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Metal-Catalyzed Organosulfur Cathodes for Rechargeable Lithium Batteries

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Abstract: Extensive studies were carried out to apply composite materials composed of polyaniline (PAn) and 2,5-dimercapto-1,3,4-thiadiazole (DMcT) to develop cathode materials which exhibit high energy densities. Previous results have established that composites of PAn and DMcT which are coated onto copper substrates exhibit greatly enhanced charge and discharge performance. It is shown that composite materials composed of DMcT, PAn, and Cu ion have the ability to be reversibly charged and discharged at ca. 260 A h per kg-cathode (ca. 830 W h per kg-cathode) for more than 80 cycles. These two results are explored in general in this contribution via investigation of the electron transfer reactions between the components using UV/Vis and investigation of the copper substrate/DMcT chemistry using electrochemical quartz crystal microbalance and phase modulated interferometric microscopy.

INTRODUCTION

Contemporary applications such as sensors, photoconversion, and energy storage demand materials with increasingly specific electronic and chemical characteristics. It has long been recognized that the ability to tailor these properties is facilitated by the use of composites.[1] For applications involving electroactive thin films, metal-polymer complex materials are particularly effective at providing flexibility in redox and chemical activity, while minimizing the shortcomings of the components.

An example of such an application is seen in the secondary lithium battery field. The development of secondary lithium batteries is currently limited by a general lack of stable cathode materials capable of reversibly storing high charge densities.[2] The complete requirements for these materials are quite stringent. Cathodes must be oxidized and reduced at potentials useful relative to the Li/Li$^+$ couple, must intercalate and deintercalate lithium ions during this redox process, and must be capable of repeatedly supporting both of these processes for hundreds or thousands of cycles.

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This paper will detail our results regarding the use of a copper/polyaniline/organosulfur composite material in secondary lithium cells. Our previous work has shown that composites of polyaniline and a dimercaptan, 2,5-dimercapto-1,3,4-thiadiazole (DMcT), can store up to 185 A h per kg-cathode.[3] In this contribution, we will discuss the effects of adding copper ion directly to the composites and of coating such composite films onto copper substrates. These alterations result in significantly improved performance of the cathode films. The reasons for these results have been explored via investigation of bulk DMcT-copper ion chemistry and via studies of the interfacial chemistry of copper substrates in solutions of DMcT.

EXPERIMENTAL

Materials

2,5-dimercapto-1,3,4-thiadiazole (DMcT) (Tokyo Kasei Organic Chemicals, 98%), $LiOH{\bullet}H_2O$ (95%), K_2DMcT (98%), methanol, H_2SO_4, $Ce(SO_4)_2{\bullet}4H_2O$ (97.5%), anhydrous $LiClO_4$, and dehydrated acetonitrile (all from Kanto Chemical Co.) were used as purchased. Polyaniline (PAn) was obtained from Nitto Denko (Japan).

The dimer form of DMcT was synthesized as: equimolar K_2DMcT and DMcT were dissolved (in that order) in de-aerated, distilled water. After dissolution, the solution was made ca. 0.1 M H_2SO_4. To that solution was added dropwise two equivalents of $Ce(SO_4)_2{\bullet}4H_2O$ in (de-aerated) 0.1 M H_2SO_4. A yellow solid precipitated immediately. The solid was filtered and dried under vacuum, then recrystallized from de-aerated methanol.

Analysis

Solution cyclic voltammetry was performed at room temperature using a Toho Technical Research potentiostat (PS-07) equipped with a Graphtec 1200 X-Y recorder. Solutions of 0.1 M anhydrous $LiClO_4$ in dehydrated acetonitrile were prepared under Ar atmosphere. Studies were done using a platinium coil counter electrode, a sodium-saturated calomel reference electrode, and a glassy carbon disk working electrode (BAS, MF-2012, 3.0 mm diameter). Solution CV's were obtained at a 50 mVs^{-1}. Solid-state cyclic voltammetry was perfomed using similar equipment. 1 M $LiClO_4$/propylene carbonate/ethylene carbonate electrolyte solutions were gelled with 10% w/w polyacrylonitrile and sandwiched between a carbon counter electrode and a glassy carbon working electrode. Silver wire was used as a quasi-reference electrode and standardized to the SCE potential scale using a ferrocene standard. Onto the 3 mm diameter working electrode was coated typically 1 to 15 μg of material (dried weight) from N-methyl pyrrolidinone casting solutions. Solid state CV's were obtained at a 5 mV s^{-1} scan rate.

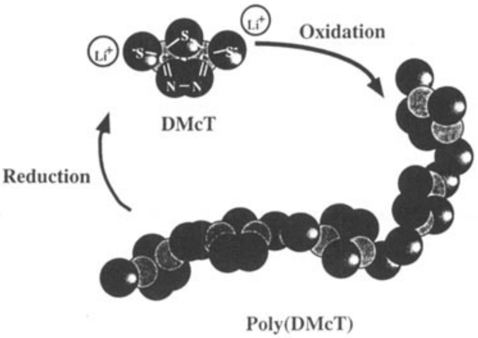
For cell testing, cathode films were coated onto silver-plated copper and placed in cells with an ethylene carbonate-propylene carbonate-LiBF$_4$ electrolyte gelled with acrylonitrile-methylacrylate copolymer (600 μm thick, 0.24 ml volume), lithium foil anodes, and carbon plate anodic current collectors. Charging of the cells was performed at constant current, 0.19 mA per cm^2, with an upper potential limit of 4.75 V, unless otherwise stated. Discharging was done at constant current, 0.19 mA per cm^2, with a lower limit of 2.0 V. Battery tests were performed at 20 C.

RESULTS AND DISCUSSION

Redox activity of DMcT

Figure 1 shows voltammograms of DMcT and of its dimer form in 0.1 M LiClO$_4$ acetonitrile. Voltammogram a is characterized by oxidation of the thiol substituents in an anodic wave at 4.1 V and reduction of the disulfide bonds of the subsequently produced oligomers in a cathodic wave at 3.0 V. This large peak separation has previously been ascribed to slow redox kinetics of this couple.[4] This redox process may be represented in general by the reaction in Scheme 1. In light of the basic properties of thiolates, it is expected that this electron transfer is proton-coupled. Furthermore, since the oligomer form of DMcT is not soluble in acetonitrile, it is expected that oxidation of DMcT results in precipitation of oligomer onto the electrode. These expectations have been borne out by a series of studies on this system.[4-12]

Scheme 1:



However, control of the protonation state and solubility of the redox species allows the observation of quasi-reversible redox waves for this system. Voltammogram b in Figure 1 shows such a case, where the electroactive species is the dimer form of DMcT. This voltammogram is characterized by reduction of the disulfide in a cathodic wave at 3.0 V, followed by oxidation of the produced thiolates in an anodic wave at 3.3 V, with a peak separation being only 300 mV. This observation suggests that the kinetics of this redox couple are not inherently slow. These observations and their implications have been discussed at length in another contribution.[11]

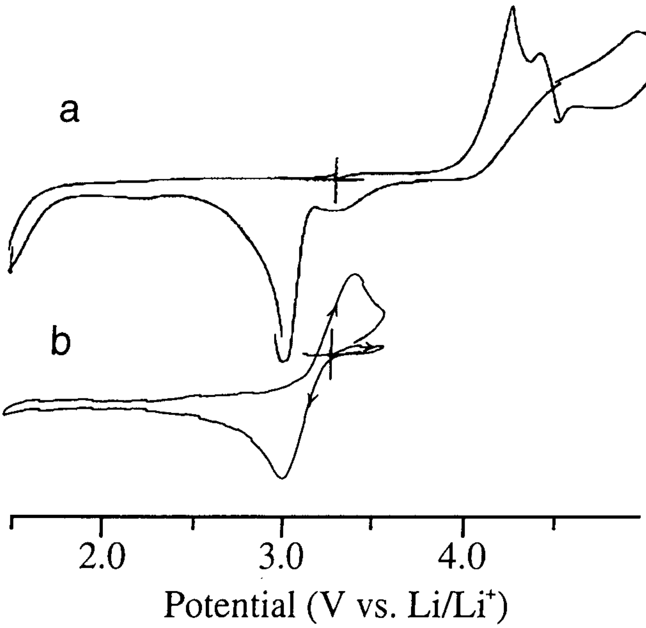


Figure 1: Solution voltammograms of a) 10 mM DMcT and b) 2 mM dimer DMcT at glassy carbon in 0.1 M $LiClO_4$/acetonitrile. Scan rate was 50 mV s^{-1}.

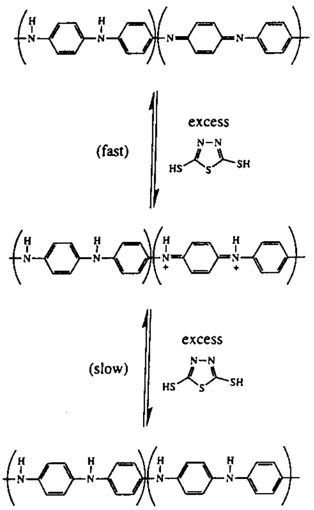
Electron and proton transfer between DMcT and polyaniline

The use of pure DMcT as a cathode material has been hampered by its limited electronic conductivity.[13,14] Dispersion of DMcT in poly(ethylene oxide) mixed with carbon have been shown to provide some measure of ionic and electronic conductivity, although the use of such cathodes at room temperature is limited.[13-17] It is well-known that conducting polymer-coated electrodes mediate electron transfer between the electrode and solution, and that conducting polymers such as polyaniline (PAn) are efficient ion conductors.[18] Thus, in this paradigm, conducting polymers provide pathways for electron and ion transport through the composite while the organosulfur provides a high density of sites which can store electrons. The primary issue in designing such a composite is to find a conducting polymer with the proper window of conductivity in which the organosulfur can be oxidized and reduced.

For DMcT, PAn appears to have the proper orbital overlap to facilitate electron transfer from the current collector to the dispersed electroactive material. To illustrate, Figure 2 shows solid-state voltammograms of 1.44 μg PAn in the absence and presence of 4.28 μg DMcT (both evaporatively deposited from N-methyl-2-pyrrolidinone(NMP)). The films were covered by a gelled propylene carbonate/ethylene carbonate electrolyte. The mixed film showed increased currents when the potential was scanned positive of ca. 0.5 V (vs. SCE), compared to the pure PAn film. This suggests that PAn mediates the oxidation of DMcT in these films.

In order to establish the character of this mediation more clearly, our group has investigated the electron and proton transfers which occur from the reduced and oxidized forms of DMcT to the oxidized and reduced forms, respectively, of Pan.[19] The use of stopped-flow technique allows clear separation of this proton and electron transfer. Time resolved stopped-flow spectra of the addition of DMcT to emeraldine base-PAn in NMP showed that a fast proton transfer from DMcT to emeraldine base-PAn occurs first, followed by a slower electron transfer from deprotonated DMcT to emeraldine-PAn, as depicted in Scheme 2.

Scheme 2:



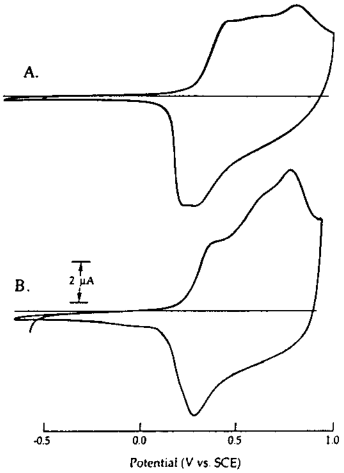


Figure 2: Solid-state voltammograms of a) 1.4 µg PAn and b) 1.4 µg DMcT mixed with 4.3 µg poly(aniline) evaporatively deposited from N-methyl pyrrolidinone onto a glassy carbon electrode. Electrolyte was a 10 % w/w poly(acrylonitrile)-gel of 1 M $LiClO_4$ in 1:1 propylene carbonate:ethylene carbonate. Scan rate was 5 mV s^{-1}.

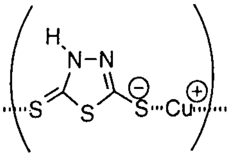
Interfacial DMcT-copper substrate chemistry

The practical use of DMcT/PAn composites as cathodes in secondary lithium batteries has been extensively studied by our group.[3,13,20,21] These composites have the ability to store extremely high densities of charge (up to 185 A h per kg-cathode). However, adding and removing electrons from these films (i.e. discharging and charging the cell, respectively) remains fairly slow.[20]

A recent discovery has shown that coating such films onto copper substrates results in significantly improved charging and discharging behavior.[22] We have found that a cell using the composite cathode coupled with a copper current collector can be cycled up to 250 times at specific capacities of 220 Ah per kg-cathode with a stable discharge voltage (data not shown). We have attributed the observed improvements to dissolution of the copper substrate, followed by formation of a complex between DMcT and copper ions.

This interfacial chemistry at the surface of copper substrates was further examined using the in-situ electrochemical QCM (EQCM) method. Figure 3 shows EQCM results accompanying Cu electrodissolution in the presence of 10 mM DMcT. In the absence of DMcT, the Cu electrodissolution was observed to start at ca. 0.4 V vs. SSCE as a concurrent increase in anodic current and frequency (data not shown). (Constant-potential electrolysis correlated with QCM frequency measurements identified the dissolving species in this case to be Cu(II).) However, in the presence of DMcT the electrodissolution of copper substrate was inhibited below 1.0V vs. SSCE (Figure 3, top). In this case, the Cu substrate dissolved as Cu(I). This is consistent with a general stabilization of Cu(I) by DMcT observed in related studies of the bulk DMcT/Cu ion chemistry.[23] One of possible structures of a complex between DMcT and Cu[I] as suggested by Raman and IR spectroscopy and elemental analysis [23] is shown in Scheme 3.

Scheme 3:



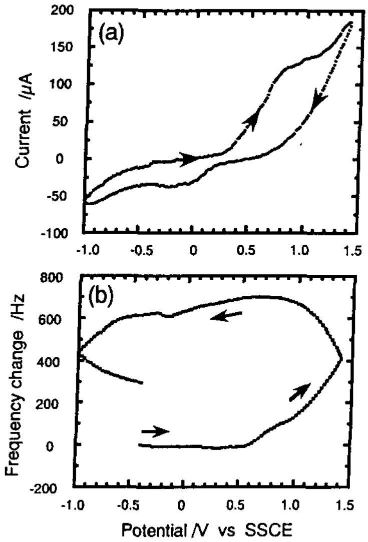


Figure 3: EQCM of a copper-coated quartz crystal in a 10 mM solution of DMcT in 0.1 $LiBF_4$ in 1:1 propylene carbonate:ethylene carbonate. a) Voltammetric and b) frequency response of the electrode during a 10 mV s^{-1} scan from -1.0 to +1.4 volts vs. SSCE (scan shown was taken after two identical conditioning scans).

Furthermore, we have observed that dissolution of copper substrates occurs spontaneously in the presence of DMcT without electrolysis. The resonant frequency of a copper-coated QCM electrode in NMP was substantially changed by addition of DMcT to the solution. An initial decrease in frequency was followed by a steady increase. This can be explained by a model where adsorption of DMcT onto the Cu surface is followed by dissolution of the Cu(I)/DMcT complex. The dissolution of Cu by DMcT can also be observed using PMIM method. In this experiment, a Cu substrate (coated on a glass plate) was soaked in NMP solution containing 100 mM DMcT and then rinsed with pure NMP and dried. Figure 4 shows a representative sectional PMIM image of the resultant substrate. The dissolution of Cu can be clearly seen as decrease in the surface height in the area B where the surface contacted with the DMcT solution. A deep trench in the image suggests the dissolution is accelerated in the presence of oxygen.

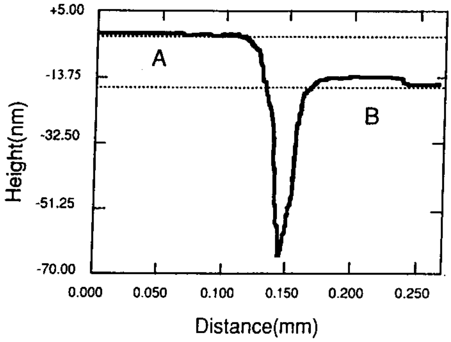


Figure 4: Sectional PMIM image of a copper electrode after partial immersion in a solution of DMcT. Region A was not in contact with the solution, while region B was soaked in 100 mM DMcT solution in N-methyl pyrrolidinone. The electrode was rinsed with pure solvent and dried prior to the measurement. After dissolution, region B was observed to be on average ca. 10 nm lower than region A.

Effect of copper on redox activity of the composite cathodes

The results of our copper substrate studies suggested that the effect of copper dissolution on the bulk electrochemistry of the DMcT/PAn films significantly contributes to the observed performance. This realization led to testing composites to which copper ion has been directly added.[24] Figures 5 shows the discharge capacity of a representative lithium cell including a copper-doped DMcT/PAn composite cathode. Stable discharge behavior was observed for at least 80 cycles in cells cycled at ca. 260 A h per kg-cathode (and up to 10 cycles for cells cycled at 300 A h per kg-cathode (not shown)).

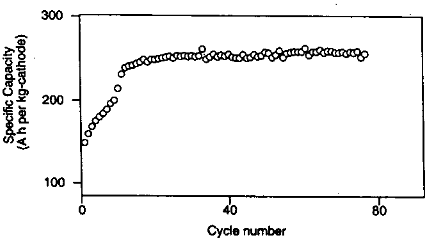
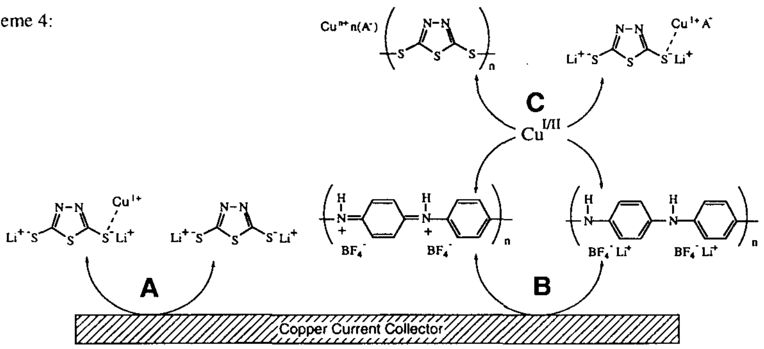


Figure 5: Discharge capacity versus cycle number of a representative cell (at 20 C) which was charged 130% of its theoretical capacity. See text for charging conditions.

Representative graphs of the cell voltage during charging and discharging are shown in Figure 6. This extremely reproducible behavior reflects new DMcT/Cu ion and PAn/Cu ion chemistry operative in the composite. Based on the results above, we propose that these processes are determined by the chemical and redox processes shown in Scheme 4. Here, in step A, DMcT adsorbs onto the copper substrate, then dissolves the substrate as a DMcT/Cu(I) complex. Electron transfer between the substrate and the PAn "molecular wire" (step B) provides the driving force for electron transfer between the PAn and DMcT. The latter electron transfer (step C) may be mediated by Cu(II) and/or facilitated by Cu(I) coordination of DMcT.

Our next efforts in this vein will focus on examination of the redox chemistry between these components using voltammetry, stopped-flow spectroscopy, and spectroelectrochemistry.

Scheme 4:



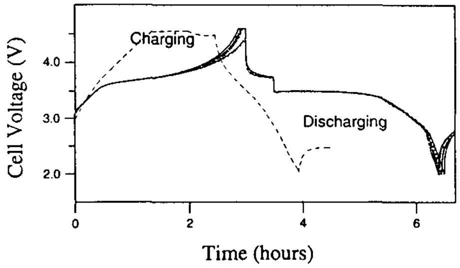


Figure 6: Cell voltage during every tenth charge-discharge cycle between the thirtieth and eightieth cycles of a cell charged to 260 A h per kg-cathode at a 0.4 C rate. The broken line shows cell voltage of a lithium cell using the PAn/DMcT composite (undoped) with a carbon current collector.

Acknowledgment

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References

1. e.g. *Macromolecular Complexes: Dynamic Interactions and Electronic Processes*, E. Tsuchida, Ed., VCH Publishers, Inc., New York (1991).
2. *Rechargeable Lithium and Lithium-ion Batteries*, S. Megahed, B. M. Barnett and L. Xie, Editors, Electrochemical Society Proceedings Series, Pennington, New Jersey (1995).
3. N. Oyama, T. Tatsuma, T. Sato and T. Sotomura *Nature*, **373**, 598 (1995).
4. S. Ye, D. Belanger *J. Electrochem. Soc.*, **141**, L49 (1994).
5. S. Picart and E. Genies *J. Electroanal. Chem.*, **408**, 53 (1996).
6. K. Naoi, Y. Oura, Y. Iwamizu and N. Oyama *J. Electrochem. Soc.*, **142**, 354 (1995).
7. E. Shouji and N. Oyama *J. Electroanal. Chem.*, **410**, 229 (1996).
8. E. Shouji and H. Matsui, N. Oyama *J. Electroanal. Chem.*, **417**, 17 (1996).
9. E. Shouji and Y. Yokoyama, J. M. Pope, N. Oyama, D. A. Buttry *J. Phys. Chem.*, **101**, 2861 (1997).
10. T. Tatsuma, Y. Yokoyama, D. A. Buttry and N. Oyama, *J. Phys. Chem.*, in press.
11. J. M. Pope and N. Oyama, in contribution.
12. X. Q. Yang, K. H. Xue, H. S. Lee, J. McGreen, T. A. Skotheim, F. Lu *Phys. Rev. B*, **45**, 5733 (1992).
13. T. Sotomura, H. Uemachi, Y. Miyamoto, A. Kaminaga and N. Oyama *Denki Kagaku*, **12**, 1366, (1993).
14. M. M. Doeff, S. J. Visco and L. C. De Jonghe *J. Electrochem. Soc.*, **139**, 2077 (1992).
15. M. Ue, S. J. Visco and L. C. De Jonghe *Denki Kagaku*, **61**, 1409 (1993).
16. M. M. Doeff, S. J. Visco and L. C. De Jonghe *J. Electrochem. Soc.*, **139**, 1808 (1992).
17. M. Liu, S. J. Visco and L. C. De Jonghe *J. Electrochem. Soc.*, **138**, 1891 (1991).
18. e.g. T. Tatsuma, K.-I. Saito and N. Oyama *Anal. Chem.*, **66**, 1002 (1994).
19. a.) T. Tatsuma, H. Matsui, E. Shouji and N. Oyama *J. Phys. Chem.*, **100**, 14016 (1996). b.) O. Hatozaki, Y. Yokoyama, M. Motomura, S. Nakamura and N. Oyama, in contribution.
20. T. Tatsuma, T. Sotomura, T. Sato, D. A. Buttry and N. Oyama *J. Electrochem. Soc.*, **142**, L183 (1995).
21. T. Sotomura, H. Uemachi, K. Takeyama, K. Naoi and N. Oyama *Electrochim. Acta*, **37**, 1851 (1992).
22. T. Sotomura, T. Tatsuma and N. Oyama, *J. Electrochem. Soc.*, **143**, 3152 (1996).
23. J. M. Pope, S. C. Paulson and N. Masuda, unpublished results (1997).
24. N. Oyama, J. M. Pope and T. Sotomura, *J. Electrochem. Soc.*, **144**, L47 (1997).