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Electrocatalytic Oxidation of Nerol with Nitroxyl Radical Covalently Immobilized to Poly(acrylic acid) Coated on Carbon Electrodes

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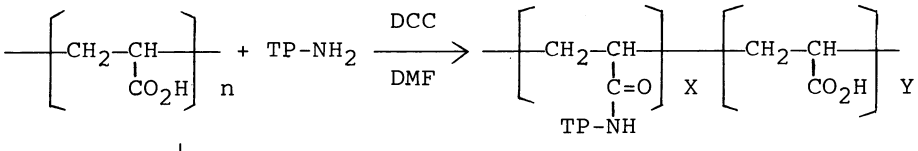
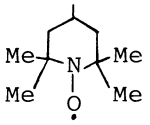
Glassy carbon electrode coating poly(acrylic acid) immobilized covalently with 2,2,6,6-tetramethylpiperydinyl-1-oxy was characterized electrochemically and a similar modified carbon felt electrode was utilized successfully to electrocatalytic oxidation of nerol.

One of the most attractive applications of chemically modified electrodes is their use in electrocatalytic syntheses of various organic substrates.[1] In this respect polymer modified electrodes possessing electrocatalytic activities are especially promising as a practical device.[2] So far, many studies[3] on polymer coated electrodes have been reported from an electrocatalytic point of view, but there is no demonstration of such an electrode for electrocatalysis of alcohol oxidation which is very important as fundamental and practical process in organic synthesis.

We report here on a useful polymer coated electrode using 2,2,6,6-tetramethylpiperydinyl-1-oxy (TEMPO) as a heterogeneous redox catalyst for nerol oxidation. TEMPO is a stable organic radical which is not only well-used as a nitroxide spin probe for biomolecular chemistry[4] but also known as a stable redox species which is characterized by property of a reversible one-electron oxidation, even in aqueous solution.[5] The oxidized species, a nitrosonium salt, is known to be specific and useful oxidizing agent.[6] The use of TEMPO as a homogeneous redox catalyst in electrosynthesis for alcohol oxidation has been already developed by Semmelhack et al.[7] Therefore the electrochemical studies on TEMPO bound to polymer are very interesting and important.[8]

The redox polymer used was synthesized by immobilization of 4-amino-TEMPO to poly(acrylic acid) by an amide-linkage with the coupling reagent, N,N'-dicyclohexylcarbodiimide (DCC) in dimethylformamide (DMF) as shown in Scheme 1.



TP-; 

I

X = 0.71 Y = 0.29

Scheme 1.

The product I was purified by the dialysis with methylene chloride and methanol for 4 days. The composition of TEMPO in I was estimated on the basis of the elementary analysis. IR and EPR spectra suggested the presence of amide-bonding and nitroxide radical immobilized to the polymer, respectively. The polymer coated electrodes were fabricated by the cast-coating of methanol-methylene chloride mixed solution of I on carbon electrodes by a microsyringe and followed to remove the solvents by air-drying.

Figure 1 shows the typical cyclic voltammograms of I coated thinly on a glassy carbon electrode in 0.2 M $NaClO_4/CH_3CN$ at low scan rates. At the scan rate less than 20 mV/s, the wave is characterized by symmetric and reversible shape with peak to peak separation less than 10 mV, and peak currents are proportional to the scan rate. With increase in scan rate, deviations from the monolayer-like voltammetric behavior occur, demonstrating the appearance of a diffusion-like charge transport across the coating layer.

Potential step chronoamperometry was carried out to get more precise information on the charge propagation because it is a very important factor to characterize a redox polymer coated electrode for electrocatalysis. The results are shown in Fig. 2. The experimental values shown in points are well-fitting to the theoretical curve obtained from Eq. 5 for the finite diffusion current-time relation given in Ref. 9. These result indicate that the redox site, TEMPO covalently bound to the polymer (I) coated on a glassy carbon electrode, can be oxidized three-dimensionally through the diffusion-like propagation of the charge.

As shown in Table 1, it was found that the charge transport diffusion coefficient, D_{ct}, in 0.2 M $NaClO_4/CH_3CN$ was three times larger than the value in 0.2 M $LiClO_4/CH_3CN$ because the film thickness, d, is equal. The reason for the difference is not clear yet, but it is interesting in the relation to charge propagation mechanism in this redox polymer.[10] This finding led us to qualitatively examine the electrocatalytic behavior of nerol oxidation with this modified electrode in the following cyclic voltammetry experiments.

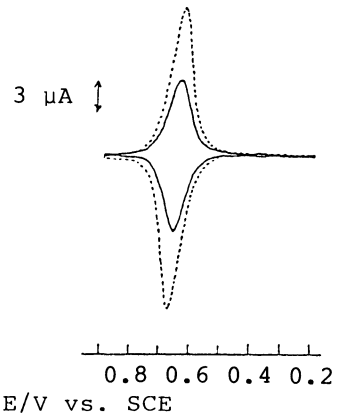


Fig. 1. Cyclic voltammograms of I coated on a glassy carbon electrode in 0.2 M $NaClO_4/CH_3CN$ at scan rate, 10 mV/s (——) and 20 mV/s (---).

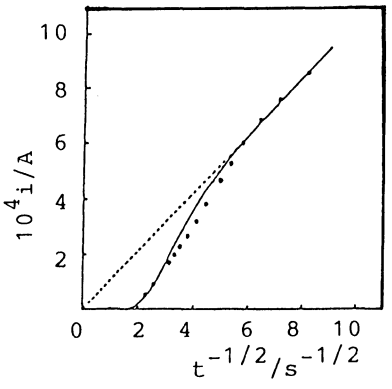


Fig. 2. Chronoamperometric current-time data of I coated on a glassy carbon electrode following potential step from 450 to 850 mV vs. SCE in 0.2 M $NaClO_4/CH_3CN$; points are experimental currents, solid curve shows theoretical currents.

Figure 3 shows the comparison of cyclic voltammograms of the electrocatalytic oxidation of nerol in 0.2 M $NaClO_4$ or in 0.2 M $LiClO_4$. In the absence of 2,6-lutidine as a base,[7] it can be seen that the oxidation currents increase only a little despite considerable disappearance of the rereduction currents. In the presence of 2,6-lutidine, however, the catalytic oxidation currents are enhanced markedly in both electrolytes, and the increment in 0.2 M $NaClO_4$ is apparently larger than that in 0.2 M $LiClO_4$. This difference is reasonable parallel to the difference in D_{ct}. These results indicate that in the absence of 2,6-lutidine the catalytic reaction itself between the nitrosonium cation formed by one-electron oxidation of a TEMPO and an alcohol is slow and a rate-limiting process, but that in the presence of 2,6-lutidine diffusion-like charge propagation across the coating layer becomes rate-limiting. Although the mechanisms for the catalysis and the regeneration in the present heterogeneous reaction are not simple as in the homogeneous case,[7] Fig. 3 proves undoubtedly that the electrocatalytic oxidation of nerol with TEMPO can successfully proceed even in this immobilized system.

Table 1. Values of Γ_T and D_{ct}/d^2 determined by potential step chronoamperometry of I coated glassy carbon electrode in CH_3CN

Electrolyte	Γ_T a) / 10^{-8} mol cm^{-2}	D_{ct}/d^2 b) / s^{-1}
0.2 M $NaClO_4$	1.1	6.0
0.2 M $LiClO_4$	1.1	1.9

a) Γ_T is coverage of TEMPO estimated from cyclic voltammetry.
b) D_{ct} is charge transport diffusion coefficient and d is thickness of the coating.

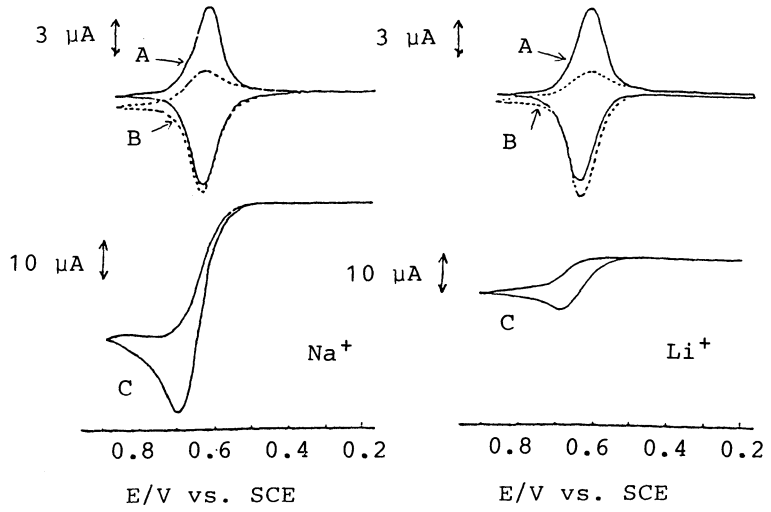


Fig. 3. Cyclic voltammograms of I coated glassy carbon electrode, in CH_3CN containing 0.2 M $NaClO_4$ (Na^+) and 0.2 M $LiClO_4$ (Li^+), respectively at 10 mV/s without additive (A), with 10 mM of nerol (B), and 10 mM of nerol plus 10 mM of 2,6-lutidine (C).

Based on these findings, preparative electrolysis using I coated carbon felt[11] (Union Carbide Co. WDF felt electrode, which possesses very large surfaces so that the coating thickness can be minimized) was carried out at a controlled potential of 0.8 V (vs. SCE). Figure 4 shows the reaction time course. The current efficiency exceeds 80% and the turnover per TEMPO-subunit used reaches more than 100 in a hour. This preliminary result strongly suggests that this kind of modified electrode is promising for a practical electrocatalytic application. A more detailed study is being made.

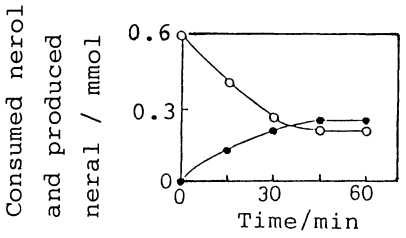


Fig. 4. Time course of consumed nerol (o—o) and produced neral (●—●) for electrocatalytic oxidation with I coated carbon felt electrode in 20 mM nerol and 0.2 M $NaClO_4/Ch_3CN$ (30 ml) containing 20 mmol 2,6-lutidine.

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11) The carbon felt electrode was 5 x 2 x 0.5 cm^3 in size.

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