

Microporous PVdF gel for lithium-ion batteries

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Abstract

A novel ionic conductor for lithium-ion batteries was developed. This electrolyte is based on a porous polymer matrix filled and swollen by a liquid. The polymer matrix obtained by phase inversion was characterized in terms of porosity and average pore size. The microporous PVdF gel formed by impregnation of this polymer matrix with liquid electrolyte exhibited a high equivalent conductivity and a good temperature stability. Complete lithium-ion batteries using this polymer-based electrolyte were manufactured with a new process. Preliminary cycling results show a good rate capability and a capacity evolution similar to that of regular lithium-ion cells. The interest of this technology, as many other lithium-polymer ones, also lies in the possibility of designing and manufacturing new battery shapes at lower cost. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium-ion batteries using polymers or immobilized electrolytes are well adapted to the new multimedia applications. Indeed, these batteries offer various possible geometries (thin/flexible cells), are expected to be safe and should be cost effective compared to regular lithium-ion batteries.

Despite extensive research on lithium polymer conductors, the conductivity of pure solid electrolytes (with no liquid) is insufficient at room temperature. A possible solution is the addition of liquid electrolyte to the polymer matrix. Different polymer matrices and processes are proposed in the literature [1–4]. However, one problem persists with all these electrolytes: it is difficult to combine a good conductivity, increasing with the percentage of liquid electrolyte, and mechanical properties in a wide temperature range, deteriorating when the percentage of liquid electrolyte increases. Various solutions are suggested in the literature. The first one is the addition of fumed silica to improve mechanical properties [5]. Another solution associates two polymers [6]; one has a very good affinity for the liquid electrolyte (liquid swelling) and the other one has no affinity (mechanical properties). Our solution consists in using a microporous matrix (to trap the liquid

electrolyte) based on a polymer, which has some affinity to the liquid. This paper presents the elaboration and the characterization of this material, and its use for manufacturing lithium-polymer batteries.

2. Elaboration and characterization of microporous polymer matrix

The chosen polymer is a commercially available PVdF homopolymer. The microporous polymer matrix is obtained by phase inversion. The principle and the different techniques used in this process have been described in a previous article [7]. A PVdF membrane prepared by selective evaporation is studied in this article.

The PVdF powder was dissolved in a mixture of a volatile solvent (acetone) and a PVdF non-solvent (butanol) with the following proportions per weight (acetone/butanol/PVdF (6/1/1)). The proportion of non-solvent was low enough to allow the dissolution and high enough to allow the phase separation during evaporation. The viscosity of the solution (0.08 Pa s for a 100 s⁻¹ gradient at 25°C) was quite low. It was, however, sufficient to cast membrane of uniform thickness either on a metallic substrate or directly on the electrode. The membrane coating on the electrode was broken in liquid nitrogen in order to observe membrane cross-section by SEM. Fig. 1 displays a SEM photograph of the bulk structure of the membrane

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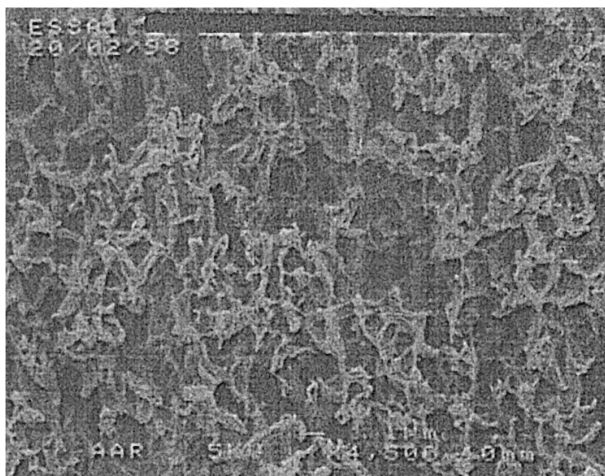


Fig. 1. SEM photo of a membrane cross-section. Bulk structure.

using a large magnification ($\times 4500$). As shown in Fig. 1, the microstructure exhibits a highly porous «sponge» structure. The porosity was found around 70%. The average pore size was estimated at about $0.5 \mu\text{m}$ by Coulter porosimetry. No skin was observed at the surface of the membrane. The adhesion of the membrane on the electrode was good. Fig. 2 shows a SEM photograph of the interface between a LiCoO_2 based composite electrode (8% electronic conductor, 6% PVdF binder and 86% LiCoO_2) and the membrane. It is clear from this photograph that the adhesion mechanism is mechanical. It can also be seen that the membrane structure penetrates the electrode porosity.

3. Characterization of microporous PVdF gel

Carbonate solvents are the basis of most liquid electrolytes used for lithium-ion batteries. Swelling tests in dimethyl carbonate (DMC) at 60°C of PVdF homopoly-

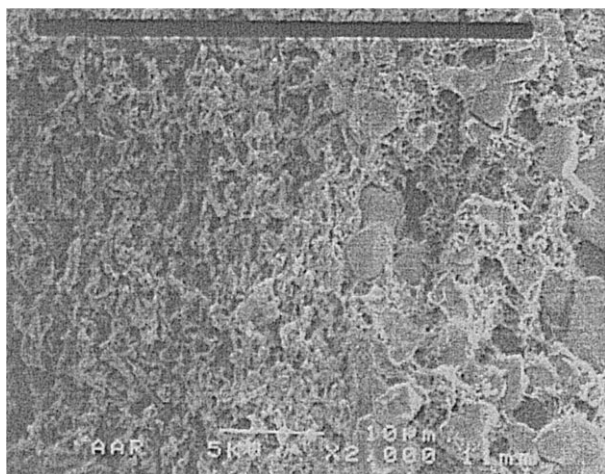


Fig. 2. SEM photo of an electrode + membrane cross-section.

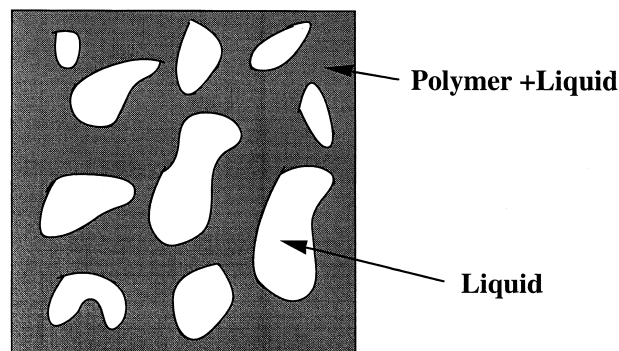


Fig. 3. Structure of microporous PVdF gel.

mers and copolymers, were made by an Elf Atochem research team on their products [8]. For PVdF Kynar 741 (homopolymer), the weight increase in DMC at 60°C was found around 25%, whereas the swelling was over 50% for a copolymer with a low amount of HFP (Kynarfex 2850, 5 wt.% HFP). A 85/15 wt. PVdF-HFP (Kynarfex 2750) would dissolve completely in these conditions. Consequently, a PVdF homopolymer swells in carbonate solvents but keeps its mechanical properties in this medium at a higher temperature than PVdF copolymers.

The microporous PVdF membrane is the matrix of the polymer gel electrolyte. Liquid electrolyte is trapped in the porosity of the membrane but also swells the PVdF homopolymer. Thus, the microporous PVdF gel has the structure depicted in Fig. 3. The liquid content of the gel is approximately 65% per weight. The conductivity of this gel with PC/EC/3DMC + 1 M LiPF_6 as liquid electrolyte was $3.7 \times 10^{-3} \text{ S/cm}$ at 25°C . The resistance due to the membrane is linked to its porosity (ε) and tortuosity (T) by the following formula:

$$R_{\text{membrane + liquid electrolyte}} = R_{\text{liquid electrolyte}} \times (T/\varepsilon).$$

The tortuosity of the membrane studied was calculated at 2.1 knowing the porosity of the membrane ($\varepsilon = 0.7$), and conductivities of liquid electrolyte (10^{-2} S/cm at 25°C) and PVdF gel ($3.7 \times 10^{-3} \text{ S/cm}$ at 25°C). The temperature stability of the microporous PVdF gel was evaluated by DSC. No phase change was observed between ambient temperature and 90°C , where a melting temperature peak was observed.

4. Manufacture of lithium-polymer batteries

Regular SAFT lithium-ion batteries electrodes were used. The PVdF membrane was cast and formed directly on top of the negative electrode as described previously. Then, the same membrane solution was used again to laminate the positive electrode to the PVdF membrane. By carefully controlling the drying procedure after lamination, a porous bonding layer can be obtained producing a unitary cell, negative electrode + microporous PVdF membrane + positive electrode. The highest boiling point of

solvents used in this process is 120°C. At this temperature, all the solvents can be eliminated, exclusively by evaporation, without damaging the PVdF membrane. These operations can be done in a non-controlled environment.

The unitary cells are then vacuum dried for removal of residual solvents and moisture at elevated temperatures (final moisture level < 200 ppm). They are transferred to a dry room where they are impregnated with a liquid electrolyte. As PVdF homopolymer is chosen, a wide selection of organic solvents can be used including low boiling carbonates like DMC or DEC. This makes possible to optimize the ionic conductivity over a wide temperature range. The cell units can be assembled into cell-stacks to deliver the required battery capacity. The cells are finally packed in a pouch, manufactured from multi-layer plastic/metal foils, which are known from the food and pharmaceutical industry, additionally optimized to minimize moisture permeability. To conclude, it should be noticed that the cells were made using a limited number of steps: electrode casting, membrane casting, bonding, electrolyte impregnation and cell sealing.

5. Performances of lithium-polymer batteries

Pouch cells with capacities ranging from 0.05 to 0.1 Ah were built and tested. The specific surface capacity of the electrodes was 1–3 mAh/cm². Graphite and LiNiO₂ or LiCoO₂ were employed as negative and positive electrode materials, respectively. Liquid electrolyte in the microporous gel was a mixture of carbonate solvents with LiPF₆ salt.

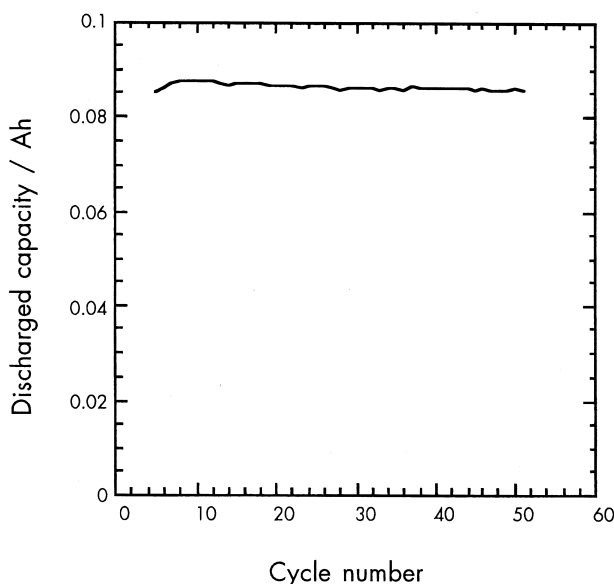


Fig. 4. Lithium polymer cells fading. Charge at C/2 up to 4.2 V with 1 h floating at 4.2 V (at R.T.). Discharge at C/2 (at R.T.) down to 2.7 V.

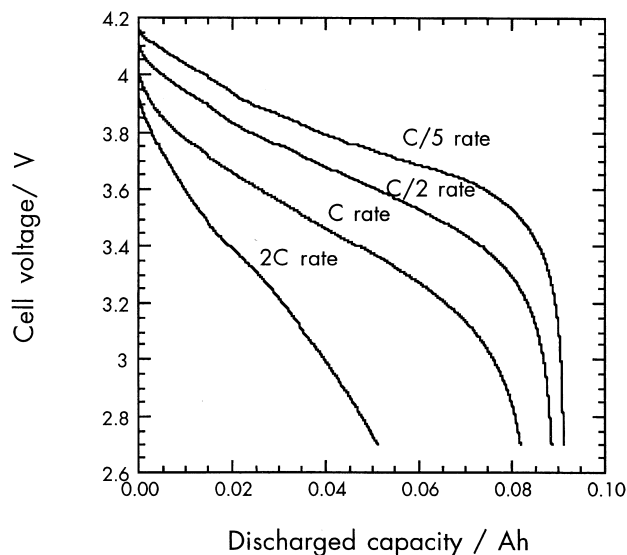


Fig. 5. Lithium polymer cells rate capability. Charge at C/10 up to 4.2 V with 5 h floating at 4.2 V (at R.T.). Discharge at various rates (at R.T.) down to 2.7 V.

orous gel was a mixture of carbonate solvents with LiPF₆ salt.

Results of cycling tests and high rate discharges are given in Figs. 4 and 5. All cycling tests were conducted between 2.7 and 4.2 V. At C/5 the capacity is stable after 50 cycles. Power tests gave over 80% of the nominal capacity at C rate and over 50% at 2C rate.

6. Conclusion

The manufacturing process of dry cells described in this paper, is based on the use of phase inversion for elaboration of a unitary cell. Each step of the process is simple (no complex extraction step) and can be adapted to the PVdF nature (homopolymer or copolymer). Dry cells can be impregnated by various organic solvents and salts, and finally assembled in a pouch cell. These lithium-polymer cells using microporous PVdF gel exhibit electrochemical performances similar to regular lithium-ion batteries with liquid electrolyte. Their main advantage is their ability to be tailored in different geometries (very thin cells).

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