

# Development of a bipolar Li/composite polymer electrolyte/pyrite battery for electric vehicles

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## Abstract

To demonstrate the concept of rechargeable polymer electrolyte bipolar lithium batteries, laboratory-type bipolar Li/pyrite 3-cell batteries were fabricated and tested. The unoptimized 5 V, 10 cm<sup>2</sup> 3-cell battery had a capacity of 30–40 mAh with 100% Faradaic efficiency. The long-term projection for a prototype sealed bipolar Li/composite polymer electrolyte/pyrite (Li/CPE/FeS<sub>2</sub>) battery, with a 45 μm-thick cathode is 250 Wh/kg specific energy. The performances of monopolar and bipolar battery designs are compared. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymer electrolyte bipolar battery; Faradaic efficiency; Li/pyrite batteries

## 1. Introduction

Lithium and lithium-ion battery usage is gradually spreading to large-scale battery systems, such as power sources for electric vehicles (EV) and energy storage for load leveling. Electric vehicles need batteries that are affordable, meet or exceed current safety standards and satisfy customer expectations for performance. The lithium polymer battery is considered to be one of the best long-term solution for powering electric vehicles. Lithium polymer batteries have been under development since the late 1970s and have been shown to be a promising technology [1]. One of the major obstacles to the commercialization of lithium polymer-electrolyte and lithium-ion batteries for EV application is their high cost [2]. The cost of materials for the Li/composite polymer electrolyte/pyrite (Li/CPE/FeS<sub>2</sub>) battery is about \$40/kWh (excluding the case), a sixth of that for lithium ion batteries and for other lithium polymer electrolyte batteries (estimated at \$250/kWh) [3–5]. There are two reasons for such low cost similar to that of the lead-acid battery: the use of lithium iodide as a salt at \$20/kg, as opposed to lithium hexafluorophosphate or lithium imide at about \$250/kg, and the use of a natural ore (pyrite) as cathode material at \$0.5/kg.

The Li/CPE/FeS<sub>2</sub> battery has many attractive properties. This all-solid-state battery utilizes metallic lithium as its anode and a thin composite polymer electrolyte which acts both as a separator and electrolyte. The flexible, multi-laminate structure of the polymer electrolyte battery makes possible very high power and energy densities. The use of a solid polymer as the electrolyte is particularly advantageous because it does not leak and emit dangerous gases. Pyrite was found to be fully compatible with the polymer electrolyte components up to 300°C [3]. The Li/CPE/FeS<sub>2</sub> battery operates over a moderate temperature range of 75–140°C. At C/10 discharge rate, thin-cathode cells operating at 90°C deliver 50% of their 135°C capacity. More than 500 100% DOD cycles (at C/3 rate) with a capacity-fading rate of less than 0.1%/cycle were carried out in small (1 cm<sup>2</sup> area) laboratory prototype cells with 10 μm-thick cathodes [4]. It was shown [5] that cells with FeS<sub>2</sub>-composite cathodes show identical electrochemical behavior and performance characteristics, independent of the pyrite source.

Internal electrochemical overcharge/overdischarge protection mechanisms were shown for the Li/CPE/FeS<sub>2</sub> battery [4]. Up to 100% overcharge and discharge down to 0.3 V are possible in this system with no significant negative effects. The existence of the buffer capacities is a very important battery feature against accidental damage. Overcharge and overdischarge protection becomes particularly important in the design of high-voltage multi-cell bipolar batteries. The bipolar battery design minimizes IR losses between adjacent cells in a cell-stack and provides uniform current and

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potential distributions over the active surface area of each cell component. Bipolar batteries are known to provide higher power than monopolar batteries, which are aimed at higher capacity [6]. At present we are developing a small laboratory prototype of a Li/CPE/FeS<sub>2</sub> battery to meet the range and power required by the USABC. This work presents preliminary results on selection and characterization of materials and cycleability of bipolar Li/CPE/FeS<sub>2</sub> battery.

## 2. Experimental

The electrochemical cells studied comprise a lithium anode, LiI<sub>1</sub>P(EO)<sub>20</sub>EC<sub>1</sub> 9% v/v Al<sub>2</sub>O<sub>3</sub> 100–150 μm thick CPE and a 35–50% (v/v) 10 and 45 μm thick pyrite-based composite cathode. The preparation of CPEs and composite cathodes is described elsewhere [3–7]. 1 cm<sup>2</sup>-button batteries, 10 cm<sup>2</sup> single cells and 3-cell bipolar experimental batteries were built and tested.

Experimental bipolar Li/CPE/FeS<sub>2</sub> batteries were assembled as shown in Fig. 1. The batteries were constructed from three cells and contained two bipolar plates. Each bipolar plate consists of a pyrite cathode on one side and a lithium anode on the other side. The bipolar substrate is 50 μm thick stainless steel, coated by a mixture of expanded graphite and 20% w/w PVDF. The graphite-aluminum laminate as cathode current collector and stainless steel-anode current collector were also examined. Stainless steel sheets

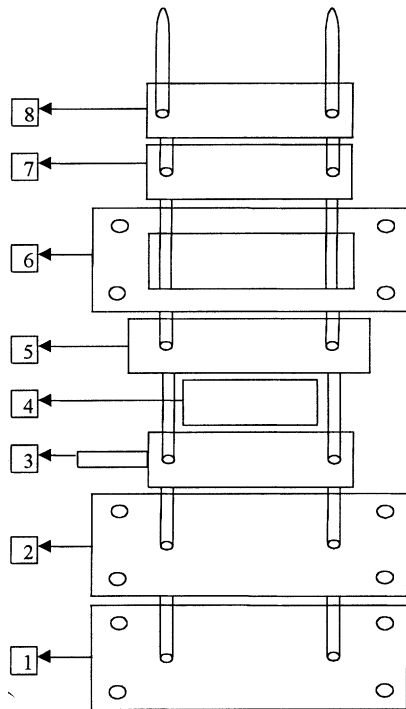


Fig. 1. Schematic presentation of the setup of one cell in the bipolar battery: (1) s.s. plate, (2) isolator, (3) anode current collector, (4) lithium, (5) CPE, (6) isolating frame, (7) cathode, (8) bipolar plate.

of 5 mm thickness were used as end plates. The plates were fixed by four equidistant stainless steel springs at periphery of the battery. Fig. 1 schematically illustrates the single-cell structure of the bipolar battery. Our calculation shows that cell expansion/extraction during charge-discharge is about  $\pm 20\%$ . An optimal spring pressure eliminating contact loss and providing maximum utilization of cathode active material in 10 cm<sup>2</sup>-area cells was found to be 4.8 kg/cm<sup>2</sup>. The 1 cm<sup>2</sup>-button batteries, 10 cm<sup>2</sup>-single cell and 3-cell experimental batteries were cycled at 120 and 135°C in a Maccor series 2000 battery test system.

## 3. Results and discussion

The corrosion of thin current collectors in lithium batteries is of particular concern whenever a large number of cells is connected in series for long-term operation [8]. In bipolar batteries overcharging of some cells may be unavoidable. Chen and co-workers [8] showed that aluminum is resistant to uniform corrosion in the PEO-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte but is susceptible to pitting corrosion on overcharging. Similar results were obtained by Munshi et al. [9] for the Li/P(EO)<sub>8</sub>-LiCF<sub>3</sub>SO<sub>3</sub>/V<sub>6</sub>O<sub>13</sub> cell. On the other hand, Shembel et al. [10] found that aluminum is corrosion resistant in the short-circuit couple FeS<sub>2</sub>-Al in nonaqueous electrolytes.

In the present work we examined the performance of the Li/CPE/FeS<sub>2</sub> battery, where the cathode current collector is immediately adjacent to a composite cathode comprising polymer electrolyte and cathode-active material. We found that the degree of degradation of small (1 cm<sup>2</sup> area) Li/P(EO)<sub>20</sub>EC Al<sub>2</sub>O<sub>3</sub>/pyrite cells is dramatically affected by the material of cathode-current collector. All the current collectors studied, namely stainless steel, aluminum, graph-foil and aluminum covered by a PVDF-graphite coating were likely to corrode to different extents during charge/discharge. Similar results were obtained for the 10 cm<sup>2</sup>-area cells (Fig. 2). A single 10 cm<sup>2</sup>-cell went through over 70 reversible cycles. The capacity loss of the cell with a

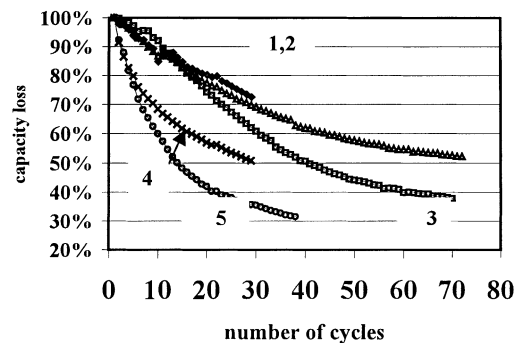


Fig. 2. Cycle life of 10 cm<sup>2</sup>-area monopolar Li/CPE/pyrite battery with different current collectors: 1 and 2, graph foil; 3, aluminum-graphite laminate; 4, homemade graphite; 5, stainless steel.

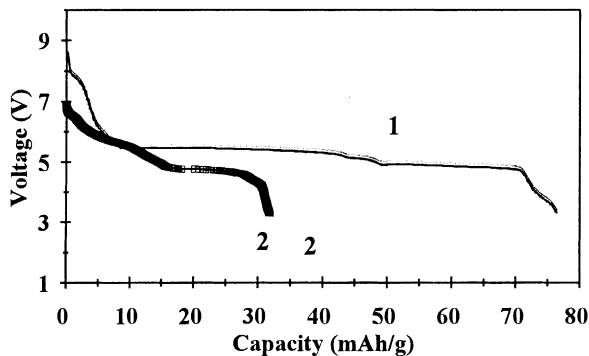


Fig. 3. First and second discharge curves of the 3-cell bipolar Li/CPE/FeS<sub>2</sub> battery  $T = 135^{\circ}\text{C}$ .

stainless steel current collector after 20 100%DOD cycles was found to be about 3%/cycle. The cells with a graph-foil current collector and graphite-aluminum laminate showed 1.2–1.8 and 1.1–1.9%/cycle, respectively. After 72 cycles, the degree of degradation of the latter cells was about 0.7%/cycle. The performance characteristics of the cells with a graphite-stainless steel laminate current collector were close to those having a graphite-aluminum current collector.

Scanning electron microscopy (SEM) micrographs showed pitting corrosion occurring on the aluminum current collector on cycling. The surface of the stainless steel current collector was subjected to intensive grain-boundary corrosion. At this stage of the investigation, graphite-aluminum and graphite-stainless steel laminates seem to be less prone to corrosion in Li/CPE/pyrite batteries and were used as cathode current collectors in bipolar batteries.

An OCV value of 8.4 V was observed in an as-built Li/CPE/FeS<sub>2</sub> 3-cell bipolar battery (Fig. 3) and the first discharge curve had a high-voltage slope at 8.4–5.4 V, corresponding to 2.8–1.8 V for a single cell. This high-voltage spike during the early stages of discharge is attributed to the reduction of surface impurities of pyrite, such as iron oxides, hydroxides and sulfates [5].

The first discharge curve at 120 and 135°C has two well defined plateaus, one at about 5.4 V and another at 4.8 V (Fig. 3) corresponding to 1.8 and 1.6 V for a single-cell pyrite battery. The first discharge cathode utilization of bipolar battery at 0.05 mA/cm<sup>2</sup> was about 70%, while for the 1 cm<sup>2</sup> cell it was 85–100%. Charge–discharge curves at subsequent cycles, were similar to those of the small 1 cm<sup>2</sup> monopolar prototype cell.

The 45 μm-thick cathode battery went through over 20 reversible 100% DOD cycles. Capacities of 30–40 mAh with 100% Faradaic efficiency were routinely obtained during discharge of this bipolar battery.

Simple calculations were carried out for Li/CPE/FeS<sub>2</sub> monopolar and bipolar batteries consisting of composite cathodes of varying thickness and pyrite content (Fig. 4). It was found that the batteries of bipolar design have about 20% higher specific energy than monopolar batteries of the

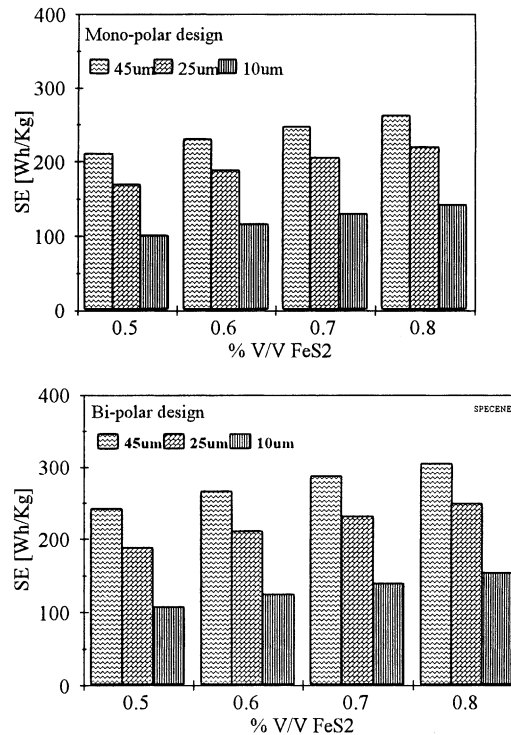


Fig. 4. Projection for the specific energy of monopolar and bipolar Li/CPE/FeS<sub>2</sub> battery.

same composition. These improvements are mainly due to the weight saving of the can and bipolar plates.

#### 4. Summary

The effect of current collector material on the performance of Li/CPE/FeS<sub>2</sub> monopolar 1 and 10 cm<sup>2</sup>-area batteries was studied. A single 10 cm<sup>2</sup> cell went through over 70 reversible cycles. The capacity loss of the cell with a stainless steel current collector after 20 100%DOD cycles was found to be about 3%/cycle. The cells with graph-foil current collector and graphite-aluminum laminate showed capacity losses of 1.2–1.8 and 1.1–1.9%/cycle, respectively. After 70 cycles the degree of degradation of the later cells was about 0.7%/cycle.

The 3-cell 5 V bipolar batteries with good performance were assembled and tested. Capacities of 30 to 40 mAh with 100% Faradaic efficiency were routinely obtained during discharge. Charge–discharge characteristics of these cells were similar to those of the monopolar prototype.

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