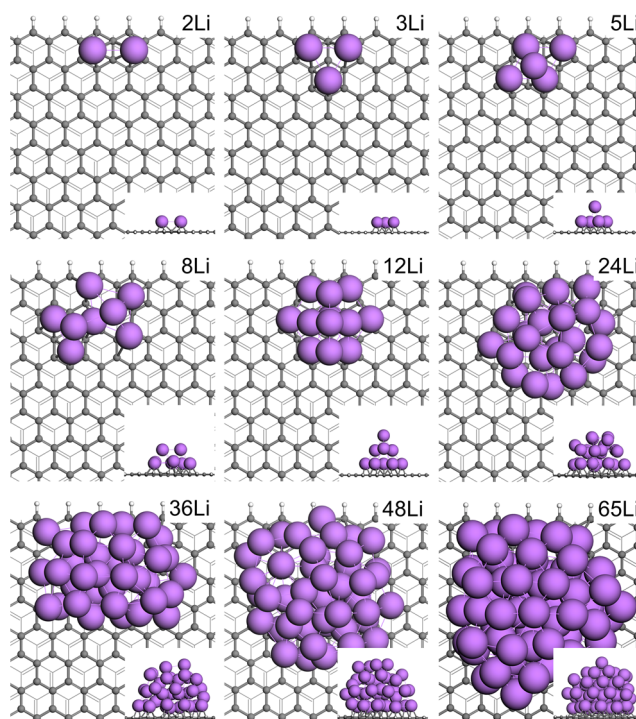
Figure S3. The structures of different sized Li clusters deposited at the zigzag edge. The white, grey and purple spheres denote hydrogen, carbon and Li atoms, respectively. This notation is adopted throughout the whole work.
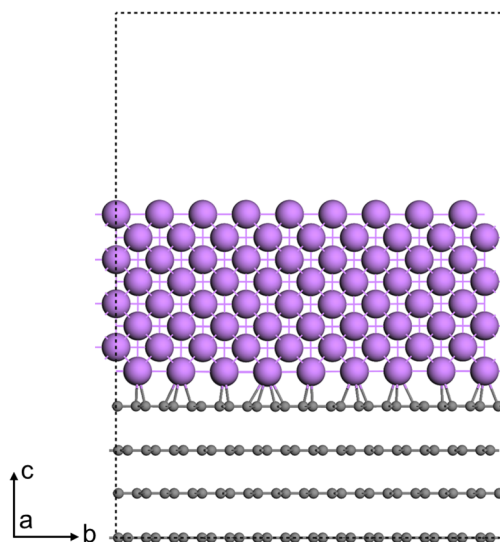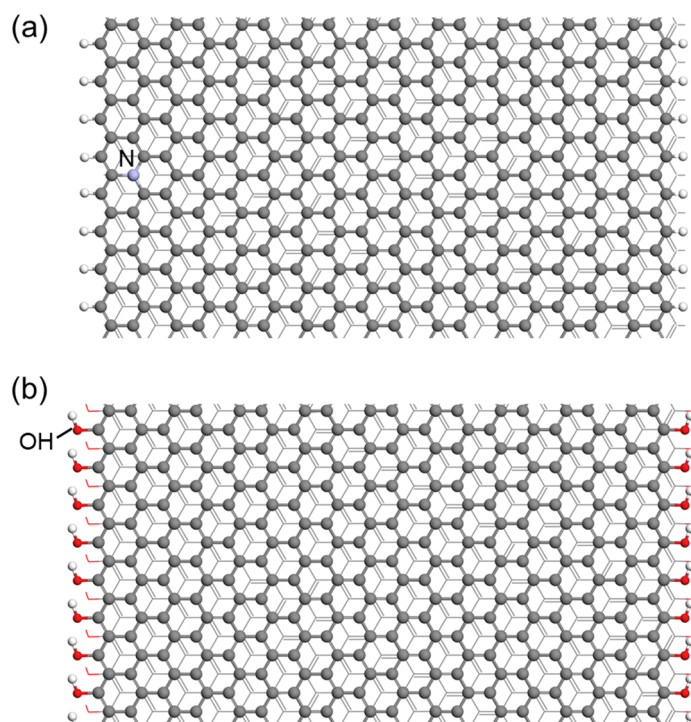

Figure S4. The structures of Li(100)@graphite(001) composite system.

Figure S5. The structures of different sized Li clusters deposited at the zigzag-edged LiC_6.

Figure S6. The structures of nitrogen doped zigzag-edged graphite (a) and OH-terminated zigzag-edged graphite (b).