**Supplementary Information**

# Theoretical Evaluation of Pristine, Single B and N-Doped, and BN Co-Doped Graphenylene as Metal-Free Cathode Catalysts for Nonaqueous Li-$O_2$ Batteries

Sima Roshan [a], Adel Reisi-Vanani [a,b,*]

[a] *Department of Physical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran*

[b] *Institute of Nano Science and Nano Technology, University of Kashan, Kashan, Iran*

* *Corresponding author: Adel Reisi-Vanani*

*E-mail*: areisi@kashanu.ac.ir, *Tel: +98 3155912358; Fax: +98 3155912397.*

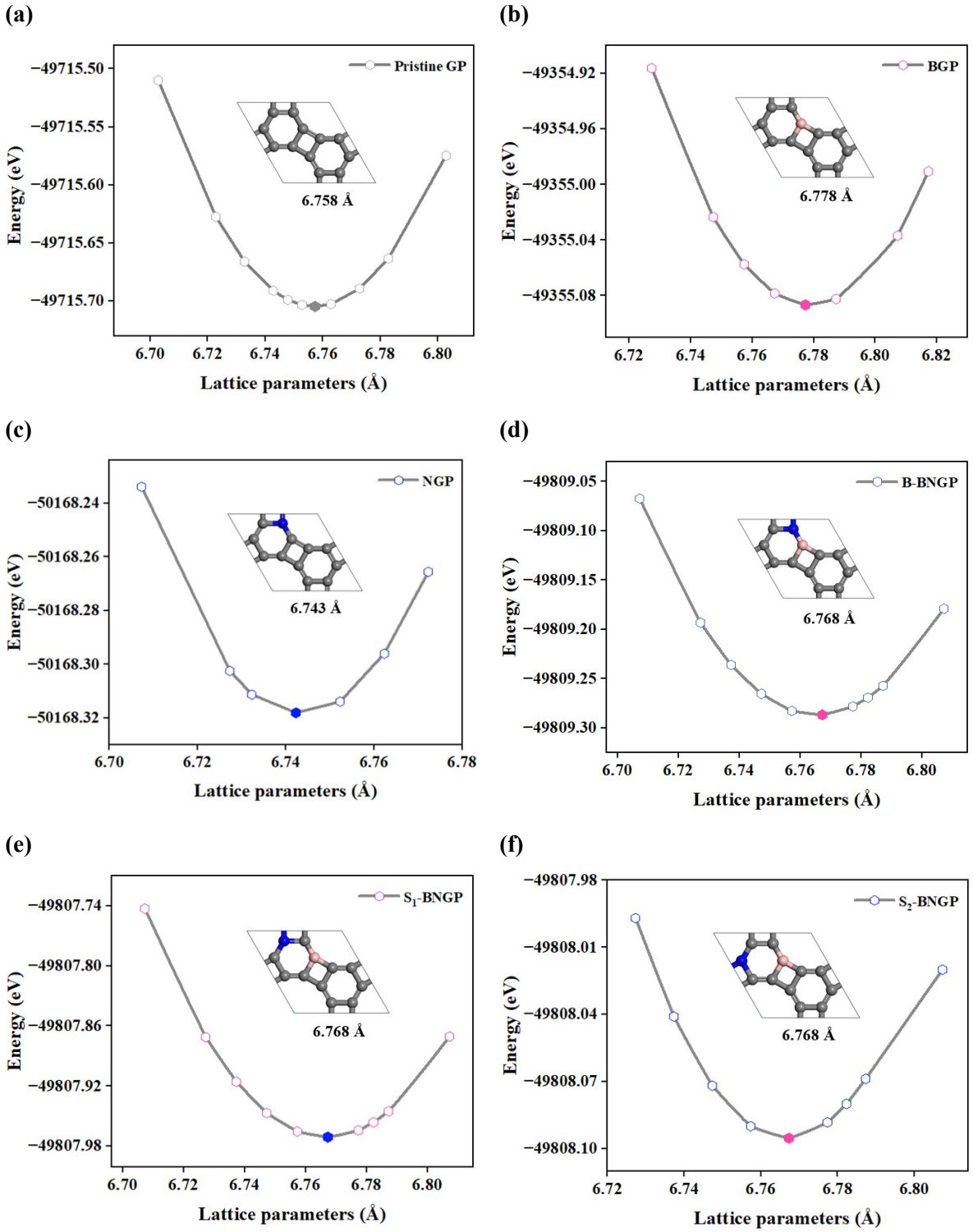



**Figure S1.** Optimized lattice constants (Å) of (a) pristine GP, (b) BGP, (c) NGP, (d) B-BNGP, (e) $S_1$-BNGP, and (f) $S_2$-BNGP.

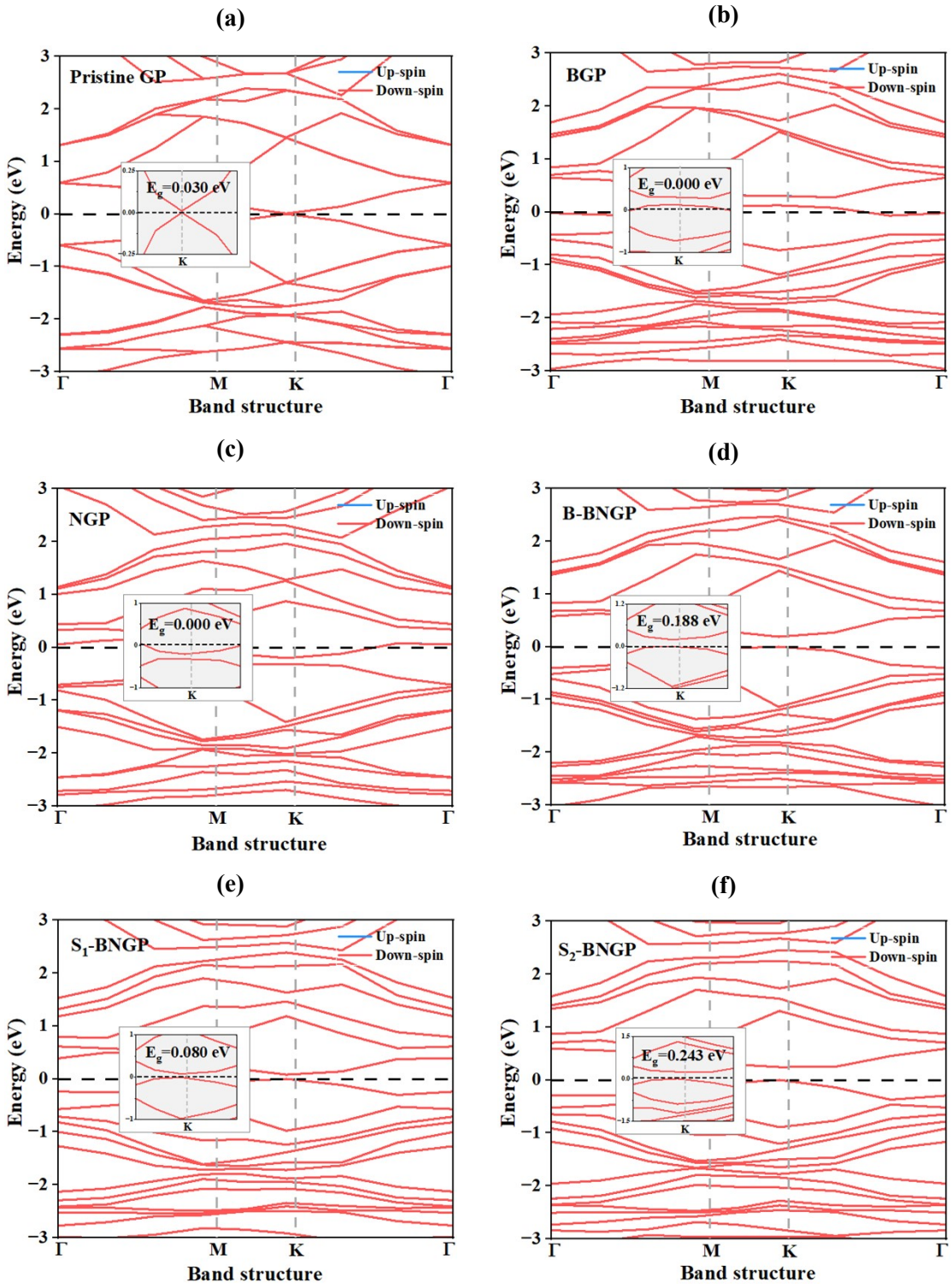



**Fig S2.** Electronic band structures of (a) pristine GP, (b) BGP, (c) NGP, (d) B-BNGP, (e) $S_1$-BNGP, and (f) $S_2$-BNGP; the Fermi level is indicated by a black dashed line set at zero energy. Blue and red lines represent spin-up and spin-down states, respectively, and the insets show magnified views around the K point and the band gaps.

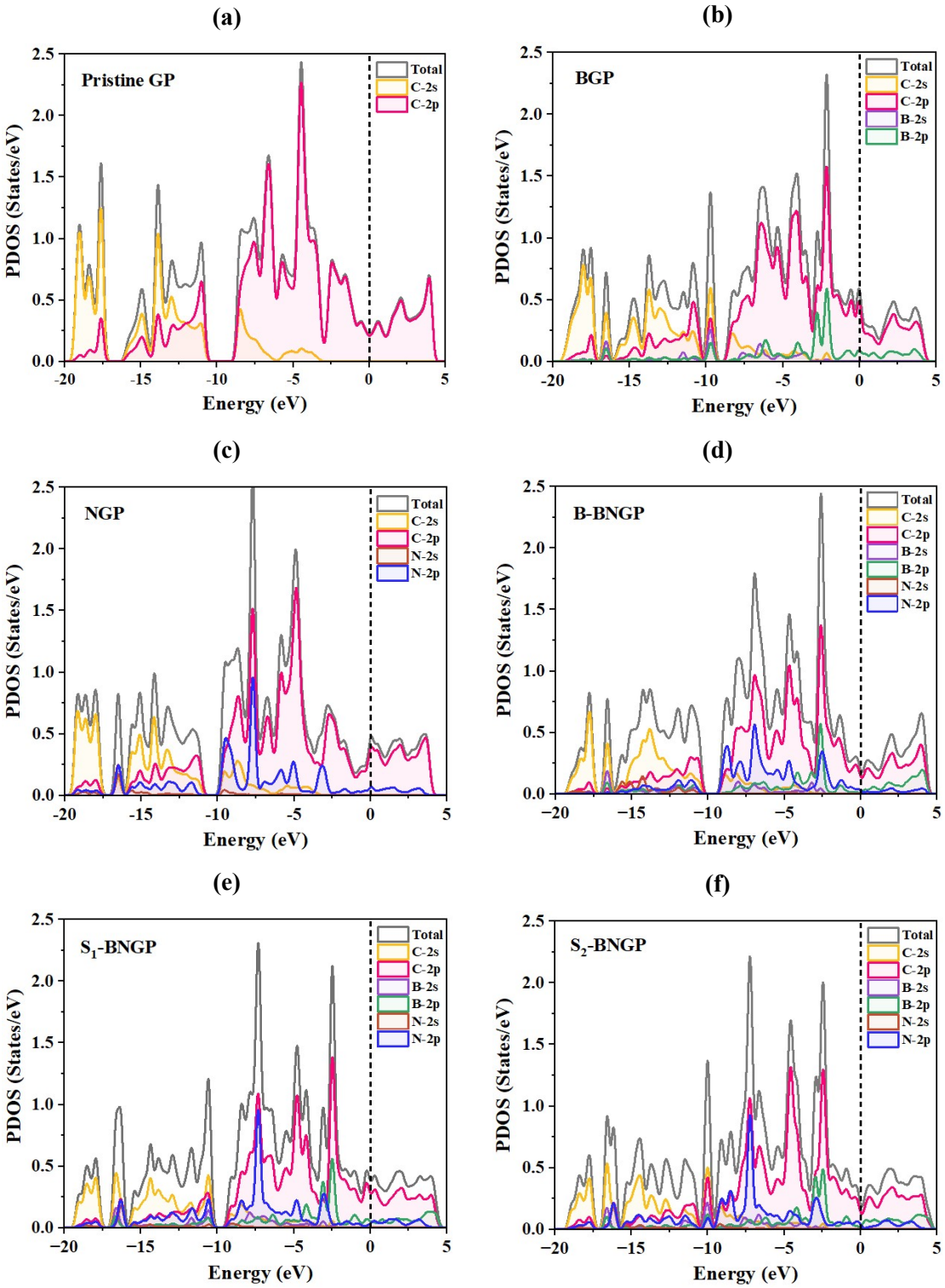



**Fig S3.** PDOS images of (a) pristine GP, (b) BGP, (c) NGP, (d) B-BNGP, (e) $S_1$-BNGP, and (f) $S_2$-BNGP; the Fermi level is indicated by a black dashed line set at zero energy.

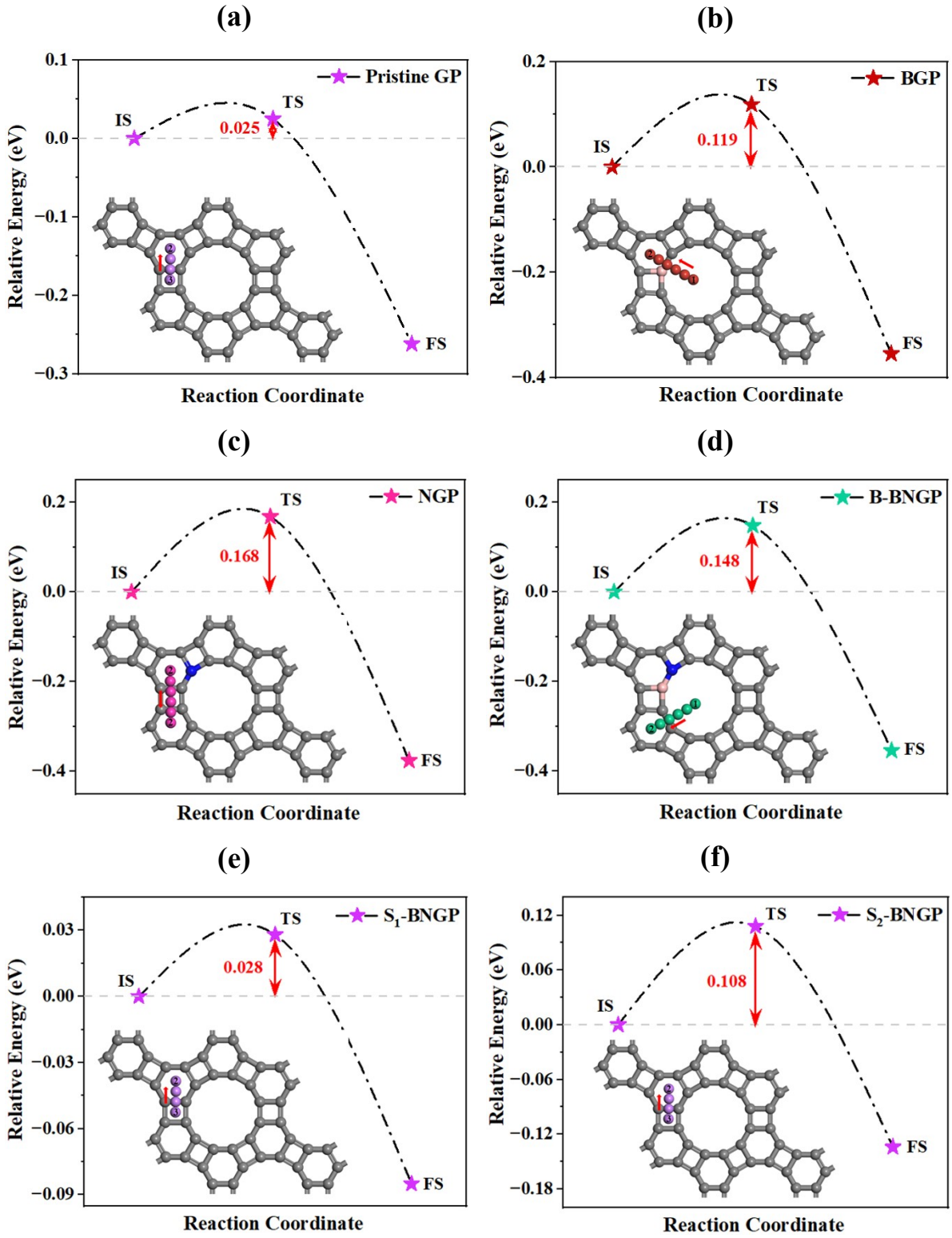



**Fig S4.** Relative energy profiles and diffusion barriers (eV) for Li atom migration on (a) pristine GP, (b) BGP, (c) NGP, (d) B-BNGP, (e) $S_1$-BNGP, and (f) $S_2$-BNGP surfaces; IS, TS, and FS denote the initial, transition, and final states, respectively; C, B, and N atoms are shown as gray, pink, and blue spheres. Migration paths H3→H2, H2→H2, and H1→H2 are marked by purple, pink, and red-green balls, respectively.

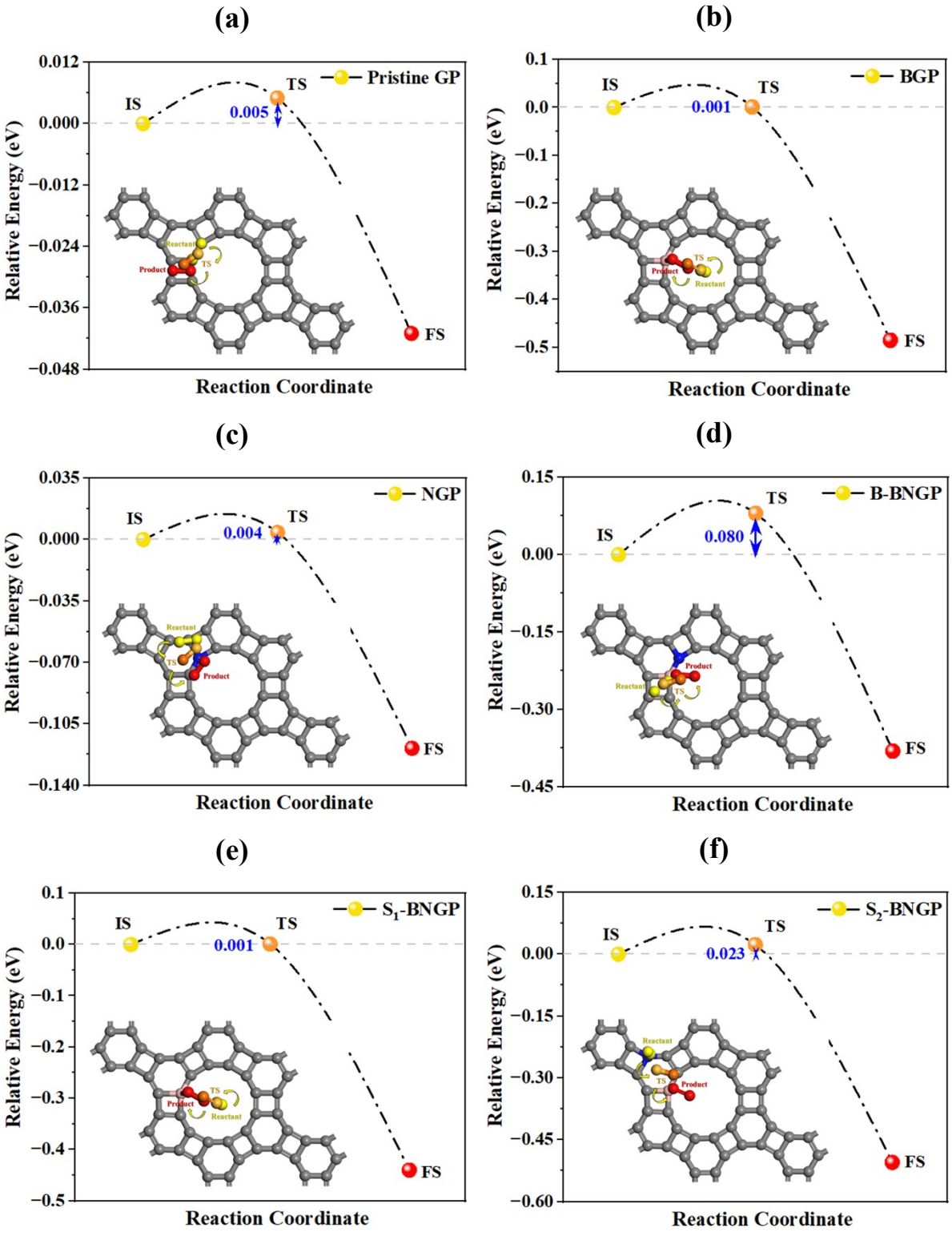



**Fig S5.** Relative energy profiles and diffusion barriers (eV) for $O_2$ molecule migration on (a) pristine GP, (b) BGP, (c) NGP, (d) B-BNGP, (e) $S_1$-BNGP, and (f) $S_2$-BNGP surfaces; C, B, and N atoms are shown as gray, pink, and blue spheres, respectively; initial (IS), transition (TS), and final (FS) states are indicated by yellow, orange, and red spheres, respectively.

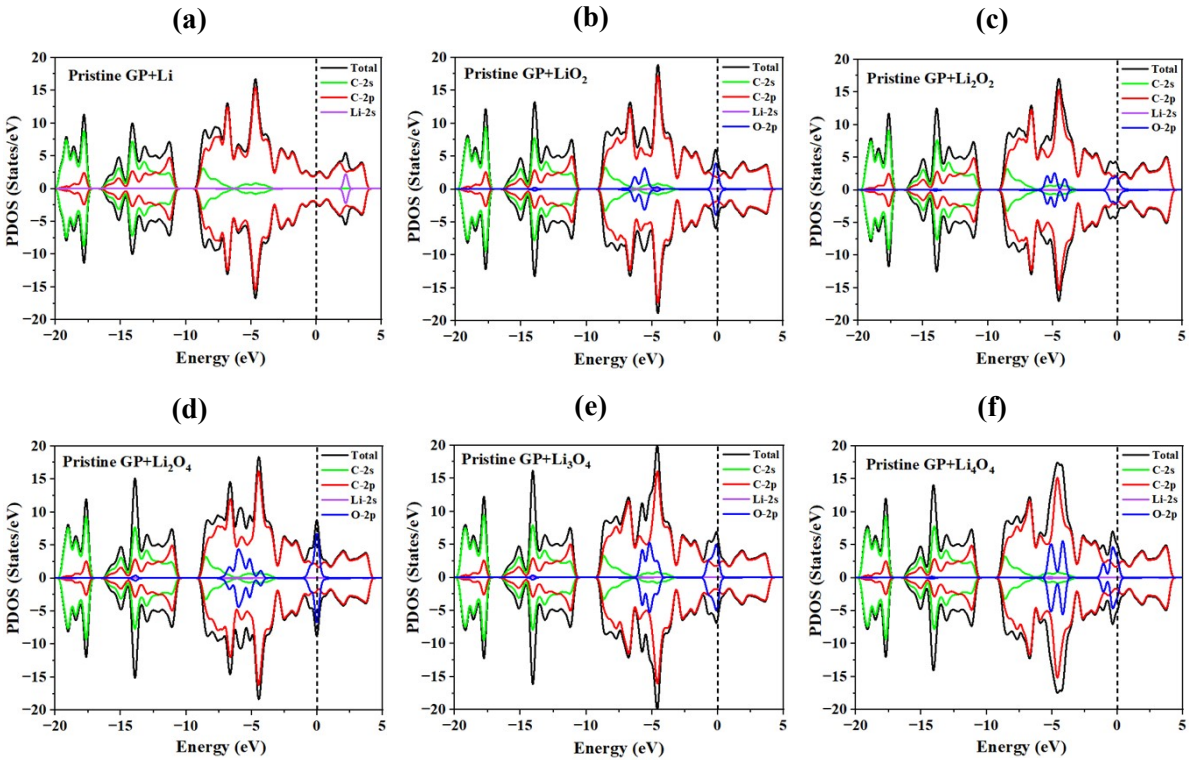
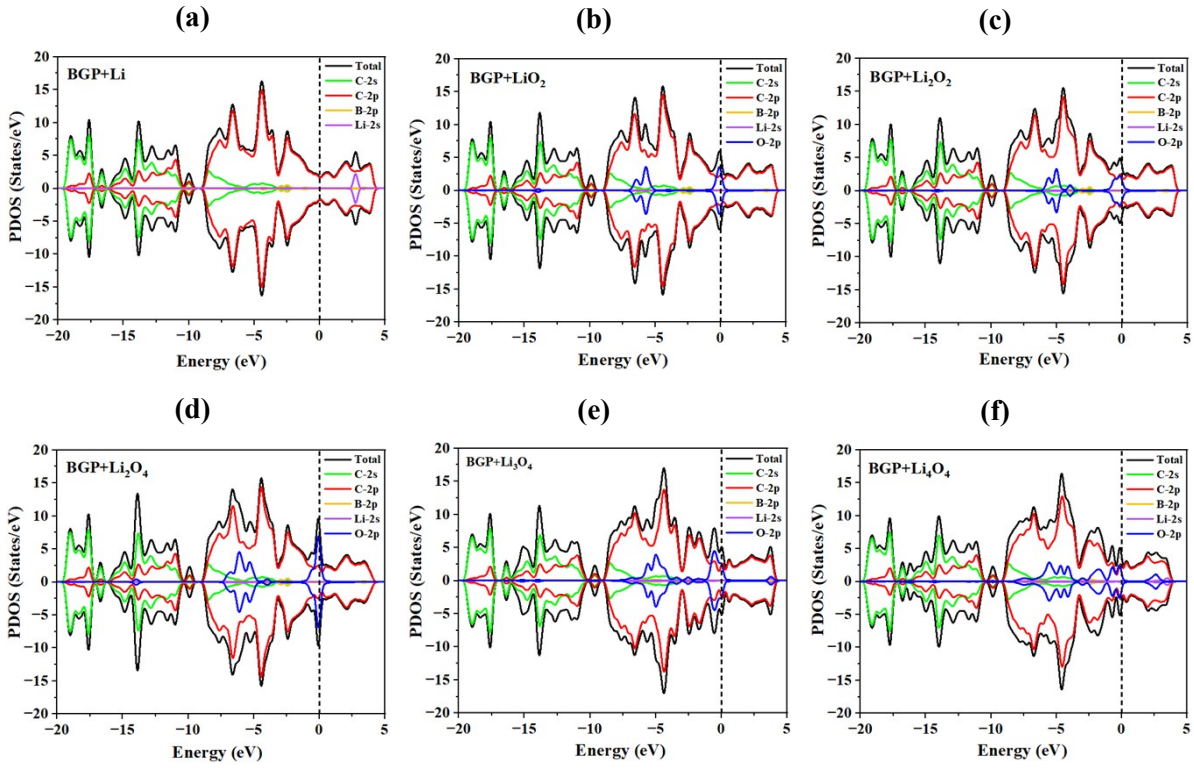



**Fig S6.** PDOS images of (a) $Li/O_2$, (b) $LiO_2$, (c) $Li_2O_2$, (d) $Li_2O_4$, (e) $Li_3O_4$, and (f) $Li_4O_4$ adsorbed on the pristine GP, BGP, NGP, $S_1$-BNGP, and $S_2$-BNGP structures, respectively; the Fermi level is indicated by a black dashed line set at zero energy.



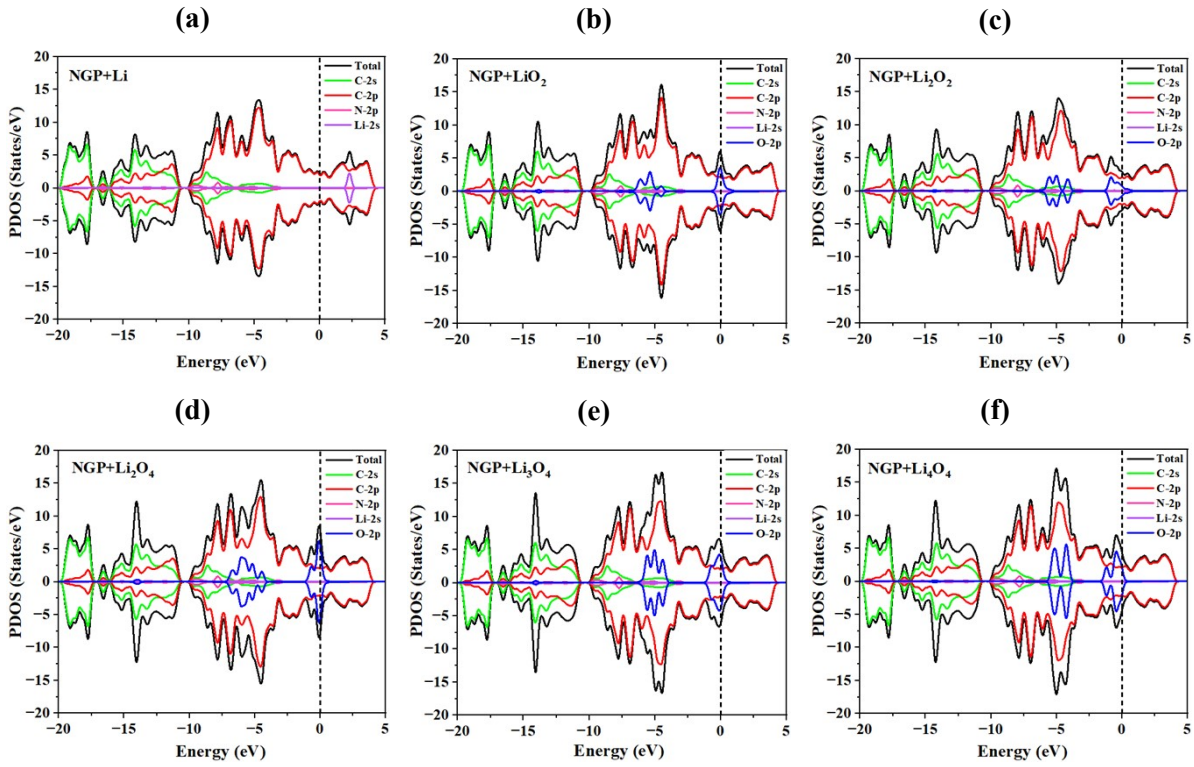




**Fig S6.** (continued).

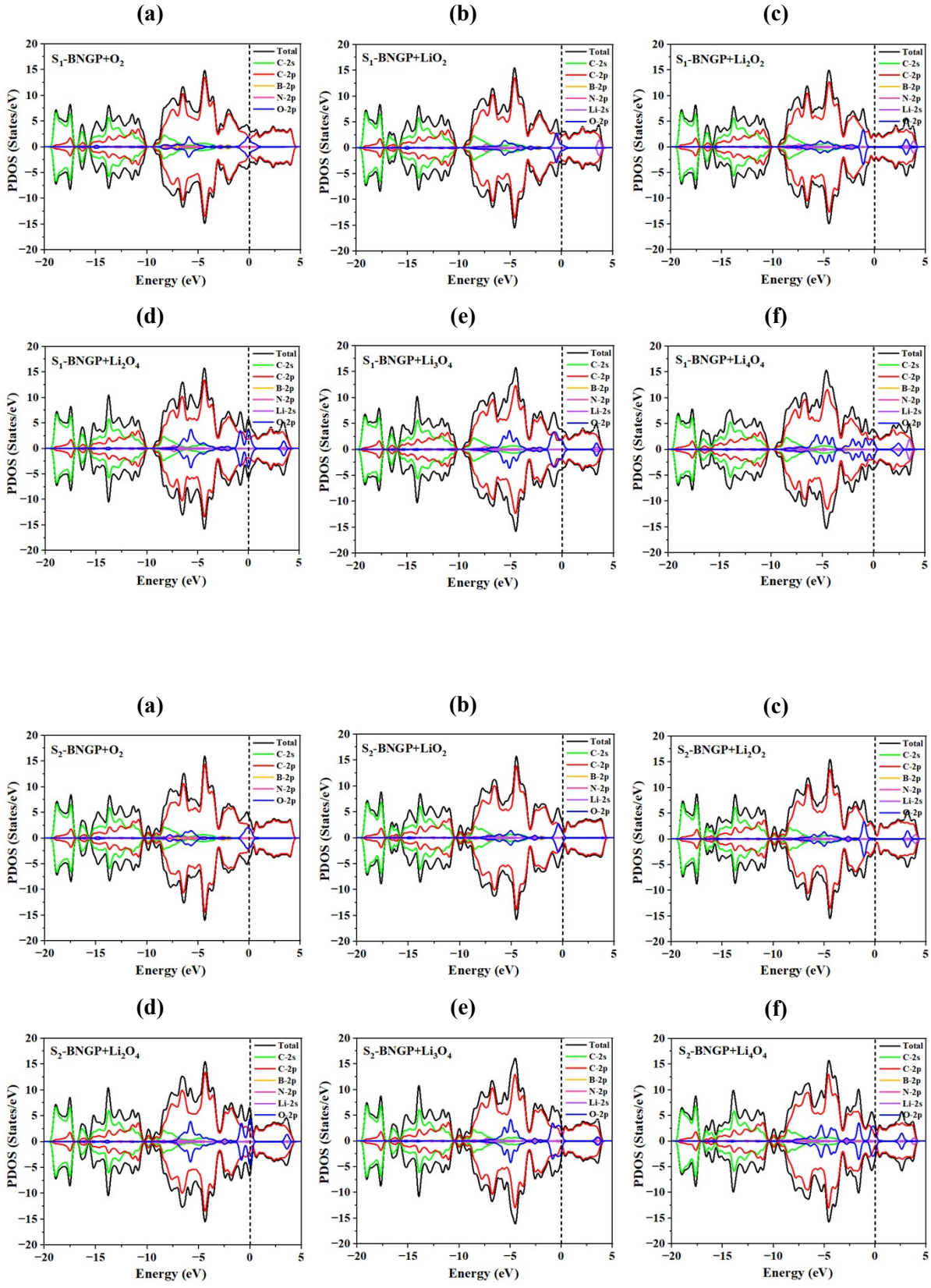



**Fig S6.** (continued).

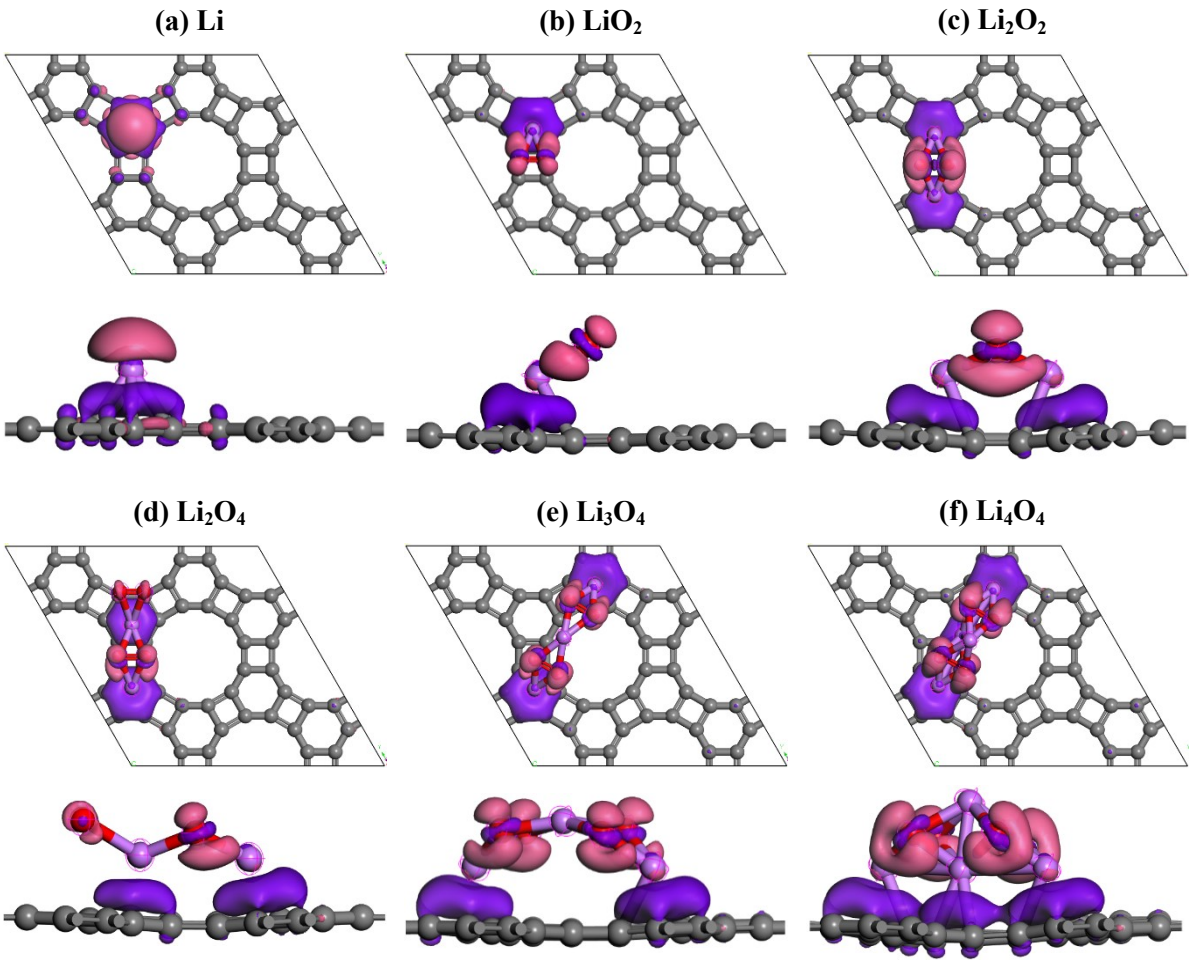



**Fig S7.** CDD images of (a) $Li/O_2$, (b) $LiO_2$, (c) $Li_2O_2$, (d) $Li_2O_4$, (e) $Li_3O_4$, and (f) $Li_4O_4$ adsorbed on the pristine GP, BGP, NGP, $S_1$-BNGP, and $S_2$-BNGP structures, respectively; purple and pink regions represent charge accumulation and depletion, respectively.

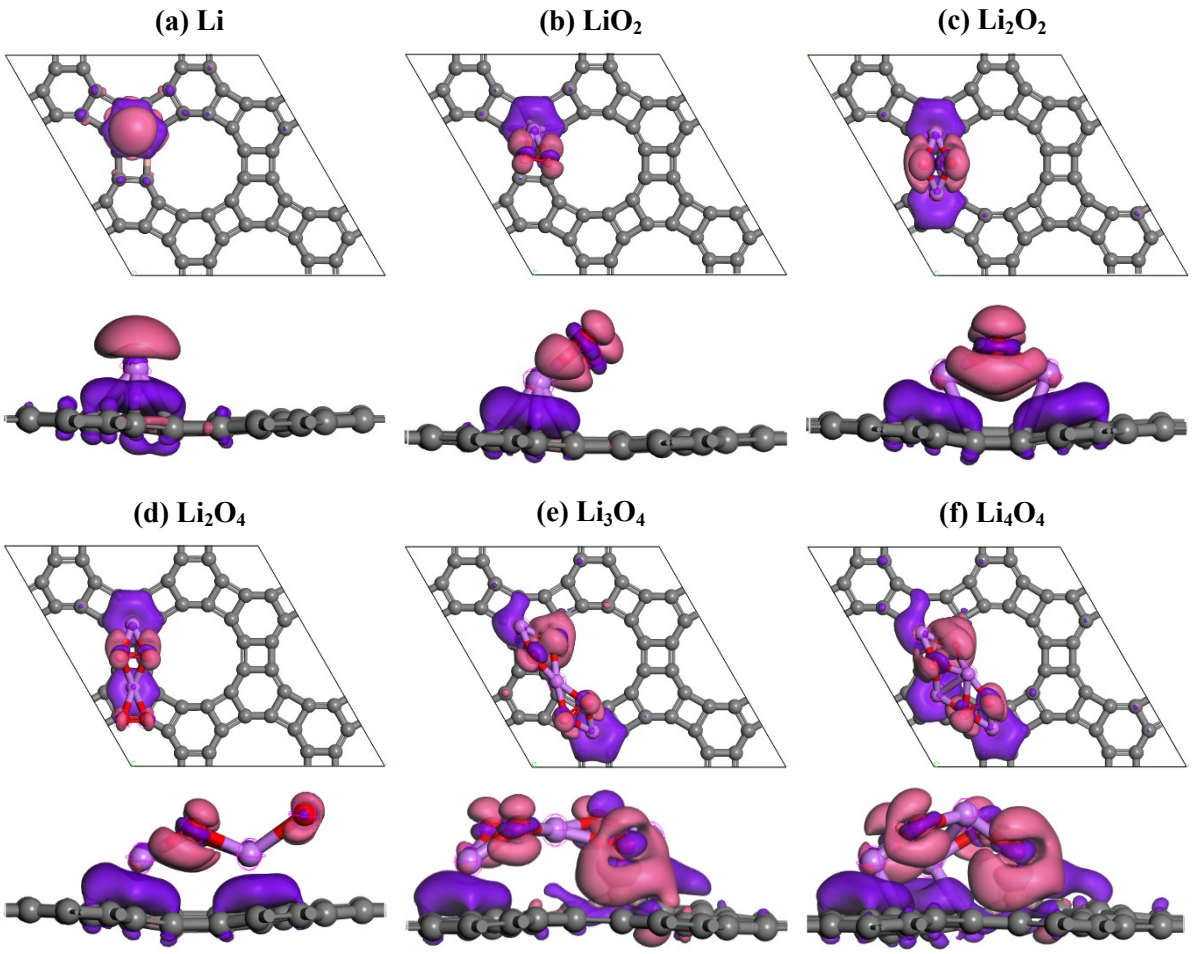



**Fig S7.** (continued).

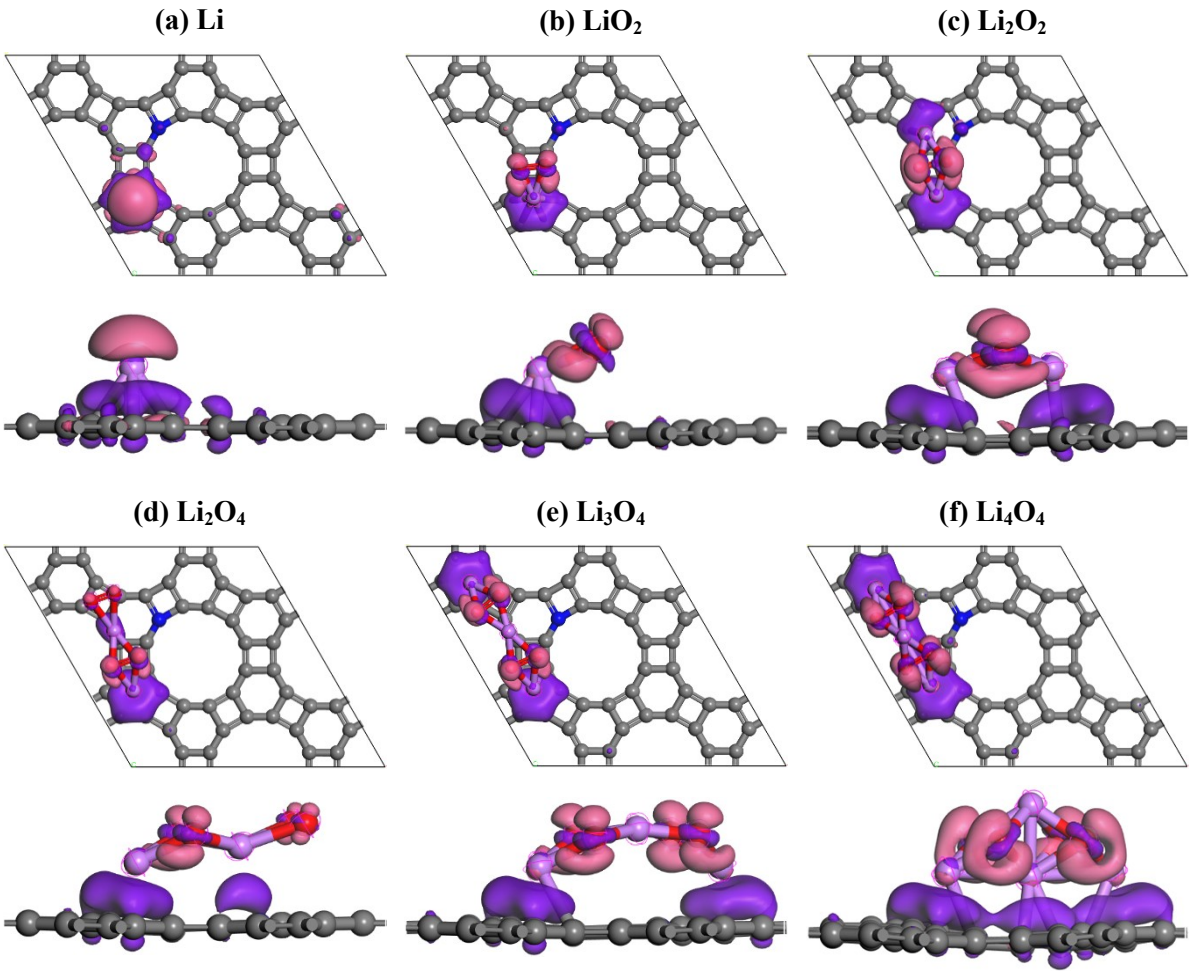



**Fig S7.** (continued).

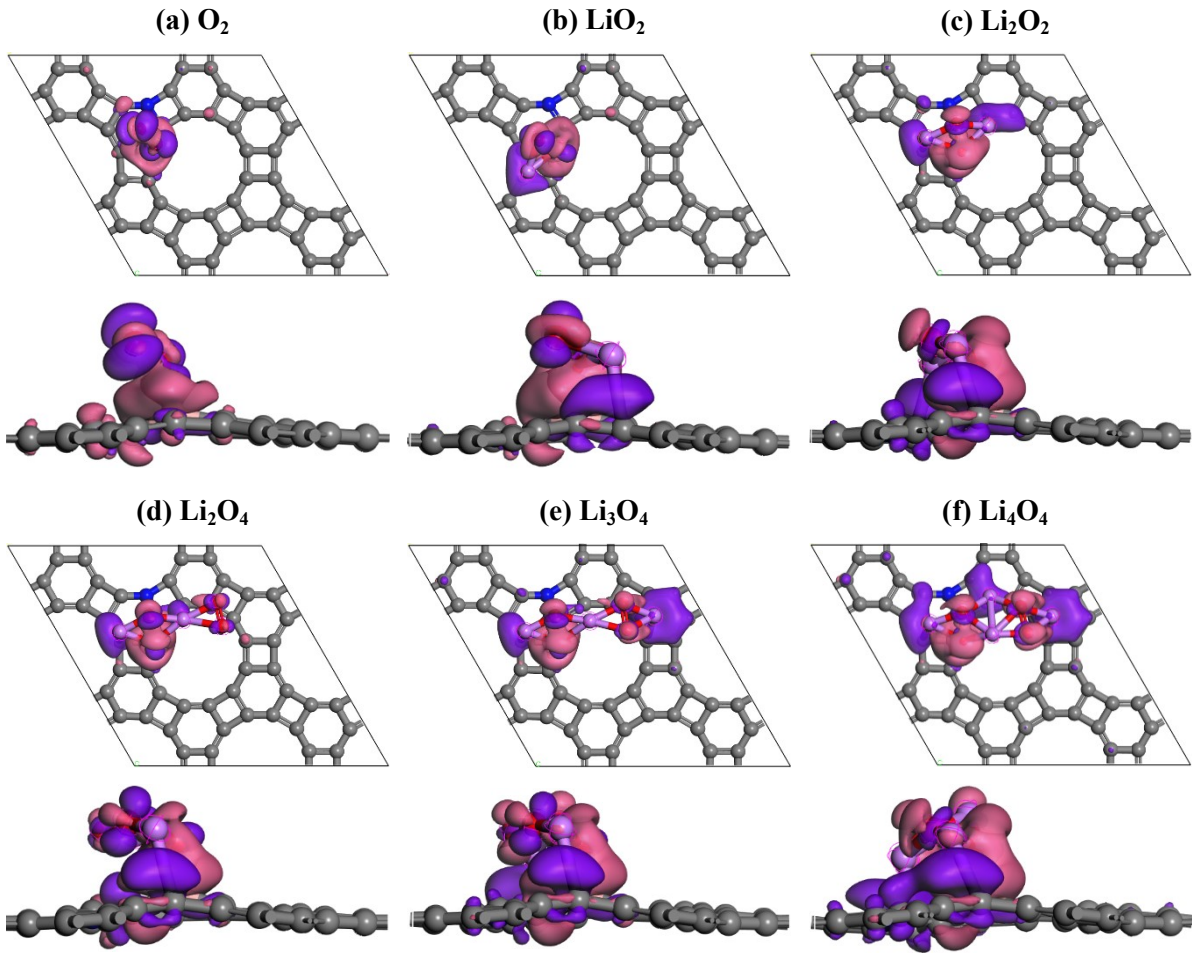



**Fig S7.** (continued).

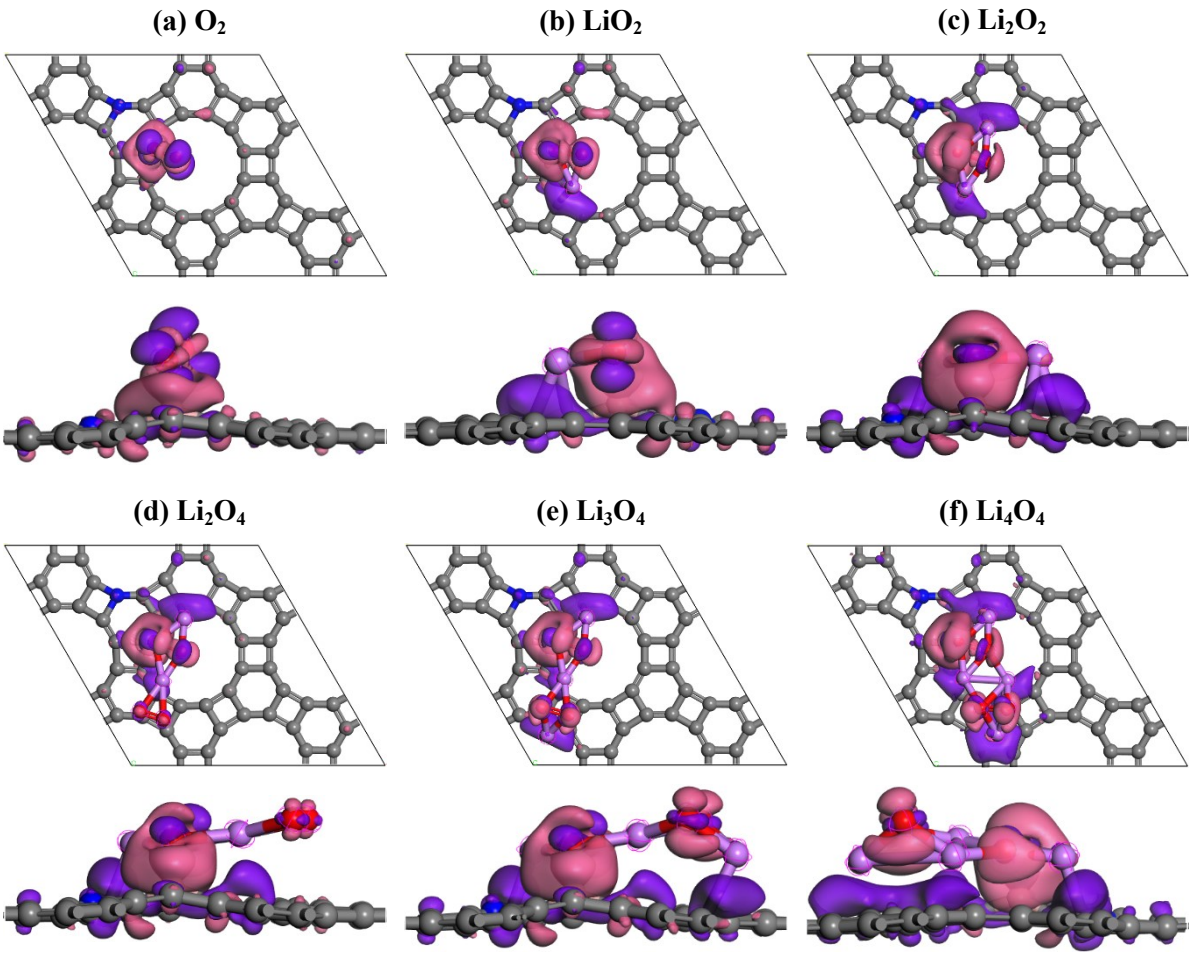



**Fig S7.** (continued).

**Table S1.** Optimized lattice constants (Å) of pristine, B-doped, N-doped, and BN co-doped structures.

| | Pristine GP | BGP | NGP | B-BNGP | $S_1$-BNGP | $S_2$-BNGP |
|---|---|---|---|---|---|---|
| a | 6.758 | 6.778 | 6.743 | 6.768 | 6.768 | 6.768 |
| b | 6.758 | 6.778 | 6.743 | 6.768 | 6.768 | 6.768 |

**Table S2.** Bond lengths of C-C, B-C, N-C, and B-N in pristine, B-doped, N-doped, and BN co-doped structures.

| System | B1 (Å) | B2 (Å) | B3 (Å) |
|---|---|---|---|
| Pristine GP | 1.366 (C-C) | 1.471 (C-C) | 1.470 (C-C) |
| BGP | 1.468 (B-C) | 1.525 (B-C) | 1.549 (B-C) |
| NGP | 1.344 (N-C) | 1.452 (N-C) | 1.459 (N-C) |
| B-BNGP | 1.401 (B-N) | 1.542 (B-C)<br>1.416 (N-C) | 1.548 (B-C)<br>1.460 (N-C) |
| $S_1$-BNGP | 1.460 (B-C)<br>1.343 (N-C) | 1.532 (B-C)<br>1.458 (N-C) | 1.542 (B-C)<br>1.458 (N-C) |
| $S_2$-BNGP | 1.463 (B-C)<br>1.350 (N-C) | 1.530 (B-C)<br>1.447 (N-C) | 1.553 (B-C)<br>1.465 (N-C) |

**Table S3.** Adsorption of Li at various sites and distances in different GP-based systems: initial position (IP), initial distance (ID), final position (FP), final distance (FD), and adsorption energy ($E_{ads}$).

| Substrate | Adsorbate | IP | ID (Å) | FP | FD (Å) | $E_{ads}$ (eV) |
|---|---|---|---|---|---|---|
| Pristine GP | Li | H2 | 0.000 | H2 | 0.003 | -0.426 |
| | | H2 | 0.500 | H2 | 1.794 | -0.807 |
| | | H2 | 1.000 | H2 | 1.787 | -0.807 |
| | | H2 | 1.500 | H2 | 1.802 | -0.807 |
| | | H2 | 2.000 | H2 | 1.805 | -0.808 |
| | | H2 | 2.500 | H2 | 1.807 | -0.806 |
| | | H1 | 1.805 | H1 | 0.099 | -0.333 |
| | | H3 | 1.805 | H3 | 1.976 | -0.547 |
| | | B1 | 1.805 | H2 | 1.824 | -0.807 |
| | | B2 | 1.805 | H3 | 1.971 | -0.547 |
| | | B3 | 1.805 | H2 | 1.809 | -0.806 |
| | | T | 1.805 | H2 | 1.781 | -0.806 |
| BGP | Li | H1 | 1.805 | H1 | 0.400 | -0.961 |
| | | H2 | 1.805 | H2 | 1.837 | -1.291 |
| | | H3 | 1.805 | H2 | 1.669 | -1.290 |
| | | B1 | 1.805 | H2 | 1.651 | -1.291 |
| | | B2 | 1.805 | H2 | 1.660 | -1.291 |
| | | B3 | 1.805 | H2 | 1.657 | -1.291 |
| | | T1 (Top C) | 1.805 | H2 | 1.647 | -1.292 |
| | | T2 (Top B) | 1.805 | H2 | 1.664 | -1.291 |
| NGP | Li | H1 | 1.805 | H1 | 0.281 | -0.206 |
| | | H2 | 1.805 | H2 | 1.832 | -0.352 |
| | | H3 | 1.805 | H2 | 1.790 | -0.726 |
| | | B1 | 1.805 | H2 | 1.811 | -0.352 |
| | | B2 | 1.805 | H2 | 1.784 | -0.725 |
| | | B3 | 1.805 | H2 | 1.806 | -0.725 |
| | | T1 (Top C) | 1.805 | H3 | 1.946 | -0.176 |
| | | T2 (Top N) | 1.805 | H3 | 1.893 | -0.181 |
| B-BNGP | Li | H1 | 1.805 | H1 | 0.178 | -0.501 |
| | | H2 | 1.805 | H2 | 1.785 | -0.746 |
| | | H3 | 1.805 | H2 | 1.692 | -0.847 |
| | | B1 | 1.805 | H2 | 1.730 | -0.749 |
| | | B2 | 1.805 | H2 | 1.696 | -0.848 |
| | | B3 | 1.805 | H2 | 1.701 | -0.847 |
| | | T1 (Top C) | 1.805 | H2 | 1.724 | -0.749 |
| | | T2 (Top B) | 1.805 | H2 | 1.694 | -0.847 |
| | | T3 (Top N) | 1.805 | H2 | 1.723 | -0.749 |
| $S_1$-BNGP | Li | H1 | 1.805 | H1 | 0.419 | -0.749 |
| | | H2 | 1.805 | H2 | 1.777 | -0.809 |
| | | H3 | 1.805 | H3 | 1.798 | -0.732 |
| | | B1 | 1.805 | H2 | 1.757 | -0.815 |
| | | B2 | 1.805 | H3 | 1.810 | -0.733 |
| | | B3 | 1.805 | H3 | 1.793 | -0.735 |
| | | T1 (Top C) | 1.805 | H2 | 1.768 | -0.815 |
| | | T2 (Top B) | 1.805 | H3 | 1.727 | -0.735 |
| | | T3 (Top N) | 1.805 | H2 | 1.767 | -0.816 |
| $S_2$-BNGP | Li | H1 | 1.805 | H1 | 0.338 | -0.706 |
| | | H2 | 1.805 | H2 | 1.773 | -0.718 |
| | | H3 | 1.805 | H3 | 1.820 | -0.655 |
| | | B1 | 1.805 | H2 | 1.784 | -0.723 |
| | | B2 | 1.805 | H3 | 1.830 | -0.656 |
| | | B3 | 1.805 | H3 | 1.811 | -0.656 |
| | | T1 (Top C) | 1.805 | H3 | 1.987 | -0.590 |
| | | T2 (Top B) | 1.805 | H3 | 1.732 | -0.653 |
| | | T3 (Top N) | 1.805 | H2 | 1.768 | -0.724 |

**Table S4.** Adsorption of $O_2$ at various sites, distances, and orientations in different GP-based systems: initial position (IP), initial orientation (IO), initial distance (ID), final position (FP), final orientation (FO), final distance (FD), and adsorption energy ($E_{ads}$).

| Substrate | Adsorbate | IP | IO [a] | ID (Å) | FP | FO | FD (Å) | $E_{ads}$ (eV) |
|---|---|---|---|---|---|---|---|---|
| Pristine GP | $O_2$ | H2 | H | 1.500 | H2 | H | 2.815 | -0.345 |
| | | H2 | V | 1.500 | H2 | V | 3.419 | -0.270 |
| | | H2 | H | 2.000 | H2 | H | 2.809 | -0.341 |
| | | H2 | V | 2.000 | H2 | V | 3.439 | -0.271 |
| | | H2 | H | 2.500 | H2 | H | 2.806 | -0.342 |
| | | H2 | V | 2.500 | H2 | V | 3.432 | -0.271 |
| | | H2 | H | 3.000 | H2 | H | 2.793 | -0.341 |
| | | H2 | V | 3.000 | H2 | V | 3.425 | -0.271 |
| | | H1 | H | 2.815 | H1 | H | 2.281 | -0.348 |
| | | H1 | V | 2.815 | H1 | V | 2.239 | -0.347 |
| | | H3 | H | 2.815 | H3 | H | 2.797 | -0.359 |
| | | H3 | V | 2.815 | H3 | V | 3.442 | -0.274 |
| | | B1 | H | 2.815 | B1 | H | 2.939 | -0.315 |
| | | B1 | V | 2.815 | B1 | O | 3.299 | -0.274 |
| | | B2 | H | 2.815 | B2 | H | 2.876 | -0.329 |
| | | B2 | V | 2.815 | B2 | O | 3.399 | -0.276 |
| | | B3 | H | 2.815 | B3 | H | 2.810 | -0.350 |
| | | B3 | V | 2.815 | B3 | H | 2.856 | -0.339 |
| | | T | H | 2.815 | B3 | H | 2.776 | -0.357 |
| | | T | V | 2.815 | T | O | 3.309 | -0.275 |
| BGP | $O_2$ | H1 | H | 2.815 | Top B | O | 2.343 | -0.859 |
| | | H1 | V | 2.815 | H1 | O | 2.387 | -0.281 |
| | | H2 | H | 2.815 | Top B | O | 2.569 | -0.855 |
| | | H2 | V | 2.815 | Top B | O | 2.362 | -0.859 |
| | | H3 | H | 2.815 | Top B | O | 2.565 | -0.855 |
| | | H3 | V | 2.815 | Top B | O | 2.567 | -0.854 |
| | | B1 | H | 2.815 | Top B | O | 2.568 | -0.854 |
| | | B1 | V | 2.815 | Top B | O | 2.364 | -0.860 |
| | | B2 | H | 2.815 | Top B | O | 2.352 | -0.859 |
| | | B2 | V | 2.815 | Top B | O | 2.349 | -0.859 |
| | | B3 | H | 2.815 | Top B | O | 2.563 | -0.856 |
| | | B3 | V | 2.815 | Top B | O | 2.567 | -0.856 |
| | | T1 (Top C) | H | 2.815 | Top B | O | 2.567 | -0.855 |
| | | T1 (Top C) | V | 2.815 | Top B | O | 2.573 | -0.855 |
| | | T2 (Top B) | H | 2.815 | Top B | O | 2.564 | -0.856 |
| | | T2 (Top B) | V | 2.815 | Top B | O | 2.564 | -0.855 |
| NGP | $O_2$ | H1 | H | 2.815 | H1 | O | 2.031 | -0.424 |
| | | H1 | V | 2.815 | H1 | V | 2.212 | -0.410 |
| | | H2 | H | 2.815 | H3 | O | 2.626 | -0.464 |
| | | H2 | V | 2.815 | H2 | O | 3.413 | -0.312 |
| | | H3 | H | 2.815 | H3 | O | 2.615 | -0.464 |
| | | H3 | V | 2.815 | B1 | O | 2.532 | -0.512 |
| | | B1 | H | 2.815 | B1 | O | 2.530 | -0.512 |
| | | B1 | V | 2.815 | B1 | O | 3.311 | -0.336 |
| | | B2 | H | 2.815 | B2 | O | 2.664 | -0.430 |
| | | B2 | V | 2.815 | B1 | O | 2.513 | -0.512 |
| | | B3 | H | 2.815 | H3 | O | 2.662 | -0.463 |
| | | B3 | V | 2.815 | B1 | O | 2.518 | -0.513 |
| | | T1 (Top C) | H | 2.815 | Top C | O | 2.925 | -0.362 |
| | | T1 (Top C) | V | 2.815 | Top C | O | 3.230 | -0.328 |
| | | T2 (Top N) | H | 2.815 | B1 | O | 2.538 | -0.512 |
| | | T2 (Top N) | V | 2.815 | Top N | O | 3.373 | -0.328 |
| B-BNGP | $O_2$ | H1 | H | 2.815 | H1 | O | 2.139 | -0.355 |
| | | H1 | V | 2.815 | H1 | V | 2.288 | -0.330 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | H2 | H | 2.815 | B1 | O | 2.469 | -0.750 |
| | | H2 | V | 2.815 | H2 | O | 3.359 | -0.261 |
| | | H3 | H | 2.815 | H3 | O | 2.634 | -0.347 |
| | | H3 | V | 2.815 | H3 | O | 2.208 | -0.269 |
| | | B1 | H | 2.815 | B1 | O | 2.471 | -0.750 |
| | | B1 | V | 2.815 | B1 | O | 3.315 | -0.271 |
| | | B2 | H | 2.815 | B2 | O | 2.512 | -0.668 |
| | | B2 | V | 2.815 | H1 | O | 2.238 | -0.751 |
| | | B3 | H | 2.815 | Top B | O | 2.465 | -0.746 |
| | | B3 | V | 2.815 | Top B | O | 2.474 | -0.750 |
| | | T1 (Top C) | H | 2.815 | B2 | O | 2.791 | -0.336 |
| | | T1 (Top C) | V | 2.815 | B3 | O | 3.263 | -0.267 |
| | | T2 (Top B) | H | 2.815 | Top B | O | 2.472 | -0.751 |
| | | T2 (Top B) | V | 2.815 | Top B | O | 2.231 | -0.752 |
| | | T3 (Top N) | H | 2.815 | Top B | H | 2.235 | -0.751 |
| | | T3 (Top N) | V | 2.815 | Top N | O | 3.382 | -0.261 |
| $S_1$-BNGP | $O_2$ | H1 | H | 2.815 | Top B | O | 2.219 | -0.825 |
| | | H1 | V | 2.815 | H1 | O | 2.253 | -0.349 |
| | | H2 | H | 2.815 | Top B | O | 2.411 | -0.837 |
| | | H2 | V | 2.815 | Top B | O | 2.232 | -0.825 |
| | | H3 | H | 2.815 | Top B | O | 2.408 | -0.836 |
| | | H3 | V | 2.815 | Top B | O | 2.410 | -0.836 |
| | | B1 | H | 2.815 | Top B | O | 2.248 | -0.826 |
| | | B1 | V | 2.815 | Top B | O | 2.412 | -0.836 |
| | | B2 | H | 2.815 | Top B | O | 2.246 | -0.826 |
| | | B2 | V | 2.815 | Top B | O | 2.234 | -0.825 |
| | | B3 | H | 2.815 | Top B | O | 2.420 | -0.836 |
| | | B3 | V | 2.815 | Top B | O | 2.404 | -0.836 |
| | | T1 (Top C) | H | 2.815 | Top C | O | 2.621 | -0.476 |
| | | T1 (Top C) | V | 2.815 | Top B | O | 2.216 | -0.825 |
| | | T2 (Top B) | H | 2.815 | Top B | O | 2.423 | -0.836 |
| | | T2 (Top B) | V | 2.815 | Top B | O | 2.410 | -0.836 |
| | | T3 (Top N) | H | 2.815 | Top B | O | 2.409 | -0.836 |
| | | T3 (Top N) | V | 2.815 | Top N | O | 3.359 | -0.305 |
| $S_2$-BNGP | $O_2$ | H1 | H | 2.815 | Top B | O | 2.253 | -0.821 |
| | | H1 | V | 2.815 | H1 | O | 2.315 | -0.343 |
| | | H2 | H | 2.815 | Top B | O | 2.474 | -0.781 |
| | | H2 | V | 2.815 | Top B | O | 2.253 | -0.821 |
| | | H3 | H | 2.815 | Top B | O | 2.473 | -0.785 |
| | | H3 | V | 2.815 | Top B | O | 2.411 | -0.705 |
| | | B1 | H | 2.815 | Top B | O | 2.469 | -0.785 |
| | | B1 | V | 2.815 | Top B | O | 2.481 | -0.785 |
| | | B2 | H | 2.815 | Top B | O | 2.253 | -0.822 |
| | | B2 | V | 2.815 | Top B | O | 2.256 | -0.821 |
| | | B3 | H | 2.815 | Top B | O | 2.472 | -0.784 |
| | | B3 | V | 2.815 | Top B | O | 2.475 | -0.785 |
| | | T1 (Top C) | H | 2.815 | Top C | O | 2.624 | -0.444 |
| | | T1 (Top C) | V | 2.815 | Top B | O | 2.479 | -0.785 |
| | | T2 (Top B) | H | 2.815 | Top B | O | 2.466 | -0.783 |
| | | T2 (Top B) | V | 2.815 | Top B | O | 2.469 | -0.785 |
| | | T3 (Top N) | H | 2.815 | B1 | O | 2.611 | -0.400 |
| | | T3 (Top N) | V | 2.815 | Top N | O | 3.431 | -0.288 |

[a] H, V, and O represent horizontal, vertical, and oblique orientations, respectively.

**Table S5.** Calculated distances between $Li_xO_{2y}$ intermediates and C atoms (Å) on pristine, B-doped, N-doped, and BN co-doped structures.

| $Li_xO_{2y}$ | Pristine GP | BGP | NGP | B-BNGP | $S_1$-BNGP | $S_2$-BNGP |
|---|---|---|---|---|---|---|
| Li | 1.805 | 1.647 | 1.790 | 1.696 | 1.767 | 1.768 |
| $O_2$ | 2.797 | 2.364 | 2.518 | 2.231 | 2.411 | 2.253 |
| $LiO_2$ | 1.939 | 1.876 | 1.926 | 1.774 | 2.095 | 1.909 |
| $Li_2O_2$ | 1.992 | 1.887 | 2.035 | 1.807 | 2.075 | 1.934 |
| $Li_3O_2$ | 1.542 | 1.551 | 2.260 | 1.294 | 1.921 | 1.507 |
| $Li_4O_2$ | 1.542 | 1.402 | 1.541 | 1.282 | 2.112 | 2.003 |
| $Li_2O_4$ | 1.846 | 1.892 | 1.976 | 1.842 | 2.128 | 1.982 |
| $Li_3O_4$ (i) | 1.967 | 1.529 | 1.965 | 1.859 | 1.849 | 1.899 |
| $Li_3O_4$ (ii) | 1.979 | 1.951 | 2.029 | 1.440 | 1.971 | 1.545 |
| $Li_4O_4$ (i) | 2.194 | 1.482 | 2.039 | 1.987 | 1.976 | 1.883 |
| $Li_4O_4$ (ii) | 1.933 | 1.558 | 1.715 | 1.246 | 2.143 | 1.957 |

**Table S6.** Adsorption energies ($E_{ads}$, eV) of $Li_xO_{2y}$ intermediates on pristine, B-doped, N-doped, and BN co-doped structures.

| $Li_xO_{2y}$ | Pristine GP | BGP | NGP | B-BNGP | $S_1$-BNGP | $S_2$-BNGP |
|---|---|---|---|---|---|---|
| Li | -0.808 | -1.292 | -0.726 | -0.848 | -0.816 | -0.724 |
| $O_2$ | -0.359 | -0.860 | -0.513 | -0.752 | -0.837 | -0.822 |
| $LiO_2$ | -2.358 | -2.627 | -2.930 | -2.392 | -2.738 | -2.400 |
| $Li_2O_2$ | -4.691 | -5.018 | -4.537 | -4.956 | -5.222 | -5.417 |
| $Li_3O_2$ | -6.031 | -6.462 | -5.830 | -6.028 | -6.254 | -6.497 |
| $Li_4O_2$ | -7.222 | -8.123 | -6.851 | -7.396 | -9.423 | -9.788 |
| $Li_2O_4$ | -6.114 | -6.501 | -6.038 | -6.148 | -6.294 | -6.548 |
| $Li_3O_4$ (i) | -8.567 | -8.727 | -8.464 | -7.872 | -8.457 | -8.219 |
| $Li_3O_4$ (ii) | -8.125 | -8.127 | -7.542 | -7.131 | -8.385 | -7.830 |
| $Li_4O_4$ (i) | -10.390 | -11.316 | -10.332 | -10.492 | -10.848 | -11.018 |
| $Li_4O_4$ (ii) | -9.365 | -9.569 | -9.359 | -9.372 | -10.727 | -10.971 |

**Table S7.** Variation of the Hirshfeld charge transferred for $Li_xO_{2y}$ intermediates formed on pristine, B-doped, N-doped, and BN co-doped structures during the reduction process. Negative and positive values of the transferred charge indicate an increase and decrease in the number of electrons, respectively.

| Structure | $Li_xO_{2y}$ | Transferred charge (\|e\|) for the adsorbed O and Li atoms | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $Li_1$ | $Li_2$ | $Li_3$ | $Li_4$ | $O_1$ | $O_2$ | $O_3$ | $O_4$ | Total |
| Pristine GP | $LiO_2$ | 0.278 | | | | -0.141 | -0.141 | | | -0.004 |
| | $Li_2O_2$ | 0.283 | 0.283 | | | -0.238 | -0.237 | | | 0.091 |
| | $Li_3O_2$ | 0.278 | 0.279 | 0.357 | | -0.314 | -0.287 | | | 0.313 |
| | $Li_4O_2$ | 0.270 | 0.270 | 0.358 | 0.355 | -0.327 | -0.326 | | | 0.600 |
| | $Li_2O_4$ | 0.168 | 0.290 | | | -0.180 | -0.180 | -0.049 | -0.049 | 0.000 |
| | $Li_3O_4$(i) | 0.286 | 0.259 | 0.260 | | -0.203 | -0.203 | -0.204 | -0.203 | -0.008 |
| | $Li_4O_4$(i) | 0.350 | 0.263 | 0.264 | 0.165 | -0.255 | -0.258 | -0.253 | -0.253 | 0.023 |
| BGP | $LiO_2$ | 0.267 | | | | -0.128 | -0.112 | | | 0.027 |
| | $Li_2O_2$ | 0.265 | 0.277 | | | -0.223 | -0.208 | | | 0.111 |
| | $Li_3O_2$ | 0.264 | 0.272 | 0.345 | | -0.297 | -0.265 | | | 0.319 |
| | $Li_4O_2$ | 0.252 | 0.266 | 0.349 | 0.343 | -0.321 | -0.314 | | | 0.575 |
| | $Li_2O_4$ | 0.275 | 0.166 | | | -0.164 | -0.158 | -0.039 | -0.040 | 0.040 |
| | $Li_3O_4$(i) | 0.357 | 0.242 | 0.266 | | -0.309 | -0.145 | -0.198 | -0.196 | 0.017 |
| | $Li_4O_4$(i) | 0.371 | 0.323 | 0.255 | 0.237 | -0.301 | -0.139 | -0.258 | -0.263 | 0.225 |
| NGP | $LiO_2$ | 0.286 | | | | -0.158 | -0.152 | | | -0.024 |
| | $Li_2O_2$ | 0.289 | 0.305 | | | -0.260 | -0.246 | | | 0.088 |
| | $Li_3O_2$ | 0.292 | 0.304 | 0.372 | | -0.322 | -0.344 | | | 0.302 |
| | $Li_4O_2$ | 0.306 | 0.296 | 0.346 | 0.344 | -0.317 | -0.336 | | | 0.639 |
| | $Li_2O_4$ | 0.285 | 0.203 | | | -0.200 | -0.199 | -0.064 | -0.070 | -0.045 |
| | $Li_3O_4$(i) | 0.270 | 0.257 | 0.266 | | -0.214 | -0.212 | -0.211 | -0.212 | -0.056 |
| | $Li_4O_4$(i) | 0.264 | 0.347 | 0.263 | 0.166 | -0.260 | -0.260 | -0.257 | -0.259 | 0.004 |
| B-BNGP | $LiO_2$ | 0.380 | | | | -0.260 | -0.094 | | | 0.026 |
| | $Li_2O_2$ | 0.376 | 0.348 | | | -0.345 | -0.158 | | | 0.221 |
| | $Li_3O_2$ | 0.402 | 0.350 | 0.328 | | -0.326 | -0.153 | | | 0.601 |
| | $Li_4O_2$ | 0.281 | 0.261 | 0.318 | 0.423 | -0.637 | -0.411 | | | 0.235 |
| | $Li_2O_4$ | 0.386 | 0.233 | | | -0.326 | -0.149 | -0.102 | -0.107 | -0.065 |
| | $Li_3O_4$(i) | 0.378 | 0.260 | 0.272 | | -0.330 | -0.148 | -0.204 | -0.209 | 0.019 |
| | $Li_4O_4$(i) | 0.371 | 0.321 | 0.269 | 0.247 | -0.307 | -0.137 | -0.269 | -0.270 | 0.225 |
| $S_1$-BNGP | $LiO_2$ | 0.277 | | | | -0.133 | -0.147 | | | -0.003 |
| | $Li_2O_2$ | 0.284 | 0.287 | | | -0.225 | -0.254 | | | 0.092 |
| | $Li_3O_2$ | 0.269 | 0.279 | 0.355 | | -0.307 | -0.294 | | | 0.302 |
| | $Li_4O_2$ | 0.260 | 0.276 | 0.363 | 0.347 | -0.318 | -0.315 | | | 0.613 |
| | $Li_2O_4$ | 0.286 | 0.173 | | | -0.192 | -0.202 | -0.080 | -0.079 | -0.094 |
| | $Li_3O_4$(i) | 0.267 | 0.262 | 0.263 | | -0.200 | -0.210 | -0.207 | -0.204 | -0.029 |
| | $Li_4O_4$(i) | 0.261 | 0.349 | 0.262 | 0.167 | -0.250 | -0.255 | -0.252 | -0.253 | 0.029 |
| $S_2$-BNGP | $LiO_2$ | 0.355 | | | | -0.098 | -0.264 | | | -0.007 |
| | $Li_2O_2$ | 0.363 | 0.347 | | | -0.157 | -0.336 | | | 0.217 |
| | $Li_3O_2$ | 0.366 | 0.335 | 0.402 | | -0.167 | -0.332 | | | 0.604 |
| | $Li_4O_2$ | 0.280 | 0.258 | 0.400 | 0.319 | -0.410 | -0.633 | | | 0.214 |
| | $Li_2O_4$ | 0.226 | 0.351 | | | -0.139 | -0.315 | -0.095 | -0.094 | -0.066 |
| | $Li_3O_4$(i) | 0.214 | 0.346 | 0.330 | | -0.136 | -0.309 | -0.209 | -0.205 | 0.031 |
| | $Li_4O_4$(i) | 0.233 | 0.357 | 0.260 | 0.284 | -0.134 | -0.295 | -0.267 | -0.272 | 0.166 |

**Table S8.** Calculated discharge, equilibrium, and charge potentials ($U_{DC}$/Ueq/$U_C$) (in V), and ORR, OER, and total overpotentials ($\eta_{ORR}$/$\eta_{OER}$/$\eta_{TOT}$) (in V) for pristine, B-doped, N-doped, and BN co-doped structures.

| Structure | $U_{DC}$ | $U_{eq}$ | $U_C$ | $\eta_{ORR}$ | $\eta_{OER}$ | $\eta_{TOT}$ |
|---|---|---|---|---|---|---|
| Pristine GP | 2.163 | 2.563 | 3.526 | 0.400 | 0.963 | 1.363 |
| BGP | 2.364 | 2.790 | 3.720 | 0.426 | 0.930 | 1.356 |
| NGP | 2.096 | 2.550 | 3.324 | 0.454 | 0.774 | 1.228 |
| B-BNGP | 2.304 | 2.584 | 2.877 | 0.280 | 0.293 | 0.574 |
| $S_1$-BNGP | 2.255 | 2.680 | 3.338 | 0.425 | 0.658 | 1.083 |
| $S_2$-BNGP | 2.432 | 2.718 | 3.013 | 0.286 | 0.295 | 0.581 |

To evaluate the effect of the $O_2$ energy correction on the calculated thermodynamic quantities, the formation free energies ($\Delta G_f$) of discharge species and the equilibrium potential ($U_{eq}$) for one representative structure in this study (B-BNGP) were compared with and without applying the $O_2$ correction ($E_{CV}$ = 0.86 eV) (Table S9). Applying this correction results in a uniform shift in the Gibbs free energies of formation and makes the $\Delta G_f$ values of Li-$O_2$ species more negative, indicating an improved thermodynamic description of these systems within the DFT framework. Furthermore, the calculated $U_{eq}$ values obtained by including this correction become closer to the experimentally reported value for Li-$O_2$ batteries (approximately 2.96 V). These results demonstrate that although the $O_2$ correction improves the absolute accuracy of the thermodynamic quantities, the main trends and key conclusions of this study remain robust and reliable with respect to this correction. Similar behavior was also observed for the other investigated structures.

**Table S9.** Effect of $O_2$ energy correction on $\Delta G_f$ (eV) and $U_{eq}$ (V) for the representative B-BNGP structure.

| | Without $O_2$ correction | With $O_2$ correction |
|---|---|---|
| $\Delta G_f$ ($Li_2O_2$) | -3.981 | -4.841 |
| $\Delta G_f$ ($Li_4O_4$) | -8.615 | -10.335 |
| $U_{eq}$ | 2.154 | 2.584 |