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Electrocatalytic Reduction of Oxygen by Viologen-Linked Polypyrrole Coated on Glassy Carbon Electrode

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Synopsis. Viologen linked-N-substituted pyrroles were prepared and polymerized by electrochemical oxidation on glassy carbon, giving viologen-modified electrodes. The electrons were transferred from the modified electrode to O_2 through the viologen moiety. The modified electrode worked as reactive electrodes for the selective electrocatalytic reduction of O_2 to H_2O_2.

Modified electrodes prepared by electropolymerization of a functional monomer[1] could be a new kind of reactive electrode. It is not known if such a modified electrode can transfer electrons to a substrate through the internal redox site of a coating polymer on the electrode. Viologens (1,1′-dialkyl-4,4′-bipyridinium, V^{2+}) act as an electron-transfer mediator,[2] and reduce O_2 efficiently.[3] Some viologen-linked polypyrroles on electrodes have been prepared[4] because of the usefulness of viologen functions. However, the practicality of the electrode has not been demonstrated. A few modified electrodes prepared by electropolymerization of functional monomers have been used in the catalytic reduction of O_2[5]

In this study, viologen-linked N-substituted pyrroles were prepared and polymerized by electrochemical oxidation on glassy carbon (GC) to make a viologen-modified electrode. The reactivity of this modified electrode was investigated by the electrocatalytic reduction of O_2 to obtain basic information about this new reactive electrode.

Experimental

Preparation of Monomers and Viologens. Two viologen-linked pyrroles were prepared by the procedure described in a previous paper.[6] 1-[3-(1-Pyrorryl)propoxycarbonylmethyl]-1′-methyl-4,4′-bipyridinium **1** was prepared by the reaction of 1-methyl-4,4′-bipyridinium iodide (0.67 mmol) with 3-(1-pyrrolyl)propyl α-bromoacetate (0.67 mmol) in DMF (20 mL) at 60 °C for 12 h. After the reaction mixture was cooled to room temperature, acetone (50 mL) was added to the solution. The precipitating yellowish solid was filtered off and dried under reduced pressure, giving the bromide iodide salt of **1** in 55% yield. The ^{1}H NMR data (Me_2SO-d_6) of this compound are: $\delta=2.06$—2.23 (m, 2H, CH_2), 4.00 (t, 2H, CH_2O), 4.23 (t, 2H, CH_2N), 4.45 (s, 3H, Me), 5.59 (s, 2H, CH_2N^+), 6.13 (t, 2H, pyrrole), 6.77 (t, 2H, pyrrole), 8.40—9.03 (m, 8H, pyridinium). The diperchlorate salt of **1** was prepared by ion exchange with $NaClO_4$ (Chart 1). 1,1′-Bis[3-(1-pyrrolyl)propoxycarbonylmethyl]-4,4′-bipyridinium **2** was prepared by the reaction of 4,4′-bipyridine (1 mmol) with 3-(1-pyrrolyl)propyl bromoacetate (2 mmol) in DMF (20 mL) at 60 °C for 12 h. By a similar procedure, the diperchlorate salt of **2** was obtained in 44% yield. The ^{1}H NMR (CD_3CN) data are: $\delta=1.90$—2.13 (m, 4H, CH_2), 4.00 (t, 4H, CH_2O), 4.10 (t, 4H, CH_2N), 6.00 (t, 4H, pyrrole), 6.76 (t, 4H, pyrrole), 8.86 (d, 4H, pyridinium), 9.32 (d, 4H, pyridinium). Other symmetric and asymmetric viologens were prepared in a similar way. The elemental analysis data of these viologens agreed well with the calculated values.

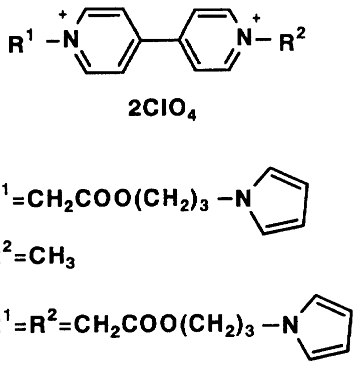

Chart 1.

Table 1. Cyclic Voltammetric Data of Viologens and Catalytic Reduction of Oxygen[a)]

Entry	Viologen[b)]	$E^{c)}_{1/2}$ / V	$E^{d)}_{pc}$ / V
1	MV^{2+}	−0.72	−0.54
2	MEV^{2+}	−0.58	−0.45
3	BV^{2+}	−0.56	−0.45
4	EV^{2+}	−0.51	−0.43
5	CV^{2+}	−0.41	−0.36
6	**1**[e)]	−0.48	−0.33
7	GC-**1**	−0.44	−0.32
8	GC-**2**	−0.38	−0.35
9	None[f)]	—	−0.55
10	None[g)]	—	−0.49

a) Conditions: Electrochemical measurements were carried out in pH 6.86 phosphate buffer (0.1 M KCl) at a scan rate of 100 mV s^{-1}. b) Abbreviations: MV^{2+}=1,1′-dimethyl-4,4′-bipyridinium diiodide; MEV^{2+}=1-ethoxycarbonylmethyl-1′-methyl-4,4′-bipyridinium bromide iodide; BV^{2+}=1,1′-dibenzyl-4,4′-bipyridinium dibromide; EV^{2+}=1,1′-bis(ethoxycarbonylmethyl)-4,4′-bipyridinium dibromide; CV^{2+}=1,1′-bis(cyanomethyl)-4,4′-bipyridinium dibromide. c) Half wave potentials due to the redox reaction between V^{2+} and $V^{+\bullet}$. d) Cathodic peak potentials due to O_2 reduction in the O_2 saturated solution. e) Bromide iodide salt of **1**. f) Bare GC electrode. g) Poly(*N*-methylpyrrole) coated GC.

Table 2. Potential-Controlled Reduction of O_2[a)]

Electrode	Potential[b)]	Coulomb[c)]	Coulomb[d)]	Current efficiency
	V	C	C	%
GC-**1**	−0.33	164	123.5	75
GC-**2**	−0.35	274	144.8	57
GC	−0.35	105	38.7	37

a) Conditions: The electrolyses were carried out in H_2O (0.1 M Na_2SO_4) for 22 h under O_2. b) Potentials were referred to SCE. c) Total amounts of coulomb during the electrolysis. d) Effective coulomb amounts of the reduction determined by the $KMnO_4$ titration.

Materials. Tetrabutylammonium perchlorate and organic reagents were purchase from Tokyo Kasei Kogyo Co., Ltd., and inorganic salts were purchased from Wako Pure Chemical Industries, Ltd. The supporting electrolyte was recrystallized and dried before use in electrochemical measurements. Solvents were purified in the usual way.

Preparation of Viologen-Modified Electrodes. A 1-mM solution (1 M=1 mol dm^{-3}) of diperchlorate salts of viologen-linked pyrrole monomers (**1**, **2**) in CH_3CN–0.1 M tetrabutylammonium perchlorate was electrolyzed at 1.7 V vs. a saturated calomel electrode (SCE) for 30 s with GC purchased from Tokai Carbon Co., Ltd. as the working electrode, giving viologen-modified electrodes GC-**1** and GC-**2**.

Measurements. Cyclic voltammetric measurements were made with an HA-501 potentiostat/galvanostat, an HB-107 function generator, and an HF-101 coulometer, all from Hokuto Denko Co., Ltd. A conventional three-electrode system was constructed with a GC (RA-5) as the working electrode, a platinum wire as the counter electrode, and an SCE (HC-205C, Toa Electronics) as the reference electrode. Electrochemical measurements were done in phosphate buffer (0.1 M KCl, pH 6.86) at a sweep rate of 100 mV s^{-1} under N_2 or under O_2 (during O_2 reduction). With the viologens listed in Table 1, the first cathodic one-electron redox reaction between V^{2+} and $V^{+\bullet}$ was reversible; that is, the wave was symmetrical and had a small ΔE_p (ca. 60 mV).

NMR spectra were recorded on a JEOL PMX-60si and a Varian Gemini 200 apparatus. Infrared spectra were recorded on a JASCO FT/IR-5MP(DR-81) spectrophotometer.

Potential-Controlled Electrolysis of O_2 by Viologen-Modified Electrode. Potential-controlled electrolysis was done in 25 mL of H_2O (0.1 M Na_2SO_4) for 22 h with bubbling with O_2 in a separate cell. After the electrolysis, H_2O_2 was assayed by the $KMnO_4$ titration.[7)]

Results and Discussion

The cyclic voltammograms of GC-**1** and GC-**2** in aqueous solution (pH 6.86 phosphate buffer–0.1 M KCl) are shown in Fig. 1a. The redox wave of viologens in the range of about −0.7 and −0.4 V (vs. SCE) in an aqueous solution is due to a one-electron reversible redox reaction between V^{2+} and $V^{+\bullet}$,[8)] so both redox waves ($E_{1/2}$) of GC-**1** (−0.44 V) and GC-**2** (−0.38 V) are regarded as arising from a one-electron redox reaction. The large residual currents observed in both viologen-modified electrodes are due to the electronic character of the polypyrrole moiety coated on the GC. With GC-**1**, the redox wave due to the one-electron reduction process of the V^{2+} moiety in the coating polymer on GC is quasi-reversible, i.e., the currents are proportional to the sweep rates between 10 and 400 mV s^{-1} and the peak separation is small ΔE_p (about 40 mV). The reversibility is less with GC-**2**. The differences between GC-**1** and GC-**2** seem to be due to the different mobility of the viologen moiety on the electrode surface when there is a pendent structure and the cross-linked structure suggested previously.[7)] The surface concentration of the electroactive species (10^{-9} mol cm^{-2}) is calculated from the charge under the anodic peak associated with the viologen group, with the assumption of

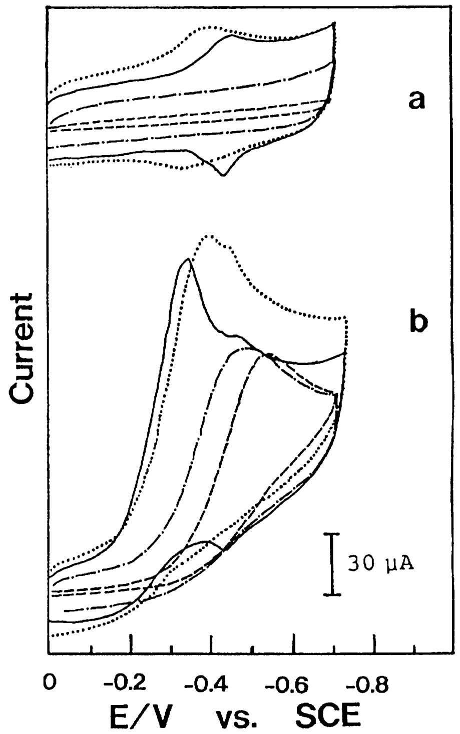

Fig. 1. Cyclic voltammograms of GC-**1** (——), GC-**2** (····), bare GC (- - -), and poly(*N*-methylpyrrole) coated GC (-·-) in pH 6.86 phosphate buffer–0.1 M KCl at a scan rate of 100 mV s^{-1} (a) under N_2 and (b) under O_2.

$1\ \mathrm{F\,mol^{-1}}$.

The redox potentials ($E_{1/2}$) due to a redox reaction between V^{2+} and $V^{+\bullet}$ and the corresponding cathodic peak potentials (E_{pc}) of oxygen reduction are summarized in Table 1. The $E_{1/2}$ values of monomeric viologens have a linear relationship with substituent constants (σ^*) and the data for $E_{1/2}$ (Entries 1—5) coincide well with reported ones.[8,9] The bromide iodide salt of monomer **1** (Entry 6) has a more positive redox potential than that of viologen with similar substituents (Entry 2), which might be due to the long substituent with the pyrrole ring. The $E_{1/2}$ values of the electrodes coated with polymeric viologen (Entries 7 and 8) are more positive than those of similar monomeric viologens (Entries 2,4, and 6), probably because of a specific environment of viologen moieties with polypyrrole substituents on the electrode. The E_{pc} values (Entries 1—5) due to the reduction of O_2 are roughly proportional to the $E_{1/2}$ values, which suggests that viologens mediate the electrochemical reduction of O_2. Figure 1b shows the cyclic voltammograms of O_2 catalytic reduction by viologen-modified electrodes under static conditions. The viologen moiety no sooner begins to be reduced at about −0.2 V than fast cathodic O_2 reduction mediated by the viologen moiety occurs. The neighboring O_2 on the electrode surface is almost completely consumed at about E_{pc} (−0.4 V), and V^{2+} moieties that remain or are produced are reduced at about −0.45 V. When the cyclic voltammograms of GC-**1** and GC-**2** are compared with those of a bare GC electrode and poly(*N*-methylpyrrole)-coated GC in the cathodic reduction of O_2 (Fig. 1b), both E_{pc} values of the modified electrodes (Entries 7 and 8) are more positive than those of the bare GC (Entry 9) or the poly(*N*-methylpyrrole)-coated GC (Entry 10). Cathodic currents due to oxygen reduction do not decrease when the electrode surface is covered.

In confirmation of the product selectivity and utility of viologen-modified electrodes in the electrochemical reduction of O_2, the redox activity of GC-**1** and GC-**2** for H_2O_2 was investigated. In the cyclic voltammograms obtained with GC-**1** and GC-**2**, the anodic currents between 0 and −0.5 V (vs. SCE) of H_2O_2 (10 mM) are little higher than those of the anaerobic solution. Selective catalytic reduction of O_2 to H_2O_2 by potential-controlled electrolysis was done. Two monomers, **1** and **2**, were electropolymerized on a large GC plate (6.5 $\mathrm{cm^2}$), and large-scale reactions were carried out (Table 2). GC-**1** has the highest current efficiency (75%) among the three but the efficiency was lowered to about 50% after one use. GC-**2** is inferior in current efficiency initially, but is stable during repeated uses, during which its activity changes little. The current loss of the electrochemical formation of H_2O_2 by the viologen-modified electrode is probably due to the slow reduction of O_2 to OH^-, mediated by $V^{+\bullet}$,[3,8] and solvent decomposition, which has been confirmed to occur by anaerobic electrolysis with a bare GC.[10]

These results show that viologen-modified electrodes GC-**1** and GC-**2** work as efficient reactive electrodes for the electrocatalytic reduction of O_2 to H_2O_2.

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