



Short communication

# Solid-state, rechargeable Li/LiFePO<sub>4</sub> polymer battery for electric vehicle application

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## ABSTRACT

A solid-state polymer lithium metal battery having a LiFePO<sub>4</sub>/C composite cathode and a poly(ethylene oxide) PEO-based solid polymer electrolyte was assembled and characterized in terms of specific energy and power according to the protocol for electric vehicle (EV) application set by the USABC-DOE. The results of these tests show that this polymer battery surpasses the goals stated by USABC-DOE and, hence, may be suitable for application in the evolving EV market.

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## 1. Introduction

Rechargeable lithium polymer batteries, LPBs, are electrochemical power sources characterized by high specific energy and power, stability to repeated charge–discharge cycles, reliability and safety [1–3]. An LPB commonly includes a cathode capable of reversibly intercalating lithium ions, a lithium conducting polymer electrolyte separator and a lithium metal anode. The safe use of a high capacity lithium metal anode and ease of cell assembly are the main advantages of these batteries. Carbon-coated lithium iron phosphate (LiFePO<sub>4</sub>/C), with a theoretical specific capacity of 170 mAh g<sup>-1</sup>, is an ideal cathode material for LPBs. The strong covalent P–O bonds in the tetragonal phosphate anion gives to the battery a high thermal stability against oxygen release and, hence, safe use and tolerance to abusive conditions.

Polymer separators represent another important factor. The most promising candidates are polyethyleneoxide–lithium salt, PEO–LiX, complexes. As is well known, PEO-based polymer electrolytes exhibit an appreciable ionic conductivity ( $\sigma > 10^{-4}$  S cm<sup>-1</sup>) only above 70 °C due to the lithium transport mechanism that is associated with the segmental motion of the polymer backbone [4–6]. High-temperature restriction may be a drawback for consumer electronic market applications but may be acceptable for electric vehicles (EVs) where thermal management is not a problem. Note too that solid-state polymer batteries are suitable power

sources for EV since their solvent-free configuration assures safety and low cost. A good choice is PEO<sub>20</sub>–LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub> because this polymer electrolyte combines high conductivity with superior interfacial stability towards the lithium metal anode, as well as good mechanical properties [7].

The present paper reports a Li/PEO<sub>20</sub>–LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C LPB and its response to electrochemical tests performed as per the EV power source condition benchmark protocol of the U.S. Department of Energy (DOE) [8].

## 2. Experimental

The cathode material LiFePO<sub>4</sub>/C was prepared as in Ref. [9] and the PEO<sub>20</sub>–LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub> polymer electrolyte as in Ref. [7]. The cathode was formed as a film electrode by lamination on a carbon-coated aluminum grid (Lamart) of a paste obtained by mixing 80 wt.% LiFePO<sub>4</sub>/C, 15 wt.% carbon conducting additive (SuperP, MMM Carbon Co.) and 5 wt.% polytetrafluoroethylene (Du Pont, 60 wt.% water dispersion) binder in a small amount of ethanol; the electrode films were dried at 80 °C under vacuum over night before use. The geometric electrode area was 0.384 cm<sup>2</sup> and the composite mass loading was 3.7 mg cm<sup>-2</sup>. The PEO<sub>20</sub>–LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub> polymer electrolyte separator (thickness of 250 μm, density of 0.95 g cm<sup>-3</sup>) was cut into the proper shape. Li metal in excess (three times the stoichiometric amount) was used as anode. The cell components were placed inside a Teflon container having two stainless-steel current collectors. Cell assembly and sealing were performed in an argon atmosphere MBraun Labmaster 130 dry box (H<sub>2</sub>O and O<sub>2</sub> < 1 ppm) and all electrochemical tests were performed

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in a Thermoblock (FALC) oven at 100 °C using a Perkin-Elmer VMP multichannel potentiostat.

### 3. Results and discussion

#### 3.1. Electrochemical tests

The Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/CLPB was characterized for specific energy and power after the EV protocol set by the USABC-DOE, as reported in “Electric vehicle battery test procedures manual” [8], focusing on “Constant Current Discharge Test” and “Peak Power Tests” to simulate battery functioning in EV. The purpose of constant current tests is to estimate the effective capacity of the cell at different C-rates. Accordingly, charge/discharge cycles at C/10, C/5, C/3 and C/2 were carried out, including C/1 discharges after C/10 charges. As stated in the manual, the specific energy of this LPB was evaluated from the C/3 discharge. The Peak Power Test (PPT) is designed to determine the sustained (30 s) discharge power capability of the battery at various depths of discharge (DOD). The value calculated at 80% DOD is of key importance because it provides the point at which the battery performance have to be compared with the USABC-DOE power target.

All the tests were performed by setting a cut-off voltage of 4.0 V for the charge and of 2.2 V for the discharge. The currents for the C-rates ranging from 2C to C/10 varied from 0.677 to 0.034 mA cm<sup>-2</sup>. Specific LPB parameters like energy and power were evaluated in reference to a total mass of 4.1 mg cm<sup>-2</sup>, which is the sum of the cathode electrode composite mass and three times the stoichiometric amount of lithium as anode.

Fig. 1 shows the voltage profiles of the constant current discharge tests at different C-rates. The discharge curves of three successive charge/discharge cycles at C/3, shown in Fig. 2, which delivered constant capacity values within 2% (123 ± 1 Ah kg<sup>-1</sup>), were used to calculate specific energy of the LPB of 275 Wh kg<sup>-1</sup>.

The PPTs were performed, starting from a fully charged LPB at C/3 at 10 depths of discharge ranging from 0% DOD to 90% DOD in 10% intervals in the course of a single discharge at a C/3 rate. At each DOD the LPB was discharged by a 30 s current pulse, and the pulse currents corresponded to 1C for the low-current and to 2C for the high-current tests; maximum pulse C-rate of 2C was selected to avoid lithium diffusion limitation in the thick PEO separator.

It is worth noting here that, before applying the first (0% DOD) discharge pulse, the LPB was discharged for 30 s at the base discharge rate (C/3) and that after the last current pulse at 90% DOD the cell was discharged at C/3 to 100% of its rated capacity. Figs. 3 and 4, which show the voltage profiles of low and high-current PPTs per-

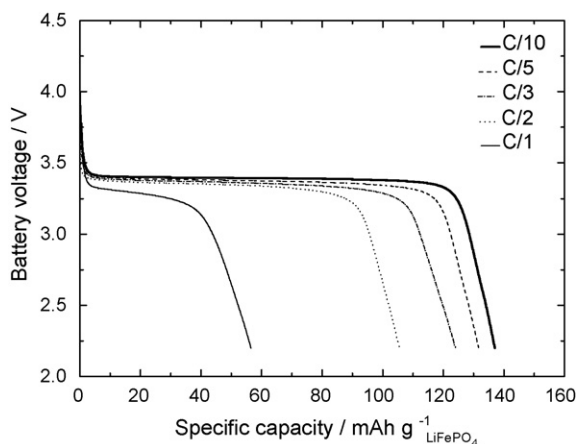


Fig. 1. Discharge profiles of the Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C LPB at different C-rates. Cut-off 4.0–2.2 V. 100 °C.

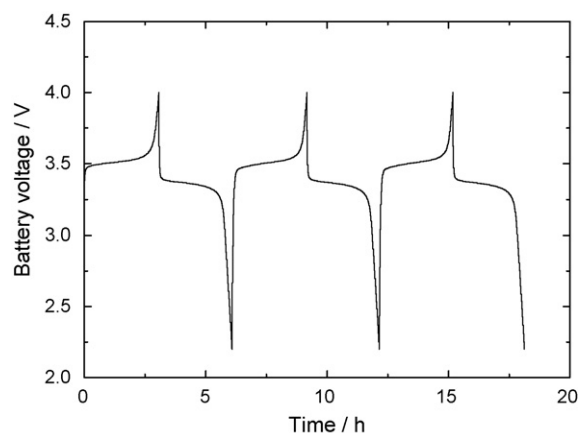


Fig. 2. Voltage profiles of three successive charge/discharge cycles at C/3 at 100 °C of the Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery.

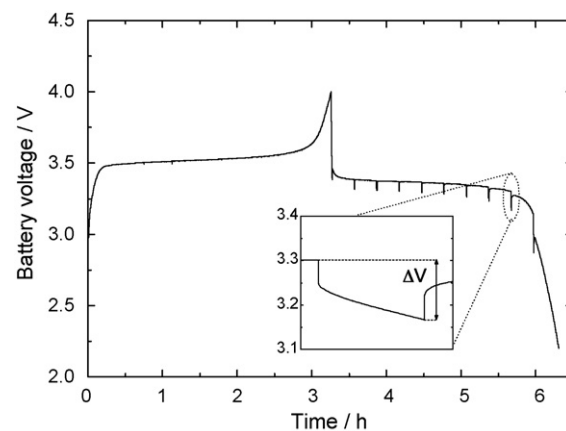


Fig. 3. Voltage profile of fresh Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery under the low-current (1C pulse) PPT at 100 °C. The inset shows the pulse voltage profile at 80% DOD.

formed on a fresh LPB clearly demonstrate that in both tests the battery always remained above the discharge voltage limit of 2.2 V.

The peak power capability of this LPB was calculated at each DOD by deriving the battery resistance and equivalent IR-free voltage from measured changes in battery voltage and current. The voltage values for  $\Delta V$  calculations were measured just prior to ( $V_1$ ) and then near the end ( $V_2$ ) of each pulse discharge current step. The

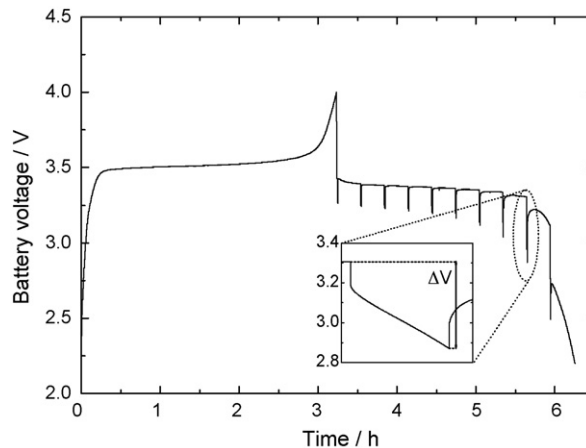


Fig. 4. Voltage profile of fresh Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery under the high-current (2C pulse) PPT at 100 °C. The inset shows the pulse voltage profile at 80% DOD.

**Table 1**  
PPT results at 100 °C and 80% DOD for fresh and cycled Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery.

	V <sub>1</sub> (V)	V <sub>2</sub> (V)	Resistance (Ω)	IR-free voltage (V)	Peak Power (mW)
Low-current pulse test (1C), fresh cell	3.30	3.17	1490	3.24	0.45
High-current pulse test (2C), fresh cell	3.31	2.90	1829	3.24	0.97
High-current pulse test (2C), cycled cell	3.30	2.85	2250	3.22	0.86

**Table 2**  
Specific power and specific energy of fresh and cycled Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery the targets set by the USABC-DOE for EV application.

	LiFePO <sub>4</sub> /PEO/Li fresh cell	LiFePO <sub>4</sub> /PEO/Li cycled cell	USABC minimum goal	USABC long-term goal
Specific power, discharge at 80% DOD/30 s (W kg <sup>-1</sup> )	615	550	300	400
Specific energy, C/3 discharge rate (Wh kg <sup>-1</sup> )	275	240	150	200

$\Delta I$  current values were taken either as the difference between the base current at C/3 and the pulse current at 1C for the low-current test, or as the pulse current at 2C for the high-current tests. Accordingly, cell resistance  $R$  and the IR-free voltage were computed as

$$\text{battery resistance} : R = \Delta V / \Delta I, \text{ and} \quad (1)$$

$$\text{cell IR-free voltage (before the pulse)} : V_{\text{IRFree}} = V - IR. \quad (2)$$

The peak power capability was calculated by Eq. (3) as:

$$\text{peak power capability} = I_{\text{Pulse}} \cdot (V_{\text{IRFree}} + RI_{\text{Pulse}}) \quad (3)$$

As suggested in the manual, this equation was selected because it yields the lowest value of peak power capability at 80% DOD. The low- and high-pulse current tests were performed twice on the same fresh battery and the results were highly reproducible. Table 1 displays (first two rows) the results of the low and high PPTs at 80% DOD for V<sub>1</sub> and V<sub>2</sub> voltage, resistance, IR-free voltage and peak power values; Table 2 (first column) shows the specific power from high-current PPT and the specific energy from the Constant Current Discharge test at C/3.

The comparison of the specific power and energy of the LPB with the USABC-DOE EV minimum and long-term targets reported in the last two columns of Table 2 demonstrates that the Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery surpasses these targets. In calculating the specific values of this LPB, the weight of the current collector and of the polymer separator were not included because they were not optimized as in a commercial battery [1]. However, even assuming a total battery weight twice that of the electrode materials, this LPB technology appears capable of meeting USABC targets.

This LPB was then galvanostatically cycled at C/3 and 100 °C for more than 375 deep cycles and Fig. 5, which displays the deliv-

ered capacity over cycles, shows the electrochemical stability of this LPB as well as its mechanical stability over more than 3 months at 100 °C.

Cell response under thermal interruption was also investigated. The test was run by lowering temperature from 100 °C to room temperature in the course of the 200th cycle and the LPB was cycled for 300 cycles at the same current and voltage cut-off used for the tests at 100 °C. Thereafter the temperature was raised again to 100 °C and the galvanostatic cycling at C/3 was restarted: no capacity loss was observed, as shown in Fig. 5, and this clearly demonstrates the mechanical stability of the battery.

Battery performance in terms of specific energy and power after 375 deep cycles at 100 °C was evaluated by constant current discharge test at C/3 and high-current PPT at 2C. The results of the PPT on this cycled cell are in the last row of Table 1 and the specific power and energy values are reported in the second column of Table 2. A comparison of the specific values of the cycled cell with those of the fresh battery shows that the decay is ca 10%, clearly indicating that the DOE targets are still met even by this long-cycled LPB.

#### 4. Conclusions

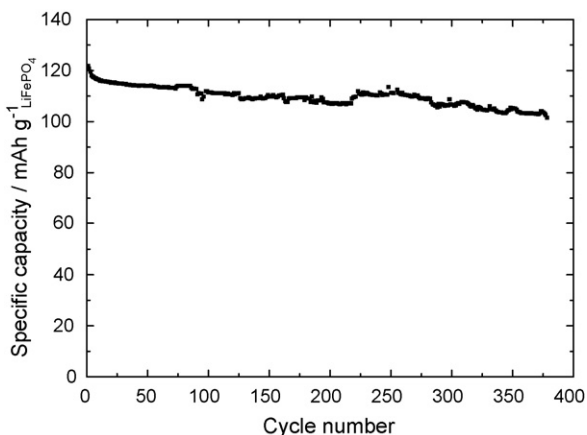
The response of the Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery reported herein under the conditions set for EV application by the USABC-DOE manual shows that the specific power and specific energy of this rechargeable LPB surpass the USABC-DOE targets. We expect that even higher values of pulse power capability can be attained by optimization of battery geometry via reducing the thickness of the polymer electrolyte separator. The encouraging results reported strongly suggest that this technology, by ensuring high performance and safety, is suitable for an effective application in the evolving EV market.

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**Fig. 5.** Delivered specific discharge capacity at C/3 and 100 °C by Li/PEO<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10%ZrO<sub>2</sub>/LiFePO<sub>4</sub>/C battery versus cycle number.