

# LiFePO<sub>4</sub> safe Li-ion polymer batteries for clean environment

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## Abstract

The performance of natural graphite-fibers/PEO-based gel electrolyte/LiFePO<sub>4</sub> cells (7 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-fiber composite anode in gel electrolyte containing 1.5 M LiFSI-EC/GBL (1:3) exhibited high reversible capacity (361 mAh g<sup>-1</sup>) and high Coulombic efficiency (92%). The LiFePO<sub>4</sub> cathode in the same gel polymer exhibited a reversible capacity of 161 mAh g<sup>-1</sup> and 93% Coulombic efficiency. A 1.5 M solution of LiFSI in ethylene carbonate (EC)/γ-butyrolactone (GBL) (1:3, v/v) mixed solvent is advantageous for use as the electrolyte in the laminated film bag because of its high flame point (135 °C), high boiling point (219 °C), low vapor pressure and high conductivity (10.2 mS cm<sup>-1</sup> at 20 °C). The Li-ion gel polymer battery shows a very low capacity fade of 5% after 500 cycles and also has high-rate capability. The Li-ion gel polymer cell using LiFePO<sub>4</sub> cathodes is suitable for HEV applications.

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**Keywords:** Natural graphite; LiFePO<sub>4</sub>; Li-ion battery; Gel electrolyte; Polymer; LiFSI salt; HEV; ARC; Safety

## 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, must actively 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 [3–6] 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. By using a high-viscosity organic liquid–polymer composite electrolyte with thermal stability, the graphite-fiber anode and the laminated film bag, the thin Li-ion batteries with high performance and safety were fabricated as thin cells.

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 Accelerated Rate Calorimetry (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,

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an organic electrolyte and gel polymer separator. The cells were sealed into an aluminum–plastic laminated film bag [7]. The electrolyte was 1.5 M lithium bis(fluorosulfonyl) imide (LiFSI) in a mixture (1:3, v/v) of ethylene carbonate (EC) and  $\gamma$ -butylacetone (GBL). Another electrolyte, 1.5 M LiFSI in a mixture (1:1:3, v/v) of (EC) + propylene carbonate (PC) and dimethyl carbonate (DMC) was used for comparison. The anode electrode was prepared from slurry of natural graphite with 10 wt% of carbon fiber (mesophase) and vapor grown carbon fiber (VGCF) and 10 wt% poly(vinylfluoride) (PVDF) dissolved in 1-methyl-2-pyrrolidone. The paste was coated by a doctor-blade process on treated copper foil current collector. 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 °C for 24 h before electrochemical evaluation. The half-cell performance of the negative and positive electrodes was evaluated separately with lithium metal (Li/electrolyte + salt/electrode). The discharge–charge cycling were performed using a constant current method (MacPile<sup>®</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 cyler was used for long-term cycling tests. In order to study the safety of the cell, a technique known as Accelerated Rate Calorimetry (Columbia Scientific, Austin, TX, U.S.A.) 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 dan-

ger under abusive conditions of battery use. ARC was used to study the exothermic reactions of anodes, cathodes, lithium salts and solvents.

A new experimental cell (see Fig. 1) that contains an optical fiber sensor was used to monitor the vapor pressure of liquid and gel electrolytes from 20 to 125 °C.

### 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.

##### 3.1.1. Solid gel

*Hard gel:* A polymer electrolyte having structure based on ethylene oxide (EO) units was coated by a doctor-blade method. The polymer based on multi branches polyether based 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 and LiFSI-EC/PC/DMC. The polymer undergoes swelling after a few minutes with 20% (v/v) increase. These gel electrolytes were used as separators in both half-cell and Li-ion cells. This technology no sue any separator such polypropylene (PP) or polyethylene or combination of PP–PE–PP.

##### 3.1.2. Thermal gel

The second gel polymer electrolyte is also based multi branches polyether, which were mixed with liquid electrolytes, 1.5 M LiFSI-EC/GBL (1:3, v/v) or LiFSI-EC/PC/DMC (1:1:3, v/v). The composition ratio of the (EO)-polymer to liquid electrolyte was 10/90 (v/v). Fifteen hundred parts per million 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 are heated at 60 °C for 1 h to complete the cross linking reaction to form the gel polymer. In these experiments, no free liquid electrolyte exists in the cells.

##### 3.1.3. Vapor pressure and conductivity of gel electrolyte

With thin Li-ion batteries using the laminated film bag at temperatures higher than 60 °C, swelling must be low to ensure safe operation. The electrolyte of thin Li-ion batteries must be more thermally stable than that of conventional Li-ion batteries using a metallic can. A promising electrolyte is a solution consisting of high viscosity solvents such as EC, PC and GBL because their boiling points and flame points are higher than those of EC/DEC and EC/DMC electrolytes used in conventional Li-ion batteries. For thin Li-ion batteries operated at high-temperatures, the vapor pressures



Fig. 1. Vapor pressure apparatus.

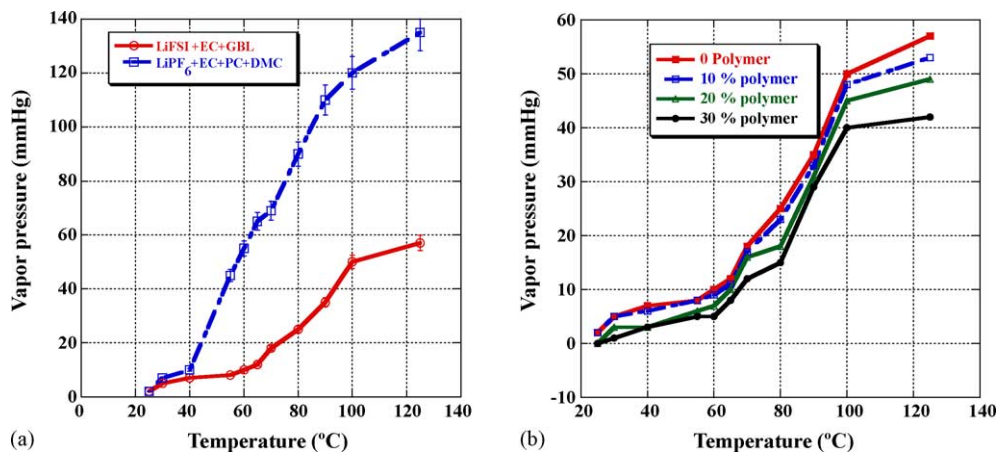


Fig. 2. Dependence of vapour pressure of: (a) 1 M LiPF<sub>6</sub>-EC/PC/DMC (1:1:3) and 1.5 M LiFSI-EC/GBL (1:3) on temperature and (b) polymer content using 1.5 M LiFSI-EC/GBL (1:3) as plasticizer on temperature.

of these promising electrolytes must be lower than those of EC/DEC and EC/DMC electrolytes. Fig. 2a shows plots of the vapor pressures of 1 M LiPF<sub>6</sub>-EC/PC/DMC (1:1:3) electrolyte and 1.5 M LiFSI-EC/GBL (1:3) electrolyte in the temperature range from 20 to 125 °C. The electrolyte containing EC/GBL and LiFSI showed lower vapor pressure than EC/PC/DMC solvent mixture. Fig. 2b shows that the vapor pressure decreases when the content of polymer in gel electrolyte increases. On the other hand, it is necessary to improve the discharge performance of thin Li-ion polymer batteries with an optimized polymer content and Li salt. Fig. 3 shows the dependence of conductivity of various electrolytes salt and polymer content. The important role of the Li salt is evident in the results showing the higher conductivities of 1.5 M LiFSI-EC/GBL (1:3) electrolyte than those of 1.5 M LiTFSI-EC/GBL (1:3) and 1.5 M LiBETI-EC/GBL (1:3) electrolyte. LiTFSI has the lowest molecular weight (197 g) compare to LiFSI (297 g) or BETI (398 g), and the cell using LiFSI has higher specific energy (Wh kg<sup>-1</sup>). The significant effect of

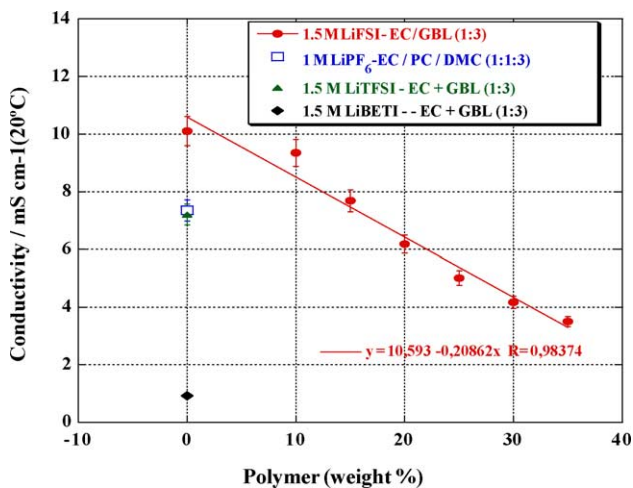


Fig. 3. Dependence of conductivities of various electrolytes on salt, solvent and polymer content.

the solvent in the electrolyte was also observed. The conductivities of 1.5 M LiFSI-EC/GBL (1:3) electrolyte was higher than that of LiBF<sub>4</sub>-EC/PC/DMC (1:1:3) electrolyte. Therefore, LiFSI-EC/GBL electrolyte is advantageous for use in the laminated film bag because of its high boiling point (219 °C), high flame point (135 °C), low vapor pressure (19 mmHg at 70 °C) and high conductivity (10.2 mS cm<sup>-1</sup> at 20 °C).

### 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. 4 shows the presence of round graphite particles with average size of about 12 μm 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 g cm<sup>-3</sup> (conventional graphite) to 0.99 g cc<sup>-3</sup> (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 + GBL, are shown in Fig. 5. The modified graphite exhibits high reversible capacity, 360 mAh g<sup>-1</sup> and 91.6% Coulombic efficiency. In order to increase the stability of cycle life of natural graphite, carbon fibers (ex-meso phase) such as Petoca and vapor-grown carbon fiber were added to the electrode. We believe that passivation layer on the graphite surface was comparable or smaller in the EC/TESA electrolyte.

#### 3.2.2. Cathode

LiFePO<sub>4</sub> powder with particle size 2 μm from Phostech is used. Fig. 6 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 reversible capacity was 160 mAh g<sup>-1</sup> for 2 μm particles; the Coulombic efficiency of the first cycle was 90%.

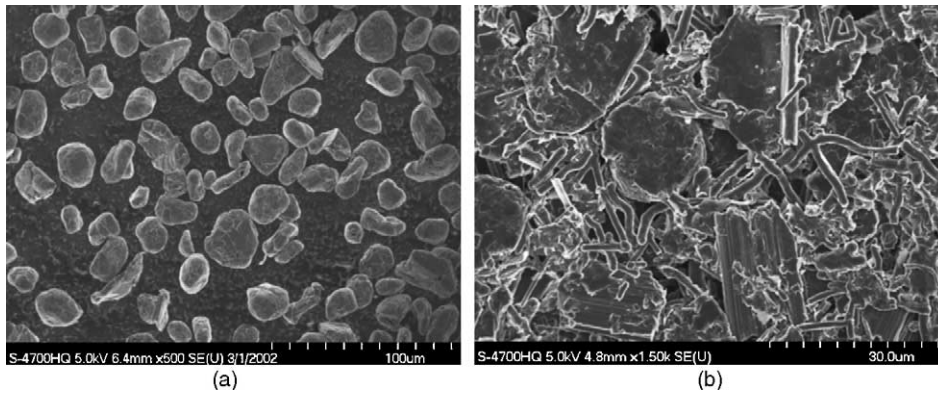


Fig. 4. SEM micrograph of (a) rounded natural graphite and (b) composite graphite VGCF-Petoca fibers electrode.

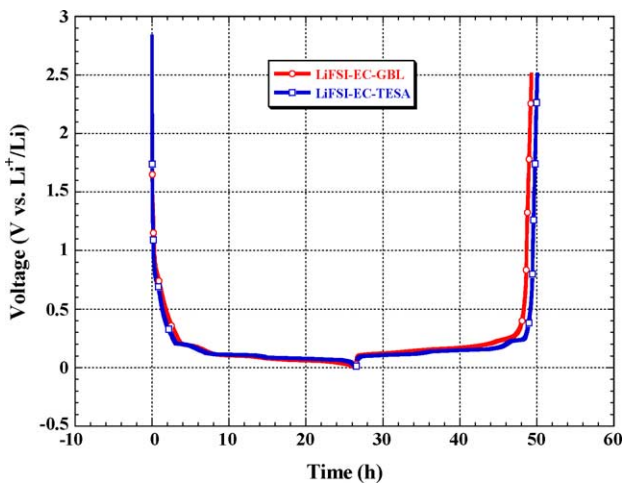


Fig. 5. The discharge–charge profiles of the half-cell, Li/graphite containing gels. Polymer electrolyte and 1.5 M LiFSI in EC + GBL at C/24 rate (cell: 4 cm<sup>2</sup>, 7 mAh).

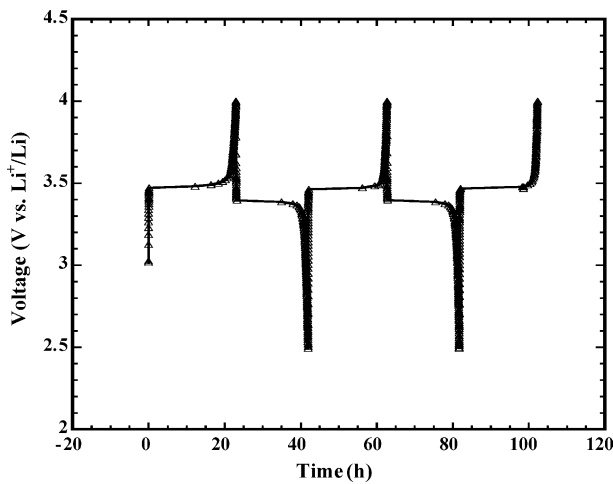


Fig. 6. The initial charge and discharge profiles of a Li/LiFePO<sub>4</sub> half-cell with the gel electrolyte at C/24 rate (cell 4 cm<sup>2</sup>, 7 mAh).

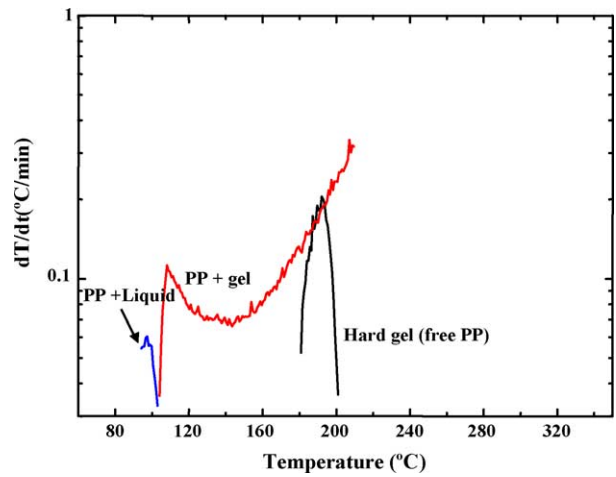


Fig. 7. Results obtained by ARC for lithiated graphite (LiC<sub>6</sub>) using liquid, hard gel (free separator) and thermal polymer gel.

### 3.3. Safety study by accelerated rate calorimetry

Fig. 7 shows a comparison of the ARC spectra of liquid-type cells containing, solid gel (no separator) and thermal gel (with PE–PP separator) on negative electrode with LiC<sub>6</sub>, the most reactive composition. It is clearly evident that thermal runaway (exothermic reaction) of the cell starts earlier with the liquid-type cell and the thermal gel; however, the solid gel is the safest compound because it encapsulates the liquid electrolyte on the polymer matrix. In addition, it can also be produced by a low-cost process because there is no need to use a solvent-free separator such as PE or PP or the combination PP–PE–PP. Fig. 8 shows a comparison of the ARC spectra between different cathode materials. These cathode materials were fully charged, which represents their most highly reactive state. The temperature at which thermal runaway is initiated increases in the following order: LiNi<sub>1.85</sub>Co<sub>0.8</sub>Al<sub>0.05</sub>O<sub>2</sub> > LiCoO<sub>2</sub> > LiFePO<sub>4</sub>. These results illustrate the excellent thermal stability of LiFePO<sub>4</sub>. These data are comparable to the findings presented by the Jiang and Dahn [9]. The ARC spectra obtained

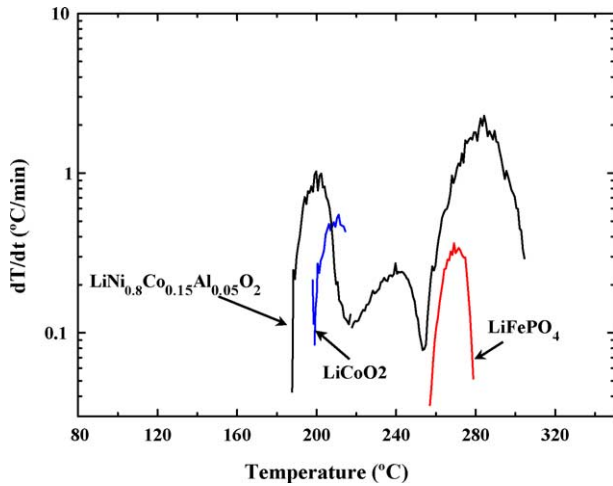


Fig. 8. Results obtained by ARC for different de-lithiated cathode materials using liquid electrolyte at the charge state, (LiPF<sub>6</sub> + EC + PC + DMC).

with a negative electrode, LiC<sub>6</sub> and different lithium salts are presented in Fig. 9. The temperature at which thermal runaway is initiated increases in the following order: LiBF<sub>4</sub> > LiPF<sub>6</sub> > LiBETI > LiTFSI > LiFSI. In particular, imide salts such as LiFSI are very suitable in cells with a graphite negative electrode. These cells exhibit long life because no HF is formed compared to cells containing LiPF<sub>6</sub>. HF formed by electrolysis of LiPF<sub>6</sub>, the dissolution of the cathode and passivation layer on the anode occurs. These tests provide a good indication of the effects of gel, salt (LiFSI) and LiFePO<sub>4</sub> from the point of view of safety. Furthermore, these components are projected to produce a low-cost Li-ion gel battery for transportation applications such HEV.

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

Fig. 10 shows typical charge–discharge profiles of a Li-ion cell (7 mAh, 4 cm<sup>2</sup> active area) using gel polymer—1.5 M

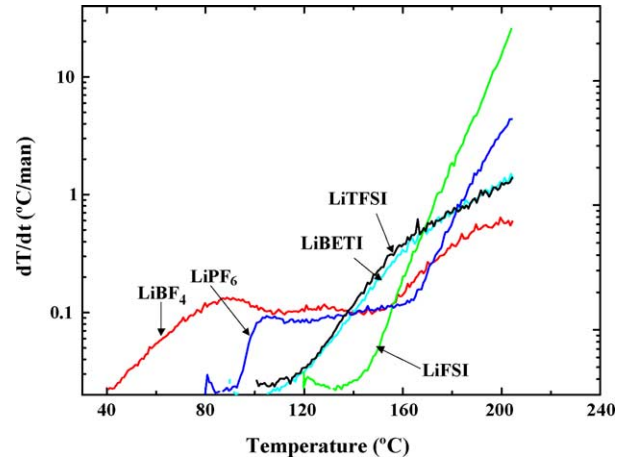


Fig. 9. Results obtained by ARC for different salts react with lithiated graphite LiC<sub>6</sub>.

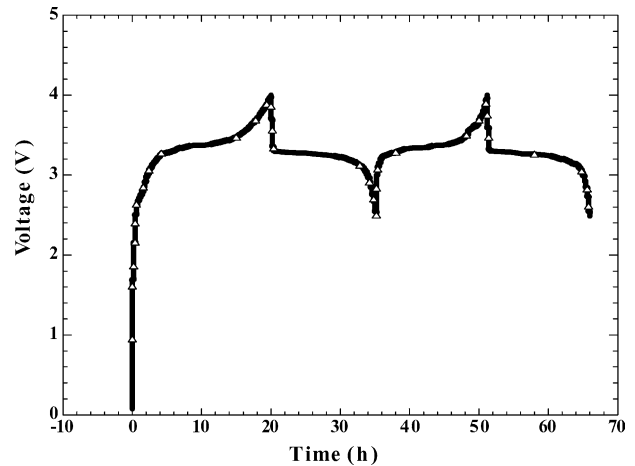


Fig. 10. A typical charge–discharge profiles of a Li-ion cell using gel polymer.

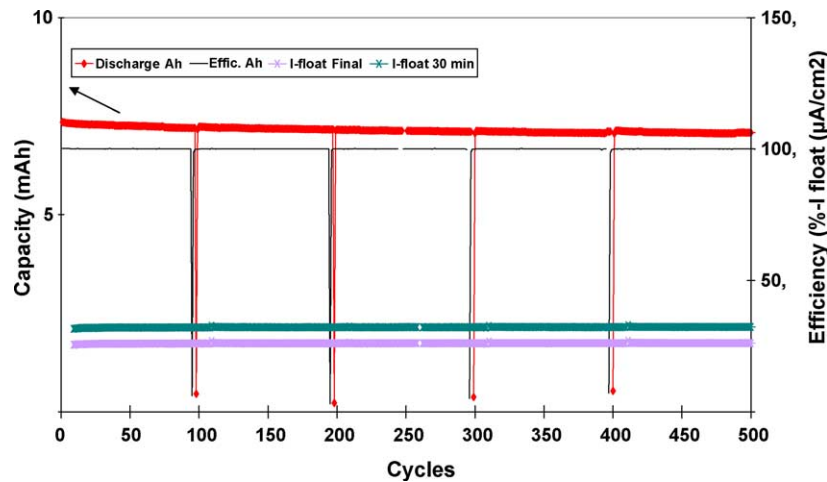


Fig. 11. The cycling performance of a Li-ion polymer cell (7 mAh, 4 cm<sup>2</sup>), discharge at C/1, charge at C/3 and constant voltage for 1 h at 4 V.

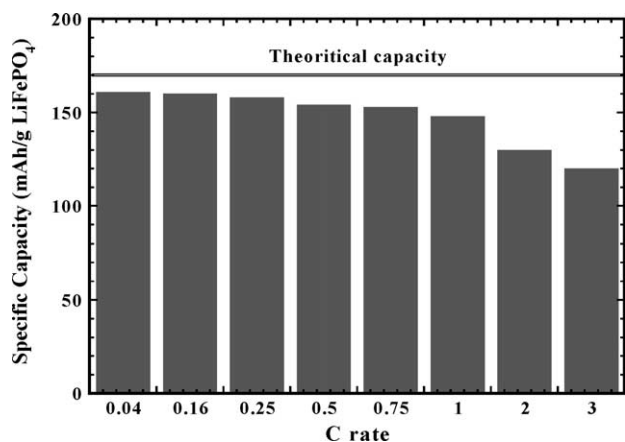


Fig. 12. Rate capability for Li-ion polymer cell (7 mAh, 4 cm<sup>2</sup>), charge at C/3 and constant voltage for 1 h at 4 V.

LiFSI-EC/GBL (1:3). The Coulombic efficiency of the first cycle was 82% and the reversible capacity was 156 mAh g<sup>-1</sup> LiFePO<sub>4</sub>. The cycling performance of a Li-ion polymer cell is shown in Fig. 11. After 500 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 97% after 100 cycles. This finding can be explained by the best performance of natural graphite mixed with 10% fibers at high-rate and the less resistive passivation film formed in EC/GBL-LiFSI electrolyte. Fig. 12 shows the high-rate capability of the cell at C/24 (161 mAh g<sup>-1</sup> LiFePO<sub>4</sub>) and at 3C (140 mAh g<sup>-1</sup> LiFePO<sub>4</sub>), which is about 87% of the nominal capacity. The capacity decreases slowly when the current density increases; this data suggest that the battery chemistry of LiFePO<sub>4</sub>/gel electrolyte–LiFSI/graphite-fiber composite is suitable for HEV application.

#### 4. Conclusion

We have evaluated Li-ion gel (EC/GBL-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 + GBL LiFePO<sub>4</sub> as cathode and composite anode graphite-fiber shows acceptable stable cycle life and high-rate capability. The system using LiFePO<sub>4</sub> is suitable for transportation application such HEV.

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