Localized Charge Induced ORR/OER Activity in Doped Fullerenes for Li-Air Battery Applications

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Table S1: Total energies (in eV) of all the considered systems using different Γ-centered k-point grids.

Systems	1 × 1 × 1 k-point	3 × 3 × 3 k-point	5 × 5 × 5 k-point
$C_{59}B$	-529.8502	-529.8501	-529.8503
$C_{59}N$	-531.8856	-531.8854	-531.8857
$C_{179}B$	-1631.5633	-1631.5587	Not converged
$C_{179}N$	-1634.3953	-1634.3912	Not converged
$C_{58}BN$	-530.7630	-530.7628	-530.7631
$C_{178}BN$	-1632.2689	-1632.2684	Not converged

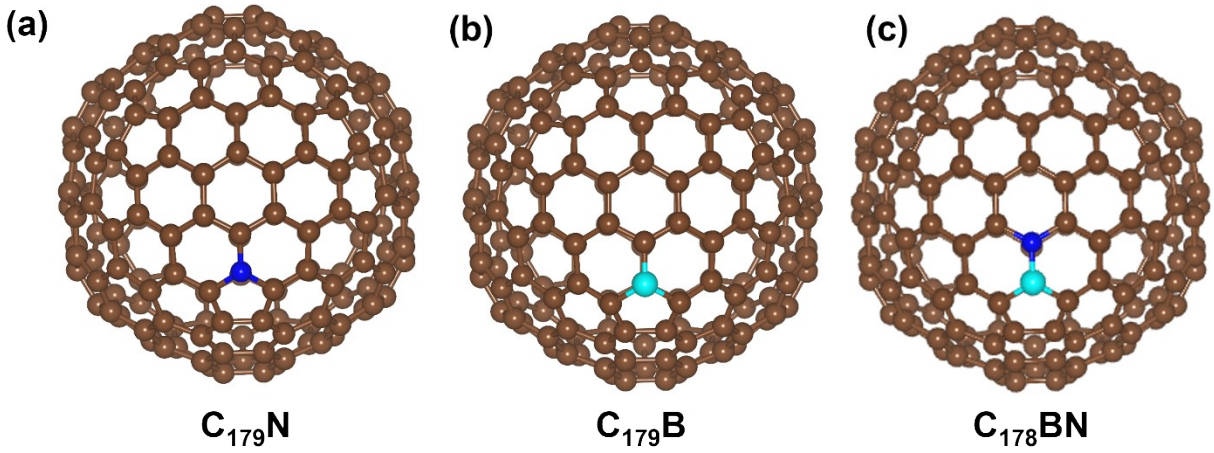

Figure S1. Optimized structures for considered (a) N, B-doped, and (b) BN co-doped C_{180} fullerenes. Here, the blue, brown, and cyan colors represent nitrogen, carbon, and boron atoms respectively.

Text S1: Stability Analysis of doped and co-doped fullerenes.

To assess the stability of the considered doped fullerenes, the formation energy[1] (E_f) has been calculated as follows,

$$E_f = E_{B_xN_yC_{m-x-y}} + (x+y)\mu_C - (E_{C_m} + x\mu_B + y\mu_N) \quad (1)$$

Here, x (=0,1) and y (=0,1,2,3) are the number of doped B and N atoms in the C_m fullerene (m=60,180). Here, $E_{B_xN_yC_{m-x-y}}$, and E_{C_m}, represents the optimized energies of the respective doped and undoped fullerenes. μ_C, μ_B, and μ_N stands for the chemical potential taken from fullerene, boron bulk, and N_2 gas, respectively. In addition, to evaluate the durability and stability of co-doped fullerenes, we examined the binding energy[1] of the B atom within these structures. The binding energy of the B atom (E_b) at the single vacancy site is calculated using the **Equation 2**,

$$E_b = E_{BN_yC_{(m-1-y)}} - E_B - E_{N_yC_{(m-1-y)}} \quad (2)$$

Where, y (=1,2,3) are number of doped N atoms around doped B atom in the C_m fullerene (m=60,180). The $E_{BN_yC_{(m-1-y)}}$ is the optimized energy of co-doped fullerene, E_B is the energy of a single B atom, and $E_{N_yC_{(m-1-y)}}$ is the energy of B vacancy defective fullerene.

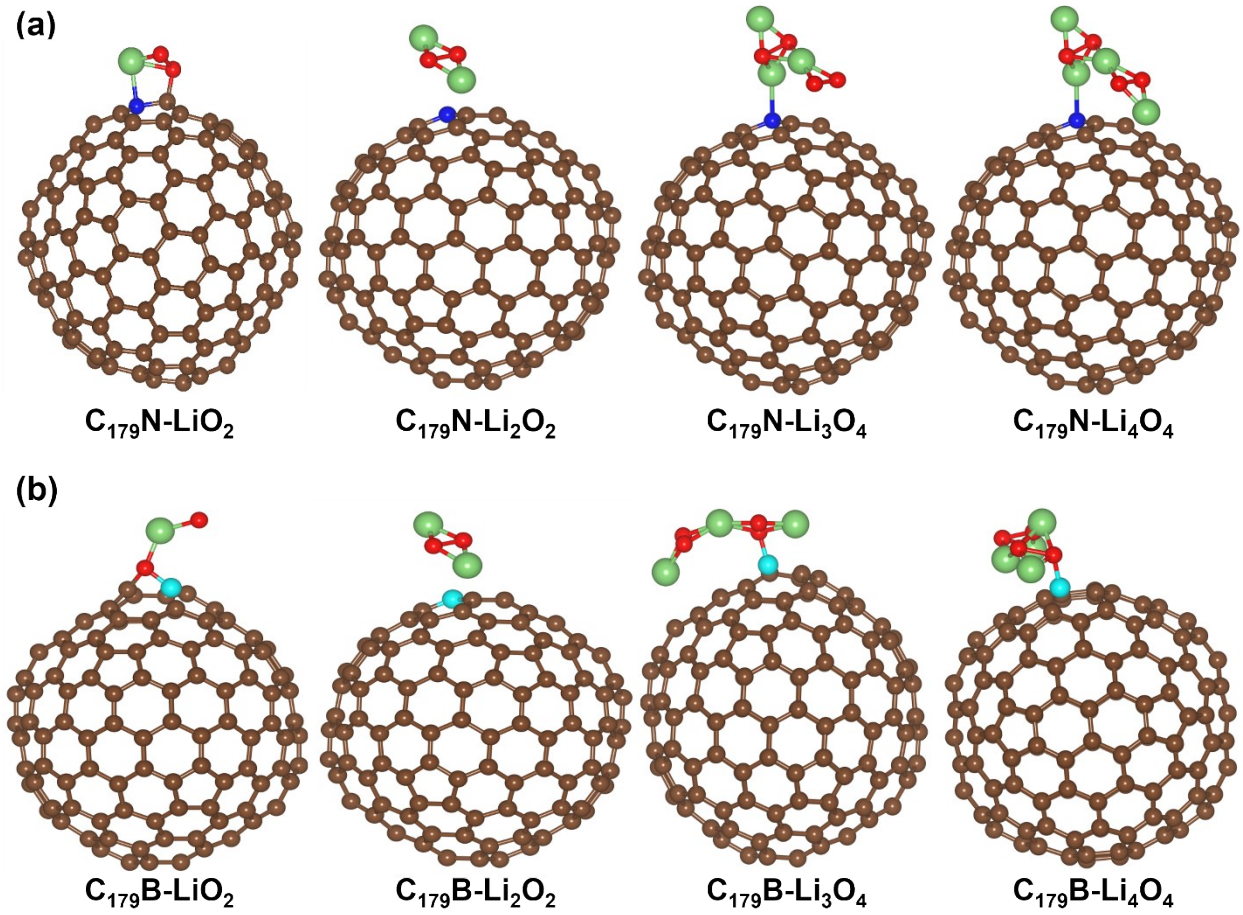

Figure S2: Adsorbed intermediate configuration corresponding to their most stable sites on (a) N-doped and (b) B-doped C_{180} fullerenes. Here, the blue, brown, cyan, green, and red colors represent nitrogen, carbon, boron, lithium, and oxygen atoms respectively.

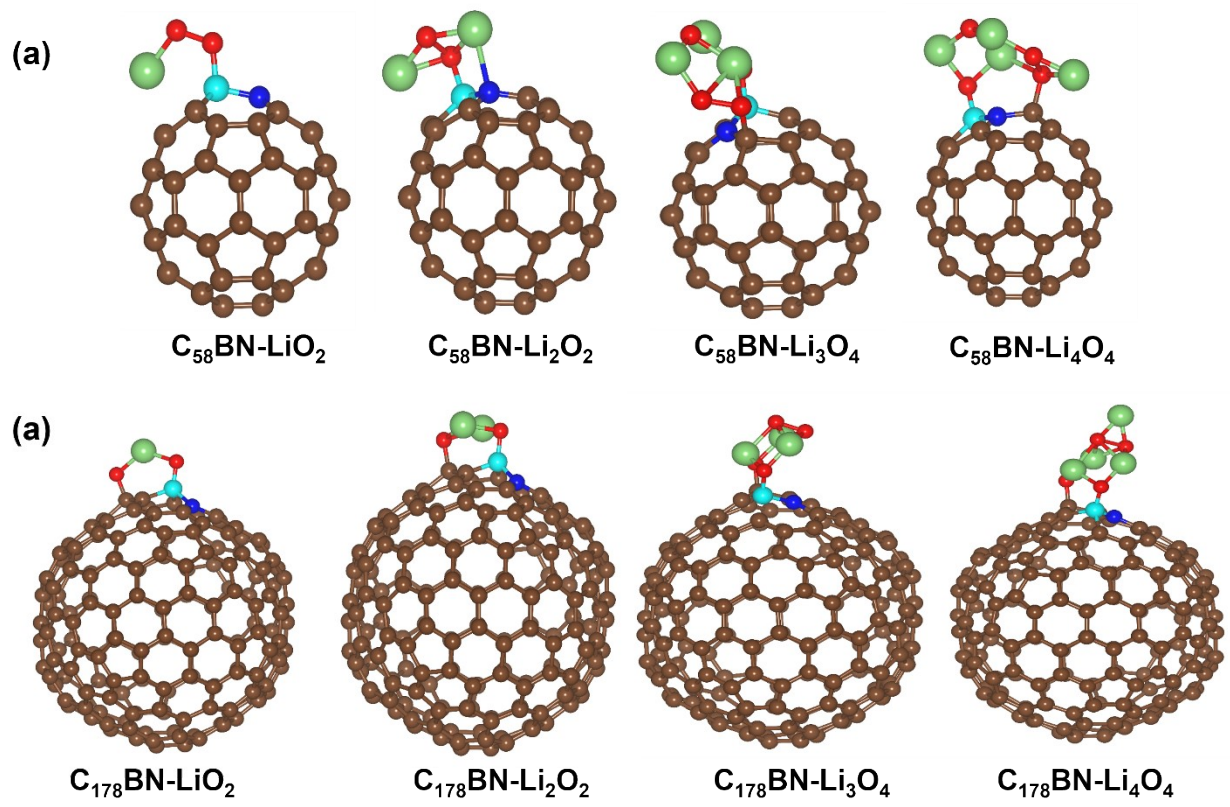

Figure S3: Adsorbed intermediate configuration corresponding to their most stable sites on (a) $C_{58}BN$ and (b) $C_{178}BN$ fullerenes. Here, the blue, brown, cyan, green, and red colors represent nitrogen, carbon, boron, lithium, and oxygen atoms respectively.

Text S2: Equations used to calculate the B-binding energy in B-doped fullerenes in the presence of oxidative intermediates.

For binding energy of B in LiO_2 adsorbed (E_{B-LiO_2}) and Li_4O_4 adsorbed systems ($E_{B-Li_4O_4}$), we have considered the following equations,

$$E_{B-LiO_2} = E_{BN_yC_{(m-1-y)}LiO_2} - E_B - E_{N_yC_{(m-1-y)}LiO_2}$$

$$E_{B-Li_4O_4} = E_{BN_yC_{(m-1-y)}Li_4O_4} - E_B - E_{N_yC_{(m-1-y)}Li_4O_4}$$

Where, $E_{BN_yC_{(m-1-y)}LiO_2}$ and $E_{BN_yC_{(m-1-y)}Li_4O_4}$ are total energies of LiO_2 adsorbed and Li_4O_4 adsorbed fullerenes, respectively. $E_{N_yC_{(m-1-y)}LiO_2}$ and $E_{N_yC_{(m-1-y)}Li_4O_4}$ are the single-point energies of the respective adsorbed fullerenes without B atom. E_B is the single point energies of B atom.

Table S2: B-binding energy in B-doped fullerenes in the presence of oxidative LiO_2 and Li_4O_4 intermediates and adsorption energies of the oxidative LiO_2 and Li_4O_4 intermediates.

Systems	E_{B-LiO_2} **(eV)**	$E_{B-Li_4O_4}$ **(eV)**	**LiO_2 Adsorption energy (eV)**	**Li_4O_4 Adsorption energy (eV)**
$C_{179}B$	-17.09	-14.12	-5.95	-9.12
$C_{59}B$	-12.72	-12.03	-2.94	-9.43
$C_{178}BN$	-14.06	-14.83	-2.59	-5.17
$C_{58}BN$	-13.18	-14.53	-3.09	-5.88

Text S3: Details of ZPE and entropy correction calculations

The zero-point energy (ZPE) can be calculated using the $\sum\frac{1}{2}h\upsilon_i$ equation, where h and υ_i define the Planck's constant and the vibrational frequencies of the intermediates, respectively. There will be contributions to entropy from each atom's translational, rotational and vibrational degrees of freedom. In general, for intermediates adsorbed on solid material-based catalysts, translational and rotational entropies are negligible, while vibrational entropy (S_v) is calculated using the following statistical thermodynamic equation.[2]

$$S_V = R\sum\left(\frac{\hbar v_i}{k_B T\left(exp\left(\frac{\hbar v_i}{kT}-1\right)\right)} - ln\left(1-exp\left(\frac{-\hbar v_i}{kT}\right)\right)\right)$$

Here, k_B is the Boltzmann constant T is the temperature, and $\hbar$ = h/2π. To incorporate the thermal energy contribution, we have calculated the free energy change of each step of the reaction at 300 K and further the entropy contribution has also been considered at the same temperature. The reaction free energies reported here are ZPE-corrected free energies.

Table S3: Stepwise LAB reaction free energies for the $C_{179}B$ fullerene in the gas phase and implicit DMSO solvent phase.

Steps	**Reaction free energy (eV)**	
	Gas phase	**Solvent phase**
$*+4(Li^+ + e^-) + 2O_2 \leftrightarrow LiO_2 *+ 3(Li^+ + e^-)$	-4.71	-1.52
$LiO_2 *+ 3(Li^+ + e^-) + O_2 \leftrightarrow Li_2O_2 *+ 2(Li^+ +$	-4.48	-0.84
$Li_2O_2 *+ 2(Li^+ + e^-) + O_2 \leftrightarrow Li_3O_4 *+ (Li^+ +$	-5.03	-1.65
$Li_3O_4 *+ (Li^+ + e^-) \leftrightarrow Li_4O_4 *$	-4.05	-0.59

References:

1. M. D, Esrafili, A. A. Khan, P. Mousavian, *RSC Adv.*, 2021, **11**, 22598 -22610.
2. D. A, McQuarrie, Harper & Row, 1973