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Insight into the Electrocatalytic Activities of Nitrogen-Doped Graphyne and Graphdiyne Families: A First-Principles Study

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Abstract : The advent of 2-D materials in the last decade has induced a fresh spur of growth in fuel cell technology as these materials have some highly promising traits that can be exploited to felicitate Oxygen Reduction Reaction (ORR) in an efficient way. Among the various 2-D carbon materials, graphyne (Gy) and graphdiyne (Gdy)1 with their intrinsic non-uniform charge distribution holds promises in this purpose and it is expected2 that substitutional Nitrogen (N) doping could further enhance their efficiency. In this regard, dispersive force corrected density functional theory is used to map the oxygen reduction reaction (ORR) kinetics of five different kinds of N doped graphyne and graphdiyne systems (namely αGy, βGy, γGy, RGy and 6,6,12Gy and Gdy) in alkaline medium. The best doping site for each of the Gy/ Gdy system is determined comparing the formation energies of the possible doping configurations. Similarly, the best di-oxygen (O_2) adsorption sites for the doped systems are identified by comparing the adsorption energies. O_2 adsorption on all N doped Gy/ Gdy systems is found to be energetically favorable. ORR on a catalyst surface may occur either via the Eley-Rideal (ER) or the Langmuir–Hinschelwood (LH) pathway. Systematic studies performed on the considered systems reveal that all of them favor the ER pathway. Further, depending on the nature of di-oxygen adsorption ORR can follow either associative or dissociative mechanism; the possibility of occurrence of both the mechanisms is tested thoroughly for each N doped Gy/ Gdy. For the ORR process, all the Gy/Gdy systems are observed to prefer the efficient four-electron pathway but the expected monotonically exothermic reaction pathway is found only for N doped 6,6,12Gy and RGy following the associative pathway and for N doped βGy, γGy and Gdy following the dissociative pathway. Further computation performed for these systems reveals that for N doped 6,6,12Gy, RGy, βGy, γGy and Gdy the overpotentials are 1.08 V, 0.94 V, 1.17 V, 1.21 V and 1.04 V respectively depicting N doped RGy is the most promising material, to carry out ORR in alkaline medium, among the considered ones. The stability of the ORR intermediate states with the variation of pH and electrode potentials is further explored with Pourbiax diagrams and the activities of these systems in the alkaline medium are compared with the prior reported B/N doped identical systems for ORR in an acidic medium in terms of a common descriptor.

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