Density functional theory study of catalytic sites for oxygen reduction in Fe/N/C catalysts used in H₂/O₂ fuel cells

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The oxygen reduction catalytic activity of carbon-supported FeN₄ moieties bridging micropores between two graphene sheets was investigated by density functional theory (DFT). Three types of Fe/N/C structures were considered: two having micropores and one structure in which the FeN₄ moiety is embedded in an extended graphene sheet. In addition, we have investigated the influence of an axial pyridine group approaching the Fe centre. The overall downhill behaviour of the relative free energy vs. reaction step suggests that most structures have catalytic activity at U = 0 V. This conclusion is further supported by calculations of the binding energies of adsorbed O₂ and H₂O and of the O-O bond lengths of adsorbed O₂ and OOH. The side-on interaction of adsorbed O₂ is preferred over the end-on interaction for the three basic structures without the axial pyridine. The pyridine coordination produces a lowering of O₂ binding energy for the dominant end-on interaction of O₂. The energy levels of the most favourable structure with and without the pyridine ligand are nearly equal for spin states S = 1 and S = 2, suggesting that both configurations are formed with similar concentration, confirming experimental findings.