New Organosulfur Polymer Lithium Battery with High Energy Density -Controlled Electron Transfer Reaction of Organosulfur Materials and Its Application to Energy Storage-

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Abstract

The redox reaction of 2,5-dimercapto-1,3,4-thiodizaole(DMcT) at electrode surfaces is slow at room temperature and influenced strongly by acidity of solutions. However, it can be accelerated when the electron transfer reaction was coupled with that of a polyaniline (PAn), PAn can be used as a molecular current collector for the insulating organosulfur compounds which are promising a high capacity energy storage materials. The charge-discharge capability of a polymer composite cathode prepared from DMcT, PAn, 3-alkylcarboxylate-4-methylpyrrole and acetylene black has been investigated on different kinds of current collectors including copper and porous carbon film in a lithium cell system with a gel-like polymer electrolyte. A battery assembled from the polymer composite cathode with a copper current collector provides a flat discharge difference from 3.4 to 2.8V and high current capability (137-194 A/kg-cathode) without undue deterioration of the energy density. The battery can be charged up to 550 Wh/kg-cathode within 1.25 hr and reversibly discharged within 1/25 hr.

1. Introduction

The increasing popularity of portable electronics has created a strong, unfulfilled demand for rechargeable batteries which possess high gravimetric energy density. The most likely products to meet this demand are those based on lithium ion (or "rocking-chair") technology. Recent advances in developing lithium-intercalated anodic materials to replace the traditional highly reactive Li metal anodes in these batteries are quite promising. However, development of active cathode materials to increase the overall stroage capacity of the cell has been slow and mainly centered on materials based on metal salts of lithium, although some works have been done on cathode materials based on conducting polymers, with limited success.

We have developed an active cathode materials based on the combination of a conducting polymer such as polyaniline (PAn) and an organosulfur compound such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT) as shown in Figure 1. Cathode made using composites of these materials exhibit extremely high energy capacities (ca. 185 Ah/kg) versus a lithium metal anode to give a gravimetric energy density of >600 Wh/kg-cathode[1]. Further improvements in our system have shown the promise of this type of chemstry to provide reliable, non-toxic, extremely high energy density batteries. These improvements have included our use of a polypyrrole dopant to increase the charging rate of the cell, our use of a copper current collector to substantially increase the cycling stability of the cell, and our recent elucidation of the proton transfer processes which may be responsible for the electrochemical behavior of the composite. These advances in the technology and our understanding of it taken together with the fact that organosulfur compounds similar to DMcT, for example N,N,N,N-tetramercapto-ethylenediamine, possess theoretical energy capacities of up to 582 Ah/kg-cathode indicate that sutdy of this general system had a great promise. In this contribution, we report some details of our recent advances regarding the chemistry of the PAn/DMcT cathode material, emphasizing our improvements in cycling stability due to the use of a copper current collector and our conceptual breakthrough in understanding the proton coupled redox processes in the cathode.

2. Experimetal

2.1 Materials

Chemically polymerized PAn in powder form (undoped, reduced form) was obtained from Nitto Denko Co. (Japan). PAMPy (reduced form) was purchased from Nippon Soda Co. (Japan). Battery-grade lithium foil of 300μm thick was obtained from Kyokuto Metal Co. (Japan). A porous carbon film of 85μm thick consisting of fluoropolymer and carbon black powder (density: 0.95 g/cm^3, volume resistivity; 0.46 Ωcm) was obtained from Japan Goretex Co. It was laminated with 30μm thick titanium foil. Copper, nickel, aluminum and titanium foil of 30μm thick were obtained from Takeuchi Metal Co. (Japan). Gold (400nm thick)-plated titanium foil was prepared by vacuum deposition method. All other chemicals were purchased from Kanto Chemical Inc. Co. and used proper purification treatments.

2.2 Preparation of gel-like polymer electrolyte

A gel-like polymer electrolyte was prepared under a dry argon atmosphere by dissolving 2.3g $LiBF_4$ in a mixture of 7.9g ethylene carbonate (EC) and 10.5g propylene carbonate (PC); dispersing 2.5g acrylonitrile-methylacrylate copolymer powder in the resulting electrolyte solution, heating the dispersion at 120 to 150°C in a sealed Teflon container until a viscous transparent liquid was obtained. The liquid was cast on a stainless steel pad (120x95mm), sealed with an aluminum laminated bag, and cooled at -20°C overnight.

2.3 Cell testing

A test cell was charged and discharged at a constant current for a given time. The charging or discharging current and time were defined on the basis of theroretical capacity (for further details see Results and Discussion). The upper potential difference of charging was limited to 4.65V. If the potential diffrence of 4.65V was reached in the course of charging, the charging was continued at a constant potential difference of 4.65V until a given charging time fully elapsed. The discharging was cut off when the potential difference of 2.0 or 2.85V was reached. The cell was allowed to stand for 0.5hr before discharging. All the charge-discharge experiments were carried out at 20°C using computer controlled

an automtic battery charging-discharging instrument.

3. Results and Discussions

3.1 Reactivity of organosulfur compounds

The reversible conversion of DMcT between polymerized and depolymerized forms corresponds to the formation and cleavage processes of the disulfide bond (Scheme 1), which accompanies electron transfer processes. The theoretical capacity of poly(DMcT) is 362 Ah/kg-cathode. However, since the redox reaction of a disulfide is very slow at room temperature, performance of a battery which consists of the organosulfur cathode is reasonable only at much higher temperatures[2]. The redox reaction processes of DMcT can be accelerated in polyaniline matrix and, thus, even at room temperature the DMcT-polyaniline composite film can act as a cathodic material in a secondary battery.

In the redox reaction processes of the DMcT-polyaniline film, it has been shown that a proton transfer reaction between DMcT and polyaniline plays an important role in the reaction activity[4-7]. Therefore, it is of interest to examine how the protonation and deprotonation processes of the mercapto thiadiazole influence the activity of the redox reaction processes. The effects of acid and base addition on the redox of thiadiazoles were examined via electrochemistry and semiempirical molecular orbital calculations[6]. It was found that the electrochemical oxidation from thiol to disulfide was promoted by the deprotonation at the thiol group. Changes of the electronic state of the thiadiazole ring due to the protonation at two nitrogen atoms in the ring or of the substituent thiolate group affect the reduction processes of the disulfide bond, whereby, the protonation of the thiadiazole ring or substituents facilitates cleavage of the disulfide bond. In addition, it was found that the reduction current of the oxidized DMcT is enhanced by the addition of pyridine[7]. The results described above predict that this acceleration will depend strongly upon the acidity within the polymer matrix.

3.2 Polydisulfide-polyaniline composite cathode

Conducting polymers such as a PAn, which possess electronic conductivity as

well as capability of storing charges, have attracted attention as electrode materials for rechargeable batteries. However, conducting polymers are not very stable in general because stored charges exist as radicals on conducting polymers. Since PAn is relatively stable conducting polymer, it has been commercialized as a cathode of rechargeable battery[8]. PAn can store one positive charge per monomer unit theoretically, so that it can potentially attain an energy density of 450 Wh/kg-cathode (Table 1). However, PAn stores only 0.5 positive charges per monomer unit in non-acidic media, otherwise it loses protons on its nitrogen atoms. Therefore, stored energy of PAn has never exceed metal oxides as a cathode.

Reversible electron transfer was observed between PAn and thiol/disulfide couples of DMcT, 2-mercapto-5-methyl-1,3,4-thiadiazole, 2-mercaptopyridine and thiophenol[4]. Thus, PAn can be used as a molecular current collector for those insulating organosulfur compounds at room temperature, probably because of the chemical interaction between organosulfur and Pan. Among those couples, DMcT exhibited the fastest reversible electron transfer. Electron transfer from other aromatic and aliphatic thiols to oxidized PAn is also observed. The reactions and reaction kinetics were affected by protons.

Then, we composed cathodes from DMcT and PAn[1]. The composite cathodes were prepared by casting N-methyl-2-pyrrolidone (NMP) solution containing both DMcT and PAn. Preparation of the cathodic materials in this way allows intimate molecular-level mixing between DMcT and PAn, both of which are redox active at the cathode. Further, rechargeable batteries were fabricated by coupling the composite cathode with a lithium anode and a polymer electrolyte. When the battery was charged at 4.75V, the cathode exhibited discharge capacity of over 185 Ah/kg-cathode and gravimetric energy density of over 600 Wh/kg-cathode. The theoretically-expected maximum discharge capacity of PAn in the composite cathode is 65 Ah/kg-cathode (one electron is assumed to be consumed per one aniline monomer unit). That of DMcT in the cathode is 159 Ah/kg-cathode (a two-electron reaction is assumed). The experimentally evaluated discharge capacity of 185 Ah/kg-cathode is thus more than 80% of the overall theoretical capacity of 224 Ah/kg-cathode.

A polymer composite cathode prepared from DMcT and PAn shows high gravimetric energy density when it is coupled with a lithium anode. However, charging and discharging currents should be 35 A/kg-cathode or less, otherwise

the cycle life is shortened. This value is not enough for the practical use. Then, we added a polypyrrole derivative to the DMcT-PAn composite to make it more conductive[9]. The addition of the polypyrrole derivative enabled the rapid charging at 87 A/kg-cathode without undue deterioration of energy density. That is, the polypyrrole derivative functions as subsidiary molecular current collector (Figure 2).

3.3 High rate capabilities of the composite cathode with a copper current collector

The cells with carbon and copper current collectors exhibited better cycle performances that the other cells with nickel, aluminum and titanium foil. Here we compare the cells with carbon and copper current collectors under the same conditions, at higher charge and discharge rates[10]. Figure 3 shows the results of charge-discharge testing of the cells with copper and carbon cathode current collectors 0.83C, where 1C is defined the charge or discharge current of [cathode theoretical capacity (Ah/kg]x[cathode weight(kg)]. The cells with a copper current collector gave a quite stable cell performance. Discharge capacities of the cells were around 150 Ah/kg-cathode. On the other hand, although the cell with a carbon current collector exhibited stable cycle ability at a charging current of 0.095C(not shown here), the larger charging current lowered the stability. That is, cycle performance of the cells with the copper current collector were much better than those of the cells with the carbon current collector.

The cell with a copper current collector exhibited a stable cycle performance over 250 cycles (at 0.5C, 220 ± 10 Ah/kg-cathode). This capacity exceeded the theoretical capacity (186 Ah/kg) calculated from the amount of PAn and DMcT contained in the cathode. This indicates that not only DMcT and PAn but also copper ion dissolving from the current collector function as a cathode active material in the present cell. Actually, we observed the dissolution of a slight amount of copper in the first charging process. In addition, the discharge curves or DMcT-conducting polymer cathode were flattened by using the copper current collector, retaining high energy-storage capability with low weight and good mechanical strength. A work is currently underway toward preparing and characterizing Cu-DMcT complexes and fabricating a cathode by coupling them with electrochemically inert current collectors.

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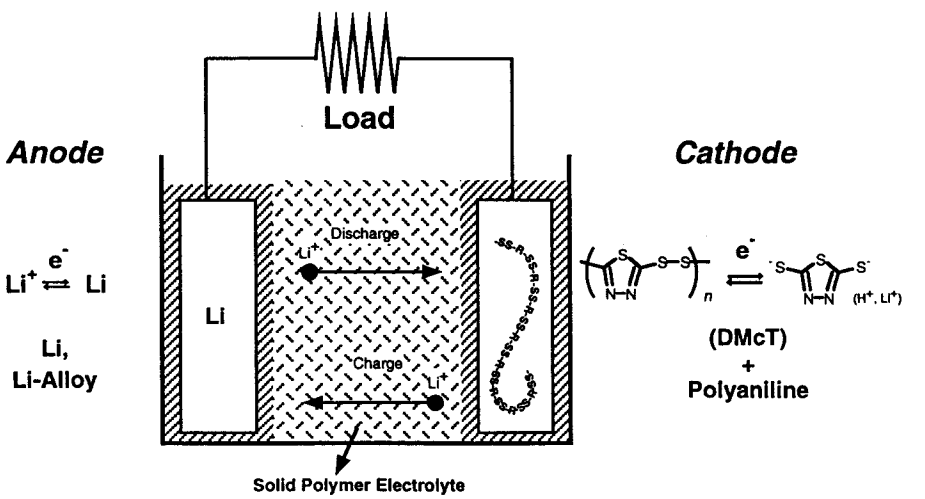

Figure 1. Configuration of lithium secondary battery which includes a PAn/DMcT cathode

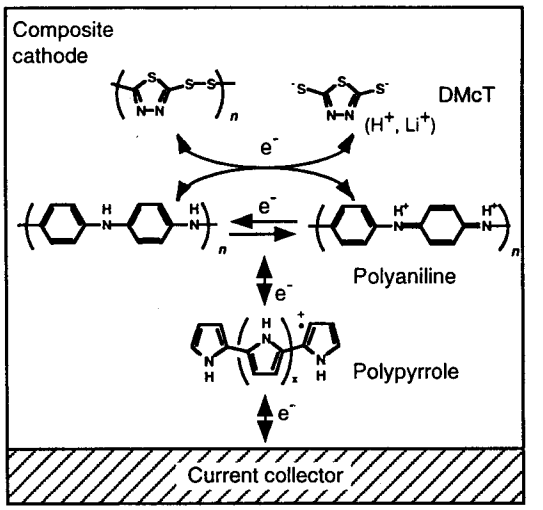

Figure 2. Modeling of charge transfer reactions in the composite cathode film

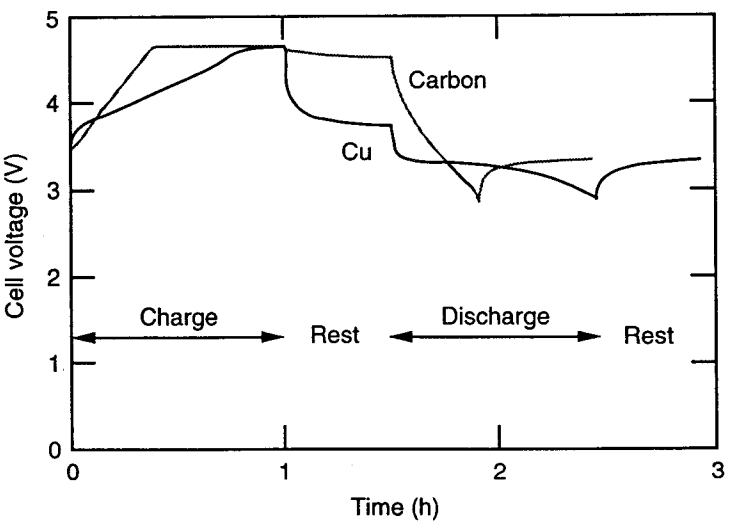

Figure 3. Charge-discharge curves of the 15th cycle of the lithium cells with a copper and a carbon cathode current collector: the cells are charged and discharged at a rate of 0.83C at 20°C