

Thin and flexible lithium-ion batteries: investigation of polymer electrolytes

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Abstract

Lithium-ion polymer batteries were investigated. These batteries used microporous PVdF filled by the liquid electrolyte as polymer electrolyte. It has been shown that the conductivity only depends on PVdF porosity, as the contribution of the swollen PVdF structure may be neglected. The loss in conductivity induced by the microporous PVdF is limited while the tortuosity is equal to 1. A shut down effect was demonstrated. Thin and flexible batteries based on this polymer electrolyte meet the specifications of GSM application.

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1. Introduction

The project developed by SAFT, in collaboration with Atofina, aims to market a new lithium-ion polymer battery. It uses a microporous separator [1,2] consisting of a high molecular weight polyvinylidene fluoride PVdF Kynar, manufactured by Atofina. Contrary to usual microporous separators such as Celgard, PVdF allows these batteries to be shaped into flexible and thin cells. If Celgard is fairly inert with respect to the liquid electrolyte, microporous PVdF is partly elasticised by the liquid electrolyte. This enables a much better wetting ability of the separator by the liquid electrolyte and a better electrode/electrolyte contact, while preserving the mechanical integrity of the polymeric membrane. In this paper, conductivities of these microporous separators are compared both to those of liquid organic electrolytes and to those of dense PVdF swollen by the same electrolyte. Special attention was also paid to safety aspects, in particular to the thermal behaviour of the set liquid electrolyte/microporous PVdF. Flexible lithium-ion batteries based on these separators were prepared and their performances were compared to those required for the GSM application.

2. Experimental details

2.1. Preparation of the PVdF microporous membrane

A 100 μm thick microporous PVdF-membrane was prepared as follows: 3.4 g of PVdF (301F Atofina) were dissolved in 16.6 g acetone at 60 °C in a hermetically closed vessel. The solution was then cast in a thickness of approximately 500 μm on an aluminium support, put into a bath made of pure ethanol for 45 s and dried, first at room temperature, then at 60 °C over night.

2.2. Preparation of the dense PVdF

The dense PVdF membranes were obtained by hot pressed PVdF powder (205 °C) and polymer film fast tempering. It was the only way to obtain easily, and in a reproducible way, true dense membranes, i.e. without any porosity.

2.3. Polymer electrolyte processing in battery

The microporous polymer electrolyte was prepared by phase inversion and processed according to the following steps: (i) laying down of an acetone solution of PVdF on the negative electrode and immersion in ethanol to generate the porosity, (ii) hot-pressing of the previous set

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(PVdF + negative) on the positive electrode, (iii) addition of the liquid electrolyte, i.e. 1 M LiPF₆ in EC, DMC, DEC (2/2/1).

The thickness of the microporous PVdF electrolytes was adjusted to between 35 and 50 μm. After the filling by the liquid electrolyte the pouches were closed and the electrical connections were inserted.

2.4. Liquid electrolyte

The “battery grade” solvents EC, DMC and DEC (<0.0003% H₂O) from Merck were dried over an activated molecular sieve (0.3 nm) before use (<0.0005 H₂O). The LiPF₆ “battery grade”, manufactured by Merck was used as received.

2.5. Positive electrode

The positive electrode consists of lithiated cobalt, carbon powder to ensure the electronic conductivity and PVdF binder to improve the mechanical characteristics.

The mixture is cast in *N*-methyl pyrrolidone (NMP) on one face of a 20 μm thick aluminium foil. The surface of the positive electrode is 4.1 cm × 8.1 cm = 33.2 cm². The calculated capacity is 106 mAh, i.e. 3.2 mAh/cm² for a cycling between voltage limits of 4.1–3.0 V.

2.6. Negative electrode

The negative electrode is based on a mixture of two carbons, namely, MCMB and graphite. The mixture of active material, additives and water is laid down on one face of a 12 μm thick copper foil. The surface of the negative electrode 4.3 cm × 8.3 cm (35.7 cm²) is higher than that of the positive. The surface capacity calculated for the negative electrode 3.4 mAh/cm² exceeds sufficiently that of the positive one.

2.7. Ionic conductivity measurements

The conductivity of the liquid electrolytes was measured using a Tacussel cell with a geometrical factor, thickness/surface, close to 1 cm⁻¹. Conductivity measurements of the dense or microporous PVdF membranes were carried out in button type coin cells (CR 2430) with stainless steel electrode of small diameter (6 mm) in order to increase the measurement accuracy. All measurements were carried out under argon by impedance spectroscopy over the frequency range 5 Hz–13 MHz, using an HP 4192A analyser.

2.8. DSC

Melting phenomena were studied using a Netzsch DSC. In order to prevent solvent evaporation, Hermetic Setaram stainless steel pans with an aluminium vent were used for the study with volatile solvents. The heating rate was 10 °C/min.

3. Results and discussion

3.1. Conductivity measurement

The conductivity of the set microporous PVdF/liquid electrolyte depends on the one hand on the polymer porosity and its wetting by the liquid electrolyte and on the other hand on the liquid electrolyte. Besides, as PVdF is swollen by liquid organic electrolytes, it may be assumed that the overall conductivity of microporous PVdF filled by the liquid electrolyte results both from the liquid filling the porosity and from the PVdF structure swollen by the same electrolyte. For that reason all these aspects were carefully investigated.

3.1.1. Liquid electrolytes

The conductivity measurements of several liquid electrolytes were performed at the same salt concentration, i.e. 1 M LiPF₆ in the temperature range –20 to 60 °C (Fig. 1). Due to its high permittivity, solvent mixtures consisting of EC provide the more conductive electrolytes. Among those, the electrolyte based on the ternary solvent mixture (EC/DMC/DEC) (2/2/1) gives the highest conductivities, in particular with respect to electrolytes consisting of pure solvent or of binary solvent mixtures. Thus, DEC addition especially improves the low temperature performances of the electrolyte (+17% at –10 °C and +7% at 20 °C) with respect to EC/DMC (1/1) electrolyte and prevents electrolyte recrystallization at –20 °C.

On the other hand, the binary mixture EC/DEC (1/1) provides conductivities which are significantly lower than EC/DMC (1/1). Besides DEC 1 M LiPF₆ is half as conductive as DMC 1 M LiPF₆. As both linear carbonates have roughly the same permittivity and donor numbers, these results must be related to the higher viscosity of DEC.

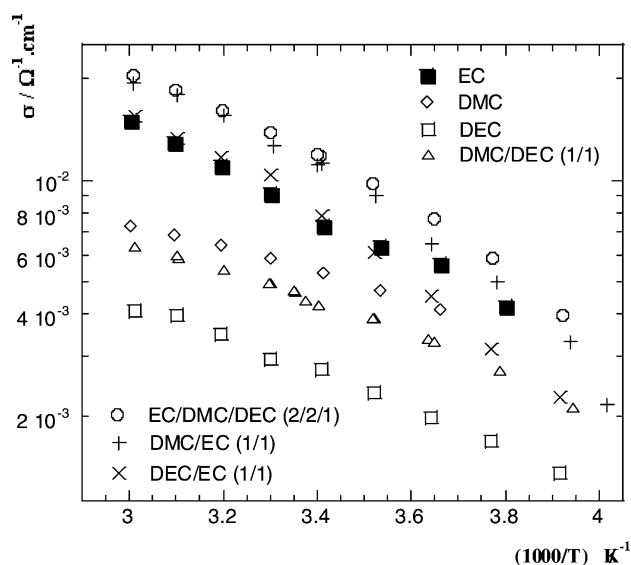


Fig. 1. Conductivity comparison of liquid electrolytes, according to solvent composition (1 M LiPF₆).

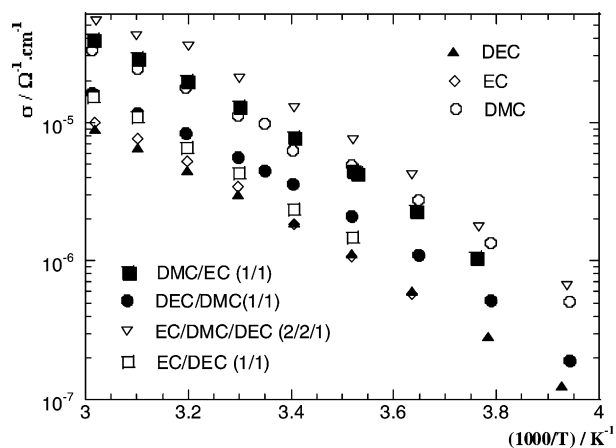


Fig. 2. Conductivity comparison of dense PVdF swollen by several electrolytes (1 M LiPF₆).

3.1.2. Dense PVdF membranes

In order to value the conductivity contribution of the PVdF structure, dense PVdF membranes swollen by several one molar solutions of LiPF₆ were investigated. Swellings were performed at 60 °C during times which were sufficiently long to reach the swelling equilibrium. Poor conductivities were obtained (Fig. 2) with only 5×10^{-5} S/cm at 60 °C for the best electrolyte.

This can be related to two factors (i) the relatively low swelling ratio of the PVdF membrane in these solvents, the higher swelling ratio in weight, 1.42, being reached with DMC/LiPF₆ (ii) the low salt content in the swollen membrane. Thus, LiPF₆ concentration in the swollen membrane only reaches 0.2 mol/l although the salt concentration in the swelling solution is 1 M. This must be related to the bad affinity, highlighted by spectroscopic studies, between PVdF and LiPF₆ [3,4]. Conductivities of the swollen microporous membranes do not particularly depend on the conductivity of the swelling liquid electrolyte, but rather on the swelling ratio. The membranes swollen in molar solutions of LiPF₆ in DMC, in mixtures DMC/EC and in the ternary mixture give higher conductivities than those swollen in DEC or EC/DEC because of the weak swelling ability of DEC [5,6].

From these results the contribution to conductivity of PVdF structure swollen by the electrolyte may be neglected with respect to that of the porous volume filled by the liquid electrolyte.

3.1.3. Microporous PVdF membranes

The PVdF membranes obtained by phase inversion have a well-defined and reproducible porous structure. The porosity, measured by mercury porosity, is close to 70% with a pore diameter distribution centred on 0.64 μm. Fig. 3 shows the Arrhenius conductivity plots of microporous membranes swollen with 1 M solutions of LiPF₆ in the ternary mixture and in EC/DEC (1/1) and those of the same liquid electrolyte free of the separator. Great attention was paid to the reproducibility of the conductivity measurements and, in

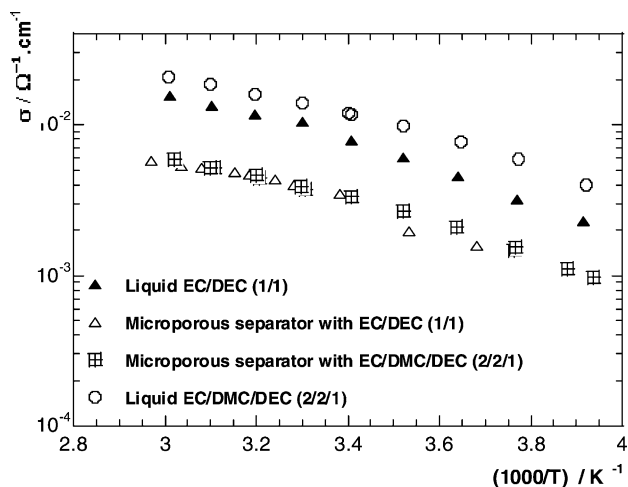


Fig. 3. Conductivity comparison of microporous PVdF filled by several electrolytes.

order to minimize the uncertainties, electrodes of low diameter were used. The conductivity loss induced by the microporous membrane incorporation depends on the liquid electrolyte used.

Assuming that PVdF structure does not significantly contribute to the conductivity, this loss is generally associated both to the reduction in the effective surface of the electrode and to tortuosity effects.

Pulse Field Gradient NMR was used to determine anion, cation and solvent diffusion coefficients, both in the liquid electrolytes and in the microporous membrane filled by these electrolytes, details will be given elsewhere [7]. A decrease, in the same proportion, of all the diffusion coefficients was observed in the polymer electrolyte. We may assume that the conductivity loss is mainly due to the decrease in diffusion coefficients and, therefore, that the tortuosity is close to 1.

The decrease in diffusion coefficients may be attributed to solvent/PVdF interactions.

The extent of the conductivity loss depends on the liquid electrolyte. It is lower with DEC/EC (1/1) (loss factor: 2.45) than with the ternary mixture (loss factor: 3.6). This may be related to the weaker affinity of PVdF for the former, highlighted by a lower polymer swelling [5,6]. The microporous membrane swollen by EC/DEC (1/1) LiPF₆ 1 M gives similar conductivities above +20 °C to that swollen by the ternary mixture. At low temperature, the conductivity provided by this electrolyte is lower, probably in relation to the higher viscosity of EC and DEC solvents.

Some influence of average pore size must be emphasized (Fig. 4). For the same porous volume, conductivity is smaller for the smaller pores, which might result from an increase in tortuosity and/or from interactions on a greater polymer solvent/interface.

3.2. Shut down effect

Shut down effect is the result of the plugging up of the pores which leads to an abrupt conductivity drop.

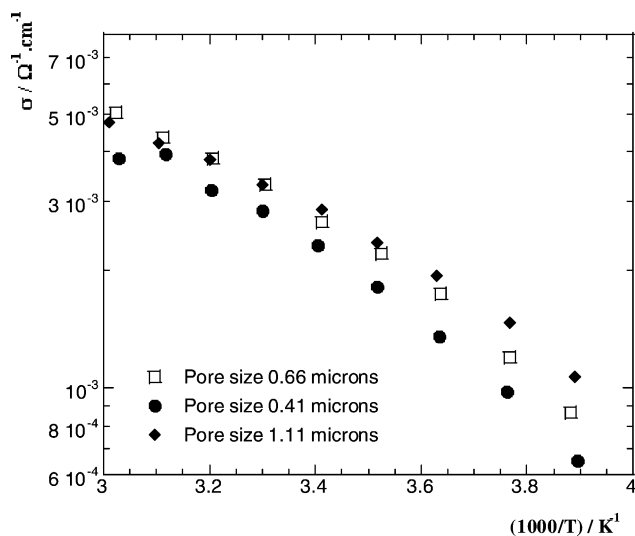


Fig. 4. Conductivity of microporous PVdF electrolyte according to the pore size.

This phenomenon is well-known for polyolefin separators. It has a good safety impact because it limits the temperature increase in the battery in the case of an exothermal incident, e.g. a short-circuit. Indeed, as the porosity vanishes, the internal resistance increases sharply, thus decreasing the current.

This study was undertaken jointly in DSC, conductivity and SEM. DSC shows that the microporous membrane swollen by the ternary electrolyte, starts to melt at 75–80 °C. For the microporous membrane free of solvent, the melting point is much higher and begins at 141 °C. Our study of dense PVdF membrane shows a continuous decrease in the melting point of the crystalline phase with the increase in the swelling ratio. Even if the solvent swelling affects the amorphous phase first the melting point and the melting enthalpy are greatly modified.

The melting point depression may be caused either by, a decrease in the lamellae thickness, or a more favourable energetic balance in the presence of solvents to the fusion.

To follow the porous structure evolution during storage at high temperature, SEM was performed both on the surface and section of the membrane (Fig. 5). The microporous samples were stored for 2 weeks at 80 and 90 °C in the presence of a large excess of the ternary electrolyte (a factor of 2 with respect to the porous volume). The plugging up of the porosity, which occurs at 80 °C, both at the surface and in the bulk of the membrane, induces a decrease in the membrane thickness. But this phenomenon depends greatly on the amount of solvent and, when the solvents are not added in excess, the porosity vanishes at a higher temperature, close to 100 °C.

This plugging up can perform a beneficial shut down effect as in polyolefin separator. The evolution of the ohmic resistance of a microporous membrane was followed during a rapid increase in temperature. Resistance was first followed by increasing temperature as long as the resistance remained stable. Then, when the resistance increased significantly, the temperature was kept constant and the resistance evolution with time was followed. The membrane shut down effect was observed roughly at 135 °C (Fig. 6). The same experiments were carried out on several membranes. A good agreement was obtained, as the difference between two shut down temperatures did not exceed 5 °C. To increase the shut down temperature, one possibility is to decrease the porosity volume. By hot pressing the initial membrane, between two spacers, we decrease its porosity. Thus, a porosity close to 40% was obtained from an initial porosity of 70%. It results in a significant increase in the shut down temperature, the sharp increase in resistance being observed at 150 °C. This may be related to a decrease in the amount of solvent filling the porous volume and available to dissolve the membrane. This shut down temperature is close to

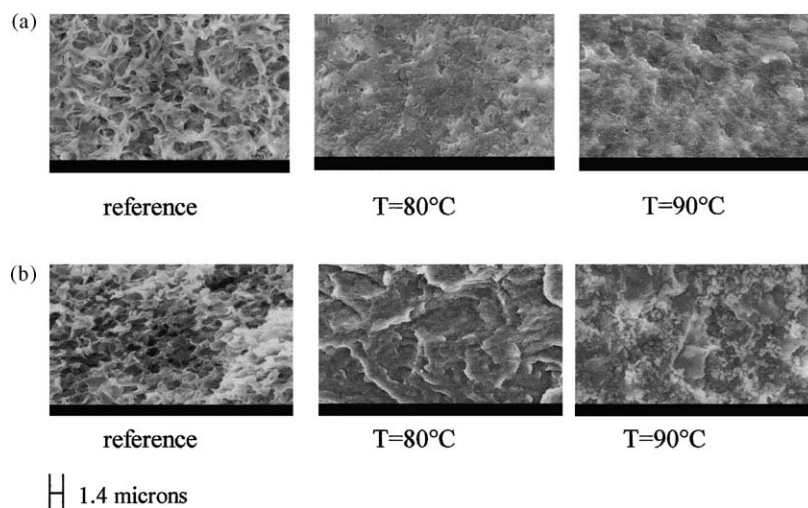


Fig. 5. SEM of microporous PVdF stored at 80 and 90 °C, for 2 weeks, in presence of a ternary liquid electrolyte excess: (a) surface of the membrane; (b) bulk of the membrane.

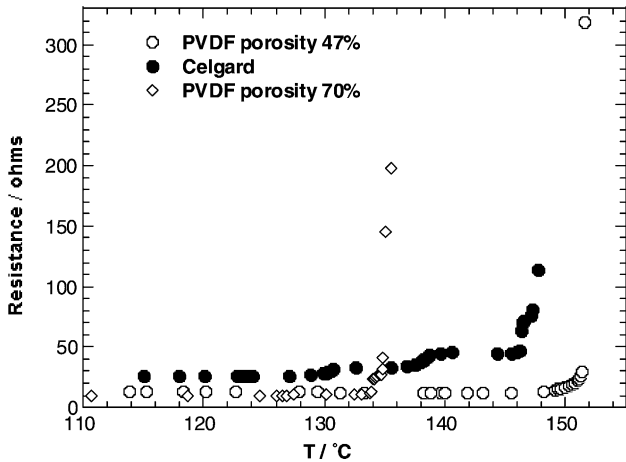


Fig. 6. Comparison of the shut down temperature of Celgard and microporous PVdF.

that—145 °C—of separators based on apolar polyolefins (polyethylene/polypropylene/polyethylene copolymers). Due to the poor affinity between these polyolefins and polar carbonate solvent the melting point of microporous polyolefin membrane is indeed unaffected by the solvent mixtures.

3.3. Battery performances

3.3.1. Battery charge

When the charge is carried out at 4.1 V, and C rate, 82% of the capacity is recovered after 1 h (Fig. 7).

3.3.2. Discharge at different rates

The capacity at slow discharge rate C/5, i.e. 20 mA ranges between 93 and 115 mAh. The discharge ability is ensured

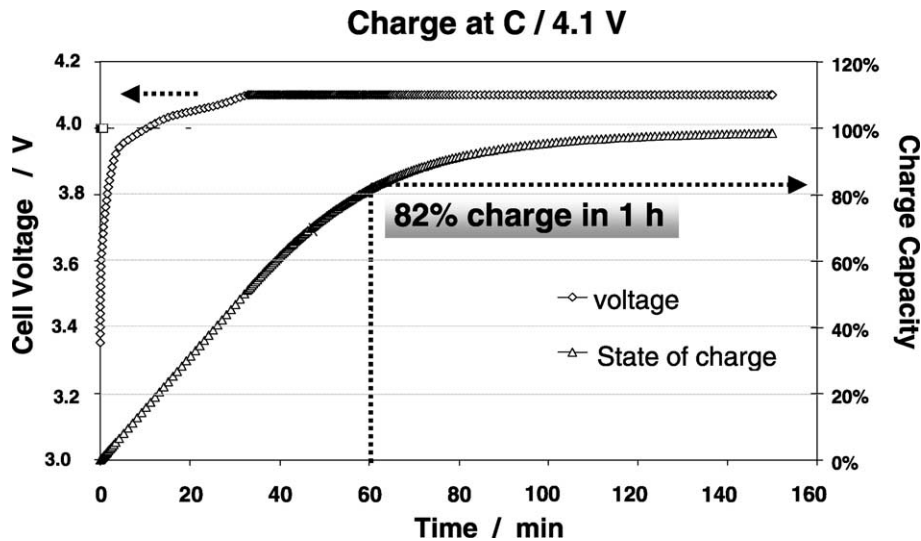


Fig. 7. Curve charge of lithium-ion battery based on microporous PVdF.

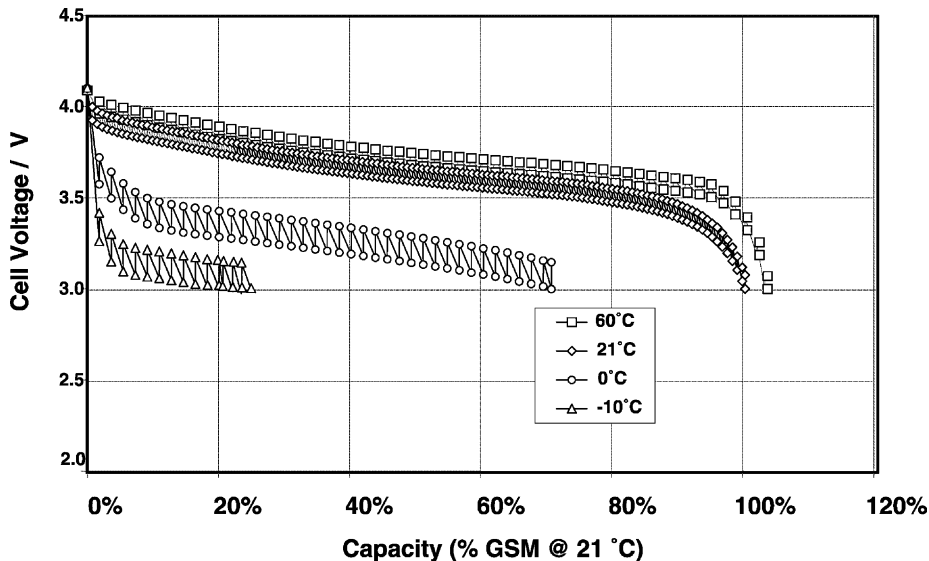


Fig. 8. GSM discharge curves at different temperatures.

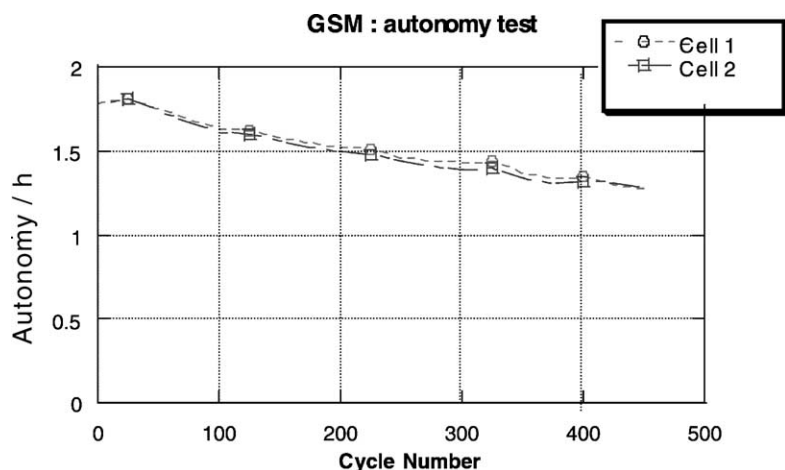


Fig. 9. Evolution of the battery autonomy with the number of cycles.

up to the continuous discharge rate C , i.e. 100 mA. In the best case, a 6% capacity loss is obtained. At $2C$, i.e. 200 mA, a significant decrease both in voltage and capacity must be emphasized. A 40% loss in capacity is observed with respect to the $C/5$ discharge rate. This phenomenon is usual in lithium-ion batteries. Indeed, beyond some current density, the diffusion limit of lithium between deintercalation and intercalation sites is reached, resulting in a decrease in the battery voltage. As $0.4C$ is a discharge rate similar to that of a cellular phone, limitations related to lithium diffusion should not occur.

3.3.3. Discharges at different temperatures

Discharge curves are shown in Fig. 8. GSM discharges are pulsed discharges, consisting in a sequence of peak current and a baseline current, which depend on cellular phone manufacturers. In this paper, a $2C$ peak current was selected for 0.5 ms, followed by a $C/2$ baseline current for 4.5 ms. The average current is roughly $(2/3)C$.

3.3.4. Specific energy

The specific energy of one monostack (in pouch) is 95 Wh/kg. The internal resistance of each monostack ranges between 360 and 860 m Ω . When 6–7 monostacks are assembled in parallel to build a battery of 6–700 mAh, an internal resistance of 60 m Ω for a weight of 18–19 g. Thereby a specific energy of 130 Wh/kg is reached.

3.3.5. Autonomy evolution with cycling

Fig. 9 plots the autonomy evolution, for a 2.7 cut-off voltage. The specifications of GSM application in terms of autonomy are 1.5 h initially and 1.2 h after 400 charge/discharge cycles.

The experimental data show an initial autonomy of 1.78 h for both cells 1 and 2 and, respectively, 1.35 and

1.32 h after 400 cycles, therefore exceeding the GSM specifications.

4. Conclusion

Polymer electrolytes based on microporous PVdF provide a good compromise between conductivity and mechanical properties. The increase in resistivity, with respect to pure liquid electrolyte, caused by using a microporous PVdF separator is lower than a factor of 4. The separator tortuosity is equal to 1. This separator gives a shut down effect, which depends on the porous volume. The battery performances allow these batteries to be used in several applications. Low temperature performances, however, remain limited.

Acknowledgements

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References

- [1] F. Boudin, X. Andrieu, C. Jehoulet, I.I. Olsen, J. Power Sources 82 (1999) 804.
- [2] F. Boudin, Thesis, University of Paris VI, Paris, 1998.
- [3] P. Mustarelli, E. Quartanone, C. Capiglia, C. Tomasi, A. Magistris, Solid State Ion. 122 (1999) 285.
- [4] M.M.E. Jacob, A.K. Arof, Electrochim. Acta 44 (1999) 2909.
- [5] J. Saunier, Thesis, INP, Grenoble, 2001.
- [6] J. Saunier, F. Alloin, J.-Y. Sanchez, B. Barrière, J. Polym. Sci. Phys., submitted for publication.
- [7] J. Saunier, W. Gorecki, F. Alloin, J.-Y. Sanchez, J. Phys. Chem., submitted for publication.