Development and characterization of bipolar lithium composite polymer electrolyte (CPE)–FeS₂ battery for applications in electric vehicles

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Abstract

A small laboratory prototype of a new lithium battery for electric vehicles and load levelling has been developed. This rechargeable battery consists of thin foils of lithium anode, composite solid electrolyte (CSE) or composite polymer electrolyte (CPE) and a composite FeS₂ (pyrite) cathode. The battery has several advantages over other state-of-the-art polymer electrolyte batteries: (i) low-cost cathode, pyrite, is a natural ore, therefore environmentally friendly, (ii) small prototype cells exhibited very high specific energy, projected to be 140 Wh/kg at a $C/6$ to $C/10$ rate (three times larger than that of a lead/acid battery), and more than forty 100% charge/discharge cycles; (iii) this battery has an internal electrochemical overcharge protection mechanism (which is essential for bipolar batteries), and (iv) for both CSE and CPE, the Li/electrolyte interfacial resistance is low and stable up to 3000 h (CPE) and 700 h (CSE) at 120 °C. The long-term projected specific energy for this battery is over 200 Wh/kg, five times larger than that of the lead/acid battery and one of the highest among all batteries in progress.

Keywords: Lithium composite batteries; Polymer electrolytes; Iron disulfide; Electric vehicles

1. Introduction

One of the most promising candidates for powering electric vehicles (EVs) is the bipolar lithium battery based on a polymer electrolyte (PE). Each cell in this battery consists of thin foils (20–70 μm thick) of bipolar conductive substrate, lithium, polymer electrolyte and cathode. The thickness of a complete cell is only 150 to 200 μm. The bipolar configuration offers a low-cost continuous manufacture, high power and improved safety due to the following reasons: the lithium anode is thin and sandwiched between two solid films, and the lithium deposit is less dendritic.

Recent activities in solid polymer electrolyte/lithium batteries are centred on the use of poly(ethylene oxide) (PEO) and other organic polymers complexes with lithium salts as the electrolyte [1–6]. These electrolytes have the following disadvantages: (i) low transference number for lithium cations ($t_+ = 0.2–0.5$) leading to a high concentration polarization and high interface resistance; (ii) salt anions (BF_4^-, AsF_6^-, ClO_4^-, $CF_3SO_3^-$) in the polymer are not compatible with lithium and cause the lithium to passivate, and (iii) low mechanical strength above 100 °C. A novel solution to these problems has been recently suggested [7–11]. A thin composite solid electrolyte (CSE) film based

on LiI–Al₂O₃–PEO was developed and characterized. It has a t_+ value of about 1, a good ionic conductivity and a low and stable Li/CSE interfacial resistance.

One of the best candidates to be used as a cathode in future EV batteries is FeS₂. It is cheap and abundantly available. The Li/FeS₂ couple has a very high theoretical specific energy (1273 Wh/kg). The four-electron discharge curve has two to four voltage plateaus [11–15]. FeS₂ can be further oxidized, a fact that can be used as an overcharge protection mechanism [11]. At elevated temperatures, the molten salt LiAl/FeS₂ system has a large positive entropy change for discharge [16]. This is very important for large batteries like EV batteries as it helps cooling the battery at high discharge rates. The Li/(CPE)(CSE)/FeS₂ batteries operate in a moderate temperature range from 100 to 140 °C; therefore, common, commercially available, low-cost hardware, materials, insulators, seals and current collectors can be used. Their electrolytes consist of a thermodynamically stable anion (I^-) and high-surface-area oxide matrix. The latter improves the mechanical strength, immobilizes the molten phases, and seems to help in achieving low and stable Li/CPE and Li/CSE interfacial resistances (low R_{SEI}). The CSEs are salt-rich electrolytes which have an n to LiI (n in $P(EO)_n$) ratio of 2.5–3 while the CPEs have an n to LiI ratio of 6–20.

It is expected that this battery will meet the power-density and energy-density requirements of EVs. In addition, it has safety and manufacturing advantages over other lithium and sodium batteries. The goal of this paper is to review our progress in the development and characterization of a small laboratory prototypes of Li/CSE/FeS$_2$ and Li/CPE/FeS$_2$ bipolar batteries.

2. Experimental

High purity, vacuum-dried components such as PEO (polyethylene oxide, 5×10^6 mol. wt. Aldrich), PMMA (polymethylmetacrylate, 12 000, mol. wt., Aldrich), EC (ethylene carbonate), and Al$_2$O$_3$, SiO$_2$ or MgO and LiI were weighed in an appropriate proportion and mixed in a flask inside VAC glove box. Homogeneous dispersion was obtained after stirring at room temperature for about 4 h. Then, partial evaporation was allowed and the viscous (about 20 cm^3 volume) slurry was cast on a 64 cm^2 Teflon tray to form a film. The film was dried in about 3 h under vacuum at room temperature and later it was dried under vacuum at 120 °C. The final product was a film of about 100 μm thickness.

The cathode foil was prepared by dispersing FeS$_2$ particles (less than 20 μm in size) in a polymer slurry and casted in the same way. The properties of the polymer materials were examined in a suitable electrochemical cell.

For the ionic conductivity measurements the 0.9 cm^2 film polymer composite electrolyte was sandwiched between the two metallic lithium electrodes. The a.c. conductivity data were obtained by analysing the impedance spectrum which was measured by a home-made computerized apparatus and two-beam oscilloscope at the frequency range from 0.02 Hz to 2 MHz.

The small laboratory prototype of Li/(CSE)(CPE)/FeS$_2$ batteries consisted of a lithium foil, a 50–200 μm thick CSE (or CPE) and a 0.9 cm^2 composite FeS$_2$ cathode. All the cells were held under spring pressure inside a hermetically sealed glass vessel. The batteries were cycled at 120 to 135 °C by using a home-made computerized cycler.

3. Results and discussions

In this work, we used a new composite solid electrolyte with $t_+ = 1$ [7–11] or composite polymer electrolyte (CPE) with low $t_+ < 0.4$ [8–11]. It was found that for both CSE and CPE the Li/electrolyte interfacial resistance, R_{SEI}, is low and stable up to 3000 h (CPE) and 700 h (CSE) at 120 °C (Table 1, Figs. 1 and 2). The apparent thickness of the SEI (solid electrolyte interphase covering the lithium [17]) was found to be in the range of 2 to 50 nm. In most cases, L_{SEI} was

Table 1
The effect of cell operating time on stability of R_{bulk} and R_{SEI} in Li/CPE/Li cell at 120 °C

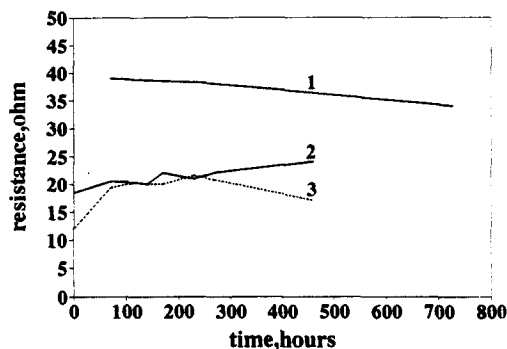| Time (h)	R_{bulk} (Ω cm^2)	R_{SEI} (Ω cm^2)
336	5.4	19.6
2640	5.9	20.9
3120	4	21.9

Fig. 1. R_{bulk} [1,2] and R_{SEI} [3] of Li/CSE/Li cells vs. operating time at 120 °C: (1) CSE composition: LiI–P(EO)$_{2.5}$–P(MMA)$_{0.25}$–EC (6%) v/v Al$_2$O$_3$; (2) and (3) CSE composition: LiI–P(EO)$_3$–T$_{0.14}$. Electrode area = 1 cm^2; stack pressure = 8 kg/cm^2.
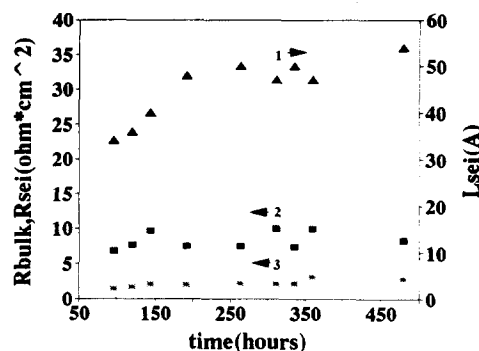

Fig. 2. Plots (1) L_{SEI} and (2) R_{CPE} (R_{bulk}) and of R_{SEI} (3) vs. time at 120 °C. CPE composition: LiI–P(EO)$_6$–PEG$_{0.3}$–P(MMA)$_{0.6}$ (6%) v/v Al$_2$O$_3$.

low and stable during storage at 100 to 120 °C (Fig. 2). Both R_{SEI} and L_{SEI} (SEI thickness) depend on the CPE and CSE composition. The minimum value measured for R_{SEI} is 2–4 Ω cm^2 (Fig. 2).

As a multi-electron system ($4e^-$/FeS$_2$), the FeS$_2$ cathode is expected to have several charge (or discharge) steps [12–15]. The first discharge curve for the Li/CSE and CPE/composite FeS$_2$ cells are shown in Fig. 3. It resembles those obtained for molten salt cells at high temperature and for non-aqueous solution cells at room temperature. The first discharge curve for the CPE cell has two plateaus, one at 1.7–1.8 V (depending on the current density) and another at 1.6 V. However, the first discharge curve for the CSE cell has four steps of about one Li/Fe for each. After a discharge to
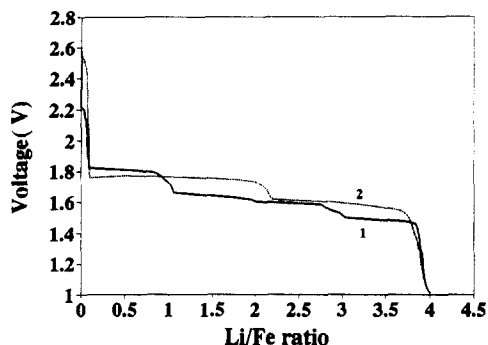
Fig. 3. The first discharge of Li/FeS₂ cells; (1) CSE, and (2) CPE at 120 °C and 27 μA. CSE composition: LiI–P(EO)₃–P(MMA)₀.₃–EC (6%) v/v Al₂O₃. CPE composition: LiI–P(EO)₁₄–P(MMA)₁–EC (6%) v/v Al₂O₃. Cathode thickness: (1) 50 μm, 40% FeS₂ and (2) 15 μm, 35% FeS₂; stack pressure = (1) 15 kg/cm², and (2) 5 kg/cm².
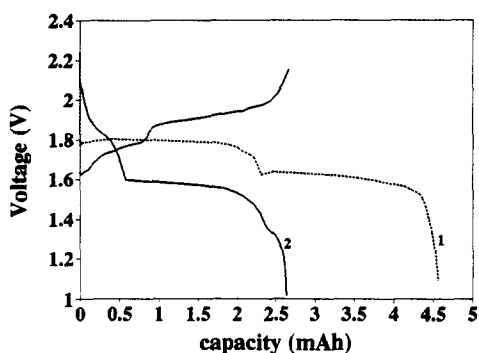

Fig. 5. Typical charge/discharge plots of: (1) Li/CSE/FeS₂ cell, and (2) Li/CPE/FeS₂ cell. CSE composition: LiI–P(EO)₃–P(MMA)₀.₃–EC (6%) v/v Al₂O₃, i_c = 36 μA, and i_d = 50 μA. CPE composition: LiI–P(EO)₉–P(MMA)₀.₅–EC (6%) v/v Al₂O₃, i_c = 71 μA, and i_d = 130 μA. Cathode thickness = 50 μ; (1) 40% FeS₂ and (2) 35% FeS₂; stack pressure = (1) 15 kg/cm², and (2) 8 kg/cm².

Fig. 4. Typical charge/discharge plots of an Li/CPE/FeS₂ cell: (1) cycle 0, and (2) cycle 4; i_c = 70 μA, i_d = 300 μA, at 135 °C. CPE composition: LiI–P(EO)₉–P(MMA)₀.₅–EC (12%) v/v Al₂O₃.

Fig. 6. Plots of open-circuit voltage (1,4) and capacity (2,3) of Li/CPE/FeS₂ cell vs. number of cycles: capacity: (2) Q_c, and (3) Q_d. Cycling conditions: Voltage range = 1.1–2.15 V; i_c = 100 μA, up to cycle 3, i_c = 70 μA, after cycle 3, and i_d = 300 mA, at 135 °C.

1.5 V the cell could not be charged effectively at a voltage lower than 1.9 V. In order to charge the cell effectively it was necessary to increase the end of charge voltage to 2.1 V. The second discharge curve is different from the first one (Fig. 4), indicating a change in the cells reactions. During consecutive cycles, over a voltage range of 1.4 to 2.1 V, all the discharge curves, of both types, behave similarly (Fig. 5). At the 1.2–2.15 V range the cells could be cycled at about 2.5e^-/Fe (560 mAh/ g) with almost no capacity loss (Fig. 6). The open-circuit voltage (OCV) at the end of charge was also stable while the OCV at the end of discharge decreased. The discharge capacity is very close to the charge capacity indicating almost 100% faradaic efficiency. Our preliminary suggestions for discharge/charge mechanisms at 100 to 135 °C are shown in Scheme 1. Both the Li/CPE/FeS₂ and Li/CSE/FeS₂ cells demonstrated a 100% overcharge protection mechanism without loss of capacity (Fig. 7). A comparison between CSE and CPE cells is presented in Table 2. The CSE has a higher t_+ but a lower conductivity. It seems that the power-limiting factor for CPE is diffusion while for CSE it is the interfacial contact. For a good operation Li/CSE cells need, in general, higher stack pressure
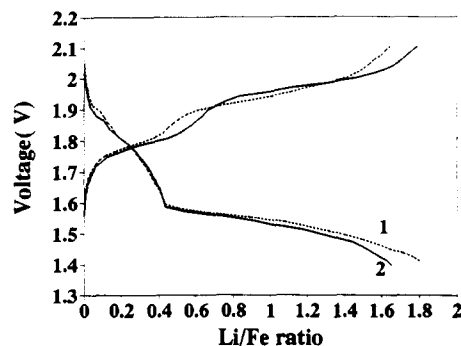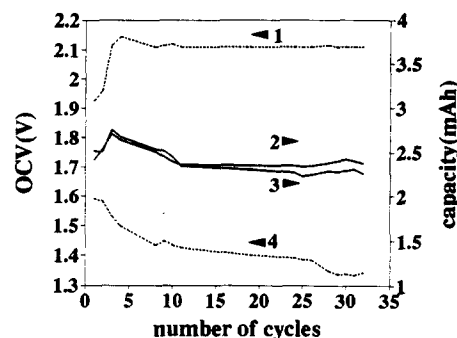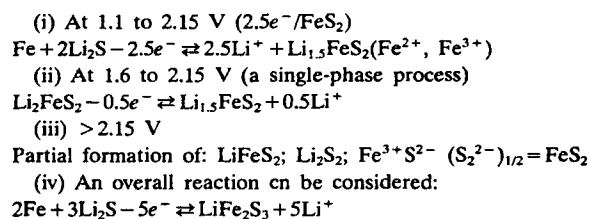
(i) At 1.1 to 2.15 V (2.5e^-/FeS₂)
Fe + 2Li₂S – 2.5e^- ⇄ 2.5Li⁺ + Li₁.₅FeS₂(Fe²⁺, Fe³⁺)

(ii) At 1.6 to 2.15 V (a single-phase process)
Li₂FeS₂ – 0.5e^- ⇄ Li₁.₅FeS₂ + 0.5Li⁺

(iii) >2.15 V
Partial formation of: LiFeS₂; Li₂S₂; Fe³⁺S²⁻ (S₂²⁻)₁/₂ = FeS₂

(iv) An overall reaction cn be considered:
2Fe + 3Li₂S – 5e^- ⇄ LiFe₂S₃ + 5Li⁺

Scheme 1. Li/CPE and CSE/FeS₂ cells: suggestions for charge/discharge mechanisms at 100 to 135 °C.

than do Li/CPE cells (having a softer solid electrolyte), indicating poor interface contacts. The maximum continuous discharge-current densities, at this stage of the research, is 1 mA cm⁻² (Fig. 8).

An Li/CPE/FeS₂ cell which consisted of a 45 μm thick composite FeS₂ cathode delivered, at C/6 5 mWh/ cm² (Fig. 8). The estimated weight of a complete cell, including the bipolar substrate, is 26.5 mg/cm² and its thickness is about 140 μm (Table 3). The specific energy calculated for the stack is 188 Wh/kg (Table 3). For a battery packing factor of 0.8 the projected specific energy for a complete battery is 150 Wh/kg. It is estimated that the geometric energy for 160 μm thick
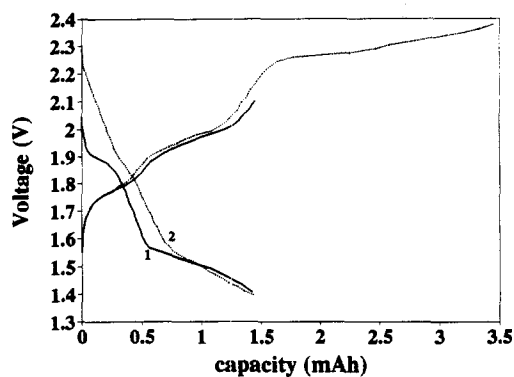
Fig. 7. Charge/discharge curves of Li/CSE/FeS$_2$ cell at 1.4 to 2.4 V; $i_c = 36$ μA, $i_d = 110$ μA at 120 °C. CSE composition: LiI/P(EO)$_3$–P(MMA)$_{0.3}$–EC$_8$ (6%) v/v Al$_2$O$_3$. Cathode thickness ≈ 50 μ, 40% FeS$_2$; stack pressure = 15 kg/cm^2. (1) Before and (2) after 100% overcharge.

Table 2
Comparisons between CSE [a] and CPE [b] cells

	CSE	CPE
Conductivity at 120 °C (mS/cm)	0.1–0.5	0.1–2
R_{SEI} at 120 °C (Ω cm^2)	15–50	2–40
Stack pressure (kg/cm^2)	7–15	1–7
t_+	0.8–1	0.2–0.4
Mechanical properties	Medium	Good
R_{bulk}, R_{SEI} stability	Excellent	Excellent
Density (g/cm^3)	1.8	1.4–1.6
Power limiting factor	Interface contacts	Diffusion

[a] CSE = composite solid electrolyte.
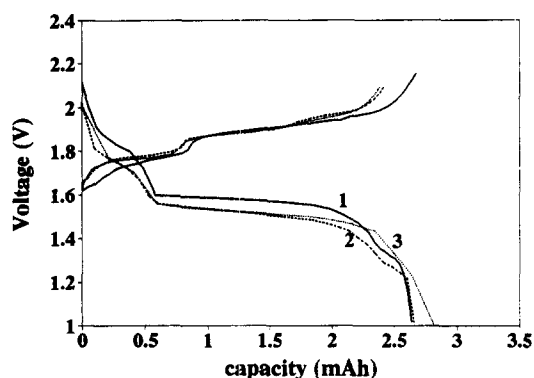[b] CPE = composite polymer–electrolyte.

Fig. 8. Charge/discharge curves of Li/CPE/FeS$_2$ cell at 135 °C; (1) 0.3 mA/cm^2; (2) 0.5 mA/cm^2, and (3) 1 mA/cm^2. CPE composition: LiI–P(EO)$_9$–P(MMA)$_{0.5}$–EC (12%) v/v Al$_2$O$_3$.

cell can be increased to over 10 mWh/cm^2. This will yield a specific energy of over 250 Wh/kg for a complete bipolar battery. A further increase in specific energy can be achieved by the use of a thin low-weight bipolar substrate. A Li/CPE/FeS$_2$ laboratory battery which consisted of a 9.5 cm^2, 25 μm thick composite FeS$_2$ cathode delivered at C/7 rate 1.4 mAh/cm^2.

Table 3
Preliminary design characteristics of bipolar battery (small laboratory prototype); geometric energy at $C/6 = 5.0$ mWh/cm^2

	Thickness (μm)	Weight (mg/cm^2)
Composite polymer electrolyte	50	7.5
Composite cathode	45	11.4
Lithium	30	1.6
Bipolar plate	15	6
Total	140	26.5

[a] At end of charge voltage of 2.35 V (30% overcharge).
Specific energy (stack) = (5 × 10^3)/26.5 = 188 Wh/kg.
Specific energy battery = 188 × 0.8 = 150 Wh/kg.

The Li/CPE/FeS$_2$ system is also a promising candidate for large high-energy density and high-power density primary battery applications. Small laboratory cells delivered, at 120 to 135 °C, from 1.8 to 20 mAh/cm^2 at 3.4 mA/cm^2 and 0.05 mA/cm^2, respectively. The projected specific energy and specific power (stack basis) for these cells are 97 Wh/kg at 257 W/kg and 634 Wh/kg at 1.5 W/kg, respectively [18].

4. Summary

We have a better understanding of the charge/discharge processes of this battery. A CSE with $t_+ = 1$ and a CPE (based on LiI–Al$_2$O$_3$–PEO) were developed and characterized. Both the CSE and CPE demonstrated excellent stability and compatibility with lithium (for 1000–3000 h at 120 °C), and a good ionic conductivity. A small laboratory prototype rechargeable Li/CPE/FeS$_2$ cell demonstrating over 40 stable C/10 100% depth-of-discharge cycles and specific energy (stack) of 177 Wh/kg and 250 Wh/kg is projected. An overcharge protection mechanism was demonstrated for these cells. These properties make the Li/(CPE)(CSE)/FeS$_2$ system a very promising candidate for EVs and load-levelling applications.

Acknowledgements

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