

Short communication

Enhanced redox processes of disulfides with partially *N*-methylated polyaniline¹

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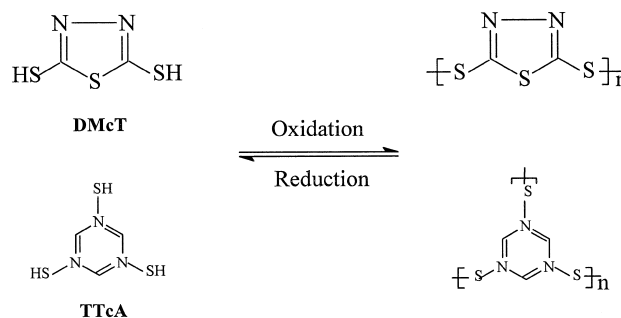
Abstract

Partially *N*-methylated polyaniline (NMPAn) is used instead of polyaniline (PAn) to make a composite with organodisulfides for cathodes of lithium secondary batteries. NMPAn displays a better electrocatalytic effect on the redox processes of organodisulfides than PAn. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Organodisulfides; *N*-methylated polyaniline; Electrocatalytic effect

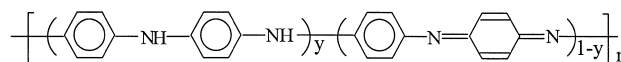
1. Introduction

Organodisulfides such as 2,5-dimercaptothiadiazole (DMcT) and 1,3,5-trithiocyanuric acid (TTcA) are of electrochemical interest due to the reversible S–S oxidation–reduction reactions (Scheme 1). DMcT and TTcA are reported to have a theoretical energy density as high as 990 and 1280 W h kg^{−1}, respectively. Thus, they are attractive electrode active materials [1–5]. Unfortunately, the redox processes of these organodisulfides, usually very slow at room temperature, must be catalyzed in order to find practical application at room temperature. It has been reported as early as in the 1960s that basic substances like amines were good catalysts for the redox processes of organodisulfides [6,7]. Recent work of Naoi et al. [8] added new information on the above catalytic effect. They found that the electrode kinetics of DMcT were greatly enhanced by polyaniline, a typical intrinsically conducting polymer whose structure is shown in Scheme 2. The batteries using polyaniline/DMcT composite as cathode materials have exhibited a specific energy of over 600 W h kg^{−1} cathode. Since *N*-substituted polyaniline derivatives such as



Scheme 1. Structure of DMcT and TTcA and the reversible redox reaction between DMcT or TTcA and their disulfides.

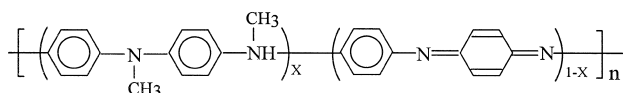
poly(*N*-methyl)aniline and poly(*N,N'*-dimethyl)aniline exerted an insignificant catalytic effect on redox processes of DMcT, it was therefore accepted that the capability of amine to form adducts with DMcT was important for its catalytic effect [8–12]. In this paper, we report that the catalytic effect of polyaniline does not decrease monotonously with an increasing degree of *N*-methylation. Moreover, in case of a suitable adduct ratio, moderately



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Scheme 2. Structure of polyaniline, *y* is between 0 and 1.



Scheme 3. Structure of partially *N*-methylated polyaniline, x is between 0.1 and 0.8.

N-methylated polyaniline can improve further the catalytic effect to DMcT.

2. Experimental

2.1. Chemicals

DMcT was recrystallized from THF/*n*-hexane solution. TTcA was purchased from Aldrich and used as received. Propylene carbonate (PC) was provided by Aldrich; it was dried over CaF₂ and distilled under reduced pressure prior to use. Lithium perchlorate (LiClO₄) of analytical purity was dried at 150°C in vacuum for 72 h and stored in a dry box under an argon atmosphere. Lithium foil was of analytical purity and was also stored in a dry box under an argon atmosphere.

2.2. Preparation of de-doped polyaniline and its completely reduced form

Polyaniline in doped form was obtained by polymerizing aniline in 1 M HCl/H₂O₂/Fe²⁺ system as described in a previous publication [13]; it was subsequently treated with 0.5 M ammonia solution to obtain de-doped polyaniline. The de-doped polyaniline was reduced by phenylhydrazine in ethanol to obtain completely reduced polyaniline (Leucoemeraldine, as indicated from its electronic spectra).

2.3. Preparation of *N*-methylated polyaniline

A total of 1.2 g of sodium was dissolved in 200 ml of dimethyl-sulfoxide at 40°C; 2 g of leucoemeraldine was added with stirring, and then 1.4 g (or 0.7 g) of iodomethane was added. The reaction was allowed to continue for 24 h at 40°C until a blue precipitate developed upon the addition of excess methanol. The precipitate was washed thoroughly with, successively, methanol, 1 M HCl, 1 M ammonia solution, water, and acetone. It was then

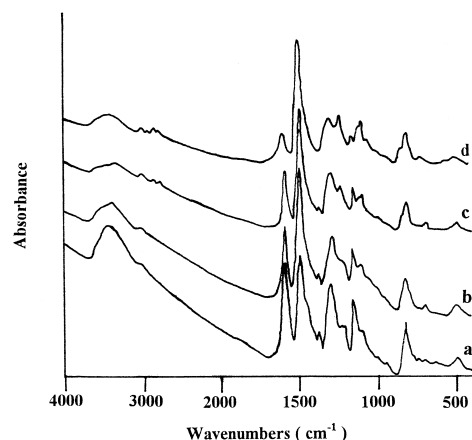


Fig. 1. FT-IR spectra of (a) PAN; NMPAn with the *N*-methylation ratio of (b) 35.8%; (c) 79.4%; (d) 100%.

dried under vacuum at 50°C. The product was denoted as *N*-methylated polyaniline (NMPAn) [14].

2.4. Measurements

Electrochemical tests were performed in a three-compartment electrochemical cell at room temperature. Lithium foil was used for both the counter and the reference electrodes, whereas bare platinum, PAN cast on platinum, DMcT cast on platinum, or PAN/DMcT composite cast on platinum was used as the corresponding working electrode. The supporting electrolyte was propylene carbonate that contained 1 M LiClO₄.

PAN or NMPAn was co-dissolved in *N*-methylpyrrolidinone with a suitable molar ratio of DMcT. The surface of the film cast from the above solution was vacuum deposited with gold prior to taking SEM images.

FT-IR spectra of PAN and its *N*-methylated derivatives were obtained from their KBr pellets. All the conductivities were measured by the standard four-probe method.

3. Results and discussion

The structure of NMPAn is shown in Scheme 3; x is between 0.1 and 0.8, as calculated from elemental analysis results. The major differences in the FT-IR spectra of PAN and NMPAn are observed in Fig. 1. The enhancing absorptional bands around 3000 to 2800 cm⁻¹ are the characteristic bands of the -CH₃ group. As listed in Table 1, the peaks around 1590 cm⁻¹ from the quinoid ring (Q) and

Table 1

FT-IR peak position of quinoid, benzenoid and imine structure in PAN and several kinds of NMPAn

Peak position (cm ⁻¹)	PAN	NMPAn ($x = 0.36$)	NMPAn ($x = 0.79$)	NMPAn ($x = 1.0$)	Group
I	1589	1595	1595	1597	quinoid
II	1496	1499	1500	1499	benzenoid
III	1167	1168	1167	1171	imine

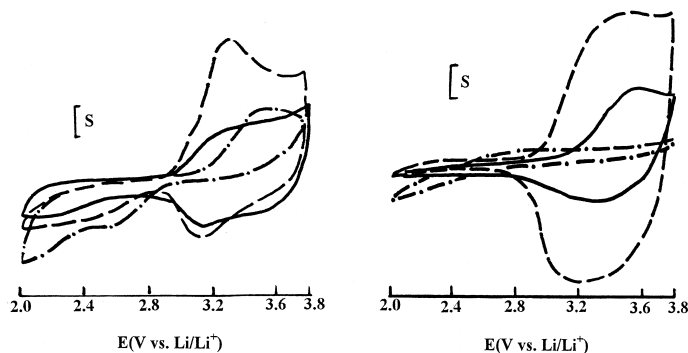


Fig. 2. CV curves of NMPAn (—), DMcT (---) ($S = 10 \mu\text{A}$) and NMPAn/DMcT adduct (— · —) ($S = 25 \mu\text{A}$) (Fig. 1a) and NMPAn (—), TTcA (---) and NMPAn/TTcA adduct (— · —) ($S = 25 \mu\text{A}$) (Fig. 1b) on Pt electrode in PC/1 M LiClO₄ solution at a scan rate of 12 mV s^{-1} , NMPAn of $x = 0.79$ was used, and the molar ratio of NMPAn/DMcT or TTcA is 1/0.8.

1500 cm^{-1} from the benzenoid ring (B) are shifted gradually with increasing of methyl substitution. Moreover, corresponding to the increase of *N*-methylation ratio, the relative intensity of the absorption band of the quinoid ring to the benzenoid ring decreases gradually, and the absorption band near 1170 cm^{-1} characteristic of the imine group becomes weaker. All these changes are consistent with nitrogen substitution of the PAn [14,15].

Cyclic voltammograms (CV) of DMcT, NMPAn ($x = 0.79$) and their composite (NMPAn/DMcT = 1/0.8) in PC/1 M LiClO₄ solution are given in Fig. 2. The CV curve for DMcT has an anodic–cathodic peak separation of more than 800 mV, and both the anodic and cathodic peak currents are very small. This suggests that the redox processes of DMcT are slow under these conditions. The anodic and cathodic peak currents are much larger for the DMcT/NMPAn composite at the same scan rate, and the

peak separation is reduced to about 200 mV. Thus, the electrode kinetics of DMcT are accelerated remarkably. Taking the area enclosed in the CV curve as the capacity of the corresponding cathode material, it is found that the capacity of the NMPAn/DMcT adduct is much higher than that of DMcT and NMPAn together, while the capacity of PAn/DMcT adduct is lower than that of NMPAn/DMcT complex at the same ratio. Thus, the redox processes of DMcT are further improved by employing NMPAn instead of parent PAn. Similar phenomena are observed when NMPAn ($x = 0.36$) is used.

The CV curves of TTcA, NMPAn and their composite (NMPAn/TTcA = 1/0.8) in PC/1 M LiClO₄ solution are shown in Fig. 2b. Though TTcA possesses a much higher energy density than DMcT at elevated temperature, it displays slow redox processes similar to DMcT at room temperature. As described for the DMcT system, pro-

Table 2

Electrical conductivities of polyaniline doped by DMcT or TTcA

Molar ratio (PAn to DMcT or TTcA)	1/0.2	1/0.5	1/0.8	1/1	1/1.2
Conductivity of PAn/DMcT (S cm^{-1})	1.2×10^{-4}	1.1×10^{-3}	3.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}
Conductivity of PAn/TTcA (S cm^{-1})	1.4×10^{-6}	4.4×10^{-6}	3.1×10^{-6}	5.2×10^{-6}	4.5×10^{-6}

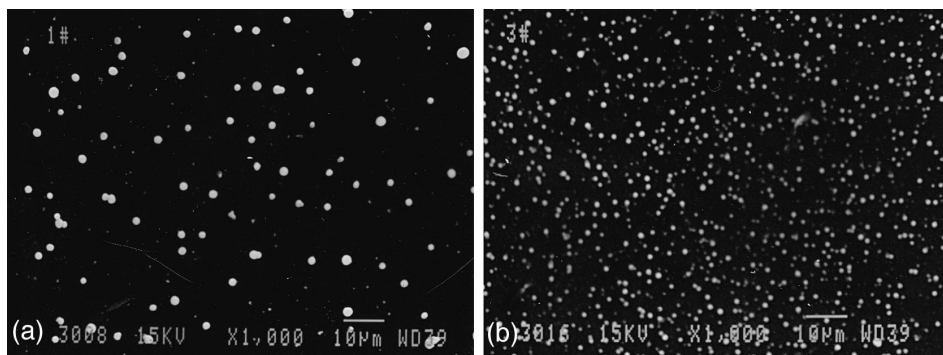


Fig. 3. Electron micrographs of PAN/DMcT (a) and NMPAn/DMcT (b) composite film, the molar ratio of PAN(NMPAn)/DMcT is 1/0.8.

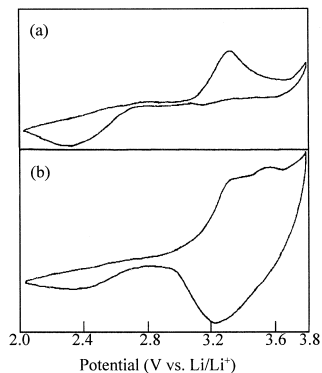


Fig. 4. Cyclic voltammograms of DMcT in PC/1 M LiClO₄ solution on NMPAn ($x = 0.36$) coated Pt electrode at a scan rate of 80 mV s⁻¹, (a) first cycle, (b) after 300 cycles.

nounced electrocatalytic phenomena are observed when PAN (results not shown) or NMPAN is used together with TTcA. Nevertheless, no significant differences in capacity is found irrespective of whether the catalyst is PAN or NMPAN. Moreover, similar CV curves are obtained when different NMPAN ($x = 0.36$) are used. This is explained by the different interaction between thiols and the catalyst (PAN or NMPAN) in the adduct. It is found from Table 2 that DMcT can dope PAN to give an electrical conductivity as high as 10⁻³ S cm⁻¹; this indicates that PAN has a very strong interaction with DMcT. In fact, a precipitate exists when PAN/DMcT is dispersed in *N*-methylpyrrolidinone (NMP). By contrast, this kind of interaction is depressed in the NMPAN/DMcT adduct as reflected by the low electrical conductivity of the corresponding composite (below 10⁻⁶ S cm⁻¹). This adduct is well dissolved in NMP; therefore, molecular level contact between DMcT and the catalyst is enhanced and leads to an improved catalytic effect. This can be verified from the electron micrographs of PAN (or NMPAN)/DMcT composite films shown in Fig. 3. The white dots in the images are DMcT molecular aggregates. The domain size is smaller in NMPAN than in PAN, and suggests that the dispersion of DMcT in NMPAN is better than in PAN. For the TTcA system, both PAN/TTcA and NMPAN/TTcA adducts display electrical conductivities below 10⁻⁶ S cm⁻¹, and thus, no significant difference in the catalytic effect is observed.

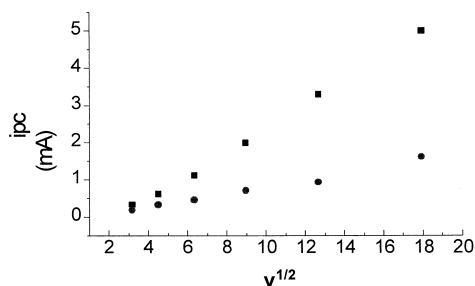
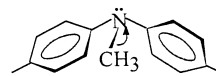


Fig. 5. i_{pc} vs. $v^{1/2}$ of (●) first several cycles, (■) after 300 cycles of cyclic voltammograms of DMcT in PC/1 M LiClO₄ solution on NMPAN ($x = 0.36$) coated Pt electrode.



Scheme 4. Electron repulsive effect of methyl group in NMPAN.

The cyclic voltammograms of DMcT in PC/1 M LiClO₄ solution on a NMPAN ($x = 0.36$) coated Pt electrode are presented in Fig. 4. During the first several cycles, the CV curves of DMcT are similar to those for a bare Pt electrode. The CV curve changes remarkably after 300 cycles; however, an anodic peak appears at around 3.2 V and both the cathodic and the anodic peak currents increase continuously. After 300 cycles, the curves are similar to that for the NMPAN/DMcT composite; this implies that DMcT permeates into the NMPAN film and the adduct is formed during the scanning. The scan rate (v) dependence of the i_{pc} (cathodic peak current) for the first several cycles and after 300 cycles is shown in Fig. 5. The $i_{pc}-v^{1/2}$ curve of the first several cycles deviates and is below the linear one. Thus, there is a slow electrode reaction of DMcT. After 300 cycles, the $i_{pc}-v^{1/2}$ curve also deviates but is above the linear one, and this indicates that DMcT is absorbed on or has penetrated into the NMPAN film.

Another explanation based on the difference of basicity between PAN and NMPAN is suggested. The basicity of NMPAN is stronger than PAN due to the electron-repulsive effect of the methyl group (see Scheme 4). Since thiols are acidic substances, formation of the organic amine–thiols adduct becomes easier if the basicity of organic amine was increased. Therefore, NMPAN displays better electrocatalytic effect to the redox processes of DMcT than parent PAN. This result is consistent with the earlier report in that alkyl amine is a better catalyst than aryl amine for the chemical oxidation of thiols [7].

4. Conclusions

Partially *N*-methylated polyaniline (NMPAN) was used as electrocatalyst for the redox reaction of disulfides. SEM images showed that NMPAN and DMcT produced better composite than PAN and DMcT. The electrochemical study indicated that the redox process of disulfides was enhanced remarkably. According to the basicity difference between NMPAN and PAN, NMPAN may be a better electrocatalyst than PAN.

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