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Theoretical Investigation of the Oxygen Reduction Reaction on h-BN Monolayer

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The oxygen reduction reaction (ORR) is a key reaction for the environment related catalysis and energy technology that allows polymer-electrolyte fuel cell (PEFC) to operate. Currently the most efficient catalysts for ORR are based on precious metals, such as platinum [1]. The high cost and limited resources of Pt prevent the wide use of PEFCs in practical applications. Therefore extensive efforts are currently devoted to search for non-precious Pt-free catalysts for ORR. Recently, it has been reported that carbon-based nanomaterials, such as graphene clusters, doped with nitrogen and boron (carbon alloy catalyst) demonstrate high ORR activity [2,3]. It was shown that B-N pair defect at the edge of graphene sheet serves as an active center for ORR [3]. Such materials can be considered as a good candidate for cathode catalyst of fuel cell. However, the concentration of N or N-B impurities in carbon alloy materials is relatively low. Therefore, the overall ORR rate can be limited.

In the present work we study theoretically whether or not nanomaterials mainly consisting of B and N atoms, such as, for example, hexagonal boron nitride (h-BN) can demonstrate activity for ORR. The binding preference and energetics of the ORR intermediates, such as O_2 , O, OOH, OH, H_2O_2 and H_2O adsorbed on the N impurity defect on free and Ni(111) supported h-BN monolayer are studied using methods of density functional theory (DFT) at the generalized gradient approximation level with the WC functional by Wu and Cohen [4]. Adsorption and catalytic activation of O_2 on various adsorption sites located on the surface of h-BN monolayer, including B and N impurity and vacancy point defects as well as adsorption sites at the H-terminated edges of h-BN nanoribbons are studied. It is shown that among all considered adsorption sites only N impurity defect on the surface of h-BN monolayer can be a good candidate for an active center of ORR. Therefore, for the case of N impurity defect we have calculated the optimized geometries and adsorption energies of O_2 and a list of intermediates of ORR on the reaction pathway (see Figs.1 and 2). The results of calculations demonstrate that adsorption energies of O_2 , O, OOH, OH and H_2O on the N impurity defect in h-BN monolayer are similar to those known for Pt(111)

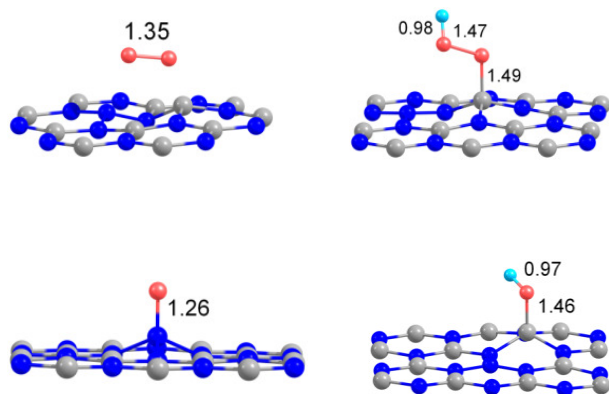


Fig. 1 Optimized geometries of O_2 , OOH , O and OH adsorbed on N doped h-BN monolayer.

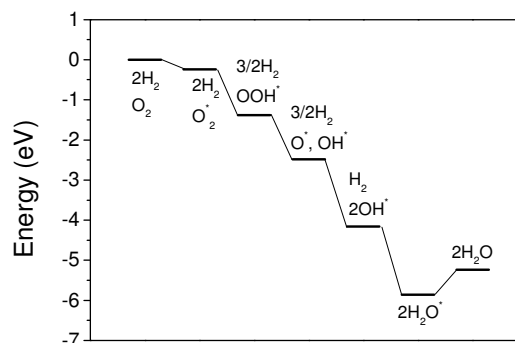


Fig. 2 Reaction energies calculated for the OOH association mechanism of ORR on N doped h-BN monolayer. Adsorbed configurations are marked by (*) upper index.

surface. We have also investigated the influence of the water solvent on binding of ORR intermediates on the h-BN monolayer with N impurity. We have demonstrated that water considerably stabilizes adsorption of O_2 and OH . It is well known that h-BN is an insulator with a large energy gap. Therefore, the problem of electron transport to the active center of ORR on the surface of h-BN monolayer is discussed. It is suggested, that electron transport can be promoted in the h-BN monolayer deposited on the surface of some transition metals. Modification of the electronic structure of the h-BN monolayer, that occurs after its deposition on Ni(111) surface, possible transition to metallicity and change in adsorption energies of ORR intermediates are analyzed.

References

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