

Supporting information

Design Principles of Nitrogen-doped Graphene Nanoribbons as Highly Effective bifunctional catalysts for Li - O₂ Batteries

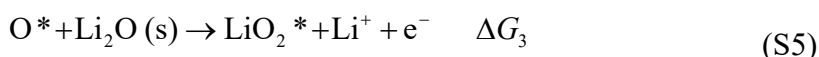
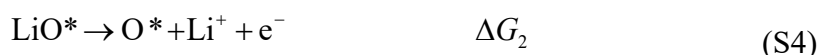
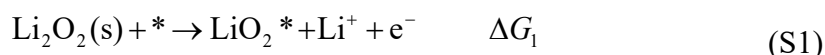
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Reaction pathways of OER through four-electron and two-electron pathway:

The steps of the two-electron pathway and the four-electron pathway of OER are shown in formulas S1-S2 and S3-S6, respectively.



where the asterisk (*) represents the chemisorption site, O*, LiO* and LiO₂* are reaction intermediates, g and s denote gas and solid phases, respectively.

Supporting table:

Table S1. ZPE corrections of adsorbates. The vibrational frequencies of intermediates were calculated with the N-GNRs fixed to obtain ZPE contribution in the free energy. $E_{\text{ZPE}} = \sum_i 1/2h\nu_i$, where h is Planck's constant and ν_i is the frequency of the vibrational mode of the binding molecule.

adsorbates	O*	LiO*	LiO ₂ *	Li ₂ O*	Li ₂ O ₂ *	Li ₂ (bulk)
E _{ZPE} (eV)	0.083	0.098	0.135	0.132	0.128	0.061

Supporting figures:

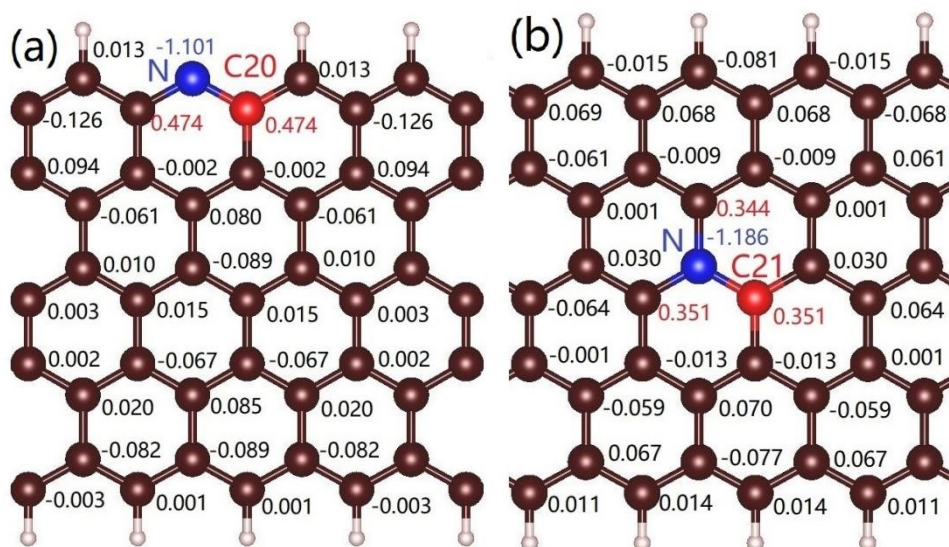


Figure S1. The Bader charge value on each atom in (a) the Z1 structure and (b) the Z5 structure.

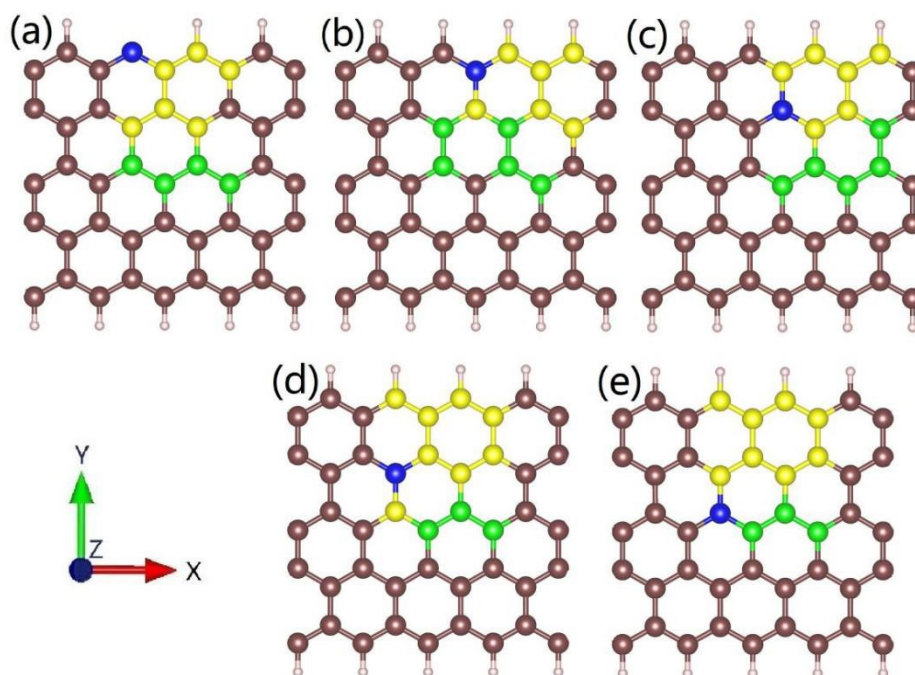


Figure S2. The dominant position of the four-electron pathway(green) and the dominant position of the two-electron pathway(yellow) in the Zigzag N-GNRs: (a) Z1 structure; (b) Z2 structure; (c) Z3 structure; (d) Z4 structure; (e) Z5 structure.

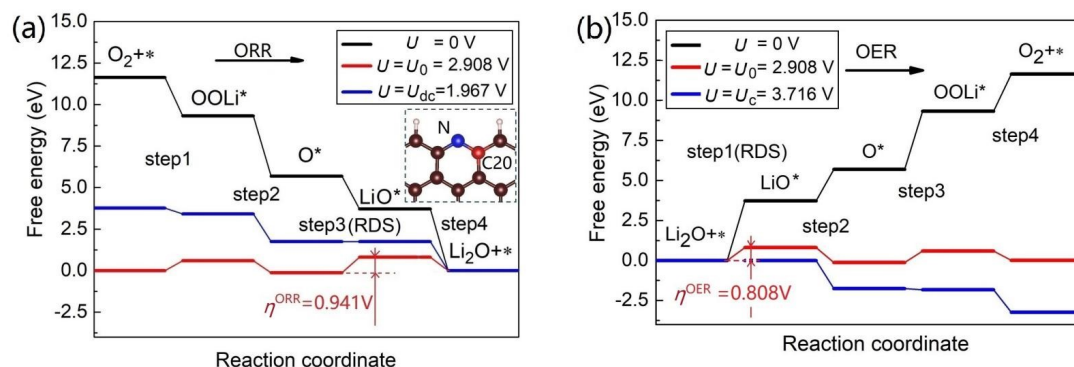


Figure S3. Free energy diagrams of (a) ORR and (b) OER under different electrode potentials at site C20 of Z1 structure. U , U_0 , U_{dc} and U_c are applied electrode potential, equilibrium potential, maximum discharge potential and minimum charge potential, respectively.

Taking site C20 of Z1 model (Z1-C20) as an example, the overpotentials are 0.941 V and 0.808 V for ORR and OER, which are considerably smaller than that of Pt(111), 1.02 V and 1.62 V, respectively, indicating a possibly high catalytic efficiency of N-doped graphene catalysts. As shown in Figure S3, all the steps are downhill at an electrode potential of 0V, indicating that each step is thermodynamically favorable, corresponding to the spontaneous discharge behavior of the battery. Among them, the third step with the least drop of free energy, limits the rate of the entire reaction, namely the rate-determining step(RDS). At the equivalent potential condition, the first step in figure S3(b) has the maximal increment in free energy, and thus it is the RDS of OER process. When the electrode potential is the equilibrium potential U_0 , the RDS possesses the largest increment of free energy in both figures. Such an increment exactly is the relevant overpotential and is indicated in red in Figure S3. In the calculations, we gain the η^{ORR} through the discharge potential U_{dc} and charge potential U_c , where $U_{dc} = -\max\Delta G_i/e$ and $U_c = -\min\Delta G_i/e$. Given the electrode potential equals to U_{dc} in Figure S3(a), other steps are keeping

downhill while the RDS is in equilibrium. Therefore the reaction is incapable in a discharge voltage higher than U_{dc} . For the free energy under U_c shown in Figure S3(b), other steps are downhill and thermodynamically favorable while the RDS remains equilibrium. The OER is incapable on a charge voltage less than U_c for there will be a positive rise in free energy of the first step. Accordingly, the overpotentials can be get from the equilibrium potential and discharge/charge potentials for $\eta^{ORR}=U_0-U_{dc}=2.908-1.967=0.941V$ and $\eta^{OER}=U_c-U_0=3.716-2.908=0.808V$.

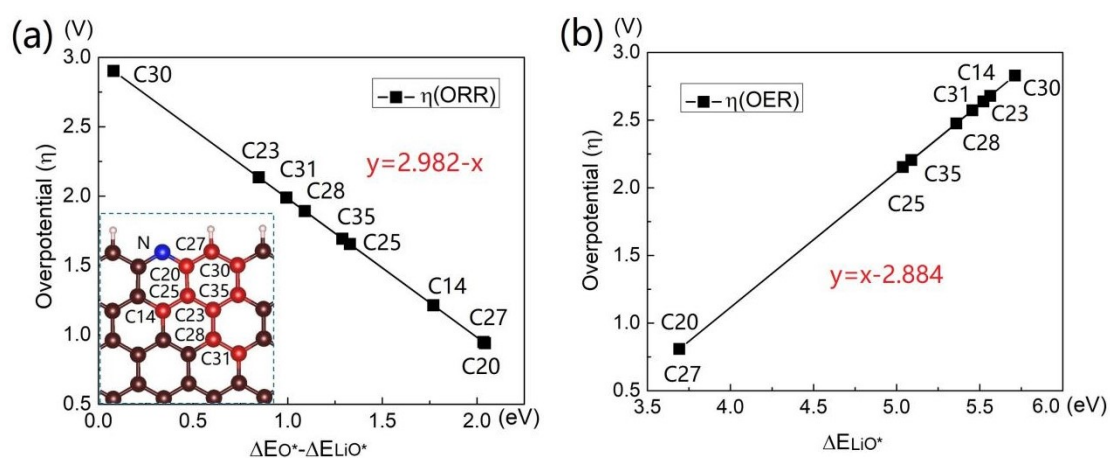


Figure S4. (a) Overpotentials of ORR varies with adsorption energies ($\Delta E_{O^*} - \Delta E_{LiO^*}$) and (b) Overpotentials of OER varies with the adsorption energies ΔE_{LiO^*} on Z1 structure. Each reactive site is labeled with symbol “C” and numbers.

Taking Z1 structure as an example, the overpotential of ORR has a linear correction with the difference of adsorption energy ΔE_{O^*} and ΔE_{LiO^*} ($\Delta E_{O^*} - \Delta E_{LiO^*}$) by an analytic expression of $y = 2.982 - x$, as shown in Figure S4(a). Large $\Delta E_{O^*} - \Delta E_{LiO^*}$ is beneficial for O^* involved in subsequent reaction step and the formation of LiO^* , which promotes the RDS, and reduces the overpotential. In Figure S4(b), the positive adsorption energy of LiO^* is hinders the RDS, so the larger adsorption energy corresponds to higher overpotential and poor catalytic activity, with a functional relationship of $y = x - 2.884$. Therefore, it would be an effective strategy to design the

catalyst to change the adsorption energy of intermediates and accelerate the RDS to improve the reaction efficiency.