Large lithium polymer battery development
The immobile solvent concept

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Abstract

The program to develop large lithium–metal, polymer electrolyte batteries for electric traction and stand-by power is reviewed. Dry polymer electrolyte conductivity improvement through research into polymers and lithium salts has led to a thin-film lithium polymer battery that operates in the range of 60 to 40 °C. Recent developments in large lithium polymer cell design and production are given, including preliminary results on lithium polymer cell production for the US Advanced Battery Consortium (USABC). Results of stand-by and cycle-life tests on small laboratory cells over several years are also presented confirming the electrolyte's exceptional stability in the lithium rechargeable-cell environment.

Keywords: Polymer electrolyte cells; Lithium batteries

1. Introduction

Ever since Armand first claimed the application of a polymer electrolyte in lithium batteries [1], research has expanded worldwide. Several new polymer electrolytes with improved conductivity has resulted from a better understanding of the major parameters controlling the ion migration, such as favorable polymer structure, phase diagram between solvating polymer and lithium salt and, the development of new lithium counter-anions.

In spite of the progress so far, the quest for a highly conductive dry polymer at room temperature is still continuing and all lithium polymer battery (LPB) developers presently face the options: whether to heat the polymer electrolyte to enable high-power performance, as required for the electric vehicle, or to use 'rediscovered' plasticized or gelled polymer electrolytes, i.e. polymer electrolytes to which a liquid solvent, a low molecular weight polymer or a real plasticizer has been added. Recent success in developing a 4 V lithium-ion rechargeable battery from liquid electrolytes and mounting pressure to come up rapidly with a high-power LPB have brought many developers to choose the second approach or at least consider it as a worthy alternative to be explored.

Each of the choices contemplated in Fig. 1 has a far-reaching impact extending from the basic cell electrochemistry to packaged lithium polymer cell (LPC) design, fabrication process and safety, especially when a large battery installation is considered. This communication covers some of the progress in developing lithium–metal-based batteries made from dry polymer electrolytes, i.e. electrolytes progressively optimized to act as an immobile solvent, i.e., those in which, ultimately, only the non-solvated lithium ion migrates, macroscopically, from one electrode to the other [2].
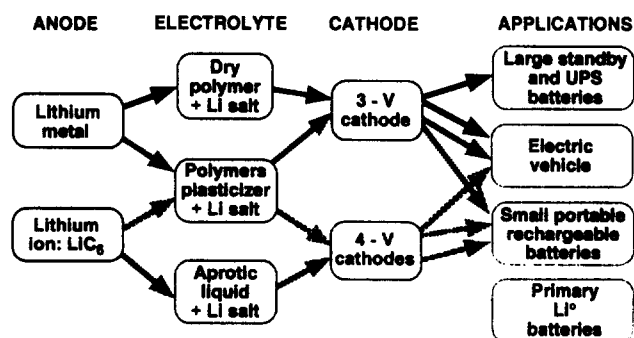
Fig. 1. Polymer electrolyte for lithium battery applications.

2. Polymer electrolyte development

Since our early work on amorphous copolyethers and chemical networks [3,4], several improvements to solvating polymer structures have been made as a result of both our own research programs and those of several other laboratories. In parallel with the polymer host improvements, research and optimization of existing and new lithium salts have made significant progress, mainly with the development of new anion structures. Among others, the development of LiTFIS, i.e. $LiN(CF_3SO_2)_2$, in combination with amorphous polymer hosts has led to better conductivities (Fig. 2) and much lower cell operating temperatures than the former poly(ethylene oxide) (PEO) + lithium triflate electrolyte formulation, e.g., from 130–120 °C down to the current 50–60 °C. More recently, a further advance has been proposed with the development of LiTFSM derivatives, $LiCR(CF_3SO_2)_2$, where R is a crosslinkable function [5]. This technologically simple approach to covalently fix the lithium counter-anion to the host polymer structure could become an important step toward an optimal LPB based on an immobilized-solvent network. It is anticipated that several electrochemical cell characteristics will benefit from the use of a pure Li^+-ion conductor, a feature that Fuller and co-workers [6] have already pointed out by modeling the power characteristics of lithium metal cells. The latter have shown that a pure Li^+-ion conductor compares well with a mixed-ion conductor, whose total conductivity is higher by almost one order of magnitude.

3. Cell chemistry and lithium polymer cell designs

Polymer electrolytes with no liquid solvent added have no vapor pressure and are less prone to react spontaneously with lithium at its melting temperature than either gelled polymers or liquid electrolytes [7]. These initial observations supported the choice of lith-

Fig. 2. Dry polymer electrolyte conductivity evolution.

ium metal as the anode in order to take full advantage of its high specific energy. The absence of any liquid phase or vapor pressure in a large operating temperature range is also deemed very important for large-battery operation, since a high power rate generally raises the normal operating temperature significantly. The initial cell chemistry selected for the large-battery development program is illustrated in Fig. 1. It is based on the following system:

Anode	Polymer electrolyte	Composite cathode

Li^0 metal | Copolymer + LiFTFI | VO_x (MnO_2)
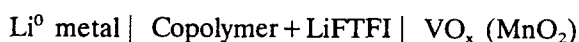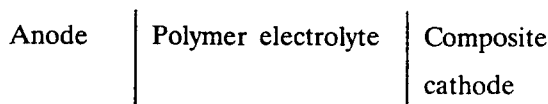
The operating temperature is normally fixed at 60 °C in order to achieve the fast lithium-ion transport necessary for an electric vehicle acceleration, e.g., a pulse power in excess of 200 W/kg for approximatively 30 s.

3.1. Large lithium battery from thin polymer electrolyte cell

Energy and power build-up from moderately conductive polymer electrolytes (10^{-4}–10^{-3} Ω^{-1} cm^{-1}) calls for the development of a large surface of the cell laminate. Several parameters must be taken into account in the design of such a large cell:

(i) individual cell balancing in a series arrangement;

(ii) low-cost current collector required by the large surface to be developed;

(iii) efficient current collection in order to minimize the IR drop and preserve the cell's electric field homogeneity at high power, and

(iv) efficient thermal exchange in and out of the large multilayered stack.

3.2. Parallel-wound cell versus the bipolar design

The need to protect individual LPC when series-mounted to obtain the battery voltage prompted the adoption of a battery design based on a large single parallel LPC as a building unit. This approach is illustrated in Fig. 3 and compared to the bipolar design, where smaller cells are first mounted in series. The high coulombic efficiency associated with lithium rechargeable batteries has one drawback: no secondary reaction is normally available as in conventional lead/acid or nickel-based batteries. Chemical shuttles for lithium cells which are essential to the bipolar design have been proposed but most of these materials are still under development. Moreover, the thermal management challenge associated with fully optimized bipolar cells, i.e. cells based on ultra-thin current col-
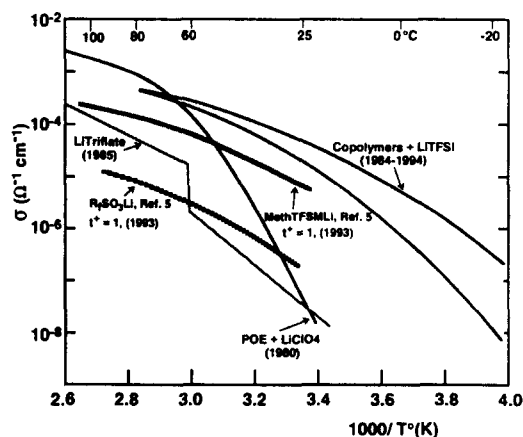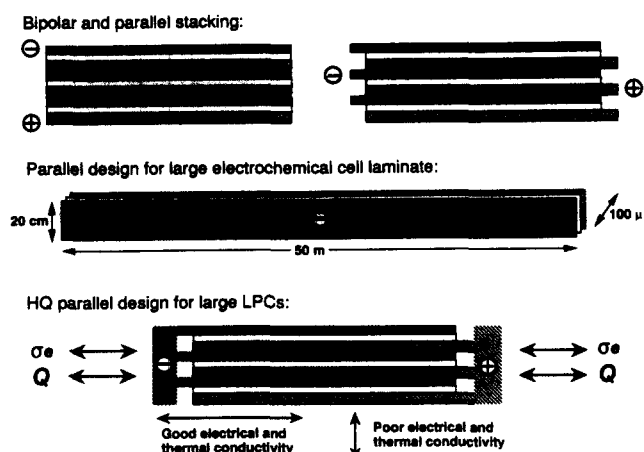
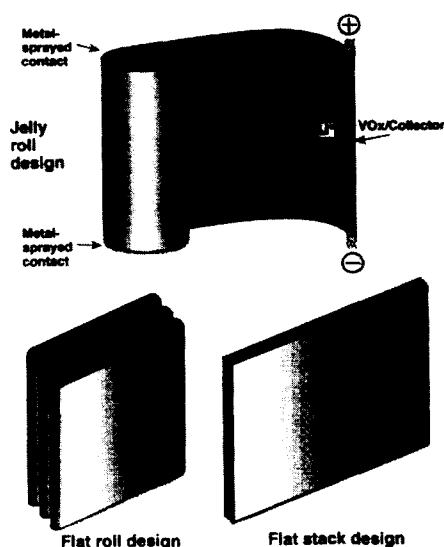Fig. 3. Large lithium polymer cell design.

Fig. 4. Lithium polymer cell designs and electrical contact.

lectors, brought us to the conclusion that this approach was premature at the present stage of development of the lithium polymer technology.

3.3. Compact and efficient lithium polymer battery design adapted from the capacitor model

In the last five years, Hydro-Québec, an electric utility, has been working on an LPC design derived from high-power electric capacitors. Thin dry polymer electrolyte films bear similarities to ultra-thin dielectric films in terms of current collection, surface area, electric field homogeneity between electrodes, and the need for efficient heat transfer from the stacked films. This analogy led to the adaptation of some of the capacitor features to an electrochemical system based on lithium metal.

Figs. (3) and (4) illustrate how the large surface of a cell laminate can be collected over a short distance at every point of a wound or stacked cell laminate that

can be several metres long. This geometry minimizes *IR* losses and allows efficient heat transfer to and from the multilayer cell. The lithium foil itself is used as both anode and collector, while a thin metal or a metallization, e.g. Al, is used for composite-cathode collection. Projection of both metals at each end of the cylindrical roll, for example, allows a very compact design. Fig. 4 also illustrates different designs for three bare electrochemical cell shapes made from the same cell laminate production. A metal spraying technique have been developed to ensure direct contact with the lithium foil anode as well as with the cathode collector metal. This technique allows contact along the full length of each lateral edge of the electrode without damaging the plastic components and avoiding lateral tabs, which would generate defects or electrical field inhomogeneity in such a thin-film system.

This cell design offers the high electric and heat-transfer efficiency essential for high power and safe operation of the large LPB. It also constitutes a light-weight, compact and simple solution for the fabrication a high-energy storage battery.

3.4. Components under development and the '10 Wh-size' development cells

The electrochemical cell laminate is about 120 μm thick at the present stage of development and bench-scale processes exist to fabricate the film components and laminate the electrochemical cell on a continuous basis, including a new process devised to make high-quality ultra-thin lithium foil. Fig. 5 illustrates two '10 Wh-size' cells from the May production covered by the USABC contract. These small development LPCs are not optimized for packaging and are used only for material and process evaluation and for establishing the electrochemical performance baseline.
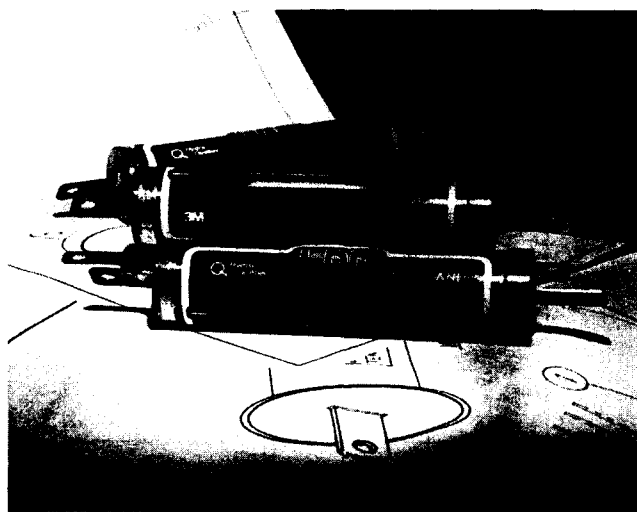

Fig. 5. Recent '10 Wh-size' lithium polymer cells produced for USABC.

4. Electrochemical performance of 4 cm² laboratory cells and '10 Wh-size' lithium polymer cells

4.1. Initial scale-up experience between laboratory cells and '10 Wh-size' jelly roll lithium polymer cells

Earlier production of '10 Wh-size' cells cycled at constant current and at a C/6 discharge rate is illustrated in Fig. 6. A cell performance similar to that of 4 cm² laboratory cells is observed, in spite of the thousand-fold surface factor; the trend in cycling is also very similar with no dendrite problem developing. Results from twelve '10 Wh-size' LPCs from USABC's May production are illustrated in Fig. 7. Initial cycling of these first twelve cells represented confirms a 100% Ah efficiency and a >85% energy efficiency between discharge and charge by cycle 9. Cell resistance observed by current interruption is essentially determined by electrochemical cell contribution as extrapolated from small laboratory cells, confirming the good quality of electrical connection of the lateral electrode obtained from sprayed metal contacts.

4.2. Laboratory cell performances for non-electric vehicle applications

4.2.1. Wheelchair

The battery size required by a wheelchair application, about 1 kWh, is an interesting first target for any new high-energy and high-power source. First, the market is already there and growing. Second, a wheelchair constitutes a smaller version of an electric vehicle (EV) with a need for power: specific energy and cycle number. The power requirement is somewhat lower than in the EV, however, as shown by the typical outdoor elementary and complete profiles in Figs. 8 and 9.

The driving-profile power needs P (W) are translated from LPB into an equivalent peak-current density
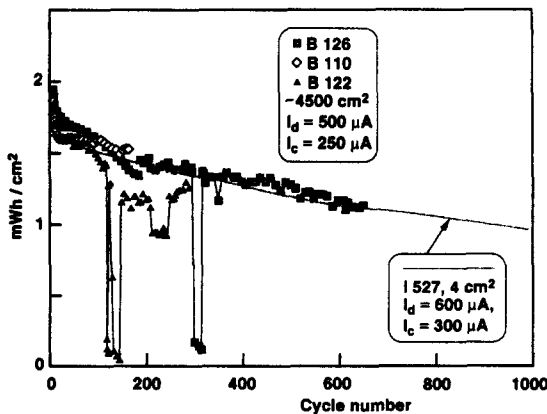

Fig. 6. Cycling performance of early '10 Wh-size' lithium polymer cells made in 1992.
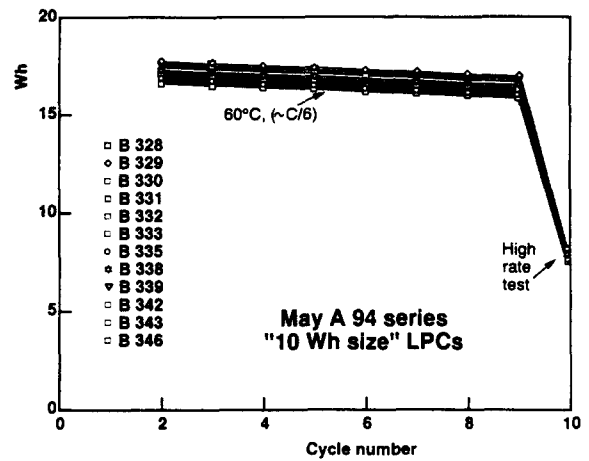

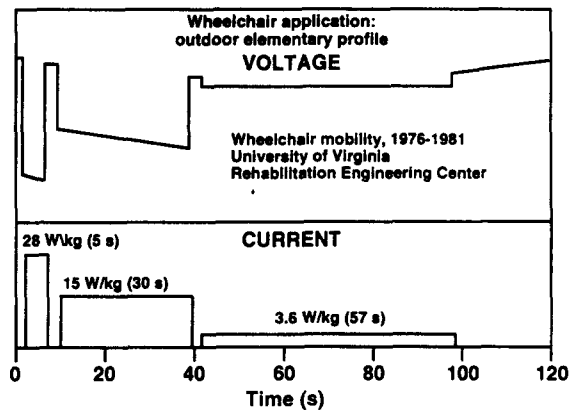Fig. 7. Initial cycling (formation) of a group of 12 '10 Wh-size' lithium polymer cells made for USABC.

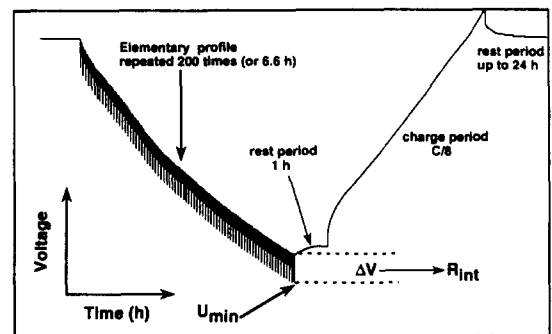Fig. 8. Wheelchair application: outdoor elementary cycling profile.

Fig. 9. Wheelchair application: complete outdoor profile.

($I_{LC\,max.}$) applied to the 4 cm² laboratory cell (LC) using the following relation:

$$I_{LC\,max.} = \frac{P(W) \times (L \times S)_{LC} \times d_{LC}}{M(kg) \times U_{LC}(V)} \tag{1}$$

where L, S and U are the LC thickness, area and voltage, respectively. A commercial 1.3 kWh, 34 kg, 24 V lead/acid battery is used to determine the equivalent LC current density required from a LPB of the same

volume. A current density $(I_{LC\,max.})$ of 760 mA for a 4 cm² LC was found to correspond to the 26 W/kg peak power requirement.

Cycling under this outdoor profile has been under way for over three years and the results in Fig. 10 are in fact an update of those presented at the previous ILBM Meeting in Münster, 1992. These results are for a Li⁰/copolymer + LiTFSI/VO$_x$ 4 cm² LC operated at 60 °C. In this cycling test, the elementary profile is repeated 200 times, roughly the equivalent of six uses per day, which correspond to partially discharging the battery every day over three years. The test is still in progress and now being completed by other tests under

Fig. 10. Wheelchair application: outdoor profile testing over three years.

more stringent conditions. However, the results clearly reveal the stability of dry polymer cells under long-term cycling at 60 °C.

4.2.2. Stand-by power

Another potential application for LPB based on a dry polymer electrolyte is suggested by their exceptional shelf life and self-discharge characteristics. Uninterrupted power sources (UPS) and other types of stand-by power sources require reliability, compactness, zero-maintenance and instantaneous power availability.

Three individual cells, 4 cm² in size, are still being tested after more than six years. The history of these cells maintained at three different temperatures, 80, 60 and 40 °C, is summarized in Fig. 11. After initial cycling and characterization, the cells were left in open-circuit voltage (OCV), fully charged, with their voltage being monitored periodically. After a 3-year stand-by period at their normal operating temperature, the cells were discharged at a 6 h rate and the voltage behavior observed closely in the first milliseconds (Figs. 12 and 13). No voltage delay was detected on cell start-up and the energy recovered during discharge confirmed exactly the same value predicted from the OCV monitoring.

Periodic evaluation of the cell capacity, cycling capability and impedance is performed alternately with long stand-by periods in the charged state. Over this long period of testing at these operating temperatures, the following self-discharge rates are observed: (i) less
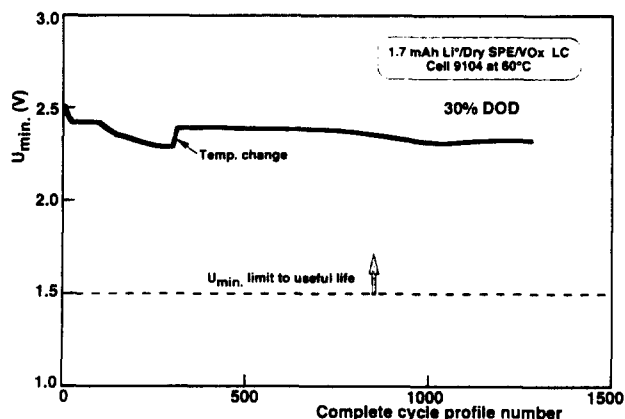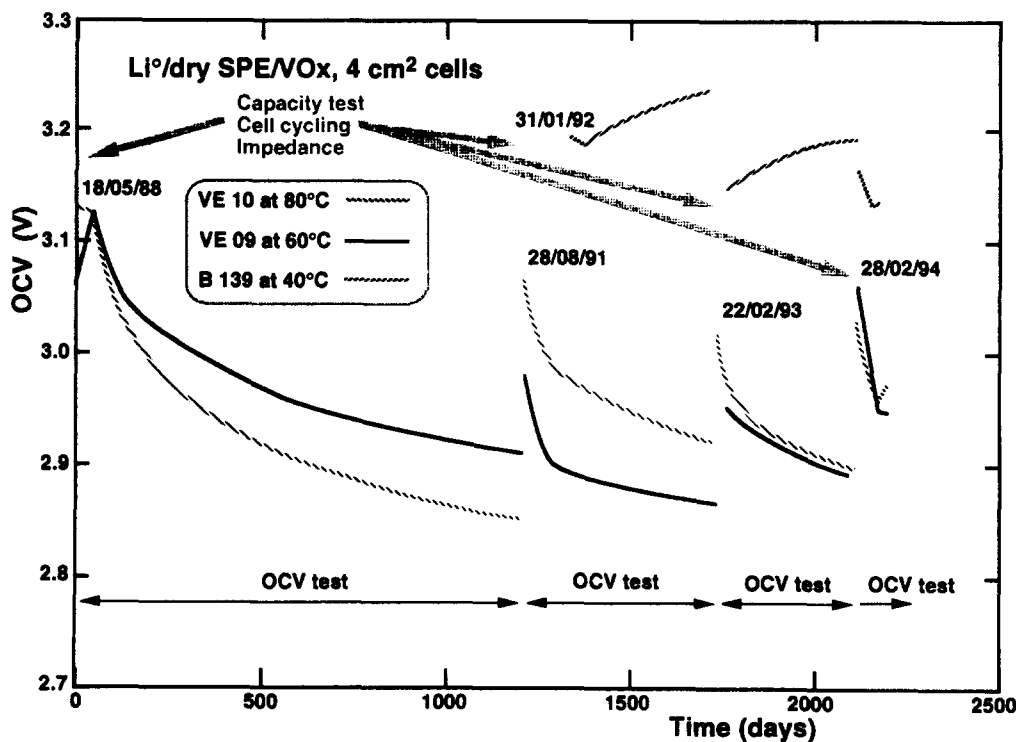

Fig. 11. Six-year stand-by test on dry polymer cells at 40, 60 and 80 °C: open-circuit voltage (OCV) vs. time.
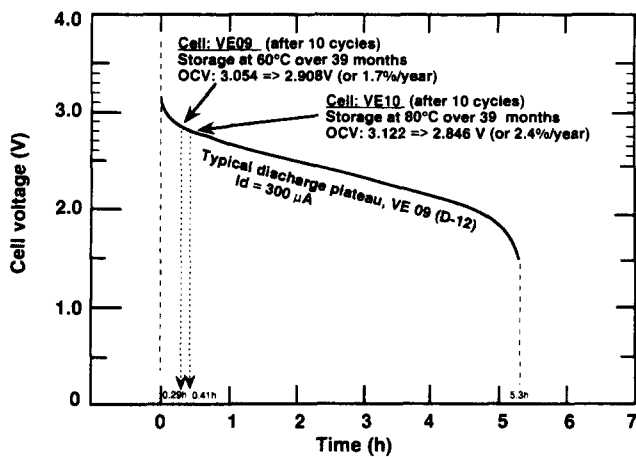
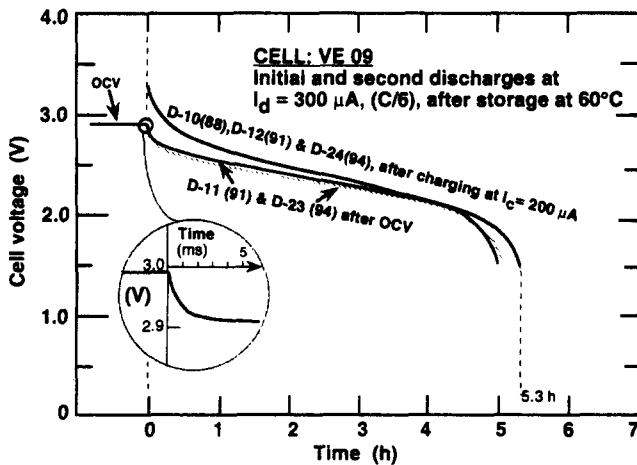Fig. 12. Self-discharge evaluation from open-circuit voltage (OCV).

Fig. 13. Shelf life after three and six years on stand-by.

than 3%/year at 80 °C; (ii) less than 2%/year at 60 °C; and (iii) nothing at 40 °C.

If scale-up, cost, thermal management and safety of the LPB confirm our expectations, we can anticipate the emergence of markets where maintenance, reliability and reproducible performance are important. A normal operating temperature of 40 °C for a stand-by battery now looks an attractive target for further demonstration activity in view of the preliminary shelf-life studies and taking advantage of the fact that the high peak power level associated with EV acceleration is not required for stationary applications.

5. Conclusions

The outlook for high-performance large lithium batteries is promising, considering the constant progress made in developing polymer electrolytes and original LPC designs adapted to the lithium polymer technology.

The association of lithium metal with dry polymer electrolyte acting as an immobile solvent still represents one of the very few candidates to reach or exceed the long-sought goal of a 200 Wh/kg specific energy for an EV power source.

Results from small laboratory cells are now being confirmed by '10 Wh-size' development cells (> 1000 times larger) now currently produced as part of the USABC program.

Other results on small laboratory cells operated between 40 and 80 °C and tested under cycling or stand-by conditions over several years confirm the excellent stability of the dry polyether + LiTFSI electrolyte in a lithium cell environment (Li^0 metal + 3 V cathode). They also suggest that other non-EV applications might exist for the present LPB technology operating between 40 and 60 °C.

Several new materials are still under development in an aim to improve the LPB rate capability, cycle life and operating temperature. The recent USABC 33M$ R&D contract granted to the 3M, Argonne National Laboratory and Hydro-Québec team will accelerate the development of this long-term technology. It is also anticipated that the complementary background of each partner will help to solve the major research, engineering, cost and safety issues to be overcome before a commercially viable EV battery becomes available.

Acknowledgements

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