New sensor for dissolved dioxygen: a gold electrode modified with a condensation polymer film of β-cyclodextrin hosting cobalt tetraphenylporphyrin

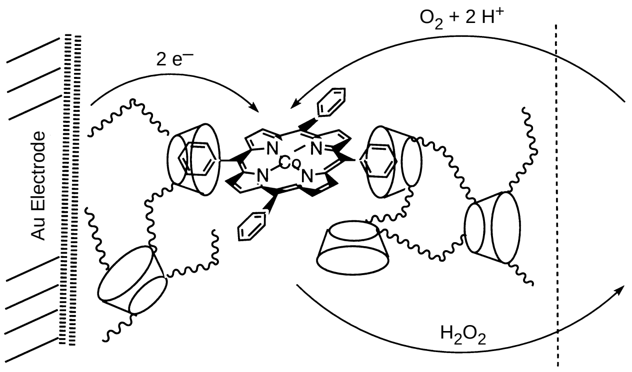
Francis D'Souza,*[a] Yi-Ying Hsieh,[a] Heang Wickman[a] and Wlodzimierz Kutner*[a,b]

[a] *Department of Chemistry, Wichita State University, Wichita, KS 67260-0051, USA*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warsaw, Poland*

A gold electrode, coated with a thin polymer film of a supramolecular complex of β-cyclodextrin and cobalt tetraphenylporphyrin, is used as an electrocatalytic sensor for determination of dioxygen dissolved in water.

Development of supramolecular transducing systems for catalytic sensor applications is an area of active research.[1] Cyclodextrin (CD) hosts are very appealing with this respect since they can form supramolecular complexes with a broad range of organic and inorganic, both ionic and neutral compounds.[2] Additional advantages arise if a thin cyclodextrin polymer (CDP) film is cast on an electrode surface.[3,4] Importantly, the stability of supramolecular complexes of CDs embedded, *e.g.* by polycondensation, in polymer matrices is virtually the same as that of solution complexes, and in some cases the stability is even increased.[5] Moreover, CDP is soluble neither in aqueous nor in non-aqueous solvent solutions and is resistant to pH changes within a wide range (pH 2–12). The structure of CDP is relatively open, so the CDP films are readily permeable to small molecules or ions present in solution while large ones are repelled.[3,5] The shelf lifetime of CDP film coated electrodes reaches months if films are stored in air of sufficiently high humidity.

Metalloporphyrins, due to their rich and well defined redox behaviour,[6] are suitable for developing redox catalysts and sensors. For instance, monomeric cobalt porphyrins reversibly bind dioxygen and catalytically electroreduce it to peroxide both in homogeneous and heterogeneous systems.[7] Recently, formation of supramolecular complexes of β-cyclodextrin (β-CD) and free-base tetraarylporphyrins have been reported,[8] thus opening the opportunity to develop new catalytic sensor devices. In the present study, we exploit this approach (Scheme 1) by demonstrating that a polymer film of a supramolecular complex of β-CD and cobalt tetraphenylporphyrin, Co(TTP), coated on the surface of a gold electrode, (β-CDP)–[Co(TPP)]/Au, can operate as a voltammetric sensor for determination of dioxygen dissolved in aqueous solution.



Scheme 1 Schematic representation of catalytic O_2 electroreduction at a gold electrode coated with a polymer film of β-cyclodextrin hosting Co(TPP)

The (β-CDP)–[Co(TPP)]/Au electrode was prepared according to a simple one-step procedure developed earlier for the β-CDP films hosting other organic compounds.[10] That is, a *ca.* 0.1 mM Co(TPP)† chloroform solution was equilibrated, by sonication for a few min, with a stock solution of 2% β-cyclodextrin soluble prepolymer (β-CDPS).‡ After partition equilibrium was attained, the stock solution turned pale red–orange. This solution was used to prepare the casting solution which was 1.5% in β-CDPS, hosting Co(TPP), 15 mM in glutaric dialdehyde and 10 mM in HCl. Then, a *ca.* 3 μm thick polymer film was prepared by dispensing a 5 μl sample of the casting solution on the Au electrode surface to form a *ca.* 4 mm diameter circular spot.[3] Polycondensation was carried out for *ca.* 1 h in a water-vapour filled container (*ca.* 40% humidity), to allow for slow water evaporation. The small thickness of the β-CDP film used in the present study is advantageous with respect to the response time of the fabricated sensor.[10b]

Cyclic voltammetry (CV)§ experiments, perofrmed with the use of the (β-CDP)–[Co(TPP)]/Au electrode in deaerated 0.1 M phosphate buffer (pH 5.6),¶ 0.1 M NaCl, exhibited an electro-oxidation peak located at E_{pa} = 0.09 V (potential scan rate, v = 0.1 V s^{-1}) corresponding to the Co^{II}(TPP)–Co^{III}(TPP) redox couple.[6] Multicyclic voltammetry experiments showed no decay of the Co^{II}(TPP)–Co^{III}(TPP) peak currents with the scan number. This indicates that Co(TPP) is not released from the film into solution, as expected for this water-insoluble catalyst. Logarithmic dependence of the Co^{II}(TPP)–Co^{III}(TPP) electro-oxidation peak current *vs.* the potential scan rate was linear, with a slope close to 0.5, indicating a semi-infinite diffusion controlled charge transport within the polymer matrix. By analogy to the earlier reported supramolecular CD–porphyrin complexes in solution,[7] one may expect that Co(TPP) is complexed predominately by inclusion of its one or more phenyl rings by the cyclodextrin host site of the polymer rather than through axial ligation of the cobalt centre. Because of the semi-infinite, and not finite, diffusion control of the CV peak current, it is also unlikely that the Co(TPP) solid is present in the form of a suspension in the film.

The voltammetric peak corresponding to electroreduction of dissolved dioxygen at a blank (β-CDP)/Au electrode, *i.e.* in the absence of the Co(TPP) catalyst in the film, occurs at E_{pc} = −0.70 V (v = 0.1 V s^{-1}). Interestingly, with the (β-CDP)–[Co(TPP)]/Au electrode, *i.e.* in the presence of the catalyst in the film, this peak is positively shifted due to electrocatalysis and occurs at E_{pc} = −0.45 V (v = 0.1 V s^{-1}). A peak current dependence on $v^{\frac{1}{2}}$ for the latter peak is linear, with zero plot intercept, for constant dioxygen concentration, indicating that dioxygen catalytic electroreduction is controlled by semi-infinite diffusion. Fig. 1 shows the effect of the dioxygen concentration on the voltammetric peak current of catalytic dioxygen electroreduction measured at the (β-CDP)–[Co(TPP)]/Au electrode. The catalytic peak current is linearly dependent on the dioxygen concentration for the entire range of dioxygen concentration (inset in Fig. 1). Voltammetry at the rotating ring-disk (platinum–glassy carbon) electrode, with a (β-CDP)–[Co(TPP)] film coated on the disk, proved that dioxygen is catalytically electroreduced to hydrogen peroxide (Scheme 1). That is, ring current was observed corresponding to the electrooxidation of hydrogen peroxide, which is the electroreduction product at the disk when its potential is scanned from 0.2 to −0.7 V and the ring potential is kept constant at E_R = 0.8 V.[11]

In summary, the Co(TPP) catalyst can be immobilized in a thin β-CDP film cast on the Au electrode surface, and the sensor thus fabricated can be successfully used for detection of dioxygen dissolved in aqueous solution. The catalyst is molecularly dispersed in the polymer matrix forming a supramolecular complex with the β-CD sites and, advantageously, this immobilization is irreversible in aqueous solutions. The catalytic peak current of dioxygen electroreduction is proportional to the dioxygen concentration in solution for the entire range of the dioxygen concentration. The (β-CDP)–[Co(TPP)]/Au electrodes show reproducible results with respect to dioxygen determination after storage for several days in air atmosphere of high humidity. Mechanistic studies on dioxygen binding to cobalt porphyrins bearing different peripheral charges, hosted by the β-CDP matrix, and hydrogen peroxide release will follow.[13]

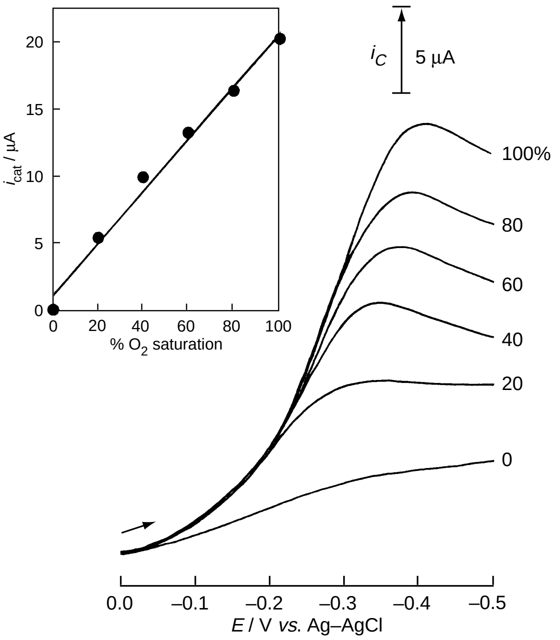


Fig. 1 Voltammograms for the (β-CDP)–[Co(TPP)] film-coated Au disk electrode for different % O_2, indicated for each curve; 0.1 M phosphate buffer (pH 5.6), 0.1 M NaCl; ν 0.1 V s^{-1}. Inset is the dependence of the catalytic peak current, i_{cat}, of O_2 electroreduction *vs.* % O_2 saturation of the solution.

Financial support to F. D. from the National Science Foundation, through Grant No. EPS-9550487, and matching support from the State of Kansas, as well as to W. K. from the Polish State Committee for Scientific Research, through Grant KBN 2P 303 10 707, is gratefully acknowledged.

Footnotes

* E-mail: dsouza@wsuhab.uc.twsu.edu; wkutner@ichf.edu.pl

† Co(TPP) was synthesized according to the literature procedure (ref. 9).

‡ β-CDPS was from Cyclolab, Cyclodextrin Research and Development Laboratory (Budapest, Hungary).

§ Cyclic voltammetry was performed by using either a Model EC/225 Voltammetric Analyzer of IBM Instruments, Inc. (Danbury, CT) or a Model 263A potentiostat/galvanostat of EG&G PAR (Princeton, NJ) and a typical three-electrode electrochemical cell. A 1.6 mm diameter disk gold electrode of Bioanalytical Systems (West Lafayette, IN) was used as the working electrode. A platinum wire and sodium chloride saturated Ag–AgCl electrode served as the auxiliary and reference electrodes, respectively. All potentials cited are against the Ag–AgCl reference electrode. All measurements were performed for a 0.1 M phosphate buffer (pH 5.6), 0.1 M NaCl solution, at 20 ± 1 °C.

¶ The pH of the working solution was chosen to be 5.6 in order to avoid hydrolysis of glycosidic bonds of the β-CDP polymer which occurs at pH $<$ 2, and also to avoid the pH dependence of the formal redox potential of the $Co^{III}–Co^{II}$ couple of Co(TPP) at pH $\geqslant$ 6, as demonstrated in ref. 12.

References

1 *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and R. Vogtle, Pergamon, New York, 1996; J.-M. Lehn, in *Supramolecular Chemistry*, VCH, Weinheim, 1995, ch., 5 and 8.
2 G. Wenz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 803.
3 W. Kutner, W. Storck and K. Doblhofer, *J. Inclusion Phenom.*, 1992, **13**, 257; W. Kutner and K. Doblhofer, *J. Electroanal. Chem.*, 1992, **326**, 139; W. Kutner, *Electrochim. Acta*, 1992, **37**, 1109.
4 J. C. Lepretre and E. Saintman, *J. Electroanal. Chem.*, 1993, **347**, 465.
5 D. Koradecki and W. Kutner, *J. Inclusion Phenom.*, 1991, **10**, 79.
6 K. M. Kadish, *Prog. Inorg. Chem.*, 1986, **34**, 435.
7 A. Bettelheim, R. J. H. Chan and T. Kuwana, *J. Electroanal. Chem.*, 1979, **99**, 93; C.-L. Ni and F. C. Anson, *Inorg. Chem.*, 1985, **24**, 4754.
8 S. Zhao and J. H. T. Luong, *J. Chem. Soc., Chem. Commun.*, 1994, 2307; F. Venema, A. E. Rowan and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1996, **118**, 257.
9 J.-H. Fuhrhop and K. M. Smith, in *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, New York, 1975, ch. 19.
10 (*a*) W. Kutner, H. Wu and K. M. Kadish, *Electroanalysis*, 1994, **6**, 934; (*b*) Q. Chen, P. V. A. Pamidi, J. Wang and W. Kutner, *Anal. Chim. Acta*, 1995, **306**, 201.
11 F. D'Souza, R. G. Deviprasad and Y.-Y. Hsieh, *J. Electroanal. Chem.*, 1996, **411**, 167.
12 R. R. Durand, Jr. and F. C. Anson, *J. Electroanal. Chem.*, 1982, **134**, 273.
13 F. D'Souza, Y.-Y. Hsieh, H. Wickman and W. Kutner, *Electroanalysis*, 1997, in press.

Received in Columbia, MO, USA, 11th March 1997, Com. 7/01704I