

Short communication

## 4.4 V lithium-ion polymer batteries with a chemical stable gel electrolyte

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### Abstract

We tested 4.2 V Li-ion polymer batteries (LIPB) with physical gel electrolyte, poly(vinylidene fluoride) (PVDF), 4.4 V LIPB and 4.4 V Li-ion batteries (LIB) with a liquid electrolyte. The discharge capacity of the 4.4 V LIPB reached 520 Wh l<sup>-1</sup> which was 9% higher than that of the 4.2 V LIPB. The 4.4 V LIPB had a high capacity retention ratio of 91.4% at 3 C because of the excellent ion conductivity of the PVDF gel. The capacity retention ratio of the 4.4 V LIPB was 82% after 500 cycles, which is comparable to those of some commercial LIBs. The 4.4 V LIPB retained its original thickness even after many cycles and after being stored at 90 °C, whereas the 4.4 V LIB swelled by over 20%. Peaks in the FT-IR spectrum of the discolored separator in the 4.4 V LIB after storage were assigned to C=C double bonds, suggesting that the separator in direct contact with the 4.4 V cathode had been oxidized. The PVDF gel electrolyte not only had a high ionic conductivity but also completely suppressed oxidation. The 4.4 V LIPB with PVDF gel electrolyte has properties suitable for practical cells, namely, high energy density, high permanence and it is safe to use. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Poly(vinylidene fluoride); High voltage; Lithium-ion polymer battery

### 1. Introduction

The Li-ion polymer battery (LIPB) was released by Sony in 1998. It is eminently suitable for use in several mobile electronic devices because of its high energy density and reliability. However, due to continual improvement in these devices and extension of their area of application, these devices continually require batteries having higher charge capacities and upper cut-off voltage limits.

High-voltage LIPBs hold out considerable promise for providing higher charge capacity batteries, since high voltage LIPBs have high average discharge voltages. In contrast, other high-capacity technologies, for example, LiNiO<sub>2</sub> cathode and negative alloy electrodes have lower average discharge voltages. The charge capacity of a 4.4 V LiCoO<sub>2</sub> battery is about 12% greater than that of a 4.2 V LiCoO<sub>2</sub> battery. Consequently, high voltage lithium ion batteries have been attracting considerable attention for many years [1–6]. However, most of the work done to date on these batteries has focused on the decay mechanism

of the cathode materials and ways for suppressing this decay [1–3,5–8]. There have been few studies that have investigated the degradation of the separator in high voltage batteries.

LIPBs with gel electrolytes are currently attracting much attention since they have both high energy densities and reliability [9–27]. In particular, LIPBs with polyvinylidene fluoride (PVDF)-based gel electrolytes have demonstrated remarkable cell performances [28–34]. The PVDF-based gel electrolyte, which is a thermo-reversible gel, is chemically stable even at potential differences exceeding 4.3 V because no radical residue is produced in the gel forming reaction. In this study, we produced 4.4 V LIPBs with PVDF and evaluated their performance. We describe the advantages of using a PVDF-based gel electrolyte to protect the separator from the cathode having a potential of greater than 4.3 V. We also report the cell performance of a 4.4 V LIPB.

### 2. Experimental/materials and methods

#### 2.1. Measurement of Ionic conductivity

The PVDF sol was prepared by mixing poly(vinylidene fluoride-co-hexafluoro-propylene) (PVDF-HFP) copolymer,

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ethylene carbonate (EC), propylene carbonate (PC) and lithium hexafluorophosphate (LiPF<sub>6</sub>) at 90 °C. The component ratio of the gel electrolytes was PVDF/EC/PC/LiPF<sub>6</sub> = 7/43/43/7 (in mol%). Cooling this sol to room temperature produced a PVDF-based gel film.

The ionic conductivity was determined by AC impedance spectroscopy using a frequency response analyzer, (Solartron 1260, Schlumberger) connected to an electrochemical interface (Solartron 1286, Schlumberger). The films were housed in a two-electrode cell which had blocking and stainless steel electrodes. Their Cole-Cole plots were calculated at various temperatures. The entire fabrication process was conducted in a dry atmosphere (dew point of air <−40 °C).

## 2.2. Cell performance

The positive electrode was prepared by combining 3 wt.% of PVDF and 2 wt.% of carbon with LiCoO<sub>2</sub>. The negative electrode was prepared by combining 5 wt.% of PVDF with mesocarbon-microbead graphite. The positive electrode and negative electrode were coated with aluminum foil and copper foil, respectively. A porous membrane made of poly(ethylene) was used for the separator material.

The gel electrolyte was coated on both electrodes by sol casting before stacking the separators between the positive and negative electrodes. We used a doctor blade to coat the hot sol solution of the PVDF-based gel electrolyte so as to achieve sufficient penetration of the deep cavities of the porous electrodes. These electrodes were then stacked together before the sol solution became the gel electrolyte. The LIPBs were fabricated by packing the stacked electrodes and separators in a laminated flexible film. In order to reduce the amount of moisture present, Al and Cu sheets were used as current collectors for the positive and negative electrodes, respectively. The prepared batteries were 3.8 mm (thickness) × 34 mm (width) × 50 mm (length) in size. The entire fabrication process was performed in a dry room having a dew point not lower than −40 °C. The LIBs with liquid electrolytes were fabricated using the same positive and negative electrodes, but they were housed in an aluminum cell. The component ratio of the liquid electrolytes was EC/DEC/LiPF<sub>6</sub> = 27/63/10 (in mol%). These batteries and their cell performance were evaluated using commercial test equipment (TOSCAT 3000, Toyo System Inc.).

## 2.3. Evaluation of resistance to oxidation

The high voltage 4.4 V LIPBs and 4.4 V LIBs were fully charged and stored at 90 °C for 4 h. After the batteries had discharged, we disassembled the batteries and removed their separators. We then washed the separators using dimethyl carbonate and dried under vacuum at 60 °C for 24 h. A Fourier-transform infrared (FTIR) spectrometer (Nicolet 380, Thermo Electron) was employed to acquire spectra, which were used to identify molecular combinations. We analyzed the surface of the PE separators of the 4.4 V LIPBs and the 4.4 V LIBs with liquid electrolyte after storage.



Fig. 1. Picture of PVDF gel electrolyte.

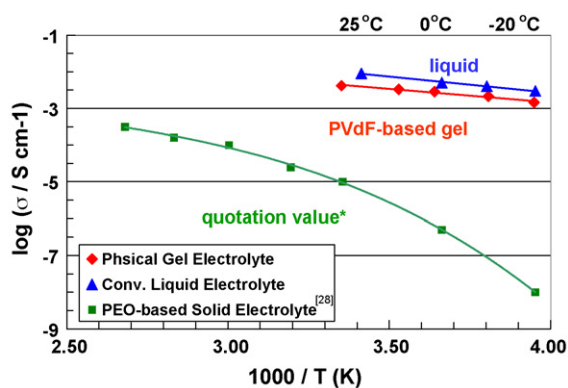
## 3. Results and discussion

### 3.1. PVdF gel

Fig. 1 shows a photograph of the PVDF gel. The gel electrolyte made by the procedure described above is self-standing. Thus a LIPB with PVDF gel electrolyte produced by trapping liquid solutions in a polymer matrix remains structurally stable during fabrication, battery assembly, storage and usage.

### 3.2. Ionic conductivity

Fig. 2 shows the ionic conductivity of PVDF-based gel film and polyethylene oxide (PEO)-based gel film at various temperatures. The ionic conductivity of a PEO-based gel film has been measured [27]. The conductivity from −20 °C to room temperature was greater than 10<sup>−3</sup> mS cm<sup>−1</sup>, which was higher than that of the PEO-based solid polymer electrolyte. The Arrhenius behavior of this gel was as good that exhibited by non-aqueous solvent electrolytes. The PEO-based electrolyte combines the advantages of the solid state with the ease of casting of thin films. However, the PEO-based electrolyte has very low ionic conductivity, typically in the range from 10<sup>−8</sup> to 10<sup>−3.5</sup> S cm<sup>−1</sup> for temperatures between 40 and 100 °C.



\*Y. Kato, M. Watanabe, K. Sanui, N. Ogata, Solid State Ionics 40&41 632 (1990)

Fig. 2. Arrhenius plot of ionic conductivity of the gel electrolyte.

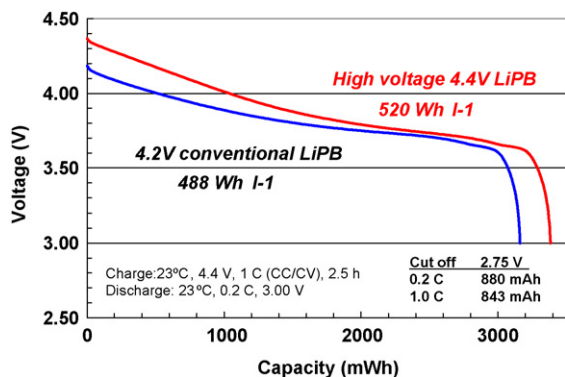


Fig. 3. Comparison of typical discharge voltage profile of a 4.4 V LiPB and 4.2 V LiPB.

### 3.3. Cell performances

Fig. 3 shows a typical discharge voltage profiles for LiPBs charged to 4.2 and 4.4 V. The discharge capacity of the 4.4 V LiPB was approximately 3.38 Wh while that of the conventional 4.2 V LiPB was 3.17 Wh. The discharge capacity of the 4.4 V LiPB is about 6% higher than the conventionally charged 4.2 V LiPB. The discharge voltage of the battery charged to 4.4 V was higher than that charged to 4.2 V in the measured voltage range, which means that the high voltage charged battery is superior to the conventionally charged battery especially when considering the constant power discharge condition. We estimated that the average discharge voltage of the 4.4 V LiPB and the 4.2 V LiPB are about 3.8 and 3.7 V at 0.2 C, respectively.

It is worth noting that the high voltage charged battery suppresses the discharge current during the power discharge condition compared with the conventionally charged battery, which has the benefit that the battery temperature rise is also suppressed. Fig. 4 shows the typical drain performance of a 4.4 V LiPB. The capacity retention ratios were 98.6, 97.1, 94.6 and 91.4% at 0.2, 1, 2 and 3 C, respectively. The observed drain performance of the 4.4 V LiPB was excellent, as high as that of some commercial 4.2 V LiBs with liquid electrolytes.

Fig. 5 shows the 1 C/1 C charge/discharge cycle performances of the 4.4 V LiPB with PVDF gel electrolyte and the 4.4 V LiB. Suppression of oxidation when the PVDF gel was used was excellent compared to that for 4.4 V LiB with liquid electrolyte, and the discharge capacity was maintained at above 80% after

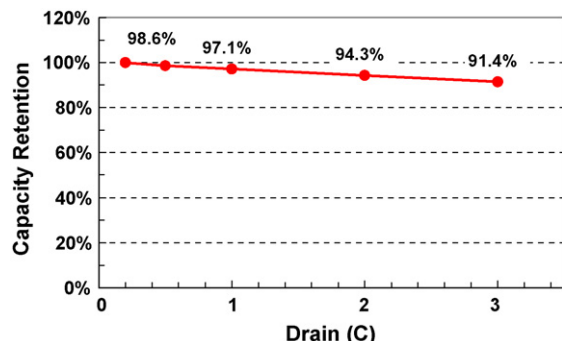


Fig. 4. Drain performance of the 4.4 V Li-ion polymer battery.

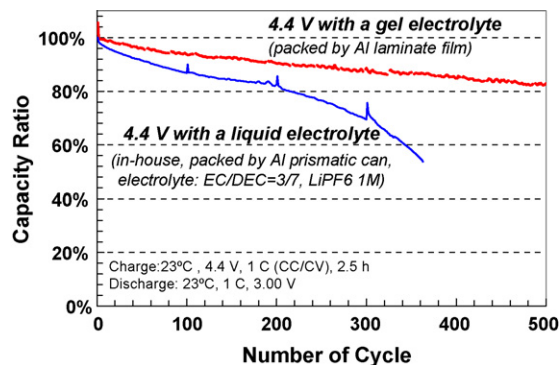


Fig. 5. Comparison of cycle performance of the 4.4 V LiPB and the 4.4 V LiB. Charge and discharge at 1 C.

500 cycles. In contrast, the capacity retention of the 4.4 V LiB fell below 80% after 200 cycles and it then decreased rapidly to be less than 60% after 340 cycles. The difference in the cycle performances of 4.4 V Li-ion batteries with and without PVDF gel clearly demonstrates that the PVDF gel suppresses separator oxidation and overcomes the problem of fading capacity retention.

Fig. 6 shows the change in the cell thickness of the 4.4 V LiPB during the cycle test. The change in the thickness of the 4.4 V LiPB before and after the cycle test was only 0.08 mm, thus the cell thickness remained almost unchanged. In contrast, the change in the thickness of the 4.4 V LiB was 1.23 mm despite being packed in a hard aluminum prismatic can. The swelling was caused by evolved gas in addition to expansion of the electrodes. The high pressure of the contents of the 4.4 V LiB can was confirmed, when we disassembled the 4.4 V LiB and the inner electrolyte poured out. The gas evolving side reaction of the 4.4 V LiB may be related with the fading capacity retention of this battery. These results demonstrate that the 4.4 V LiB has a low reliability despite having a poor cycle performance.

Fig. 7 shows the change in the cell thickness for 4.4 V LiPB during the storage test. The 4.4 V LiPB with PVDF gel and the 4.4 V LiB without PVDF were fully charged and stored at 90 °C for 4 h. The change in the thickness of the 4.4 V LiPB before and after the storage test was only 0.11 mm, which is very similar to the cycle test result. The cell thickness change of the 4.4 V LiB

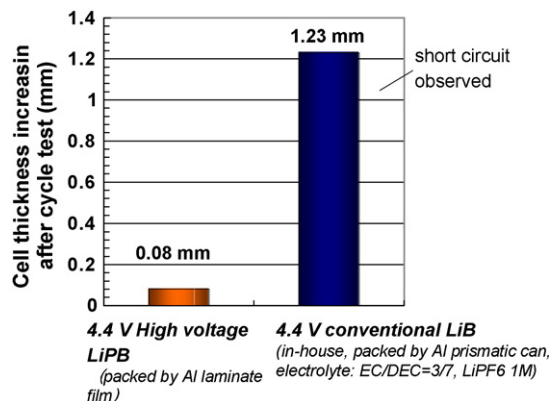


Fig. 6. Comparison of cell thickness of the 4.4 V LiPB and the 4.4 V LiB after cycle test.

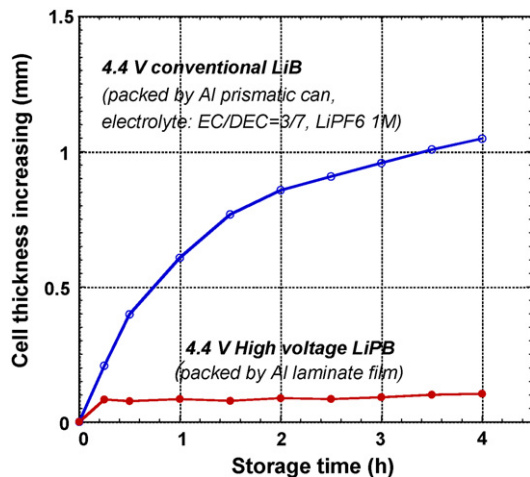


Fig. 7. Comparison of cell thickness increasing with 4.4 V LiPB and 4.4 V LIB at 90 °C storage test.

exhibited a rapid increase and reached a value of 1.14 mm. The swelling of the 4.4 V LIB was considerably worse than that of the 4.4 V LIPB. This demonstrates the high reliability that of the 4.4 V LIPB, since it maintained its cell size and the shape after both the storage and cycle tests.

### 3.4. FT-IR analysis

Fig. 8 shows FT-IR spectra of the surface of the PE-based separator after the storage test at 90 °C for 4 h. The 4.4 V LIPB and the 4.4 V LIB were fully charged and stored at 90 °C for 4 h. Both batteries used pure poly(ethylene) as the separator. We found that the color of the disassembled separator of the conventional 4.4 V LIB during the storage test changed from white to black. The peaks of the FT-IR spectra of the LIPB separators after the storage test were located at approximately 700, 1500, 2800 and 2950  $\text{cm}^{-1}$ . These are clearly indicative of the C–C single bonds of pure poly(ethylene), thus demonstrating that no degradation of the LIPB separators had occurred during storage. On the other hand, the peaks of the FT-IR spectrum of the LIB separator after the storage test were located in the range 700–1900  $\text{cm}^{-1}$ . These broad peaks were composed of many peaks that could be assigned to as the C=C double bond. The

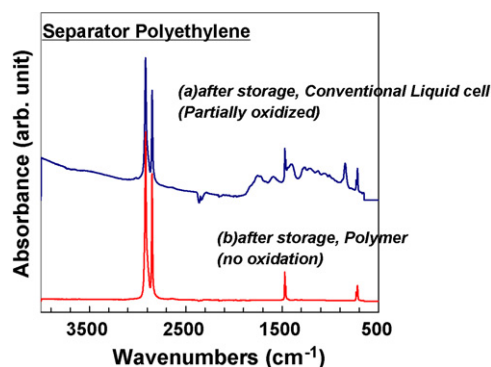


Fig. 8. FT-IR spectra of surface of the PE-based separator after storage test at 90 °C for 4 h.

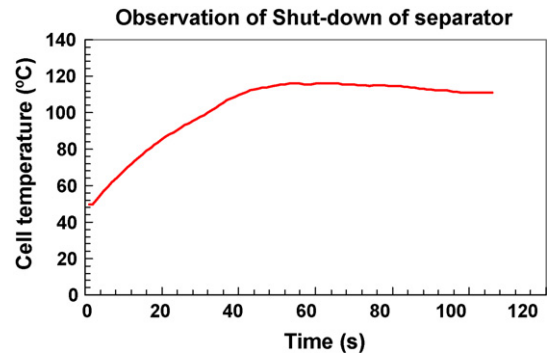


Fig. 9. Surface temperature of the 4.5 V “over charged” Li-ion polymer battery on the nail test.

observed discoloration of separator indicates that a separator, which is in direct contact with a cathode having a potential of more than 4.3 V, is oxidized. It was demonstrated experimentally that oxidation of the separator of the 4.4 V LIPB with PVDF gel was entirely suppressed, due to the fact that the separator with polymer electrolyte was not in direct contact with the cathode and the PVDF was chemically stable at voltages exceeding 4.3 V.

### 3.5. Safety tests

Safety is the most important requirement for commercial Li-ion batteries. We tested the safety of the 4.4 V LIPB intensively and developed two in-house tests.

Fig. 9 shows a plot of the change in the cell temperature as a function of the time after it had been penetrated by a 2.5 mm  $\varnothing$  metal nail. We observed no thermal runaway. The voltage of the LIPB immediately dropped to 0 V after inserting the nail. However, the surface temperature of the LIPB increased to 120 °C. The result indicates that the shutdown of the separator of 4.4 V LIPB behaves well.

Overcharging the battery is a common safety test. The overcharge test is designed to simulate a malfunctioning charger. The battery is charged by a constant galvanostatic current, and the battery voltage is only limited by the power supply capability. We performed the test by charging a LIPB with a constant current of 870 mA with a voltage limit of 12 V at 45 °C for 2.5 h. Since the 4.4 V LIPB did not explode or ignite, it passed the overcharge test. These results show that the 4.4 V LIPB is safe to use in addition to having a high charge capacity and good cell properties.

## 4. Conclusions

We have demonstrated that the cell performance of 4.4 V LIPB with a highly chemical stable PVDF-based gel electrolyte is sufficient for practical use. We have shown the high reliability of this battery by demonstrating that the 4.4 V LIPB with PVDF retained its original thickness after the cycle test and the 90 °C storage test. By FT-IR analysis we have shown that the poor cell performance of the 4.4 V conventional LIB is due to oxidation of its separator. The PVDF gel electrolyte not only had a high ionic conductivity but also entirely suppressed oxi-

dition. Two safety tests indicate that the 4.4 V LIPB is safe to use in addition to having a high charge capacity and good cell properties.

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