

# Structure, porosity and conductivity of PVdF films for polymer electrolytes

A. Magistris<sup>a</sup>, P. Mustarelli<sup>a,\*</sup>, F. Parazzoli<sup>a</sup>, E. Quartarone<sup>a</sup>, P. Piaggio<sup>b</sup>, A. Bottino<sup>b</sup>

<sup>a</sup>Department of Physical Chemistry and CSTE CNR, Università di Pavia, Via Taramelli 16, 27100 Pavia, Italy

<sup>b</sup>Department of Chemistry and Industrial Chemistry, Via Dodecaneso, 16132 Genova, Italy

Received 15 June 2000; received in revised form 11 November 2000; accepted 28 December 2000

## Abstract

Semicrystalline porous films of poly(vinylidene fluoride) (PVdF) were prepared by a phase-inversion method. The microstructure of the films depends on the preparation conditions, and can be classified in two categories: sponge-like and finger-like. Porosities higher than 75% can be reached with finger-like texture, and all the pore structure is accessible to the electrolyte solution. Conductivity higher than 2 mS/cm is easily obtained by soaking the films into standard electrolyte solutions. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lithium batteries; Gel electrolytes; Poly(vinylidene fluoride); Phase inversion; Porous membranes

## 1. Introduction

Poly(vinylidene fluoride-hexafluoropropylene) P(VdF-HFP) copolymers have been widely studied for applications in rechargeable lithium batteries [1]. Polymer electrolytes with room temperature conductivity of the order of 1 mS/cm have been obtained both by the standard casting procedure [2,3], and by the absorption/extraction method [4,5]. On the other hand, casting technology is discouraged for large-scale applications, whereas the preparation by extraction of dibutylphthalate leads to porosities not higher than 50% in volume.

Phase separation by liquid immersion [6] is a well known method for preparing porous membranes with controlled properties from various polymers. The use of this technique for obtaining PVdF membranes with different porosities and structures, these latter ranging from the so-called ‘finger-like’ structure to the ‘sponge-like’ one, is described in a previous work [7]. Scanning electron microscope (SEM) micrographs of these structures are shown as an example in Fig. 1a and b. PVdF, which is widely used for making ultrafiltration and microfiltration membranes [8] owing to its excellent chemical resistance and good thermal stability, has attracted in the recent years much attention as trunk material for the preparation of separators in lithium batteries [9].

In order to obtain the best compromise among conductivity and thermal stability, it is mandatory to characterize the pore structure and the interactions between the host polymer and the electrolyte solution, which are translated at a macroscopic level by quantities like surface tension and solution viscosity.

In this paper we perform a microstructural, thermal and electric characterization of PVdF porous membranes activated by non-aqueous electrolyte solutions. The results of simple bulk measurements like membrane density and uptake rate are correlated with the membrane structure and data obtained from conductivity measurements.

## 2. Experimental section

### 2.1. Membrane preparation

Asymmetric porous PVdF (Forafion 1000HD, Atochem,  $M_v = 4.5 \times 10^5$ ) membranes were prepared by the phase inversion method starting from solutions whose composition is listed in Table 1. Solutions were first cast at room temperature (20°C) onto a glass plate to form films with ~350 μm thickness that after 30 s at 20°C were immersed in a water bath at 10°C to precipitate the polymer and form the membrane. The membranes were leached for 48 h under running water and then immersed in deionized water for the same period prior to be dried by simple exposition in air. Dried membranes whose thickness varied from 120 to

\* Corresponding author. Tel.: +39-0382-507776; fax: +39-382-507575.  
E-mail address: mustarelli@matsci.unipv.it (P. Mustarelli).

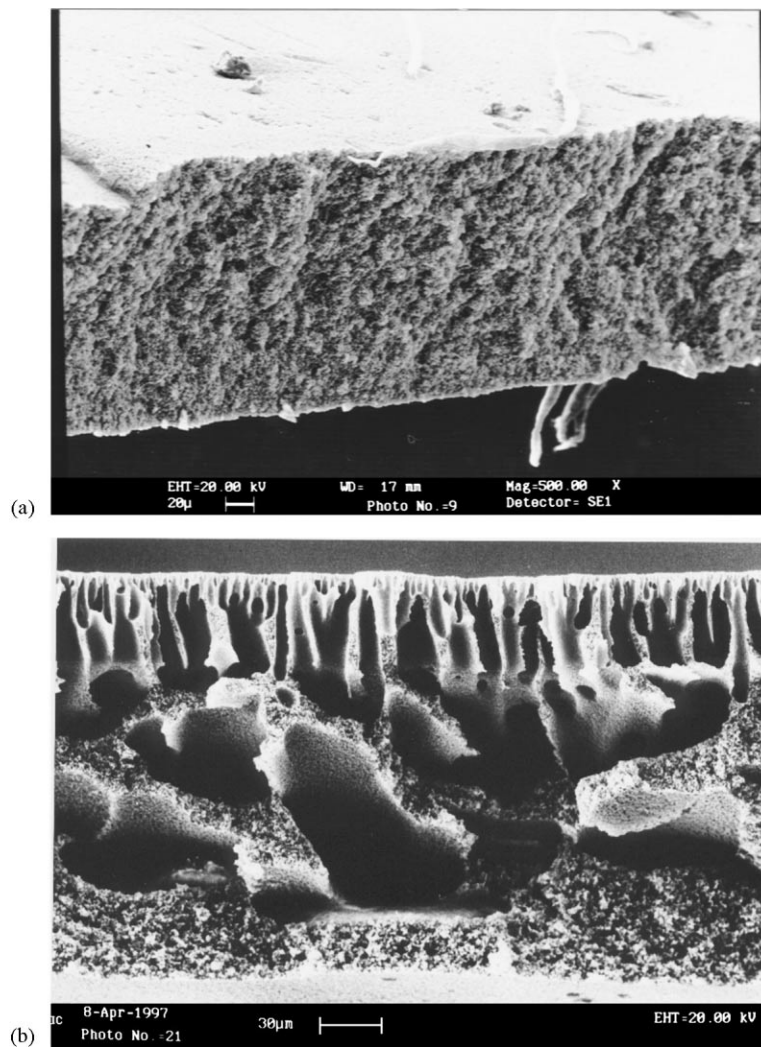


Fig. 1. SEM micrographs of two samples characterized by sponge-like (a) and by finger-like (b) structures.

Table 1

List of compositions of the PVDF starting solutions

Membrane and morphology	Solvent	PVdF concentration (wt.%)	SiO <sub>2</sub> concentration <sup>a</sup> (wt.%) <sup>b</sup>	Density (g/cm <sup>3</sup> )	Crystallinity (%)	Uptake <sup>c</sup> (%)
Compact PVdF	–	–	–	1.82	49	15
PF-100 finger-like (small cavities)	<i>N,N</i> -dimethylformamide (DMF)	20	–	0.826	–	152
PF-900 sponge-like	Triethyl phosphate (TEP)	20	–	0.650	–	182
PF-901 sponge-like	Triethyl phosphate (TEP)	20	–	0.529	–	233
PF-419 finger-like	<i>N</i> -methyl-2-pyrrolidone (NMP)	20	–	0.475	–	288
PF-421 finger-like	<i>N</i> -methyl-2-pyrrolidone (NMP)	20	10	0.402	–	275
PF-413 finger-like	<i>N</i> -methyl-2-pyrrolidone (NMP))	15	–	0.342	–	386
PF-423 finger-like	<i>N</i> -methyl-2-pyrrolidone (NMP)	10	–	0.286	60	403
PF-424 finger-like	<i>N</i> -methyl-2-pyrrolidone (NMP)	10	10	0.264	–	476

<sup>a</sup> Fumed silica (Sigma).

<sup>b</sup> With respect to PVdF.

<sup>c</sup> Determined as  $(W_w - W_d)/W_d \times 100$ , where  $W_w$  and  $W_d$  are the weights of the wet and dry membrane, respectively.

220  $\mu\text{m}$ , depending on the composition of the cast solution, were finally soaked for 18 h in a dry box in two different electrolyte solutions, EC-DEC 1:1 (w/w) 1.0 M  $\text{LiPF}_6$ , (Selectipur<sup>TM</sup>, Merck) pure and mixed with 20 vol.% of TEGDME– $\text{LiPF}_6$  1.0 M.

## 2.2. Characterization

The thermal properties of the membranes were studied by a modulated differential scanning calorimeter (MDSC 2910, TA Instruments<sup>TM</sup>, USA). The measurements were carried out at 5°C/min with a modulation period of 40 s and a modulation amplitude of 0.5°C/min. The structure of the surface and cross-section of the dry PVdF membranes was observed by a SEM (Leica Stereoscan 440).

The ionic conductivity was measured at room temperature by impedance spectroscopy, using a frequency response analyser (Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 10 Hz to 1 MHz at an ac amplitude of 100 mV. Scans at 10 mV were also performed in order to check the current/voltage linearity.

The density values were determined by a standard pycnometric method, using water as the reference liquid. Finally, the uptake rate was calculated by considering the amount of liquid electrolyte absorbed by the porous membrane ( $W_w - W_d$ , where  $W_w$  and  $W_d$  are the weights of the membrane, respectively, after and before the immersion), normalized to 1 g of dried membrane,  $W_d$ .

## 3. Results and discussion

Fig. 2 shows the entity of the uptake by volume against a quantity ( $1/d_a - 1/d_c$ ) which is related to the porosity of the film. Here,  $d_a$  is the apparent density of the porous films, whereas  $d_c$  the density of the non-porous PVdF film pre-

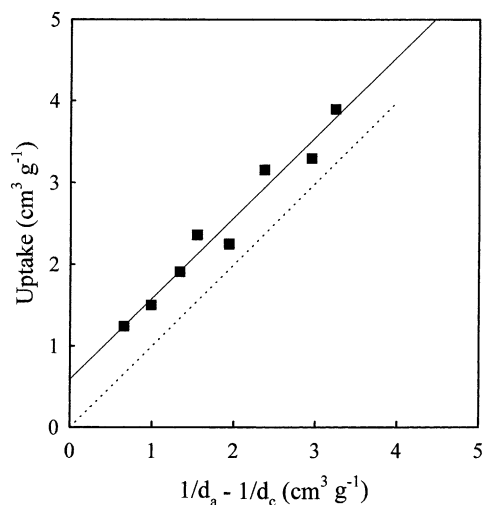


Fig. 2. Behavior of the uptake by volume against the quantity ( $1/d_a - 1/d_c$ ) (see text).

pared by casting ('compact film') as determined by pycnometry. The dotted line represents the theoretical absorption if the solution enters all the pore structure. The experimental points are well-fitted by a regression line having slope  $m \cong 0.99$ , which means that all the pore structure is accessible to the solution. We stress here that the time required to reach the equilibrium uptake is generally very short (<1 min).

The uptake excess displayed by our samples with respect to the theoretical line is due to that part of the solution which enters the amorphous polymer strands to form a gel phase. This fraction is invisible to the pycnometric measurements performed in the electrolyte solution itself, under the hypothesis that the solution density does not change in the gel phase. The excess uptake due to the gel formation is nearly constant for the different samples, and it is related to the amount of amorphous content in the membrane (see Table 1). The amounts of solution forming the gel phase have been checked, in some selected cases, by a geometric determination of the swelling of the films.

Fig. 3 shows the behavior of the electric conductivity,  $\sigma$ , against the pores fraction,  $v_p = 1 - d_a/d_c$ , for all the samples activated with the two different electrolyte solutions described in Section 2. In both cases the behavior is strongly non-linear, with the samples containing TEGDME which display conductivity higher by roughly a factor 1.2 with respect to the other ones. This is nearly the same ratio we observe between the conductivity of the pure Selectipur<sup>TM</sup> solution ( $\sigma = 7.22$  mS/cm at room temperature), and that of the solution with TEGDME ( $\sigma = 9.50$  mS/cm at room temperature). We can conclude that the host polymers do not change the transport properties of the solutions, but for a constant term (an added resistance) which depends on the sample morphology. Finally, the addition of silica does not seem to play a relevant role on the conductivity (see Table 1).

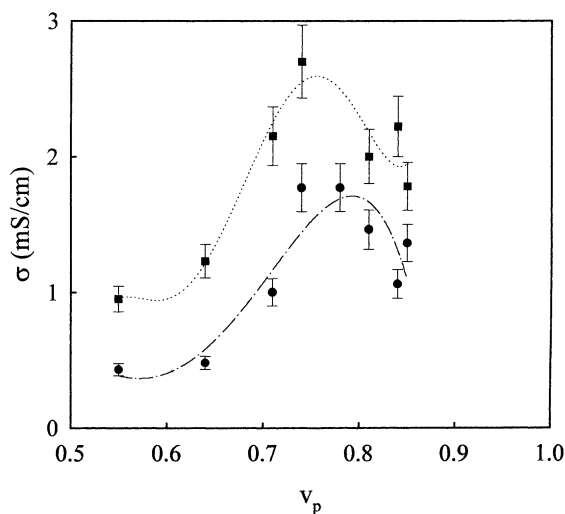


Fig. 3. Behavior of the room temperature conductivity of the solution EC-DEC 1:1 (w/w) 1.0 M  $\text{LiPF}_6$  (circles) and of the one mixed with 20 vol.% of TEGDME– $\text{LiPF}_6$  1.0 M (squares) against the pore fraction,  $v_p$ . The dashed and dotted lines are only guides for the eyes.

The behavior of the pure electrolyte solution for different ratios (EC/DEC)/TEGDME will not be discussed here. Let us focus our attention, instead, on how the conductivity changes with the morphology. For  $v_p < 0.75$ , the conductivity sharply increases with the pore fraction, i.e. with the solution content, and this is also in agreement with the results of Michot et al. [9]. At  $v_p \sim 0.75$ , a maximum is attained, which is grossly placed where a finger-like structure is obtained, with the fingers which have dimensions comparable to the film thickness. After that, we observe a decrease of the conductivity in concomitance with a further increase of the pore fraction. This apparently contradictory result may be tentatively explained in terms of variation of tortuosity inside the membranes, related to differences in depth, crystallinity and pore density of the skin. The dashed and dotted lines of Fig. 3 are only guides for the eyes.

Tentative electrical models can be hypothesized in terms of series of resistors in parallel: this work is in progress and will be the object of a future paper.

#### 4. Conclusions

The phase-inversion method is well suited to prepare free-standing PVdF films for application as separators in lithium

batteries. We showed that a proper tailoring of the porous structure of PVdF allows to easily obtain conductivity higher than 2 mS/cm at room temperature. The electrolyte solution goes mainly to occupy the porous structure, which is completely accessible. However, a certain part of the solution gives origin to a swollen gel phase.

#### References

- [1] Z. Jiang, B. Carroll, K.M. Abraham, *Electrochim. Acta* 42 (1997) 2667.
- [2] J.-M. Tarascon, A.S. Gozdz, C. Schmutz, F. Shokkahi, P.C. Warren, *Solid State Ionics* 86–88 (1996) 49.
- [3] E. Quartarone, M. Brusa, P. Mustarelli, C. Tomasi, A. Magistris, *Electrochim. Acta* 44 (1998) 677.
- [4] A.S. Gozdz, C.N. Schmutz, J.M. Tarascon, P.C. Warren, US Patent 5,456,000 (1995).
- [5] V. Arcella, A. Sanguineti, E. Quartarone, P. Mustarelli, *J. Power Sources* 81/82 (1999) 790.
- [6] H. Strathmann, K. Kock, *Desalination* 21 (1977) 241.
- [7] A. Bottino, G. Camera-Roda, G. Capannelli, S. Munari, *J. Membr. Sci.* 57 (1991) 1.
- [8] M. Cheryan, *Ultrafiltration and Microfiltration Handbook*, Technomic Publishing Co., Lancaster, PA, 1998.
- [9] T. Michot, A. Nishimoto, M. Watanabe, *Electrochim. Acta* 45 (2000) 1347.