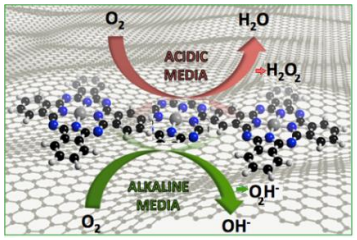
Reactivity descriptors for the electrocatalytic activity of MN4 molecular catalysts for O_2 reduction and other reactions: implications in energy conversion

Jose H. Zagal

Laboratorio de Electrocatalisis, Departamento de Ciencias de los Materiales, Facultad de Quimica y Biologia, Universidad de Santiago de Chile



The success of developing low cost fuel cells depends on the development of inexpensive non precious metal catalysts for oxygen cathode. We discuss here the similarities between well-established reactivity descriptors for classical metal electrodes for their activity for the reduction of O_2 (ORR) with the reactivity of molecular catalysts, in particular MN4 macrocyclic metal complexes confined to electrode surfaces. The M(III)/M(II) redox potential gives linear and volcano activity correlations. A correlation between catalytic activity (as log *i* at constant *E*) vs. calculated M-O_2 binding energies [1] gives a volcano correlation. Specifically, the binding energy of O_2 (and other O species) tracks the M(III)-OH/M(II) redox transition for MnN4 and FeN4 metal complexes. This strongly suggests that the M(III)-OH/M(II) redox transition is a suitable reactivity descriptor, and that M(II) is the active oxidation state. FeN4 and MnN4s catalyze the 4-electron reduction of O_2 and the ORR onset potential follows the pH dependence of the M(III)-OH/M(II) redox transition. FeN4 and MnN4 behave similar to Pt (the best known ORR catalyst): intermediate oxygen binding strength, 4-electron transfer (maximum energy released), with OH^- desorption determining the onset of ORR, leading to a 60 mV/pH dependence of the onset potential on the SHE scale. In contrast, CoN4 complexes (with very few exceptions) only promote the 2-electron ORR (less energy released), the ORR onset potential is pH independent and far removed from the Co(III)-OH/(II). The ORR onset potential tracks the pH insensitivity of the II/I redox transition of the CoN4 complex in the pH = 4-13 range. CoN4 is somehow similar to gold: weak oxygen binding strength, 2-electron transfer, with an onset potential that is does not depend on pH on SHE scale. This suggests that the II/I transition is a suitable reactivity descriptor. The descriptors proposed in this work also apply to heat-treated pyrolyzed MN4 catalysts and to other reactions like peroxide and hydrazine oxidation.

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References

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* **e-mail do autor principal:** jose.zagal@usach.cl