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A readily-prepared, convergent, oxygen reduction electrocatalyst†

Jun Chen,[a] Weimin Zhang,[a] David Officer,[a] Gerhard F. Swiegers*[b] and Gordon G. Wallace*[a]

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Monomeric cobalt(II) tetraphenylporphyrin immobilized in high concentrations within vapour-phase polymerized polypyrrole deposited on an ITO electrode catalyzes the 4-electron reduction of dioxygen to water, a reaction requiring concerted action by two separate catalytic groups.

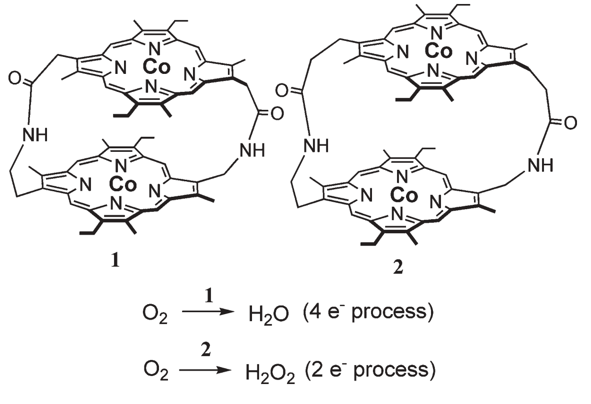
Homogeneous catalysts in which multiple functional groups participate in the catalytic process are termed “multi-centred” in their action.[1] The catalytic groups in such species may act in either a *concerted* or a *non-concerted* fashion.[2] A concerted action involves a *coordinated interplay* between the different catalytic groups so as to ensure that the bound reactant functionalities are always brought into reactive contact, or pulled apart, in a very specific and highly repeatable way.[2] Such actions are more correctly termed “*convergent*” since the catalytic groups are disposed to act in a synchronized way; that is, their movements *converge* to create a concerted action.[2] The best examples of multi-centred catalysts that employ concerted catalytic actions are the enzymes in biology.[2] Enzymes typically depend on a very particular spatial arrangement and conformational movement in their active site for their catalytic effect.[2,3] Their need for, and use of, a coordinated action creates the great catalytic specificities for which they are famous. With only a few exceptions, man-made multi-centred homogeneous catalysts do not act in a convergent manner however.[2] This is because the required synchronization is typically not readily achieved in a simple, molecular species. There is, nevertheless, great interest in developing catalysts that are capable of coordinated actions.[4] The rare few examples that exist in this respect rely on carefully designed and complicated structures to bring about the necessary convergence.[5] However, the complexity of synthesizing such catalysts severely restricts their practical utility. Discovering simple and inexpensive means with which to create convergence in multi-centred homogeneous catalysis is therefore of particular interest.[2] In this work, we describe a catalytic system in which coordinated actions by commercially available, monomeric catalytic groups appear to be made statistically favoured by the use of high concentrations.

An example of a convergent non-biological homogeneous catalyst is the cofacial dicobalt porphyrin **1** first described by Collman *et al.* (Scheme 1).[6] Compound **1** catalyzes the 4-electron reduction of O_2 to H_2O at potentials negative of 0.71 V (*vs.* NHE) and below pH 3.5 when adsorbed on a graphite electrode.[6] Under identical conditions, the corresponding Co-porphyrin monomer and the equivalent diporphyrin **2** catalyze the 2-electron formation of H_2O_2.[6,7] Extensive studies have revealed that, in this class of catalyst, the O=O molecule must be *simultaneously* bound to both Co centres at the instant of reduction for O–O bond cleavage to be successful.[6] One of the Co centres needs, in fact, only to act as a Lewis acid.[8] Because of the brevity of Co–O_2 binding, the likelihood of this sort of coordinated, synchronized interplay between the Co catalytic groups in the corresponding monomers or in **2**, is too low to yield substantial 4-electron reduction. Instead, a slower 2-electron reduction, involving O_2 bound to a single Co centre at the instant of reduction, is favoured.[6]

While **1** has potential utility as an oxygen reduction catalyst in H_2–O_2 fuel cells, this is limited, in practice, by the cost and complexity of its synthesis. How, then, can one utilize the effect present in **1** in an uncomplicated and practical manner?

Several approaches have been proposed in this regard. For example, when adsorbed on graphite, some mononuclear metalloporphyrins and phthalocyanines that normally catalyze 2-electron reduction of O_2 facilitate the 4-electron reduction to H_2O in the same way as the cofacial metallodiporphyrins. This has elicited suggestions—as yet unconfirmed—that these species may adsorb in a side-on, pairwise arrangement that makes a coordinated interaction inevitable.[9]

Another proposal involves covalently binding monomers in high densities to the backbone of a polymer, thereby increasing the likelihood of concerted action. For example, a cobalt phthalocyanine[9,10] and an iron(III) tetra(*o*-aminophenyl)porphyrin[9,11] that catalyze 2-electron reduction of O_2 in open solution, are reported to catalyze 4-electron reduction when bound in high densities within polymers. These cases cannot, unfortunately, be unequivocally assigned as concerted, multi-centred processes because the covalent connections with the support may alter the electronic



Scheme 1

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[a] *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, New South Wales 2522, Australia. E-mail: gwallace@uow.edu.au*
[b] *CSIRO Molecular and Health Technologies, Bag 10, Clayton, Victoria 3169, Australia. E-mail: Gerry.Swiegers@csiro.au*
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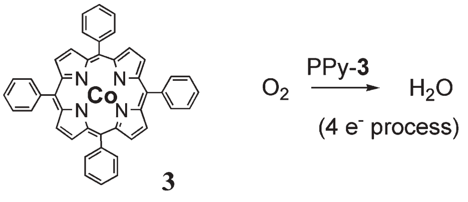
structure of the monomer metal, allowing it to unilaterally facilitate O–O bond cleavage without participation by a second monomer.[2] An electron rich monomeric Ru-appended Co-porphyrin has, for example, been shown to catalyze O–O bond cleavage without involvement by a second monomer.[12] Polymer supports may influence the catalytic process in other ways as well.[9]

To eliminate these complications, it is hypothetically also possible to concentrate the equivalent free, neutral monomers within a restricted volume in the hope that coordinated action becomes statistically inevitable. This approach has been described as a "statistical" version of the proximity effect employed by enzymes, leading it to be termed a "statistical proximity" effect.[2] Certain electrocatalytic hydrogen-generating conducting polymers have been shown to employ such an effect when deposited as thin, porous layers on electrode surfaces.[2,13] However, it has not been demonstrated for 4-electron dioxygen reduction. This is, presumably, because no means has existed to immobilize sufficiently high concentrations of neutral Co-porphyrin monomers within polymer layers.

In recent work, we have discovered a new technique for trapping small molecules within a thin-layer conducting polymer. This process employs a polypyrrole (PPy) film grown using so-called vapour phase polymerization (VPP).[14] During VPP, polypyrrole is deposited as a swollen and porous layer on the electrode. When this layer is subsequently washed, it undergoes dramatic shrinkage, becoming exceedingly dense. In so doing, it may be used to securely immobilize and concentrate molecular species upon an electrode surface.[14] Given the catalytic properties of **1**, we wondered whether we could induce a neutral Co-porphyrin monomer to undertake concerted catalysis of 4-electron O_2 reduction to H_2O when concentrated within VPP-grown polypyrrole. A convenient test species in this respect is commercially available, neutral Co-tetraphenylporphyrin **3** (Scheme 2), which is known to be exclusively a catalyst of 2-electron O_2 reduction to H_2O_2 in open solution; when adsorbed on graphite it generates a product mix containing >60% H_2O_2.[9]

Using standard vapour-phase polymerization techniques, applied using an initial 0.5 mM solution of **3**, a thin film of polypyrrole (PPy) containing Co-tetraphenylporphyrin **3** was deposited on an ITO glass slide.† Linear sweep voltammograms (LSV's) of the resulting PPy–**3**/ITO electrode immersed (and stationary) in an aqueous 0.5 M H_2SO_4 solution indicated a substantial reduction process negative of *ca.* 0.41 V (*vs.* Ag/AgCl) under an O_2 atmosphere (Fig. 1). No response was observed in this region under an N_2 atmosphere. The former current is therefore unequivocally due to dioxygen reduction. The current profile is, however, not expected for a first-order reaction under diffusion control. Rather, it is more typical of a reaction at steady-state on, for example, a microelectrode/microelectrode array or a rotating disk electrode.



Scheme 2

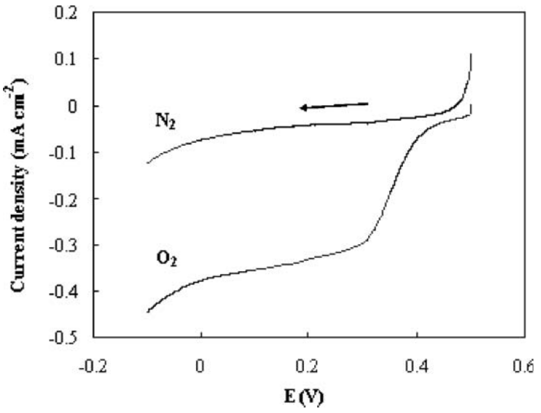


Fig. 1 Linear sweep voltammograms (*vs.* Ag/AgCl) for O_2 reduction at PPy–**3**/ITO glass in 0.5 M H_2SO_4. Scan rate 5 mV s^{-1}.

In order to determine the number of electrons transferred during this O_2 reduction, LSV's were obtained at different rotation speeds for PPy–**3** similarly deposited on a glassy carbon electrode. The number of electrons involved in the O_2 reduction was calculated using the Koutecky–Levich equation, which relates the current *i* to the rotation rate of the electrode ω

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\omega^{0.5}} \qquad (1)$$

where i_k is the kinetic current and *B* is the Levich slope.†

$$B = 0.2nFA(D_{O_2})^{2/3}v^{-1/6}C_{O_2} \qquad (2)$$

The kinetic current i_k can be obtained by extrapolation of the Koutecky–Levich plots for $\omega^{-1/2} \rightarrow 0$.† The observed need for a Koutecky–Levich rather than a Levich plot indicates that the currents are not controlled by O_2 diffusion within the polymer. Table 1 depicts representative data, including the number of electrons transferred during O_2 reduction in the potential range −50 mV to 100 mV. As can be seen, between 3.3 and 4.0 electrons are involved in the reaction. This corresponds to a product distribution of 65–100% H_2O and 35–0% H_2O_2, respectively. The fact that 4-electrons are involved indicates that the reduction comprises direct conversion of O_2 to H_2O at a single catalytic site by, effectively, a concerted process; this may possibly involve a short-lived, bound H_2O_2 intermediate. It cannot involve two 2-electron reductions at separate sites in a sequence of $O_2 \rightarrow H_2O_2$ followed by $H_2O_2 \rightarrow H_2O$. The variation in product distribution as a function of applied voltage may be due to differences in the rate of electron transfer, which has previously been proposed to influence product distribution.[6,12]

Table 1 Slopes k_i of the Koutecky–Levich plots and corresponding number of electrons transferred for O_2 reduction (n_i) at PPy–**3**/glassy carbon in an O_2-saturated 0.5 M H_2SO_4 solution

I	E_i/mV *vs.* Ag/AgCl	k_i	$1/i_k$ (mA^{-1})	n_i
1	−50	32.4	−0.771	4.0
2	0	35.0	−0.769	3.7
3	50	37.4	−0.759	3.5
4	100	38.8	−0.815	3.3

These results were separately confirmed from a controlled rotating ring disk electrochemical (RRDE) study which employed Pt ring and disk electrodes rotating at 1500 rpm. In such studies, the ring electrode is poised at 1.0 V in order to oxidize any H_2O_2 released during O_2 reduction at the disc electrode;[6] H_2O is not oxidized at this potential. The released H_2O_2 travels by convection from the disc to the ring electrode during rotation.[6] The collection efficiency of the ring disk was measured in an independent experiment with the $Fe(CN)_6^{3+/4+}$ couple and found to be $N_0 = 0.22$ (that is, 22% of the products released by the disk were detected at the ring).

Using RRDE, a LSV was applied at the disk (Fig. S6).† At +50 mV, a current of 0.011 mA was observed on the ring electrode (oxidation of H_2O_2) while the disk electrode produced a current of 0.352 mA (overall O_2 reduction). The low current observed at the ring confirms the efficiency of the 4-electron reduction of O_2 to H_2O;[6] this corresponds to at least 86% of the charge consumed at the disk electrode being involved in the conversion of O_2 to H_2O; the remaining 14% is involved in converting O_2 to H_2O_2.

Studies also examined the influence on the $H_2O_2 : H_2O$ product distribution of the relative proportion of **3** in the PPy–**3** layer. The data in Table 1 were obtained using PPy–**3** that had been deposited from an initial solution containing 0.5 mM **3**. However, PPy–**3** prepared from a 5-fold more dilute solution (0.1 mM **3**) yielded substantially larger $H_2O_2 : H_2O$ ratios, around 1 : 3 at −50 mV (Table 1 shows 100% formation of H_2O at −50 mV). Under these circumstances, nearly 26% of the charge consumed is involved in the conversion of O_2 to H_2O_2.

These data indicate that, whereas monomeric **3** mainly facilitates 2-electron reduction of O_2 to H_2O_2 in open solution or when adsorbed on graphite, it generates predominantly H_2O by 4-electron reduction when trapped in a concentrated form within polypyrrole. Moreover, the proportion of H_2O_2 generated declines as the concentration of **3** in the polypyrrole is increased. This is consistent with the neutral Co-tetraphenylporphyrin becoming statistically more disposed to a coordinated bi-molecular interaction that favours 4-electron H_2O formation upon concentration within polypyrrole. Additionally, the apparent steady-state response observed in Fig. 1 is consistent with, effectively, a microarray of a few highly active H_2O-generating electrocatalytic sites surrounded by a sea of less active H_2O_2-generating sites. At this stage we cannot definitively say whether polypyrrole is involved in the catalytic process or not (as a possible Lewis acid?); Co-polypyrrole composites have recently been shown to offer useful catalysts in H_2–O_2 fuel cells.[15] Nor can we say whether H_2O_2 is a short-lived intermediate in the catalysis. The reduction potential of O_2 in Fig. 1 (0.41 V *vs.* Ag/AgCl) is similar to 2-electron reduction of O_2 to H_2O_2 ($E^\circ = 0.68$ V *vs.* NHE), suggesting the presence of such an intermediate.

Detailed investigations are ongoing and will be described in a full paper.

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