

A flexible Li polymer primary cell with a novel gel electrolyte based on poly(acrylonitrile)

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Abstract

The performance of a Li polymer primary cell with fire-retardant poly(acrylonitrile) (PAN)-based gel electrolytes is reported. By optimizing electrodes, electrolytes, the packaging material, and the structural design of the polymer cell, we succeeded in developing a “film-like” Li polymer primary cell with sufficient performance for practical use. The cell is flexible and less than 0.5 mm thick, which makes it suitable for a power source for some smart devices, such as an IC card. Fast cation conduction in the gel electrolyte minimizes the drop of the discharge capacity even at -20°C . The high chemical stability of the gel electrolytes and the new packaging material allow the self-discharge rate to be limited to under 4.3%, which is equivalent to that of conventional coin-shaped or cylindrical Li-MnO₂ cells. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Li polymer batteries using gel electrolytes are currently attracting much attention since they can take various forms, such as that of a thin flexible plastic film and also have high energy density and reliability [1–5].

There has been extensive research on the physical and electrochemical properties of gel electrolytes [6–19] but comparatively little research on practical polymer batteries using gel electrolytes themselves [20–23].

Recently, we found that a poly(acrylonitrile) (PAN)-based gel electrolyte with ethylene carbonate, propylene carbonate, and LiPF₆ shows fire-retardance which ensures the reliability of a Li polymer battery even though an organic electrolyte solution is immersed in the gel electrolyte [24,25]. In previous papers [24,26,27], we reported that the PAN-based gel electrolyte has good cation transport mechanism and chemical stability for use in batteries.

We report here the performance of a new flexible Li polymer primary cell based on a fire-retardant gel electrolyte and composed of Li metal and MnO₂.

2. Experimental

2.1. Preparation of the gel electrolyte

The gel electrolyte was synthesized from ethylene carbonate (EC, Li-battery grade, Mitsubishi Chemical), propylene carbonate (PC, Li-battery grade, Mitsubishi Chemical), poly(acrylonitrile) (PAN, Polyscience Inc., $M_w = 1.5 \times 10^4$), and lithium hexafluorophosphate (LiPF₆, Tomiyama). The PAN was dried under vacuum at 80°C for 24 h. EC, PC, and LiPF₆ were used as received. 49 mol% of EC, 24 mol% of PC, and 10 mol% of LiPF₆ were mixed together at room temperature to ensure wetting of 17 mol% of PAN powder, then the mixture was placed on a preheated hot plate at 110°C and stirred until a clear viscous solution was formed. Films for complex impedance measurements were fabricated by pouring the hot viscous solution onto a flat glass plate. The solutions formed a freestanding flexible film upon cooling to room temperature. All sample manipulations were performed in a dry room at a dew point lower than -40°C .

2.2. Measurement of ionic conductivity of the gel electrolyte

The level of ionic conductivity was determined by complex impedance measurements utilizing an impedance ana-

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lyzer (HP4192A, Yokogawa) with a desktop computer (Macintosh II-Si with “LABVIEW” National Instruments) for controlling devices and data acquisition. The applied voltage was 10 mV. The scanning frequency range was from 13 MHz to 5 Hz. The cell configuration is shown in Fig. 1.

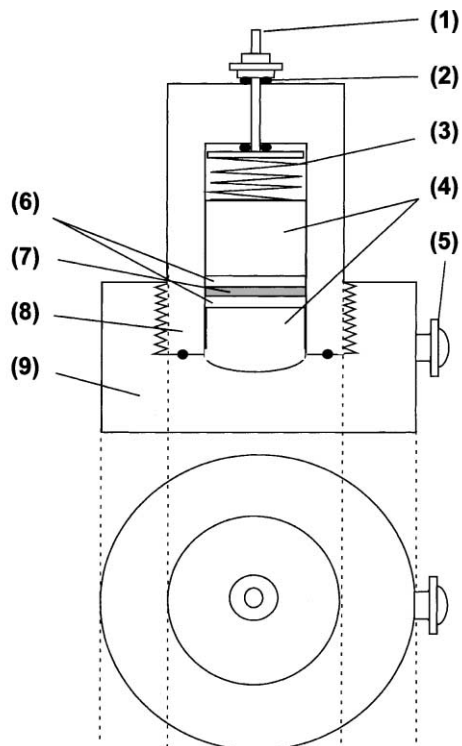


Fig. 1. Cell configuration for impedance measurements. (1) Terminal (SUS), (2) O-ring, (3) spring (SUS), (4) pellet (SUS), (5) terminal (SUS), (6) blocking electrode (Pt), (7) gel electrolyte, (8) casing (PTFE), (9) casing (SUS).

2.3. Fabrication of the Li-MnO₂ polymer cell

The positive-electrode plate (1), shown in Fig. 2, was prepared as follows:

Eighty-five wt.% of electrolytic manganese dioxide (Mitsui Kinzoku Kogyo), 10 wt.% of graphite (KS15, Lonza) and 5 wt.% of poly(tetrafluoroethylene) (Aldrich) were mixed and an approximately equal amount of *N*-methyl pyrrolidone (Wako) was mixed into the resulting mixture and kneaded to prepare material for the positive-electrode. This positive-electrode material was coated on a 2 cm × 2 cm area on a stainless steel mesh operating as a current collector and the resulting product was dried in a drier maintained at 120 °C and pressed by a calender machine. The electrode plate was molded to a shape in which a strip-shaped current collector (1b) was extended from coating area (1a) of the positive-electrode material to prepare the positive-electrode plate (1), as shown in Fig. 2.

A Li metal plate 30 μm thick (2a) was cut to a size of 2 cm × 2 cm and press-fitted to the current collector (2b) with the same shape as the positive-electrode plate to prepare the negative-electrode plate (2).

The gel electrolyte was coated over both the positive-electrode plate (1) and the negative-electrode plate (2), respectively. The gel electrolyte was then coated on a separator (3) poly(propylene) (a non-woven fabric, 40 μm). The positive-electrode plate (1), the separator (3), the gel electrolyte (4) and the negative-electrode plate (2) were stacked together to prepare a pair of the stacked electrodes, as shown in Fig. 2.

The stacked electrodes was covered with a heat-fusible laminated film, which constituted the exterior material for the cell (5), and the upper (5a) was packed in vacuum to

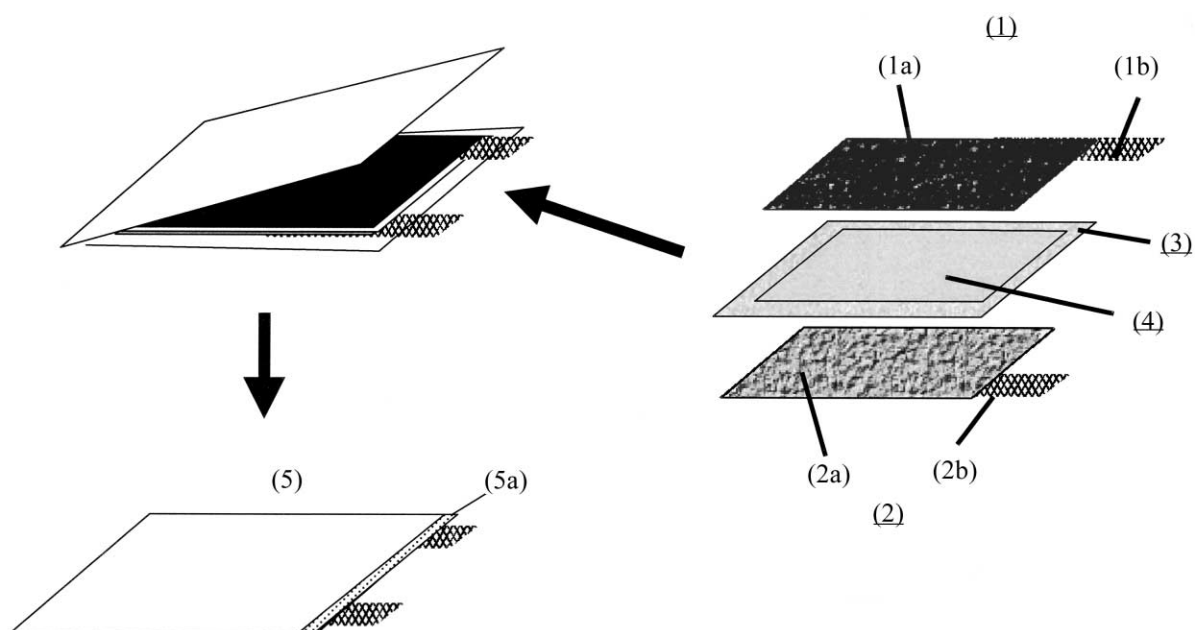


Fig. 2. Schematic images of the Li polymer primary cell.

make the film-like Li polymer primary cell. The surface area of the cell was ca. 5.2 cm^2 . The thickest part of the cell was not more than $500 \mu\text{m}$, and the average thickness was $400 \mu\text{m}$.

All fabrication work took place in a dry room with a dew point lower than -40°C .

The laminated film consists of three layers. The outer layer is poly(ethylene terephthalate) (PET) of $12 \mu\text{m}$, the middle layer is aluminum foil of $7 \mu\text{m}$, and the inner layer is poly(propylene) (CCP) of $70 \mu\text{m}$. The three layers were laminated by a calender machine. The PET was used for mechanical strength and thermal stability of the packaging film. The CCP is thermally stable up to 140°C plays a role of a heat-fusible layer.

We tested the cell performances using a discharge test system (BTS series, Nagano) in the galvanostatic mode.

2.4. Gas barrier of the heat-fusible laminated film

The effectiveness of the gas barrier of the heat-fusible laminated film was measured by monitoring the change in the weight of the package wrapped by the laminated film. Two grams of a silica gel (a desiccating agent) were completely wrapped by the heat-fusible laminated film in the dry room. The package was $10 \text{ cm} \times 10 \text{ cm}$ and it was stored at 60°C and a relative humidity over 95% in a test chamber. By monitoring the weight of the package for 2200 h, the gas-barrier effectiveness of the film was measured.

3. Results and discussion

3.1. Ionic conductivity of the gel electrolyte

The typical temperature dependence of the ionic conductivity of the PAN-based gel electrolytes is shown in Fig. 3. The ionic conductivity of the gel electrolyte reached

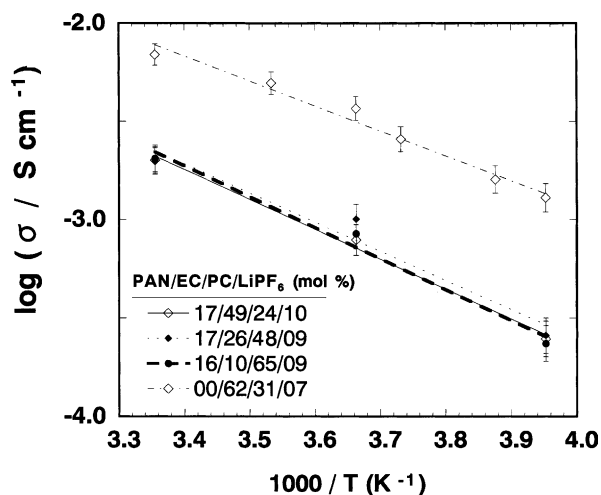


Fig. 3. Typical Arrhenius plot of ionic conductivity for several PAN-based gel electrolytes. The data for the liquid electrolyte was plotted for comparison.

over 10^{-3} S/cm at room temperature. In the entire temperature range from 23 to -20°C , the temperature dependence of ionic conductivity exhibited Arrhenius behavior. Compared to a conventional liquid electrolyte solution, for example EC/PC/LiPF₆ = 62/31/7 in mol%, the ionic conductivity of the gel electrolyte was slightly lower, however, the activation energy was similar.

Generally, the temperature dependence of ionic conductivity of a solid polymer electrolyte, such as a polymer complex of poly(ethylene oxide) and certain Li salts, obeys WLF behavior [28] because charge transport occurs with a corresponding short segmental movement of the polymer chain [28–32]. Therefore, the activation energy of the ionic conductivity is larger than that of the liquid electrolyte solution.

On the other hand, the activation energy of the ionic conductivity of the gel electrolyte is about 0.3 eV which is almost same as that of the liquid electrolyte solution. The corresponding of the activation energy of those electrolyte materials mean that the charge transport in the gel electrolyte is independent of the segmental movements of the PAN, and thus a “fast” charge transport might occur in the gel electrolyte [27].

The component ratio PAN/EC/PC/LiPF₆ = 17/49/24/10 (mol%) gave the better fire-retardance and mechanical strength for the gel electrolyte, thus, we adopted the component ratio for the cell.

3.2. Heat-fusible laminated film for the flexible Li polymer primary cell

In order to avoid penetration of moisture into a Li polymer primary cell and also give the cell flexibility, we developed a new heat-fusible laminated film which has the highly gas barrier performance enough for practical use.

Variations in the weight of the packaging over time are shown in Fig. 4. The weight of the package with the heat-fusible laminated film ($89 \mu\text{m}$) did not change over the entire time range. By contrast, the weight of the other package with a poly(ethylene) (“PE (1)”, $100 \mu\text{m}$), poly(ethylene) (“PE (2)”, $30 \mu\text{m}$), and the film made of a poly(ethylene-co-tetrafluoroethylene) (“ETFE”, $300 \mu\text{m}$) increased considerably over the time. The observed difference of permeability between PE (1), PE (2) and ETFE may be explained by the thickness of the films [33]. Although, the laminated film was thinner than PE (1) and ETFE, no moisture penetration was observed. These results indicate that the aluminum foil layer ($7 \mu\text{m}$) plays an important role as a barrier against moisture.

3.3. Positive-electrode design for a flexible Li polymer primary cell

3.3.1. Thickness of electrode

A thick positive-electrode gives the cell with a high discharge capacity but causes limits of the output power, for example the drain performance or the temperature

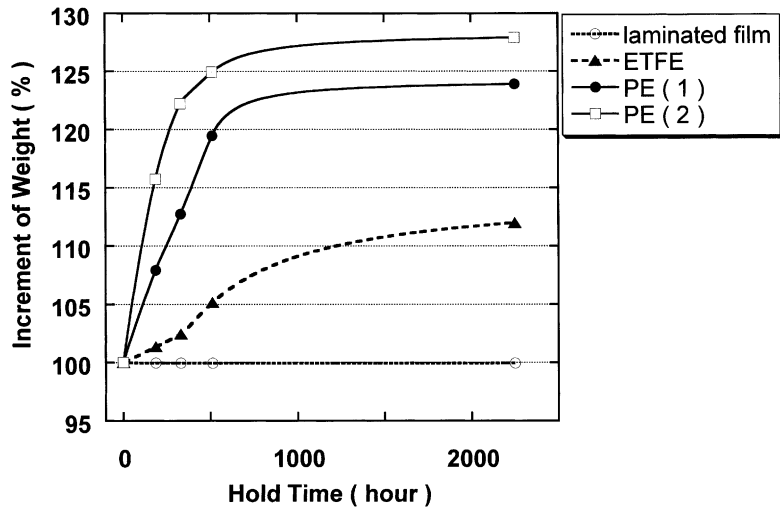


Fig. 4. Fluctuations in the weight of various packages were plotted against storage time. ETFE, PE (1), and PE (2) were shown for comparison.

performance. Therefore, optimization of the thickness of the positive-electrode is important to achieve a thin and flexible cell that has a high energy density.

Fig. 5 shows typical discharge profiles for a Li polymer primary cell with the positive-electrodes of different thicknesses. The positive-electrode made use of a stainless steel mesh (the diameter of the mesh was approximately 100 μm) for a current collector. Every cell showed a flat curve at 50 μA/cm², similar to a commercial cell with a liquid electrolyte solution. The average voltage for the 120 μm cell was 2.9 V, which is higher than those of the other cells. The average voltage is defined as the voltage at 50% in depth of discharge. The observed difference in the average voltage can be explained by the difference in the load current per weight of the positive-electrode.

Fig. 6 shows the relationship between the thickness of the positive-electrode and capacity density. The capacity density has a linear relation to the thickness of the positive-

electrode. The relationship between the thickness of the positive-electrode and the capacity density was defined by the Eq. (1). The correlation coefficient also indicates that the PAN-based gel electrolyte provides suitable interface between the electrolyte and the relatively thicker positive-electrodes.

$$Y = -3.34 + 8.05 \times 10^{-2}X \quad R = 0.997 \quad (1)$$

X: the thickness of the the positive-electrode (μm); Y: The capacity density of the positive-electrode (mAh/cm²).

Because of a trade-off of the cell capacity and cell thickness (size), we settle on an optimum for the thickness of the positive-electrode of 90 μm.

3.3.2. Polymeric binder

We investigated various polymeric binders for the positive-electrode. Fig. 7 shows two typical discharge profiles for the Li polymer primary cells with a PTFE binder and a

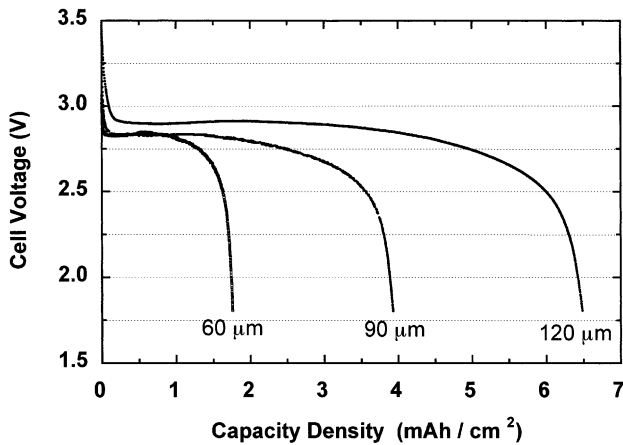


Fig. 5. Typical discharge profile for the Li polymer primary cells with the positive-electrode of different thicknesses. Load current 50 μA/cm², cut-off voltage 1.8 V.

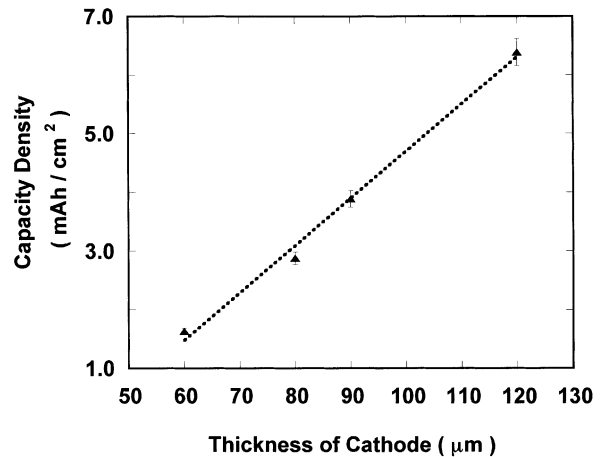


Fig. 6. Relationship between the thickness of the positive-electrode and capacity density. Load current 50 μA/cm², cut-off voltage 1.8 V.

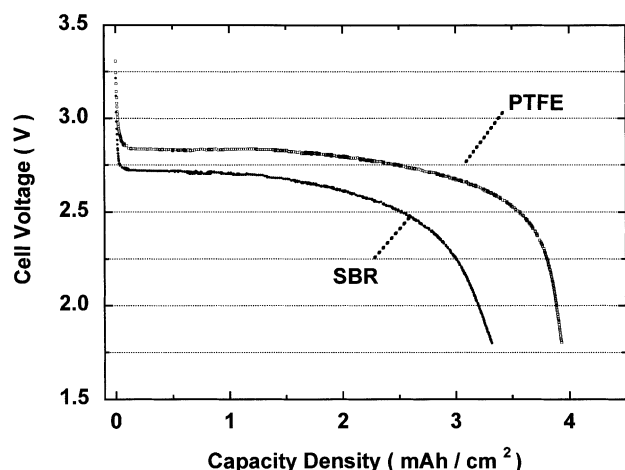


Fig. 7. Typical discharge profiles for Li polymer primary cells with a poly(tetrafluoroethylene) (PTFE) binder and a styrene butadiene rubber (SBR) binder. The thickness of the positive-electrode was 90 μm . Load current and cut-off voltage were 50 $\mu\text{A}/\text{cm}^2$ and 1.8 V.

styrene butadiene rubber (SBR) binder. The thickness of the positive-electrode was 90 μm and the load current was 50 $\mu\text{A}/\text{cm}^2$.

The closed circuit voltage (CCV) of the SBR cell tended to be lower than that of the PTFE cell. The average voltage was estimated to be less than 2.7 V, which was decrease of about 100 mV as compared with the PTFE cell. The discharge curve of the SBR cell also dropped gradually in the range from about 2.3 V to the end of measurements, thus, the capacity density of the SBR cell was inferior to that the PTFE cell. These results indicate that SBR used as a polymeric binder increased charge transfer resistance remarkably during discharge reaction, compared to PTFE. Therefore, we settle on an optimum for the binder of PTFE.

The difference observed in the discharge behavior arises from the difference in adhesion between the polymeric binder and the positive-electrode. The positive-electrode particles seem to be over-covered with the SBR, but not with the PTFE.

3.4. Cell performance

3.4.1. Typical discharge profile

Fig. 8 shows a typical discharge profile of the optimized flexible Li polymer primary cell. The capacity and an average voltage reached 16.4 mAh and 2.7 V at 200 μA , respectively. An error in the capacity values is less than 4%. The utilization of the MnO_2 used is found to be 94.2% at 200 μA . The thickness of the polymer primary cell is less than 0.50 μm . The volumetric energy density is ca. 210 Wh/l. The cell has enough capacity to operate IC cards with a transmitter at least for 3 years.

3.4.2. Drain performance

A serious problem for a polymer cell used to be poor drain performance. By optimization of the ionic conductivity of

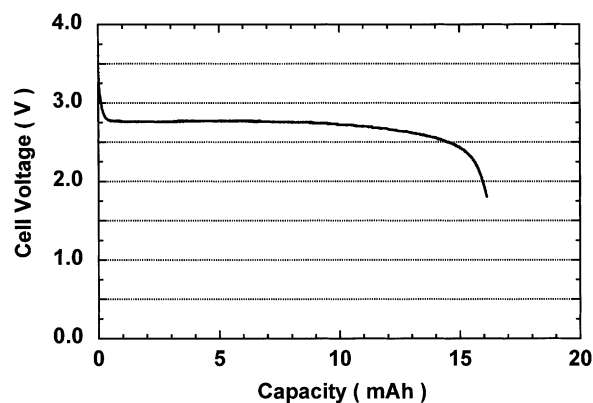


Fig. 8. Typical discharge profile of the optimized flexible Li polymer primary cell. Load current 200 μA , cut-off voltage 1.8 V.

the PAN-based gel electrolyte and the cell structure, the drain performance of the Li polymer primary cell improved sufficiently for practical use. Fig. 9 shows the relationship between load current and capacity density. The capacity density gradually decreased from 4.1 mAh/cm^2 (100%) to 3.6 mAh/cm^2 (88%) in the range from 50 to 500 $\mu\text{A}/\text{cm}^2$.

3.4.3. Pulse discharge condition

Fig. 10 shows a typical discharge profile of the Li polymer primary cell under a pulse discharge. The voltage slightly changed by about 37 mV, when the cell output a relatively high pulse current (500 μA). The low polarization arises from the low inner resistance of the Li polymer primary cell.

3.4.4. Temperature performance

Fig. 11 shows the relationship between cell temperature and capacity at 200 μA . The capacity density fluctuated with the cell temperature. The capacity retention decreased by 90% at -20°C . The higher ionic conductivity of the PAN-based gel electrolyte at -20°C might provide the sufficient capacity for practical use even at low temperatures. The capacity retention increased by 124% at 90°C . The electrolyte solution is chemically attached to the polymer chains in

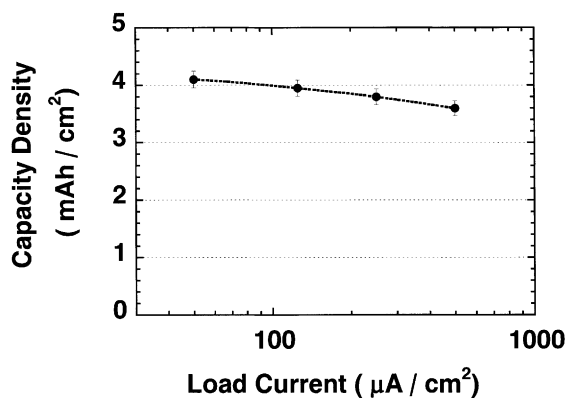


Fig. 9. Relationship between load current and capacity density of the Li polymer primary cell. Cut-off voltage 1.8 V.

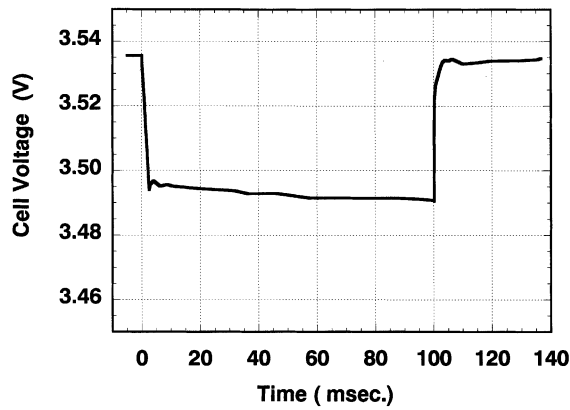


Fig. 10. Typical discharge profile of the Li polymer primary cell under a pulse discharge condition. Load current 500 μ A, discharge time 100 msec.

the PAN-based gel electrolyte, therefore, the Li polymer primary cell does not swell nor its capacity performance significant degraded even at 90 °C.

3.4.5. Storage performance

The self-discharge rate (SDR) of the Li polymer primary cell was investigated by measuring discharge capacity at 200 μ A at 23 °C. Before these measurements the cell was stored for 20 days at 60 °C, which is assumed to be equivalent to storage for a year at 23 °C.

The discharge capacity is plotted against the storage time in Fig. 12. The data of a commercial Li/MnO₂ cell (CR2320) with a liquid electrolyte is plotted for a comparison. It is well known that the SDR of the commercial cell is lower than that of most other cells. The capacity remaining of the Li polymer primary cell decreases linearly over time. This behavior is similar to that of the CR2320. The estimated SDR of the Li polymer primary cell and the CR2320 were almost same, and so the good storage performance of the Li polymer primary cell was confirmed. The storage performance of the Li polymer primary cell can be explained by the chemical stability of the PAN-based gel electrolyte [26]

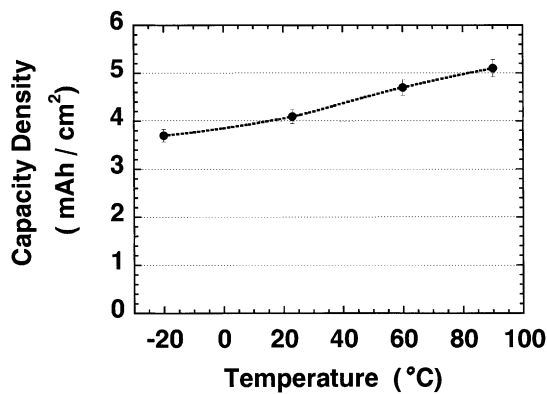


Fig. 11. Relationship between cell temperature and capacity density of the Li polymer primary cell. Load current 200 μ A, cut-off voltage 1.8 V.

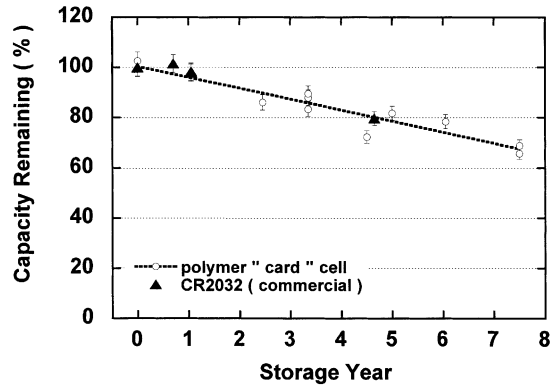


Fig. 12. Discharge capacity of the Li polymer primary cell plotted against storage time. Load current 200 μ A, cut-off voltage 1.8 V.

and, as mentioned earlier, the good gas barrier of the new heat-fusible laminated film.

3.4.6. Bending and safety evaluation

Flexibility is needed for a cell used such for an IC card. To test the cell's flexibility it was bent 1000 times from about +45 to -45° as shown in Fig. 13.

Table 1 shows the results of the storage and safety evaluation. The capacity drop of the cell was not observed after those 1000 bends. This result might be attributed to the adhesive nature of the gel electrolyte. The gel electrolyte played to bind the three layers—the positive-electrode, the gel electrolyte, the negative-electrode—in the cell during the flexibility test, so the interface of the three layers, an important factor in good cell performance, was not destroyed.

The result of the safety evaluation is also investigated. A behavior when the cell was cut into two pieces by a pair of scissors was observed. No violently exothermic reaction occurred after cutting the cell and no leakage of the liquid electrolyte from the gel electrolyte was observed. The outer temperature of the cell was below 25 °C.

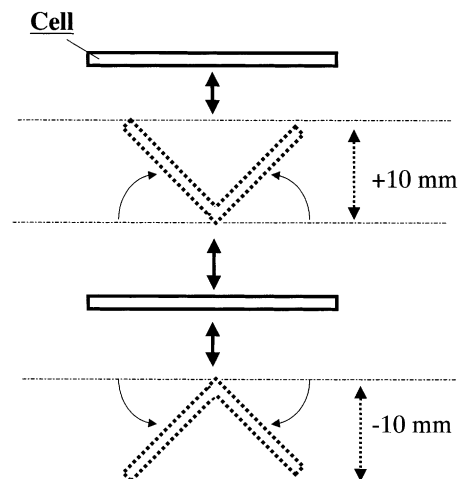


Fig. 13. Schematic image of bending evaluation.

Table 1
Bending evaluation and safety evaluation of the Li polymer primary cell

Number of repeats	Discharge capacity (mAh)	Appearance (after cutting by a scissors)
1000	16.2	* No violently exothermic reaction * No leakage of the liquid electrolyte from the cell

4. Summary

We have shown that the performance of the Li polymer primary cell with a fire-retardant PAN-based gel electrolyte is sufficient for practical use.

The volumetric energy density of the cell was found to be ca. 210 Wh/l. A breakthrough in mass-product technology, such as making the Li metal (negative-electrode) and the separator thinner, should improve the energy density of the cell with this gel electrolyte and our cell design. Fast ion conduction in the PAN-based gel electrolyte contributes to the excellent cell performance even at -20°C . The chemical stability of the PAN-based gel electrolyte and effective gas barrier of the new laminated film achieve a self-discharge rate for the Li polymer primary cell to be equivalent to that of the commercial cell, CR2320. It is also clear that the adhesive nature of the gel electrolyte is effective to maintain the cell performance during the flexibility test. In addition, the liquid absorbency of the gel electrolyte helped to prevent leakage of the liquid electrolyte even when the cell was cut into two pieces by scissors.

These results lead us to conclude that the novel fire-retardant PAN-based gel electrolyte is not only a fast ion conductor over a wide temperature range from -20 to 60°C but also a desirable electrolyte material for a practical Li primary cell with MnO_2 .

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