

# Vinylidene fluoride–hexafluoropropylene copolymers as hybrid electrolyte components for lithium batteries

V. Arcella<sup>a</sup>, A. Sanguineti<sup>a</sup>, E. Quartarone<sup>b,\*</sup>, P. Mustarelli<sup>b</sup>

<sup>a</sup> Ausimont, Viale Lombardia 20, Bollate, Italy

<sup>b</sup> CSTE-CNR and Department of Physical Chemistry, University of Pavia, Via Taramelli 16, 27100 Pavia, Italy

## Abstract

Hybrid polymer electrolytes based on P(VdF–HFP) copolymers exhibit high ionic conductivity and fair mechanical performances. Two preparation methods are tested in order to optimise the properties of P(VdF–4.5 mol% HFP)-based matrices, activated by different concentrations of a 1.5 M solution of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in an EC/PC mixture: (1) the extraction/absorption procedure; (2) the conventional solvent casting. Conductivity values exceeding  $10^{-4} \Omega^{-1} \text{cm}^{-1}$  are found in samples containing 60 wt.% of electrolyte solution. In general, the films obtained by casting show a lower conductivity than the samples prepared by the extraction/absorption method, and such a difference decreases when the electrolyte fraction increases. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Poly(vinylidene fluoride); Hybrid electrolytes; Conductivity; Lithium batteries

## 1. Introduction

Hybrid lithium-based polymers represent a very promising class of ionic conductors for lithium batteries. They, in fact, combine the high conductivity at room temperature ( $\sigma_{\text{rt}} > 10^{-3} \Omega^{-1} \text{cm}^{-1}$ ) and the high power rate of liquids with the shape flexibility typical of polymers [1]. However, many drawbacks prevent them from large-scale use in practical cells. Due to their gel nature, in fact, the mechanical performances are poor and syneresis effects are observed over ageing and thermal treatments [2]. Recently, in order to improve the mechanical properties of such systems, random copolymers based on vinylidene fluoride have been employed and suitable comonomers, as hexafluoropropylene and chloroethylene, were used to modulate the crystalline-to-amorphous ratio [3,4].

However, the problem related to the loss of the electrolyte solvents is not yet completely solved. In a recent work [5] we have shown that a slight heating under primary vacuum of some P(VdF–HFP)-based hybrid electrolytes causes a loss of 20%–30% of liquid, and a consequent decrease of the conductivity of such systems. Some studies for controlling and reducing the syneresis and loss of liquid phenomena have been performed by Abraham et al. [6] and Fuller et al. [7], who have proposed the use of

only one high-boiling-point solvent in the electrolyte solution, instead of the usual ethylene carbonate–propylene carbonate solvent mixture.

In this paper we compare different procedures of films preparation, in order to optimise the transport and mechanical properties of P(VdF–4.5 mol% HFP)-based electrolytes. Two methods are tested, as discussed below.

(1) Activation with the above mentioned liquid electrolyte of porous membranes obtained by plasticising the copolymer with different amounts of dibutylphtalate (DBP), and subsequent solvent extraction with methanol or ethylene glycol (phase separation method).

(2) Conventional casting of a solution containing the copolymer dissolved in THF, and different amounts (up to 60 wt.%) of the electrolyte solution 1.5 M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in 1:1 v/v ethylene carbonate (EC) and propylene carbonate (PC).

## 2. Experimental details

### 2.1. The raw materials

The host matrix is a random copolymer of VdF with 4.5 mol% of HFP, characterised by a melting point of  $\sim 140^\circ\text{C}$  and by a melting enthalpy of 37 J/g. The corresponding degree of crystallinity is of the order of 35%, as estimated

\* Corresponding author. E-mail: eliana@chifis.unipv.it

by attributing to the totally crystalline PVdF a melting enthalpy of  $\Delta H_m = 105 \text{ J/g}$  [8]. This polymer has been provided by Ausimont (Italy).

The 1.5 M electrolyte solution was prepared by dissolving the appropriate amount of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (Fluka) in a 1:1 v/v mixture of ethylene carbonate (EC) (Aldrich) and anhydrous propylene carbonate (PC) ( $< 5 \text{ ppm H}_2\text{O}$ , Aldrich).

## 2.2. The preparation of the films

### 2.2.1. The extraction–absorption method

The P(VdF–HFP) copolymer was blended at  $200^\circ\text{C}$  for 30 min with di-butyl phthalate (DBP) (Fluka,  $> 98\%$ ), using a Brabender internal mixer. First the dried polymer was statically melted in the mixer, then DBP was slowly added under mixing. Any possible polymer overheating was avoided by carefully monitoring both the torque and the temperature.

Films having a thickness of about  $100 \mu\text{m}$  were prepared by compression moulding at  $200^\circ\text{C}$ . If not stated otherwise, all the investigated films were quenched in a large water bath within few seconds (QS samples). The effect of the thermal history was checked by comparison with another film cooled slowly in the press without any applied pressure (SCS sample). In the latter case, the cooling rate across the crystallisation range was estimated to be about  $0.1^\circ\text{C}/\text{min}$ . The actual amount of DBP in the films was determined by thermogravimetric analysis.

Plasticiser extraction was carried out in a large excess of methanol. No agitation was used in order to avoid film damaging. A time of 24 h was enough to exchange completely the solvent at room temperature, then allowing methanol to evaporate.

The film with the lowest electrolyte uptake was prepared by the phase separation method (PSM), putting in contact the polymer solution above its melting point with ethylene glycol (non-solvent at high temperature) for some minutes, and by subsequent cooling down.

### 2.2.2. The solvent casting method

Copolymer (0.8 g) was dissolved in 4–5 ml of anhydrous THF ( $< 5 \text{ ppm of H}_2\text{O}$ , Aldrich), slowly heated at  $50^\circ\text{C}$ . After complete dissolution, the required amount of the electrolyte solution was added, then stirred for 1 h. In order to perform correct comparisons, each film was prepared by using the same amount of electrolyte solution that was taken by the corresponding sample prepared by the extraction/absorption method. The absorbed quantities were determined by weighing. The resulting homogeneous and highly viscous solutions were cast onto a PTFE disk in order to allow the solvent to evaporate. Films with thickness in the range  $80\text{--}150 \mu\text{m}$  were obtained. Each step of the sample preparation was performed in a dry box ( $< 10 \text{ ppm of H}_2\text{O}$ ).

## 2.3. Apparatus

WAXD experiments were performed with an X-rays 5100 Philips Diffractometer, equipped with a scintillation counter and a pulse-height analyser, using  $\text{CuK}_\alpha$  radiation.

Optical microscope investigations were carried out with an Universal II Microscope (Karl Zeiss) at a magnification of  $256 \times$ .

Thermogravimetric analysis was performed at  $5^\circ\text{C}/\text{min}$ , under  $\text{N}_2$  flow, using a 951 TGA (Du Pont, USA).

The conductivity was measured by the Impedance Spectroscopy (IS) method, with a Solartron 1255 Frequency Response Analyzer (FRA), in the temperature range of  $20\text{--}80^\circ\text{C}$  and in the frequency range  $1 \text{ Hz--}1 \text{ MHz}$ . The disk-shaped samples were kept in a static helium atmosphere during the measurement.

Differential Scanning Calorimetry scans were carried out with a Perkin Elmer DSC7.

## 3. Results and discussions

### 3.1. Comparison of the preparation methods

During a conventional casting procedure the liquid electrolyte is directly introduced in the host polymer dissolved in a proper solvent. After the evaporation of the solvent an homogeneous film is obtained, which is plasticised by the electrolyte solution. In contrast, the extraction of DBP from the homogeneous blend with the copolymer creates a highly microporous structure in which the liquid electrolyte is absorbed and through which the ionic transport takes place. However, it has been reported in literature [9] that, in PVdF-based films, the absorbed quantity of electrolyte solution is generally less than the extracted DBP. Table 1 shows the results of some thermogravimetric investigations performed in order to check the real amounts of DBP and liquid electrolyte which were extracted and absorbed, respectively. Although the plasticiser is fully extracted, the electrolyte solvent does not replace it completely, but a quantity of  $\sim 10 \text{ wt.}\%$  less than the original amount is usually absorbed. This likely means that a fraction of the pores is not accessible to the electrolyte

Table 1

Sample	DBP <sup>a</sup> (wt.%)	Electrolyte <sup>b</sup> (wt.%)	Solvent <sup>c</sup> (wt.%)	Electrolyte <sup>d</sup> (wt.%)
QS	50	39.0	30.0	40.2
QS	70	60.3	44.0	59.3
PSM	50	15.0	9.54	13.4

<sup>a</sup>Weight fraction of DBP used to plasticise the copolymer. This quantity is fully extracted, as demonstrated by TGA experiments.

<sup>b</sup>Weight fraction of the electrolyte solution absorbed by the film after 2 days of immersion at room temperature (microbalance measurements).

<sup>c</sup>Solvent loss in TGA during a heating ramp at  $5^\circ\text{C}/\text{min}$  up to  $310^\circ\text{C}$ .

<sup>d</sup>Electrolyte losses calculated on the basis of the data of column (3).

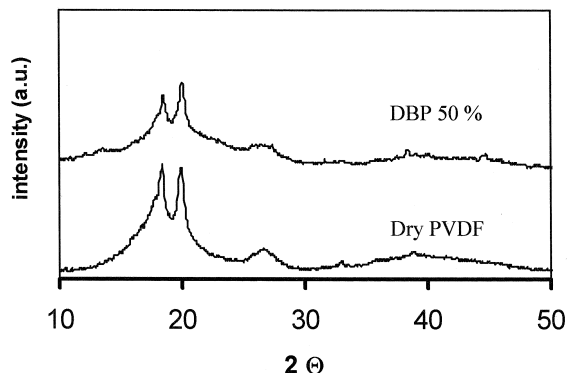


Fig. 1. WAXD spectra of the dried PVdF copolymer and the film with 50 wt.% of DBP, in a  $2\theta$  range of  $10^{\circ}$ – $50^{\circ}$ .

solution, or that an irreversible shrinkage of the polymeric structure occurs as a consequence of the extraction process. Such a phenomenon is much more evident when the sample is prepared by the phase-separation method (PSM): in fact, starting from 50 wt.% of DBP, just only 15 wt.% of the electrolyte liquid can be trapped in the membrane after the total removal of the plasticiser.

In order to highlight the influence on the transport properties of the microstructural differences related to the preparation method, the cast samples have been prepared by using the same electrolyte quantities that were found in

the homologous samples prepared by the absorption/extraction method.

### 3.2. Structure and morphology of the pure and plasticised membranes (method 1)

Fig. 1 compares the WAXD spectra of the dried PVdF copolymer and the film containing 50 wt.% of DBP. Both the films show two main reflections in a  $2\theta$  range around  $18^{\circ}$ – $20^{\circ}$  and a smaller and broader reflection of  $2\theta \sim 27^{\circ}$ . Therefore, the crystalline cell of these samples can be ascribed to the so-called ‘form II’ [10].

Though the diffraction peaks become slightly less sharp upon addition of the plasticiser, there is still clear evidence of a crystalline structure in the films containing 50 wt.% of DBP. Moreover, no evidence of new reflections can be recorded, suggesting that neither the solvent co-crystallises with the polymer, as reported in other systems [11], nor the solvent induces a change in the crystallographic organisation of PVdF, as observed for PVdF homopolymers in some polar solvents [12].

Further information on the crystalline phase can be obtained from DSC. In particular, the plasticisation with 50 wt.% of DBP induces a decrease of the melting temperature to  $124^{\circ}\text{C}$ . Such a variation is a typical and well-known effect of low molecular weight diluents on the melting

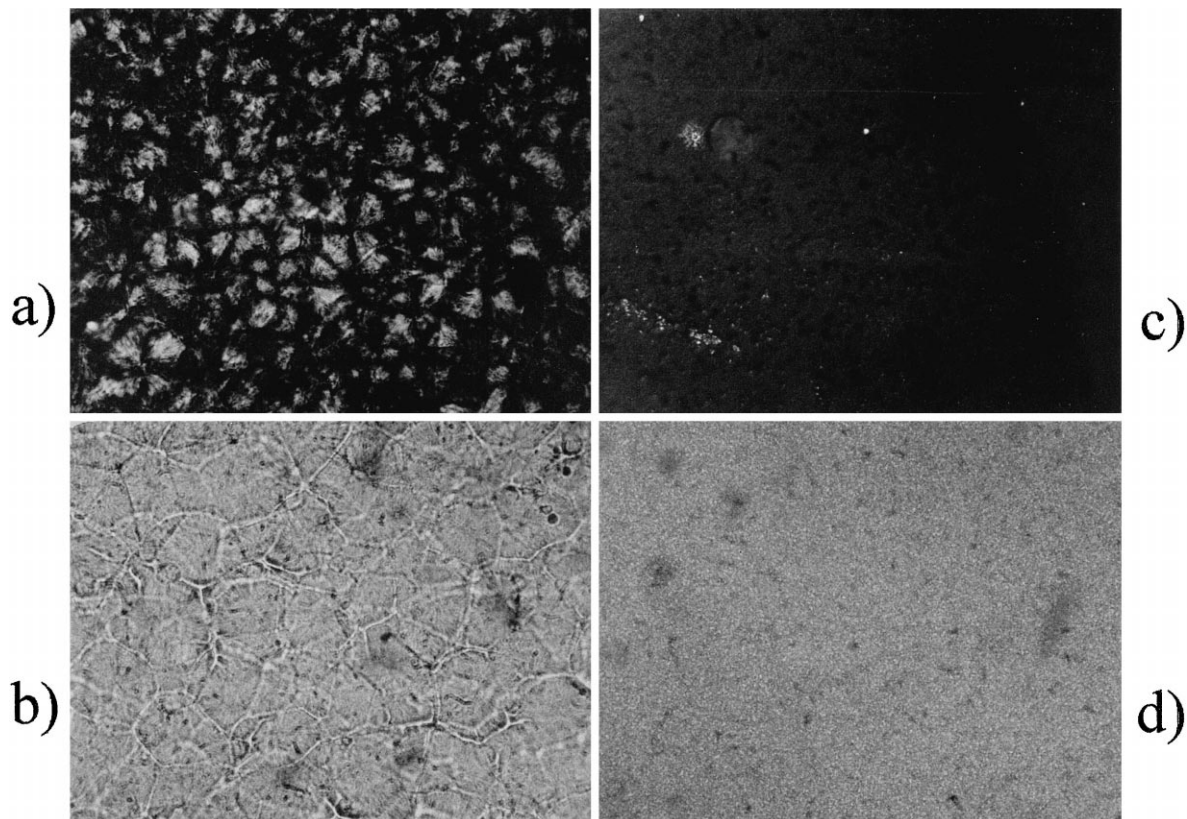


Fig. 2. Optical micrographs of the slowly cooled film (SCS) (a and b) and on a quenched film (QS) (c and d). (a) and (c) are obtained by keeping the samples between two crossed polarizers (magnification  $256\times$ ).

point of high molecular weight polymers [13]. The melting enthalpy,  $\Delta H_m$ , of the same film is 18 J/g, i.e., half of the pure polymer value. A linear scaling of the gel melting enthalpy with the polymer weight fraction has already been reported for other polymer-solvent systems and ascribed to an unchanged unit cell upon solvent addition [14].

According to these preliminary results, the plasticisation of PVDF copolymers with DBP, i.e., the gelification of an homogeneous polymer solution upon cooling, would seem to occur through the simple dilution of the crystalline phase in an amorphous swollen polymer matrix. However, it is well known that in semicrystalline polymers gelation is usually a complex phenomenon that may involve different phase separation mechanisms (solid-liquid, liquid-liquid), often taking place in a competitive way and leading to different morphology [11].

As an example, the variation of the cooling rate on the film with 50 wt.% of DBP is able to induce strong morphological effects. Fig. 2 shows four optical micrographs of the slowly cooled film (Fig. 2a and b) and of the quenched one (Fig. 2c and d). Fig. 2a and c were obtained with the film kept between two crossed polarizers. The SCS exhibits a spherulitic texture with a characteristic size of about 50  $\mu\text{m}$ . Without polarizers, QS shows a minute granular structure having a size comparable to the wavelength of the light, while no evidence of crystalline superstructures is observed when it is viewed between the polarizers. It is worth recalling that the same quenched film is crystalline according to WAXD and DSC.

### 3.3. Thermal properties

Fig. 3 shows the TGA losses of the samples prepared by the two methods and activated with 40 wt.% of elec-

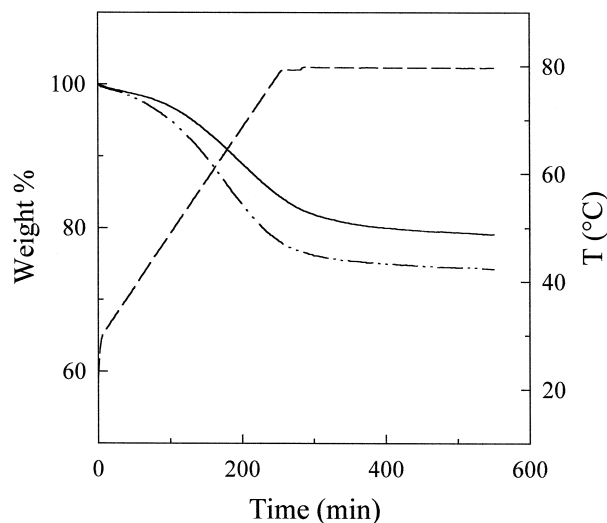


Fig. 3. TGA losses of two films prepared by the casting method (solid line) and by the extraction/absorption method (dashed/dotted line), after a 0.2°C/min ramp up to 80°C and a subsequent isotherm for 200 min.

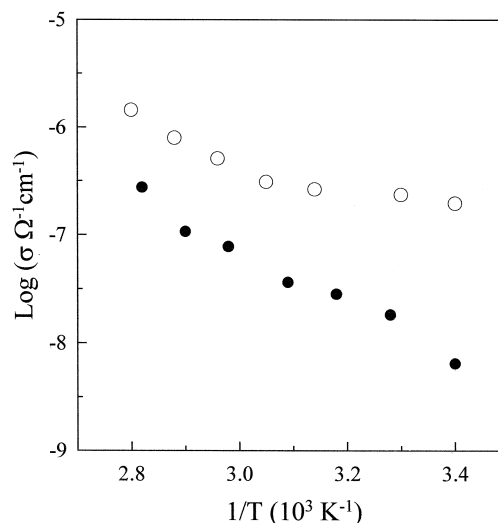


Fig. 4. Arrhenius plots between 20 and 80°C of the cast sample (filled circles) and of the one prepared by absorption/extraction (open circles), activated with 40 wt.% of liquid electrolyte.

trolyte solution. After an isotherm of about 200 min at 80°C the two samples lose about 25 and 20 wt.% of solution, respectively.

Differences in the loss kinetics are also observed, the cast film being the more resistant to the solvent loss. Rather than to reveal errors in the starting quantities of the electrolyte solution, these differences are probably related to the morphology and the microstructure of the films. We speculate that host polymer prepared by the method (1) has a highly porous and somewhat rigid structure which renders easier the solvent flow towards the surface, whereas the samples prepared by casting are more similar to true gel materials.

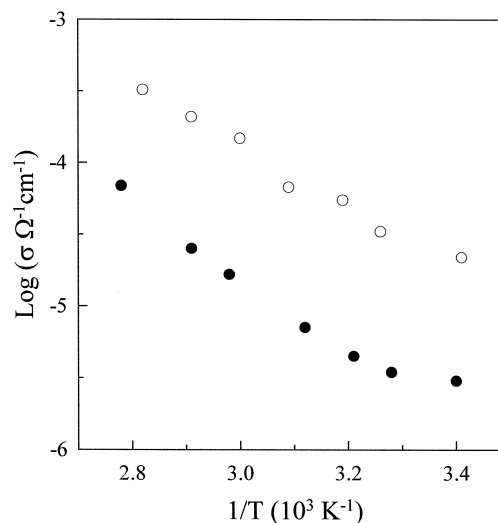


Fig. 5. Arrhenius plots between 20 and 80°C of the cast sample (filled circles) and of the one prepared by absorption/extraction (open circles), activated with 15 wt.% of liquid electrolyte.

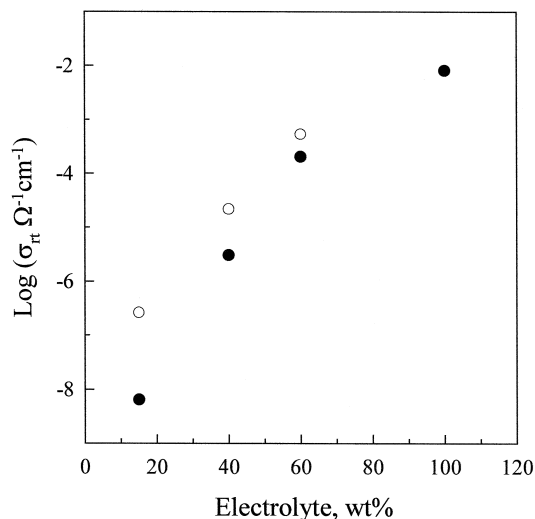


Fig. 6. Behaviour of the  $rt$  conductivity vs. the electrolyte content of the samples prepared by method (1) (open circles) and method (2) (filled circles).

### 3.4. Ionic conductivity

Fig. 4 shows the Arrhenius plots of two P(VdF–4.5 mol% HFP)-based membranes, activated with 40 wt.% of liquid electrolyte, in the temperature range 20–80°C. Filled and open circles represent the conductivity of the films prepared by solvent casting and by the extraction/absorption method, respectively. It can be noted that the second procedure allows the increase of the conductivity of one order of magnitude with respect to the values of the cast films, nearly over the entire temperature range.

Fig. 5 shows the Arrhenius plots between 20 and 80°C of the same membranes of Fig. 4 activated with 15 wt.% of electrolyte. Again, the filled circles represent the cast samples and the empty ones the films obtained by the extraction/absorption method. The difference in conductivity is still more evident, especially near room temperature, than in the case of Fig. 4.

These results are well summarised in Fig. 6, that is a sort of ‘master curve’ in which the  $rt$  conductivities of the cast films (filled circles) and of the activated ones (open circles) are plotted against the electrolyte weight fraction. An interesting non-linear behaviour is clearly observed. It can be also observed that the differences in conductivity decrease by increasing the electrolyte fraction. Again, this result can be explained by supposing that the extraction/absorption method give samples with a highly porous structure, where well interconnected pathways are easily accessible to the solution. In contrast, the cast films are characterised by a microstructure less suitable for the

ionic transport. However, when the solution content exceeds  $\sim 60$  wt.%, it has been shown [15] that liquid regions are formed in the cast films, which tend to suppress the differences related to parameters like morphology or microstructure in influencing the ionic transport.

## 4. Conclusions

In this paper we have compared some P(VdF–4.5 mol% HFP)-based hybrid electrolytes prepared by two methods: absorption/extraction and solvent casting. The samples prepared by the former method do not allow to be activated with an electrolyte weight fraction equal to the quantity of extracted plasticiser. Small differences in the solvent loss kinetics are observed among the cast film and the ones prepared by the extraction/absorption method.

The conductivity shows a non-linear behaviour against the liquid electrolyte content. In general, the films obtained by the extraction/absorption method display higher conductivity values in comparison with the ones prepared by solvent casting and containing the same quantity of liquid electrolyte. However, the differences decrease as the liquid electrolyte fraction increases. Conductivity values of the order of  $10^{-4} \Omega^{-1} \text{cm}^{-1}$  are obtained for 60 wt.% of electrolyte solution.

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