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Roles of Metal Nanoparticles on Organosulfur-Conducting Polymer Composites for Lithium Battery with High Energy Density

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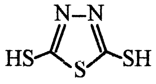
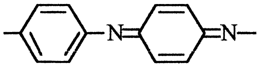
Summary: Ag nanoparticles were added to DMcT-PAn composites to improve charge-discharge performance of the composites as a cathode material for lithium rechargeable batteries. Addition of Ag nanoparticles successfully enhanced the redox activity of the composites, possibly due to electrocatalytic activity of the nanoparticles. Increased conductivity of the composite films could be another possible origin for the enhanced redox activity. UV/vis spectroscopic analysis suggested strong interactions between DMcT and nanoparticles, while only weak interactions were observed between PAn and nanoparticles. XPS measurements further confirmed the interactions between DMcT and Ag nanoparticles based on a signal indicative of a silver-sulfur bond.

Introduction

High energy density attainable only with a lithium battery is mainly contributed from an anodic material such as lithium ion intercalating carbon materials, theoretical capacity of which is 372Ah/kg. Therefore, cathode materials possessing higher capacity than 137Ah/kg of lithium cobalt oxide ($LiCoO_2$), which is employed in a commercially available lithium-ion battery, are in great demand. Among various inorganic and organic compounds now examined as a cathode active material is a series of organosulfur compounds with two or more thiol groups (-SH).[1-3] Theoretical capacity of, for example, 2,5-dimercapto-1,3,4-thiadiazole (DMcT), which has two thiol groups, is 362 Ah/kg, which far exceeds the capacity of $LiCoO_2$. However, although a redox conversion between thiol and disulfide is a chemically reversible process, the kinetics of the redox reaction is too slow at room temperature to be used in a lithium battery.[2]


DMcT


PAn

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Previously we have shown that conducting polymer polyaniline (PAn) accelerates the sluggish kinetics of the redox reactions of DMcT.[3-8] It was also found that a Cu-DMcT complex on copper current collector enhanced the charge-transfer kinetics.[9-12] In the present study, Ag nanoparticles[13-15] are added to the DMcT-PAn composites as an electrocatalyst in an attempt to further activate the organosulfur redox reactions, and the positive effects of metal nanoparticle addition on electrochemical activity of organosulfur-based composite cathode materials are confirmed.

Experimental

4.1wt% Ag nanoparticles dispersed in water was obtained from Catalysts & Chemicals Ind. Co. (Japan). To prepare DMcT-PAn composite films containing nanoparticles, the nanoparticle sol solution was added to an *N*-methyl-2-pyrrolidinone (NMP, Aldrich) solution dissolved with DMcT (Tokyo Kasei Co., Japan) and PAn (Nitto Denko Co., Japan). The solution obtained was then cast on electrode surfaces and dried. Typical thickness of the composite films thus prepared was approximately 1 μm.

Electrochemical measurements were conducted using a conventional three-electrode configuration. A glassy carbon electrode (area : $0.25cm^2$) coated with a composite film was used as a working electrode. A Pt spiral and Ag wire were used as the counter and pseudo-reference electrode, respectively. Electrolyte solution for the electrochemical measurements was a propylene carbonate (PC) solution dissolved with 0.1M $LiClO_4$.

Scanning tunneling microscopy (STM) observations were carried out using a Nanoscope III STM apparatus (Digital Instruments). UV/vis absorption spectra were recorded using a UN/Vis spectrophotometer (Shimadzu, Model UV-160). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCA-3400 electron spectrometer (Shimadzu Co., Japan).

Results and Discussion

1. Electrochemistry of DMcT-PAn composites containing Ag nanoparticles

STM measurements gave clear images of unaggregated Ag nanoparticles on a HOPG surface and an average diameter of 15nm was estimated from the STM images. STM images for surface morphology of DMcT-PAn composite films containing <5wt% of Ag nanoparticles did not clearly show the presence of nanoparticles on the surface, indicating nanoparticles were embedded in the composite films. However, at a higher content above 10wt%, it appeared that some of the nanoparticles aggregated on the composite film surface.

Electrochemistry of DMcT-PAn composites with Ag nanoparticles was examined using cyclic voltammetry and AC impedance measurements. As seen from cyclic voltammograms shown in Figure 1, addition of Ag nanoparticles lead to enhancement of the redox activity of the DMcT-PAn composite in a whole potential range between –0.8 and +0.4V vs. Ag/Ag^+, while Ag nanoparticles solely applied to electrode surfaces gave a sharp oxidation wave in a potential range between 0 and +0.2V vs. Ag/Ag^+. Electrocatalytic activity of Ag nanoparticles[13] and increased conductivity of the composite films are expected as a possible origin for the enhanced redox activity of the DMcT-PAn composites.

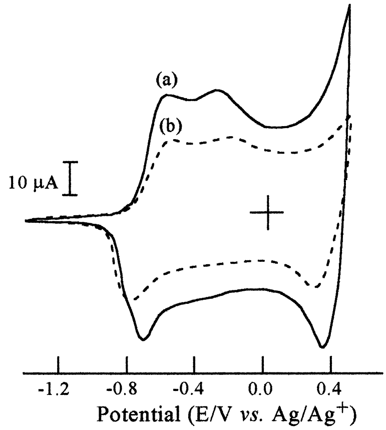


Figure 1. Cyclic voltammograms of DMcT-PAn composite films on glassy carbon. Films (a) containing 5wt% Ag nanoparticles and (b) without nanoparticles. Electrolyte solution : 0.1M $LiClO_4$/PC.

The redox activity of the composites depended on the amount of Ag nanoparticles added to composites. Although initially addition of Ag nanoparticles brought about the current increase, further addition resulted in current decrease. The maximum enhancement of the redox current was observed when 5wt% of nanoparticles was added (Figure 1a). The current decrease observed at a high Ag nanoparticle content may be attributed to the aggregation of the nanoparticles observed by STM measurements. Conductivity of composite films measured by four-probe method showed similar dependence on the Ag nanoparticle content, the highest conductivity being obtained at nanoparticle contents between 5-10wt%. However, interfacial charge-transfer resistance estimated by AC-impedance measurements was observed to decrease monotonically with increasing the content of nanoparticles.

2. UV/vis spectroscopic measurements for the interactions among the components

To further examine the enhanced redox activity of DMcT-PAn composites induced by the addition of Ag nanoparticles, UV/vis spectroscopic measurements were carried out. Ag nanoparticles, which were stabilized and well-dispersed in NMP solutions, showed a characteristic surface plasmon bands at λ_{max} = 430nm and 680nm as shown in Figure 2a. When a DMcT/NMP solution was added to Ag nanoparticle/NMP solution, the surface plasmon bands of Ag nanoparticles disappeared (Figure 2b). It was also found that abosbances at λ = 270nm and 360nm due to DMcT in thiol and thiolate ($-S^-$), respectively,[7] were smaller in the presence of Ag nanoparticles compared to those without nanoparticles. These changes in the spectrum suggested the existence of strong interactions between DMcT and Ag nanoparticles in NMP solutions. It can be considered that bonding of sulfur atom to Ag nanoparticle induced a dumping effect on surface plasmon absorption.[16]

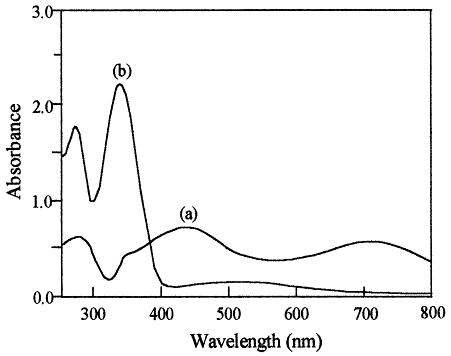


Figure 2. Uv/vis spectra of NMP solutions (a) containing 80μM Ag nanoparticles and (b) 0.25mM DMcT and 80μM Ag nanoparticles.

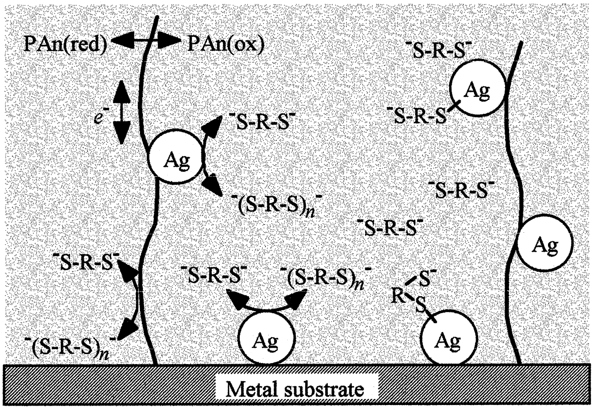
Similar spectroscopic experiments were carried out to examine interactions between PAn and Ag nanoparticles. A PAn/NMP solution was blue in color and showed absorption bands at λ_{max} = 340nm and 640nm (not shown), indicating PAn employed in this study was partially oxidized. Addition of a Ag nanoparticle/NMP solution to PAn/NMP induced only small blue shift and increase in the magnitude of the absorption band at λ_{max} = 640nm. Furthermore, the surface plasmon absorption peaks of Ag nanoparticles were clearly observed for the mixed solution. These results implied in the absence of strong interactions between PAn and Ag nanoparticles. Recent studies using a model compound for PAn, 2,5-diphenyl-p-phenylenediamine in different oxidation states, however, suggested the presence of electrochemical interactions between PAn and Ag nanoparticles.[17]

3. Chemisorption of the thiol group on Ag nanoparticles

One of the diagnostic procedures for chemical interactions between DMcT and Ag nanoparticles is to examine XPS spectra for binding energy of Ag(3d) and S(2*p*). Although detailed analysis of XPS for the DMcT-PAn composite film containing Ag nanoparticles is not described in this report, briefly an XPS spectrum recorded over S(2p) binding energy region gave a signal which was indicative of sulfur species involved in a silver-metal bond. The XPS spectrum also indicated the presence of a disulfide bond, i.e., DMcT being partially oxidized to poly(DMcT). A high-resolution curve-fit Ag(3d) spectrum revealed peaks assigned to Ag(0) (70%) and Ag(I) (30%).

Conclusion

The effects of metal nanoparticle addition on the redox reactions of organosulfur-conducting polymer composites were investigated in this study. Adding 5wt% Ag nanoparticles, DMcT-PAn composite film-coated electrodes showed the enhanced redox



Scheme 1. Electron-flows in DMcT-PAn composite containing Ag nanoparticles. ($^-$S-R-S$^-$) and $^-$(S-R-S)n^- represent DMcT and poly(DMcT), respectively.

activity, possibly due to electrocatalytic activity of the nanoparticles and/or increased conductivity of the composite films. However, the composite film electrode containing more than 10wt% nanoparticle showed the decreased electroactivity. We expect that metal nanoparticles are capable of activating the redox reactions of DMcT in the composites, leading to the enhanced redox activity (Scheme 1).

We have obtained similar positive effects on the redox activity of the DMcT-PAn composites by adding other metal nanoparticles such as Pd and carbon nanoparticles.[18] Organosulfur-conducting polymer composites containing metal nanoparticles as an electrocatalyst will be of practical use as a cathode material for lithium rechargeable batteris.

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