Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for "An *Ab-initio* Study for Probing Iodization Reactions on Metallic Anode Surfaces of Li–I_2 Batteries"

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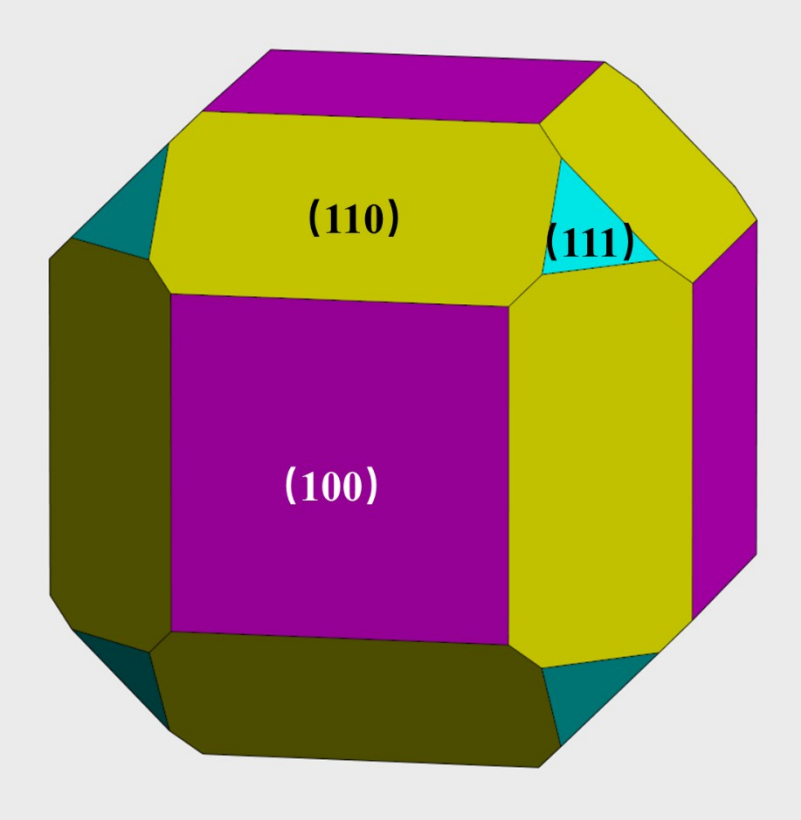

Figure S1. Wulff construction of crystalline Li. The magenta facets belong to the family of (100) surface, the yellow facets belong to the family of (110) surface, and the cyan facets belong to the family of (111) surface. The Wulff construction is visualized by the Wullfmaker code developed by Zucker *et al*.[1]

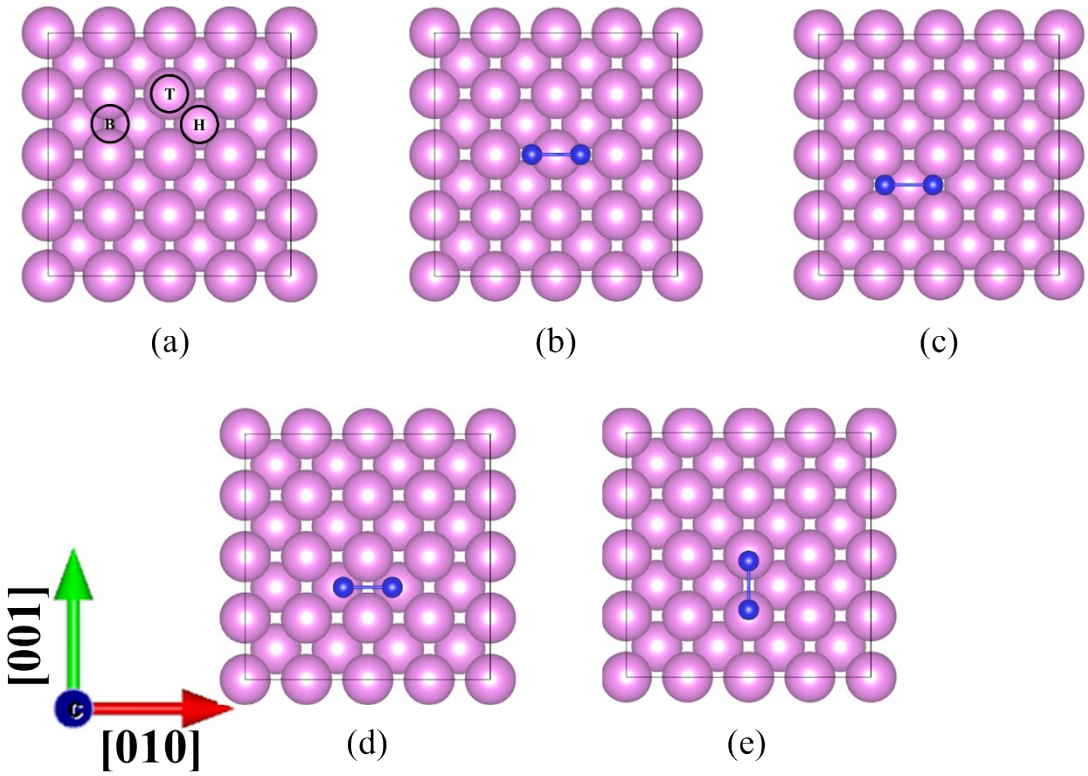

Figure S2. (a) Three typical adsorption sites on the Li (100) surface. The top site (labelled by "T") is directly above a Li atom in the topmost layer; the hollow site (labelled by "H") is the center of a square consisted of four Li atoms in the topmost layer; and the bridge site (labelled by "B") is the middle point of two adjacent Li atoms in the topmost layer. To model the adsorption behavior, the I_2 molecule is parallelly placed on (b) the top site, (c) the hollow site, (d) and (e) the bridge site. For I_2 on the bridge site, the I-I bond can be either along the [010] direction, or along the [001] direction.

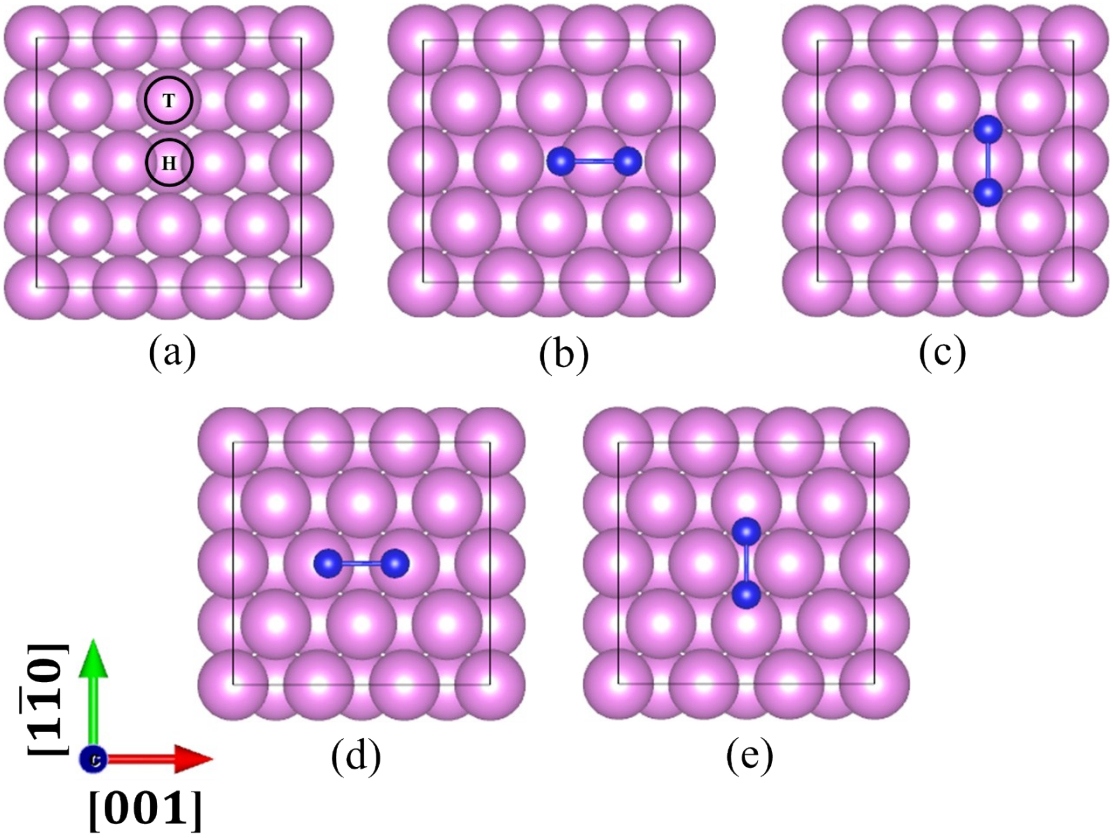

Figure S3. (a) Two typical adsorption sites on the Li (110) surface. The top site (labelled by "T") is directly above a Li atom in the topmost layer, and the hollow site (labelled by "H") is the center of a parallelogram consisted of four Li atoms in the topmost layer. The I_2 molecule can be placed on the top site with I-I bond paralleling to (b) [001] orientation or (c) [1$\bar{1}$0] orientation, or be placed on the hollow site with I-I bond paralleling to (d) [001] orientation or (d) [1$\bar{1}$0]orientation.

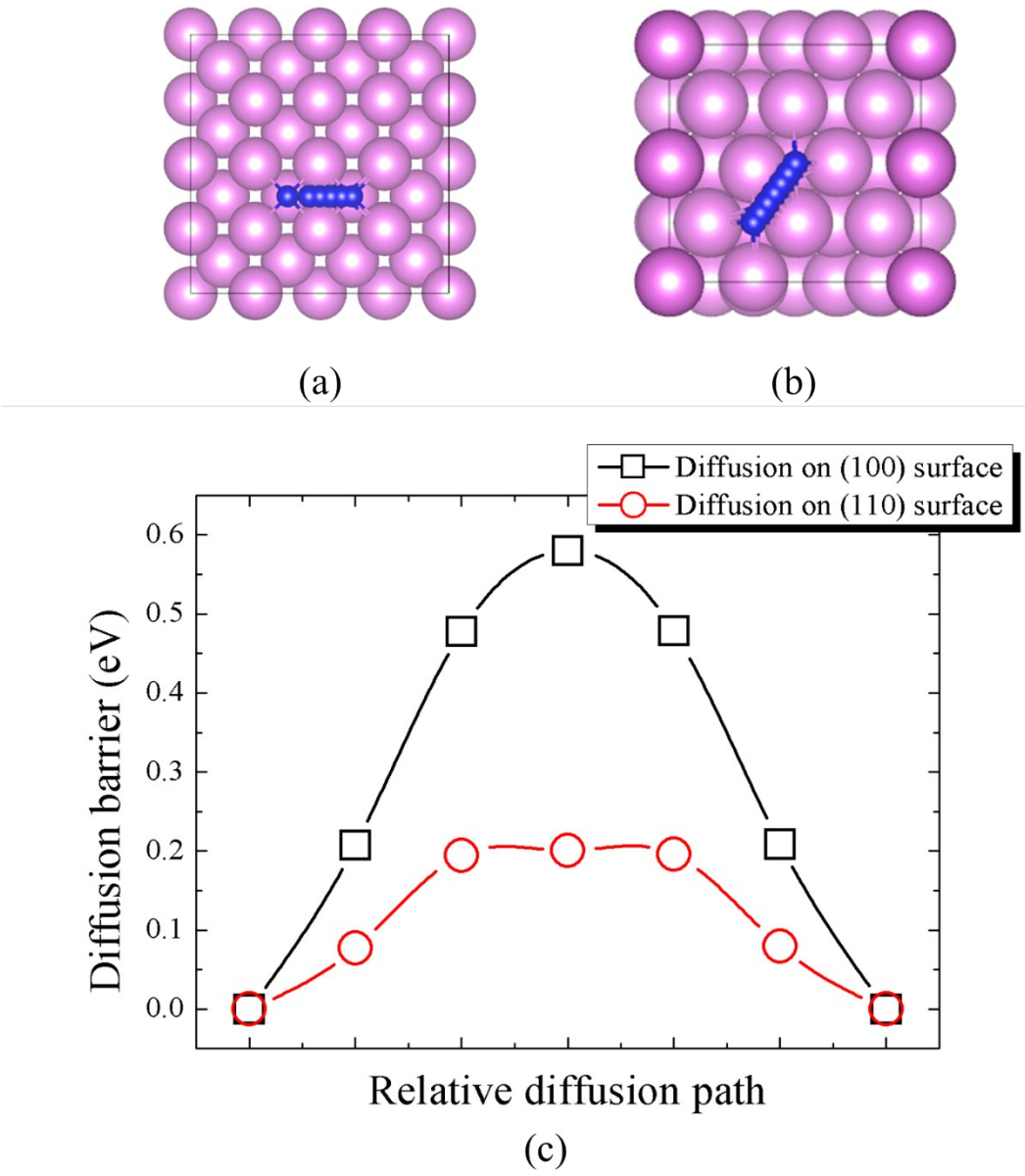

Figure S4. Proposed paths of I diffusion on (a) the I (100) surface and (b) the I (110) surface. The I atom is jumping from one hollow site to the nearest adjacent hollow site. The diffusion barriers are depicted in (c).

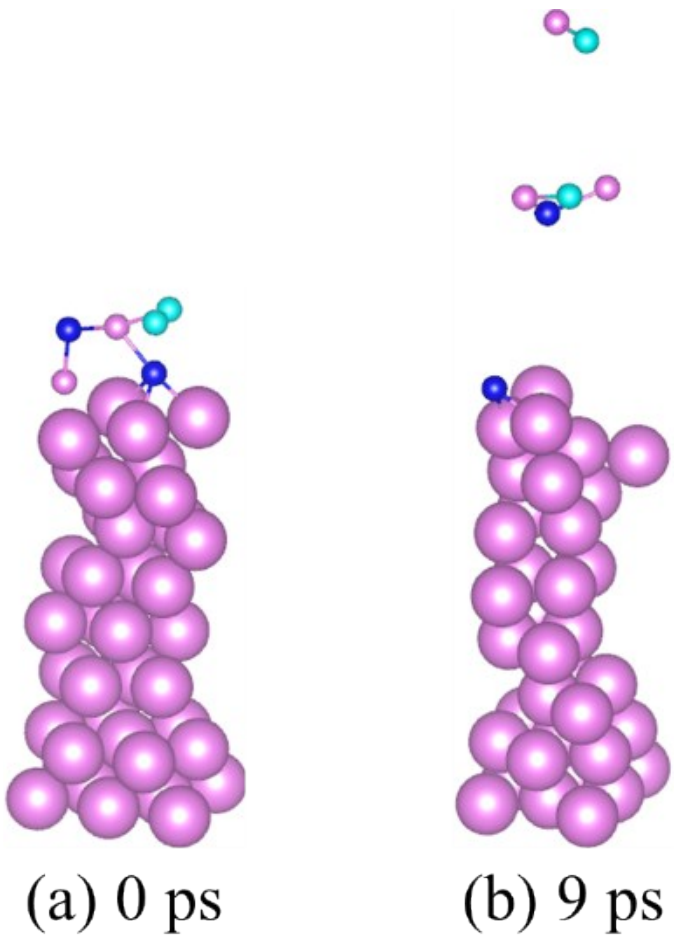

Figure S5. (a) A new I_2 molecule (cyan spheres) is introduced to the iodized Li (110) surface. (b) After 9 ps, the I_2 molecule dissociate and I atoms take Li atoms away from the anode surface.

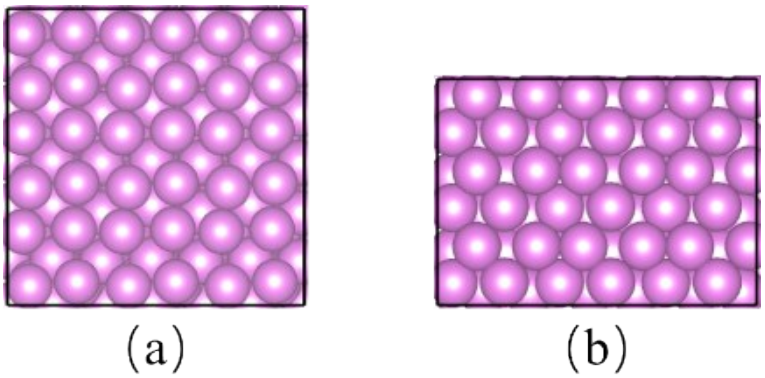

Figure S6. Top view of atomistic structures of (a) (100)-($3\sqrt{2} \times 3\sqrt{2}$) surface cell after removing LiI species and (b) (100)-(6×3) surface unit cell after removing LiI species.

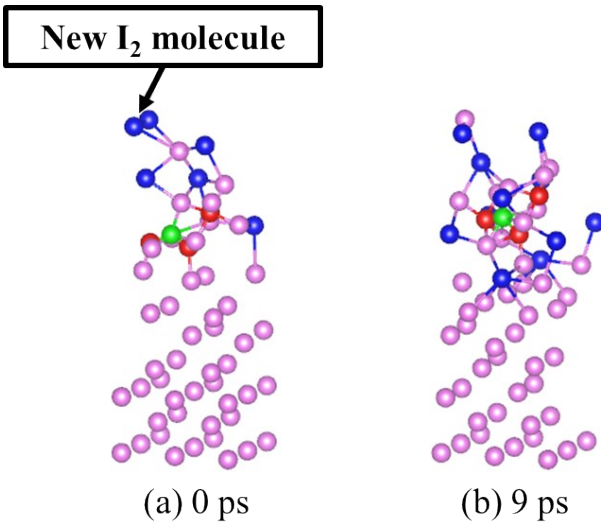

Figure S7. (a) A new I_2 molecule is introduced to the $LiNO_3$ treated Li (100) surface which is shown in Figure 6b. (b) Atomistic structure after 9 ps simulation.

References

S1. Zucker, R. V.; Chatain, D.; Dahmen, U.; Hagege, S.; Carter, W. C., New Software Tools for the Calculation and Display of Isolated and Attached Interfacial-Energy Minimizing Particle Shapes. *Journal of Materials Science* **2012**, *47*, 8290-8302.