

Performance characteristics of lithium-ion cells using in situ polymerized electrolytes

Luying Sun, Katsuhiro Higaki, Robert C. McDonald

Battery Engineering Inc., 1636 Hyde Park Avenue, Hyde Park, MA 02136, USA

Accepted 25 November 1996

Abstract

Complete lithium-ion cells have been cycled to demonstrate the effectiveness of a new type of solid polymer electrolyte (SPE). The polymer electrolyte was developed with a eye toward manufacturability and reliability. Monomers are reacted in place, either on a thin supporting fabric or directly onto one electrode surface, just prior to assembly. This approach leads to an interface between the electrolyte and electrodes which permits excellent ion transport during charge and discharge. When combined with a disordered carbon lithium-ion anode and a metal oxide lithium intercalation cathode, the new electrolyte supports over 500 cycles of reliable capacity down to 80% of the initial capacity. The cell load voltage averages 3.3 V at $C/1$ rate. These cells have also shown some tolerance to moderate (600%) overcharge and can be cycled at a wide range of current densities. © 1997 Elsevier Science S.A.

Keywords: Solid polymer electrolytes; Lithium ion batteries; Cycle life. Overcharge; Rechargeable batteries

1. Introduction

Portable equipment tracking devices, wireless modems, PC-based telephones, electronic credit and debit cards will require safe, light-weight, inexpensive rechargeable cells for power. Currently available lithium-ion cells achieve about 500 cycles at the 0.5C rate, but these must be housed in metal cases. Solid polymer electrolytes and polymer gel electrolytes with dissolved lithium salts permit the development of thin, lithium-ion anode cells in lightweight plastic containers [1]. Solid polymer electrolytes also help control self-discharge parasitic reactions which might occur on storage because ions and solvent molecules have reduced diffusion rates. Polyethylene oxide (PEO) [2–4], fluorocarbons [5,8] and polyacrylonitrile (PAN) [6,7] in combination with lithium salts and organic plasticizers have been used in successful demonstrations of full cells. However, attempts to commercialize polymer batteries have been plagued by the rapid fall-off in capacity with cycle life and cell failures associated with overcharge and overdischarge. The fall-off with cycling is primarily due to electrolyte decomposition and physical changes in the active materials and interfaces which gradually increase cell internal resistance. As resistance increases, the cell reaches the charging target voltage prematurely, causing declining current during the constant voltage portion of the charge. On discharge, cells with increasing internal resistance

operate at decreasing load voltages in latter cycles so that the discharge voltage cutoff is prematurely reached. Both of these effects cause the capacity to decline steadily.

The cell performance results described below stem from an effort to tailor the electrolyte polymer structure in order to optimize ionic conductivity and processability. The objective was to find an electrolyte which could be polymerized in place so that intimate contact and wetting on the molecular level could be achieved between the solid polymer electrolyte and the electrodes.

2. Experimental

Anode, cathode and electrolyte materials and cells were prepared in a dry atmosphere. The anode in this cell uses a non-crystalline carbon as the lithium host with a suitable binder. The binder and carbon were combined with a lithium electrolyte salt dissolved in a solution of organic carbonates. The cathode contained the same binder and organic electrolyte solution along with the intercalation compound Li_xCoO_2 . The 6 cm² electrodes were hot-pressed with a final thickness ranging from 75–125 μm .

The polymer-based electrolyte was prepared from a mixture of three monomers, a carbonate-based plasticizer solution containing a lithium salt [9]. These monomers have a low molecular weight in order to insure distribution of lithium

Table 1
Mechanical strengths of BEI solid polymer electrolytes/fabric composites

Sample no.	Thickness of film (μm)	Mullen burst strength (kPa)
BEI-9	38	207
BEI-10	75	310
BEI-11	100	351
Microporous polypropylene	25	110

ions at the molecular level, and to provide a low viscosity working solution which is easy to handle. The polymerization was carried out on a glass plate, Mylar film, or directly on one of the electrodes. A synthetic fabric was incorporated for ease of handling. The liquid can be sprayed, poured or spread prior to polymerization [10]. The final electrolyte thickness ranged from 20 to 100 μm . The preparation consisted of the spreading of the free-flowing liquid mix, containing a polymerization initiator, onto the appropriate surface, followed by a thermal cure under modest compression. The three monomers are comprised of the following: (i) one with a diacrylate group which serves as a crosslinker; (ii) one with an allyl or acryloyl-containing group with a polar side group, and (iii) one with an oligo (oxyethylene) group.

Copper foil substrates were used for the anode and aluminum foil substrates for the cathode. The electrolyte was either directly polymerized on an electrode surface or prepared separately on a non-woven fabric and sandwiched between the electrodes with modest pressure. The electrode package was then sealed within an evacuated metallized plastic case. The foil electrode tab feed-troughs were heat-sealed against the case walls to create a sufficient barrier to atmospheric moisture.

Cells were cycled on a Maccor automated controller. They were charged at a constant current density of 0.5 mA/cm^2 ($0.4C$ rate) up to a target voltage of 4.2 V. The cells were held at this voltage until the total accumulated charge time

Table 2
Measured conductivities for BEI solid polymer electrolytes with and without fabric reinforcement at room temperature

Polyester fabric	Thickness (μm)	Conductivity (S/cm)
No	56	$(2.3\text{--}2.6) \times 10^{-3}$
Yes	140	$(1.3\text{--}1.4) \times 10^{-3}$

reached 2.5 h. The cells were discharged at the $0.4C$ rate down to a cutoff voltage of 2.75 V. SPE conductivities were measured using a Princeton Applied Research Model 273A galvanostat/potentiostat. A.c. measurements were conducted up to 10 000 Hz and the extrapolated value taken at zero reactance. SPE films were submitted to Ionics Inc. in Watertown, MA, for Mullen burst testing.

3. Results and discussion

The mechanical and physical properties of the resulting electrolytes have been investigated. Table 1 summarizes typical burst strengths of the polymer and polymer-fabric composite electrolytes in comparison with commercial microporous polypropylene. Table 2 summarizes the measured bulk conductivity values found for the pure polymer electrolyte and the polymer/fabric composite structure.

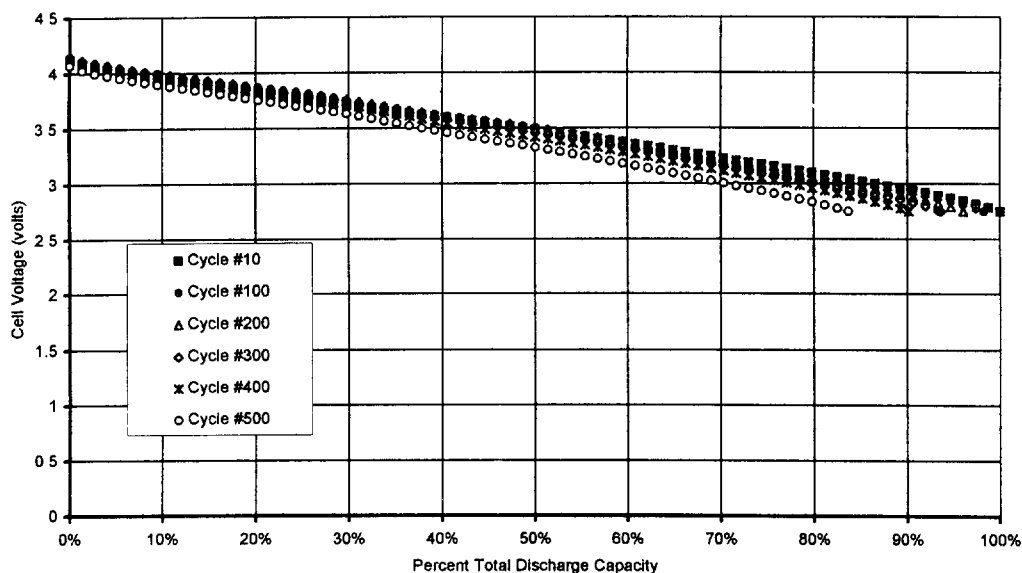


Fig. 1 Typical discharge voltage profiles of a polymer cell, charged and discharged at the $0.4C$ rate at room temperature

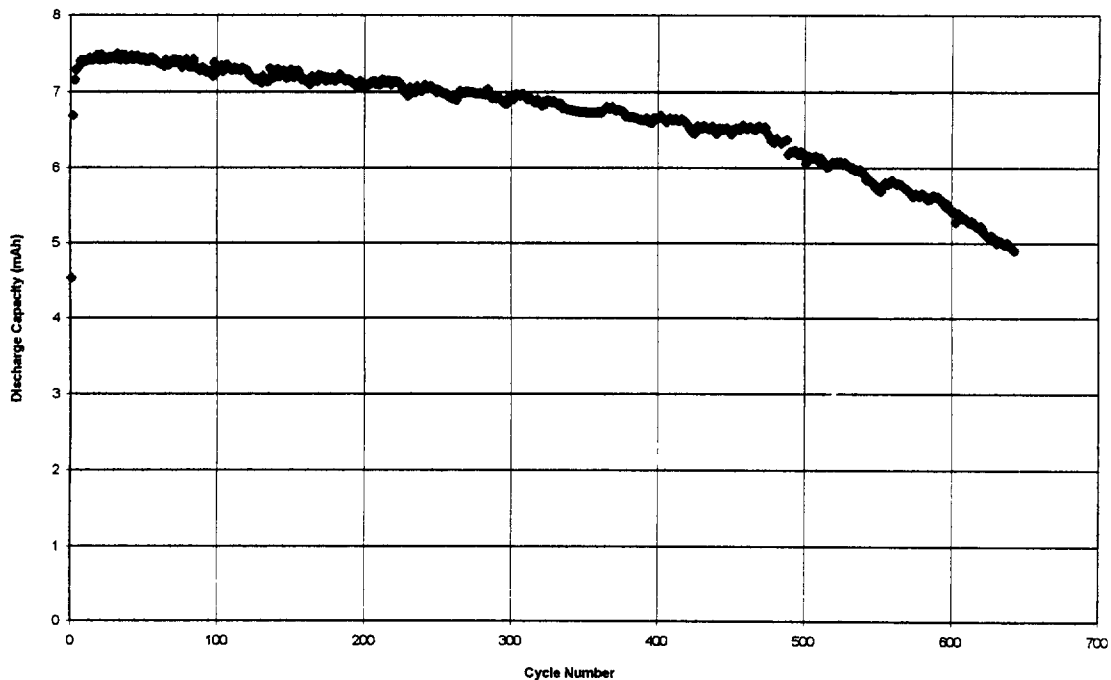


Fig. 2. Cell discharge capacity at the 0.4C rate and at room temperature as a function of cycle number.

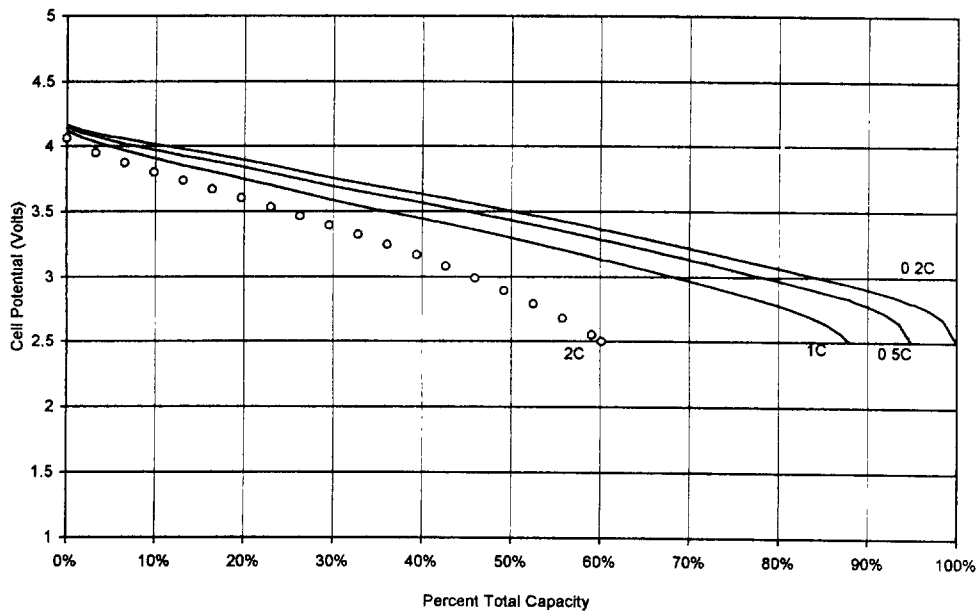


Fig. 3. Cell discharge voltage profiles at different discharge rates.

Based on the softness of the material and the exceptional conductivity, we believe the SPE is a true polymer gel system. The presence of the fabric does not greatly diminish the ionic conductivity of the material which provides mechanical strength, dimensional control and ease of handling. This electrolyte represents an improvement over electrolyte structures consisting of microporous Celgard impregnated with various poly(tetraethylene glycol diacrylate) gels with conductivi-

ties to be $(1.2\text{--}3.0) \times 10^{-4} \text{ S/cm}$ [11]. Performance results below are from cells using the polymer/fabric electrolyte structure.

Typical discharge voltage profiles are shown in Fig. 1. At the 0.5 mA/cm^2 (0.4C rate), the charge results in a continuous increase in a cell voltage up to the target 4.2 V. This is followed by a constant voltage charge at a declining current for the remainder of the 2.5 h period. Following a 5 min rest

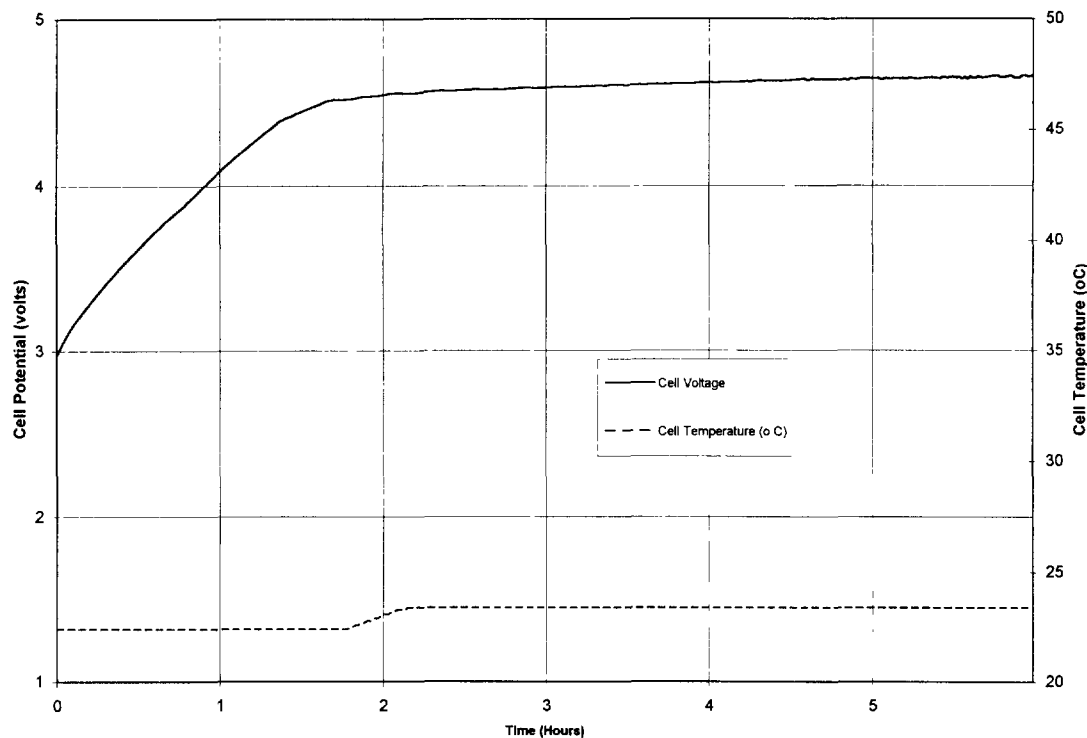


Fig. 4. Overcharge test at the 1C rate.

period, the cells were discharged with the same current density to the 2.75 V cutoff. The cells were placed on a 5 min rest period prior to the next charge. The shape of the charge voltage profile remains constant for several hundred cycles. Fig. 2 shows the relative variation of a cell capacity over 600 cycles. The efficiency with which the cell can utilize the capacity added during charge ranges from 98 to 100%. This represents a significant improvement over previously reported attempts at using polyester-based electrolytes in lithium-ion polymer cells [12].

The cell chemistry has been tested over a range of discharge currents from 0.2 to 2.0C. The results show a 40% falloff in discharge capacity over this range (Fig. 3). At the 0.4C rate the utilization of the electrode active materials is comparable with that of commercial liquid electrolyte lithium-ion cells (e.g. >145 mAh/g of anode carbon and >85 mAh/g LiCoO₂). Overcharge, which might be anticipated in the event a battery charger fails to detect a target charge voltage, was examined. Cells were charged at a constant current beyond the normal 4.2 V cutoff 6 h (Fig. 4). The test shows that, at least initially, the constant current charge results in an elevated voltage of 4.65 V during which chemical recombination results. The cell rose 2 °C before reaching thermal equilibrium. The nature of this control mechanism is under investigation.

4. Conclusions

The use of a battery electrolyte which can be applied as a free-flowing liquid to a surface prior to polymerization, pro-

vides a substantial advantage in the manufacture of polymer lithium-ion cells. The composition of the polymer, plasticizer and salt must be carefully optimized. The method also provides for an optimized, wetted interface between electrodes and the electrolyte. This improved interface permits a large number of cycles before cell failure. The incorporation of a synthetic fabric into the electrolyte layer provides added strength for handling and processing. The lithium-ion carbon/LiCoO₂ cells tested demonstrate a capacity of 1.25 mAh/cm² of electrode surface with over 500 cycles to 80% capacity.

References

- [1] G. Schmutz, J.M. Tarascon, A.S. Gozdz, P.C. Warren and F.K. Shokoobi, in S. Megahed, B.M. Barnett and L. Xie (eds.), *Proc. Symp. Rechargeable Lithium and Lithium-Ion Batteries*, The Electrochemical Society, Pennington, NJ, USA, 1995, pp. 330–335.
- [2] E. Newnham, N. Scholey and K.J. Green, *Power Sources 15. Research and Development in Non-Mechanical Electrical Power Sources*, International Power Sources Committee, Brighton, UK, 1990, pp. 285–293.
- [3] W.J. Macklin, R.J. Neat and R.J. Powell, *Power Sources 15: Research and Development in Non-Mechanical Electrical Power Sources*, International Power Sources Committee, Brighton, UK, 1990, pp. 1–15.
- [4] G. Nagasubramanian, D.H. Shen, S. Surampudi and G. Halpert, in S. Megahed, B.M. Barnett and L. Xie (eds.), *Proc. Symp. Rechargeable Lithium and Lithium-Ion Batteries*, The Electrochemical Society, Pennington, NJ, USA, 1995, pp. 408–422.

- [5] A.S. Gozdz, C. Schmutz and J.M. Tarascon, *US Patent No. 5 296 318*
- [6] G. Nagasubramanian, A.I. Attia and G. Halpert, *J. Electrochem. Soc.*, 139 (1992) 3043–3046
- [7] S. Passerini, S. Loutzky and B. Scrosati, *J. Electrochem. Soc.*, 141 (1994) L80–L81
- [8] A.S. Gozdz, J.M. Tarascon, O.S. Gebizlioglu, C.N. Schmutz, P.C. Warren and F.K. Shokoohi, in S. Megahed, B.M. Barnett and L. Xie (eds.), *Proc. Symp. Rechargeable Lithium and Lithium-Ion Batteries*, The Electrochemical Society, Pennington, NJ, USA, 1995, pp. 400–407.
- [9] L. Sun, *US Patent Applic. Ser. No. 08/511 470* (Aug. 1995).
- [10] L. Sun, *US Patent Applic. Ser. No. 08/531 198* (Sept 1995).
- [11] K.M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, 142 (1995) 683–687.
- [12] T. Oshawa, O. Kimura, T. Kabata, N. Katagiri, T. Fujii and Y. Hayashi, in S. Megahed, B.M. Barnett and L. Xie (eds.), *Proc. Symp. Rechargeable Lithium and Lithium-Ion Batteries*, The Electrochemical Society, Pennington, NJ, USA, 1995, pp. 481–486.