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THE DEACTIVATION/REACTIVATION OF COBALT(III) TETRAKIS(4-PYRIDYL)PORPHYRIN ELECTROCATALYST

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Cobalt tetrakis(4-pyridyl)porphyrin (abbr:CoTPyP) absorbed on a glassy carbon electrode (abb:GCE) catalyzed the reduction of oxygen to hydrogen peroxide at a rate of 1.0×10^{6} mol^{-1} dm^{3} s^{-1}. Although the CoTPyP exhibited deactivation, it was found that the activity could be restored by open-circuit relaxation.

There has been much interest in modifying various carbon surfaces via the adsorption of metal porphyrins for the electrocatalytic reduction of oxygen.1-3) We have emphasized the study of water-soluble iron and cobalt porphyrins. For example, cobalt(III) tetrakis(4-methylpyridyl)porphyrin (abbr:CoTMPyP)4) electrocatalyzed oxygen reduction to hydrogen peroxide while FeTMPyP further catalyzed hydrogen peroxide reduction to water.5,6) We also proposed that these reactions proceeded via an ec mechanism where the potential of the oxygen reduction was governed by the redox potential of the metal porphyrin. Evidence also indicated that both CoTMPyP and CoTPyP were strongly adsorbed on GCE surfaces in contrast to their iron analogs. This letter will focus on the activity (redox turnover rate of the catalyst), stability (change of activity with time) and an open-circuit reactivation phenomenon of adsorbed CoTPyP. Similar results can also be obtained with CoTMPyP.

Voltammetric experiments with stationary and rotating disk electrodes (RDE) were conducted with a Pine Instrument (Grove City, PA) model RDE-3 potentiostat and a three-electrode cell; a glassy carbon working electrode which was mounted in a teflon rod with an exposed disk area of (0.48±0.01) cm^{2}, a shielded Pt foil auxiliary electrode and a Ag/AgCl (sat'd. KCl) reference electrode. Potentials are reported here with respect to a normal hydrogen electrode. The GCE was polished successively with 1.0, 0.3, and 0.05 μm alumina and then washed well or sonicated 5 min with doubly distilled water. Adsorption was accomplished by immersing this electrode into a solution of 0.5 mM (1 M = 1 mol dm^{-3}) CoTPyP in 0.05 M H_2SO_4 for 30 min, and then washed with doubly distilled water. The amounts of adsorbed CoTPyP, as calculated from the charges under the cyclic voltammetric current-potential (i-E) curves, averaged $(9.0\pm1.1)\times10^{-11}$ mol cm^{-2}. The CoTPyP, as the chloride salt, was synthesized according to Adler's method.7)

Figure 1 shows typical RDE voltammograms at different rotation rates of the adsorbed CoTPyP in the presence of oxygen in 0.05 M H_2SO_4. The potential at the onset of current for oxygen catalysis corresponded closely to the redox potential of adsorbed Co(II(/II)TPyP. The stoichiometry of the catalysis, as determined from cyclic voltammetric and controlled potential coulometric results, was ascertained to be a two electron conversion of oxygen to hydrogen peroxide, consistent with other cobalt macrocycles for the reduction of oxygen. The rate of the catalysis, assuming a single rate determining step in the two electron process, was determined from the RDE voltammograms.

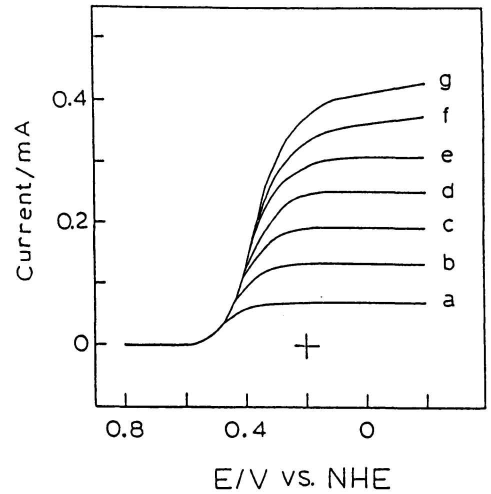

Fig. 1. RDE voltammograms of adsorbed CoTPyP on a GCE in air-saturated 0.05 M H_2SO_4; Rotation rates; a. 100, b. 400, c. 900, d. 1600, e. 2500, f. 3600, g. 4900 rpm.

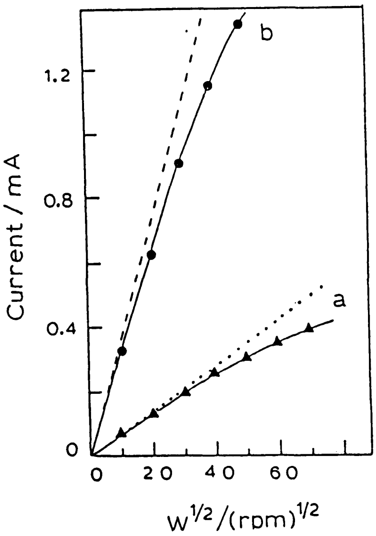

Fig. 2. Plot of RDE i_L vs. $w^{1/2}$ for a) air and b) pure O_2 saturated 0.05 M H_2SO_4 solutions. Calculated (dotted) for n=2 diffusional process.

As seen in Fig. 2, the Levich[8)] plots of the limiting current, i_L, versus the square-root of the rotation rate, $w^{1/2}$, deviated from linearity at high scan rates, for the solutions saturated with air (0.24 mM oxygen) and with pure oxygen (1.2 mM oxygen). The deviations were an indication of a kinetically limiting step between the reduced Co(II)TPyP and oxygen. The rate constant, k_f, for this step was resolved from the corresponding Koutecky-Levich plots[9)] of $1/i_L$ vs. $1/w^{1/2}$, where:

$$1/i_L = 1/i_K + 1/i_{lev} \quad (1)$$

and

$$1/i_{lev} = 0.62nFAD^{2/3}w^{1/2}v^{-1/6}C^* \quad (2)$$

The electrochemical parameters of F, A, D, w, and C* have their usual significance. The number of electrons (n) per oxygen was assumed as 2 in Eq. 2; the kinematic viscosity, v, was taken as the value of pure water and

$$i_K = nFAk_f\Gamma C^* \quad (3)$$

where the i_K values were the intercepts on the i_L axis of the extrapolated plots of $1/i_L$ vs. $1/w^{1/2}$. Equation assumes that the reaction controlling the limiting current is first order in the amount of the catalyst on the RDE surface (in mol cm^{-2}) and in the bulk concentration of oxygen.

From the experimental intercepts of i_K for both air and pure oxygen saturated solutions, a value of k_f equal to $(1.0\pm0.2)\times10^6$ M^{-1} s^{-1} was calculated. This value is ca. one order larger than those reported previously$^{10)}$ for several Co(II) complexes reacting oxygen.

During the RDE experiments, the current was observed to decrease gradually with time, indicating a loss of the catalyst activity. For the first time, it was found that this activity could be restored by open-circuiting the electrode for various time intervals. Curves a and b of Fig. 3 show the normalized limiting current, i_N, as a function of time for RDE's with adsorbed CoTPyP in air- and pure oxygen-saturated 0.05 M H_2SO_4 solutions. The $i_N = i_L/i_i$ (where i_i was the initial current measured 1 min after the application of a potential step from 0.60 to 0.05 V to the RDE rotating at 100 rpm) decreased linearly with time. If the ratios of $(1.0-i_N)$ for the two solutions were plotted as a function of time, steady-state values of ca. 5 were attained at times greater than 30 min. The deactivation rate is apparently proportional to the oxygen concentration and hence, also to $w^{1/2}$.

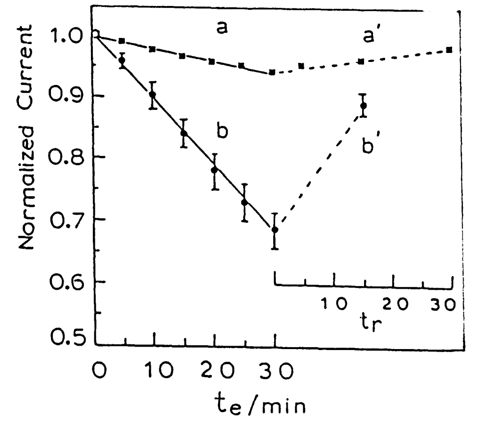

Fig. 3. Plot of i_N vs. time during catalysis, t_e, and during reactivation, t_r (see text for explanation); curves a and a' (air); b and b' (pure O_2).

The extent of the reactivation appeared to be directly related to the length of time, t_r, that the RDE was open-circuited. The activity could be restored to ca. 90% of the original value after a t_r of 15 min. The reactivation values of i_N are plotted as a function of t_r in Fig. 3, traces a' and b'. The deliberate addition of hydrogen peroxide to the solution did not affect the rate of deactivation or reactivation.

A possible explanation for the deactivation is that a slow accumulation of an intermediate species, such as a peroxy-cobalt porphyrin,$^{10)}$ prevents the quantitative regeneration of Co(II)TPyP. Restoration of the catalyst activity may be due to the dissociation of the peroxy ligand from the cobalt during the open-circuited period, returning the catalyst to its original state.

Evidence for the presence of such an intermediate is given by the slowing of deactivation when thiocyanate ion ($<10^{-4}$ M) is added. This ion is known to complex with Co(III)TPyP and thereby may accelerate the displacement of the peroxy group. The thiocyanate ion dissociates when Co(III)TPyP is reduced to the catalytic-active, cobaltous state.

The enhanced stability or regeneration of the active form of metal complexes as catalysts for oxygen reduction is important if practical applications are to be achieved for energy conversion or electrosynthetic purposes.$^{11)}$ Such restoration of activity of an oxygen electrocatalyst by open-circuit relaxation has not been observed previously. Further studies on this mechanism are underway and will be reported subsequently.

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