

Density Functional Theory Study of Oxygen Reduction Reaction on Non-Precious Transition Metal/Nitrogen Doped Carbon Catalysts

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Proton exchange membrane fuel cell (PEMFC) can convert chemical energy stored in hydrogen fuels to electricity and produce environmentally benign product water. However, the commercialization of PEMFCs is hindered by the present requirement of expensive Pt group metals as their electrocatalysts. To advance PEMFC technology, it is of great interests to develop earth-abundant, non-precious metal based catalysts in replacement of Pt, especially for oxygen reduction reaction (ORR) occurring at the cathode of PEMFCs. Recently, non-precious transition metal/nitrogen doped carbon (TM-N-C) catalysts have drawn much attention since they exhibit promising ORR activity close to Pt. However, the chemical structure of the active sites in these TM-N-C catalysts and their catalytic mechanism for ORR have not been fully understood. To gain insight into the nature of the active sites in the TM-N-C catalysts, we have performed density functional theory (DFT) calculations to investigate the progression of ORR on various types of TM-N₄ (TM = Fe, Co) moiety substitutionally embedded into a graphene layer. On each possible TM-N₄ active site, we calculated the adsorption energies of all the relevant chemical species, namely, O₂, O, OH, OOH, HOOH and H₂O, and the activation energies for O-O dissociation reactions involved in ORR using the DFT method. On FeN₄ and/or CoN₄ embedded in an intact graphene plane, our DFT calculations predicted that the ORR could happen through 4e⁻ associative pathway on the FeN₄ site, whereas follow a 2e⁻ pathway on the CoN₄ site due to high activation energy for O-O bond splitting and extremely weak adsorption of H₂O₂ on the CoN₄ site. These theoretical results are in agreement with experimental observations. In addition, we studied the ORR on a FeN₄ moiety bridging two adjacent armchair like graphene edges as well as a FeN₄ moiety bridging two adjacent zigzag graphene edges with a porphyrinic architecture. Among the three FeN₄ moieties, the porphyrin-like FeN₄ moiety was predicted to catalyze ORR with the highest onset potential. Moreover, we found that the O-O bond scission had lower activation energy on the FeN₄ moieties bridging graphene edges than on the FeN₄ moiety embedded in an intact graphene layer. Consequently, our computation results suggest that introduction of micropores in the TM-N-C catalysts would enhance their catalytic activity for ORR through improving not only the specific area but also the intrinsic activity of the active sites.