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Polymer Battery R&D in the U.S.

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SUMMARY: Polymer electrolytes that have been developed for battery applications fall into two general classes, neat or “pure” polymer and plasticized or gel in which the polymer is combined with a conducting organic electrolyte. The polyethylene oxide (PEO) and its modifications are typical of the “pure” polymer electrolytes. They have poor conductivity at room temperatures, but at elevated temperatures, their conductivity is of the order of 10^{-3} to 10^{-4} S/cm. The PEO electrolytes have found application in the high temperature (>60°C) lithium metal anode battery systems. The high temperature necessary for good operation makes them unsuitable for use in small consumer appliances. The polymer electrolyte battery development activities have resulted in several high performance battery systems now just entering the market. Not all of the developments have resulted in commercial cell production. The commercialization activities of high performance lithium-ion (Li-Ion) batteries have been based on two general plastic polymer systems: poly-vinylidene difluoride-hexafluoropropylene copolymer (PVdF-HFP) and polyacrylates. The polymer cells are expected to have advantages in manufacturing, flexibility, thin cell formats and lightweight packaging. Important parameters in PVdF gel electrolyte performance include the electrolyte type (combination of organic carbonates), temperature, and HFP copolymer content. Li-Ion coin cells fabricated with a polyolefin separator with either liquid electrolyte or with the PVdF gel polymer electrolyte have equivalent performance.

Introduction

Polymer batteries have been under intense research and development over the past 10 years. This year several commercial Li-Ion polymer batteries were introduced to the market place. Batteries have a set of general criteria for commercialization as listed in Table I. Polymer battery systems are capable of meeting all of these general criteria.

Polymer batteries are lighter weight than the equivalent non-polymer battery because they utilize a low cost, light weight polymer-foil container to replace the thick walled steel or aluminum can of non-polymer cells. Polymer batteries offer shape flexibility in design and are capable of very thin, large footprint constructions. Polymer cells are internally bonded and do not require external pressure on the electrode separator interface for good operation. They are essentially insensitive to shock and vibration.

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Table I. General Criteria for Commercial Batteries

Attribute	Benefit
High Energy Density	Smaller More Powerful Devices
Light Weight	Portable, Hand Held Devices
Long Life	Lower Life Cycle Costs
Flexibility	Adaptable for Many Applications
Safe Operation	Reduced Commercial Risk
Environmentally Friendly	Easy, Low Cost Disposal

Polymer electrolytes for use in batteries must be resistant to oxidation and reduction by strong oxidizing agents such as lithium cobalt oxide and by strong reducing agents such as lithium metal. This means that the range of stability is at least 4.5 volts vs. lithium. In addition, this resistance to oxidation and reduction applies over the temperature range of –40C to +85C. It is preferred that the polymers have good mechanical strength for ease in manufacturing. They can form conductive electrolytes either neat or when plasticized by addition of organic electrolytes.

Polymer Electrolyte Development

The phenomenon of complexation of salts with polyethylene oxide (PEO) or polypropylene oxide (PPO) was observed in the mid-1960s[1)]. Almost ten years later, P.V. Wright and coworkers discovered that PEO and PPO complexed with alkali metal salts exhibit high ionic conductivity at elevated temperatures[2,3)]. For example, the ionic conductivity of a $(PEO)_{4.5}KSCN$ complex reached roughly 10^{-3} S/cm at 120°C. Shortly afterward, M. B. Armand and coworkers recognized the potential of these polymer electrolytes for use as separators in solid state batteries, especially in rechargeable lithium batteries[4)]. Since that time, considerable effort has been directed towards the development of polymer electrolytes for use in lithium cells[5-8)]. Although the ionic conductivity of the archetypal PEO solid polymer electrolytes (SPEs) is high at elevated temperatures, their conductivity is low (10^{-6} to 10^{-8} S/cm) at ambient temperatures[2)]. A room temperature conductivity of at least of 10^{-3} S/cm is needed for a polymer electrolytes to function well in consumer battery systems.

Approaches to enhance the room temperature conductivity of the archetypal PEO-based “dry” SPEs include: reduction of the crystallinity level of the polymer electrolytes[9)], use of polymers that have flexible backbones[10, 11)], attachment of flexible pendent polar groups to the main polymer chains[12)], use of special salts with large anions to form more dissociated species in polymer electrolytes[13)], preparation of ionic rubbers (polymer-in-salt)[14)], addition of inorganic fillers[15)] etc. These approaches have not resulted in "dry" (no added liquids) and easily processible polymer electrolytes with good room temperature conductivity.

The incorporation of liquid electrolyte solutions into solid polymer matrices to produce “wet” or “plasticized” gel polymer electrolytes (GPEs) is very effective in lowering the ionic conductivity of GPEs to the level of 10^{-3} S/cm at room temperature[16, 17)]. The increased ionic conductivity occurs at the expense of mechanical strength of the prepared films. The magnitude of the mechanical strength reduction depends mainly on the type of polymer, the type of solvent and the amount of solvent used. For example, propylene carbonate (PC), an active solvent for linear or branched-chain PEO[16)], is a latent solvent for polyacrylonitrile (PAN)[17)] and polyvinylidene fluoride (PVdF)[18)]. Therefore, if heavily plasticized with PC (~40-60 wt%), dimensionally stable films can be prepared from PAN- and PVdF-based gel electrolytes, but not from linear or branched-chain PEO-based gel electrolytes. This is because active solvents will dissolve polymers at room temperature, whereas latent solvents will form gels with polymers at room temperature, although the gelled polymers may turn into liquid state again at elevated temperatures.

Among the GPEs investigated for use as separators in Li-Ion cells, PAN-, and PVdF-, and polyacrylate-based gel systems have attracted most R&D efforts[16, 18, 19)]. Dimensionally stable films have been made from these GPEs containing as much as 80 wt% liquid solvent[17)]. Although liquid solvents in these gels are immobilized macroscopically, they still behave much like liquid molecules at the microscopic level. It has been reported that the reactivity of gelled PAN-PC-EC-$LiClO_4$ electrolyte has similar behavior towards lithium metal to that of liquid PC-EC-$LiClO_4$ electrolyte[16)].

Hooper [20,21)] was able to obtain acceptable conductivity with plasticized PEO films but suffered from poor cycling with lithium metal electrodes. This is typical of the behavior of lithium in liquid organic electrolytes. Shackle et al[22)] developed a plasticized radiation cross-linked acrylate electrolyte system with excellent conductivity for lithium systems. The low cycling efficiency of lithium coupled with the tendency of cycled lithium to form lithium dendrites are well known problems for cells with a liquid electrolyte and those with GPE separators. This difficulty is largely responsible for the shift away from lithium metal cells toward the Li-Ion technology with GPE constructions.

Of the three types of polymers mentioned above, PVdF-based polymers have attracted most R&D work of GPE Li-Ion cells because they readily swell in carbonate solvents, possess good chemical and electrochemical stability, and have good mechanical processability. Feuillade and Perche observed in 1975[23)] that P(VdF-HFP), the copolymer of vinylidene fluoride (VdF) and hexafluoropropylene (HFP), possessed good ionic conductivity ($5x10^{-4}$ S/cm) and good mechanical strength after swollen in a PC solution of NH_4ClO_4. In the early 1980s, Tsuchida and coworkers also reported that ionic conductivity of PVdF, P(VdF-TFE)[1] and P(VdF-TrFE)[1] polymers, when gelled with some liquid electrolytes (e.g. $LiClO_4$ dissolved in PC), reached 10^{-5} to 10^{-6} S/cm at room temperature[24)]. The ionic conductivity of these GPEs was low because only 21.9 to 35.2 wt% solvents were incorporated into the polymer matrices, rather than the 50-60 wt% level needed to reach 10^{-3} S/cm at room temperature. Gozdz and coworkers at Bellcore reported that P(VdF-HFP)[25, 26)] and P(VdF-CTFE)[27)] polymers[1], after swollen in carbonate-based electrolyte solutions, had very good ionic conductivity ($\sim10^{-3}$ S/cm) and good mechanical strength at room temperature. These copolymers dissolve in carbonate solvents only under some extreme conditions[28, 29)].

Current GPE Li-Ion batteries are flat in format and packaged in thin plastic-foil pouches. A single battery often contains multiple bicells stacked together. Cells using P(VdF-HFP) and P(VdF-CTFE) copolymer as binders, and/or separator materials, have been reported to have good performance characteristics[25)] and are currently under active development by some battery manufacturers. We have recently compared the manufacturing processes and performance characteristics of GPE Li-Ion cells with those of liquid electrolyte Li-Ion cells[30)].

In this paper, we report our experimental results of the effects of HFP concentration, solvent type, temperature and salt on the swelling behavior of the P(VdF-HFP) in electrolyte solutions, since the cell performance depends, to a large extent, on the amount of electrolyte solution present in GPEs. We then demonstrate that Li-Ion coin cells using P(VdF-HFP) separator can have rate capability equal to or better than those using a microporous separator

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[1] TFE-tetrafluoroethylene; TrFE-trifluoroethylene; CTFE-chlorotrifluoroethylene.

when appropriate GPEs are selected. Finally, we will discuss several developments in the early stages of commercialization.

PvDF Polymer Experiments

P(VdF-HFP) polymers containing 0%, 8% and 15% of HFP by weight were used for electrolyte solution uptake study. The PVdF polymer samples were from Solvay. The pure homopolymer had the designation 1010, the 8% HFP sample had the designation 20810 and the 15% HFP had the designation 21510. Polymer samples with a diameter of 18 mm were punched out of 2 mm. thick polymer plaques and immersed in 1 M $LiPF_6$ electrolyte solutions at 21°C or 55°C. The solvents for the electrolyte solutions were DMC, DEC, EC/DMC (1:0.82 by weight), EC/DEC (1:0.82 by weight), and EC/DMC/DEC (1:2:2 by weight), respectively. After immersion in the electrolyte solution for 1, 7, 14 and 30 days, the polymer samples were removed from the electrolyte solutions contained in poly(propylene) bottles, wiped dry and weighed. All experimental procedures, including cell assembly, were carried out inside a dry glove box. The amount of electrolyte solution absorbed by a polymer sample is $(W_b - W_a)$ and the percentage of the weight increase of the polymer sample is calculated from $100*(W_b-W_a)/(W_a)$. Here, W_a and W_b are the weight of the polymer samples before and after immersion, respectively.

Flooded Li-Ion coin cells were built using the 2016 coin cell hardware, 3.2 mil thick $LiCoO_2$ cathode electrodes and 3.6 mil thick MCMB anode electrodes. The binder for both the cathode and the anode electrodes is a PVdF homopolymer. Because the rate capability of GPE Li-Ion cells is much affected by the GPE separators, a design of experiments was carried out for five variables - solvent type, 55 °C pre-conditioning, filler type, polymer type, and separator thickness – to explore the relative importance of these variables in affecting the discharge rate capability at room temperature. The preparation of the GPE separator followed the method described in reference32). Methanol was used to extract dibutyl phthalate (DBP), a processing and performance-enhancing agent, from P(VdF-HFP). The Li-Ion coin cells were first charged to 4.1 V and then discharged to 3.0 V at C/10 rate at room temperature. The discharge rate capability was determined from subsequent discharge to 3.0 V at C/10, C/5, C/2 and 1C rates and at room temperature. Before each discharge, cells were charged to 4.1 V using constant current (C/2 rate) and then held at 4.1 V until the current dropped to 10% of the C/2 current level.

Results and Discussion

Fig. 1 shows the percentage of weight gain of three P(VdF-HFP) polymer samples immersed in 1 M $LiPF_6$ solutions of DMC, DEC, EC/DMC, and EC/DEC at room temperature. It can be seen from Fig. 1 that increasing the co-monomer content in P(VdF-HFP) increased the degree of swelling of the polymer samples studied. The increased absorbency of the electrolyte solution by the copolymers is related to the lower crystallinity level in the copolymers. It was reported that the crystallinity decreased from 38% for the PVdF homopolymer to 27-29% for P(VDF-8%HFP) and to 22% for P(VDF-15%HFP)$^{28,29)}$. The effect of solvents on the polymer swelling can also be seen from Fig. 1. When the solvent was changed from DEC to DMC, the electrolyte solution absorbed by the polymer samples increased from 1 wt% to 13 wt% for the PVdF homopolymer and from 41 wt% to 170 wt% for the P(VdF-15%HFP) copolymer. The swelling data of P(VdF-HFP) in pure EC-containing electrolyte is not available at room temperature (21°C) because EC's melting temperature is around 37°C. Therefore, the effect of EC on the swelling of P(VdF-HFP) was estimated from the weight gain of P(VdF-HFP) in electrolytes using EC/DMC and EC/DEC solvent mixtures. It is clear from the data in Fig. 1 that EC is similar to DEC but poorer than DMC as a solvent for swelling P(VdF-HFP) because the trend of solvent uptake by P(VdF-HFP) is DMC>EC/DMC and DEC≈EC/DEC.

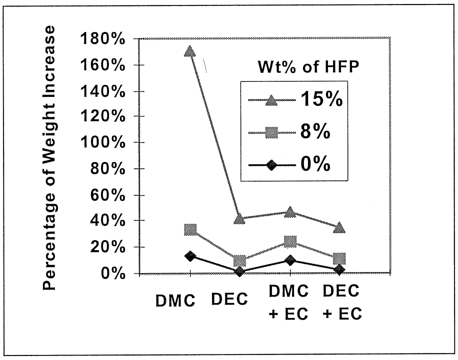

Fig. 1: Percentage of weight increase of P(VdF-HPF) samples soaked in 1 M $LiPF_6$ solutions of DMC, DEC, DMC/EC, and DEC/EC for 30 days at 21 °C.

Increasing the temperature from 21°C (room temperature) to 55°C substantially increased the swelling of P(VdF-HFP) in the carbonate electrolytes (Fig. 2). The amount of 1M $LiPF_6$-EC/DEC electrolyte absorbed by PVdF homopolymer increased from 2 wt% to 11 wt% when the temperature was raised from 21°C to 55°C. For P(VdF-15%HFP), an increase of the electrolyte absorbency (from 35 wt% to 75 wt%) resulted by this temperature increase. It is interesting to notice that a temperature "memory effect" was observed for these swollen polymers. After the swollen polymers were cooled from 55°C to 21°C and stored for 140 days, less than ~5-10 wt% of the total absorbed electrolyte was excuded from the swollen polymers, to the surrounding electrolytes.

GPE Li-Ion cells may operate at temperatures higher than 55°C in actual use. Therefore, it is necessary to carefully evaluate the mechanical integrity of P(VdF-HFP) copolymers in carbonate electrolytes at elevated temperatures because polymers may loose their mechanical strength or dissolve in carbonate electrolytes if there is sufficient solvent in contact with them. Recently, Meunier[28)] reported that almost all P(VdF-HFP) copolymers studied by him, dissolved in EC/DEC, EC/DMC/DEC, EC/PC/DMC, and EC/PC/DEC solvents at 87°C.

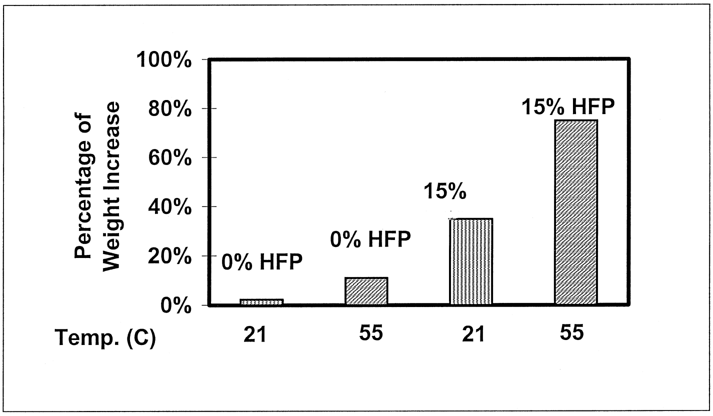

Fig. 2: Effect of temperature on the swelling degree of P(VdF-HFP) in 1 M $LiPF_6$ EC/DEC electrolyte solution.

Fig. 3 compares the swelling behavior of selected P(VdF-HFP) in pure carbonate solvents with that in $LiPF_6$ containing carbonate electrolytes. The data for the pure solvents were taken from reference[26)]. The homopolymer exhibited a similar degree of swelling in both the pure solvents and the $LiPF_6$-containing electrolyte solutions, showing no salt effect. A significant salt effect on polymer swelling existed in some cases when the HPF comonomer reached 15% by weight and the solvents used were DMC, EC/DEC and EC/DEC/DMC. The presence of $LiPF_6$ (1M) in the solvents reduced the weight increase of P(VdF-15%HFP) from

86% to 35% if the solvent was EC/DEC or from 276% to 99% if the solvent was EC/DMC/DEC. At 55°C, P(VdF-15%HFP) dissolved completely in pure EC/DEC and EC/DEC/DMC solvents but still possessed the initial circular shape in the corresponding 1 M $LiPF_6$ electrolyte solutions.

Although Li-Ion cells using SPE separators have low discharge rate capability at room temperature, cells using highly conductive GPE separators have at least an equivalent discharge rate capability as that of Li-Ion cells using microporous polyethylene separators. This is because the ionic conductivity of a GPE film can be higher than that of a microporous polyolefin separator immersed in a liquid electrolyte. Fujita and coworkers reported that the room temperature ionic conductivity for a microporous polyolefin separator immersed in 1M $LiPF_6$-EC/DMC/DEC is about $8x10^{-4}$ S/cm which is lower than 1-3 $x10^{-3}$ S/cm reported for some GPEs$^{32)}$. It may be that the internal surface charge can enhance the conductivity.

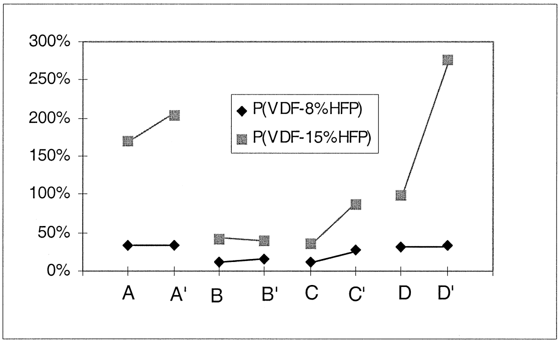

Fig. 3: Percentage of weight increases of P(VdF-HFP) in 1 M $LiPF_6$ electrolyte solutions and pure solvent solutions at room temperature. A' stands for DMC, B' for DEC, C' for EC/DMC, and D' for EC/DMC/DEC. A, B, C and D are 1 M $LiPF_6$ in A', B', C' and D', respectively.

The good discharge rate capability of a Li-Ion cell using a polymer electrolyte film can be seen in Fig. 4 which displays the voltage profiles of a coin cell discharged at rates C/5, C/2 and 1C, at room temperature. The separator employed in the cell was a P(VdF-HFP) composite film. The 1C discharge capacity is 92% of that discharged at C/5. Replacing the PVdF separator with a conventional microporous polyethylene separator reduced the 1C discharge capacity to 62% of the C/5 capacity. This difference may be related to a contact resistance at the electrode-polyethylene separator interface in the coin cell construction.

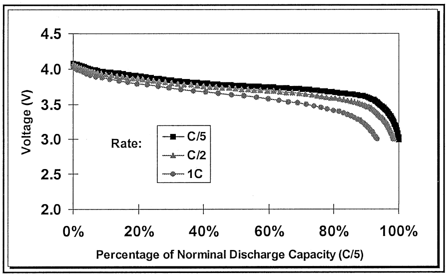

Figure 4. Discharge profiles of a flooded Li-ion coin cell using a GPE separator.

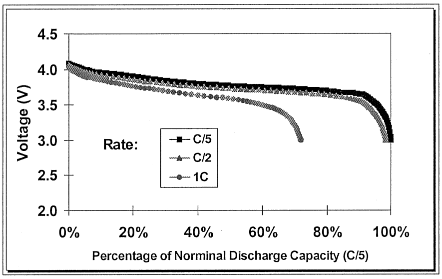

Figure 5. Discharge profiles of a flooded Li-ion coin cell using a microporous polyethylene separator.

Because the cell discharge rate capability of a GPE Li-Ion cell using thin electrodes is closely related to the conductance of the GPE separator use, a variable search experiment was designed to find factors (or parameter changes) that have a large influence on cell discharge rate capability at room temperature. Five factors–solvent type (A), high temperature formation treatment (B), silica vs. alumina separator filler type (C), HFP content polymer type (D), and separator thickness (E) were considered in this experiment. A 1 M $LiPF_6$-EC/DMC/DEC electrolyte, 55°C pre-conditioning, SiO_2 filler, P(VdF-15%HFP), and 2 mil thick separator were used in the construction of cells that gave the best performance, whereas, cells made with 1M $LiPF_6$ EC/DEC electrolyte, no high temperature treatment, Al_2O_3 filler, and P(VdF-11%HFP) gave the worst performance.

Among all parameter changes considered in this experimental design, changing temperature (variable B) from 21 °C to 55°C is the most effective way for increasing high rate discharge capability. Changes in variables C, D and E in the specified ranges have moderate effects on discharge rate capability. Replacing an EC/DEC-based electrolyte by an EC/DEC/DMC-based electrolyte seemed to be less effective than other changes on affecting the rate capability.

Commercialization Efforts and the "Bellcore" Process

The greatest activity has concentrated on developing and commercializing the Bellcore (now Telcordia) process based on a PVdF plastic electrolytes. The embodiment of the PVdF based battery system has been described by Tarascon et al[25, 26, 27, 31]. This has become known as the Bellcore process. A schematic of the Bellcore process is given in Fig. 6. Films of the anode, cathode and separator are cast using PVdF polymer as binder and electrolyte materials. The essential element of the process is the incorporation of dibutyl phthalate (DBP) as a plasticizer in the manufacture of the electrode films. The DBP plasticized films allow easy handling and processing of the laminate materials into finished cells. The DBP also functions as a pore-former for the absorption of electrolyte into the polymer. The DBP must be completely extracted from the polymer material, before the electrolyte is added to the assembled cell. Failure to reduce the concentration of DBP below 350 ppm results in poor cycle life for the finished product[33)]. DBP is electrochemically active and must be completely removed before the cell is activated by addition of the electrolyte. The removal of DBP creates minute fissures and voids in the solid PVdF that are filled by the addition of electrolyte during cell activation.

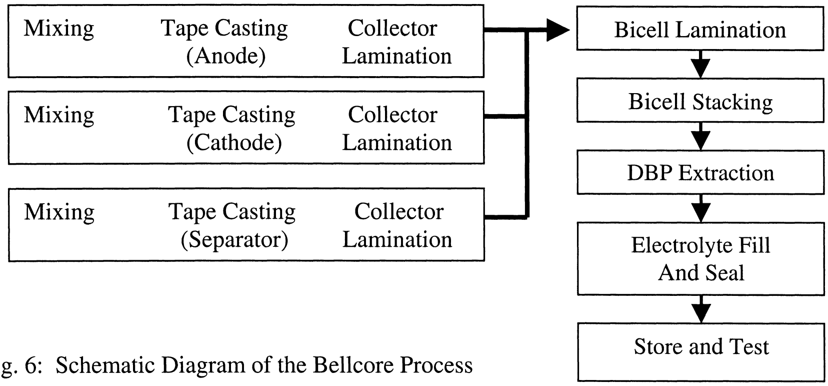

Fig. 6: Schematic Diagram of the Bellcore Process

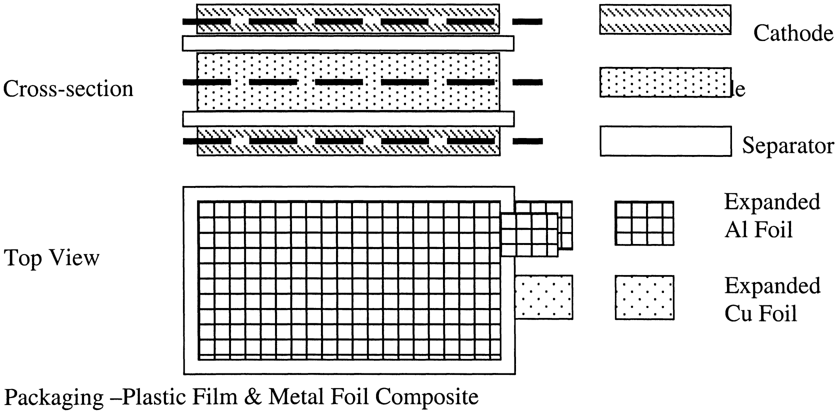

Fig. 7: Typical construction of a polymer Bicell. The separate layers and current collectors are heat laminated together

Typical construction of the polymer cell is shown in Fig. 7. This construction with two electrodes on each side of a center electrode, is termed a "bicell." These are the basic units of construction of complete batteries and may be combined to produce higher capacity cells. Polymer batteries can be fabricated in sheets that result in large footprint batteries. Since the same polymer is used throughout the active components, the polymer effectively bonds the cell components together as a single unit. There are no phase boundaries between the active cell components and the separator to introduce unwanted resistance. Consequently, the cells do not require application of external pressure for good operation. The PVdF electrolytes are very stable and can accommodate the 4-volt nickel, cobalt and manganese cathode systems. The PVdF electrolytes are reported to be "transparent" to the chemistry.

The performance characteristics of the Bellcore type Li-Ion cells are illustrated in Figs:8, 9 and 10. The cells are constructed as in Fig. 7. The cathode is a manganese spinel, $Li_{1+0.05}Mn_2O_4$, the anode is graphite and the electrolyte is 1 M $LiPF_6$ in a 50:50 mixture of ethyl carbonate and dimethyl carbonate solvents. Excess lithium is incorporated into the manganese spinel cathode material to stabilize its crystal structure and enhance long term operation. The cells have good rate capability and cycle life. The discharge curve in Fig. 8, shows little difference between the capacity delivered at a five hour (termed C/5) discharge rate and the capacity of the cell when discharged at the one hour (termed 1C) rate discharge.

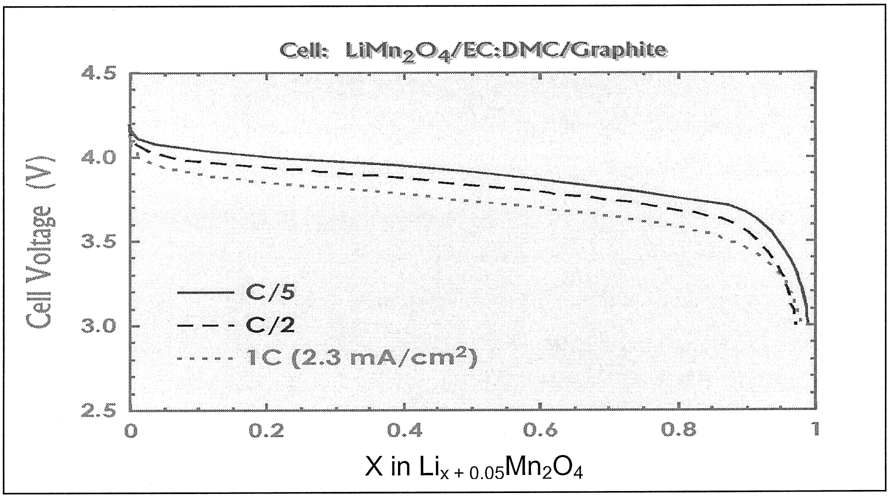

Fig. 8: Discharge Curve of a Bellcore technology cell at the five hour (C/5), 2 hour (C/2) and one hour (1C) rates. (Courtesy of Bellcore (now Telcordia))

This performance is very similar to that for a liquid electrolyte Li-Ion cell. The discharge curve is fairly flat with an average discharge voltage of 3.7 volts. The manganese cathode has about a 0.1-volt higher discharge voltage than does the lithium cobalt oxide cathode of the liquid electrolyte cells.

The cycle life for the Bellcore cells is illustrated in Fig. 9. The cells are discharged at a three hour (C/3) rate and then recharged using a current limited constant potential regime. Here the current is limited to the two hour rate. As the cell approaches full charge, the voltage limit forces the current lower. The charge is stopped when the charge current falls to 10% of its initial value. The laboratory and cellular phone cells show acceptable cycle life. The capacity falls slowly and reaches 80% of their initial capacity after more than 500 cycles.

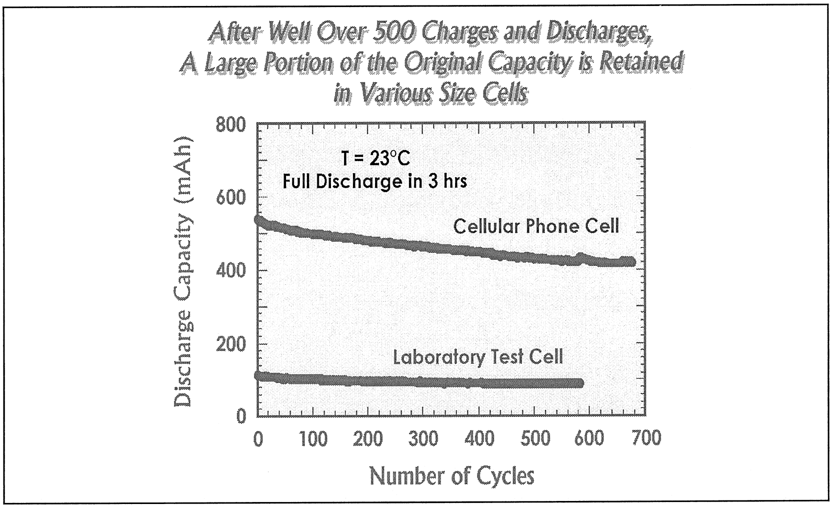

Fig. 9 Cycle Life of 2 in. X 3 in. X 0.032 in. bicells at the two hour discharge rate. (Courtesy of Bellcore)

Thomas and Betts (High Energy Technology) and Ultralife have introduced polymer batteries based on Bellcore-type technology. Several others including Valence Technology, have also been developing polymer batteries based on this technology. All told, there are over 20 licensees of the Bellcore technology worldwide.

Polymer cells can handle the high current pulses of the GSM cellular phone application. Fig. 10 shows the performance comparison of the polymer cell with that for a Ni-Cd cell of similar capacity on a simulated GSM protocol with 95 millisecond pulses for both transmission and receive. The 3C rate simulates the 1.5 ampere GSM transmission pulse. Because of the difference in unit cell voltages, two Li-Ion cells are compared with 5 Ni-Cd cells connected in series. The two systems gave essentially the same performance. There is little difference between the high current transmit and standby performance of each system. This difference in voltage between transmit and receive is directly related to the internal resistance of the battery. Both batteries have similar internal resistance. Overall, the polymer cells have demonstrated equivalent performance to that of a typical Li-Ion liquid electrolyte cell.

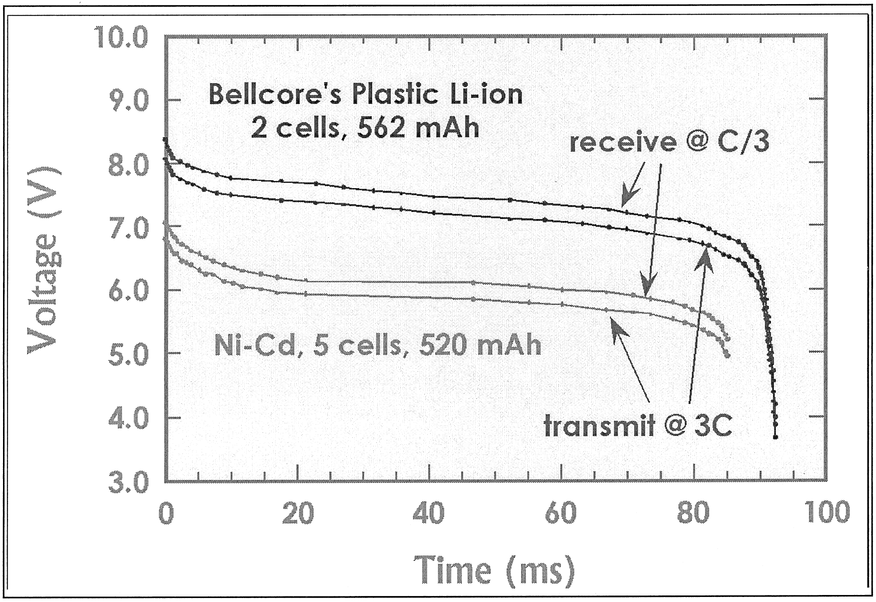

Fig. 10: Comparison of the characteristics of a 562 mAh, two-cell polymer Li-Ion and 520 mAh five cell nickel cadmium battery on a simulated GSM discharge regime. (Courtesy of Bellcore (now Telcordia))

The field of polymer batteries is a very active technical area. There are many efforts to develop Li-Ion polymer cells in various stages of development. It is estimated that over 30 different companies have development efforts that can lead to commercial production. Battery Engineering has introduced a Li-Ion battery based on acrylate electrolyte[34, 35]. The electrolyte is thermally polymerized in situ after the cell is assembled of three monomer moieties. A plastic mesh is embedded in the electrolyte layer to impart mechanical strength to the polymer. The cells do not contain a volatile solvent as the boiling point of the plasticizer is 210ºC. The flexible polymer chain provides free volume for good ion transport and conductivity.

Saft America has announced a Li-Ion polymer cell using a similar approach but has not disclosed the identity of the polymer electrolyte[36, 37)]. The polymer is based on PVdF and consists of two different interpenetrated phases: the swollen polymer and free liquid. The polymer electrolyte is prepared by a phase inversion process and has good conductivity. The process results in a separator material with a 60% void volume and pore size of 0.1m to 1.0 m. The polymer swells about 20% to 30% by weight based on electrolyte absorption.

Electrofuel in Canada announced a 160 Wh thin flat battery for notebook computers that takes advantage of the thin flat format possible with polymer cells[38)]. The battery measures 220 mm. X 206 mm. X 9.5 mm. and weighs 0.999 kg with a titanium case. This translates to 250 Wh/l and 160 Wh/kg. The fully charged battery is said to be able to power a notebook computer for about 8 hours. The identity of the polymer electrolyte was not revealed. The battery was enclosed in a titanium case and attaches directly to the bottom of a notebook computer. The company claimed that energy densities of 175 Wh/kg and 475 Wh/l were possible.

Several Japanese companies including Sony, Sanyo, Matsushita and A&T are now actively marketing polymer Li-Ion batteries. At this point in time, very little is known about the technology basis for these developments.

Conclusion

Given proper internal cell design, polymer Li-Ion cells exhibit equivalent performance to that of the regular liquid filled Li-Ion cells. They may have a weight advantage given the use of polymer foil packaging materials. Polymer Li-Ion cells are internally bonded and do not need external pressure to maintain good contact between the electrodes and the separator. Polymer Li-Ion batteries are available from several suppliers based on a variety of technologies and polymer systems. The absorption of 1 M $LiPF_6$ electrolyte solutions by P(VdF-HFP) polymers depends on the concentration of HFP unit in the polymer, solvent type, and temperature. Increasing the HFP unit content in P(VdF-HFP) and temperature increased the swelling degree of the polymers considerably. The amount of the electrolyte solution absorbed by P(VdF-HFP) at room temperature showed the following trend: DMC>EC/DMC>DEC≈EC/DEC. The presence of $LiPF_6$ in carbonate solvents did not affect the degree of swelling of PVdF and P(VdF-8%HFP) in all solutions studied but lowered the swelling degree of P(VdF-15%HFP) in DMC, EC/DEC and EC/DMC/DEC solution at room temperature or prevented dissolution in the them at 55 °C. The swelling and memory effect related to gel formation at higher temperatures may limit the use of batteries using PVdF materials to 55°C or less.

Acknowledgements

D. J. Allessio and S. E. Osmialowski carried out the experiments and summarized some of the data used in this paper. The authors also gratefully acknowledge Dr. Vassillis Keramidas of Bellcore for supplying the performance curves for their polymer cells.

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