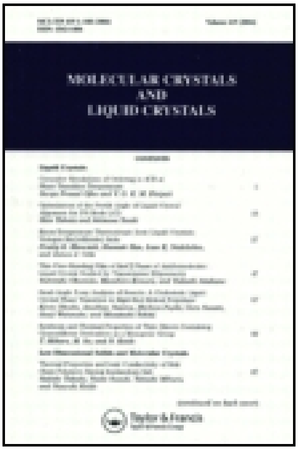

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New Composite Cathodes for Lithium Rechargeable Batteries

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New Composite Cathodes for Lithium Rechargeable Batteries

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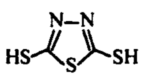
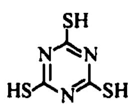
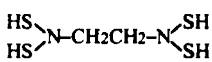
New organic composites based on thiol-compounds are developed as a cathode material for lithium batteries. A conducting polymer polyaniline (PAn) accelerates slow redox reactions of the organic sulfur compounds with multiple thiol groups, such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT). A composite cathode composed of DMcT and PAn on a copper current collector provides high charge density exceeding 225Ah/kg-cathode and is capable of being charged and discharged at high rates with excellent cyclability (>500 cycles). Surface analysis and electrochemical studies indicate that a DMcT-Cu complex plays an important role in the observed battery performances of the composite on a copper current collector. Large increase in the charge density to 550Ah/kg-cathode is achieved by adding elemental sulfur (S_8) to the composite cathode.

Keywords: lithium battery; composite cathode material; organosulfur compound; polyaniline; copper complex; elemental sulfur

INTRODUCTION

Recently, various organic materials with new electronic properties have become of significant interest in many fields. One of examples is seen in the rechargeable battery field. Although inorganic compounds have been exclusively employed as anode and cathode materials in the progress of battery technology, increasing demands for compact, lightweight rechargeable batteries prompt development of organic electrode materials with high energy density. An organic sulfur compound with multiple thiol groups is one of promising compounds as a cathode material for lithium rechargeable batteries. Organic sulfur compounds store a charge every thiol group and, thus, theoretical charge capacity of, for example, 2,5-dimercapto-1,3,4-thiadiazole (DMcT), which has two thiol groups, is calculated to be 362Ah/kg-DMcT, far exceeding that of $LiCoO_2$ (137Ah/kg-$LiCoO_2$). Higher capacity will be obtained for organic sulfur compounds with three or four thiols as shown in Table 1.

TABLE 1 Theoretical gravimetric capacity of some organic sulfur compounds.

thiol-compound		number of thiol	theoretical capacity / $Ahkg^{-1}$
	DMcT	2	362
	1,3,5-triazine-2,4,6-trithiol	3	462
	*N,N,N',N'*-tetramercapto-ethylenediamine	4	582

In this paper, we present our recent results obtained for an organic composite cathode composed of DMcT and a conducting polymer polyaniline (PAn). Improved battery characteristics of DMcT/PAn composites due to a copper current collector and elemental sulfur (S_8) are described.

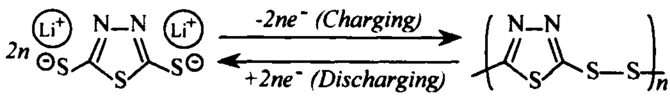
EXPERIMENTAL

To obtain a DMcT/PAn composite solutions DMcT and PAn were dissolved into NMP in that order. The obtained black inky solution was spread over current collectors and dried at 80° C under vacuum. DMcT/PAn composites containing elemental sulfur were obtained by adding S_8 into the inky solution dissolved with DMcT and PAn. Charge-discharge characteristics of the composite cathodes were evaluated using a test cell with a lithium metal anode and polymer gel electrolyte[1]. Preparation of the composite cathodes and fabrication of the test cells were carried out in a glove box under argon atmosphere.

RESULTS AND DISCUSSIONS

DMcT/PAn Composite Cathodes on Copper Current Collector

A DMcT molecule stores two charges based on the oxidation (charging) and reduction (discharging) reactions which are accompanied by reversible transformations between the thiol and disulfide as shown in Scheme 1:



SCHEME 1 Charging and discharging reactions of DMcT.

We have reported that making a well-mixed composite with PAn accelerates sluggish kinetics of the DMcT redox reactions by virtue of electrocatalytic activity of PAn[1]. Simultaneously, PAn imparts electron conductivity to the cathode and serves as an electrode active material (100Ah/kg-PAn with BF_4^- as a dopant). Charge capacity of a DMcT/PAn composite was estimated to be 185Ah/kg-cathode, which corresponds to 80% of theoretical capacity of 224Ah/kg-cathode. Average discharge voltage was 3.4V against a Li metal anode.

Although charge-discharge characteristics (e.g., cyclability) of DMcT were significantly improved by using as a composite with PAn[1], charging-discharging rates remained still low for the practical application to cathode materials. Addition of a polypyrrole derivative resulted in the increase in charging rate[2].

We have recently found that using a copper cathode current collector enables discharging as well as charging at a higher rate compared to rates with other current collectors such as titanium, gold and carbon[3,4]. Furthermore, when a copper current collector was used, the charge capacity of the composite cathode was estimated to be 233Ah/kg-cathode, exceeding theoretical capacity estimated based on the weights of DMcT and PAn in the composites[3]. The apparent increase in the charge capacity indicated that not only DMcT and PAn but also the copper serve as a cathode active material.

In our recent results, the discharge capacity of the composite has been increased to 260Ah/kg-cathode by adding copper salts to the composite without undue deterioration of battery performance[4].

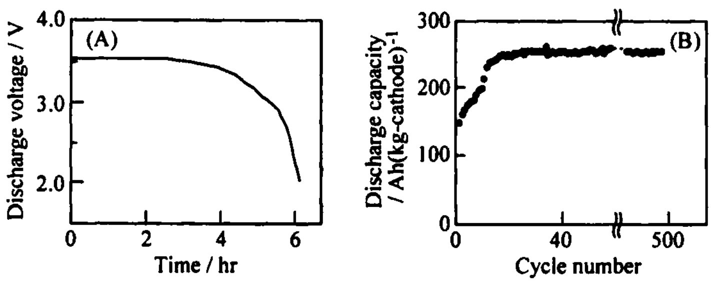


FIGURE 1 (A) Time course change of discharge voltage and (B) plot of discharge capacity vs. cycle number of a test cell with DMcT/PAn composite cathode containing copper salts. Rate: 0.4C.

Recently, surface analysis has shown that DMcT strongly interacts with copper[5,6]. Using electrochemical quartz crystal microbalance (EQCM), X-ray photoelectron spectroscopy (XPS) and IR-Raman spectroscopy, it was found that copper was mainly oxidized to cuprous ion (Cu^{I})[5]. It was also proved that surface of a copper current collector was covered with a thin layer containing DMcT and copper ions. In the surface layer, Cu^{I} formed a complex with DMcT dimer ($DMcT_2$) as a ligand. Furthermore, cyclic voltammetric studies confirmed that $DMcT_2$-Cu complex showed electrocatalytic activity toward the redox reactions of DMcT[7].

Based on the results described above, it is expected that the formation of $DMcT_2$-Cu complex plays an important role for the improved charge-discharge characteristics of DMcT/PAn composites on copper current collectors.

Composite Cathode Containing Elemental Sulfur

We have tried to increase the energy density of DMcT/PAn composite cathodes by adding elemental sulfur (S_8), the theoretical capacity of which is 1675Ah/kg-S_8 provided each sulfur atom being reduced to S^{2-} (16 electrons per S_8). S_8-containing composite cathode gave extremely high discharge capacity exceeding 550Ah/kg-cathode as shown in Figure 2[8]. The value of the discharge capacity implied that more than half of sulfur atoms in the composite was reduced to S^{2-}, though the 2-electron reduction of sulfur at electrode surfaces has not been observed. Furthermore, discharge voltage of a test cell with the S_8-containing composite cathode was observed to be 3.5V, which was much higher than that expected from the reported reduction potentials of S_8 (<2.6V vs. Li/Li$^+$)[9]. These unusual electrochemistry of S_8 was possibly due to strong interactions between S_8 and DMcT and/or S_8 and PAn in the composite.

Extensive research is under way on interactions among S_8, DMcT and PAn and mechanisms of redox reactions of S_8 in the composite.

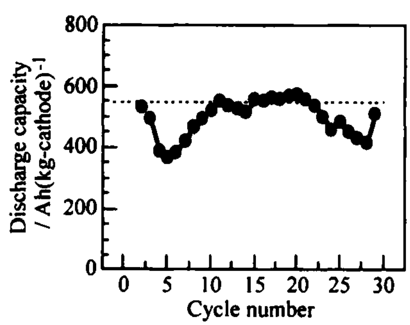


FIGURE 2 Plot of discharge capacity vs. cycle number of a representative test cell with S_8 containing DMcT/PAn composite cathode.

SUMMARY

Organic composites based on thiol-compounds showed a high promise as lightweight cathode materials for lithium batteries. Development of these organic cathodes will contribute to increase in energy density of lithium batteries. Furthermore, using organic cathodes with polymer gel electrolyte, lithium batteries will be fabricated to be thinner and unit cells can be stacked. Lithium batteries with organic cathodes and gel electrolytes will be useful as power sources for not only portable electronic devices but also for electric vehicles and space crafts.

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