

Effect of anion adsorption on the activity of M-N₄ catalysts

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The lack of a good catalyst for the oxygen reduction reaction (ORR) significantly limits the efficiency of hydrogen fuel cells. The slow kinetics of the ORR arises from the intrinsically large overpotential, but can further be affected by adsorption of anions from the electrolyte. This has been studied extensively for platinum based materials, which are currently some of the most effective catalysts for the ORR. Here the anions of common electrolytes such as phosphoric and hydrochloric acid are known to adsorb on the surface and decrease the catalytic efficiency by blocking active sites.

Concerns about the price and availability of Pt has led to intensive efforts to develop non-precious metal catalysts. Inspired by nature many investigations have focused on porphyrin-like M-N₄ (M = transition metal) motives embedded in carbon based structures. Interestingly, these materials also appear to be more resilient to anion poisoning.[1] Here we use density functional theory calculations to investigate anion adsorption on M-N₄ catalysts, considering a number of different metals and electrolytes. We find that the 2-dimensional nature of these catalysts is key to their different behaviour towards poisoning, because the adsorption of an anion on one side of the M-N₄ motif affects the adsorption of ORR intermediates on the other side. A suitable choice of anion can therefore act to reduce the overpotential, making it possible to increase the catalytic activity for a given metal by choosing the right electrolyte.

[1] J. Phys. Chem. Lett. 2011, 2, 295–298