Macromol. Symp. ***156,*** *171–178 (2000)*

Lithium Polymer Battery with High Energy Density

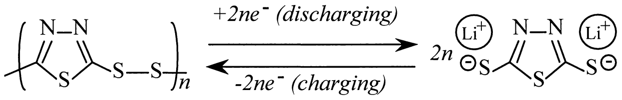
Noboru Oyama*, Osamu Hatozaki

Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

SUMMARY: Polymer cathode materials based on organosulfur compounds are developed for lithium rechargeable batteries with high energy density. Making a well-mixed composite with a conducting polymer polyaniline (PAn) accelerates slow redox reactions of organosulfur compounds such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT). Using a copper cathode current collector, battery performances of the DMcT/PAn composite cathode are significantly improved due to a formation of a complex between DMcT and a copper ion: discharge capacity exceeding 225Ah/kg-cathode and cyclability more than 500 charge-discharge cycles being achieved. Furthermore, addition of elemental sulfur (S_8) to the composite further augments the discharge capacity of the composite cathode to more than 500Ah/kg-cathode.

Introduction

In recent years, increasing demand for compact, lightweight rechargeable batteries prompts development of cathode and anode active materials based on polymer compounds with extremely high energy density. 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), is one of promising candidates as a lightweight cathode material with high charge capacity. Polydisulfides are capable of storing two charges every disulfide bond (-S-S-) based on the reversible transformations between a disulfide bond and thiolate (or thiol) as shown in Scheme 1:



Scheme 1: The reversible depolymerization/polymerization reactions between poly(DMcT) and DMcT monomer.

where a disulfide bond in poly(DMcT) is reduced and broken to yield DMcT monomers

CCC 1022-1360/00/$ 17.50+.50/0

during discharging process and the reverse change for charging. Based on the reaction, theoretical charge capacity of poly(DMcT) is calculated to be 362Ah/kg-DMcT (330Ah/kg, including two lithium ions as a counterion for the monomer).

One of drawbacks that retard application of polydisulfides to batteries of practical use is sluggish kinetics of the electron-transfer reactions at ambient temperature. Therefore, acceleration of the electron-transfer reactions has to be attained, otherwise batteries should be operated at impractically low charge-discharge rates or at higher temperatures. Additionally, lack of high conductivity in polydisulfides is another drawback for the application as electrode materials.

We have recently reported that the two problems in the application of polydisulfides are partially solved by making composites with a conducting polymer polyaniline (PAn): PAn accelerates the electron-transfer reactions and simultaneously confers electron conductivity1). Combining with a lithium metal anode and polymer gel electrolyte, the DMcT/PAn composites gave discharge capacity of 185A/kg-cathode and average discharge voltage at 3.4V.

We have carried out experimental and theoretical studies on polydisulfide/conducting polymer composite cathode materials for lithium rechargeable batteries2-9). In this paper, charge-discharge characteristics of the DMcT/PAn composite cathode and effects of a copper current collector are described. For the observed improvements of charge-discharge performance of the composite cathode, a formation of a complex between DMcT and copper ions are discussed based on surface analysis at the interface between the composite and copper substrate and electrochemical characterization of DMcT-Cu complexes. Increase in the energy density of the composite cathode by addition of elemental sulfur (S_8) is also described.

DMcT/PAn Polymer Composite Cathode

DMcT/PAn composite materials were prepared by dissolving DMcT monomer in *N*-mthyl-

2-pyrrolidinone (NMP) and subsequently adding PAn into the DMcT/NMP solution. The presence of DMcT aided in dissolving PAn in NMP, which implied that chemical and/or physical interaction(s) were operating between DMcT and PAn. We expect that this simple preparation method develops molecular-level interaction between DMcT and PAn enough to fully derive the advantages from the composite formation.

To characterize DMcT/PAn composite cathode (thickness: ca.20μm), we fabricated a test cell using a lithium metal anode (thickness: 300μm) and polymer gel electrolyte (thickness: 600-700μm)(1). The polymer gel electrolyte was prepared by dissolving a copolymer of acrylonitrile and methyl acrylate in a mixture solvent of propylene carbonate and ethylene carbonate containing 1M $LiBF_4$(1).

When poly(DMcT) alone was used as an electrode material, only poor charge-discharge performance was observed (Figure 1A). For example, discharge capacity plummeted below one-third of an initial value in the repeated charge-discharge cycling. On the contrary, a composite cathode of poly(DMcT) and PAn as prepared above showed much better cycle performances (Figure 1B). Furthermore, composite cathodes gave very high energy density, the value of which far exceeded that of lithium cobalt oxide. The observed charge capacity of 185Ah/kg-cathode corresponds to 80% of the theoretical capacity (224Ah/kg-cathode)(1).

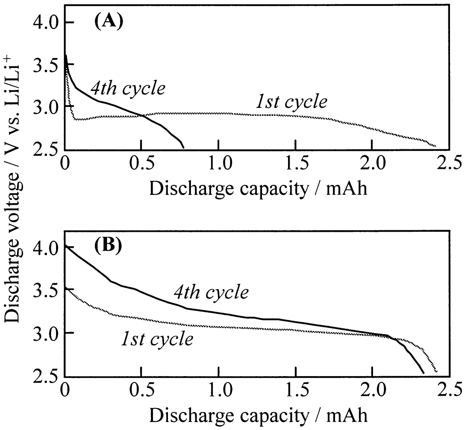
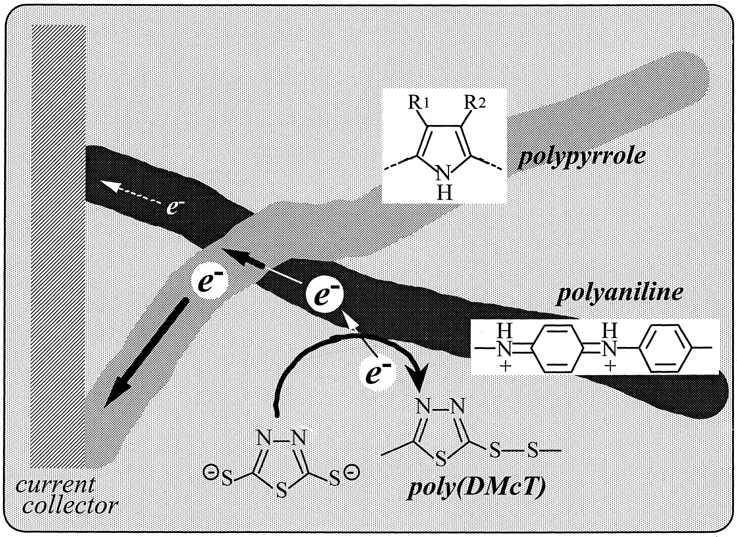


Figure 1 Charge-discharge curves of a test cell with cathodes of (A) poly(DMcT) and (B) composite of poly(DMcT) and PAn.

The high ratio of the observed capacity to the theoretical capacity confirms that both DMcT and PAn serve as an active material. It is also expected that during charging process both of the thiols on DMcT monomer are oxidized and polymerized to poly(DMcT) which is reduced and depolymerized to the monomer during discharging process as expected in Scheme 1. The DMcT redox reaction was considered to proceed via electron-exchange reaction with PAn.

Although DMcT/PAn composite materials provided high energy density exceeding 600Wh/kg-cathode as a cathode for lithium batteries, charge-discharge rates remained still too low for practical applications. This was ascribed to insufficient acceleration of the DMcT redox reactions and poor conductivity of the composite. The conductivity of the composite has been improved by adding another conducting polymer with higher conductivity to the composite[10)]. The addition of a polypyrrole derivative to the composite enabled charging at a higher rate. In this composite, PAn mediates the oxidation and reduction of DMcT and the polypyrrole derivative conveys electrons between PAn and a current collector as shown in Scheme 2. Thus, the polypyrrole derivative serves as a subsidiary molecular current collector as well as electrode active material.



Scheme 2 Electron flow in the DMcT/PAn composite cathode containing a polypyrrole derivative during the charging process.

Effects of Formation of Copper-DMcT Complexes

While characterizing DMcT/PAn composite cathodes with various current collectors, it was found that composite cathodes prepared on a copper current collector could be charged and discharged at a rate of 0.83C with excellent cyclability, compared to other current collector materials as shown in Figure 2[11]. Furthermore, with a copper current collector discharge capacity increased up to 233mA/kg-cathode, which corresponded to 125 % of the theoretical capacity value calculated based on the amounts of DMcT and PAn in the composite. The observed capacity value indicates that not only DMcT and PAn but also the copper current collector serves as a cathode active material. The energy density of the DMcT/PAn composite on a copper current collector was estimated to be >550Wh/kg-cathode at average discharge voltage at 3.2V (*taking the weight of active copper into account*).

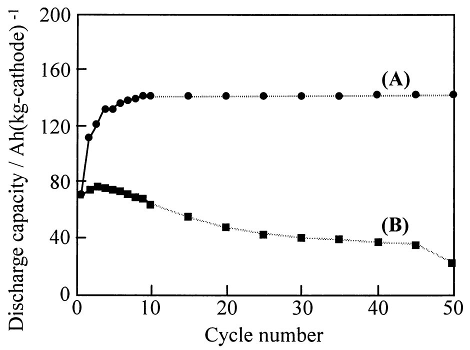


Figure 2 Changes in the discharge capacity of composite cathodes with a (A) copper and (B) carbon current collector. Discharge rate : 0.83C.

It has been reported that copper ions affect chemical and electrochemical reactions of organosulfur compounds such as DMcT[12]. In our electrochemical experiments coupled with surface analysis technique such as phase measurement interferometric microscopy (PMIM) and quartz crystal microbalance (QCM), it was observed that a large overpotential (ca. 600mV) was required for copper oxidation and dissolution in the presence of DMcT, compared to the oxidation in the absence of DMcT[13]. This observation suggested the presence of surface layer on the copper substrate. Furthermore, it was found that the copper substrate was mainly oxidized to cuprous ion (Cu^I) rather than cupric ion (Cu^{II}), which implies stabilization of Cu^I possibly due to formation of a DMcT-Cu complex. Formation of a complex has been reported between DMcT and copper ions and other metal ions[14)]. In the absence of DMcT, a copper substrate was oxidized to Cu^{II} at a more negative potential.

To prove the formation of a complex between DMcT and Cu ion in the composite, we carried out surface analysis on a copper substrate soaked in a DMcT solution. PMIM and QCM studies have clearly shown that a copper substrate spontaneously dissolves in the presence of DMcT[15)]. IR-Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) studies have revealed that the copper surface is covered with a layer of complex comprised of DMcT dimer ($DMcT_2$) and Cu^I ion, which protects the copper surface from further dissolution. The presence of a similar complex layer was proved at the interface between the composite and copper current collector and within the composite after several charge-discharge cycles. Cyclic voltammetric studies confirmed that the complex possessed electrocatalytic activity toward the redox reaction of DMcT in a solution[16)]. It seemed that the electrocatalytic activity of $DMcT_2$-Cu complex was based on the redox reaction of the copper center from XPS and cyclic voltammetric studies.

Based on the results described above, it is concluded that the formation of $DMcT_2$-Cu complex at the composite/copper and within the composite plays an important role for the acceleration of the redox reaction of DMcT and thus the observed improvements in battery performance of DMcT/PAn composite cathodes on copper current collectors.

Composite Cathode Containing Elemental Sulfur (S_8)

Sulfur compounds other than organosulfurs with thiols are also of our interest as cathode materials for lithium batteries. Recently we have succeeded in increasing the energy density of DMcT/PAn composite cathode by adding elemental sulfur (S_8) to the composite[17)]. S_8-containing composite cathodes gave charge capacity exceeding 550Ah/kg-cathode in more than 30 charge-discharge cycles. To attain the observed capacity, it was required that during discharging process a sulfur atom was, at least partially, reduced to S^{2-}, i.e., 16-electron per S_8 (1675Ah/kg-S_8). Furthermore, as shown in Figure 3A, average discharge voltage was 3.5V, which is far more positive compared to reduction potentials of S_8 (Figure 3B). In general, S_8 is reduced to a radical anion, $S_3^- \cdot$, at about +2.6V vs. Li/Li$^+$ as shown in Figure 3B (280Ah/kg-S_8), and it is mostly impossible to electrochemically reduce S_8 to $8S^{2-}$, i.e., 16-electron reduction$^{18)}$. Thus, we expect that S_8 strongly interacts with DMcT and/or PAn in the composite to attain the excellent battery performance. Extensive research on reactions in the S_8-containing composite is in progress.

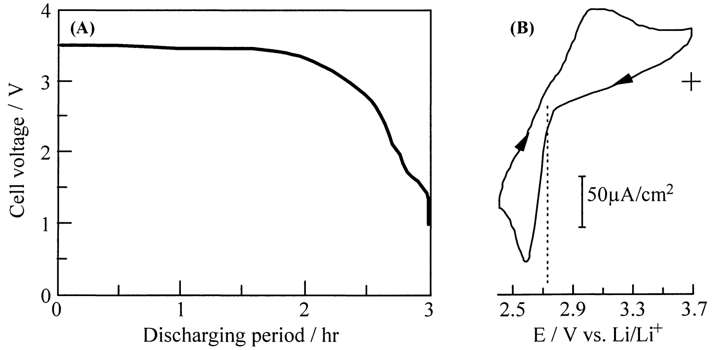


Figure 3 (A) Time course change of the discharge voltage of a test cell with DMcT/PAn composite cathode containing S_8 (6th cycle). (B) Cyclic voltammogram of 2mM S_8 in 0.25M tetrabutylammonium perchlorate (TBAP)/NMP at glassy carbon electrode.

Conclusion

Polymer composite cathodes based on polydisulfides and polyaniline were developed for polymer lithium batteries with high energy density. Test cells using the polymer composites combined with polymer gel electrolytes and lithium metal anode provided extremely high energy density with excellent cyclability. These polymer lithium batteries with high energy density will be useful as power sources for not only portable electronic devices such as cellular phones and camcorders but also for electric vehicles, spacecrafts and robots.

Acknowledgement

The authors are grateful to Drs. T. Tatsuma, F. Matsumoto, J. M. Pope, Q. Chi, E. Shouji, S. C. Paulson and T. Sotomura. This study was supported in part by the Proposed-Based New Industry Creative Type Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

1. N. Oyama, T. Tatsuma, T. Sato, T. Sotomura, *Nature* **373**, 598 (1995)
2. A. Kaminaga, T. Tatsuma, T. Sotomura, N. Oyama, *J. Electrochem. Soc.* **142**, L47 (1995)
3. E. Shouji, N. Oyama, *J. Electroanal. Chem.* **410**, 229 (1996)
4. E. Shouji, H. Matsui, N. Oyama, *J. Electroanal. Chem.*, **417**, 17 (1996)
5. T. Tatsuma, H. Matsui, E. Shouji, N. Oyama, *J. Phys. Chem.* **100**, 14016 (1996)
6. E. Shouji, Y. Yokoyama, J. M. Pope, N. Oyama, D. A. Buttry, *J. Phys. Chem.*, B **101**, 2861 (1997)
7. T. Tatsuma, Y. Yokoyama, D. A. Buttry, N. Oyama, *J. Phys. Chem., B* **101**, 7556 (1997)
8. N. Oyama, T. Tatsuma, T. Sotomura, *J. Power Sources* **68**, 135 (1997)
9. N. Oyama, J. M. Pope, T. Sotomura, *J. Electrochem. Soc.* **144**. L47 (1997)
10. T. Tatsuma, T. Sotomura, T. Sato, D. A. Buttry, N. Oyama, *J. Electrochem. Soc.* **142**, L182 (1995)
11. T. Sotomura, T. Tatsuma, N. Oyama, *J. Electrochem. Soc.* **143**, 3152 (1996)
12. For example, S. Jeannin, Y. Jeannin, G. Lavigne, *Inorg. Chem.* **18**, 3528 (1979)
13. Q. Chi, T. Tatsuma, M. Ozaki, T. Sotomura, N. Oyama, *J. Electrochem. Soc.* **145**, 2370 (1998)
14. M. R. Gajendragad, U. Z. Aqarwala, *Anorg. Allg. Chem.* **415**, 84 (1975)
15. F. Matsumoto, M. Ozaki, Y. Inatomi, S. C. Paulson, N. Oyama, *Langmuir* **15**, 857 (1999)
16. F. Matsumoto, Y. Inatomi, N. Oyama, in preparation (1999)
17. N. Oyama, S. Hirakawa, O. Hatozaki, T. Sotomura, in preparation (1999)
18. For example, E. Levillain, F. Gaillard, P. Leghie, A. Demortier, J. P. Lelieur, J. Electroanal. Chem. 420, 167 (1997)