

Short communication

## Safe Li-ion polymer batteries for HEV applications

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### Abstract

The performance of natural graphite/PEO-based gel electrolyte/LiFePO<sub>4</sub> cells (5 mAh, 4 cm<sup>2</sup>) is reported. The gel polymer electrolytes were produced by electron-beam irradiation and then soaked in a liquid electrolyte. The natural graphite anode in gel electrolyte containing lithium bis(fluorosulfonyl)imide (LiFSI)-EC + PC + DMC exhibited high reversible capacity (360 mAh/g) and high coulombic efficiency (91.6%). The LiFePO<sub>4</sub> cathode in the same gel polymer exhibited a reversible capacity of 160 mAh/g and 92% coulombic efficiency. Better performance was obtained at high-rate discharge with 6% carbon additive (carbon and graphite) in the cathode. The Li-ion gel polymer battery shows a very low capacity fade of 1% after 100 cycles.

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### 1. Introduction

Hybrid electric vehicles (HEVs) offer one important step towards improved energy efficiency and reducing global warming. As the world population grows at a rate of 80 million inhabitants a year, there will be an urgent need for more automobiles. It is estimated that there will be 1.5 billion vehicles in the year 2020, the total emission of CO<sub>2</sub> from transportation will be about 65% higher. The automotive industries, as well as the battery and fuel cell companies, could pursue new technologies to mitigate this problem. One example of advanced batteries, Li-ion gel polymer batteries, is a good candidate for HEVs that utilize an internal combustion engine and a rechargeable battery. The successful commercialization of Li-ion gel polymer batteries for portable electronic devices has led to other applications where the size and weight of batteries are important. A considerable investment in this battery technology that utilizes LiCoO<sub>2</sub> cathodes has been made. However, lower-cost cathode materials are required for many applications such as in EVs and HEVs [1,2]. Recently, LiFePO<sub>4</sub> was investigated intensively as a potential cathode material for rechargeable Li-ion batteries [3,4,5,6] because of its low cost and improved safety. The objective of this work is to develop Li-ion batteries with

gel polymer electrolyte using a cell chemistry selected in the battery technology for transportation (BATT) program from the United States Department of Energy. This cell chemistry is based on use of low-cost materials such as natural graphite in the anode. In this paper, we report the electrochemical and ARC results obtained with natural graphite/gel electrolyte/LiFePO<sub>4</sub> cells.

### 2. Experimental

The thin Li-ion gel polymer cells contained natural graphite (purified and processed at Hydro-Québec) for the anode, LiFePO<sub>4</sub> (Phostech, Québec, Canada) for the cathode, an organic electrolyte, and gel polymer separator. The cells were sealed into an aluminum–plastic laminated film bag. The electrolyte was 1.5 M lithium bis(fluorosulfonyl)imide (LiFSI) in a mixture (1:3, v/v) of ethylene carbonate (EC) and g-butylacetone (GBL) [7]. Another electrolyte, 1.5 M LiFSI in a mixture (1:1:3, v/v/v) of (EC) + propylene carbonate (PC) and dimethyl carbonate (DMC) was used for comparison. Experiments were also conducted with a mixed salt, 1 M LiFSI + 0.5 M LiBF<sub>4</sub>, to compare with a single salt. The anode electrode was prepared from a slurry of natural graphite with 10% (w/w) of carbon fiber (mesophase) and vapor grown carbon fiber (VGCF) and 10% (w/w) poly(vinylfluoride) (PVDF) dissolved in 1-methyl-2-pyrrolidone. The paste was coated by a doctor-blade process on a treated copper foil current col-

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lector. The cathode was prepared by combining 10% PVDF with 4% Shawinigan carbon black and  $\text{LiFePO}_4$  mixed in NMP. The paste was coated on aluminum foil current collector. The electrodes were dried under vacuum at  $85^\circ\text{C}$  for 24 h before electrochemical evaluation. The half-cell performance of the negative and positive electrodes was evaluated separately with lithium metal ( $\text{Li}^0/\text{electrolyte} + \text{salt}/\text{electrode}$ ). Discharge–charge cycling was performed using a constant current method (MacPile<sup>R</sup>, Claix, France). ac impedance spectroscopy was used to investigate the interface phenomena. The test cells were maintained at an optimum compression of 10 psi. Both half-cells and complete cells were evaluated at different rates between the voltage limits of 2.5–4 V. A Bitrode cycler was used for long-term cycling tests. In order to study the safety of the cell, a technique known as accelerated rate calorimetry (ARC) (Columbia Scientific, Austin, Texas, USA) was used, this technique involves successively raising the temperature of the sample to high temperatures until a spontaneous thermal reaction between the elements of the battery produces additional heat (stabilization of the temporary rise in temperature). This technique is sensitive to exothermic reactions which can present a danger under abusive conditions of battery use. ARC was used to study the exothermic reactions of anodes, cathodes, lithium salts, and solvents.

### 3. Results and discussion

#### 3.1. Preparation of the gel polymer electrolyte

We have tested two types of gel polymer electrolytes obtained by electron-beam irradiation of a solid gel and a thermal gel.

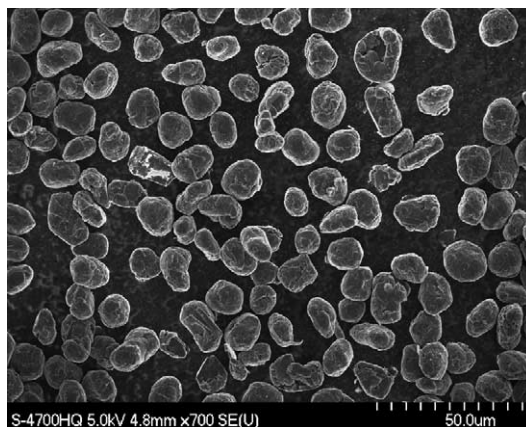


Fig. 1. SEM micrograph of rounded natural graphite.

#### 3.1.1. Solid gel

A polymer electrolyte having structure based on ethylene oxide (EO) units was coated by a doctor-blade method. The polymer based on a four branch polyether film was cross linked by using an electron beam with an energy of 5 Mrad. A hard, free standing uniform film was obtained, which was soaked in liquid electrolyte solutions, 1.5 M LiFSI-EC/GBL, LiFSI-EC/PC/DMC. The polymer underwent swelling after a few minutes with a 20% volume increase. These gel electrolytes were used as separators in both half-cell and Li-ion cells. In these studies, a free liquid electrolyte was present in the cells.

#### 3.1.2. Thermal gel

The second gel polymer electrolyte is also based on a multi branch polyether which was mixed with liquid electrolytes, 1.5 M LiFSI-EC/GBL (1: 3, v/v) or LiFSI-EC/

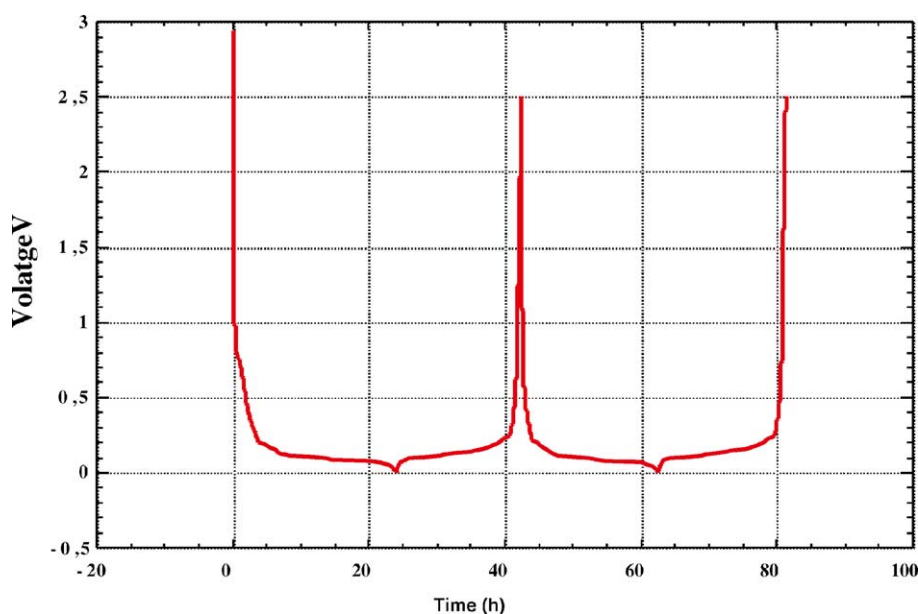


Fig. 2. The discharge–charge profiles of the half-cell, Li/graphite containing gel polymer electrolyte and 1.5 M LiFSI in EC + DMC + PC at C/24 rate (cell:  $4\text{ cm}^2$ , 5 mAh).

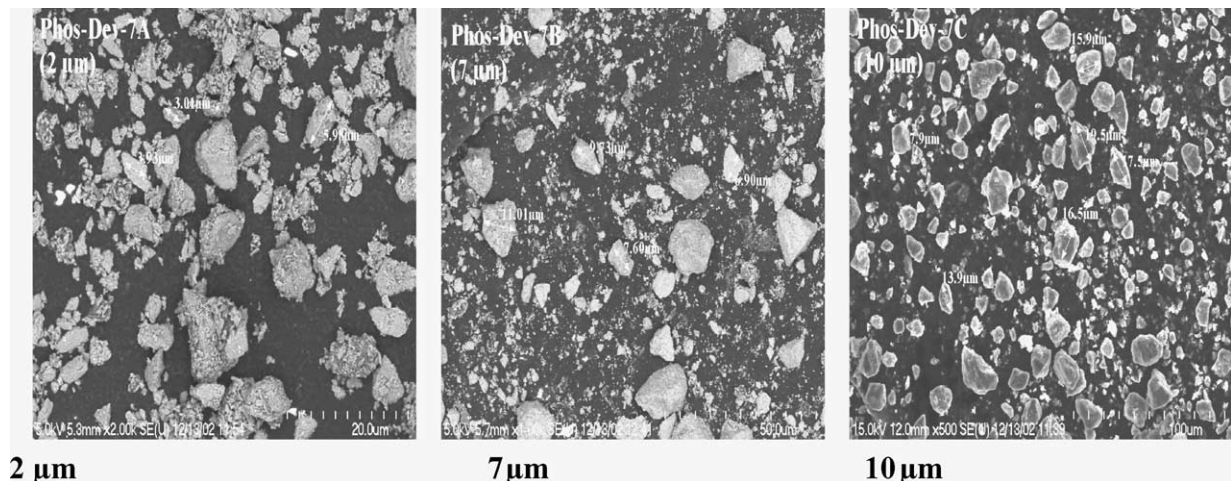


Fig. 3. SEM micrograph of  $\text{LiFePO}_4$  with different particle size (2, 7, 10  $\mu\text{m}$ ).

PC/DMC (1:1:3, v/v/v). The composition ratio of the (EO)-polymer to liquid electrolyte was 10/90 (v/v). 1500 PPM of thermal initiator Perkadox (16 type from Akzo Nobel) was added to the polymer-liquid composition. The gel electrolyte was coated on the electrodes to fill the pores in the electrodes. All the gel preparation steps and cell assembly took place in a glove box. After the cell assembly, the cells were heated at  $60^\circ\text{C}$  for 1 h to complete the cross linking reaction to form the gel polymer. In these experiments, no free liquid electrolyte existed in the cells.

### 3.2. Half-cell characterization

#### 3.2.1. Anode

Commercial Brazilian natural graphite was modified and purified by the Hydro-Québec process [8]. The

scanning electronic microscopy (SEM) results in Fig. 1 show the presence of round graphite particles with average size of about  $12\ \mu\text{m}$  diameter. By using these particles rather than the conventional natural graphite, an improved electrode coating was obtained with an electrode density that increased from  $0.60\ \text{g/cc}$  (conventional graphite) to  $0.99\ \text{g/cc}$  (modified natural graphite). The discharge-charge profiles of the first and second cycles obtained between 2.5 and 0 V at  $C/24$  rate with the half-cell, Li/graphite containing gel polymer electrolyte and 1.5 M LiFSI in EC + DMC + PC, are shown in Fig. 2. The modified graphite exhibits highly reversible capacity,  $360\ \text{mAh/g}$  and a 91.6% coulombic efficiency. We believe that passivation of the graphite surface was comparable to or lower in the EC/TESA electrolyte.

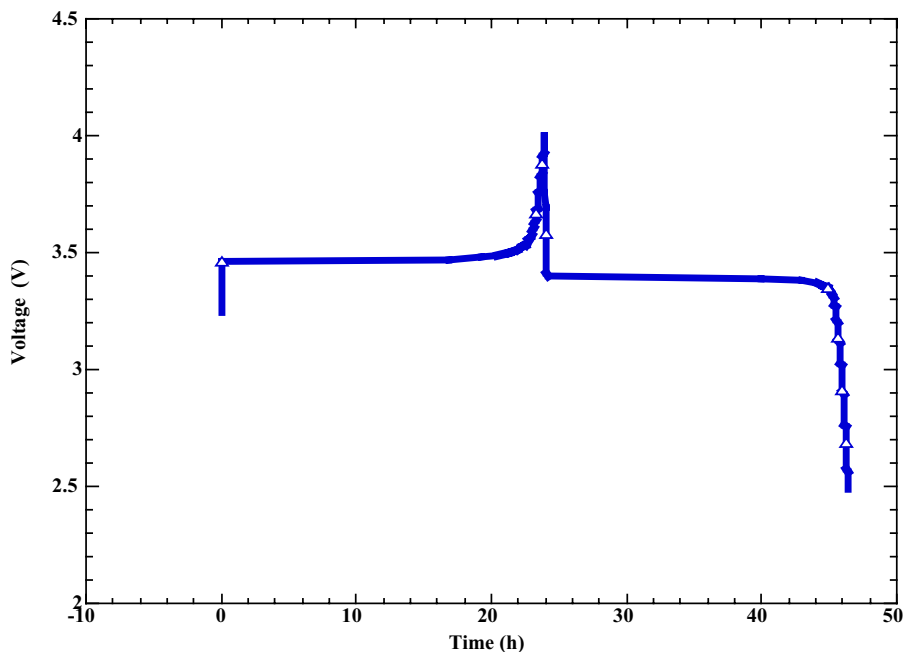


Fig. 4. The initial charge and discharge profiles of a  $\text{Li/LiFePO}_4$  half-cell with the gel at  $C/24$  rate (cell:  $4\ \text{cm}^2$ , 5 mAh).

3.2.2. Cathode

LiFePO<sub>4</sub> powders with different particle sizes (2, 7, 10 μm) (batch-Dev-7) and 2 μm (batch-Dev-10) from Phostech were used. The SEM photographs in Fig. 3 show the shape of these particles. Fig. 4 shows the initial charge and discharge profiles between 2.5 and 4 V at C/24 rate for the first and second cycles of a Li/LiFePO<sub>4</sub> half-cell with the gel electrolyte. The coulombic efficiency of the first cycle was 83% and the reversible capacity was 150 mAh/g, which is 88% of the theoretical capacity. The effect of particle size of LiFePO<sub>4</sub> was investigated. Fig. 5 shows a typical discharge–charge profile at C/24 rate of the half-cell with gel polymer. Cells containing the smallest particle size show the best performance at this rate. The reversible capacity was 160 mAh/g for 2 μm particles, and only 110 mAh/g with the 7 μm particles. The capacity can be stated as following: 2 μm > 10 μm > 7 μm. The relation is not linear with particle size. These results can be related to the synthesis methods used to prepare these different particle sizes.

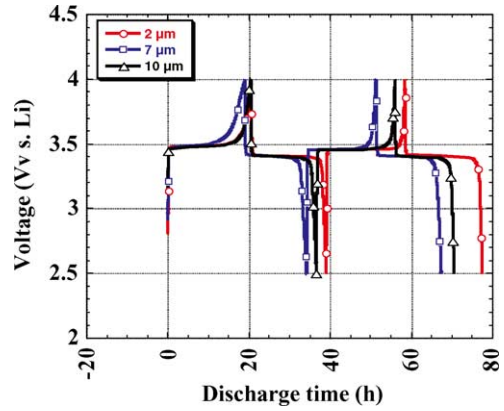


Fig. 5. Typical discharge–charge profile at C/24 rate (cell: 4 cm<sup>2</sup>, 5 mAh) of the Li/gel polymer LiFePO<sub>4</sub> half-cell with different particle size.

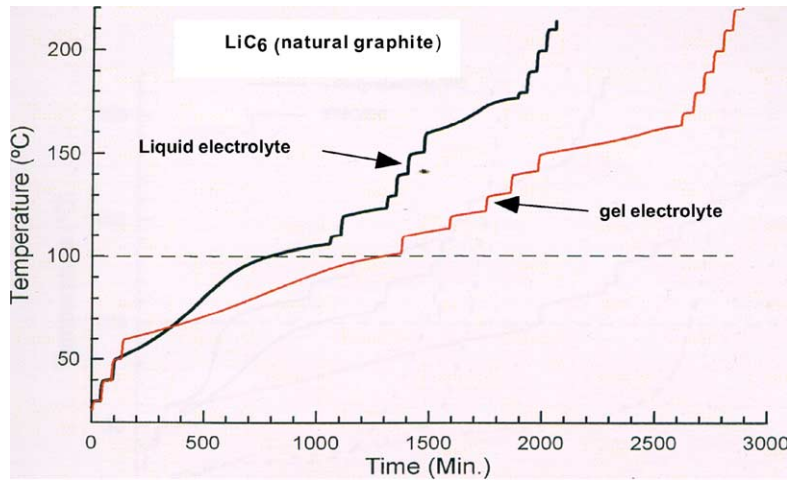


Fig. 6. Results obtained by ARC for lithiated graphite (LiC<sub>6</sub>) using liquid and gel electrolyte.

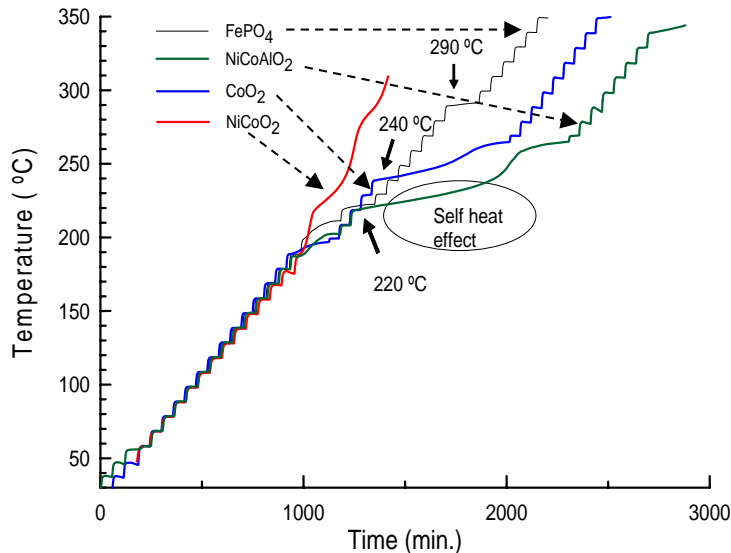


Fig. 7. Results obtained by ARC for different de-lithiated cathode materials using liquid electrolyte at the charge state.

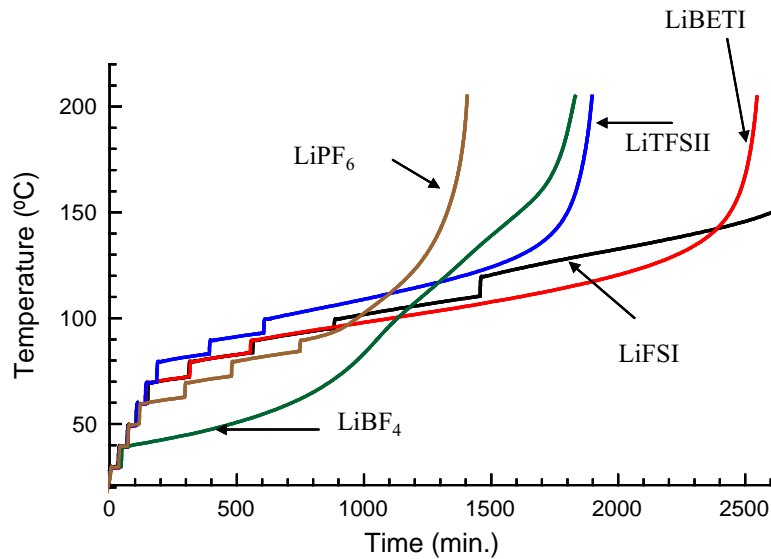


Fig. 8. Results obtained by ARC for different salts react with lithiated graphite  $\text{LiC}_6$ .

### 3.3. Safety study by accelerated rate calorimetry

Fig. 6 shows a comparison of the ARC spectra between gel- and liquid-type cells containing a negative electrode with  $\text{LiC}_6$ , the most reactive composition. It is clearly evident that thermal runaway (exothermic reaction) of the cell starts earlier with the liquid-type cell. Fig. 7 shows a comparison of the ARC spectra between different cathode materials. These cathode materials were fully charged, which is their most highly reactive state. The temperature at which thermal runaway is initiated increases in the following or-

der:  $\text{LiNi}_x\text{Co}_y\text{O}_2 > \text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2 > \text{LiCoO}_2 > \text{LiFePO}_4$ . These results illustrate the excellent thermal stability of  $\text{LiFePO}_4$ . The ARC spectra obtained with a negative electrode,  $\text{LiC}_6$ , and different lithium salts is presented in Fig. 8. The temperature at which thermal runaway is initiated increases in the following order:  $\text{LiBF}_4 > \text{LiPF}_6 > \text{BETI} > \text{LiTFSI} > \text{LiFSI}$ . These tests provide a good indication of the effects of gel, salt ( $\text{LiFSI}$ ) and  $\text{LiFePO}_4$  from the point of view of safety. Furthermore these components are projected to produce a low-cost Li-ion gel battery for transportation applications.

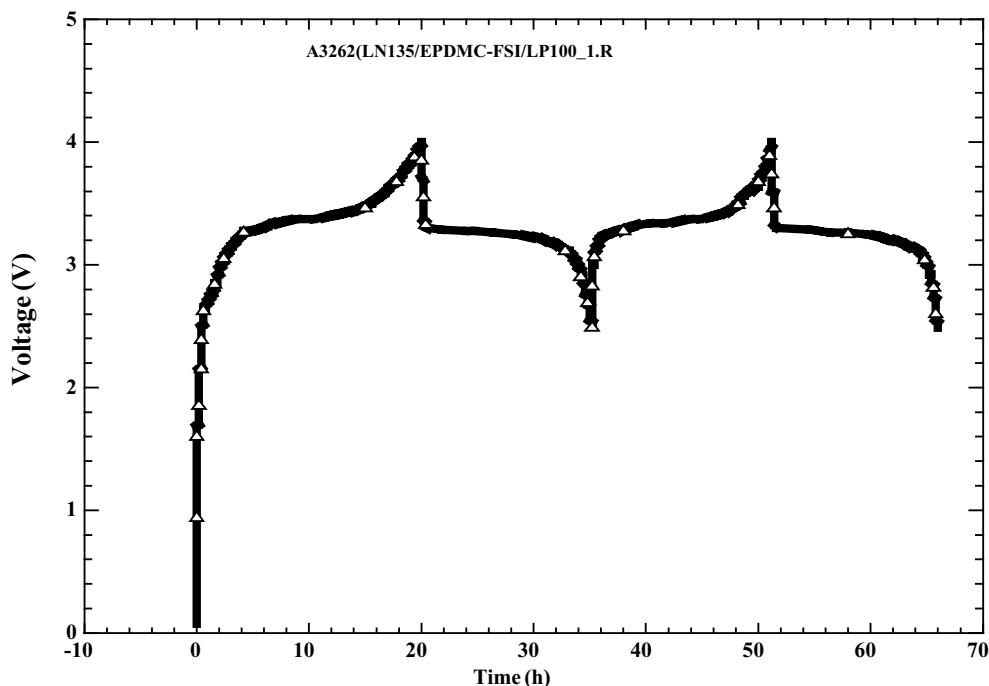


Fig. 9. A typical discharge-charge profiles of a Li-ion cell using gel polymer.

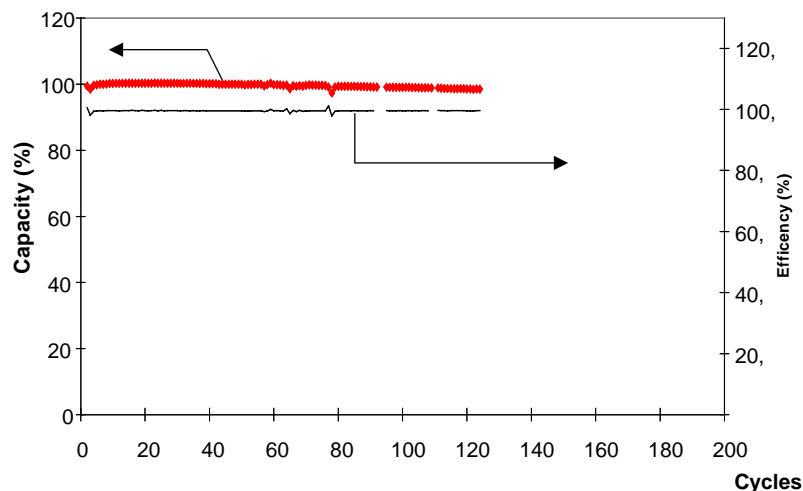


Fig. 10. The cycling performance of a Li-ion polymer cell (5 mAh, 4 cm<sup>2</sup>), discharge at C/1: 5 mAh, charge at C/3: 1.66 mA and constant voltage for 1 h at 4 V.

### 3.4. Cell performance of Li-ion polymer batteries using LiFSI salt

Fig. 9 shows typical discharge–charge profiles of a Li-ion cell (5 mAh, 4 cm<sup>2</sup> active area) using gel polymer—1.5 M LiFSI–EC/PC/DMC (1:1:3). The coulombic efficiency of the first cycle was 76% and the reversible capacity was 156 mAh/g LiFePO<sub>4</sub>. The cycling performance of a Li-ion polymer cell is shown in Fig. 10. After 100 cycles at C/2-rate and with cut off voltage 4–2.5 V, a constant capacity was observed. The capacity ratio of its initial capacity was 99% after 100 cycles. This finding can be explained by the best performance of natural graphite mixed with 105 fibers at high rate and the less resistive passivation film formed in EC/PC/DMC-FSI electrolyte.

## 4. Conclusion

We have evaluated Li-ion gel (EC/PC/DMC-LiFSI) cells with low-cost materials such as natural graphite anode, LiFePO<sub>4</sub> cathode and LiFSI salt. We have evaluated their safety by ARC, comparing LiFePO<sub>4</sub> to different cathode materials. The thermal measurements show that LiFePO<sub>4</sub> exhibits the highest stability. The ionic conductivity of LiFSI is high, and it is thermally stable. A Li-ion gel battery containing 1.5 M LiFSI in EC + DMC + PC shows acceptable and stable cycle life.

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