Oxygen Reduction Reaction

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Metallocorroles as Nonprecious-Metal Catalysts for Oxygen Reduction

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Abstract: *The future of affordable fuel cells strongly relies on the design of earth-abundant (non-platinum) catalysts for the electrochemical oxygen reduction reaction (ORR). However, the bottleneck in the overall process occurs therein. We have examined herein trivalent Mn, Fe, Co, Ni, and Cu complexes of β-pyrrole-brominated corrole as ORR catalysts. The adsorption of these complexes on a high-surface-area carbon powder (BP2000) created a unique composite material, used for electrochemical measurements in acidic aqueous solutions. These experiments disclosed a clear dependence of the catalytic activity on the metal center of the complexes, in the order of Co > Fe > Ni > Mn > Cu. The best catalytic performance was obtained for the Co^{III} corrole, whose onset potential was as positive as 0.81 V versus the reversible hydrogen electrode (RHE). Insight into the properties of these systems was gained by spectroscopic and computational characterization of the reduced and oxidized forms of the metallocorroles.*

Climate change and oscillating oil prices have renewed interest in fuel-cell technology over the past two decades.[1] The practicality and energy conversion efficiency in polymer electrolyte membrane (PEM) fuel cells are limited by two major aspects: a) the rate-limiting oxygen reduction reaction at the cathode; and b) the low abundance and high cost of platinum, which is still the most efficient catalyst and most expensive component (more than 37 % of the overall price) in the fuel cell.[2] Intensive effort has hence been devoted to developing alternative nonprecious-metal catalysts (NPMCs) for oxygen reduction.[3] Biological processes, in which transition-metal complexes of porphyrins play a major role, have inspired many of the approaches,[4] but studies conducted with synthetic metalloporphyrins revealed that their activity and stability is much lower than that of the state-of-the-art platinum-based catalysts.[5] Later studies indicated that the pyrolysis of these transition-metal macrocycles and even that of separate nitrogen, carbon, and transition-metal precursors could lead to significant improvement in both activity and stability of NPMCs.[6] A major drawback of the pyrolyzed catalysts is that they are not well defined, and therefore it is much more difficult to control their structure and improve their performance. In fact, it is not even clear if the transition metal is important for ORR catalysis.[7] Quite a wide range of non-noble metal materials were determined to be applicable as ORR catalysis in alkaline media, but Pt still remains the only catalyst to offer a high enough free energy of adsorption for O_2 that is crucial for catalyzing ORR in acidic media.[8]

Metallocorroles have been recently considered as a relatively new class of potential NPMCs[9] because the slightly contracted metal-coordinating core and the tri-anionic charge of these ligands greatly affect the chemistry of the chelated transition-metal ions.[10] Several key properties of metallocorroles render them of relevance for ORR catalysis: a) high oxidation states are much more accessible;[11] b) low oxidation states are very reactive;[11a] and c) the tendency of forming inert six-coordinate complexes is comparatively small.[11a] Taken together, metallocorroles may be anticipated to display promising features as catalysts for oxygen reduction reaction. Several reports confirmed this hypothesis,[12] but not all the desired properties required for optimal performance were reported. The main goal of this work was to elucidate the factors that affect both the electrochemical onset potential and the kinetics of ORR. This was successfully done by tuning the properties of metallocorroles by changing the metal center, leading to one catalyst whose onset potential is almost as positive as that of platinum.

This study focused on five first-row transition-metal complexes of 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(pentafluorophenyl)corrole [M(tpfcBr$_8$)], (Figure 1, inset), which are very resistant to oxidative self-destruction and may hence be expected to be robust catalysts. Replacement of the eight β-pyrrole hydrogen atoms of metallocorroles by bromine

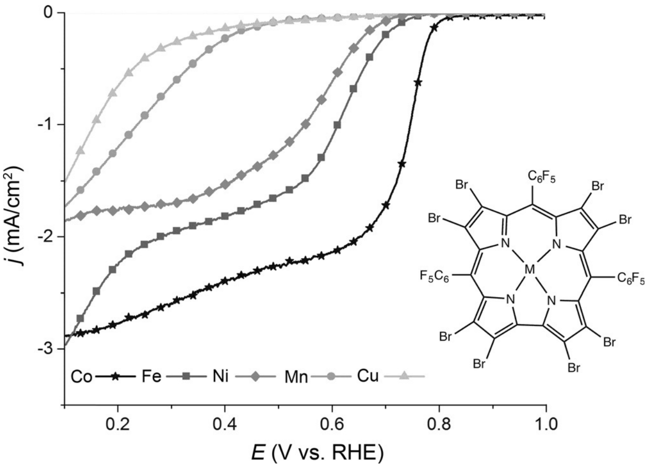

Figure 1. Linear sweep voltammograms of [M(tpfcBr$_8$)]/BP2000 carbon (M = Mn, Fe, Co, Ni, Cu) with the RDE at 900 rpm in a solution of H_2SO_4 (0.5 M) and a scan rate of 5 mV s^{-1}. Inset: The chemical structure of the brominated metallocorroles [M(tpfcBr$_8$)].

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atoms also induces very large positive shifts in the redox potentials of the complexes,[13] which could be beneficial for shifting the ORR onset potential towards the desired direction. The required complexes were prepared by either the reaction of the non-brominated metallocorroles with Br_2 (for M = Mn, Fe, Co)[13] or by metallation of the β-pyrrole-brominated free-base corrole (for M = Cu, Ni).

Composite carbon–corrole electrodes for the catalytic performance investigations were prepared by mixing BP2000 carbon (10 mg) and metallocorrole (0.8 mg) with isopropanol (1 mL) for 48 h, followed by standard treatments (see the Experimental Section). The kinetics of the adsorption of the corroles onto the carbon surface were investigated by measuring the changes in the absorbance of corrole/isopropanol solutions during the adsorption process (see the Supporting Information, Figure S1). Cyclic voltammetry (CV) and the rotating disk electrode (RDE) method were used to evaluate the activity of the electrodes prepared with the various [M(tpfcBr_8)] complexes. The quite high capacitance current measured in the CVs conducted under an inert atmosphere, resulting from the very large surface area of the utilized carbon, was deducted from the total current measured under an O_2-saturated atmosphere for isolating the faradaic current that is due to the ORR electrocatalysis (Figure S6, S7). Figure 1 presents the results obtained from linear sweep voltammetry RDE measurements during forward scans from 1.0 to 0.1 V (versus RHE, where RHE is the reversible hydrogen electrode) at a rotation speed of 900 rpm, revealing that the cobalt and iron corroles clearly display the most significant catalytic effect on the ORR.

The rate-limiting step of the ORR by metal-based catalysts is generally assumed to be the one-electron reduction of the metal ion,[14] required for binding the oxygen molecule and its reduction to either hydrogen peroxide or its complete reduction to water. It was hence of interest to investigate the electronic structure of the catalysts by computation and to examine how they are related to the experimentally determined redox potentials of the complexes and the catalytic onset potentials for ORR. Gas-phase cluster calculations at the UM06-L/6-31G(d,p) level of theory indicated that the LUMO energy (eV) of the trivalent [M(tpfcBr_8)] complexes decreases upon moving from Mn to Ni and Cu along the first-row transition-metal corroles: Mn(−4.38) > Fe(−4.82) > Co(−4.99) > Cu(−5.22) > Ni(−5.28). A similar trend of LUMO energies (eV) was obtained at the UB3LYP/6-31g(d,p) level of theory: Mn(−3.66) > Fe(−4.28) > Co(−4.30) > Cu(−4.87) > Ni(−4.89). The LUMO energies, which reflect the electron affinities, qualitatively agree with the experimentally measured reduction potentials (V versus Ag/AgCl, in CH_3CN) of the trivalent [M(tpfcBr_8)] complexes: Ni(0.97) > Cu(0.64) > Co(0.36) > Fe(0.05) > Mn(−0.37).[13,15] The computed frontier molecular orbital isovalue surfaces of [M(tpfcBr_8)] revealed that for Mn, Fe, and Co, their calculated LUMO has a significant amplitude at the metal center (Figure S2 a–c). This was however not the case for the Ni and Cu corroles. The calculations for the neutral state of [Ni(tpfcBr_8)] showed that the coefficients of the LUMO are largest on the corrole ring (Figure S2 d) and that there is also significant ligand-to-metal charge transfer, resulting in a nonmagnetic nickel ion and an open-shell ligand cation radical.[16] Two thermally accessible states were obtained for the Cu corrole: a triplet with a quite planar corrole and a singlet with the corrole in a saddled conformation.[15b,17] The coefficients of the LUMO of both conformers were largest on the corrole ring (Figure S2 e-i, e-ii). The shapes of the LUMOs hence indicate that the one-electron reduction will occur on the metal for Mn, Fe, and Co, but will occur on the corrole for Cu and Ni.

This prediction was confirmed by looking at the singly occupied highest molecular orbitals (SOHMOs) of the $1e^-$ reduced corroles. The molecular orbital is mainly located on the metal center for Co, Mn, and Fe (Figure 2 a; Figure S2 f, g), but on the corrole moiety for Cu and Ni (Figure 2 b; Figure S2 i). This implies that electron transfer to dioxygen will be faster for the Mn, Fe, and Co complexes than for the Cu and Ni complexes.[18] The low reduction potential of the Mn corrole relative to the Fe and Co complexes (−0.37, +0.05, and +0.36, respectively) explains why the former is a much less potent ORR catalyst. The above analysis also suggests that the Ni corrole should be as inactive as the Cu corrole, which is however not the case (Figure 1). Plausible explanations rely on the fundamental differences between d^8 Ni^{II} and d^9 Cu^{II} complexes in terms of the binding and activation of dioxygen,[19] a point that will be addressed in future studies.

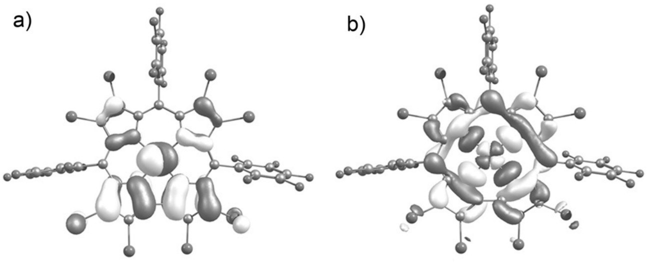

Figure 2. The SOHMO isovalue surfaces for a) $[Co(tpfcBr_8)]^-$ (which is similar to that of $[Mn(tpfcBr_8)]^-$ and $[Fe(tpfcBr_8)]^-$) and b) $[Cu(tpfcBr_8)]^-$ (which is similar to that of $[Ni(tpfcBr_8)]^-$).

An in-depth experimental investigation was performed on the most active cobalt corrole, by utilizing linear sweep voltammetry (LSV) from 1.0 to 0.1 V (versus RHE) at selected electrode rotation speeds (225 to 1600 rpm; Figure 3 a). That data was used for the construction of a Koutecky–Levich plot, which disclosed a linear relationship between i^{-1} and $w^{-1/2}$ (Figure S3). The corresponding Tafel plot (Figure S4) yielded a transfer coefficient (α) of 0.75 and an exchange current density of 6.36×10^{-7} mA cm^{-2}. This implies that the rate limiting step is the one-electron reduction of the metal center. This conclusion is reminiscent of what has been obtained for porphyrin metal complexes,[20] suggesting that this type of ligand is particularly suitable for ORR.[21]

The mechanism by which the cobalt corrole catalyzes the ORR is of obvious importance for its end applications, and several potential mechanisms have been proposed: $2e^-/2H^+$

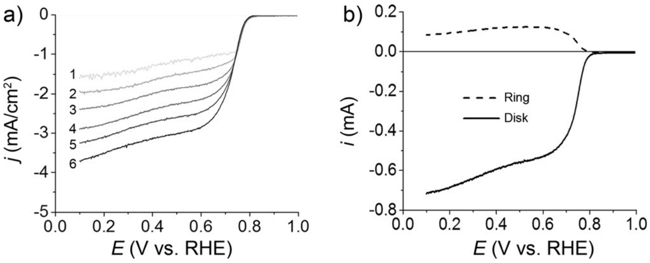

Figure 3. a) Linear sweep voltammograms of [Co(tpfcBr$_8$)]/BP2000 carbon in H_2SO_4 (0.5 M) at a scan rate of 5 mV s^{-1} with the RDE at different rotation speeds: 1) 225, 2) 400, 3) 625, 4) 900, 5) 1225, and 6) 1600 rpm. b) RRDE measurements of ORR in H_2SO_4 (0.5 M). The disk ([Co(tpfcBr$_8$)]/BP2000) potential was linearly swept at a scan rate of 5 mV s^{-1} and the potential of the ring was kept constant at 1.2 V versus RHE. i = current.

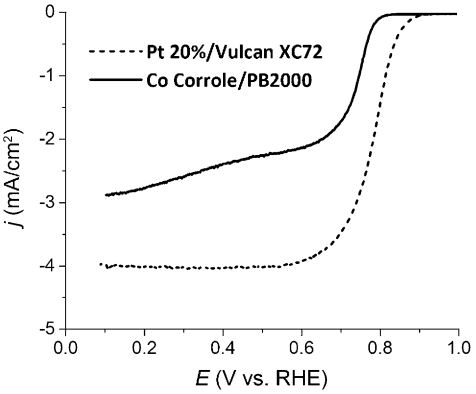

Figure 4. Linear sweep voltammograms of Co corrole/BP2000 and a commercial 20%Pt/VulcanXC72 electrode in a solution of H_2SO_4 (0.5 M) with the RDE set at 900 rpm and a scan rate of 5 mV s^{-1}.

reduction of O_2 to H_2O_2, two consecutive $2e^-/2H^+$ reductions leading to water, or the direct $4e^-/4H^+$ reduction to H_2O.[22] Earlier studies of macrocyclic compounds revealed that monometallic macrocyclic compounds tend to reduce oxygen to peroxide in most cases,[23] whereas bimetallic complexes have a clear tendency for the 4-electron pathway.[24] This aspect was addressed for [Co(tpfcBr$_8$)] using the rotating ring disk electrode (RRDE) method, where the disk potential was linearly scanned from 1.0 to 0.1 V versus RHE and the platinum ring potential was set at 1.2 V versus RHE. A current of 550 μA was obtained on the disk and 125 μA on the ring at high potentials (Figure 3 b; shown without the ring's collection efficiency correction), indicating that about two thirds of the electrons transferred in the catalytic reaction were utilized for the 2-electron reduction of oxygen to H_2O_2. Independent supporting evidence was obtained by calculating the number of electrons transferred (n) using the Levich equation and the slope from the Koutecky–Levich linear plot in the steady-state region (Figure S5). This calculation led to an average value of $n = 2.6$ at high potentials and up to $n = 3.6$ at lower potentials, thus demonstrating the sensitivity of the $2e^-/2H^+$ versus $4e^-/4H^+$ pathways to the reaction conditions.[22b] The number of electrons transferred in the reactions catalyzed by the analogous Fe and Ni complexes was much smaller ($n = 2.05$ and 1.73, respectively) at the voltages of limiting currents. Keeping in mind the goal of developing first-row transition-metal complexes for replacing platinum as ORR catalysts, the performance of the [Co(tpfcBr$_8$)]/BP2000 electrode was compared with an industry standard, namely 20% Pt/Vulcan XC72.[25] Figure 4 shows that the onset potential of the Co-based electrode is only about 80 mV lower than that of the industry standard, although its limiting current is about a third (or about 50% at an applied voltage of 600 mV). Nevertheless, the cobalt corrole still displays the lowest overpotential relative to all other reported non-pyrolyzed NPMC catalysts.[23,24,26]

The comparison of a series of first-row transition-metal corroles as electrocatalysts for the oxygen reduction reaction revealed that the activity increased in the order of Co > Fe > Ni > Mn > Cu. The Cu complex was found to be a poor catalyst as a result of both thermodynamic and kinetic considerations: the reduction potential indicates that Cu$^{\mathrm{II}}$ in [Cu(tpfcBr$_8$)]$^-$ is too stable to reduce oxygen, and the spin density in the corresponding SOHMO is corrole-based and not metal-centered. The one-electron reductions of [Mn(tpfcBr$_8$)], [Co(tpfcBr$_8$)], and [Fe(tpfcBr$_8$)] are all metal-centered, but the reduction potential of [Mn(tpfcBr$_8$)] is very negative and it consequentially displays a very low onset potential. The highest onset potential was obtained with [Co(tpfcBr$_8$)], followed by [Fe(tpfcBr$_8$)], consistent with the more positive reduction potential of the former. The cobalt corrole not only displayed the best catalytic activity when compared to other corroles tested herein and in previous studies,[26b] but it also exhibited comparable results to precious-metal catalysts used by the fuel-cell industry, with an onset potential of 0.81 V versus RHE. This work shows that the overpotential required for the ORR is strongly influenced by the metal center of the brominated corrole. We also show that catalysis by this group of complexes proceeds according to the electrochemical–chemical (EC) pathway, where the metal center must be reduced before reduction of dioxygen can take place. The role of the carbon surface is currently under investigation.[27]

Experimental Section

Materials: All solvents and reagents were of high purity grades and purchased from Sigma–Aldrich. The corroles [Fe(tpfcBr$_8$)],[13] [Mn(tpfcBr$_8$)],[13] and [Co(tpfcBr$_8$)][15a] were prepared according to published procedures.

Synthesis of [Cu(tpfcBr$_8$)]: A solution of H_3(tpfcBr$_8$)[13,28] (30 mg, 21 μmol) and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 200 μmol) in pyridine (15 mL) was stirred at room temperature and the reaction was monitored by UV/Vis spectroscopy and fluorescence measurements. After 30 min of stirring, the solvent was evaporated and [Cu(tpfcBr$_8$)] was isolated (27 mg, 87 yield) after column chromatography on silica gel (using 5:1 n-hexane:ethanol as eluent). HRMS (ESI) in negative ion mode m/z: calcd. for $C_{37}N_4F_{15}Br_8Cu$ 1487.2564 [M^-]; Found 1487.2571. The other spectral properties of the product are consistent with literature data.[15b,29]

Synthesis of [Ni(tpfcBr$_8$)]: A solution of H_3(tpfcBr$_8$) (30 mg, 21 μmol) and $Ni(OAc)_2 \cdot 4H_2O$ (200 mg, 805 μmol) in pyridine (15 mL) was heated to reflux and the reaction was monitored by UV/Vis spectroscopy and fluorescence measurements. After 1 hour, the solvent was evaporated and [Ni(tpfcBr$_8$)] was isolated after column chromatography on silica gel (4:1 *n*-hexane:ethanol as eluent for impurities separations, followed by 1:1 *n*-hexane:ethanol for product separation). Recrystallization from mixtures of dichloromethane/*n*-hexane afforded [Ni(tpfcBr$_8$)] in 28 mg (90 % yield). ^{19}F NMR (CD_3OD, 188 MHz): $\delta_F = -139.6$ (dd, 2F, $^3J_{FF} = 24.2$ Hz, $^4J_{FF} = 8.1$ Hz, *ortho*-F), -140.0 (dd, 4F, $^3J_{FF} = 24.2$ Hz, $^4J_{FF} = 8.0$ Hz, *ortho*-F), -157.5 (t, 2F, $^3J_{FF} = 19.9$ Hz, *para*-F), -157.7 (t, 1F, $^3J_{FF} = 19.9$ Hz, *para*-F), -167.6 ppm (m, 6F, *meta*-F). UV/Vis (acetonitrile): λ_{max}, nm (ε, $M^{-1}cm^{-1}$) = 420 (63 000), 586 (11 800), 610 (16 600). HRMS (ESI) in negative ion mode *m*/*z*: Calcd for $C_{37}N_4F_{15}Br_8Ni$ 1482.2621 [M^-]; Found 1482.2985.

Preparation of the composite carbon–corrole electrode: A sample of 10 mg BP2000 carbon (10 mg; Cabot Corporation) and 0.8 mg corrole (0.8 mg) were mixed with 1 mL Isopropanol (1 mL; Daejung > 99.7 %) for 48 h, in order to allow the corrole to adsorb on to the carbon surface. The sample was then centrifuged (6000 rpm) and the carbon was separated from the excess corrole. A 1 mL solution of 2:1 (volumetric) isopropanol/deionized water containing 0.2 % Nafion (Ion Power DUPONT D2020 NAFION Solution) was added to the carbon–corrole composite. 10 μL of the catalyst slurry was applied as a drop on the glassy carbon surface of a rotating ring-disk electrode (0.247 cm^2) and was left at room temperature to dry.

Electrochemical characterization: Cyclic voltammetry (CV), rotating disk electrode (RDE), and rotating ring disk electrode (RRDE) measurements were all performed with a Bio Logic VSP and VMP-300 potentiostats. RDE (disk area = 0.196 cm^2) and RRDE (disk area = 0.2475 cm^2) were measured using a PINE rotator and electrodes. The collection efficiency of the ring electrodes was measured using a $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reversible redox couple and it was found to be 40 % (should be 37 % according to the manufacturer). All measurements were conducted in an aqueous solution of H_2SO_4 (0.5 M; Acros Organics 96 %), unless otherwise stated. The counter electrode was a glassy carbon rod ($\phi = 3$ mm) and the reference electrode was a homemade hydrogen reference electrode $[Pt\,|\,H_{2(g)}\,|\,H^+_{(aq)}(0.5\,M)]$. When background currents were measured, the cell was purged with Ar gas (99.999 % purity) and when the reaction of the catalyst with oxygen was tested, the cell was purged with O_2 gas (99.999 % purity) for at least 20 min to saturate the solution with dissolved oxygen.

Adsorption measurements: Insight into the adsorption kinetics was obtained by placing 3 mg BP2000 carbon at the bottom of quartz cuvettes that contained 300 μL of 0.5 mM [M(tpfcBr$_8$)]/isopropanol solutions and recording the absorption above the carbon every 10 min for many hours.

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