Electrocatalytic Activation of Organosulfur Redox Reactions by Metal Nanoparticles

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(Received September 2, 2002; CL-020745)

The effect of Ag nanoparticles on the redox reactions of organosulfur compounds was investigated. Adding the nanoparticles to 2,5-dimercapto-1,3,4-thiadiazole (DMcT)-polyaniline composites, redox activity of the composites was enhanced due to electrocatalytic activation of DMcT by the nanoparticles. It was expected that adsorption of DMcT to the nanoparticles would make a positive contribution to the electrocatalysis.

Recently organosulfur compounds with two or more thiol groups (-SH) have been attracting considerable attention as an alternative cathode material for lithium metal oxides in lithium secondary batteries due to high capacity.[1,2] However, practical application of organosulfur compounds to batteries requires acceleration of the sluggish kinetics of organosulfur redox reactions. Oyama et al. have reported that conducting polymer polyaniline (PAn) is capable of electrocatalytically accelerating a slow redox reaction of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and DMcT-PAn composite was proposed as a cathode material for lithium rechargeable batteries.[3–5]

To develop organosulfur-based cathode materials, in this study metal nanoparticles were employed as an electrocatalyst to further activate the redox reaction of DMcT. Because of large surface area and a high ratio of surface-to-bulk atoms, metal nanoparticles have shown enhanced catalytic activity compared to corresponding bulk metals. Especially, it has been reported that metal nanoparticles imbedded in conducting polymer matrix serve as an efficient electrocatalyst toward oxidation and reduction reactions of various redox species.[6–8] In this study it was found that addition of Ag nanoparticles to DMcT-PAn composites successfully enhanced the redox activity through electrocatalytic activation of the DMcT redox reactions.

Partially oxidized, deprotonated PAn and DMcT were obtained from Nitto Denko Co. (Japan) and Aldrich, respectively. A colloidal Ag (0.9 wt%) in diacetyl alcohol containing citric acid (2 wt%) to stabilize the nanoparticles was given by Catalysts & Chemical Ind. (Japan). An average diameter of the nanoparticle was 17 nm.

To prepare DMcT-PAn composite electrodes which contained Ag nanoparticles, the nanoparticle solution was first added to *N*-methyl-2-pyrrolidinone (NMP). To the nanoparticle-containing NMP solution were then dissolved 16 mg DMcT and 8 mg PAn successively, and stirred for 24 h. The composite solution was applied onto a glassy carbon (GC) electrode surface and dried under vacuum for 4 h at room temperature.

Electrochemical measurements were conducted using a conventional three-electrode cell with a Ag/Ag$^+$ reference electrode (0.05 M $AgClO_4$) and Pt spiral counter electrode.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCA-3400 electron spectrometer (Shimadzu Co., Japan). Uv/vis spectra were recorded using a spectrophotometer (U-Best-55, JASCO, Japan).

Figure 1a shows a typical cyclic voltammogram of a DMcT-PAn composite film on a GC electrode in 0.1 M $LiClO_4$/propylene carbonate solution (10th scan, steady-state). While DMcT dissolved in PC gives oxidation and reduction current peaks at +0.35 V and −1.2 V vs Ag/Ag$^+$, respectively, at a bare GC electrode, both the oxidation and reduction currents of the composite electrode were larger than that of a PAn film-coated electrode at the same loaded amount in a whole potential region where PAn showed its electrochemical activity, indicating electrocatalytic activation of the oxidation and reduction of DMcT by PAn.[3]

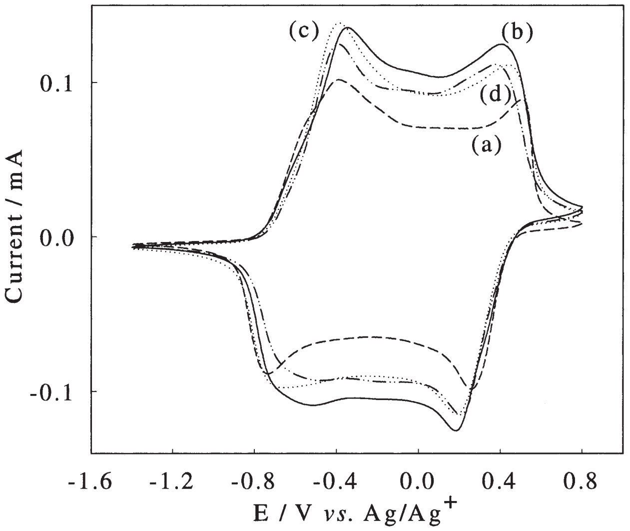

Figure 1. Cyclic voltammograms of DMcT-PAn composite films (2:1 by weight) containing Ag nanoparticles. The content of the nanoparticles: (a) (dash line) 0, (b) (solid line) 5, (c) (dot line) 10, and (d) (dach-dot-dot line) 20 wt%. The amount of DMcT-PAn in the film: 0.42 mg/cm^2.

Inclusion of Ag nanoparticles further enhanced the redox activity of DMcT-PAn composites, the extent of which was dependent on the content of the nanoparticles in the composites. Addition of 5 wt% Ag nanoparticles to the composite induced large increase in both the oxidation and reduction current with a small shift in the peak potentials as shown in Figure 1b. Similar current increase was not observed when the nanoparticles were added to PAn films. Further addition of the nanoparticles to 10 wt% and higher to DMcT-PAn composites, however, resulted in the current decrease, although the current magnitude remained still higher than that of the composite electrode without the nanoparticles (Figure 1c and 1d). The results shown in Figure 1 indicate the presence of an optimum nanoparticle content to obtain the highest redox activity of DMcT-PAn composite electrodes. It is worth noting that redox activity of Ag nanoparticles was totally absent from the steady-state voltammograms of DMcT-PAn-Ag composite electrodes.

The observed current enhancement was ascribed to the improved efficiency of DMcT utilization in the composites due to electrocatalytic activation of the DMcT redox reactions in the presence of the nanoparticles. It has been observed that metal nanoparticles dispersed in conducting polymer matrices show high electrocatalytic activity toward various redox reactions.[6–8] Nanometer size imparts high surface area to metal nanoparticles for adsorption of reactants, leading to enhanced electrocatalytic activity.[9]

It is well known that thiol compounds show high tendency to be adsorbed onto metal surfaces including Ag.[10] XPS experiments were carried out to confirm adsorption of DMcT onto Ag nanoparticles. Figure 2 shows XPS spectra in the sulfur 2p region for DMcT (Figure 2a) and a DMcT-Ag nanoparticle composite (Figure 2b). A sulfur 2p peak at a binding energy of 162.0 eV observed for the DMcT-Ag composite system was characteristics of thiolate species adsorbed on metals such as Ag.[11] The peak at 162.0 eV was also observed for DMcT-Ag nanoparticle system with PAn. Additionally, the XPS spectrum in the silver 3d region obtained for the DMcT-Ag composite electrode indicated that Ag nanoparticles were not fully oxidized during a potential cycling but remained mainly as a metal state.

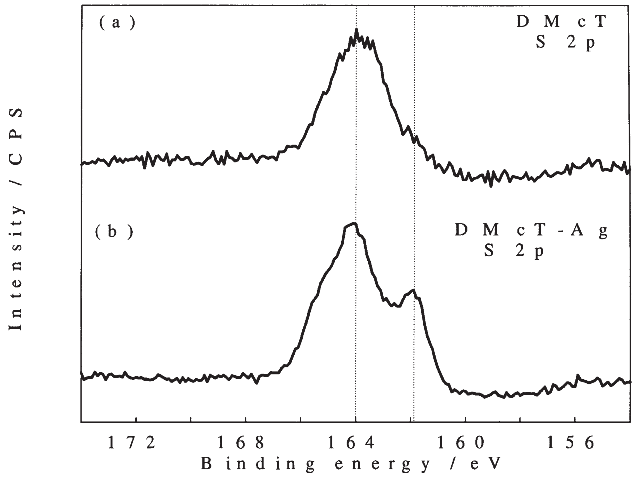

Figure 2. XPS spectra obtained for (a) DMcT and (b) DMcT + 10 wt% Ag particles in the S 2p region.

Furthermore, interaction between DMcT and Ag nanoparticles was examined by UV–vis spectroscopy. It is well-known that Ag nanoparticles show characteristic plasmon absorption peaks at $\lambda_{max} = 430$ and 700 nm.[12] Adding 0.25 mM DMcT to the nanoparticle solution, the both peaks disappeared. The observed spectral change was ascribable to a dumping effect on the plasmon absorptions of the nanoparticles due to the strong adsorption of DMcT to the nanoparticles.[13] It is also appreciated that an absorption peak of DMcT at $\lambda_{max} = 360$ nm underwent a blue shift in the presence of the nanoparticles.

Enhanced redox activity of DMcT-PAn composite electrodes was attained by adding metal nanoparticles to the composites. Since the use of Ag plate as a current collector failed to improve battery performance of DMcT-PAn composite, nanometer size of metal particles should be essential for the observed enhanced redox activity of the composite electrodes. It was expected that adsorption of DMcT onto the nanoparticle surface made a positive contribution to electrocatalytic reactivity. In DMcT-PAn-Ag composites, PAn is expected to play an important role in the electrocatalysis by Ag nanoparticles, because high electrocatalytic activity observed in Figure 1b was attained only in the presence of PAn matrix. The further study is currently under way to investigate a mechanism of the electrocatalysis in DMcT-PAn-Ag composites.

It has been reported that addition of a conductive material improved kinetic properties of DMcT-PAn composite cathodes.[5] Therefore, conductivity increase due to the addition of metal nanoparticles could be an origin of the enhanced redox activity. However, the current decrease with increasing the nanoparticle content from 5 to 20 wt% in Figure 1 would render a contribution from the conductivity increase less important than the electrocatalysis in the present system. The reason for the decrease in the redox current at a higher nanoparticle content is not clear.

The authors would like to thank Dr. T. Ohasaka at Tokyo Institute of Technology for useful discussion. This work was partially supported by Grant-in-Aid for Scientific Research (B) (No. 13450350 for OH) from Japan Society for the Promotion of Science and by Oosaka Community Foundation for NO.

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