Electrocatalytic Oxidation of 2,5-Dimercapto-1,3,4-thiadiazole by Polyaniline. 1 Use of *N,N'*-Diphenyl-*p*-phenylenediamine as a Model Compound of Polyaniline

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In the present study, electrocatalysis by polyaniline was investigated using a model compound of polyaniline, *N,N'*-diphenyl-*p*-phenylenediamine (DPPD). Electrochemical measurements indicated that the highest oxidized form of DPPD, diimine, showed high electrocatalytic activity toward the oxidation of 2,5-dimercapto-1,3,4-thiadiazole, DMcT. On the contrary, one-electron oxidized form of DPPD, radical cation, shows only poor activity in the oxidation. Different electrocatalytic activity observed for polyaniline in the emeraldine salt form and the DPPD radical cation suggests that conductivity of polyaniline in the emeraldine salt form plays an important role in electrocatalysis by polyaniline. Based on the results it was expected that the use of DPPD and its oxidized form as model compounds for polyaniline in the different oxidation states is useful for discussion of relative contributions from redox polymer character and conducting polymer character of polyaniline in electrocatalysis.

Key Words : Polyaniline, Organosulfur Compound, Electrocatalysis, Lithium Battery

1 Introduction

An organosulfur compound with two or more thiol groups is expected from a thermodynamic point of view as one of possible candidates for a cathode material of batteries, because of high theoretical capacity based on chemically reversible redox transformations between thiol and disulfide.^{1, 2)} However, considerable electrochemical irreversibility of the redox reactions only leads to a low energy efficiency, which hinders the application of organosulfur compounds as a practical cathode material at room temperature.^{3, 4)} Recently, Oyama *et al.* has shown that polyaniline is capable of catalytically accelerating the organosulfur redox reactions to an extent which allows one to use an organosulfur compound such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT) in rechargeable batteries.⁵⁾

Electrocatalysis by polyaniline has been observed for redox reactions of various organic and inorganic compounds which only show sluggish electron-transfers at unmodified electrode surfaces.^{6, 7)} It is expected that

polyaniline behaves as a redox polymer and/or a metal substrate in electrocatalytic reactions.⁸⁾ In this study homogeneous electrocatalytic oxidation of DMcT was studied by cyclic voltammetry using *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) which has been used as the smallest model compound for polyaniline redox reactions (Scheme 1).^{9, 10)}

2 Experimental

DPPD was purchased from Tokyo Kasei (Japan) and purified by recrystallization from toluene. DMcT and propylene carbonate were obtained from Aldrich and used as received.

Cyclic voltammetry was performed using a potentiostat (HABF 1510 m, Hokuto Denko, Japan) and a conventional three-electrode cell with a glassy carbon disk electrode as working electrode, a Pt spiral counter electrode and a Ag/Ag⁺ (50 mM (M = mol dm⁻³) AgClO₄) reference electrode. All electrochemical measurements were carried out under Ar atmosphere in a glove box (Miwa, Japan). Spectroscopic measurements were carried out using a spectrophotometer (Multi Spec-1500, Shimadzu, Japan) and a stopped-flow/rapid scan spectrometer (RSP-601, UNISOKU, Japan).

3 Results and Discussion

Figure 1 shows cyclic voltammograms of DPPD and DMcT in propylene carbonate (PC) containing 0.1 M LiClO₄. As shown in Fig. 1B, DPPD gives a cyclic voltammogram with two reversible redox waves in PC as previously observed in acetonitrile.^{10, 11)} The redox responses

Scheme 1 Redox transformations of (A) polyaniline and (B) the model compound.

Fig. 1 Cyclic voltammograms of PC solutions containing (A) DPPD and DMcT, (B) DPPD, and (C) DMcT. Concentrations were 2 mM for all compounds. Supporting electrolyte: 0.1 M LiClO₄. Scan rate: 100 mVs⁻¹.

at $E = -0.25$ V vs. Ag/Ag⁺ and $+0.2$ V are attributed to one-electron transfer processes of DPPD/DPPD⁺ and DPPD⁺/DPPD²⁺ redox couples, respectively, which correspond to the redox interconversions of polyaniline between emeraldine/leucoemeraldine and leucoemeraldine/pernigraniline forms, respectively, as shown in Scheme 1.^{9,10} The voltammogram characterized with the two well-defined redox waves indicates that the oxidation products of DPPD retain the protons in PC (Scheme 1).^{10,11}

DMcT molecule, which has two thiol groups, is also capable of undergoing two one-electron redox reactions at electrode surfaces, leading to the formation of disulfide polymers (Scheme 2).^{1,2} However, DMcT only gives highly irreversible redox waves due to sluggish kinetics as shown in Fig. 1C. Figure 1A shows a cyclic voltammogram obtained in a PC solution containing equimolar DMcT and DPPD. It is clearly seen that the second oxidation of DPPD, which corresponds to the oxidation of the intermediate radical species to the protonated diimine form, was significantly enhanced in the presence of DMcT. The current enhancement indicates that DMcT is catalytically oxidized by the diimine form of DPPD (DPPD²⁺) at a more negative potential by *ca.* 180 mV compared to a bare glassy carbon electrode and DPPD²⁺

Scheme 2 Schematic of the electrocatalytic oxidation of DMcT by DPPD²⁺.

Fig. 2 (A) Changes in the absorbance of (a) 0.1 mM DPPD²⁺ at $\lambda = 515$ nm and (b) 0.1 mM DPPD⁺ at $\lambda = 380$ nm observed after mixing with 0.6 mM DMcT in PC. (B) UV-vis spectra of DPPD at the different oxidation states in PC.

was reduced to DPPD⁺ (Scheme 2) (Oxidation products of DMcT from the electrocatalysis are not clear at this stage of our research). It is expected that the electrocatalytic oxidation of DMcT by DPPD²⁺ would correspond to that by polyaniline in the pernigraniline form. Additionally, it is also expected that DMcT would prevent polyaniline from degradation by reducing the pernigraniline form which is subject to degradation,^{12,13} sustaining highly stable charge-discharge cyclic performance of the DMcT-polyaniline composite cathode.

While the electrocatalytic activity of DPPD²⁺ toward the oxidation of DMcT was confirmed as described above, electrocatalytic oxidation by the intermediate oxidized species DPPD⁺, which corresponds to polyaniline in the emeraldine salt form, was not clearly observed from the electrochemical measurements (Fig. 1). Spectroscopic experiments, however, showed that DPPD⁺ is also capable of electrocatalytically oxidizing DMcT as shown in Fig. 2. When mixing with excess DMcT, the absorbance at $\lambda = 380$ nm due to DPPD⁺ gradually decreased, indicating one-electron reduction of DPPD⁺ to DPPD by DMcT, although the oxidation of DMcT proceeded more slowly compared to that by DPPD²⁺ (Fig. 2 b), possibly due to poorer driving force.

Although the electrocatalytic oxidation of DMcT by DPPD⁺ was confirmed in this study, it appeared that the oxidation of DMcT by DPPD⁺ was much slower than that by polyaniline in the emeraldine salt form, since the current enhancement was clearly observed in a cyclic voltammogram of a DMcT-polyaniline composite electrode even in a potential region where leucoemeraldine was oxidized to emeraldine.⁴ Kinetic analysis suggested that the electrocatalytic oxidation of DMcT by the DPPD oxidized species were strongly affected by proton dissociation equilibria of the DPPD oxidized species.¹⁴

4 Conclusion

In this study, electrocatalytic oxidation of an organosulfur compound by polyaniline was investigated using a model compound of polyaniline, DPPD, for the first time. The model compound in the highest oxidation state, diimine form, showed high electrocatalytic activity toward the oxidation of DMcT, which would confirm the electrocatalytic oxidation of DMcT by polyaniline in the pernigraniline form.

graniline form. The result would confirm that the redox polymer mechanism can be applied to the electrocatalytic oxidation of DMcT by polyaniline in a potential region where pernigraniline is a predominant form. On the contrary, slower oxidation of DMcT by DPPD⁺ compared to that by the emeraldine salt form of polyaniline may suggest high conductivity of the emeraldine salt form would contribute to the electrocatalytic oxidation of DMcT by the emeraldine polyaniline.

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