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Electrocatalytic Reduction of Dioxygen at Glassy Carbon Electrodes with Irreversible Self-assembly of N-hexadecyl-N'-methyl Viologen

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The electroreduction of dioxygen at glassy carbon electrodes with irreversible self-assembly of N-hexadecyl-N'-methyl viologen ($C_{16}VC_1$) proceeds at potentials more positive than those where the reduction occurs at bare electrodes. The electrocatalyzed reduction takes place at potentials well ahead of those where the catalyst is reduced in the absence of dioxygen and the limiting currents observed at rotating disk electrodes did not deviate from the theoretical Levich line up to 6400 rpm, indicating that the electrocatalysis is extremely rapid. The rate constant for the heterogeneous reaction between $C_{16}V^+C_1$ immobilized on the electrode surface and O_2 in solution was estimated to be *ca.* $10^8 M^{-1}s^{-1}$. The half-wave potential of dioxygen reduction was independent of solution pH.

Introduction

We describe here the results of electrocatalytic studies of dioxygen reduction at glassy carbon electrodes with irreversible self-assembly of N-hexadecyl-N'-methyl viologen ($C_{16}V^+C_1$). Because of the very high specific rates between viologen radical cations and dioxygen in homogeneous aqueous solutions,¹⁻³ several different forms of viologens immobilized on carbon electrode surfaces were employed to accelerate the electroreduction of dioxygen.⁴⁻⁶ Anson used poly(xylylviologen) coatings on basal plane graphite electrodes to catalyze the electroreduction of dioxygen to hydrogen peroxide in order to make the most of the very high concentrations of redox catalyst sites at positions within the polymer where they could be cycled between oxidation states electrochemically.⁴ However, the expected advantages inherent with polymeric coatings⁷ were not apparent in the study, because the rate of the cross reaction between dioxygen and the viologen radical cations appeared to proceed more slowly within the polyelectrolyte films than in homogeneous solution and therefore only the outermost monolayer was concluded to participate in the electrocatalysis.⁴ The intermolecular complexes of poly(xylylviologen)-polystyrene sulfonate and poly(xylylviologen)-Nafion on graphite electrodes were applied to study the effects of the metal-free organic electrocatalyst on dioxygen reduction by Oyama,⁵ based on the facts that the polymer complexes were fixed on electrode surfaces more stably and that the polymer functional groups were well solvated⁸. Advantageously for electrocatalysis the coating films of poly(xylylviologen)-poly(sulfonates) had a high permeability of dioxygen but the reaction rates between the viologen radical cations and dioxygen were found to be lower than that with the case of poly(xylylviologen) only.^{4,5}

Differently from these previous studies with polymeric forms of viologens, we began to investigate the electroreduction of dioxygen by irreversible self-assembly of viologens at carbon electrodes.⁶ Bard was the first to report that $C_{16}VC_1$ formed a monomolecular self-assembly on glassy carbon surfaces in the concentration range of 1-20 μM in the aqueous solution of 50 mM NaCl.⁹ We thought that the monomolecular self-assembly of $C_{16}VC_1$ could serve as a better electrocatalytic model system to closely examine the dynamics of the electroreduction of dioxygen by viologen moieties at electrode surfaces, because small variations in electroactive species at monolayer level can be differentiated more effectively through the changes in electrochemical signal than those at polymeric forms and because the electrochemical theory with monolayer catalyst is much simpler to rationalize electrode reactions than the corresponding one with polymer coatings on electrode surfaces.¹⁰ The present results show that the rate of dioxygen reduction by irreversibly adsorbed viologen radical on carbon surfaces is higher than those reported earlier⁴⁻⁶.

Experimental Section

The $C_{16}V^{2+}C_1$ was prepared by a literature procedure.^{9,11,12} Other chemicals were of the best quality available from Aldrich Chemical Company. Solutions were prepared from laboratory deionized water that was passed through a Millipore purification system. Solutions were buffered with hydrochloric acid (pH 1-2), phthalate (pH 3-4), acetate (pH 4-5), phosphate (pH 6-8), carbonate (pH 9-11) and sodium hydroxide (pH 12-14), and contained 0.1 M NaCl. All experiments were performed in the electrochemical cell thermostated at $23(\pm 2)^\circ C$. UV/Vis spectra were obtained by using Shimadzu UV-2100. Cyclic and

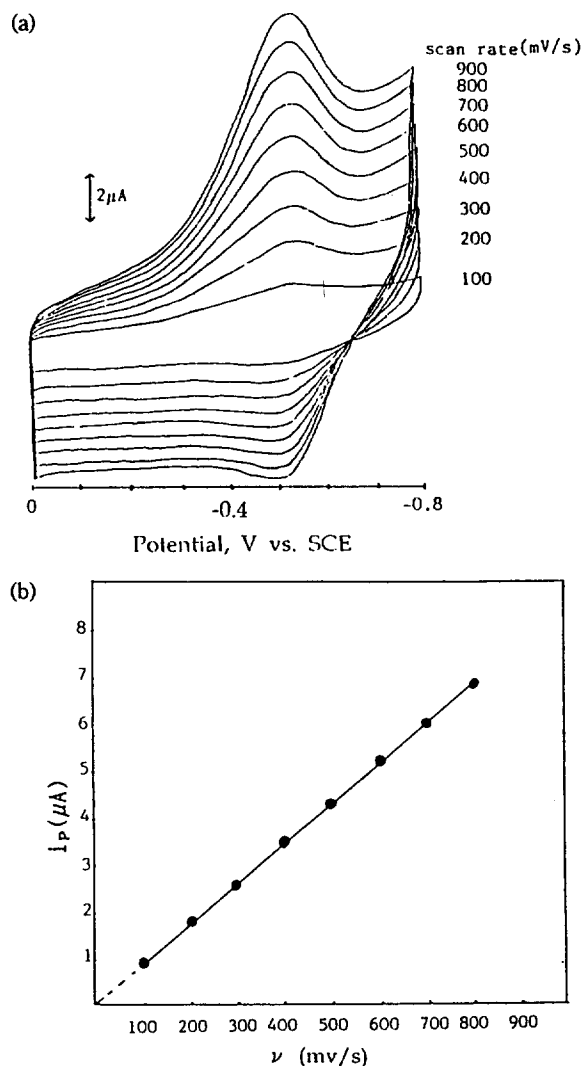


Figure 1A. Cyclic voltammograms obtained with glassy carbon electrode immersed for two hours in aqueous solution of $5 \mu\text{M}$ $\text{C}_{16}\text{V}^{2+}\text{C}_1$ and 0.1 M NaCl at pH 7.0 (0.02 M phosphate) under nitrogen atmosphere. B. Plot of cathodic peak current (i_p) versus scan rate (ν).

rotating disk voltammetry was performed by using a pine bipotentiostat AFRDE 4 and rotator AFMSRX. Voltammograms were recorded by a Yokogawa 3025 recorder. Prior to and after measurements of electrocatalytic currents the self-assembled viologen electrodes were inspected voltammetrically under inert atmosphere to measure the change in the amount of the viologens immobilized on electrode surfaces. The glassy carbon electrodes were polished with $3 \mu\text{m}$ and $0.05 \mu\text{m}$ alumina/water slurry successively, washed with copious amounts of water, and sonicated immediately before use. The area of working electrode was 0.071 cm^2 unless described otherwise. A platinum wire was used as counter electrode. All potentials were measured and are quoted with respect to a saturated calomel electrode (SCE).

Results

Cyclic Voltammetry. Cyclic voltammetry is an impor-

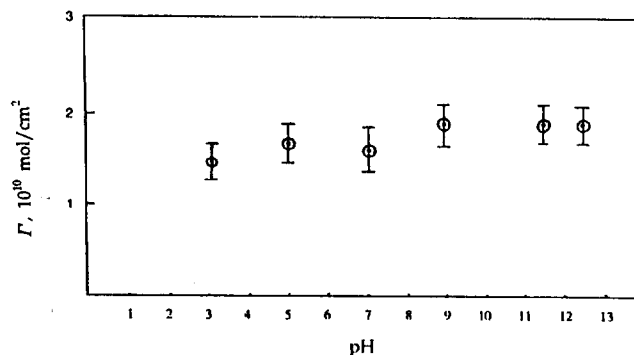
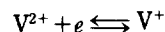


Figure 2. pH dependence of the amount of C_{16}VC_1 adsorbed (Γ) on glassy carbon electrode.

tant tool to ascertain the existence and stability of catalyst for the viologen-dioxygen reaction. Figure 1A shows a series of cyclic voltammograms for the glassy carbon electrode immersed for two hours in an aqueous solution of $5 \mu\text{M}$ $\text{C}_{16}\text{V}^{2+}\text{C}_1$ and 0.1 M NaCl at pH 7.0 (0.02 M phosphate) under nitrogen atmosphere. The potential was scanned only over the first of the two viologen reduction waves¹³ so that the responses observed arise from the electrode reaction,



The voltammogram is characterized by a single broad cathodic and corresponding anodic wave, and was independent of electrode rotation. The cathodic peak current varied linearly with scan rate in the range of 100 to 1000 mV/s with zero intercept (Figure 1B). Thus the experimental evidences show that the electroactivity originates from the surface-bound electroactive viologen ($2+/+$) species.¹⁴ The integration of the voltammogram gives an estimate of the surface coverage of $\Gamma = 1.7(\pm 0.2) \times 10^{-10} \text{ mol/cm}^2$. In Figure 2 is shown the pH dependence of the amount of the viologen immobilized on electrode surfaces. At lower pHs, background currents were so large that the voltammetric measurement of anchored viologens was thwarted. The self-assembly of C_{16}VC_1 on glassy carbon did not lose its electroactivity significantly within several hours when it is transferred to the solution not containing viologens. Therefore, the irreversible self-assembly of C_{16}VC_1 on glassy carbon ($\text{C}_{16}\text{VC}_1/\text{GC}$) is formed to study the reaction between molecular oxygen and viologen radical cation immobilized on electrode surfaces in the pH range of 3 to 13.

When the cyclic voltammetric experiments were performed with $\text{C}_{16}\text{VC}_1/\text{GC}$ under oxygen atmosphere, the voltammograms with sharply defined cathodic currents were obtained without any measureable anodic currents (Figure 3A). Cyclic voltammograms with $\text{C}_{16}\text{VC}_1/\text{GC}$ under nitrogen atmosphere are shown for a direct comparison in Figure 3B. Salient feature is that the cathodic peak potential under oxygen atmosphere is more positive than that under nitrogen atmosphere. The observed experimental facts manifest the very fast electrocatalytic reaction between substrate oxygen and the catalyst viologen radical cation on electrode surfaces.¹⁵ After the catalytic experiments for a half an hour, however, cyclic voltammograms under nitrogen atmosphere were obtained with the peak currents smaller than those before the catalytic experiments. Therefore, the electrocatalysts appear to be de-

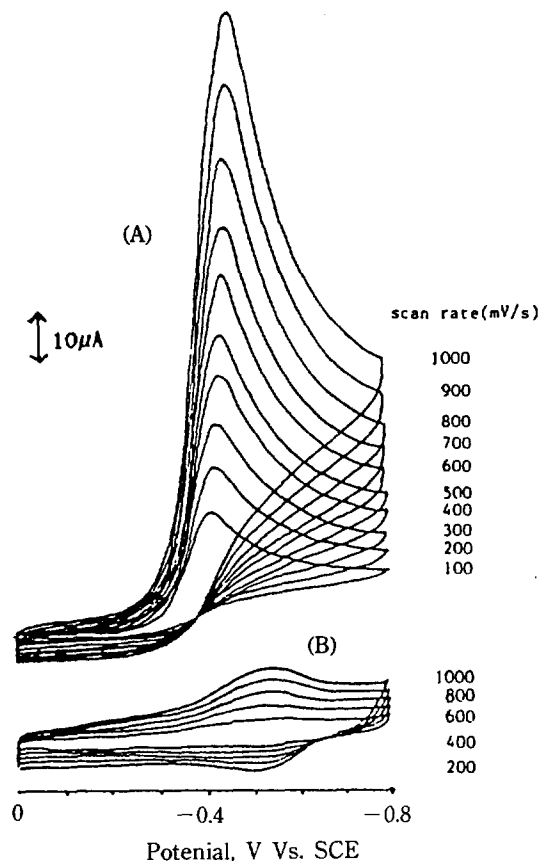


Figure 3. Cyclic Voltammograms of $C_{16}VC_1/GC$ in aqueous solution of $5 \mu M C_{16}V^{2+}C_1$ and $0.1 M NaCl$ under oxygen atmosphere (A) and nitrogen atmosphere (B).

stroyed during the catalytic reaction.

Rotating Disk Voltammetry. To investigate the kinetics of the electrocatalytic reaction, rotating disk voltammetric techniques¹⁶ were employed. The results are shown in Figure 4. Also shown in Figure 4 are the background responses at rotating glassy carbon disk electrode under oxygen atmosphere. The electroreduction of O_2 with $C_{16}VC_1/GC$ proceeds at potentials more positive than those where the reduction occurs at bare glassy carbon electrodes. Therefore the observed currents at $C_{16}VC_1/GC$ are catalytic. To obtain the reliable limiting catalytic currents, voltammetric experiments with $C_{16}VC_1/GC$ were performed under nitrogen atmosphere before and after the catalytic experiments under oxygen atmosphere. Rotating disk voltammograms were taken only when the surface coverage remained little changed before and after rotating disk voltammetric measurements under oxygen atmosphere. The rotating disk voltammograms in Figure 4 are well-defined without potential-dependent inclination in limiting currents, corresponding to the diffusion-convection limited reduction of dioxygen.¹⁷ The Levich plot¹⁶ derived from the voltammograms was linear with zero intercept up to 6400 rpm (Figure 5), indicating that the catalytic rate is very large. The slope in the Levich plot corresponds to $n=2$, as expected from the reaction product hydrogen peroxide found in homogeneous solution studies.¹² Further employment of rotating disk voltammetric techniques was made to investigate the pH dependence of limiting currents and half-wave poten-

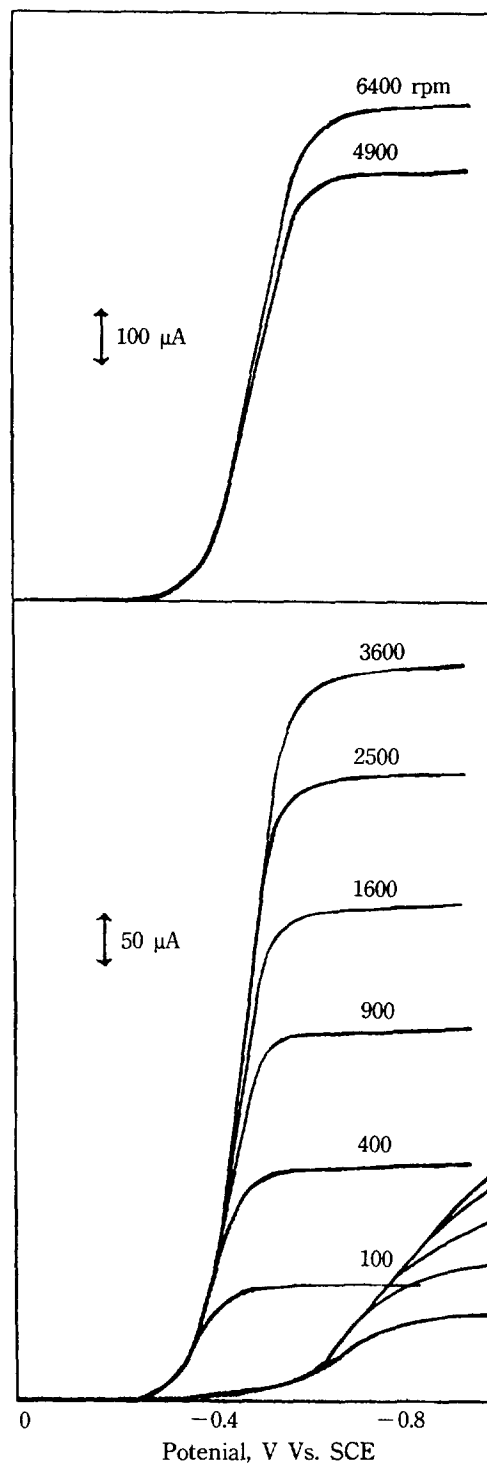


Figure 4. Rotating disk voltammograms with $C_{16}VC_1/GC$ (A) and bare glassy carbon electrode (B) under oxygen atmosphere. Solution had the same composition as in Figure 1A. Scan rate; $4 mV/s$, Electrode area; $0.20 cm^2$.

tials of the electrocatalytic reaction. The results are shown in Figure 6. Although cation radical viologens (+1) are well known to react with molecular oxygen to produce hydrogen peroxide in aqueous solutions and therefore it is expected that the electrode reaction should depend on pH, the limiting current depends on pH only above 12, which was not obser-

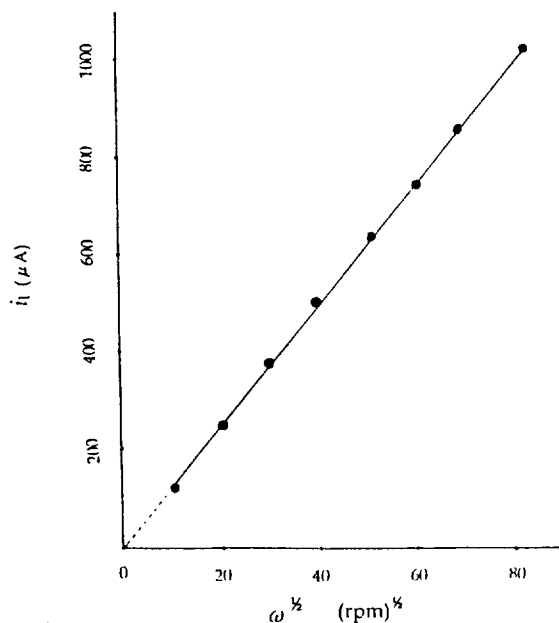


Figure 5. Levich plot of the data in Figure 4 A.

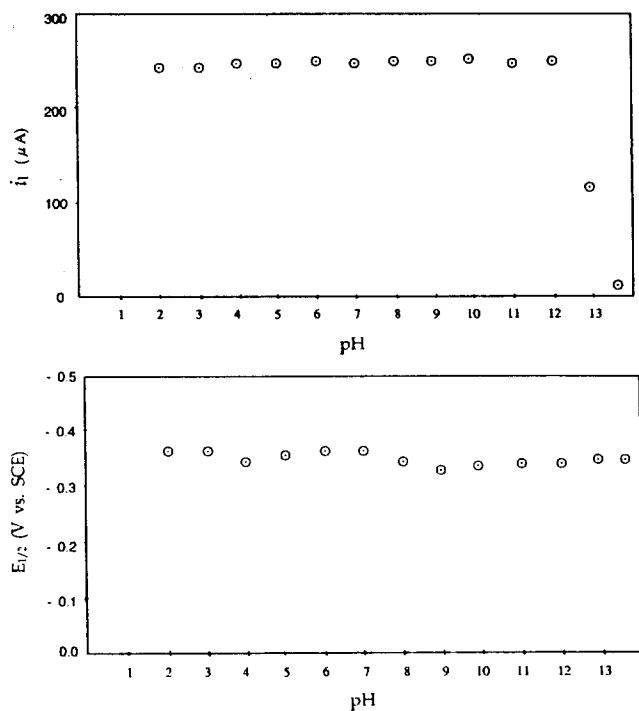


Figure 6. pH dependence of limiting current (A) and half-wave potential (B) at rotating disk ($C_{16}VC_1/GC$) electrode under oxygen atmosphere.

Rotation rate; 400 rpm.

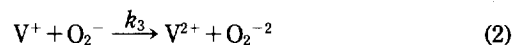
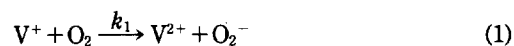
ved in similar studies with polymer complexes by Oyama,⁵ and the half-wave potential appears to be completely independent of pH of the solution medium.

Discussions

The electrode reaction between molecular oxygen and vi-

ologen radical cation immobilized on electrode surface appears to be very fast but the catalyst degraded during the experiments. In nonaqueous solutions, superoxide ion was reported to attack to open the aromatic ring.¹⁸ We believe that similar catalyst poisoning reaction takes place in the present electrode reactions, although the deactivation of electrocatalyst is not so rapid to prohibit the kinetic investigation of the catalytic reaction. The experimental data were taken only when the catalyst activity was believed to remain unperturbed, as judged from the negligible change in the voltammetric signals under nitrogen atmosphere before and after the catalytic experiments.

Notable experimental facts obtained in this study are that the half-wave potentials of the catalytic waves are much more positive than the formal potential of $C_{16}V^{2+/+}C_1$ and that the limiting currents do not deviate from the theoretical Levich line up to a very high rotation rate. This is the case expected when the electrocatalytic rate with which the substrate consumes the active form of the catalyst is very large. In fact, kinetic studies of electron transfer reactions between methyl viologen radical MV^+ and molecular oxygen in aqueous solutions by using stopped-flow techniques concluded that the bimolecular rate constant had the lower limit of $k > 5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.² In addition, pulse radiolysis studies in homogeneous solution measured that k_1 value was $10^9 \text{ M}^{-1}\text{s}^{-1}$ and that k_2 value was higher for the following reaction scheme.^{1,3}



The number of electrons involved in the electrocatalytic reaction is determined to be two from the slope of the plot of limiting currents versus rotation rates, which is in agreement with previous electrochemical studies on dioxygen reduction by viologens with different functional groups.^{4,5,19} The pH independence of the half-wave potential and limiting current in rotating disk voltammograms indicates that the proton transfer step is not rate limiting in the present reaction system. The electrocatalytic system of cobalt-porphyrin for dioxygen reduction, where the reaction product was hydrogen peroxide in aqueous solution as is in the current case, was shown to depend strongly on the pH of solution, because hydroxyl group was coordinated to the axial position of cobalt metal center.^{20,21} Viologens do not have such a position available for coordination of hydroxyl group or proton. In any case, the proton transfer step can be excluded in the reaction mechanism of reduction of molecular oxygen by viologen radical cation on electrode surfaces. The above reaction scheme (1) and (2) was taken to analyze the kinetic data for the present system. Decay in limiting currents at $\text{pH} > 12$ may originate from the attack of hydroxyl group on the aromatic ring resulting in ring opening.^{22,23} Another important implication of the pH independence of the half-wave potential and limiting current is that the electrocatalytic system becomes more efficient at higher pH. The reduction potential of molecular oxygen to hydrogen peroxide at the standard states is 0.68 V but it changes to -0.10 V at pH 13. Thus at higher pH, less thermodynamic energy is required to obtain the same catalytic current. However, the practical appli-

cation of the present electrocatalytic system should be limited below pH 12 because of the rapid decay in limiting current above it.

The reaction rate between $C_{16}V^+C_1$ on electrode and molecular oxygen can not be determined from the conventional Koutecky-Levich analysis, because the Levich plot follows the theoretical expectation for the diffusion-convection controlled reactions.¹⁶ The following functional relationship, which Murray²⁴ and later Oyama⁵ has driven for such fast electrocatalytic reactions, can be applied to extract the rate constant k_1 of the rate determining step (1),

$$\Delta E = \frac{RT}{nF} \ln \left(1 + \frac{i_k}{i_L} \right)$$

with $i_k = nFAk_1C^0\Gamma$

$$i_L = 0.62nFAC^b D_o^{2/3} \omega^{1/2} \nu^{-1/6}$$

where ΔE denotes the shift in formal potential and Γ the amount of immobilized catalyst. Other symbols have their usual meanings. With $\Delta E = 200$ mV and $\Gamma = 1.7 \times 10^{-10}$ mol/cm² the bimolecular rate constant was estimated to be ca. 10^8 M⁻¹s⁻¹. This is much larger than those obtained by us with limited instrumentation previously⁶ or by Anson⁴ or Oyama⁵ using the polymeric forms of viologens. The difference observed from polymeric forms of viologen might be attributed to the different reaction conditions and thermodynamic potentials of viologen sites. The deactivation of electrocatalysts (vide supra) in these cases might have been unnoticed because the catalyst deactivation is not as fast to be detected unless extreme care is taken of during the experiments, especially so in measuring large voltammetric signal of polymeric films.

In conclusions, the peak potential of electroreduction of molecular oxygen at $C_{16}V^+C_1/GC$ is more positive than that of $C_{16}V^{2+/+}C_1/GC$ in the absence of molecular oxygen, the rotating disk voltammograms are well-defined, the limiting catalytic currents follow the Levich line up to 6400 rpm and thus the $C_{16}V^+C_1/GC$ catalyzes the reduction of molecular oxygen at electrode surfaces very rapidly. The catalyst was deactivated slowly during experiments. The electrocatalytic reaction does not depend on pH of the solution.

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