

# Advanced electrolyte and electrode materials for lithium polymer batteries

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## Abstract

The most recent results obtained in our laboratory on the characterization of two classes of polymer electrolytes and of olivine-type lithium iron phosphate electrodes are reviewed and discussed, especially in view of their application in advanced lithium batteries.

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*Keywords:* Lithium batteries; Polymer electrolytes; Lithium phosphate electrodes

## 1. Introduction

The next step in the advancement of the lithium battery technology is expected to be the replacement of the common liquid electrolyte with a highly conducting polymer membrane. Indeed, thin-film, solid polymer electrolyte rechargeable lithium batteries are expected to overcome the performance of conventional liquid electrolyte systems. In addition, the large-scale production of solid-state batteries can benefit from the well-established technologies developed in the polymer industry [1].

The key component of the lithium polymer battery is the electrolyte. The proper choice of this component is ruled by a series of requirements which include high ionic conductivity, good mechanical properties and compatibility with the electrode materials. Two classes of electrolytes can be considered. One involves solvent-free membranes formed by blending poly(ethylene oxide) (PEO) with a lithium salt, LiX and the other includes gel-type membranes formed by immobilization and/or swelling of selected liquid solutions in polymer matrices. In this paper, we discuss the application of both classes in advanced, rechargeable lithium polymer batteries.

## 2. Lithium polymer batteries

Polymer electrolytes formed by blending poly(ethylene oxide) with a lithium salt, LiX, are of interest for application

as advanced separators in rechargeable lithium cells. The useful operating temperatures of these polymer electrolytes are in the 70–100 °C range since below 70 °C the poor conductive PEO crystalline phase is stable [2]. We have shown that the conductivity can be improved by the addition to the PEO–LiX matrix of “active” ceramic powders at nano-particle size in order to form nano-composite polymer electrolytes [3]. A typical example is obtained by dispersing 10 wt.% of Al<sub>2</sub>O<sub>3</sub> (or SiO<sub>2</sub>) in a PEO–LiCF<sub>3</sub>SO<sub>3</sub> blend. This nano-composite electrolyte is hereafter simply noted as PEO–LiCF<sub>3</sub>SO<sub>3</sub> + 10w/o SiO<sub>2</sub>.

It has been demonstrated that the ceramic filler enhances both the polymer chains flexibility and the polymer chains solvating power [4], thus finally leading to consistent improvements in conductivity. For instance, the conductivity of the PEO–LiCF<sub>3</sub>SO<sub>3</sub> + 10w/o Al<sub>2</sub>O<sub>3</sub> electrolyte varies from 10<sup>-3</sup> to 10<sup>-5</sup> S cm<sup>-1</sup> passing from 100 to 20 °C (versus the 10<sup>-3</sup> to 10<sup>-7</sup> S cm<sup>-1</sup> values of the ceramic-free counterpart in the same temperature range).

In addition to high conductivity, nano-composite electrolytes have a series of favorable properties which make them of particular value in view of battery application. One is the improved interfacial stability towards the lithium metal electrode. This is shown in Fig. 1 which illustrates the time evolution of the impedance of a symmetrical Li/nano-composite/Li cell kept under open-circuit conditions at 95 °C [5]. The impedance response evolves as a semicircle whose low-frequency intercept is representative of the Li/electrolyte interface resistance,  $R_i$  [6]. It may be clearly seen that the semicircle does not consistently expand upon time, thus finally demonstrating the invariance of  $R_i$  and thus, the stability of the interface.

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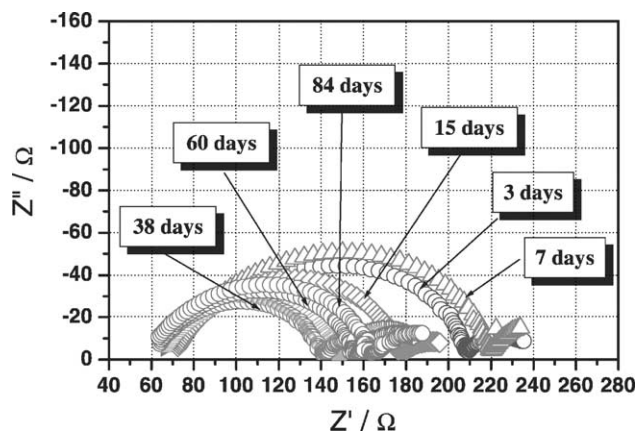


Fig. 1. Time evolution of the impedance spectra of the Li/P(EO)<sub>20</sub>-LiCF<sub>3</sub>SO<sub>3</sub> + 10w/o Al<sub>2</sub>O<sub>3</sub>/Li cell stored under open-circuit conditions at 95 °C.

This high stability, which is welcome in terms of the efficiency of the lithium cycling process, is supposed to be promoted by the dispersed ceramic powders, e.g. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> powders, by specific shielding and scavenging actions. In fact, the ceramic dispersion reinforces the mechanical properties of the electrolytes, thus leading to hard interfaces which are expected to inhibit lithium dendrites. In addition, due to their affinity for liquids, the ceramics trap away from the interface traces of liquids (e.g. residual casting solvent), i.e. of those impurities which are generally very aggressive versus lithium metal.

Another beneficial effect of the dispersed ceramics is the enhancement of the lithium transference number,  $t_{Li^+}$ . This effect, which reflects positively on the kinetics of the charge–discharge process of the lithium battery, is associated to the ceramics' surface states which compete with the polymer chains in coordinating the lithium salt cations and anions [7]. This correlation has been demonstrated by dispersing ceramics characterized by different extent of surfaces, and observing a corresponding different increase in one of the  $t_{Li^+}$  of the resulting nano-composites [7]. To be noticed that by a proper selection of the ceramic filler, enhancement in  $t_{Li^+}$  up to 30% respect to ceramic-free electrolytes can be achieved [7].

All these favorable properties are somewhat contrasted by the relatively low electrochemical stability window, since nano-composite electrolytes suffer of the limited oxidative stability of PEO. Fig. 2 shows the current–voltage curve of a stainless-steel electrode in a P(EO)<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> + 10w/w Al<sub>2</sub>O<sub>3</sub> polymer electrolyte cell. The onset of the current, which is representative of the decomposition of the electrolyte, occurs around 4.0 V versus Li, this indeed suggesting that the choice of the cathode to be used with this electrolyte may be a critical factor. Among the various possible cathode materials, iron phospho-olivines, i.e. LiFePO<sub>4</sub> [8] seem particularly convenient. Indeed, LiFePO<sub>4</sub> is the perfect cathode for PEO-based lithium batteries due to the flatness of its two-phase, charge–discharge process which evolves in

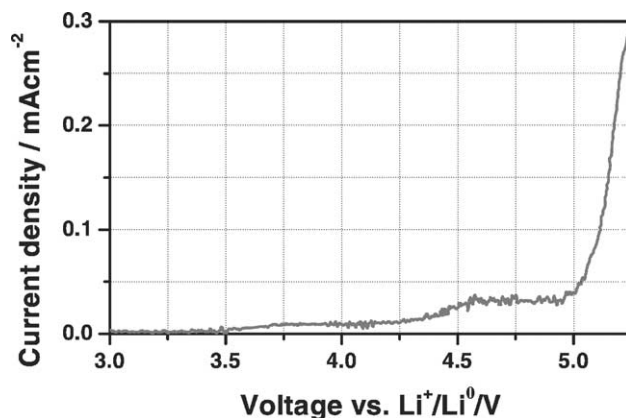


Fig. 2. Current–voltage curve of a stainless-steel electrode in a P(EO)<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> + 10w/w Al<sub>2</sub>O<sub>3</sub> polymer electrolyte cell. Counter and reference electrode: Li;  $t = 70$  °C; scan rate = 0.1 mV s<sup>-1</sup>. The onset of the current occurs at the decomposition voltage of the electrolyte.

the 3.5 V range, i.e. within the stability window of the electrolyte. However, common iron phosphate electrodes suffer from loss of capacity with increasing current density, associated to the diffusion-limited transfer of lithium across the two-phase interface [8]. We have shown that an effective way to by-pass the aforementioned kinetic limitation is to enhance the iron phosphate inter-particle electronic contact by suitable doping [9].

Indeed, optimized metal-doped LiFePO<sub>4</sub> cathodes behave quite well in lithium, nano-composite electrolyte batteries, as demonstrated by the typical example reported in Fig. 3. The battery, which operates on the basis of the following charge–discharge process:



can be cycled several times with a very limited capacity fading [10].

It is also to be noticed from Fig. 3 that the cycles evolve with a charge–discharge efficiency approaching 100%, this

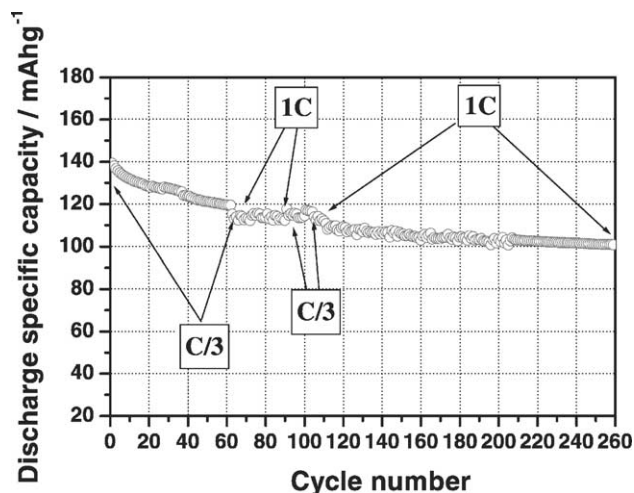


Fig. 3. Cycling response of a Li/P(EO)<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> + 10w/w Al<sub>2</sub>O<sub>3</sub>/LiFePO<sub>4</sub> polymer cell at various rates and at 105 °C.

confirming the ongoing of a smooth and reversible lithium stripping-deposition process, as that assured by the above discussed lithium/nano-composite interfacial stability. Finally, the high rates at which the battery operates confirm that the metal-doped iron phosphate electrode is indeed characterized by fast kinetics.

However, although quite satisfactory in terms of cycle life and rate capability, the lithium–iron phosphate, nano-composite polymer battery can efficiently operate only above 70 °C since the conductivity of the electrolyte is still too low at lower temperatures. Therefore, this battery can be profitably addressed to those applications where temperature is not a critical parameter, e.g. in the electric vehicle area.

For all the other cases, a different class of polymer electrolytes is required. A good choice is provided by gel-type membranes formed by the immobilization and/or swelling of selected liquid solutions in a polymer matrix. A typical example of these membranes is that prepared by swelling a poly(vinylidene fluoride) (PVdF) matrix with a LiPF<sub>6</sub> ethylene carbonate–propylene carbonate solution [11]. Hereafter, this membrane will be simply noted as LiPF<sub>6</sub>-EC-PC-PVdF.

Also these gel-type membranes can be profitably used as polymer electrolytes in lithium batteries since, despite the liquid component, they retain a good mechanical integrity (see Fig. 4). Furthermore, the conductivity of these membranes is quite high over a wide temperature range, which include ambient and subambient regions. For instance, the conductivity of the LiPF<sub>6</sub>-EC-PC-PVdF gel membrane varies from  $2 \times 10^{-3}$  to  $5 \times 10^{-4}$  S cm<sup>-1</sup> passing from 20 to -20 °C.

Metal-added, modified lithium iron phosphate can be the cathode of choice also for lithium batteries based on the gel polymer electrolytes. Fig. 5 compares the cycling response of one example of these batteries with that of a similar battery where the gel polymer electrolyte is replaced by the swelling liquid electrolyte. There is no consistent difference between

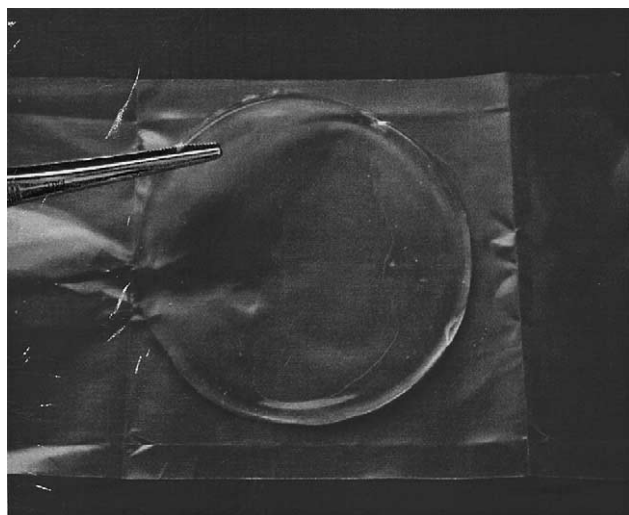


Fig. 4. Appearance of the LiPF<sub>6</sub>-EC-PC-PVdF gel membrane.

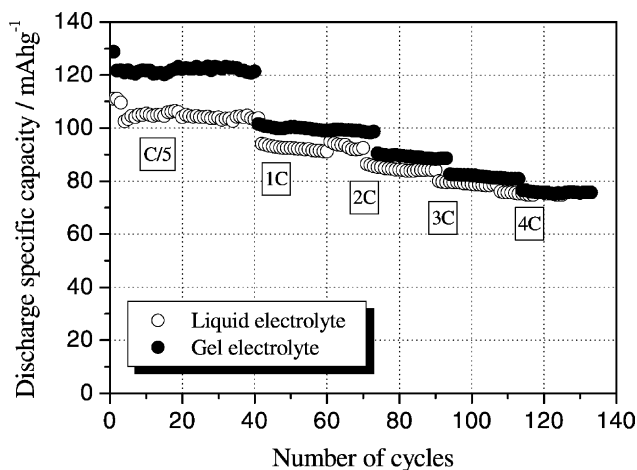


Fig. 5. Cycling response of Li/electrolyte/Ag-added LiFePO<sub>4</sub> batteries at various discharge rates and at room temperature. Electrolyte: LiPF<sub>6</sub>-EC-PC-PVdF gel membrane and LiPF<sub>6</sub>-EC-PC liquid solution, respectively. The cycling capacity is referred to the LiFePO<sub>4</sub> cathode. Charge rate: first 40 cycles, 0.2 C; remaining cycles, 1 C.

the two cases, with even a slightly improved response for the gel battery. This demonstrates that the selected gel electrolytes may indeed be competitive with common liquid solutions, probably because of their high chemical and electrochemical stability. Finally, Fig. 5 shows that the batteries may operate at very high rates, this confirming the improved kinetics of the modified iron phosphate cathode.

### 3. Conclusion

The results here reported show that two classes of electrolytes can be profitably used for the development of advanced lithium polymer batteries. The first class considers PEO-LiX-based, low particle size ceramic-added, nano-composite membranes. These electrolytes can be addressed to batteries operating in the 70–100 °C temperature range with relevance for the electric vehicle market. The second class includes gel-type membranes prepared by swelling suitable polymer matrices, e.g. PVdF matrices, with liquid lithium salt solutions. These electrolytes have a high conductivity over a wide temperature range and thus, they can be profitably used for the development of various types of batteries, including lithium ion batteries.

### Acknowledgements

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