

## Application of solid-polymer electrolyte in lithium batteries: ultra-thin film battery

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### Abstract

With the recent rapid progress in the electronics industry, the trend towards making electronic equipment more compact and lightweight has been accelerating. In addition to the need for batteries for use in such electronic equipment to be more lightweight and more compact, emphasises the need for a battery to be able to meet any shape requirement. We developed a solid-polymer electrolyte that has a high ionic conductivity of  $\sigma = 2 \times 10^{-3}$  S  $\text{cm}^{-1}$  at 25 °C, and using this electrolyte, we then developed an ultra-thin film primary battery of the size of a credit card and with a thickness of 0.1 mm. This battery is composed of  $\text{MnO}_2$ , a solid-polymer electrolyte and lithium, and has a volumetric energy density of 400 W h/l. In addition to this primary battery, we are currently developing an ultra-thin film secondary battery. An ultra-thin film battery, which employs our solid-polymer electrolyte, is advantageous in reducing risks such as the high reactivity of metallic lithium, heat accumulation inside the battery and internal shorting due to growth of deposited lithium.

### Introduction

It was proposed by Armand in 1986 [1] that the transfer of alkali metal ions in polyether, which form complexes with these ions, takes place through the amorphous parts of the complex structure. Watanabe *et al.* [2] advocated in 1986 that the ionic conductivity can be increased at low temperatures by inhibiting the crystallization of these complexes by means of three-dimensional cross-linking. We have developed a solid-polymer electrolyte that can be used over a wide temperature range by preventing crystallization through cross-linking the polyethylene oxide chains using a polyether-type copolymer to form a network structure. We have also succeeded in increasing the ionic conductivity at low temperatures by addition of a special plasticizer [3]. Figure 1 shows the ionic conductivity of this solid-polymer electrolyte at various temperatures T (K).

A polymer obtained by the three-dimensional cross-linking reaction of polyether that has an acrylated-reaction group is used in the solid-polymer electrolyte. This cross-linking reaction is attained by the application of heat, ultraviolet rays or electron beams to the polyether.

### Primary ultra-thin film battery

#### Designing

Figure 2 shows a general and a cross-sectional view of our ultra-thin film battery. The current collectors serve also as outer packaging. We made calculations by computer

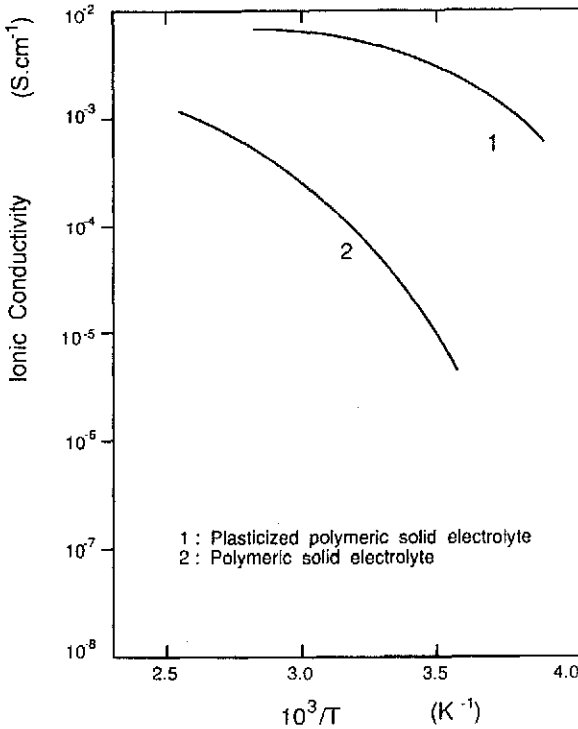


Fig. 1. Ionic conductivity as an inverse function of temperature.

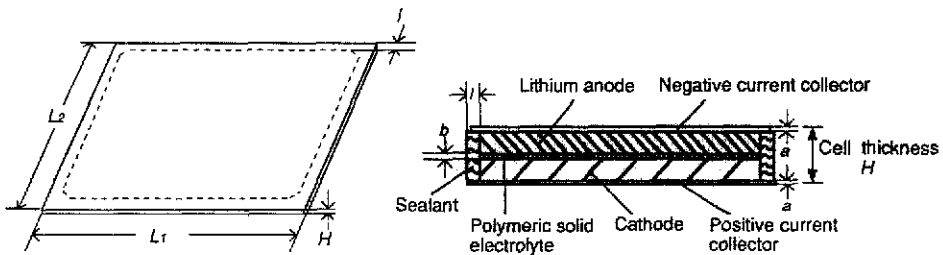


Fig. 2. General and cross-sectional views of ultra-thin film primary battery.

simulation regarding the effects of dimensional factors of each cell component on the volumetric energy density of the ultra-thin film battery. These dimensional factors include cell size and thickness, each component size and thickness and sealing width.

Figures 3 and 4 show the results of the volumetric energy density with respect to dimensional factors.

From these Figs. it can be seen that the volumetric energy density of an ultra-thin film battery is greatly influenced by the dimensions of each cell component. Therefore, in order to maintain the volumetric energy density at a high level, it is important to minimize the dimensions of those sections which do not contribute to the electrochemical reaction to generate electricity, such as current collectors, outer packaging and sealing sections.

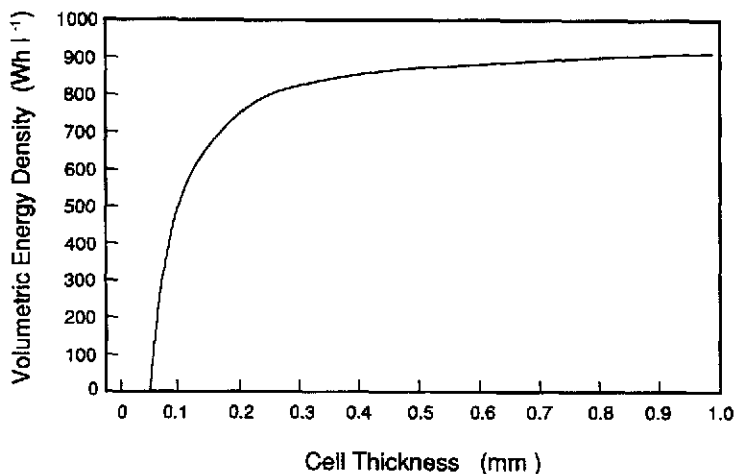


Fig. 3. Relationship between cell thickness and volumetric energy density from computer simulation.

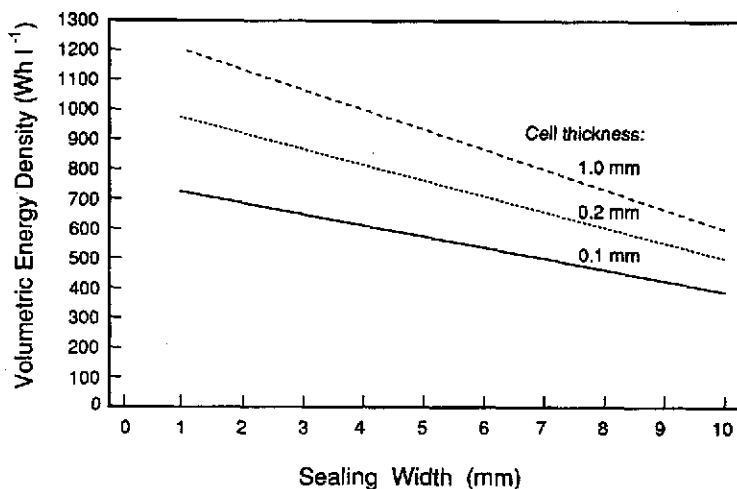


Fig. 4. Relationship between sealing width and volumetric energy density from computer simulation.

#### *Battery configuration and performance*

The cathode is a composite material consisting of the cathode-active material, carbon and a solid-polymer electrolyte. For this cathode-active material, we used  $\beta$ - $\text{MnO}_2$  which was obtained by subjecting electrolytic manganese dioxide to heat treatment. We then carried out various investigations on the composition of this composite material in an attempt to increase the volumetric energy density.

The anode was prepared by means of pressure-fitting metallic lithium foil onto the negative current collector. This foil was prepared by rolling to a thickness of  $30 \mu\text{m}$ .

The following describes our ultra-thin film primary battery we have produced on a test basis. The battery size is  $85 \text{ mm} \times 53 \text{ mm}$ , which is the same size as a credit card. Figure 5 shows a comparison of the energy density between our film battery

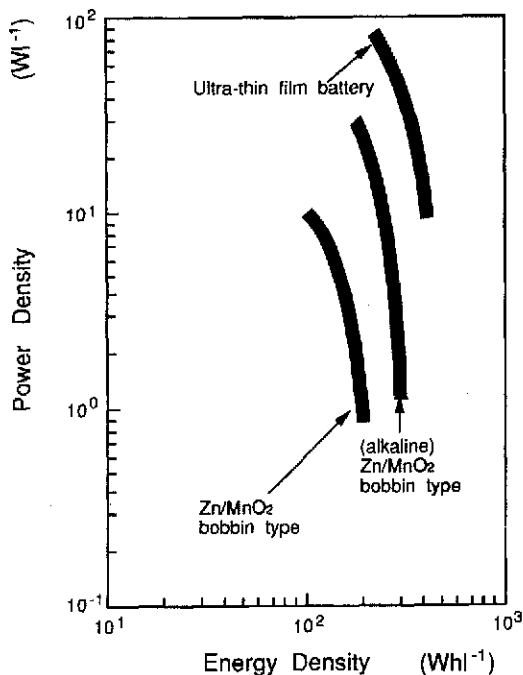


Fig. 5. Specific power vs. specific energy curves on volume basis for ultra-thin film battery compared with conventional cells.

and other general-purpose batteries. Despite the shortcoming in designing due to its extreme thinness, our battery exhibits a higher volumetric energy density than the other two batteries. Figure 6 shows continuous discharge curves for the ultra-thin film battery at ambient temperatures of 25 and 0 °C, respectively. These curves were obtained during discharge at a constant current of 0.1 mA/cm<sup>2</sup>. From this Fig. it can be seen that discharge of this battery at low temperatures has been made possible by the effect of preventing the crystallization of the complex by forming the polyether into a three-dimensional cross-linked structure, and also by the effect of an added plasticizer.

### Safety

What is most important for existing lithium batteries is safety, because metallic lithium shows a high reactivity with other materials.

Our ultra-thin film battery is soft and flexible; this fact demands even greater safety requirements against folding and cutting.

#### *Test by dropping cut cell into water*

To examine the safety features of our film battery, it was cut into halves using scissors and they were dropped into a water tank. One half of the battery came up to float on the surface and the other half was made to sink to the bottom. We expected that the floating half would be in a more dangerous situation because the reaction of lithium with water was thought to be accelerated by the three-phase interface of gas, liquid and solid. However, nothing happened to this floating cell as far as we

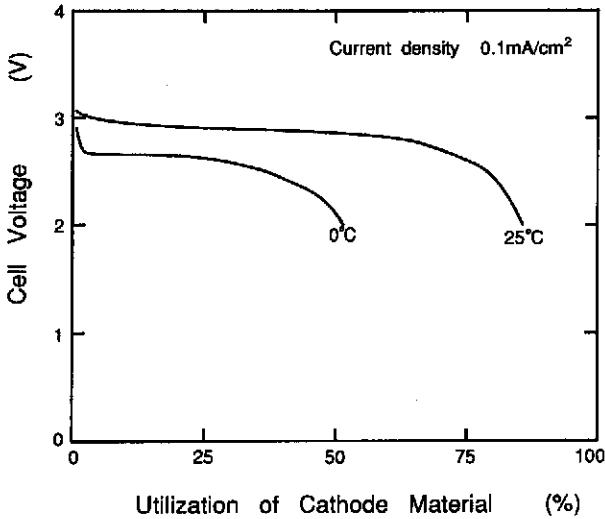


Fig. 6. Effect of temperature on cell discharge of ultra-thin film battery.

could see; the other half at the bottom of the tank was only observed to be bubbling gently. In the end, no ignition took place in either of them.

After this test was finished, we took out the floating piece, peeled off the outer packaging to open the battery and found the lithium on the negative current collector showing a metallic sheen. This means that the lithium was firmly covered and protected from water by the solid-polymer electrolyte.

#### *Crushing test*

For ordinary lithium batteries, crushing is fatal. For commercial lithium batteries, which employ liquid electrolyte, deformation of the battery itself causes the electrodes to be shorted to each other inside the battery, thereby creating a large current flow that results in an explosion-like ignition.

When an ultra-thin film battery is trampled on, it easily becomes deformed. We imagined what would happen if such a thin battery were stamped on by stiletto heel shoes. With this situation in mind, we carried out a crushing test to obtain the results.

A metallic bar with a diameter of 13 mm was placed on a film battery, and pressure was gradually applied using a hydraulic press. During the test, we observed changes in cell voltage, cell temperature and cell outside appearance. Table 1 shows the results. At 530 kgf/cm<sup>2</sup> (52 MPa), the cell voltage suddenly began to decrease, and finally reached nearly 0 V at 1000 kgf/cm<sup>2</sup> (98 MPa). During this period, however, no changes were observed in the cell temperature and the outside appearance of the cell. When the applied pressure was released, the cell voltage immediately recovered to 0.2 V. Although it was thought from the monitored cell voltage results that internal shorting apparently occurred, no increase was seen even in cell temperature. One of the possible reasons for this is that the ultra-thin design allows a large ratio of cell surface area to cell volume, which is, in turn, extremely helpful in radiating heat.

Figure 7 shows a comparison of surface area/internal volume ratios among various lithium batteries. The ratio of the ultra-thin film battery is approximately 15 times larger than that of a coin-type battery, and 60 times that of a cylindrical-type battery.

TABLE 1  
Crushing test results

Applied pressure (kgf/cm <sup>2</sup> )	Cell voltage (V)	Cell temperature (°C)	Change in outside appearance
0	3.23	26	none
100	2.93	26	none
530	1.6 → 0.2	26	none
1000	0.01	26	none
Released	0.2	26	none

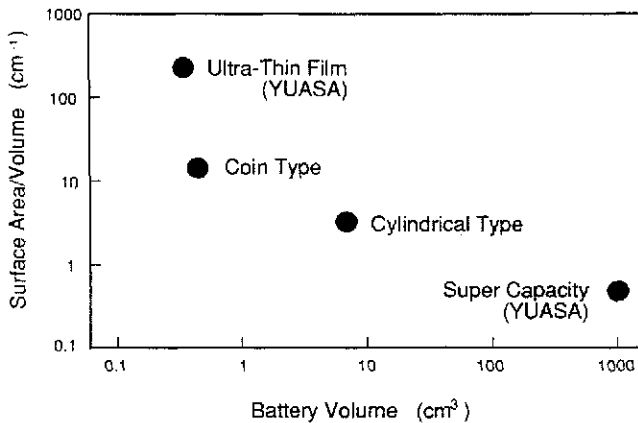


Fig. 7. Surface area/volume ratio of various lithium batteries.

### Secondary ultra-thin film battery

A secondary battery which employs metallic lithium in an electrode has more safety problems than do primary batteries which have been described above. The first problem is a limited cycle life due to the formation of dendrite-like lithium deposits, and the second is also a limited cycle life, but due to soft shorting caused by the formation of such lithium deposits. The third problem is that soft shorting results in heat generation inside the cell. Therefore, when dissipation of the heat, thus generated, is insufficient an explosion-like ignition will certainly occur. The third problem in particular results in fatal consequences for safety in the lithium secondary battery.

#### *Growth conditions of deposited lithium*

We made a comparison of lithium deposition conditions during charge between the solid-polymer electrolyte and the liquid-polymer electrolyte [4].

We used a LiClO<sub>4</sub>/propylene carbonate solution for the liquid-electrolyte system, and for the solid-polymer electrolyte we also used LiClO<sub>4</sub> as the salt. The cell, as shown in Fig. 8, was used to observe lithium-deposition conditions in the horizontal direction against the cross section, namely, the deposition plane. We continuously observed the deposition process using an optical fiber image pick-up type microscope. Figure 9 shows a morphological comparison of deposited lithium between the liquid-

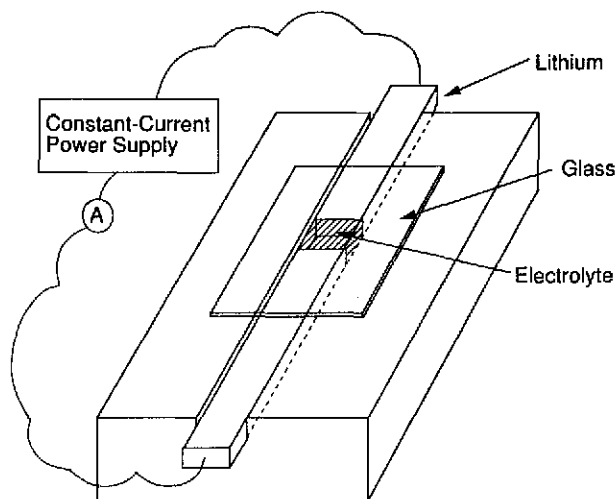


Fig. 8. Setup for observation of lithium deposits.

electrolyte system and the solid-electrolyte system, and these deposits were produced at the same amount of electricity under the same conditions. For the solid-polymer electrolyte, the deposits are actually globe-like and far from 'dendrite-like', as is generally observed in the liquid-electrolyte system. The growth distance from the lithium interface to the deposited lithium end in the solid-polymer electrolyte system is only approximately 1/10 of that of the liquid-electrolyte system.

Some of the possible causes of the difference in growth distance are as follows:

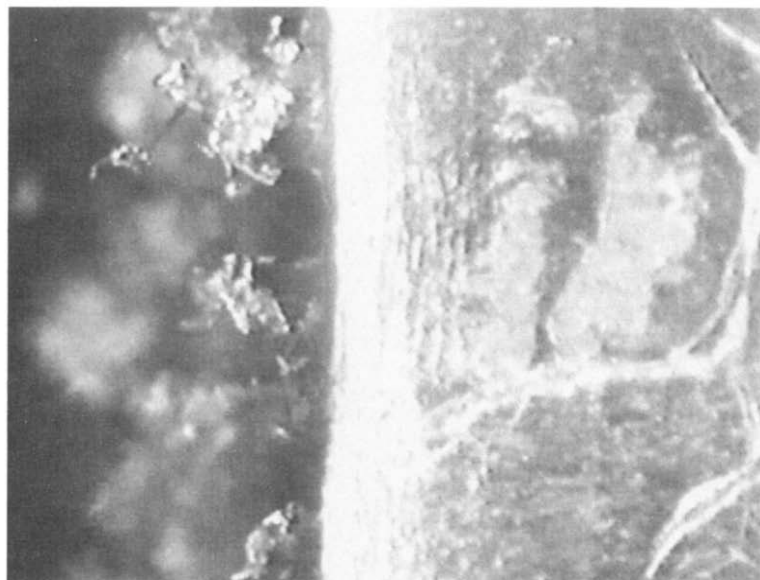
(i) Since a solid-polymer electrolyte is higher in molecular density than a liquid electrolyte, this provides a physical obstacle against growth of deposits.

(ii) The theory that lithium ions in the liquid-electrolyte system are considered to be transported to a lithium electrode in a solvate condition in the solvent by means of migration potential is generally accepted. However, in the solid-polymer electrolyte system there is no low molecular weight compound which is capable of migration, except for the plasticizer. Furthermore, since even such a low molecular weight compound as a plasticizer is captured by the polyether chains, the lithium ions' level of flexibility in selecting easy-to-deposit places, through which the lithium ions migrate, can be considered to be small.

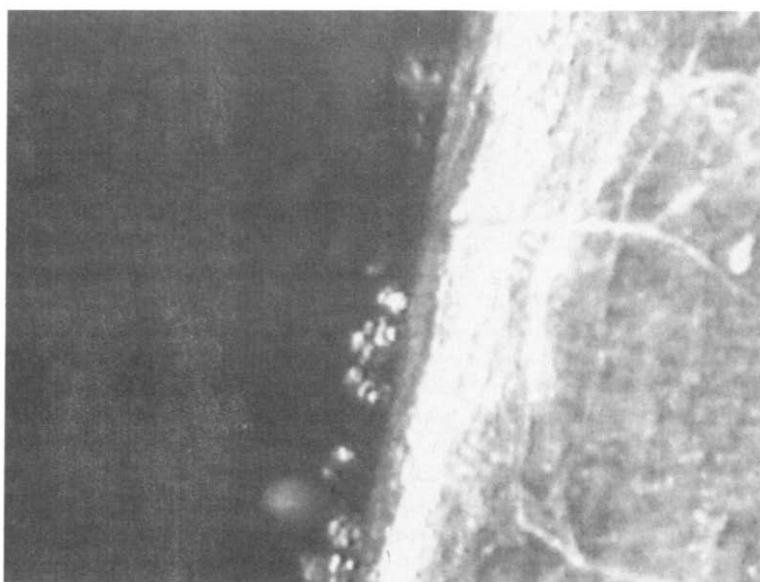
#### *Follow-up characteristics of solid-polymer electrolyte for electrode deformation*

One of the most characteristic problems with the application of solid-polymer electrolyte to a lithium secondary battery is the follow-up characteristics for physical deformation of electrodes which is caused through charge/discharge cycling.

In the lithium electrode, it is expected that repeated charge/discharge cycling will gradually change the morphology of the lithium deposits into finer particles. If such fine deposits are gradually accumulated on the electrode as cycling is going on, it would be difficult for a polymer electrolyte in a solid state to penetrate sufficiently into each corner of this fine structure. Thus, if a solid-polymer electrolyte can not penetrate into fine void spaces because it is solid, this would be one of the factors in limiting the cycle life.



(a)



(b)

Fig. 9. Morphology of deposited lithium in (a) 1 M  $\text{LiClO}_4$ /polypropylene carbonate, and (b) in solid-polymer electrolyte system.

We prepared two symmetrical lithium/separator/lithium cells (cell A and cell B) and simulated charge and discharge cycles for the lithium electrode by changing the direction of current every 12 h at a current density of  $0.1 \text{ mA/cm}^2$ . As a separator



we used a solid-polymer electrolyte for cell A, and a polypropylene non-woven sheet impregnated with a liquid electrolyte for cell B, so that we could make a comparison between the solid-electrolyte system and the liquid-electrolyte system. We used a  $\text{LiAsF}_6$ /propylene carbonate-based solvent solution as the liquid electrolyte. We also used  $\text{LiAsF}_6$  as the salt for the solid-polymer electrolyte.

With two changes of current direction counted as one cycle, we determined the interface resistance of the cell at each cycle by means of Cole-Cole plotting using the a.c. measurement method.

Figure 10 shows the results of the interface resistance in relation to cycle number obtained by means of Cole-Cole plotting. In the liquid-electrolyte system the interface resistance hardly increased even after 160 cycles, whereas in the solid-electrolyte system it sharply increased after 120 cycles. Although it can not be said that the difference between these phenomena is attributed solely to the above-mentioned poor follow-

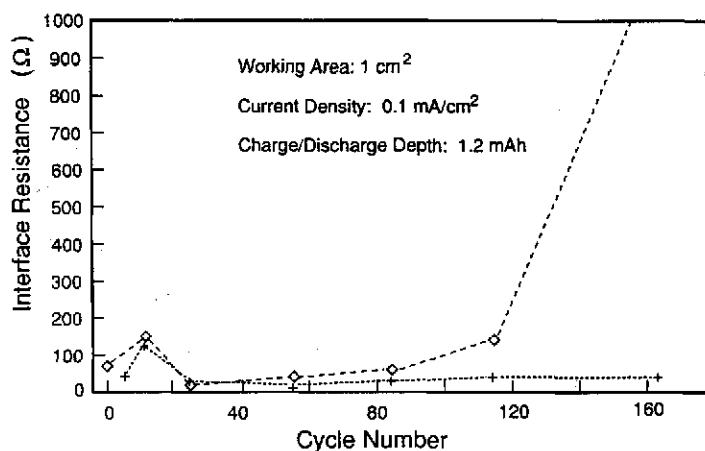


Fig. 10. Changes in resistance at lithium/electrolyte interface in lithium/electrolyte/lithium symmetrical cell: (+) liquid-electrolyte system, and (◇) solid-polymer electrolyte system.

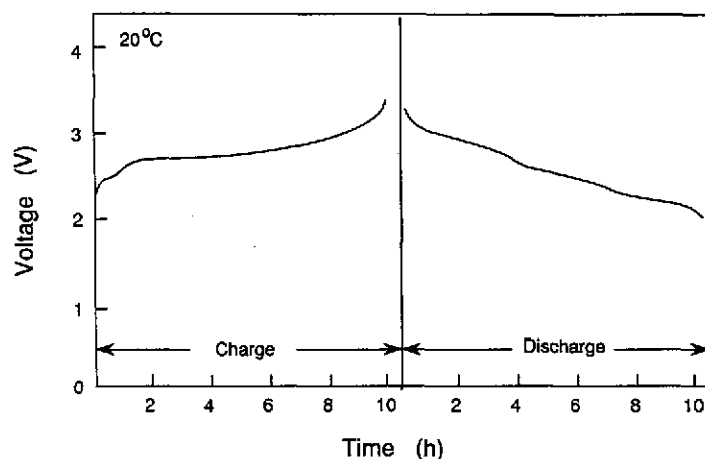


Fig. 11. Charge and discharge characteristics of lithium/vanadium oxide battery.

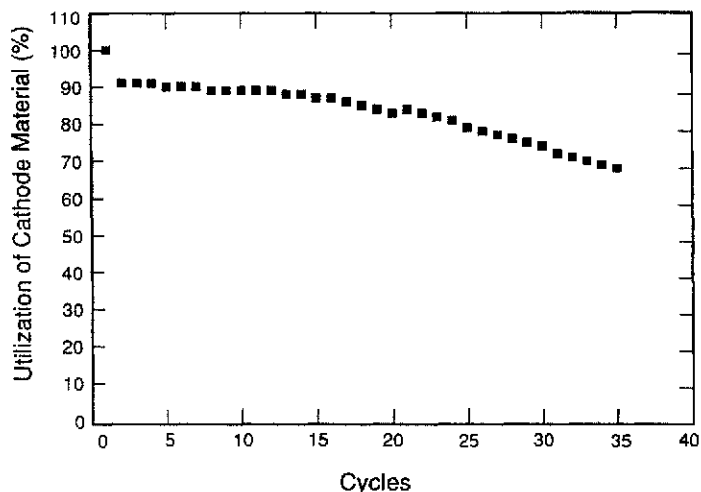


Fig. 12. Capacity change of ultra-thin film secondary battery during cycling.

up characteristics, we must pay attention to the electrode-interface behavior due to cycling.

It is generally known that a composite electrode is subjected to increases and decreases in its active-material volume due to charge and discharge cycling. Here, also with the ultra-thin film secondary battery, we can regard the following as parameters which will control the cycle life: (i) the follow-up characteristics of a solid-polymer electrolyte used inside the electrode to deal with repeated expansion and shrinkage of active-electrode material particles, and (ii) the follow-up characteristics of a solid-polymer electrolyte used as a separator to deal with expansion and shrinkage of electrode plates.

#### *Performance of secondary ultra-thin film battery*

An example of the configuration of a prototype secondary cell we have test-produced is as follows:

- electrode working area: 4 cm<sup>2</sup>
- cathode: vanadium oxide-carbon solid-polymer electrolyte composite
- separator: solid-polymer electrolyte
- anode: metallic lithium

Figure 11 shows the typical charge and discharge curves, and Fig. 12 shows a cell capacity change curve on repeated 100% charge and discharge cycling. As shown here, the capacity deterioration of our ultra-thin film secondary battery due to cycling is significantly larger than that obtained in the liquid system using the same active material. Therefore, improvement of this capacity performance is a future research subject.

#### **Conclusions**

1. Our 0.1-mm thick ultra-thin film primary battery has a volumetric energy density of 400 W h/l.

2. Our solid-polymer electrolyte firmly covers the lithium surface inhibiting the reactivity of lithium.

3. The ultra-thin film design allows efficient radiation of heat generated inside the battery, which is advantageous to safety.

4. Our solid-polymer electrolyte improves the shape of lithium which deposits during charge and inhibits also the growth of lithium deposits.

5. For a solid-polymer electrolyte, follow-up characteristics to deal with electrode deformation due to charge/discharge cycling are required.

## References

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