

Reactivity descriptors for the electrocatalytic activity of macrocyclic metal complexes confined on electrode surfaces for electrochemical reactions relevant to energy conversion

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MN4 macrocyclic complexes resemble some natural occurring catalysts [1-2]. The reactivity of these molecules is related to the redox potential of the complex [1-2]. The activity of a given family of macrocyclics for a specific reaction follows a non-linear volcano correlation versus the $M^{n+}/M^{(n-1)+}$ redox potential of the metal chelate. Most of the work published have modulated the redox potential using electron donating or electron-withdrawing substituents on the macrocyclic ligand. However, this parameter can also be modulated by axial ligation [3] and can then play a key role in the electrocatalytic process. Pristine and chemically modified single and multiwalled carbon nanotubes are excellent materials to anchor metal complexes via axial ligation. It is generally accepted that for achieving the highest catalytic activity it is necessary that the reacting molecules interact with the active site to a degree that it is not too weak or not too strong (Sabatier Principle [4]). Too strong of adsorption leads to the blockage of the active sites. In the particular case of the reduction of O_2 [4], its interaction with a metal complex can be described by the M- O_2 binding energy. We find volcano correlations with this parameter when comparing several complexes. Further, a linear correlation between the M(III)/(II) redox potential and the M- O_2 binding energy is found [4]. We will discuss also the key role of axial ligand on enhancing the catalytic activity of MN4 macrocyclics for ORR and for the oxidation and reduction of thiols: cysteine/cystine, cysteamine and glutathione. Axial ligation of these complexes to carbon nanotubes enhance both the activity and long term stability for oxygen reduction and this is required for fuel cell opera-

tion. Axial ligands also shift the M(III)/(II) redox potential in both directions, depending on the nature of the ligand and then can move up or down a particular complex on any side of the volcano correlation. There is a very interesting interplay between ligand substitution and axial substitution. These two effects are not necessarily additive and depend on the nature of the particular complex. Finally, the beneficial effect of back ligands for O_2 reduction mimick the effect of similar ligands in the reduction of O_2 catalyzed by cytochrome c, containing a Fe porphyrin unit. Co phthalocyanine in the presence of an axial ligand changes from a 2-electron reduction catalyst to a 4-electron reduction catalyst mimicking vitamin B12, a Co corrin 4-electron O_2 reduction catalyst [5].

To summarize, we have found volcano correlations of \log of reaction rate as $(\log i)E$ versus the redox potential or versus the M- O_2 binding energy so an optimal redox potential does exist for the reduction of O_2 . We have found similar correlation when studying other reactions like hydrazine oxidation, glucose oxidation and for the oxidation of sulfur-containing species like thiols and thiocyanate.

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