Cobalt Corroles as Electrocatalysts for the Oxygen Reduction Reaction

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Recent years have seen an increased urgency in research dedicated to the development of sustainable energy systems as a result of growing energy demands and environmental concerns related to our continued reliance on fossil fuels.[1,2] In an ideal scheme, energy from renewable resources such as wind or solar power could be stored in chemical bonds through the generation of hydrogen by water electrolysis. The resulting hydrogen fuel could then be used as needed to power systems ranging from personal transportation to back-up generators via combustion in hydrogen fuel cells – a clean process which affords heat and water as its only by-products.[1] However, realization of this strategy relies in great part on efficient energy conversion, a process which is dictated by the kinetics of the hydrogen oxidation (HOR) and oxygen reduction (ORR) half reactions within fuel cells **(Figure 1)**. Because ORR is quite sluggish, five orders of magnitude slower than HOR, and can proceed via multiple pathways, the development of ORR catalysts which are both efficient and selective is of predominant interest.[3] The activity of state-of-the-art Pt-based ORR catalysts has already proven sufficient for the development of fuel cell technologies capable of powering vehicles,[2] however, the cost and scarcity of this precious metal is prohibitive to the widespread implementation of fuel cell technologies and there remains room for improvement with regard to both catalyst durability and efficiency.[3]

Hydrogen Oxidation Reaction: $2H_2 \rightarrow 4H^+ + 4e^-$, $E^0 = 0V$ vs. RHE

Oxygen Reduction Reaction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, $E^0 = 1.23$ V vs. RHE

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$, $E^0 = 0.68$ V vs. RHE

Figure 1: Fuel cell half reactions for HOR and ORR with their respective redox potentials.

Nature addresses the issue of slow ORR kinetics through the implementation of metalloenzymes such as cytochrome c oxidase (CcO) which possesses an iron porphyrin motif in its active site.[4] The impressive activity and selectivity of CcO toward the 4 electron ORR pathway[4] has inspired the investigation of a variety of porphyrin derivative transition metal complexes in the search for non-precious metal ORR catalysts.[3] Among those derivatives investigated are metal corroles **(Figure 2)** which afford a trianionic coordinating environment making them especially suitable for the stabilization of high-valent metal-oxo intermediates, and providing low-valent metal centers with increased reducing power. While corroles were first synthesized in 1964 by Johnson and Kay,[5] work by Gross and coworkers in 1999 made the synthesis and modification of these macrocycles accessible to the general research community.[6] Kadish and coworkers were

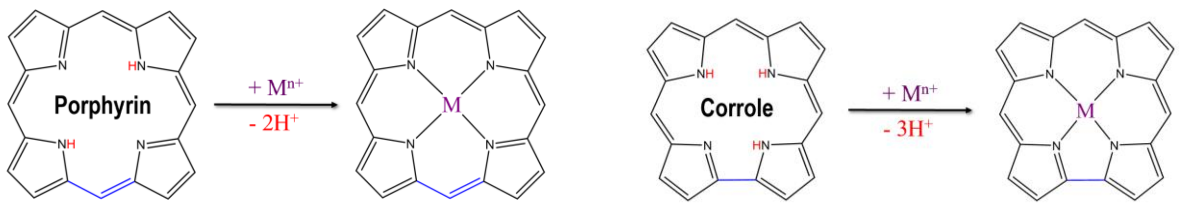

Figure 2: Comparison of porphyrin and corrole derivative skeletal structures.

among the first to investigate metal corroles for their electrocatalytic properties in 2005, demonstrating the ability of these complexes to catalyze ORR[7] and prompting the ongoing study of structural modification toward the understanding and optimization of catalytic activity.[8] Changing the metal center of a given corrole has been shown to predominantly affect the onset potential, and thereby activation energy, of ORR. A comparison of 5 analogous first row transition metal corroles revealed the cobalt corrole to be the most active for ORR catalysis with an onset potential (0.81V vs. RHE) approaching that of the platinum industry standard **(Figure 3)**.[9] This activity was attributed to the cobalt corrole's relatively low lying, metal-centered LUMO promoting fast metal center reduction and subsequent electron transfer to dioxygen. Another structural modification, meso-substitution, was found not to greatly influence onset potential, however, it was found that the electron withdrawing (vs. electron donating) character of these substituents had a significant effect on pathway selectivity.[10,11] Koutecky-Levich analysis of electrocatalytic data collected using a rotating disk electrode revealed that increasingly electron withdrawing substituents promote the desired 4 electron pathway to water **(Figure 4)**, likely by decreasing the charge density at the metal center and thus increasing the binding affinity of partially reduced oxygen species.[10]

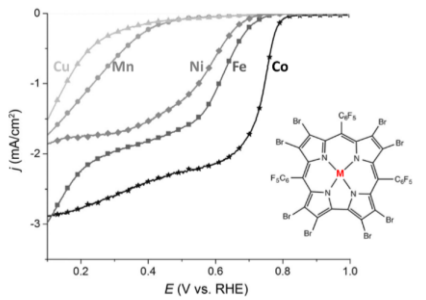

Figure 3: Linear sweep voltammograms obtained using a rotating disk electrode for various transition metal centered corroles.[9]

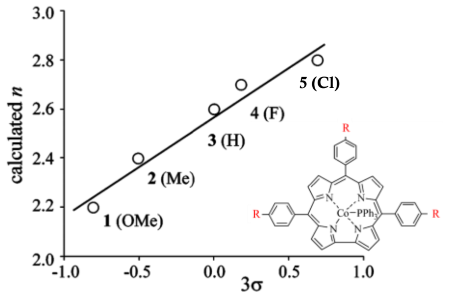

Figure 4: Plot of calculated electron transfer number against the sum of the substituent Hammett constants.[10]

Finally, the effect of beta-substitution has been studied with an initial emphasis on the effect of halogen substituents. Substituents with lower electronegativity were found to afford higher onset potentials with both electron withdrawing and pi-donating ability thought to contribute to overall performance.[12] Interestingly, when the electrode material was changed from glassy carbon to high surface area BP2000 carbon, a uniform increase in onset potential to 0.85V vs. RHE was observed and significant differences in reaction pathway appeared **(Figure 5)**.[12]

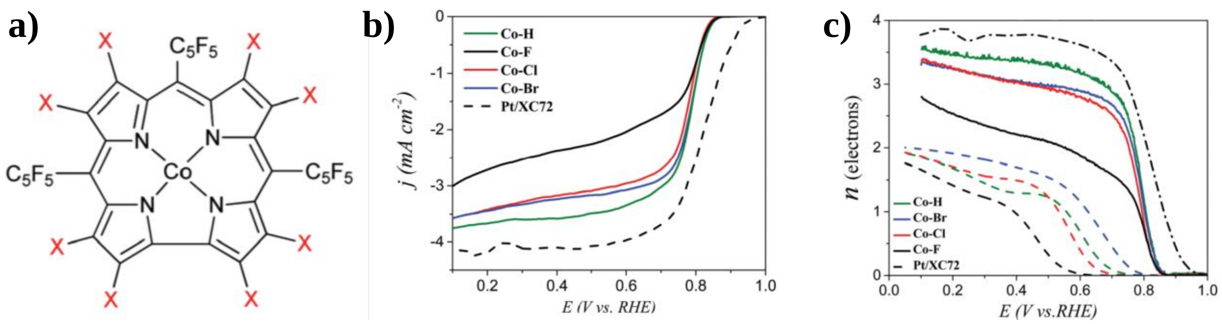

Figure 5: a) Chemical structure of the halogenated corroles under investigation, **b)** Linear sweep voltammograms of halogenated corroles on BP2000 carbon and **c)** their calculated electron transfer numbers on both BP2000 carbon (solid) and glassy carbon (dashed).[12]

Furthermore, initial electrochemical characterization of a series of cobalt corroles with purely electron withdrawing beta-substituents raised the Co^{III} /Co^{II} redox potential above that reported for beta-halogenated complexes, suggesting the possibility for an increased onset potential from these complexes under ORR conditions.[13]

In conclusion, cobalt corroles have been demonstrated to be a versatile class of ORR catalyst with activities approaching those of Pt industry standards. While the onset potentials afforded by cobalt corroles still lag behind those of pyrolyzed non-precious metal catalysts (~1V vs. RHE),[14] they provide an excellent platform for the investigation of structural effects on catalytic activity. Going forward, additional work to understand the role of carbon electrode material on catalytic performance is necessary, as well as an examination of catalyst durability over time.

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