

Graphitic Materials for Fuel Cell Development

Computational investigations of catalytic processes in doped graphitic materials

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In Short

- Doped graphitic materials have potential as electrocatalysts for oxygen reduction reaction (ORR).
- Synergistic interactions among the dopants can modify the binding affinity towards oxygen and create new active sites.
- DFT studies on various binding motifs can reveal possible binding motifs and explain the microscopic picture behind the ORR activity.

With the rising global demands for cleaner and more sustainable energy sources, fuel cells are gaining relevance as a pollution-free alternative to the conventional combustion-based energy sources. The proton exchange membrane fuel cell (PEMFC), for example, have already paved its way into the transportation market as the power source for electric vehicles, boasting the advantages of low working temperature, high energy density and zero carbon emission. The energy output of a fuel cell is driven by the exothermic oxidation of fuels such as H_2 and methanol into thermodynamically stable products such as CO_2 and H_2O . In the case of PEMFCs, the thermodynamic driving force behind the energy production is the relatively simple oxidation of H_2 to H_2O by atmospheric oxygen. Unfortunately, the use of globally abundant oxygen as the oxidant does have its drawbacks. The oxygen reduction reaction (ORR) which occurs at the cathode of a fuel cell is usually much slower compared to the fuel oxidation processes at the anode and therefore serves as the limiting factor to the fuel cell efficiency. As a result, most studies on the development of fuel cells are focused on the improvement of ORR kinetics via the introduction of electrocatalysts. The typical catalyst of choice in PEMFCs is Pt, but the high cost and rarity of Pt catalysts pose a limitation on the achievable scale of fuel cell production, thus driving the search for cheaper alternatives that can achieve similar or better ORR efficiency.

Recently, doped graphitic materials have been developed as potential alternatives to the conventional but more expensive Pt-based ORR electrocatalysts. Graphitic materials containing multiple dopants, typically N in combination with metals like Fe and Co or a non-metal like P, B and S exhibit excellent ORR activity [2]. However, the microscopic explanation

behind the synergistic interactions between different dopants in the synthesized graphitic material can be challenging to obtain experimentally since they are mostly highly amorphous and disordered materials. In that regard, quantum chemical calculations of various possible binding motifs can assist in identifying feasible binding sites in terms of stability of formation during the synthesis as well as ORR activity.

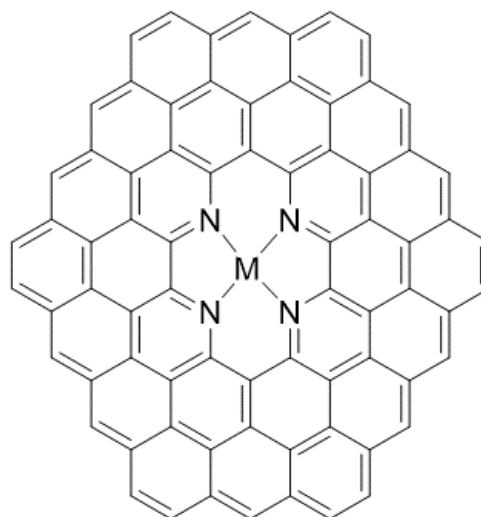


Figure 1: Structure of a $M-N_4$ embedded graphene model.

In general, multi-doped graphitic materials containing N-dopants along with a metal like Fe and Co are thought to bind in a square planar metal- N_4 motif (Figure 1) that is reminiscent of metal-bound porphyrin complexes such as the heme complex in blood. P-bound porphyrin complexes containing P- N_4 motifs are also known to exist and could also possibly be incorporated into the graphitic system. Preliminary calculations on a graphitic cluster model have shown that transition metals like Fe and Co are very strongly bound in the N_4 sites, but the binding have a significant covalent character compared to closed shell $Mg-N_4$ and $Zn-N_4$ motifs [1]. This implies that the requirement for a strongly ionic N_4^{2-} binding site as in porphyrin complexes is relaxed for these transition metals, and the substitution of N atoms at the binding sites with C could be possible to increase the strength of the covalent binding of the transition metals. The substitution of N with C at the binding site leads to various $M-(C,N)_4$ binding motifs which may exhibit different behavior towards ORR activity.

Cluster calculation of the $P-(C,N)_4$ motifs and respective oxidized variants with various combinations of C and N atoms bonded to P revealed that a mix-

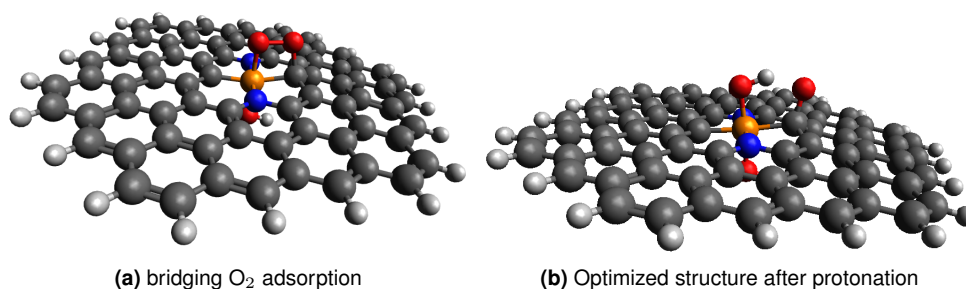


Figure 2: Optimized structures of O_2 -adsorbed $POH-C_2N_2$ cluster (a) before protonation and (b) after protonation [1].

ture of P-C and P-N bonds is optimal for the relative stability of the binding motif as well as the ORR activity [1]. In particular, the bridging adsorption of O_2 across a P-C bond led to a significant elongation of the O_2 bond which was spontaneously broken upon geometry optimization after protonation (Figure 2). The dissociation signifies a preference towards the 4-electron ORR pathway which is generally desired compared to the 2-electron pathway and can possibly explain the enhanced ORR activity of these doped graphitic materials. In addition to P, the N-C substitution at the binding site can be further applied to other atoms, especially the covalently bound transition metals Fe, Co and Ni to determine whether similar effects and behavior could be observed.

The study of ORR mechanism on doped graphitic materials is an important step towards understanding the microscopic picture behind their catalytic activity will pave the way towards the development of cheaper and better carbon-based electrocatalysts. Dispersion-corrected DFT calculations will be performed on a periodic graphene lattice as well as on a finite-sized aromatic cluster with H-termination at the boundary. Periodic calculations are performed with the Vienna Ab Initio Simulation Package (VASP) [3] and cluster calculations are performed with the TURBOMOLE program [4].

WWW

<https://www.bcp.fu-berlin.de/chemie/chemie/forschung/PhysTheoChem/agpaulus/index.html>

More Information

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