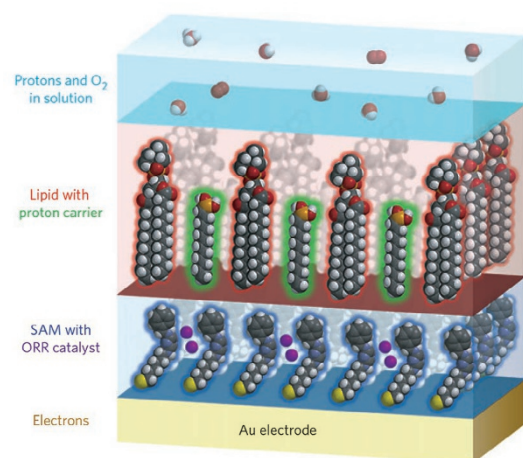


IN BRIEF

HETEROGENEOUS CATALYSIS

Substrate flux dictates selectivity



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Photosynthesis is perhaps nature's illustration par excellence of the value of proton-coupled electron transfer (PCET), and the exquisitely orchestrated transfers of 24 electrons and 24 protons ensure efficient light-driven conversion of water and carbon dioxide into chemical fuel. Many man-made energy technologies, ranging from fuel cells to water electrolyzers, also exploit PCET. A better understanding of the complexities of PCET could help improve such systems.

Writing in *Nature Materials*, Andrew Gewirth and colleagues show that adjusting the relative transfer rates of protons and electrons to a copper-based electrocatalyst for oxygen reduction changes the reaction mechanism. The desired four-electron reduction of dioxygen to water occurs only when rates are matched; high and low proton fluxes give rise to one- and two-electron reductions that generate the undesired products superoxide and hydrogen peroxide, respectively.

The observations are made with the catalyst attached to an electrode and covered with a lipid monolayer in contact with an aqueous solution. Carriers move protons through the lipid layer to the catalyst, so the amount of added carriers controls the proton flux. As this experimental platform also allows for systematic tuning of the electron transfer rates, all is set for further exploration of PCET, a process that has a pivotal role in energy conversion processes in biology and technology.

Magdalena Helmer, Senior Editor, Nature

ORIGINAL ARTICLE Tse, E. C. M. et al. Proton transfer dynamics control the mechanism of O₂ reduction by a non-precious metal electrocatalyst. *Nat. Mater.* **15**, 754–759 (2016)