The search for non-platinum-group electrocatalysts

“A Theoretical Study of Possible Active Site Structures in Cobalt-Polypyrrole Catalysts for Oxygen Reduction Reaction;” Z. Shi, H. Liu, K. Lee, E. Dy, J. Christunoff, M. Blair, P. Zelenay, J. Zhang, Z-S. Liu, *J. Phys. Chem. C*, **115**, 16672-80 (2011).

Recommended and a Commentary by Albert Migliori,

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Energy storage is today the weakest component in grid-scale implementation of all forms of renewable energy. One solution, the storage of energy in liquid chemical fuels, has the highest gravimetric energy density of any electrical energy storage strategy, and uses the cheapest storage systems (a plastic tank is cheaper than a Li-ion battery). However, the efficiency of electrochemical energy storage is limited by electrocatalysts, not thermodynamics, and the cost remains high because often platinum group metals must be used as the electrodes (or electrocatalysts).

In the last several years, advances in electrocatalysis have increased the activity (reduced the overpotentials) and durability of non-precious metal catalysts (NPMCs), which can now be regarded as potential competitors to Pt-based catalysts. We review here some of these new directions, with some conclusions on where to go.

The basic reactions are:

$2\ H_2 \rightarrow 4H^+ + 4e$ Anode reaction

$O_2 + 4H^+ + 4e \rightarrow 2H_2O$ Cathode reaction

So, the reactions are simple, but the details of the processes are not.

Beginning with Ref. 1 below, the hint provided some years ago led to work on polymer-supported transition metal (Fe), C, and N based catalysts with weak activity (activity is measured by amps per unit area for a given cell voltage). Ref. 1 described very careful chemical preparation leading to unusual stability of a low-activity catalyst. The approach was primarily heuristic and phenomenological, with the correlation between catalytic activity and the exposure of Fe being the primary driver, and the use of standard chemistry techniques to modify systematically the structure. Microscopic models have not yet entered into the research, not surprising when one considers that the macroscopic measurement of an I-V characteristic (called voltammetry) is a primary diagnostic. As research progressed, successful attempts, described in Ref. 2, the *Chemical*

Communications “hot article”, were made to include things like TiO_2, a tough oxide, as part of the catalyst structure in an attempt to improve durability. But the difficulty of correlating activity with processing remained, partly because the activity of these non-precious metal catalyst sites is strongly dependent on the heat treatment temperature. In that work IR spectroscopy, in addition to the usual I-V measurements did expand understanding some. Microscopics still have not yet entered the picture, thus the nature of the active oxidation reduction reaction (ORR) catalytic sites in N-M-C (M is a transition metal) catalysts continues to be at the center of an ongoing debate, (Ref. 3 below). Deeper understanding is complicated because results strongly depend on the type of nitrogen and transition-metal precursors used, heat treatment temperature, carbon support morphology, and synthesis conditions. However recently, a non-PGM catalyst synthesized with Fe and cyanamide has demonstrated an open cell voltage (OCV) of 1.04 V and current densities of 165 A cm^3 at 0.80 V, exceeding the 2010 US DOE target for the volumetric ORR activity of non-PGM catalysts (130 A cm^3 at 0.80 V, Ref.(4)).

But at this point, without microscopic guidance, it is difficult to understand why this material works, and what alternatives might exist. Thus we come to the featured paper above. In this paper are laid out both measurement challenges and theory approaches to understanding what makes a good electrocatalyst. The key issue today is that “The debate about whether or not the transition metal is a part of the catalytic site is at the center of active-site discussion in the non-PGM catalyst research community.”When one considers this statement, it is incredible that we do not know whether the transition metal is the key. The root problem is lack of microscopic information, either by theory or by experiments. Hints at the problem come from the referenced x-ray photoemission spectroscopy studies that finally show two nitrogen sites, infrared absorption studies that show a Co-N resonance, and electron paramagnetic studies that indicate isolated Co ions. Coupled with detailed chemistry, one site, Co-N site, could, finally be identified as the key catalyst site.

The computational methods using Density functional methods have been calibrated against available data and “have demonstrated that the computational methodology provides satisfying geometric structures and electronic properties, such as ionization potential and oxygen binding energies for this type of system”. Of importance though, is that the results, though ignoring entropy, produce potentials that agree well with published measurements. Nice arguments are presented that begin to identify structural details even if the quantitative computations are off because the results provide geometric constraints on the $C-N_x$ complexes that provide qualitative selection criteria. That is, if the complex that is stable is not planar, then it won’t work on a catalyst surface. Or if the reaction occurs on the sides of the M-N complex it is less favorable that on the ends.

Additionally, using X-ray diffraction and EXAFS (Extended x-ray absorption fine structure) bond distance could be measured and then correlated with computational results for various trial structures.

So we see here that even computations that are not comprehensive in the inclusion of physical effects can constrain what must be happening at an electrocatalytic site, but that this is only possible by coordinating with several experimental measurement techniques. In the end, this general approach may bear fruit if a model can be tested experimentally on other systems with experiments with many different techniques. Advances may provide the future ability to improve electrocatalysis.

References:

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