

Exploring of catalytic oxygen reduction reaction activity of lattice carbons of vanadium and niobium doped nitrogen codoped carbon nanotubes by density functional theory

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Abstract

The oxygen electroreduction mechanism on the V- and Nb-doped nitrogen-codoped (6,6)armchair carbon nanotube with incorporated MN₄ fragment has been studied using the ω B97XD and PBE density functional theory approaches. The metal center in MN₄ fragment and the adjacent NC=CN double bond (C_2 site) of the support have been revealed as active centers. The metal active centers turned out to be irreversibly oxidized at the first step of ORR affording stable O*, 2O*, or O*HO* adsorbates depending on the applied electrode potential U , that makes them no longer active in ORR. Therefore, the C_2 site comes at the forefront in ORR catalysis. Among the metal oxidized forms M(O)N₄⁻, M(O)(O)N₄⁻ and M(O)(OH)N₄-CNT, the C_2 site of the latter turned out to be most active for 4e dissociative ORR. For both metals the last protonation/electron transfer step, HO* + H* = H₂O, is the rate-limiting step. The alternative hydrogen peroxide formation is not only thermodynamically less favorable but also kinetically slower than the 4e dissociative ORR route on the C_2 site of model M(O)(OH)N₄-CNT catalyst.

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