Electronic Supplementary Information for:

Graphdiyne as an ideal monolayer coating material for lithium-ion battery cathodes with ultralow areal density and ultrafast Li penetration

Sheng Gong‡, Shuo Wang‡, Junyi Liu‡, Yaguang Guo†, ‡ and Qian Wang†, ‡*

†Center for Applied Physics and Technology, HEDPS, College of Engineering, Peking University, Beijing 100871, China

‡Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

1. AIMD Simulation with Li and graphene plane with divacancy sites.

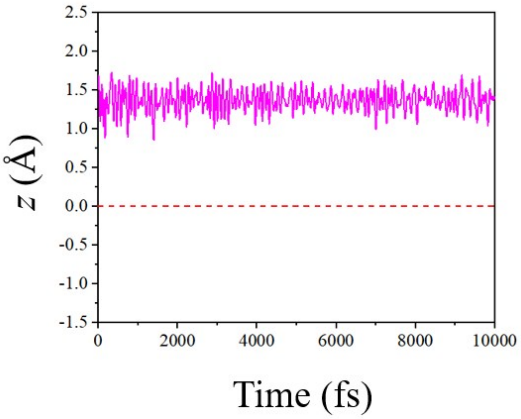

Figure S1. Time-dependent distance between a Li atom and the graphene plane with divacancies during the AIMD simulations.

2. Information about the other four trial orientations of EC molecules.

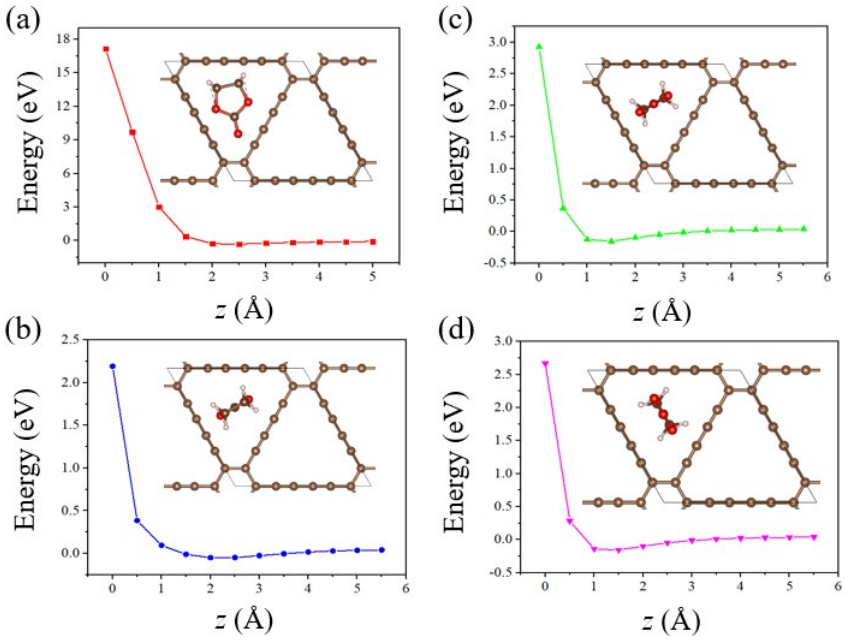

Figure S2. (a-d) Potential energy profiles of the other four trail orientations of EC molecule approaching the pore in graphdiyne. *z* denotes the distance between the geometric center of EC and the graphdiyne plane. The inset images show the configurations of EC approaching graphdiyne.

3. **Discussion about reaction (4):** although a single C^+ cation should not be one of the final products of the decomposition reaction of graphdiyne, we consider the decomposition as a two steps reaction. In the first step, graphdiyne adsorbs energy from the circuit to be activated and release a reactive group. I the second step, the reactive group reacts with other substances in the environment and releases energy. Here the first step is decisive to the whole reaction and easy to be estimated, while the path of the second step depends on the components of certain environment and is hard to be estimated. In order to estimate the first step more convincingly, we further consider the possibility of releasing a C_2 dimer group, and estimate the activation voltage as below:

$$C_{18} \rightarrow C_{18-2\delta} + \delta C_2^+ + \delta e^-,\ eV_c = E(C_{18-2\delta}) + E(\delta C_2^+) + E(\delta e^-) - E(C_{18})$$

Here, V_c is calculated to be 11.78 V, which is much larger than the value of releasing a single C^+ cation (7.85 V), suggesting that graphdiyne is stable against C_1 and C_2 fragmentation.

4. Electron work functions of graphdiyne, $LiCoO_2$ (101), $Li_{0.5}CoO_2$ (101), $LiMn_{0.5}Ni_{0.5}O_2$ (101) and $LiFePO_4$ (010) surfaces, respectively.

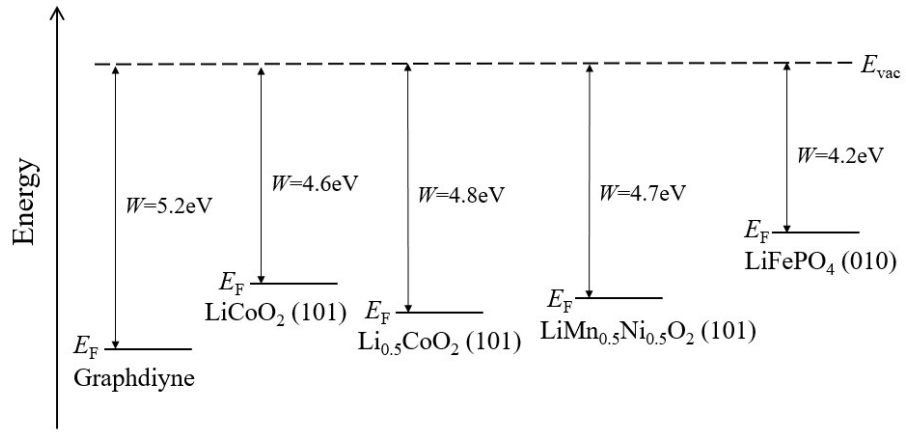

Figure S3. Schematic plot of the electron work functions of graphdiyne, $LiCoO_2$ (101), $Li_{0.5}CoO_2$ (101), $LiMn_{0.5}Ni_{0.5}O_2$ (101), and $LiFePO_4$ (010) surfaces. E_{vac} and E_F denote the energies of the vacuum and Fermi energy, respectively. W represents the electron work function.