

Development of Polymer-Based Lithium Secondary Battery

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SUMMARY: Novel polymer composites based on polydisulfide compounds are developed as a high energy density cathode material for lithium rechargeable batteries. A polymer composite composed of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and conducting polymer polyaniline (PAn) on a copper current collector provides high charge density exceeding 225Ah/kg-cathode with average discharge voltage at 3.4V. The composite cathode showed excellent rate capability and cyclability (>500 cycles). Surface analysis and electrochemical studies indicate that a DMcT-Cu complex plays an important role in the observed improvement of the battery performances with a copper current collector. Large increase in the charge density to 550Ah/kg-cathode is achieved by adding elemental sulfur (S_8) to the DMcT/PAn composite cathode.

Introduction

The last decade has witnessed rapid but steady spread of various portable electronic devices with reducing the size and weight. Because those advanced devices such as cellular phones almost exclusively depend on rechargeable batteries for power source, increase in energy storage capability of batteries has been pursued to downsize the devices with extending operation time. The strong demand for a compact, lightweight rechargeable battery with high energy density has promoted the development of novel electrode materials : for example, lithium cobalt oxide and carbon intercalating materials for lithium ion batteries. Recently, in addition to inorganic compounds, a functional polymer material is expected as one of promising candidates for the electrode materials with high energy density, as well as other major components of rechargeable batteries such as electrolytes and separators as shown in Figure 1. It is expected that the use of various polymer materials instead of inorganic compounds will make rechargeable batteries thinner and lighter in weight and also less hazardous to environment.

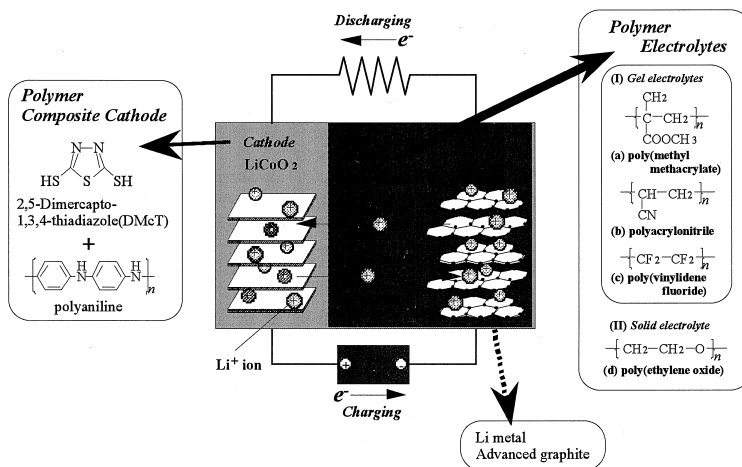
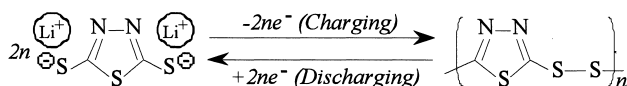


Fig. 1: Schematic depiction of the charge-discharge processes of a conventional lithium-ion battery and the structure of representative polymer materials for a polymer-based lithium battery.

Polydisulfide, which is an oxidation product of an organosulfur compound with multiple thiol groups (-SH) such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT, Fig. 1), is one of promising candidates as a lightweight cathode material with high charge capacity. A polydisulfide compound is capable of storing two charges every disulfide bond (-S-S-) based on the reversible transformations between a disulfide bond and thiolates (or thiols). Based on the reaction, theoretical charge capacity of poly(DMcT) can be calculated to be 362Ah/kg-DMcT (330Ah/kg, including two lithium ions as a counterion for the monomers).

We have conducted experimental and theoretical studies on composite polymer materials composed of polydisulfide and conducting polymer as a cathode material for lithium rechargeable batteries¹⁻⁸⁾. In this paper, we will present our recent results obtained for a polymer composite cathode composed of DMcT and conducting polymer polyaniline (PAN) which accelerates sluggish redox reactions of DMcT at room temperature. Improved battery characteristics of the DMcT/PAN composites obtained when using a copper substrate as a current collector for the composite cathode are presented. Preparation and properties, especially high energy density, of a composite cathode material containing

A DMcT molecule can store 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:



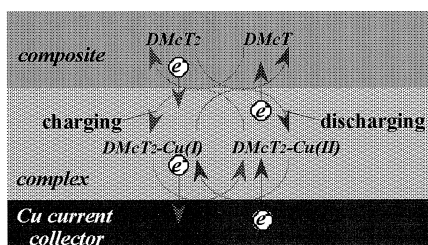
We have already reported that PAN accelerates sluggish kinetics of the DMcT redox reactions by virtue of electrocatalytic activity of PAN and making a well-mixed composite of DMcT and PAN, a cathode material with high energy density is obtained¹⁾. Composite formation with PAN solves another problem with organosulfur compounds as electrode active materials, i.e., PAN imparts electron conductivity to the composite cathode. PAN also serves as an electrode active material (100Ah/kg-PAN with BF_4^- as a dopant). Charge capacity of a DMcT/PAN composite was experimentally estimated to be 185Ah/kg-cathode, which corresponds to 80% of the theoretical capacity of 224Ah/kg-cathode. Average discharge voltage was 3.4V against a Li metal anode¹⁾.

We have recently found that use of a copper substrate as a current collector for DMcT/PAn

composite cathode improves rate capability for both discharging and charging, compared to other current collectors such as titanium, gold and carbon^{10,11}. Furthermore, when a copper current collector was used, apparent 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 composites¹⁰. The apparent increase in the charge capacity suggested that not only DMcT and PAn but also the copper serve as a cathode active material and contribute to the observed capacity^{10,11}.

Recently, surface analysis has shown that DMcT strongly interacts with copper^{12,13}. Surface analysis using phase measurement interferometric microscopy (PMIM) and quartz crystal microbalance (QCM) showed that copper surface spontaneously dissolved in a solution containing DMcT¹³. Using electrochemical QCM, X-ray photoelectron spectroscopy (XPS) and IR-Raman spectroscopy, it was found that copper was mainly oxidized to cuprous ion (Cu^{I})¹². It was also observed that surface of a copper current collector was covered with a thin layer containing DMcT and copper ions from XPS. Cyclic voltammetric studies have confirmed that $\text{DMcT}_2\text{-Cu}$ complex showed electrocatalytic activity toward the redox reactions of DMcT¹⁴.

Based on the results described above, it is expected that DMcT-Cu complexes accelerate the electron-transfer reactions at the interface between the composite and current collector as well as within the composite as shown in Scheme 2.



Scheme 2 A proposed mechanism for the acceleration of the DMcT redox reactions by DMcT-Cu complex formed on a copper current collector.

DMcT/PAn Composite Cathode Containing Elemental Sulfur

As shown above, the composite cathode composed of DMcT and PAn with a copper current collector possess much higher charge capacity than LiCoO_2 with good rate capability and cyclability. In this study, to further increase the energy density of the DMcT/PAn composite cathodes, elemental sulfur (S_8) was added to the composites.

S_8 -containing composites were prepared by adding S_8 to inky solutions dissolving DMcT and PAn at high concentration. The obtained viscous solution containing S_8 was applied to current collector and dried under vacuum. A test cell was assembled using the S_8 -containing composite (DMc/PAn/ S_8) as a cathode, a foil of lithium metal as an anode and polyacrylonitrile gel containing 0.1M LiBF_4 /propylene carbonate and ethylene carbonate as an electrolyte.

The theoretical capacity of S_8 is 1675Ah/kg- S_8 , assuming that each sulfur atom is reduced to S^{2-} (16 electrons per S_8). However, in general, S_8 is reduced to a radical anion, $\text{S}_3^{-\cdot}$, at about +2.6V vs. Li/Li^+ . $\text{S}_3^{-\cdot}$ is further reduced at more negative potentials, but it is mostly impossible to electrochemically reduce to 8S^{2-} , i.e., 2-electron reduction of every sulfur atom of S_8 ¹⁵. DMcT/PAn/ S_8 composite cathodes prepared in this study, on the other hand, showed high discharge capacity exceeding 550Ah/kg-cathode with average voltage at 3.5V as shown in Fig. 2¹⁶). The value of the discharge capacity implied that the sulfur

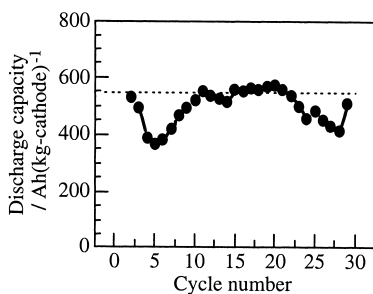


Fig. 2: Plot of discharge capacity vs. cycle number of a representative test cell with S_8 containing DMcT/PAn composite cathode.

was reduced to S^{2-} state in the composite. The observed unusual electrochemistry of S_8 in the DMCT/PAn/ S_8 composite is possibly due to strong interactions among the components of the composite.

Conclusion

Organic composites based on thiol-compounds showed a high promise as lightweight cathode materials for lithium batteries. Development of these polymer cathodes will contribute to increase energy density of lithium batteries. Furthermore, using a polymer gel electrolyte, lithium batteries will be fabricated to be thinner and unit cells can be stacked. Lithium rechargeable batteries with polymer-based 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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