Electrocatalytic Reduction of Dioxygen in the Presence of *N,N'*-Dipentyl Viologen

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An excellent electrocatalysis of *N,N'*-dipentyl viologen, which is based on not the dissolved species but the adsorbed one, has been observed for the electroreduction of O_2 to H_2O_2 at glassy carbon electrode in neutral aqueous media. The rate constant for the catalytic reaction was estimated to be ca.$10^6 \sim 10^7$ $M^{-1}s^{-1}$ based on cyclic and hydrodynamic voltammetry.

Viologen radical cations have been well known to reduce O_2 molecules with very high specific rates[1-3] and can be thus expected as potential catalysts for the electroreduction of O_2. However, contrary to our expectations, there have been only a few papers on the "electrocatalysis" of viologens for O_2 reduction.[4-8] This is surprising in comparison with a large number of papers concerning homogeneous and heterogeneous redox properties of various viologens.[9-13]

In the present work we examined the electrocatalysis of *N,N'*-dipentyl viologen(C_5V^{2+}•$2Br^-$), which gives the clear two couples of redox response (for the dication/monocation radical (C_5V^{2+}/ C_5V^+) couple) ascribed to the dissolved species as well as the adsorbed one, for O_2 reduction. It is thermodynamically possible for these both species to catalyze O_2 reduction. We are interested in clarifying which species (state) has, in practice, an electrocatalytic activity for O_2 reduction, *i.e.*, both, either or neither of them.

All electrochemical experiments were performed at laboratory temperature (25 ±2 ℃) using a standard three-electrode, two-compartment configuration with a glassy carbon (GC, Tokai Carbon Co., Ltd., area: 0.0707 cm^2) as the working electrode, a spiral platinum counter electrode and a KCl-saturated Ag/ AgCl reference electrode.

Figure 1 shows typical cyclic voltammograms demonstrating the electrocatalytic activity of C_5V^{2+} for the reduction of O_2 in 0.2 M (1 M = 1 mol dm^{-3}) KBr aqueous solution. The voltammogram (a) observed in the presence of C_5V^{2+} shows a greatly enhanced reduction current and a large positive shift in the cathodic peak of about 400 mV in comparison with that (b) obtained in the absence of C_5V^{2+}. The voltammogram (b) corresponds to the reduction O_2 to H_2O_2. These facts clearly demonstrate the electrocatalytic reduction of O_2 via a redox cycling of the C_5V^{2+}/C_5V^+ redox couple. The redox response of C_5V^{2+} itself was observed as three couples of waves (c) under N_2 atmosphere, that is, a broad wave around −0.45 V, the cathodic and anodic peaks for the dication/ monocation radical couple at −0.6 V and those for the monocation radical/ neutral species couple at ca. −1.0 V (not shown here). Based on the fact that the cathodic peak current of the most positive wave around −0.45 V is proportional to potential scan rate v (not $v^{1/2}$), this wave was ascribed to the redox reaction of the adsorbed C_5V^{2+} species (its surface coverage: (1.0 ± 0.5) × 10^{-10} mol cm^{-2}).[14] On the other hand, the cathodic peak current at −0.63 V was almost proportional to $v^{1/2}$ as expected for a diffusion-controlled, nernstian reaction. The anodic peak current for the reoxidation of the monocation radical to its dication is much larger than the corresponding cathodic one, possibly due to a precipitation of the monocation radical species on the electrode surface (as usually observed[9]). Here it should be noted that the redox wave of the dissolved C_5V^{2+} species at −0.63 V is essentially unaffected by the presence of O_2. The dissolved C_5V^{2+}/ C_5V^+ couple (its formal potential $E^{\circ\prime}_{soln}$ = ca. −0.61 V) is expected to catalyze O_2 reduction even more strongly than the adsorbed couple since the difference of its formal potential ($E^{\circ\prime}_{ad}$ = ca. −0.44 V) with that (0.22 V at pH 7) of the O_2/H_2O_2 couple is smaller. These show that a total consumption of O_2 in the reaction layer occurs in the potential range where the redox reaction of the adsorbed C_5V^{2+}/C_5V^+ couple occurs, that is, the reduction of O_2 is actually catalyzed by the adsorbed species, not by the dissolved one under the present experimental conditions.[16] The catalytic cathodic peak current i_p^c at −0.37 V is thus considered to be essentially controlled by the diffusion of O_2 from the bulk of the solution to a thin reaction layer adjacent to the electrode where the concentration of O_2 is actually zero. This was supported from the fact that

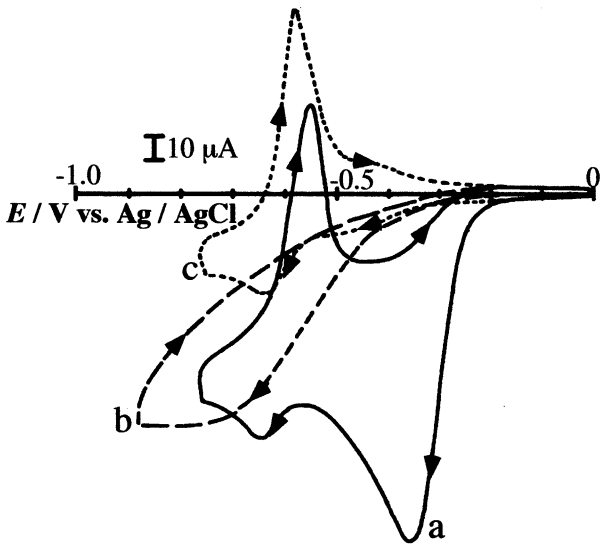

Figure 1. Cyclic voltammograms (a,c) obtained at GC electrode in 0.2 M KBr solution containing 1.0 mM C_5V^{2+} under the atmosphere of O_2 (a) and N_2 (c). The voltammogram (b) was obtained in O_2-saturated 0.2 M KBr solution. Potential scan rate: 500 mVs^{-1}.

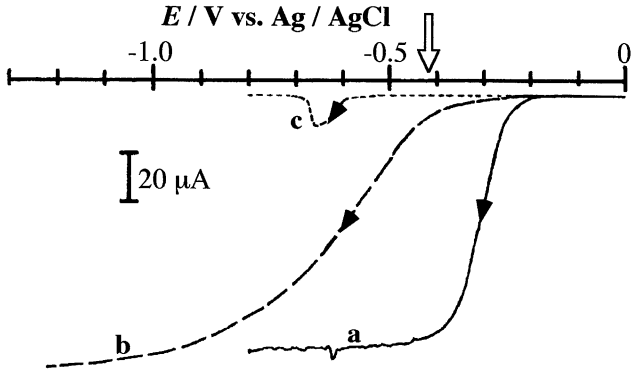

Figure 2. Typical steady-state voltammograms (a,c) obtained at rotating disk GC electrode in 0.2 M KBr solution containing 1.0 mM C_5V^{2+} under the atmosphere of O_2 (a) and N_2 (c). The voltammogram (b) was obtained in O_2-saturated 0.2 M KBr solution. Potential scan rate:2 mVs^{-1}. Electrode rotation rate: 400 rpm. The arrow (⇩) represents $E^{\circ\prime}_{ad}$.

i_p^c was proportional to $v^{1/2}$ at $v < 100$ mVs $^{-1}$ with its value almost comparable to that expected for a two-electron, reversible reaction of O_2 to H_2O_2. The rate constant (k) for the electrocatalytic O_2 reduction was estimated to be $(7 \pm 3) \times 10^6$ $M^{-1}s^{-1}$ [18] from the values of E_p^c (the electrocatalytic cathodic peak potential) and $E^{\circ\prime}_{ad}$, being comparable to those at viologen polymer-coated electrodes.[4,6]

The catalytic reduction of O_2 by the adsorbed C_5V^+ could be also observed as the positive shift of the half-wave potential, $E_{1/2}$ (at i = 0.5 i_{lim}) of the hydrodynamic voltammogram in the presence of C_5V^{2+}, compared with that in its absence (Figure 2 a,b). The value of k could be estimated to be $(5 \pm 2) \times 10^6$ $M^{-1}s^{-1}$ [18] from the potential difference between $E_{1/2}$ (in the presence of C_5V^{2+}) and $E^{\circ\prime}_{ad}$, [5,20] being in fair agreement with that obtained from cyclic voltammetry. The small spike-like signal on the limiting current of voltammogram (a) is due to the one-electron reduction of the dissolved C_5V^{2+} species and the subsequent precipitation of the resulting monocation radical species on the electrode surface (see (c)).[21] The fact that the limiting current is almost the same as that in the absence of C_5V^{2+} indicates that the overall catalytic process is two- electron reaction of O_2 to H_2O_2 and at the same time that it is actually diffusion-controlled of O_2 in agreement with the above-mentioned cyclic voltammetric results. Note that the reciprocal slope of the log plot (*i.e.*, log $[i/(i_{lim}-i)]$ vs. E plot) had a value of $72 \pm$ 5 mV rather than the 59 mV value expected from Nernst's equation for the C_5V^{2+}/C_5V^+ couple. This could be because the electrochemical waves of surface-confined redox species show substantial activity effect, as previously pointed out.[5,22]

In conclusion, the present study demonstrates an excellent electrocatalysis of the adsorbed species of *N,N'*- dipentyl viologen on the GC electrode surface, which is in equilibrium with the dissolved one, for the electroreduction of O_2 in neutral aqueous solutions. The electrocatalysis of the dissolved species, which is also possible thermodynamically, could not be observed under the present experimental conditions.

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