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High temperature stable lithium-ion polymer battery

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Abstract

The electrochemical performance of polymer lithium-ion batteries was studied as a function of the hexafluoro propylene (HFP) content in the PVDF–HFP copolymers used as electrode binders and separator membranes. The HFP content in electrode binders was found to have a significant impact on the cycle life performance at elevated temperatures. Best results were achieved with a 5% HFP level, where good cycle life was demonstrated at 60°C, combined with good rate capabilities and low temperature performance. In contrast to electrode binders, the HFP content in separator membranes was found to have no significant impact on cell performance. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium-ion batteries are presently one of the major rechargeable power sources for portable electronic devices because of their high output voltage and high energy density, based on weight and volume. The first lithium-ion cells were based on liquid electrolyte technologies and these still make up the majority of the cells currently in use. However, in recent years, there has been considerable interest in polymer lithium-ion batteries because of their enhanced design flexibility and potential safety advantages [1–3]. Among the different polymer technologies being evaluated, Telcordia's PLION technology is one of the most promising for commercialization.

An important requirement for all rechargeable batteries for use in portable electronic applications is that they be able to cycle at elevated temperatures (at least up to 60°C). However, Telcordia-type batteries, typically do not cycle well under these conditions. One possible cause of the poor high temperature performance is the hexafluoro propylene (HFP) unit substituted poly(vinylidene fluoride-co-hexafluoro propylene) (PVDF–HFP) copolymer used in the separator membranes and as the electrode binder and which typically employs 12% HFP. The HFP makes the polymer more soluble in solvents such as acetone, thus improving its

processability and increases the uptake of electrolyte solution in the cell, thus enhancing ionic conductivity. However, the relatively high level of HFP (12%) could also increase swelling and the solubility of the polymer in the electrolyte solution at elevated temperatures, thereby contributing to the observed poor cycle life performance. The purpose of the present investigation was to explore the use of PVDF–HFP polymers with lower HFP contents as a means of improving the high temperature performance of lithium-ion polymer cells.

2. Experimental

Three different PVDF–HFP compositions (Solvay) were selected for evaluation as electrode binders and separator membranes. The electrode binder compositions employed 0, 5, and 12% HFP while the separator membranes used 5% (separator C), 12% (separator B), and a 1:1 blend of 5 and 12% HFP (separator A). Electrodes were prepared by first dry mixing the active material (Seimi LiCoO₂ for the cathode and Osaka MCMB for the anode) and conductive carbon [4] (Chevron Acetylene Black), followed by the addition of binder, predissolved in NMP (Aldrich), and plasticizer (Aldrich DBT). The resulting slurries were thoroughly mixed and then coated directly onto aluminum (cathode) or copper (anode) mesh (Delker) using a laboratory coater (Allience EC) and a process developed at SKC

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[5]. With the exception of the binder compositions, the electrode formulations were the same for all tests. For determining the electrical conductivity of the electrode coatings, a small amount of each slurry was coated onto PET film (SKC, 50 μm), dried, and cut into rectangular strips. The resistivities of the strips were then measured using a two-probe technique.

Separator membranes were prepared by slurry coating onto PET film, using NMP as the slurry solvent, followed by lamination to the electrodes at elevated temperature. The experimental cells employed a bicell construction and a 1 M $\text{LiPF}_6/\text{EC}-\text{DMC}-\text{DEC}$ (1:1:1) electrolyte solution (Ferro). Separator melting points were determined by DSC (TA Instruments DSC2920) and cell tests were conducted using a Maccor cyler. Cell charging was done in two-steps: a constant current step at $C/2$ to 4.2 V followed by a constant voltage step at 4.2 V to a $C/20$ current cut-off. All discharges were conducted under constant current conditions to a 3.0 V cut-off at specified C -rates. Nonambient temperature tests were carried out in a Tenney 942 series test chamber.

3. Results and discussion

Table 1 shows the measured electrical conductivities of cathode coatings on PET using the three different binder compositions. The conductivity of the coating with PVDF homopolymer was significantly lower than that of the others. We attribute this to the lower solubility of the PVDF homopolymer in NMP with the plasticizer, resulting in incomplete mixing and a nonhomogeneous distribution of the binder in the electrode coating.

The separator membrane with a 1:1 blend of 5 and 12% HFP had a melting point of 142°C, while the membrane with 12% HFP had a melting point of 121°C. Separator membranes with 5% HFP could not be reliably laminated to electrodes at temperatures under 150°C and, thus, were not considered further. The separator thicknesses were approximately 40 μm and the membranes were laminated to electrodes at 130°C (separator A, blend) or 120°C (separator B, 12% HFP).

Fig. 1 shows the 23 and 60°C cycle performance for polymer cells with the three different binder compositions. All cells employed separator A (blend) and were discharged at $C/2$. At 23°C, the 5 and 12% binder compositions gave similar performance with good capacity retention through 150 cycles while the PVDF homopolymer exhibited a sig-

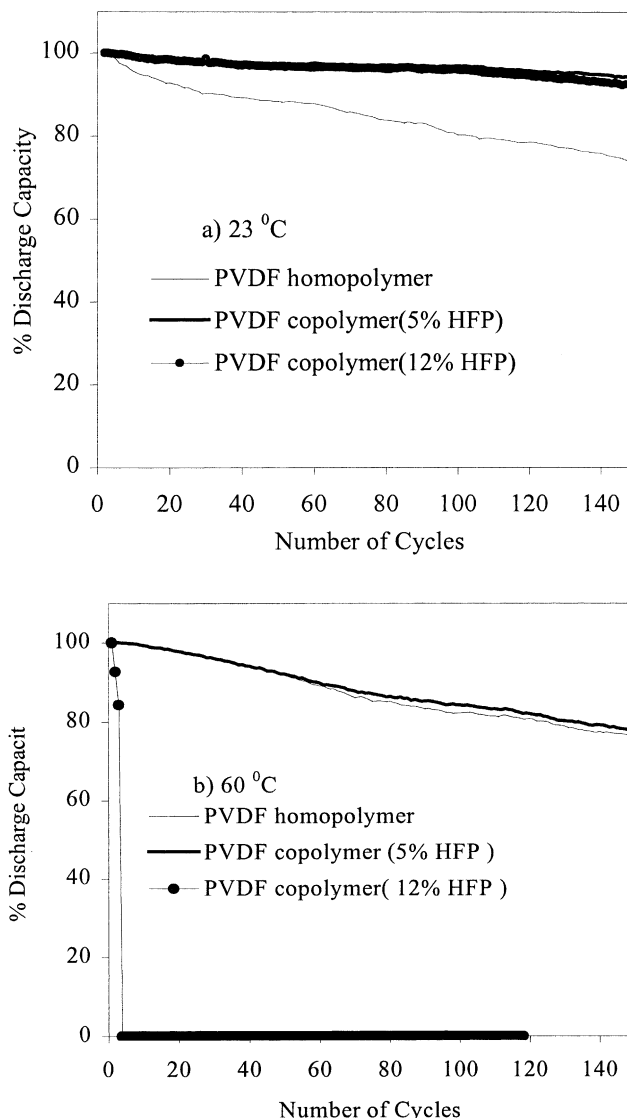


Fig. 1. Cycle performance of polymer cells with different electrode binders at (a) 23°C and (b) 60°C.

nificantly higher rate of capacity fade, reaching 80% of initial capacity after only 112 cycles. At 60°C, the homopolymer and 5% HFP binders both gave good performance, delivering approximately 150 cycles to 80%. In sharp contrast, the 12% binder dropped below 80% after only two cycles. These results show that the dramatic effect binder composition can have on polymer lithium-ion cells at elevated temperatures and the significant improvements that can be achieved by reducing the HFP content. Again, we believe the poor performance of the 12% HFP binder, which is due to either increased swelling or higher solubility in the electrolyte solution.

Rate capabilities at 23°C were determined by conducting sequential constant current discharges at $C/5$, $1C$, and $2C$. After each discharge, the cells were charged using the standard two-step procedure. At the $2C$ rate, the cells using 5 and 12% HFP binders showed good capacity

Table 1

Electrical conductivities of cathode coatings incorporating three different binder compositions

	PVDF homopolymer	PVDF copolymer (5% HFP)	PVDF copolymer (12% HFP)
Conductivity (10^{-1} S/cm)	1.1	1.8	1.8

retentions of 86 and 84%, respectively, versus their $C/5$ capacities. The cells employing the homopolymer, on the other hand, yielded only 75% retention at the $2C$ rate. The poorer high-rate performance of the electrodes with the homopolymer is consistent with their lower electrical conductivity.

At -20°C , the measured capacity retentions at the $1C$ rate were 18, 14, and 5, for the 5% HFP, 12% HFP, and the homopolymer binders, respectively. Here, the capacity retentions were based on the $C/5$ discharge capacities at 23°C . These trends were similar to those obtained at the $2C$ rate at 23°C , as described above. However, when the discharge rate at -20°C was reduced to $C/5$, the performance of the homopolymer improved significantly. Under these conditions, the capacity retentions were 85, 72, and 80% for the 5% HFP, 12% HFP, and the homopolymer binders, respectively. This trend can be explained, at least in part, by the electrolyte content of the composite electrodes, expressed by the ratio of the volume of added electrolyte solution to the volume of extracted DBP plasticizer (V_e/V_p). The higher the value of this volume ratio, the greater the amount of electrolyte that will be taken up by the polymer (for a given plasticizer content), and the greater the ionic conductivity of the resulting composite electrode. As might be expected, we have found this ratio to have a strong influence on both rate capabilities and low temperature performance. The measured volume ratios were 1.17, 1.09, and 1.21 for the 5% HFP, 12% HFP, and the homopolymer binders, respectively. The volume ratio of the 12% HFP electrodes was lower than that of the 5% HFP electrodes, consistent with their slightly poorer rate capabilities and low temperature performance. The lower melting point of the 12% HFP binder, leading to a loss of porosity during the thermal lamination process, is the suspected cause of its lower volume ratio. The homopolymer had the highest volume ratio, which apparently helped its performance at moderate rates of discharge through partial

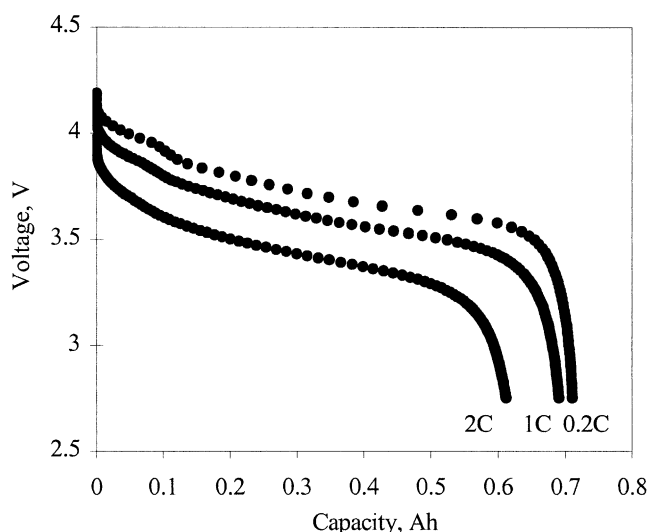


Fig. 2. Discharge curves of polymer batteries at different discharge rates.

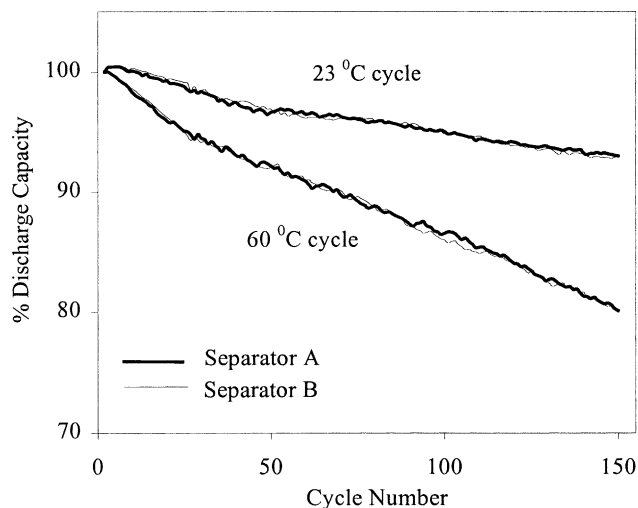


Fig. 3. Cycle performance of polymer batteries with different separator membranes at 23 and 60°C .

compensation of the lower electrical conductivity of the electrode by a slightly higher ionic conductivity. Fig. 2 shows typical discharge curves for a 393,562-size polymer battery employing the 5% HFP binder with separator A at different discharge rates.

Fig. 3 shows cycle life performance results of polymer batteries with the two different separator membranes at room temperature and at 60°C . The electrode binder used in these polymer batteries contained 5% HFP. The results show that the HFP content in the separator membrane had no significant effect on the performance of the cells at either temperature. Likewise, we have found the rate capabilities and low temperature performance of polymer lithium-ion batteries to be unaffected by the HFP content in the separator membranes.

4. Conclusions

We have found the HFP content in the PVDF–HFP copolymer used as an electrode binder in polymer lithium-ion batteries to have a significant impact on high temperature performance. The 12% HFP binder typically used in Telcordia's PLION technology provides good rate capabilities and low temperature performance, but extremely poor cycle life performance at 60°C . By reducing the HFP content to 5%, we have demonstrated significantly improved cycle life performance at 60°C with no degradation in rate capabilities or low temperature performance. The homopolymer also gave good performance at elevated temperatures, but at room temperature and subambient temperatures its performance was inferior to that of the 5% HFP composition.

In contrast to the electrode binder, we have found the HFP content in separator membranes to have no significant impact on cell performance.

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