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Electron-Transfer Kinetics of Nitroxide Radicals as an Electrode-Active Material

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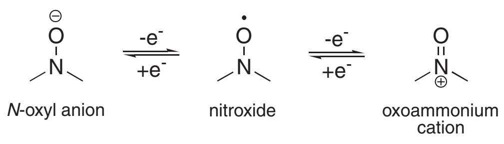
The electron-transfer rate constants of nitroxide derivatives, 4-(*N*-*t*-butyl-*N*-oxylamino)-*t*-butylbenzene, 4-(*N*-*t*-butyl-*N*-oxylamino)methoxybenzene, and 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl, were investigated by electrochemical methods, which demonstrated that these radicals can potentially be used as a high power-rate electrode-active material due to their fast electron-transfer process.

Nitroxide radicals, such as 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO), are known to be very stable, based on both the sterically protected structure around the radical center and the resonance effect involving the center.[1] The nitroxide radicals can often be reversibly oxidized into the corresponding oxoammonium cations both chemically and electrochemically, and reduced into the corresponding *N*-oxyl anions, as shown in Scheme 1.

The Oxoammonium salt, the oxidative form of TEMPO, is known to oxidize alcohols into aldehydes and ketones.[2] These nitroxide radicals have been extended to their polymeric radical molecules as heterogeneous catalytic reagents for the oxidation of alcohols.[3] In addition to such chemical applications, we have recently reported the application of such nitroxide polymers as an electrode-active material. Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) displayed a quantitatively reversible redox behavior, and has been successfully applied as a cathode-active material in a rechargeable lithium battery.[4,5] This nitroxide polymer electrode is expected to have a high capacity due to the localized small redox site compared with the π-conjugated conductive polymer electrodes, such as doped polypyrrole and polythiophene. In view of a further improvement of the specific capacity, poly(4-(*N*-*t*-butyl-*N*-oxylamino)-styrene) is designed as an electro-active material with a higher capacity, since the molecular weight per nitroxide redox site of the poly(4-(*N*-*t*-butyl-*N*-oxylamino)styrene) (i.e., the unit molecular weight) is lower than that of poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) ($M_w = 190$ and 242, for the former and the latter, respectively). In addition to the high capacity, a high power-rate performance is also expected for an organic radical battery, because the redox process of nitroxide radicals does not contain any bond-formation and -breaking, and hence the process is expected to be very rapid. In this paper, we focus on the electrode kinetics of nitroxide radicals, 4-(*N*-*t*-butyl-*N*-oxylamino)-*t*-butylbenzene (**1**) and 4-(*N*-*t*-butyl-*N*-oxylamino)methoxybenzene (**2**) (Chart 1), with a view to prognose the redox property of poly(4-(*N*-*t*-butyl-*N*-oxylamino)styrene). Their high rates of heterogeneous electron transfers are ensured by various electrochemical methods, such as cyclic voltammetry (CV), chronoamperometry (CA), and an AC technique.[6] The redox property of the reference material, TEMPO, was also characterized by the same analytical methods and discussed in comparison with previous data.[7]



Scheme 1.

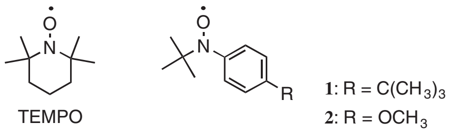


Chart 1.

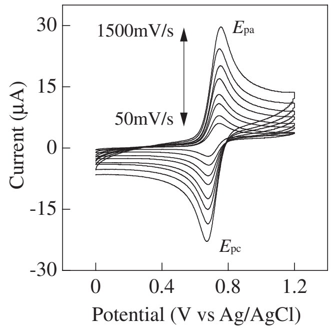


Fig. 1. Cyclic voltammogram of **1** in acetonitrile.

Cyclic voltammograms of **1** at different scan rates are shown in Fig. 1, which reveal the reversible response at $(E_{pa} + E_{pc})/2 = 0.75$ V vs Ag/AgCl. The potentials for **2** and TEMPO were 0.56 V and 0.68 V, respectively. The peak separation widths ($E_{pa} - E_{pc}$) were approximately 60 mV at low rates, which increased at the higher scan rates. The heterogeneous electron-transfer rate constant (k_0) was estimated using the Nicholson method.[6] The diffusion coefficient (D) was also calculated from the slope of the linear region between the anodic peak current and the square root of the sweep rate; the D values were in good agreement with those estimated from the magnitude of the diffusion-limited current at a rotating disc electrode (RDE). The data for TEMPO (Table 1) were in agreement with those in previous reports.[7]

Added evidence for the rapid electrode kinetics of **1** and **2** is provided from various electrochemical measurements on short time scales. In chronoamperometry, the kinetic parameters can be evaluated from the current decays after potential steps (Fig. 2). The diffusion coefficient (D) can also be determined from the Cottrell equation. Assuming that this redox process is a quasi-reversible process, the forward rate constant (k_f) was calculated from the intercept of the current decay, and it was

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Table 1. Standard Rate Constants and Diffusion Coefficients for Nitroxide Derivatives

Nitroxide	**1**		**2**		TEMPO	
	$k_0/\text{cm s}^{-1}$	$D/\text{cm}^2\text{ s}^{-1}$	$k_0/\text{cm s}^{-1}$	$D/\text{cm}^2\text{ s}^{-1}$	$k_0/\text{cm s}^{-1}$	$D/\text{cm}^2\text{ s}^{-1}$
CV	1.1×10^{-1}	1.6×10^{-5}	1.7×10^{-1}	1.3×10^{-5}	1.0×10^{-1}	2.6×10^{-5}
RDE	—	1.5×10^{-5}	—	9.9×10^{-6}	—	2.2×10^{-5}
CA	3.8×10^{-2}	4.8×10^{-5}	3.2×10^{-2}	3.5×10^{-5}	2.3×10^{-2}	3.2×10^{-5}
AC ($\cot\phi$)	1.3×10^{-1}	2.6×10^{-5}	7.9×10^{-2}	1.9×10^{-5}	6.4×10^{-1}	2.7×10^{-5}

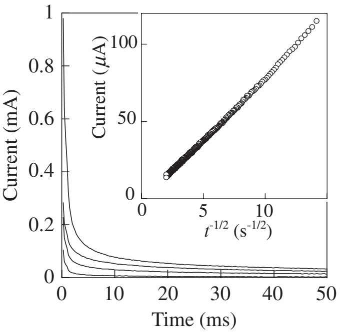

Fig. 2. Current decay of **1** after application of potential steps (0.5, 0.7, 0.75, and 1.2 V in ascending order). Inset: Cottrell plot ($E = 1.2$ V).

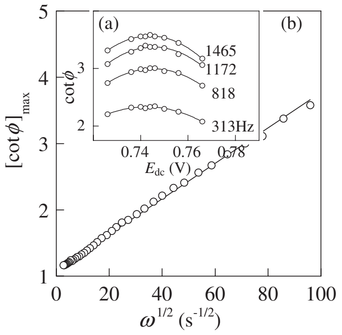

Fig. 3. (a) The dependence of $\cot\phi$ on E_{dc}. (b) Frequency dependence of $\cot\phi$ for **1** at $[E_{\text{dc}}]_{\text{max}}$ ($= 0.744$ V).

transformed into the standard rate constant (k_0). An chronoamperometric analysis tends to underestimate k_0, but the obtained values were comparable with those evaluated by CV (Table 1).

An AC technique[6] was used to more accurately determine the kinetic parameters. The AC technique is a strong method for the analysis of rapid electrode reactions. From an AC impedance measurement, the relationship between the mean potential (E_{dc}) and $\cot\phi$ ($\phi =$ the phase angle) was obtained as shown in Fig. 3a. $\cot\phi$ has its maximum value at $[E_{\text{dc}}]_{\text{max}}$, where $[\cot\phi]_{\text{max}} = 1 + (2\omega D)^{1/2}/[k_0\{\alpha/(1-\alpha)\}^{-\alpha} + \{\alpha/(1-\alpha)\}^{(1-\alpha)}]$ and $[E_{\text{dc}}]_{\text{max}} = E_{1/2} + (RT/nF)\ln[\alpha/(1-\alpha)]$. The transfer coefficient (α) was calculated from the latter equation. The rate constant (k_0) was obtained from the slope of the $[\cot\phi]_{\text{max}}$–$\omega^{1/2}$ plots (Fig. 3b).

The standard rate constant (k_0) of **1**, **2**, and TEMPO determined by the three techniques are given in Table 1. The rate constants of the nitroxide derivatives were approximately 10^{-1} cm/s, which demonstrates that the electron-transfer processes are sufficiently fast, and that these radicals can potentially be used as high power-rate electrode-active materials. The electrochemical property of poly(4-(*N*-*t*-butyl-*N*-oxylamino)-styrene) and its charge-discharge performance in a radical battery will be reported in the future.

Experimental

Electrochemical measurements were performed using a conventional cell under an atmosphere of dry argon. A platinum disk, coiled platinum wire, and Ag/AgCl were used as the working, auxiliary, and reference electrodes, respectively. A normal potentiostat system (BAS/100BW) was used for cyclic voltammetry, potential step and ac techniques. All of the electrochemical measurements were carried out in 1.0 mM acetonitrile in the presence of 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NBF}_4$ as the supporting electrolyte. The formal potential of the ferrocene/ferrocenium redox couple was 0.44 V vs this reference electrode.

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) was purchased from Kanto Chemical Co. The precursors of the *p*-substituted aryl nitroxides **1** and **2** were prepared by the lithiation of *p*-substituted bromobenzene, followed by a reaction with 2-methyl-2-nitrosopropane.[8] The obtained hydroxylamine derivatives were oxidized with silver(I) oxide in the presence of potassium carbonate. After purification by silica-gel column chromatography, the corresponding nitroxides, **1** and **2**, were obtained as an orange powder and red oil, respectively.

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References

1 H. G. Aurich, "Nitrones, Nitronates and Nitroxides," ed by S. Patai and Z. Rappoport, John Wiley & Sons (1989), pp. 313–399.

2 M. F. Semmelhack, C. R. Schmid, D. A. Cortés, and C. S. Chou, *J. Am. Chem. Soc.*, **106**, 3374 (1984).

3 T. Osa, U. Akiba, I. Segawa, and J. M. Bobbitt, *Chem. Lett.*, **1988**, 1423.

4 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, and E. Hasegawa, *Chem. Phys. Lett.*, **359**, 351 (2002).

5 H. Nishide, S. Iwasa, Y.-J. Pu, T. Suga, K. Nakahara, and M. Satoh, *Electrochim. Acta*, in press.

6 A. J. Bard and L. R. Faulkner, "Electrochemical Methods," 2nd ed, John Wiley & Sons (2001).

7 P. Krzyczmonik and H. Scholl, *J. Electroanal. Chem.*, **335**, 233 (1992).

8 J. Fujita, M. Tanaka, H. Suemune, N. Koga, K. Matsuda, and H. Iwamura, *J. Am. Chem. Soc.*, **118**, 9347 (1996).