

초청강연 1

Solid State Batteries using Copper Ion Conductive Solid Electrolyte and Copper Chevrel Phase Compound Electrode Sheets with Rubber Binder

Tadashi Sotomura

Battery Research and Development Center
Matsushita Electric Ind. Co. Ltd., Osaka, Japan

Solid state batteries using solid electrolytes and electrodes have been extensively studied because their advantages of longer shelf life and no electrolyte leakage. Inorganic powders are mainly used as solid electrolyte and electrode. The powders are press-moulded in to three layered pellets of cells. The solid pellets are rigid and brittle; so they have disadvantages of being fabricated in a limited form of tablets and not absorbing volume change accompanied by cell discharge or charge. Steele ¹⁾ pointed out that solid material with plasticity or elasticity was required to obtain stable cell performance. To develop solid batteries in a flexible or elastic sheet form, solid polymer electrolytes were introduced by Wright ²⁾ and extensively studied by Armand et. al ³⁾. Armand reported a polyethylene oxide based solid polymer electrolyte and tried to fabricate lithium batteries with flexible film form ⁴⁾. At present, polymer lithium ion rechargeable batteries using polymer gel electrolytes have been developed and commercialized and are used widely in mobile electronics appliances including cellular phones or note book computers.

Here, we report another way to get solid batteries in a flexible or elastic form. We have tried to mix synthetic rubber with solid electrolyte and electrode powders to obtain flexible solid electrolyte and electrode sheets with higher ionic conductive and good elasticity ⁵⁾ : $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ copper ion conductive solid electrolyte with an ionic conductivity of 3×10^{-1} S/cm was used to form electrolyte sheets; $\text{Cu}_x\text{Mo}_6\text{S}_{7.8}$ ($x = 0$ to 4) copper Chevrel phase compound was used for electrode sheets. The cell system is $\text{Cu}_x\text{Mo}_6\text{S}_{7.8}/\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{14}/\text{Cu}_x\text{Mo}_6\text{S}_{7.8}$ ($x = 0$ to 4). This, so-called rocking chair type cell, was firstly introduced by Kanno et. al. ⁶⁾, providing a higher current output of over 10 mA/cm^2 at room temperature. We fabricated test cells in a $15 \times 15 \text{ mm}$ form packaged with aluminum-laminated films (Fig. 1).

-
- (1) B. C. H Steele, Proceedings of NATO Advanced Study Inst., 163 (1985).
 - (2) P. V. Wright, Polymer, 7, 319 (1975).
 - (3) M. B. Armand and M. Duclot, USP4,303,748 (1978).
 - (4) M. B. Armand and D. Deroo, J. Electrochem. Soc., 132, 1333 (1985).
 - (5) T. Sotomura, S. Itho, S. Kondo, and T. Iwaki, DENKIKAGAKU, 59, 129 (1991).
 - (6) R. Kanno, Y. Takeda, M. Ohya, and O. Yamamoto, Mat. Res. Bull., 22, 1283 (1987).

This paper describes the effect of synthetic rubber binder on the charge-discharge performance and storage characteristics of the solid state rechargeable batteries. Styrene-ethylene-butadiene-styrene (SEBS) copolymer rubber was admixed with the electrolyte and electrode powders to make the cell elastic and to minimize the leak current through the solid electrolyte sheet. The volume fraction of the rubber was optimized to be 65 % in the electrolyte and 10 % in the electrode sheets. The cell with optimized electrolyte and electrode sheets provided a high current output of 10 mA/cm² with over 60 % of utilization of the copper Chevrel compound electrode, keeping 70 % of its initial capacity even after 78 day storage at 80 deg.C.

This paper also describes the mechanistic aspect of the copper Chevrel compound electrode reaction, namely the apparent diffusivity of copper ions in this electrode. Potential sweep and current pulse measurements were carried out to evaluate the apparent diffusivity of copper ions in the electrode sheet.⁷⁾ The diffusivity depended on the potential of the electrode and the mixing amount of the solid electrolyte: a larger value of 510×10^{-9} cm²/sec was obtained at 0.051 V (vs Cu, or $x =$ around 3.5 in $\text{Cu}_x\text{Mo}_6\text{S}_{7.8}$) for the electrode with 50 wt.% of solid electrolyte; and a smaller value of 0.13×10^{-9} cm²/sec at 0.509 V (vs Cu, or $x =$ around 0.5 in $\text{Cu}_x\text{Mo}_6\text{S}_{7.8}$) for the one with 20 wt.% of solid electrolyte. Dudley et. al reported the diffusivity at a high temperature of 441 K; 7×10^{-7} cm²/sec at $x = 1.5$ in $\text{Cu}_x\text{Mo}_6\text{S}_{7.8}$ and 4.8×10^{-5} cm²/sec at $x = 3.37$ ⁸⁾. The difference in the apparent diffusivity brought a marked effect on the charge-discharge cycle performance of the cell.

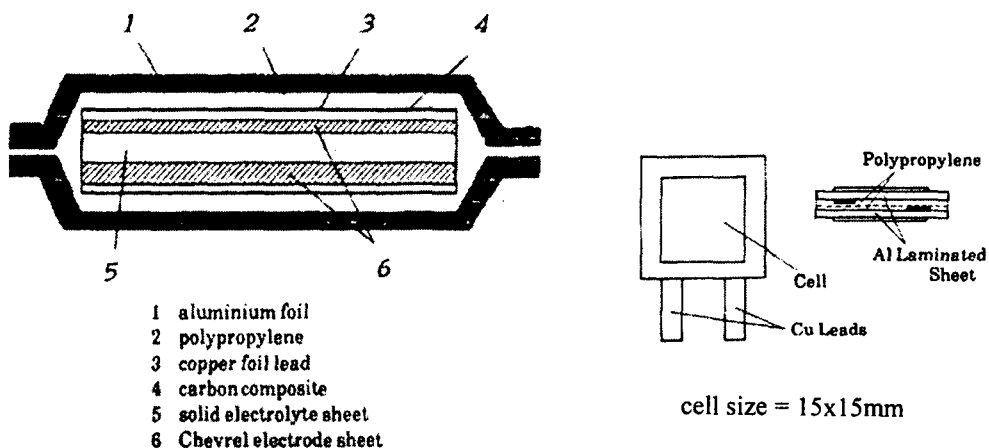


Fig. 1 Construction of the Test Cell.
 Solid state rechargeable cell using copper ion
 conductive solid electrolyte sheet of $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$
 and copper Chevrel electrode sheet of $\text{Cu}_2\text{Mo}_6\text{S}_{7.8}$

- (7) T. Sotomura and T. Iwaki, DENKIKAGAKU, 60, 44 (1992).
 (8) G. J. Dudley, K. Y. Cheung, and B. C. H. Steele, J. Solid State Chem., 32, 259. (1980).