Development of Energy Storage Rubber

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A new concept was proposed as the energy storage rubber to develop the batteries involving electrode materials in rubber matrix. The cathode active material (LiMn_2O_4) and conductive carbon were mixed with rubber material to give flexible electrode. Some rubber materials were tested for this purpose, and the acrylic rubber matrix cathode gave the good charge/discharge cycle. The initial discharge capacity was 123 mAh/g, which value corresponded to that obtained in electrolyte solution.

Key Words : Energy Storage Rubber, Lithium Ion Battery, Rubber Cathode

1 Introduction

Many characteristics such as power, electrical property, suitability in working environment, etc. are required for the production of batteries, which are designed so as to work well under this conditions.¹⁾ The battery shape is also one of the important factors. The flexibility in the shape is required in some cases such as the electronic papers and organic EL displays.²⁾

It is necessary to use wide electrode surface in lithium ion battery, because the conductivity of organic electrolyte is lower than that of aqueous one. According, the Jelly roll type electrode is used by mixing and coating active material, conductive carbon and binder on metal sheet counter electrode.^{3,4)} It is, forever, difficult to give flexibility this type electrode.

On the other hand, the development studies are actively being carried out to apply the rubbers to new areas except for car industry. A few examples are in practice, however further studies are required for the development of higher-functional rubber.⁵⁾ Since rubbers are one of polymer liquid, it is possible to dissolve or disperse many kinds of materials. For example, conductive and magnetic rubbers are in practical application by disperse metals, carbon, and magnetites.⁶⁾

The rubbers are usually prepared by molding and vulcanization including chemical reaction of mixture of raw materials, and hence the resulting products are easily reformed to give flexibility and elasticity.⁷⁾ These characteristics can be differentiated from the plasticity of polymers. If the functions of energy storage are added to the rubbers, it is possible to realize the lithium ion batteries with the characteristics of rubbers. In this communication, we report the preparation and charge/discharge characteristics of cathode in a series of studies on the development of energy storage rubber.

2 Experimental

2.1 Rubber materials and swelling test

The following 12 kinds of rubbers were used as raw materials; silicone rubber (Q), butyl rubber (IIR), butadiene rubber (BR), isoprene rubber (IR), styrene-butadiene rubber (SBR), ethylene propylene rubber (EPDM), chloroprene rubber (CR), fluorocarbon-rubber (FKM), acrylic rubber (ACM), nitrile rubber (NBR), epichlorohydrin rubber (ECO), and hydrogenated nitrile rubber (HNBR).

The mixture of raw rubber, vulcanizing agent and vulcanizing accelerator was mixed by roll, and then vulcanized at 170°C for 10 minutes under hot press to give the sheet of 2 mm thickness. The test piece was cut out from this rubber sheet and soaked in propylene carbonate (PC), dimethoxyethane (DME), and PC+DME (50 : 50 by volume %) at 40°C for 72 h for swelling test. The change in the volume ($\Delta V\%$) before and after the soaking was evaluated as the degree of swelling.⁸⁾

2.2 Preparation of test electrode

Acrylic rubber (ACM) and EPDM were selected as the rubbers from the result of swelling test. The mixture of rubber, LiMn_2O_4 and graphite (or carbon black) was mixed by open roller, and then vulcanized at 170°C by hot press on Al foil. The resulting electrode was subjected to secondary vulcanization in air oven at 150°C for 1 h. The ratio of rubber, LiMn_2O_4 and conductive carbon was 100, 40, and 75 by weight for chronopotentiometry, and 100, 30, and 75 for cyclic voltammetry, respectively. This electrode was prepared at Fukoku Co. Ltd., and subjected to the measurements. Since the aluminum current collector was used, the flexibility was sacrificed because the measurements were carried out to confirm the charge and discharge characteristics.

2.3 Electrochemical measurement

The chronopotentiometry and cyclic voltammetry

were carried out for the electrode (surface area: 1.5 cm²) prepared as shown in 2.2. Counter and reference electrodes were Li, and the electrolyte was 1mol dm⁻³ LiBF₄/PC + DME (50 : 50 by volume%) with water content below 50 ppm in chronopotentiometry. The measurements were carried out in glove box of Ar gas atmosphere at room temperature. The applied current and cut-off potential were 0.1 mA and 3.0-4.4 V vs. Li⁺/Li, respectively. The cyclic voltammograms were recorded at 0.1-0.01 mV/s between 3.4-4.4 V vs. Li⁺/Li.

3 Results and Discussion

3.1 Selection of rubber

Table 1 show the results of swelling test in PC + DME. It is considered that the degree of swelling ($\Delta V\%$) is PC + DME was classified into two groups of $\Delta V > 100\%$ and $\Delta V < 100\%$. Therefore EPDM and ACM were selected as the rubber matrix for electrodes with lower and higher ΔV values, respectively. Table 2 shows the solubility parameter (SP) of organic solvents and rubbers. It is known that the rubber swells well in the solvent with similar SP value. There is no data of SP for DME in text. The SP value of DME may be estimated to be about 9, because the tested rubbers swell in this solvent. The SP value of PC was higher than that of rubbers. In PC + DME solution, that the characteristics of

PC become a dominant factor.

3.2 Charge and discharge characteristics of cathode

Figures 1 and 2 show the charge and discharge curves of the electrodes with EPDM and ACM. The rest potential of the electrode with ACM and EPDM matrixes was about 3.25 V. As shown in Fig. 1, when the EPDM with lower ΔV value was used as a rubber matrix, the electrode resulted in the poor charge and discharge characteristics.

On the other hand, the potential of the electrode with ACM gradually increased in the charge process at 0.1 mA. The charge capacity up to 4.4 V was 142 mAh/g, and corresponded to the theoretical value. In the discharge process, the potential decreased gradually from 4.4 V to 3.8 V, and then dropped rapidly to 3.0 V. The discharge capacity from 4.4 to 3.0 V was 123 mAh/g and the efficiency of charge and discharge was 87%. This value corresponded to that obtained in electrolyte solution.

The content of active material (LiMn₂O₄) and carbon were about 20 and 40%, respectively. This experiment was carried out to confirm the feasibility of charge/discharge in the rubber matrix. It is required to increase the content of active material, and to apply to the battery assembly with negative electrode. Further studies are now in progress.

Table 1 The swelling ratio PC + DME (50:50).

$\Delta V/\%$	Polymer
<100	Q, IIR, IR, BR, SBR, EPDM, CR
100<	ECO, FKM, ACM, NBR, H-NBR

Table 2 Solubility parameter of rubber and organic solvent.

Fig. 1 Charge and discharge curves of the electrode with EPDM matrix.

Fig. 2 Charge and discharge curves of the electrode with ACM matrix.

Fig. 3 Cycle performance of ACM matrix electrode.

Figure 3 shows the cycle performance of ACM matrix electrode. The capacity decreased slowly, and decreased rapidly after 50th cycle. After the charge/discharge cycle test, the electrode taken out from the cell was observed to be loose contact between the rubber and aluminum foil. The good charge/discharge may be expected by improving the loose contact.

3.3 Evaluation by cyclic voltammetry

Figure 4 shows the cyclic voltammograms of ACM matrix electrode at various scan rates. A characteristic two step-reaction process was observed from 0.01-0.05 mV/s. The increase in scan rate resulted in the large

Fig. 4 Cyclic voltammograms curve of ACM matrix electrode.

potential shift by IR drop. In the voltammogram from 3.8-4.4 V at 0.05 mV/s, C rate evaluated by the scan rate and current was 0.3 C.

4 Conclusion

The cathode of lithium ion batteries was prepared by mixing rubber, conductive carbon and LiMn_2O_4 as active materials, and the charge and discharge properties were investigated. The obtained results are as follows.

1. This electrode worked as the cathode of lithium ion batteries, and the capacity corresponded to that in electrolyte solution.
2. It was preferable to select the rubber with higher swelling property in the electrolyte.

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