Hot-pressed, solvent-free, nanocomposite, PEO-based electrolyte membranes II. All solid-state Li/LiFePO$_4$ polymer batteries

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Abstract

The application and characteristics of hot-pressed, nanocomposite, polyethyleneoxide (PEO)-based electrolyte membranes in all solid-state rechargeable, Li/LiFePO$_4$ polymer cells are presented and discussed. Both electrolyte separators and LiFePO$_4$ composite cathodes were prepared by hot-pressing by a completely dry, solvent-free procedure. The thermal stability of both the PEO membranes and the composite cathodes was investigated. The cells were assembled by the direct lamination of the components, namely a lithium foil anode, the PEO-based electrolyte membrane and the composite LiFePO$_4$ cathode tape. The Li/LiFePO$_4$ polymer cells perform well in terms of specific capacity, charge/discharge efficiency and cycle life. At temperatures above 90 °C, the cells are capable of delivering capacities exceeding 100 mAh/g, even at moderately high rates. More than 400 cycles were obtained with a charge/discharge efficiency approaching 100%.
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1. Introduction

Rechargeable lithium polymer batteries represent an excellent choice for electrochemical power sources characterized by high energy and/or power densities, good cyclability, reliability and safety [1–4]. A rechargeable lithium polymer battery is generally formed by a lithium metal anode, a polymer electrolyte separator and a metal oxide cathode capable of reversibly intercalating and releasing (deintercalating) lithium ions. The polyethyleneoxide–lithium salt, PEO–LiX, complexes are very promising candidates as electrolyte separators [5,6]. Nevertheless, the PEO-based polymer electrolytes show an appreciable ionic conductivity ($\sigma > 10^{-4}$ S cm^{-1}) only above 60 °C, typically in the 80–100 °C range due to the increase in amorphous and fluid character of the polymer [5,7–9]. This high temperature limitation is, of course, a drawback for applications in the consumer electronic market, but it is an advantage for

numerous other applications such as for electric vehicles, energy storage and load leveling. Therefore, considerable R&D efforts have been devoted to the formulation and development of PEO-based electrolytes capable of combining high conductivity systems with superior interfacial stability towards the lithium metal anode, and good mechanical properties [10–19]. Our laboratory is involved in a systematic study on PEO-based, nanocomposite, polymer electrolyte membranes prepared by hot-pressing through a completely dry, solvent-free procedure [20]. The results [20] have demonstrated the favorable basic properties of these membranes, which show an ionic conductivity higher than 10^{-4} S cm^{-1} at 70 °C, as well as high homogeneity and excellent mechanical properties. Therefore, these membranes are expected to be suitable for use as an electrolyte separator in lithium polymer cells and batteries operating at medium to high temperatures.

Another crucial aspect for the development of a practical lithium polymer battery is the selection of a proper cathode. The most common cathodic materials such as LiCoO$_2$, LiNiO$_2$, LiCo$_x$Ni$_{1-x}$O$_2$, and LiMn$_2$O$_4$ all exhibit capacity loss and fade above 70 °C, mainly due to electrolyte

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reactions and detrimental phase transitions above 70 °C [6]. On the other hand, thermally stable materials such as vanadium oxides, i.e. V_2O_5, V_3O_8 [6,21,22], are rather expensive and constitute a possible toxicity problem. In view of these properties and concerns, we selected lithium iron phosphate, $LiFePO_4$ as the cathode material since it appears to be a very promising alternative cathode material candidate due to its capability to operate within a very flat voltage plateau (around 3.5 V), high theoretical specific capacity (about 170 mAh g^{-1}), high thermal stability, low cost and benign environmental properties [23]. A possible drawback of $LiFePO_4$ is its low electronic conductivity. However, recent work carried out in our laboratory has demonstrated that the electronic conductivity may be substantially enhanced by dispersing low particle size metallic (e.g. silver) powders into the $LiFePO_4$. With this modification, the $LiFePO_4$ cathode is capable of providing long cycle life and high rates when operated above 90 °C [24]. These favorable properties have prompted us to extend the use of this cathode material in other types of lithium polymer batteries, and in this work we report the characteristics and the performance of a all solid-state cell (battery) obtained by lamination of a lithium foil anode, an optimized PEO-based electrolyte membrane and a $LiFePO_4$ composite cathode film. All the components were prepared by hot-pressing through a completely dry, solvent-free procedure.

2. Experimental

2.1. Nanocomposite electrolyte membranes

The PEO-based, nanocomposite, polymer electrolyte membranes were prepared by a completely dry solvent-free procedure described in detail in our previous paper [20]. Linear poly(ethylene oxide) (Aldrich), having a molecular mass of 1×10^5 was dried under vacuum at 60 °C for at least 24 h before use. Nanoscale fumed SiO_2 (Aldrich) filler was dried under vacuum at 300 °C for 24 h. $LiCF_3SO_3$ (Aldrich, Battery Grade product having a water content lower than 20 ppm) was used as received. The sieved and dried components were intimately mixed by ball-milling and, subsequently hot-pressed at about 80–100 °C in an aluminum mold as described in our initial paper [20]. This preparation procedure resulted in very homogeneous, semi-transparent, composite membranes with very good mechanical strength. The ionic conductivity exceeded 10^{-4} S cm^{-1} at 70 °C [20]. The composition of the membrane selected as the electrolyte separator of choice for the cell/battery is the $P(EO)_{35}LiCF_3SO_3$ with added 5 mass% SiO_2. Although the concentration of the salt may appear low in respect to the compositions generally adopted in common PEO-based electrolytes, an EO/Li ratio of 35 still corresponds to a concentration approaching 1 mol dm^{-3}. In a previous paper [20], we showed that there is practically no effect on conductivity in the 20–50 EO/Li salt concentration range.

Accordingly, $P(EO)_{35}LiCF_3SO_3$ was chosen as the most convenient concentration for this work.

2.2. LiFePO₄ cathode material

$LiFePO_4$ was obtained by a sol–gel synthesis described in detail in a previous paper [26]. Basically, to a $Li(OH)_2$ and $Fe(NO_3)_3$ solution, we added ascorbic acid and then phosphoric acid, H_3PO_4. The pH of the resulting solution was adjusted by ammonia addition. The solution was then heated at 350 °C for 12 h under nitrogen flux to prevent iron (Fe^{2+}) oxidation. The resulting residue was annealed at 800 °C for 24 h, still under nitrogen flux, to finally obtain $LiFePO_4$ powder samples having particle sizes within a few micrometers. $LiFePO_4$ was ground to break down large particles and/or aggregates and then dried under vacuum at 120 °C for 10 h.

The lithium iron phosphate cathode films were prepared by blending the $LiFePO_4$ active material (60 mass%) with Super-P carbon electronic conductor (15 mass%) and a PEO binder (25 mass%). Linear poly(ethylene oxide), PEO (Aldrich), having a molecular mass of 6×10^5 was dried under vacuum at 60 °C for 24 h before use. A higher molecular weight PEO was used in the composite than for the electrolyte, i.e. 600,000 versus 100,000 which confers good mechanical stability to the composite cathode, particularly when operated at the higher temperatures. The Super-P carbon (MMM Carbon, Belgium) was dried under vacuum at 200 °C for 24 h. The cathode components (i.e. the $LiFePO_4$ active material, the PEO polymer and the carbon) were carefully sieved and only the smallest particle size fraction was used. The active material and the carbon were intimately mixed by ball-milling for at least 24 h. Then, PEO was added and the resulting mixture was homogenized by ball-milling for 24 h. The resulting powder mixture was hot-pressed in an aluminum mold at 70–80 °C by applying an 8 t pressure to obtain homogeneous cathode films having a thickness ranging from 200 to 250 μm. Then, the cathode films were cold-calendered in order to reduce their thickness down to 50–70 μm with an active material ($LiFePO_4$) loading of approximately 7 mg/cm^2. All preparation steps were performed in a controlled argon atmosphere environment (dry-box) having a humidity content below 10 ppm. However, it was not possible to carry out some operations (i.e. sieving, mixing, hot-pressing) inside the dry-box. In these cases, the materials were housed in sealed, coffee-bag envelopes and then removed from the dry-box for processing. The composite cathode membranes were stored under argon in order to avoid any contamination with the external environment.

2.3. Thermal analysis

Differential scanning calorimetry (DSC) measurements on the PEO electrolyte membranes and on the composite cathodes were performed using a Mettler DSC mod.821^e calorimeter. The samples (about 2 mg) were sealed in

aluminum pans inside the argon-filled box and, then, measured under an argon flow in the −100 to 200 °C temperature range at a 5 °C/min heating rate.

Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer mod. TG7 instrument. The samples (about 1.5 mg) were loaded into aluminum pans and heated in air over the 20–180 °C temperature range at a scan rate of 5 °C/min.

2.4. Li/LiFePO₄ polymer battery

The Li/LiFePO₄ polymer cells were assembled by laminating, in sequence, a lithium metal disc, the nanocomposite PEO electrolyte membrane and the LiFePO₄ composite cathode film. The components of the cells were placed inside Teflon containers having two stainless-steel current collectors. Care was taken to avoid direct contact between the metallic Li anode and the Teflon container. The cell area was

about 1 cm². The cells were assembled in a controlled, argon atmosphere dry-box (MBRAUN LabMaster 130) having both a humidity and an oxygen content below 1 ppm. After lamination, the cells were housed in sealed coffee-bag envelopes filled with argon, and then removed from the dry-box for testing.

The polymer cells were characterized by galvanostatic cycling in the 3.0–3.8 voltage range at different current densities (from 0.025 to 0.8 mA cm⁻²), and at different temperatures (from 76 to 100 °C). The performance of the cells were evaluated in terms of specific capacity, charge/discharge efficiency and cycle life. Temperature control was provided by a forced air circulation oven. Before the measurements, the cells were kept at 100 °C for at least 24 h to reach the thermal equilibrium as well as to allow the diffusion of the lithium salt inside the cathode film.

All the measurements were carried out in a controlled, argon atmosphere dry-box (MBRAUN LabMaster 130).
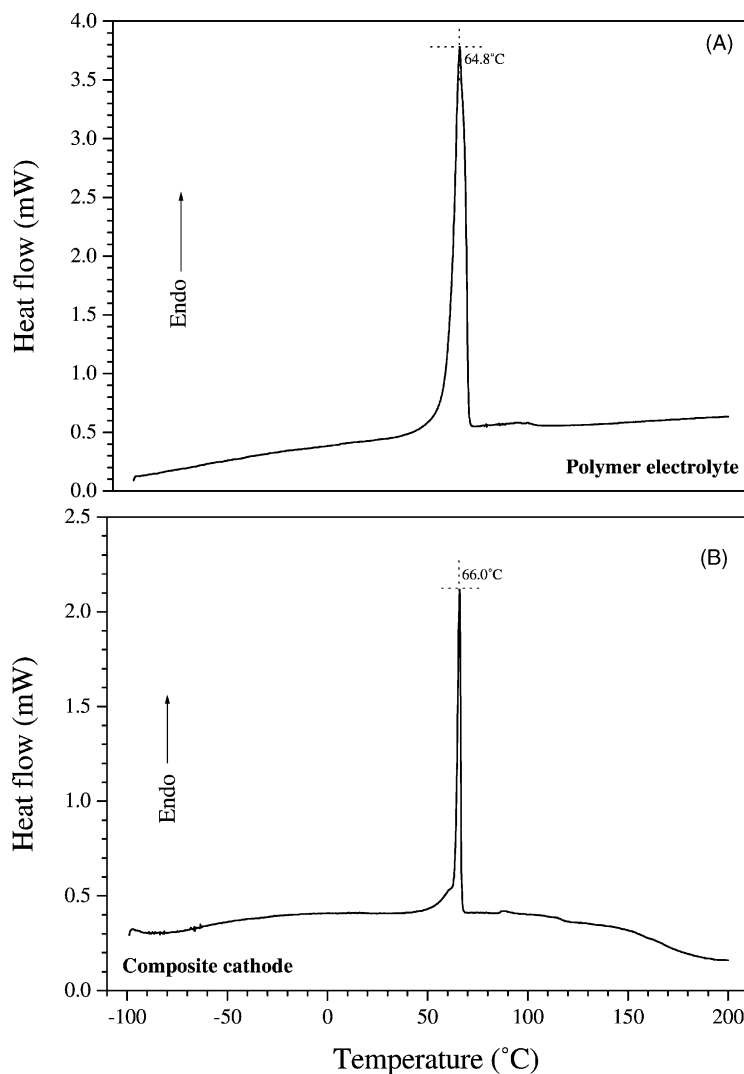

Fig. 1. Differential scanning calorimetry traces for the P(EO)₃₅LiCF₃SO₃:5% SiO₂ polymer electrolyte membrane (panel A) and the LiFePO₄:C:PEO composite cathode (panel B). Heating rate: 5 °C/min.

3. Results and discussion

3.1. Thermal analysis

The thermal behavior of the PEO composite polymer electrolyte membrane and the LiFePO$_4$ composite cathode are illustrated in Fig. 1 (DSC traces) and Fig. 2 (TGA curves).

The DSC traces of the P(EO)$_{35}$LiCF$_3$SO$_3$:5 mass% SiO$_2$ polymer electrolyte (panel A of Fig. 1) and of the LiFePO$_4$:C:PEO composite cathode (panel B of Fig. 1) show a large endothermic peak at 64.8 and 66.0 °C, respectively, associated with the melting point of the pure PEO [8]. No other features were observed in the thermal curves.

The thermogravimetric analysis of the polymer electrolyte and the composite cathode were performed in open air to evaluate the stability of the materials. Apart from an initial mass loss of 3 mass% below 50 °C, most likely due to the release of water absorbed during handling, very good thermal stability was detected up to 150 and 132 °C, respectively, for the polymer electrolyte and the composite cathode. No appreciable mass loss (3.6–4.6%) was observed in the 50–150 (130) °C temperature range, thus indicating that the materials do not undergo any reaction in air at temperatures below 130–150 °C, and that no deterioration is induced by the thermal steps of the hot-pressing process. The slightly lower thermal stability of the composite cathode may be attributed to the capability of carbon particles to catalyze material decomposition.

3.2. Li/LiFePO$_4$ polymer battery tests

The performance of the Li/LiFePO$_4$ polymer cells was investigated as a function of temperature at various current densities. Accordingly, the measurements were successively carried out at temperatures decreasing from 100 to 76 °C. After an initial low current density (0.025 mA cm^{-2}) cycling test, six different charge/discharge cycle sets were carried out at four different temperatures. The cycles were performed
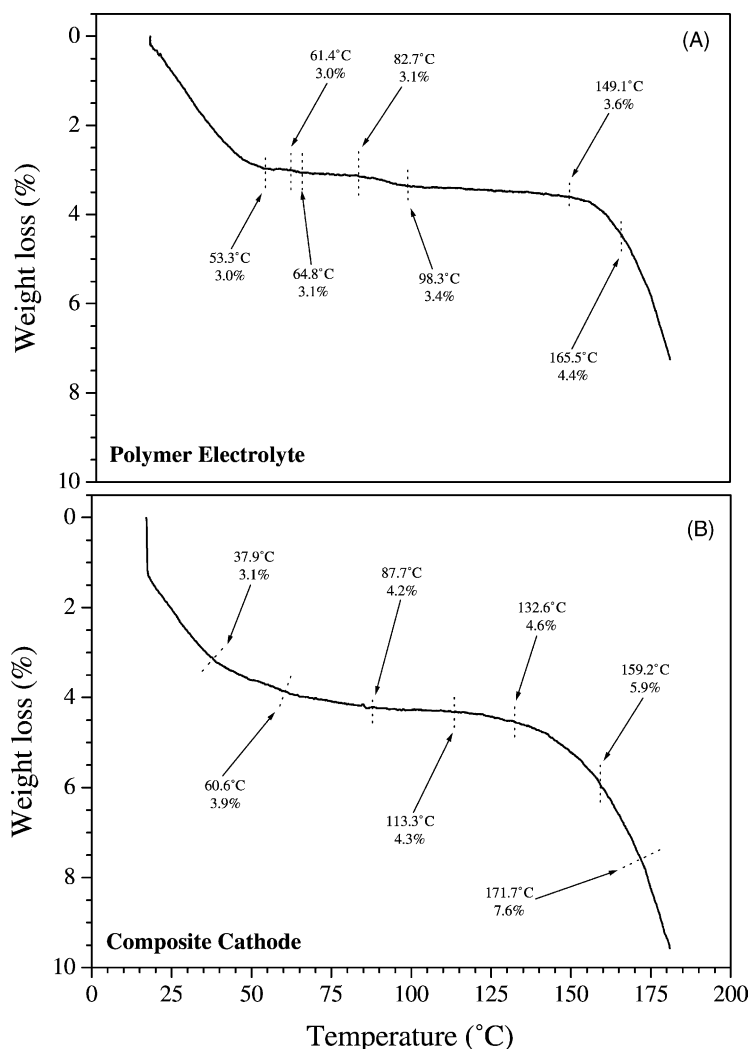

Fig. 2. Mass loss vs. temperature curves for the P(EO)$_{35}$LiCF$_3$SO$_3$:5% SiO$_2$ polymer electrolyte membrane (panel A) and the LiFePO$_4$:C:PEO composite cathode (panel B). Heating rate: 5 °C/min.
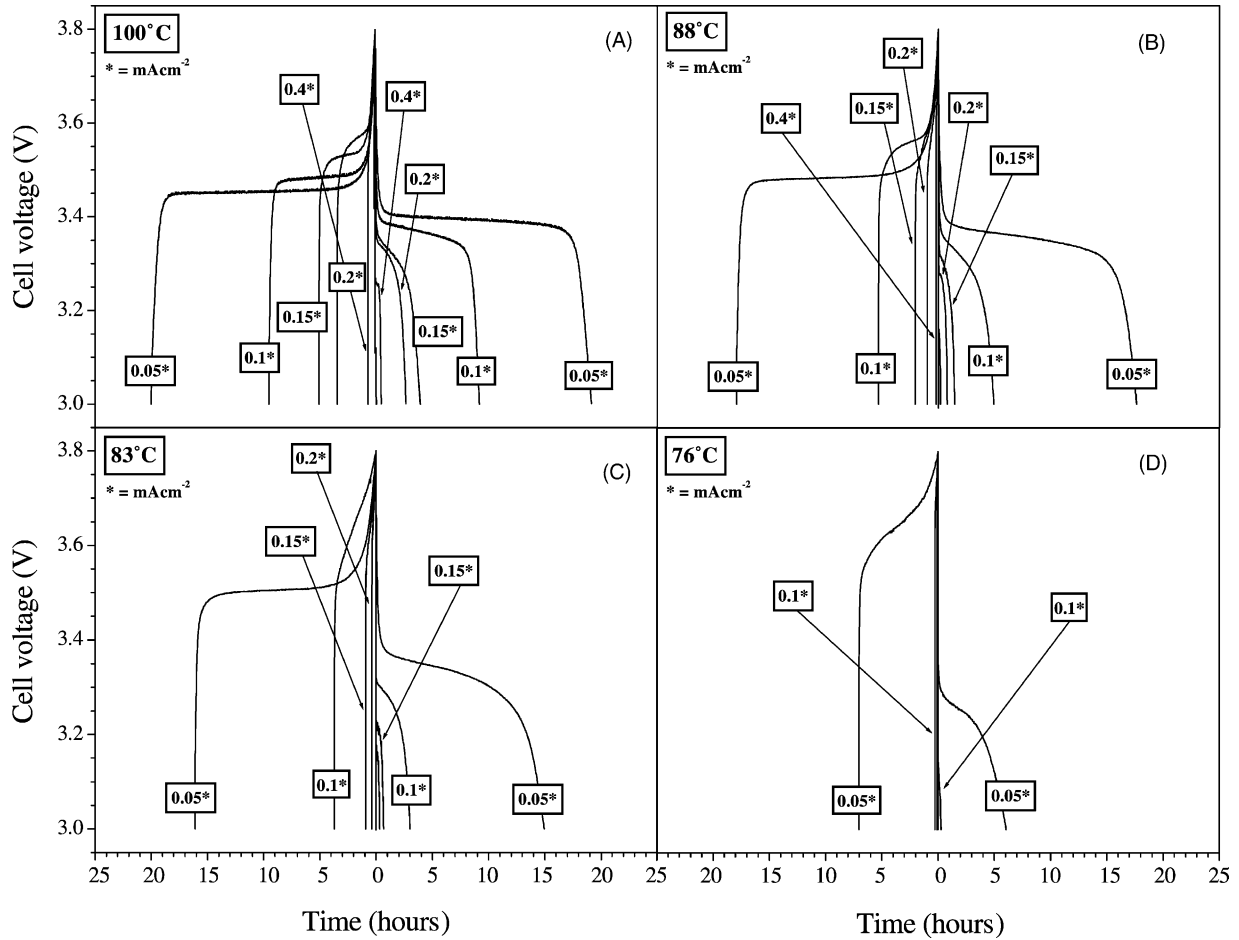
Fig. 3. Voltage/time profile of selected charge/discharge cycles obtained at different current densities (see legend) for a Li/P(EO)$_{35}$LiCF$_3$SO$_3$:5% SiO$_2$/LiFePO$_4$ polymer cell held at different temperatures (see legend). Panels from A to D are referred to the measurements performed, respectively, at 100 °C (panel A), 88 °C (panel B), 83 °C (panel C) and 76 °C (panel D).
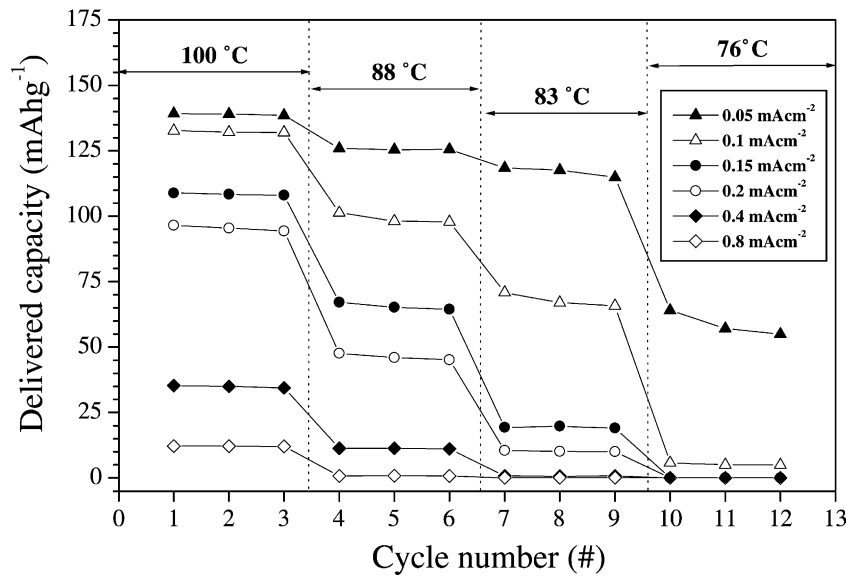

Fig. 4. Discharge cycling behavior of a Li/P(EO)$_{35}$LiCF$_3$SO$_3$:5% SiO$_2$/LiFePO$_4$ polymer battery at different temperatures (see legend) and current densities (see legend).
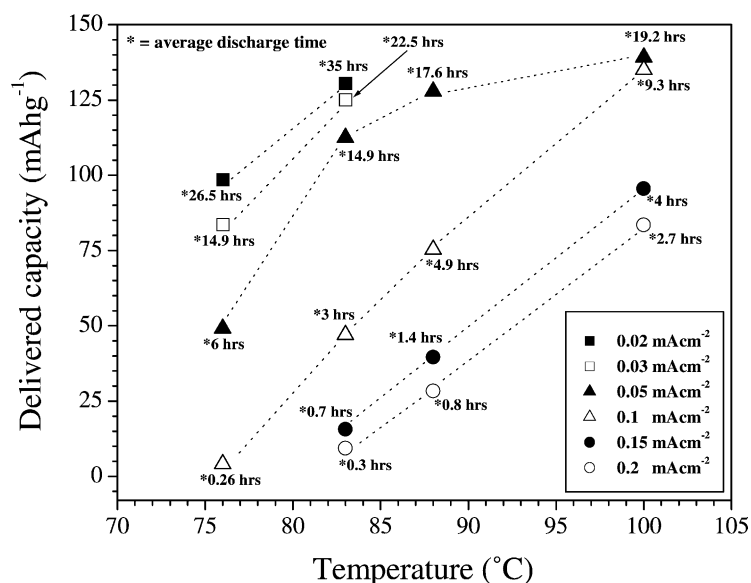
Fig. 5. Delivered specific capacity vs. temperature dependence at different current densities (see legend) for a Li/P(EO)$_{35}$LiCF$_3$SO$_3$:5% SiO$_2$/LiFePO$_4$ polymer cell. The average discharge times are also indicated.

at current densities increasing from 0.05 mA cm^{-2} (first set) to 0.8 mA cm^{-2} (sixth set). The results are reported in Figs. 3–5.

Fig. 3 shows the voltage/time profiles of selected charge/discharge cycles obtained at different current densities (see legend). Panels from A to D are referred to the cycles performed, respectively, at 100 °C (panel A), 88 °C (panel B), 83 °C (panel C) and 76 °C (panel D). The charge (lithium extraction) and discharge (lithium insertion) processes are revealed by two very flat plateaus around 3.45 V (charge) and 3.40 V (discharge), respectively. Moreover, the polymer cell is capable of maintaining the same voltage during almost the whole discharge step, which is a desired requisite for a practical battery system. The well-defined and reproducible shape of the voltage curves indicates the good behavior of the Li/LiFePO$_4$ polymer cell, especially when cycled at temperatures above 88 °C. A progressive change of the feature of the charge/discharge plateaus occurs at lower temperatures and at higher current densities. An increase of the ohmic drop in passing from the charge to the discharge step is also observed. This decay in performance is expected due to the corresponding increase of the ionic resistance of the PEO electrolyte membrane and of its diffusive properties [20], as well as of the decrease of the electronic conductivity of the LiFePO$_4$ active material [23,25] and the increase of the charge transfer resistance at the PEO membrane/LiFePO$_4$ cathode interface.

Fig. 4 summarizes the discharge cycling performance of a Li/LiFePO$_4$ polymer cell in terms of temperature (see legend) and current density (see legend). At temperatures above 88 °C, the cell is capable of delivering higher capacities, i.e. >100 mAh g^{-1}, referred to the cathode, even at moderately high current density, i.e. 0.2 mA cm^{-2} corresponding to a rate of ~C/3. Under these operating conditions, the

Li/LiFePO$_4$ polymer cell performance is comparable to that obtained with a liquid electrolyte cell at room temperature [23,27]. No dramatic decrease of capacity is observed up to 0.2 mA cm^{-2} discharge current suggesting that the limiting current density is above this value. At temperatures below 83 °C, reasonably good capacity is delivered only at moderate current densities, i.e. <0.1 mA cm^{-2}. Indeed, at low rates (≤0.05 mA cm^{-2}) no relevant difference in capacity is observed in passing from 100 °C (about 140 mAh g^{-1}) to 83 °C (120 mAh g^{-1}). A further decrease in temperature leads to increased rate of capacity decay in the performance of the cell. At high rate (>0.4 mA cm^{-2}), a moderate capacity value (about 35 mAh g^{-1}) is obtained only at high temperature. These low kinetics demonstrate that the diffusion phenomena inside the PEO electrolyte membrane are indeed strongly related to the temperature. The charge/discharge efficiency, η (not reported in Fig. 4), levels quickly above 95% for all temperatures and current densities investigated. This confirms the reversibility of the lithium ion intercalation-deintercalation process of the LiFePO$_4$ active material, as well as the electrochemical stability of the PEO membrane at the operating voltage of the cell.

Fig. 5 summarizes the delivered capacity versus temperature at various current densities (see legend). The average discharge times are also reported. Generally, an increase in cell performance is observed with increase in temperature. No relevant difference in capacity with the current density is noticed up to 0.1 mA cm^{-2} in the high temperature region (88–100 °C) where the polymer cell is able to deliver capacities exceeding 130 mAh g^{-1}. In this range, a good discharge capacity (about 80 mAh g^{-1} at 100 °C) is delivered also at moderately high rates, i.e. at 0.2 mA cm^{-2} corresponding to ~C/3. This is of particular practical interest since C/3 is the typical discharge rate for EV applications.
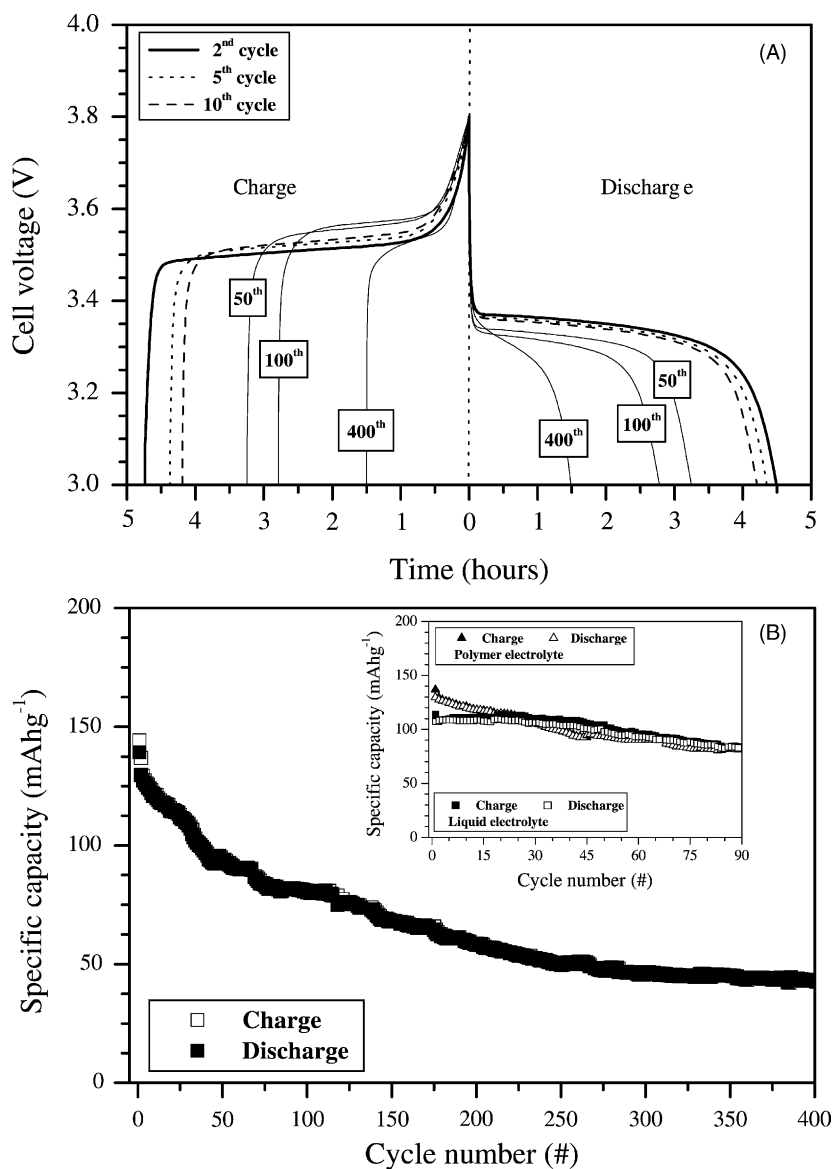
Fig. 6. Cycling performance of a Li/P(EO)$_{35}$LiCF$_3$SO$_3$:5% SiO$_2$/LiFePO$_4$ polymer cell held at 100 °C. Current density: 0.2 mA cm^{-2}. Panel A: voltage/time profile of selected charge/discharge cycles. Panel B: specific capacity vs. cycle behavior. The insert of panel B shows the performance of two LiFePO$_4$ composite cathodes in a 1 M LiClO$_4$:EC (50 mass%):DEC solution (square markers) and in the P(EO)$_{35}$LiCF$_3$SO$_3$:5 mass% SiO$_2$ polymer membrane (triangle markers), respectively.

At medium temperatures (i.e. in the 76–83 °C range), high capacity (80–130 mAh g^{-1}) is delivered only at low rates, i.e. <0.05 mA cm^{-2} corresponding to ∼C/19. An increase of the current density to 0.1 mA cm^{-2} leads to a decrease in the discharge capacity to 50 and 5 mAh g^{-1} at 83 and 76 °C, respectively. This decay in performance is due to the well-known diffusion limitations of the PEO-based electrolyte membranes and of the LiFePO$_4$ active material. We may then conclude that the Li/LiFePO$_4$ polymer battery performs well in terms of both specific energy and power density above 90 °C: below this temperature, a practical capacity can be delivered only at low power densities.

The cycling behavior of the Li/P(EO)$_{35}$LiCF$_3$SO$_3$:5 mass% SiO$_2$/LiFePO$_4$ polymer battery was evaluated

at 100 °C and 0.2 mA cm^{-2} (<C/5), following a first charge/discharge cycle (not reported) run at 0.05 mA cm^{-2}. The results are illustrated in Fig. 6 in terms of voltage/time profiles of selected charge/discharge cycles (panel A) and of capacity versus cycle behavior (panel B). Apart from a modest capacity fade, the shape of the voltage curves did not change substantially up to the 100th cycle. Also, no relevant increase of the ohmic drop was detected after more than 400 charge/discharge cycles. The polymer cell delivered an initial capacity of 130 mAh g^{-1} which decreased to 85 and 50 mAg^{-1} at the 100th and 400th cycle, respectively, i.e. with a fade lower than 0.17% per cycle. Possibly, this fade is due to a composite cathode composition which has not been optimized. This hypothesis seems

to be confirmed by the comparison between the cycling behavior of the polymer cell here under study (triangle markers) and that of a Li/LiFePO$_4$ cell using a 1 mol dm^{-3} LiClO$_4$:EC (50 mass%):DEC solution (square markers) (see insert in panel B of Fig. 6). The liquid cell was cycled at 0.135 mA cm^{-2} and at room temperature while the polymer one was tested at 0.2 mA cm^{-2} and 100 °C. Apart from an initial larger capacity for the polymer cell due to the higher electronic conductivity of the LiFePO$_4$ active material at 100 °C [23], the two cells exhibit very similar cycling performance suggesting that the capacity fading is probably associated with cathode failures rather than to polymer electrolyte degradation, although cells with a reference electrode would be required to definitely identify the failing electrode. Finally, it is important to note that the performance of the LiFePO$_4$ active material is capable of further improvements [27], thus warranting continued development of this type of an all solid-state cell/battery system.

4. Conclusions

Nanocomposite PEO:LiCF$_3$SO$_3$:SiO$_2$ membranes, prepared via an industrially feasible solvent-free procedure, appear promising candidates as electrolyte separators for all solid-state lithium cells and batteries. An example of these cells using a LiFePO$_4$-based composite cathode, fabricated with the same hot-pressing procedure used for the electrolyte, has been assembled and tested. The results confirm the good performance of this Li/LiFePO$_4$ polymer cell in terms of capacity, charge/discharge efficiency and cycle life. The capacity decay observed at medium operating temperatures and at high rates is mainly attributed to a decrease of conductivity of the polymer electrolyte. However, the Li/LiFePO$_4$ polymer battery performs well in terms of both specific energy and power density for temperature above 90 °C. A capacity fade of 0.17% per cycle was observed at 100 °C and 0.2 mA cm^{-2}. Possibly, this fade is due to cathode failures as suggested by a comparison with a parent Li/LiFePO$_4$ liquid electrolyte cell. It is also expected that passing from the laboratory type cells tested in the work to a more suitable geometry may result in an improvement of overall cell performance.

Acknowledgements

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