

Improved electrochemical redox performance of 2,5-dimercapto-1,3,4-thiadiazole by poly(3-methoxythiophene)

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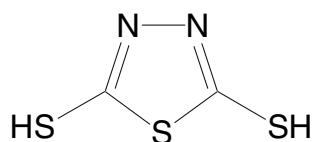
Abstract

High electrocatalytic activity of an electropolymerized film of poly(3-methoxythiophene) (PMOT) is reported toward the redox reaction of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) as a promising cathode material for the lithium ion battery. Cyclic voltammetry showed improved electrochemical performance of DMcT on PMOT-coated Pt electrode, indicating accelerated redox kinetics. Moreover, charge-discharge tests exhibited higher discharge capacity and slower capacity fading of the PMOT-doped DMcT composite cathode compared with pure DMcT.

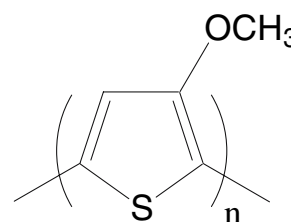
1. Introduction

Organodisulfides such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT, Structure 1) with two thiol groups can be polymerized and depolymerized reversibly during their electrochemical redox process. As a promising cathode material for the lithium ion battery, DMcT has attracted much attention, due to its high stability to temperature and high theoretical energy density (1070 Wh kg⁻¹) than other lithium metal oxides such as LiCoO₂, LiNiO₂ and LiMn₂O₄. Unfortunately, DMcT shows slow redox kinetics and poor electrical conductivity at room temperature. Therefore it requires accelerated redox kinetics by electrocatalysis for commercial application [1, 2]. Recently, it has been reported that the redox performance of DMcT can be improved by electrocatalysts such as polyaniline (PAn) and polypyrrol (PPy). For example, Visco et al. [3] and Oyama et al. [4] reported that PAn can serve as an electrocatalyst to improve the

redox kinetics of DMcT at room temperature. Park also reported that the charge-discharge transfer kinetics of DMcT can be enhanced by Ag and Pd nanoparticles [5–7]. As a conducting polymer, poly(3-methoxythiophene) (PMOT, Structure 2) possesses excellent chemical and physical stability, high redox potential and high electronic conductivity. In addition, as an electron donating group, the alkoxy substituted in the 3- and 4-positions can prevent the overoxidation of conducting polymer at higher potential, lower the oxidation potential of the monomer and stabilize the oxidation form of the polymer [8, 9]. Therefore, we were encouraged to study the electrocatalytic effect of PMOT on the redox process of DMcT. In this study, we investigated the further electrochemical improvement of DMcT by adding an appropriate quantity of PMOT. As a conducting polymer of thiophene derivatives, PMOT shows



Structure 1.



Structure 2.

a significant electrocatalytic effect on the redox process of DMcT.

2. Experimental

2.1. Reagents

3-Methoxythiophene (MOT) was purchased from Fluka Company and distilled prior to use. DMcT was obtained from Aldrich Chemical Company and recrystallized from tetrahydrofuran (THF)/*n*-hexane solution. Other chemicals of analytical grade were obtained as reagents and used without further purification.

2.2. Preparation of PMOT-coated Pt electrodes

PMOT was electropolymerized on a Pt electrode in 0.1 mol l⁻¹ LiClO₄/0.1 mol l⁻¹ MOT/AN solution as described in the literature [10]. Prior to each use, oxygen was removed from solution using pure nitrogen gas, and the polymerization potential was maintained at 2 V. The polymer was removed from the Pt electrode and dried under vacuum at room temperature. The obtained polymer was then dissolved in *N*-methyl-2-pyrrolidone (NMP); the slurry was coated on a Pt foil and subsequently dried under vacuum. Finally a PMOT-coated Pt electrode was obtained.

2.3. Cyclic voltammetry

Cyclic voltammetry was performed using a potentiostat (AUTOLAB-PGSTAT30, Switzerland Metrohm Ltd.) at room temperature. Measurements were carried out in a three-electrode configuration in which either the Pt foil or PMOT-coated Pt foil was used as a working electrode, while a Pt foil and a Ag/AgCl as counter and reference electrodes, respectively. All the experiments were performed in 0.1 mol l⁻¹ LiClO₄/5 mmol l⁻¹ DMcT/AN solution and the oxygen was removed from the solution using nitrogen gas for 30 min prior to each measurement.

2.4. Fabrication and measurement of experimental cells

The charge-discharge experiments were performed in an electrolyte of 1 mol l⁻¹ LiClO₄ EC/DEC (1:1, volume ratio) at 20 °C. PMOT was obtained by electropolymerization as described above. Either DMcT or PMOT/DMcT mixture was dissolved in NMP, and then cast on the Pt foil as a cathode after drying under vacuum at 80 °C for 2 h. The amount of PMOT in PMOT-doped DMcT was controlled at 3 wt%, the thickness and area of active material (~1.4 g cm⁻³) were about 40 μm and 2 cm², respectively. Lithium foils were used as both the counter and reference electrodes. Test cells were fabricated in a glove box under argon. The charge and discharge current were controlled at 0.2 mA cm⁻².

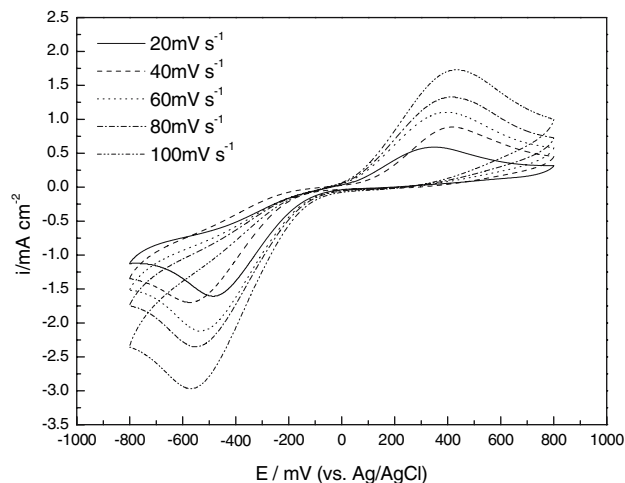
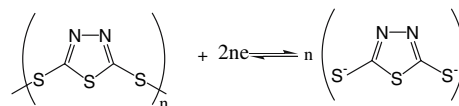


Fig. 1. Cyclic voltammograms of 5 mmol l⁻¹ DMcT on bare Pt electrode in 0.1 mol l⁻¹ LiClO₄/AN solution at different scan rate.

3. Results and discussion

Figure 1 shows a cyclic voltammogram (CV) of 5 mmol l⁻¹ DMcT on bare Pt in 0.1 mol l⁻¹ LiClO₄/AN solution. The oxidative and reductive current peaks were observed at 0.36 V and -0.49 V (vs. Ag/AgCl) at a scan rate of 20 mV s⁻¹, and the corresponding peak currents were 0.35 mA cm⁻² and -1.26 mA cm⁻², respectively. Generally, the peak separation between the oxidative and reductive current peaks was related to the electrochemical polarization. It can be seen that the peak current and peak separation increased with increase in scan rate. The electrochemical reaction during the redox process is depicted as Scheme 1. The polymeric disulphide DMcT_n was reduced to form dithiolate monomer DMcT²⁻ which can re-polymerize to poly-organodisulphide during the reversible oxidation process.

In our experiment, PMOT was used as an electrocatalyst to improve the redox activity of DMcT, and typical CV curves of 5 mmol l⁻¹ DMcT on a PMOT-coated Pt electrode in 0.1 mol l⁻¹ LiClO₄/AN are shown in Figure 2. The thickness of the PMOT layer is about 15 μm. Compared with Figure 1, it can be seen that the CV curves of the DMcT on PMOT-coated Pt electrode showed more symmetry than that on bare Pt. This phenomenon suggests the improved reversibility of DMcT on the PMOT surface. The peak current and peak separation parameters collected from CV curves at different scan rates are shown in Figure 3. The enhanced anodic peak current on the PMOT-coated Pt electrode



Scheme 1. Electrochemical reaction of DMcT.

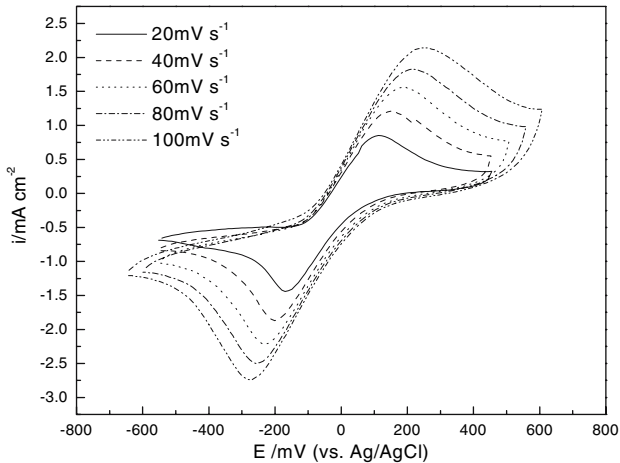


Fig. 2. Cyclic voltammograms of 5 mmol l^{-1} DMcT on PMOT-coated Pt electrode in 0.1 mol l^{-1} LiClO_4/AN at different scan rate.

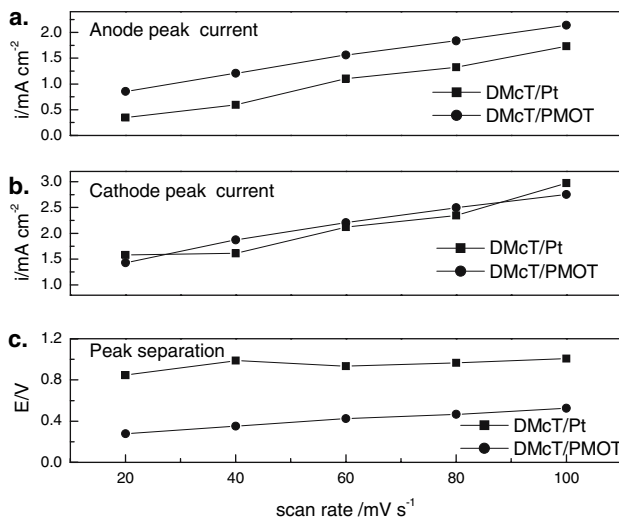
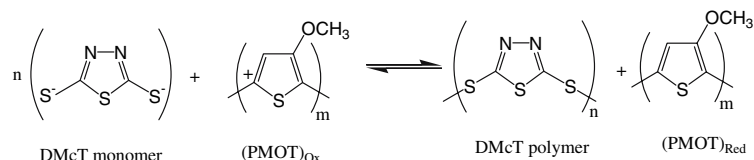


Fig. 3. Peak current and peak separation of DMcT on bare and PMOT-coated Pt electrode at different scan rate.

demonstrates the improved kinetics of DMcT by the catalysis of PMOT, the smaller peak separation implies the decreased electrochemical polarization of DMcT on the PMOT-coated Pt electrode. Based on the previous mechanism for the catalysis of the redox reaction between DMcT and poly(3,4-ethylenedioxythiophene)(PEDOT) [11], a similar mechanism between DMcT and PMOT can be deduced as in Scheme 2.

In addition, it can be seen from the CVs that the cathodic current was always higher than the anodic current. Usually, the extra discharge capacity disappears



Scheme 2. Mechanism for the catalysis of the redox reaction between DMcT and PMOT.

in organic electrolyte or becomes very large if the soluble oxygen is not removed prior to an experiment. Therefore, the extra discharge capacity in our study is attributed to chemically polymerized poly-DMcT by the remnant oxygen in the aqueous solution.

We further investigated the effect of PMOT thickness on the redox process of DMcT. As can be seen from Figure 4 and 5, the peak separation of DMcT increased

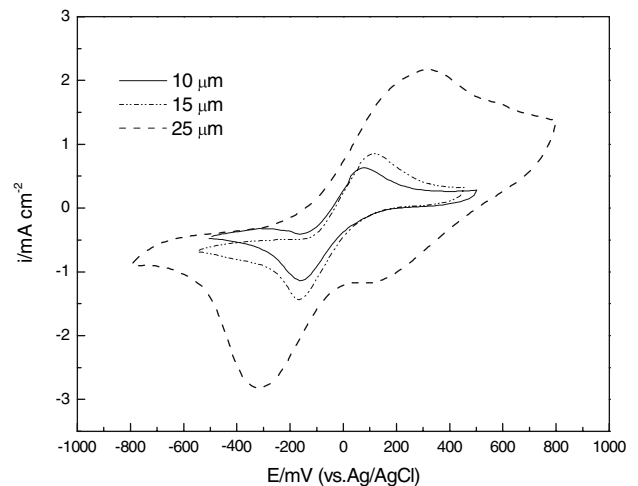


Fig. 4. Cyclic voltammograms of 5 mmol l^{-1} DMcT on PMOT-coated Pt electrode with different thickness in 0.1 mol l^{-1} LiClO_4/AN solution at a scan rate of 20 mV s^{-1} .

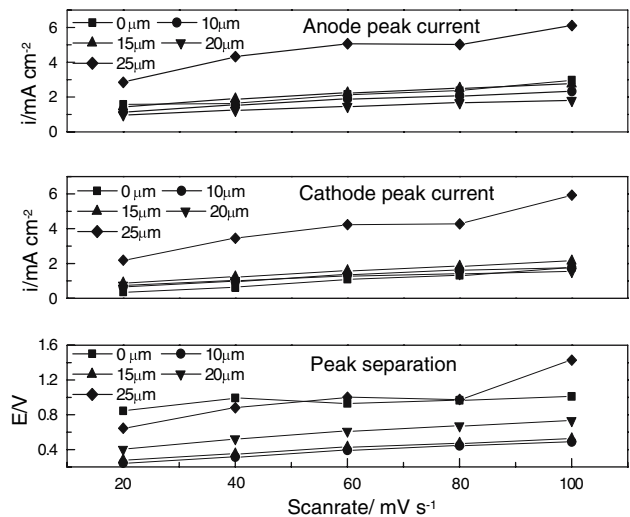


Fig. 5. Peak current and peak separation of DMcT on PMOT-coated Pt electrode in 0.1 mol l^{-1} LiClO_4/AN solution with different thickness and scan rate.

slightly as the thickness of PMOT increased from 10 to 20 μm , but showed a smaller value than that of DMcT on bare Pt. The peak current magnitude was the same as that on bare Pt. However, as the thickness of PMOT reached 25 μm , the peak current increased to almost 3 times than that on bare Pt, but the peak separation became the same as on bare Pt.

Based on the above results, we believed that the PMOT film leads to the enhancement of conductivity and redox activity of DMcT, and the electrochemical performance of DMcT can be improved on the PMOT-coated Pt electrode. The CV experiment of the PMOT-coated Pt electrode in DMcT-free solution further proved that PMOT was electrochemically inactive in the DMcT redox potential region. The conjugated thiophene ring in PMOT can adsorb or desorb charge during DMcT redox process as shown in Scheme 2, therefore PMOT served as an electrocatalyst and a conductive agent instead of electro-active material towards the DMcT redox process.

According to Scheme 1, the relationship between the theoretical discharge capacity and the degree of polymerization of poly-DMcT can be deduced as equation 1, where C_{Theo} denotes theoretical discharge capacity and n the degree of polymerization of poly-DMcT.

$$C_{\text{Theo}} = \frac{362(n-1)}{n} (\text{mAh g}^{-1}) \quad (1)$$

The calculated results are listed in Table 1, while the degree of polymerization is low, the discharge capacity is low but strongly related to the degree of polymerization. According to Oyama [4], the high charging voltage resulted in high discharge capacity of DMcT. This phenomenon can be explained by the high charging voltage resulting in a high degree of polymerization of poly-DMcT. Therefore, the degree of polymerization of poly-DMcT strongly affects its electrochemical performance. It can be concluded that the high degree of polymerization of poly-DMcT is unfavorable to its reversibility, but favorable to its charge-discharge capacity [12]. Now, it is easy to understand that DMcT showed the better reversibility but lower capacity with lower peak separation and peak current on the surface of thin PMOT film of thickness 10–20 μm ascribed to its low degree of polymerization. However, the high electro-catalyzed activity and conductivity on the surface of thick PMOT film of thickness 25 μm resulted in higher capacity but poor reversibility with higher peak current and peak separation ascribed to the high degree of polymerization of poly-DMcT.

The charge-discharge curves of DMcT and PMOT-doped DMcT in 1 mol l⁻¹ LiClO₄ EC/DEC (1:1)

electrolyte are shown in Figures 6 and 7, respectively. DMcT showed decreased coulombic efficiency (ratio of discharge capacity to charge capacity) with increase in cycle number. The voltage plateau for PMOT-doped DMcT (~ 3.5 V vs. Li/Li⁺) is obviously higher than that for DMcT (~ 3.2 V vs. Li/Li⁺) due to its higher degree of polymerization. The cycling performance of the DMcT and PMOT-doped DMcT cathode is shown in Figure 8. The discharge capacity of DMcT is relatively low and decreases dramatically with increase in cycle number. The first discharge capacity is 69 mAh g⁻¹, and then approaches 25 mAh g⁻¹ after the 80th cycle. This low discharge capacity of DMcT can be attributed to the

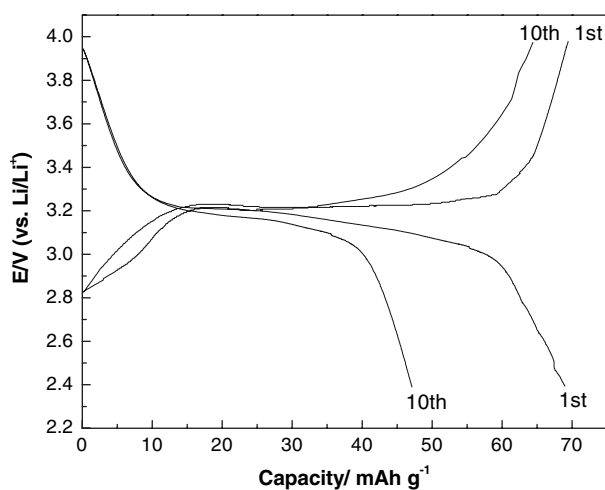


Fig. 6. Charge-discharge curves of DMcT in 1 mol l⁻¹ LiClO₄ EC/DEC (1:1) electrolyte.

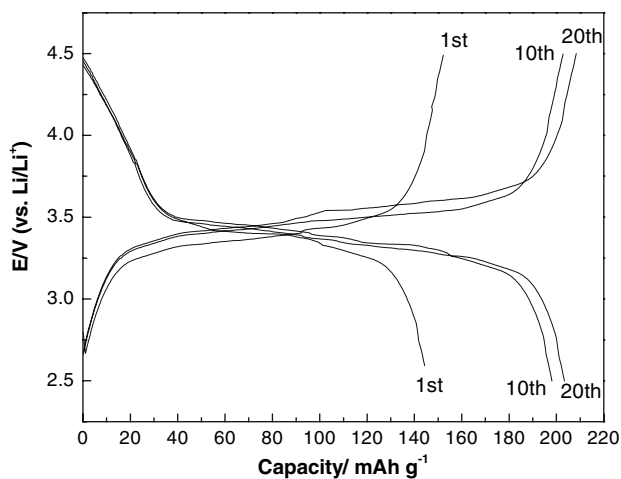


Fig. 7. Charge-discharge curves of PMOT-doped DMcT in 1 mol l⁻¹ LiClO₄ EC/DEC (1:1) electrolyte.

Table 1. Relationship between the theoretical discharge capacity and the degree of polymerization of poly-DMcT

Degree of polymerization (n)	2	3	4	5	6	7	8	9	10	∞
Theoretical discharge capacity mAh g ⁻¹	181	241	271	290	301	310	317	322	326	362

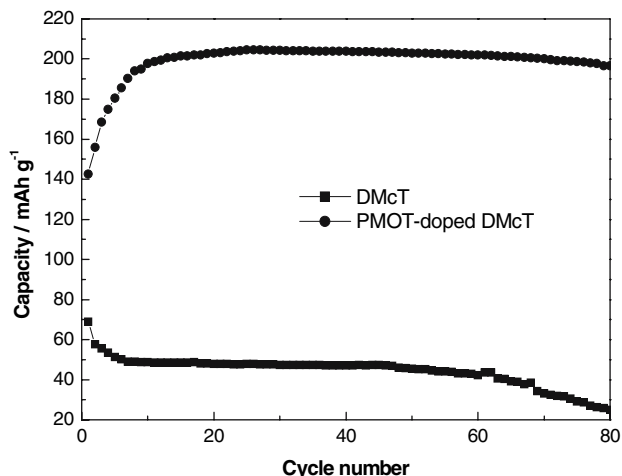


Fig. 8. Discharge capacity vs. cycle number of the test cells with DMcT and PMOT-doped DMcT cathode.

cathode without any conductive additive. However, the cycling performance of DMcT was improved by doping with PMOT. The first discharge capacity of the PMOT-doped DMcT composite electrode approaches 142 mAh g^{-1} , which is much higher than that of DMcT. Especially in the initial cycles, the discharge capacity increases rapidly with the increase in cycle number and reaches the highest capacity of 204 mAh g^{-1} at the 24th cycle. Continuous polymerization and de-polymerization of DMcT during cycling process leads to the contact from initial inter-particle to inter-molecule between DMcT and PMOT, the improved catalysis was thought to be the main reason for the increase in its capacity. After the 24th cycle the discharge capacity of the PMOT-doped DMcT composite cathode decreases slowly with cycle number and finally remains at 196 mAh g^{-1} after 80 cycles. Obviously, both the discharge capacity and reversibility are greatly improved by doping with PMOT.

4. Conclusions

Poly(3-methoxythiophene) (PMOT) can be used as an effective electrocatalyst for the redox process of 2,5-dimercapto-1,3,4-thiadiazole (DMcT). CV showed that the redox peaks had more symmetry in the electrochemical process of DMcT on the PMOT-coated Pt electrode,

and that PMOT on the surface of the Pt foil led to enhancement of the redox current of DMcT and reduction of its CV peak separation. A low thickness of PMOT favored the reversibility of the poly-DMcT due to the low degree of polymerization. Greater PMOT thickness resulted in high capacity but poor reversibility due to its high degree of polymerization. Moreover, the PMOT-doped DMcT cathode demonstrated an obvious improvement in discharge capacity and cycling performance. The contact from inter-particle to inter-molecule between DMcT and PMOT led to the increased capacity in the initial cycles.

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