

Enzyme-catalyzed Direct Electron Transfer: An Inspiration for Electrocatalyst Design

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Enzymes can be highly efficient and selective Oxygen Reduction Reaction (ORR) catalysts. At the same time, due to their size, when immobilized, enzymes can have low active site density, usually are tainted by short operational life spans, and are limited to narrow pH and temperature operating conditions.¹⁻²

During the last decade we have studied intensively the phenomena of enzyme-catalyzed direct electron transfer (DET) and particularly the cases of multi-copper oxidases (MCO).³⁻⁸ We have demonstrated that MCO when adsorbed or chemically immobilized on electrode surface reduce molecular oxygen with a similar mechanism that the one observed in solution. This mechanism is of formal 4e- pathway and has a relatively fast intermolecular charge transfer step.⁹⁻¹⁰ The rate-limiting step appears to be the water formation (as is the case in solution). Our group has demonstrated that MCO can be successfully integrated into electrode structures including those of tri-phase gas-diffusion air-breathing electrodes.¹¹⁻¹³

We are applying the lessons learned from this enterprise in bio-electrochemistry of enzymes to building of new design principles for inorganic catalyst discovery. We have thus introduced for the first time the concepts of biologically-inspired (biomimetic) “materials genomics” or “metriolomics” to electrocatalysts discovery. This paper will discuss our approach in search of structural motifs that would bring us closer to being able to intelligently build catalyst for oxygen reduction reaction (ORR). It starts with recognizing the structure of the active site of 4 Cu oxidases (such as laccase, bilirubin oxidase, ascorbate oxidase) and the contribution of protein electrostatics (PE) that play critical role in both intermolecular and intramolecular charge transfer. Fig. 1 gives a charge map of ascorbate oxidase at pH 6 (close to its maximum activity point) and the direction of the dipole created between its T2/T3 oxygen binding and T1 primary electron accepting sites.

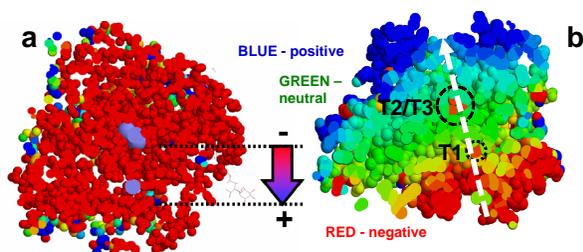


Fig. 1 Electrical charge map of surface charges (a) and cross-section of charge distribution of the changes (b) in ascorbate oxidase showing the dipole (a) and the direction of intramolecular charge transfer (b) from T1 to T2/T3 sites.

We have then set the question to look for a “design” motif that would resemble the T2/T3 tri-nuclear Cu cluster with inter-metallic bond that would allow increment/docking of oxygen molecule and a strongly polarizing metal center (analog of T1) that would be at a distance of some 13.5 Å axially from the center of the tri-nuclear cluster. Such motif (see Fig. 2) happened to be found in a list of mixed

metal oxides from the perovskite family. Many of them are electron conductive: some were studied as high-temperature super-conductors. Further selection shows that several have conductivity that allows their use as electrode materials in power sources.

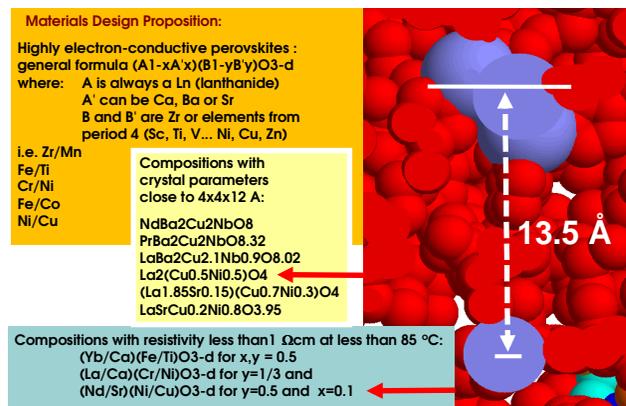


Fig. 2 Schematic of copper center of oxygen reduction enzyme used as template for deriving biomimetic copper-based mixed oxide oxygen reduction reaction catalysts.

The Ln₂CuO₄ group materials, where Ln is the lanthanide series, most closely matches the geometric requirements of an ORR enzyme and can be tuned for electronic and bonding configuration while also offering the electronic conductivity and stability needed for an efficient ORR catalyst.

A range of pure Copper Lanthanide Oxides was made using La/Pr/Nd and copper-like metals doped into the copper positions. This series of Ln-Cu electrocatalysts were synthesized, characterized, tested for ORR and OER using RDE in alkaline environment. Catalysts were characterized for surface area, composition, crystal structure, nano-structure, and surface chemical state using XRD, BET, SEM/EDS HRTEM/STEM/EDS, and XPS.

It was found that the La and Pr -based materials performed best. Doping of the Lanthanide and Copper components changes the ORR performance.

The reactivity trends observed demonstrate a successful synthesis of copper-based mixed oxides which structurally mimic enzymes active for oxygen reduction reaction, and that these bio-mimetic oxides are catalytically active. Further, this work demonstrates a successful “materials genomics” approach to creating biomimetic electrocatalysts.

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