

Reaching Your Full (Over)Potential: A Novel Approach to Electrocatalytic Oxygen Reduction

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As global energy demands continue to grow, identifying catalysts capable of interconverting small molecule feedstocks for energy production and storage has become an increasingly important research goal. In particular, inexpensive and efficient catalysts for the oxygen reduction reaction (ORR)—wherein molecular oxygen is reduced to water—are necessary for the development of more efficient hydrogen fuel cells (Figure 1). In the most

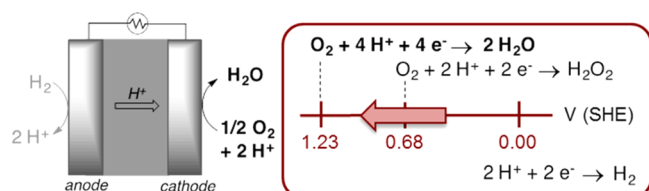


Figure 1. For efficient fuel cells, catalysts for several chemical reactions are necessary, including oxygen reduction. The intermediate reduction to hydrogen peroxide is a common side product of small-molecule oxygen reduction reaction (ORR) catalysts. Reprinted with permission from ref 1. Copyright 2015 American Chemical Society.

recent issue of *ACS Central Science*, Gerkin and Stahl report an exciting and novel approach to ORR electrocatalysis that makes use of two discrete small-molecule redox mediators — nitrogen oxides (NO_x) and the stable nitroxyl radical TEMPO.¹ While neither is a competent electrocatalyst on its own, together they cooperatively effect ORR at overpotentials that are significantly lower than those of more conventional ORR platforms.

This work finds its basis in the known ability of nitric oxide, NO, to react with O_2 , directly cleaving the O–O bond and forming NO_2 .² Much of the free energy available from O_2 as an oxidant is captured in this process, which is kinetically facile and occurs without the generation of hydrogen peroxide byproducts, a common complication in other ORR systems. However, the rates for heterogeneous reduction of NO_2 at an electrode are slow, complicating the use NO_x reagents as single component electrocatalysts. Gerken and Stahl recognized that it should be possible to turn over the NO_2 in solution using a second redox mediator, itself more

The next century's energy needs demand novel catalysts. Robert Knowles discusses Gerken and Stahl's system for oxygen reduction.

readily reducible. To this end they drew inspiration from the reports in the synthetic organic literature, where the use of dual nitroxyl/ NO_x systems has frequently been employed as catalysts for the aerobic oxidation of alcohols.³ The reduced hydroxylamine form of TEMPO readily reacts with NO_2 to form water and return NO. Moreover, proton-coupled reduction of the resulting oxoammonium cation at the electrode is a facile process that regenerates the hydroxylamine (Figure 2). This idea was successfully demonstrated as constant-potential electrolysis of solutions of nitroxyl/ NO_x (under 1 atm of O_2 in acidified MeCN) resulted in sustained ORR activity.

Beyond the impressive ORR activity reported, several other features of this report are significant and warrant further comment. First, as ORR is formally a four-electron/four-proton process, many conventional catalysts are transition metal (or bimetallic) complexes that can access a range of oxidation states.⁴ The fact that two very simple small molecules can jointly mediate a completely selective four electron reduction of O_2 in such an efficient manner is

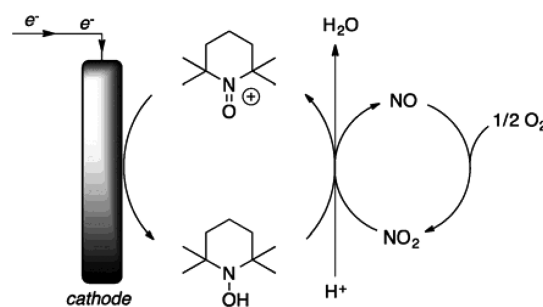


Figure 2. TEMPO and NO_x systems work together as an efficient oxygen reduction catalyst system. Reprinted with permission from ref 1. Copyright 2015 American Chemical Society.

Published: August 6, 2015

remarkable and represents a significant departure from dominant ORR catalyst design principles. Moreover, these reagents are so tunable and inexpensive one could imagine that that fuel cells based on this technology might ultimately become economically attractive.

While perhaps most relevant to the fuel cell and electrocatalysis communities, this paper has the potential to make an impact on the broader synthetic organic community as well.

Second, to be maximally efficient, an ideal ORR catalyst must exhibit fast kinetics at electrochemical potentials close to the thermodynamic potential of the substrate. Any additional driving force beyond the thermodynamic potential necessary to enable a given reaction is described as overpotential. As such, reactions operating at lower overpotential are effectively able to extract more energy from the ORR half reaction than those that operate at higher overpotentials. Many of the most common metal-based ORR catalysts must first be reduced to a lower oxidation state in order to bind and activate O₂. Typically, the potentials required for catalyst reduction are often significantly more negative than the thermodynamic potential of oxygen, limiting the overall reaction efficiency. However, in the reported system, the potentials required for effective ORR are pinned to the nitroxyl/oxoammonium couple, which occurs at comparatively high potentials. As such, this system operates at a much lower overpotential (~300 mV) than other state of the art ORR catalysts.

While perhaps most relevant to the fuel cell and electrocatalysis communities, this paper has the potential to make an impact on the broader synthetic organic community as well. Specifically, the realization that systems commonly used for redox manipulations of organic substrates can be adapted for small molecule activations relevant to renewable energy concerns will likely be an eye-opener for many and may prompt a large and vibrant catalysis community with different perspectives and expertise to start thinking more carefully about energy-relevant transformations.

Taken together, this is an exciting and significant finding that will certainly prompt further research, investigation, and refinement. Whether or not NO_x/nitroxyl fuel cells are ultimately viable remains to be seen. However, no matter the outcome this work represents a significant advance and provides the conceptual blueprints for the design of

complementary dual component systems that may function via a similar principle.

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