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Performance of Solupor[®] separator materials in lithium ion batteries

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Abstract

It is shown that Solupor is an attractive material for lithium ion batteries. The key properties of low tortuosity, high strength and puncture resistance, and excellent wettability combined with the high rate capability and low-temperature performance are due to the UHMWPE network structure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A separator in a battery is an inactive, although prerequisite material. Despite the fact that the theoretical battery capacity is determined by the amount of active materials, the practical capacity is strongly dependent on the C-rate and the temperature during the charge/discharge procedure. The total design should be considered and much effort has been paid to optimise the percolation in the electrodes with regard to porosity and electronic conductivity, e.g. Doyle et al. [1] and Abraham et al. [2].

However, the measured battery capacity can also vary noticeably for batteries containing different separator materials. Apart from important properties like thickness, puncture resistance, chemical resistance and thermal-shutdown behaviour (e.g. Laman et al. [3], Japanese Patent [4]), the key properties of separator materials are also porosity and permeability.

Some studies have been conducted to characterise these properties for commercial separators, e.g. Venugopal et al. [5], or relate the membrane resistance to the Gurley value for Celgard separators (Callahan et al. [6]). Other studies have explored new materials like composite cellulose separators, Kuribayashi [7], or combinations of polyolefin separators with solid polymer electrolyte (Abraham et al. [8]).

In this study, a series of DSM Solupor[®] separator materials, which vary in permeability, are compared with a series

of commercially available separators. Solupor is a micro-porous polyethylene separator material composed of a unique combination of randomly oriented thick and thin fibrils of UHMWPE (ultra high molecular weight polyethylene). Solupor is produced by DSM Solutech. This company develops and manufactures films for high-tech applications based on proprietary UHMWPE gel technology (extrusion and bi-axial stretching).

The separators will be compared in a rate capability test and a cycling test in the temperature range -10 to $+30^{\circ}\text{C}$. These measurements are vital for the validation of separator materials in lithium ion batteries.

2. Experimental

A series of test cells have been made using CR2320 coin cells (Hohsen Corp.). All metal cell parts were made from SUS304 steel. Cathodes and anodes were punched out of the coated active materials with a typical diameter of 14 mm. The cathode material was LiCoO_2 on aluminium (90% active material, PVDF binder) and the anode material was graphite on copper (90% active) or 0.3 mm lithium ribbon (Chemetall Foote Corp.). The electrodes were dried overnight at 80°C under vacuum. The separators were punched out with a diameter of 21 mm. The electrolyte was 1 M LiPF_6 in EC/EMC 1:2 volume (Mitsubishi Chemical).

The assembly of the cells was done in a helium-filled glove box (water content < 20 ppm). The electrodes and the separators were separately impregnated with electrolyte using a standard procedure including a vacuum step. The

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stacking of the cells was always: can, LiCoO₂ (~2 mAh), separator, gasket (pp), anode, Ø 17 mm × 0.5 mm pressing plate (SUS304), wave-spring and cap. After stacking, the cells were closed using a CR2320 crimper (Hohsen Corp.).

Prior to the cycling tests, an impedance plot was recorded for the fresh cells. The frequency range was 10⁵–10¹ Hz with a 20 mV signal amplitude using a Solartron 1260 Gain/Phase Analyser.

The cells were cycled in a Vötsch VT4004 climate room using a Maccor S4000 tester. For the rate test, the cells were kept at a constant temperature of 30°C. Charging and discharging was done with a constant current step followed by a constant voltage step. The measured capacities in the constant-current discharge step were used to compare the different cells. The current densities were varied between 0.3 and 2.4 mA/cm² (~C/7–1C rate) with cut-off voltages of 3.1 and 4.2 V. The constant voltage steps were used to make sure that the cells started at the same composition. The constant voltage steps were ended when the current dropped below 100 µA.

For the temperature test, the cells were cycled with a fixed current density of 0.6 mA/cm². The temperature was varied between –10 and +30°C in steps of 10°C. After changing the temperature, the cells were allowed to equilibrate for 1 h.

3. Results

During the construction of the cells, it was clear that the uptake of electrolyte in the pores of the various materials was good but clearly faster in the Solupor separators.

The Nyquist impedance plots of four typical fresh cells show the classical picture of a cell with one ionically conducting electrode and one blocking electrode (see

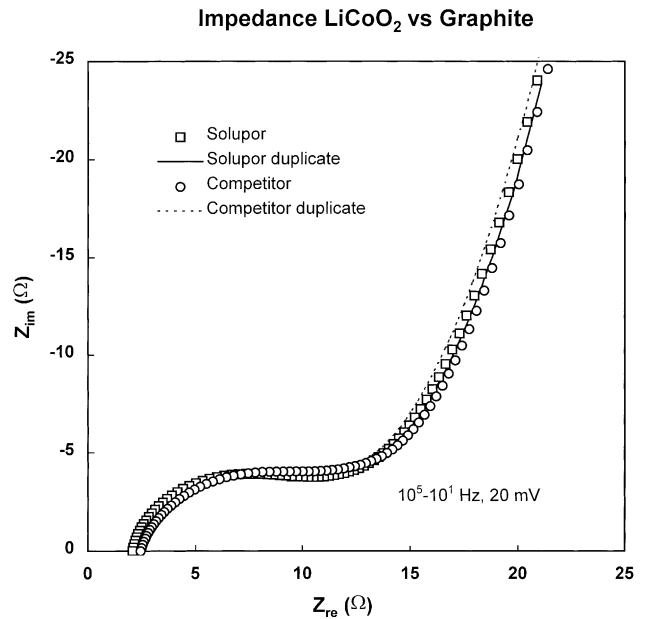


Fig. 1. Nyquist plots of typical fresh cells of LiCoO₂ vs. graphite.

Fig. 1). At the high frequency part, a pure resistance, originating in the separator/electrolyte combination, is visible. This resistance varies for the separators tested and is about 2.0–2.5 Ω in these cells. The semi-circle at medium frequencies can be attributed to the LiCoO₂ electrode and the steep increase at low frequencies to the empty graphite electrode. The Nyquist plots also show that the cells could be made quite reproducible.

Fig. 2 shows the rate capability of the cells at 30°C in the form of the discharge capacity in the constant current regime. At low rates, the performance of the cells with different separators is quite similar. At rates of 2.4 mA/cm²

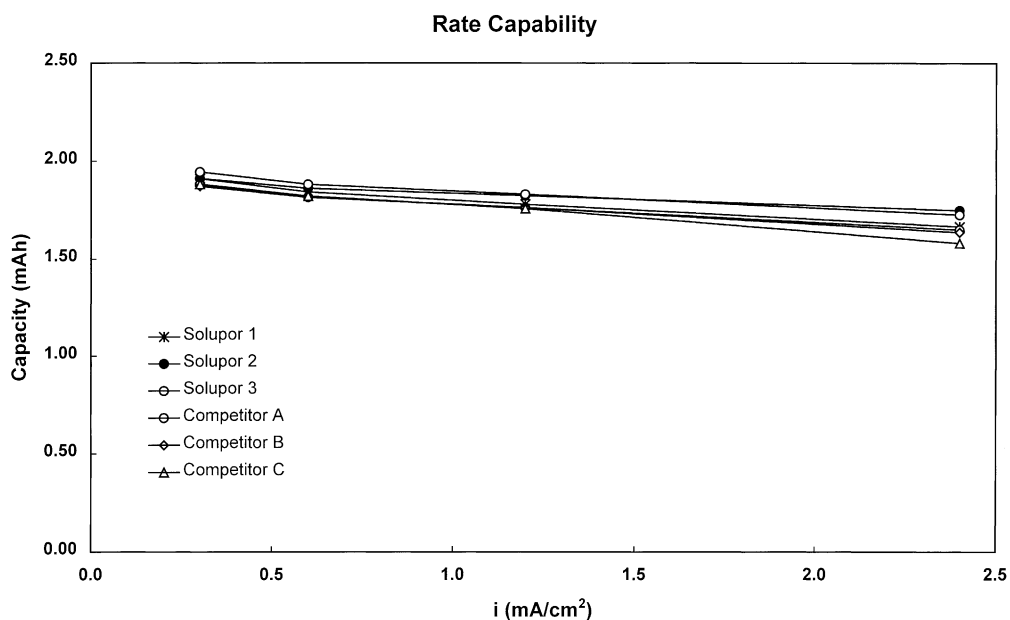


Fig. 2. The rate capability of cells with different separators. The capacity is determined from the constant-current discharge step.

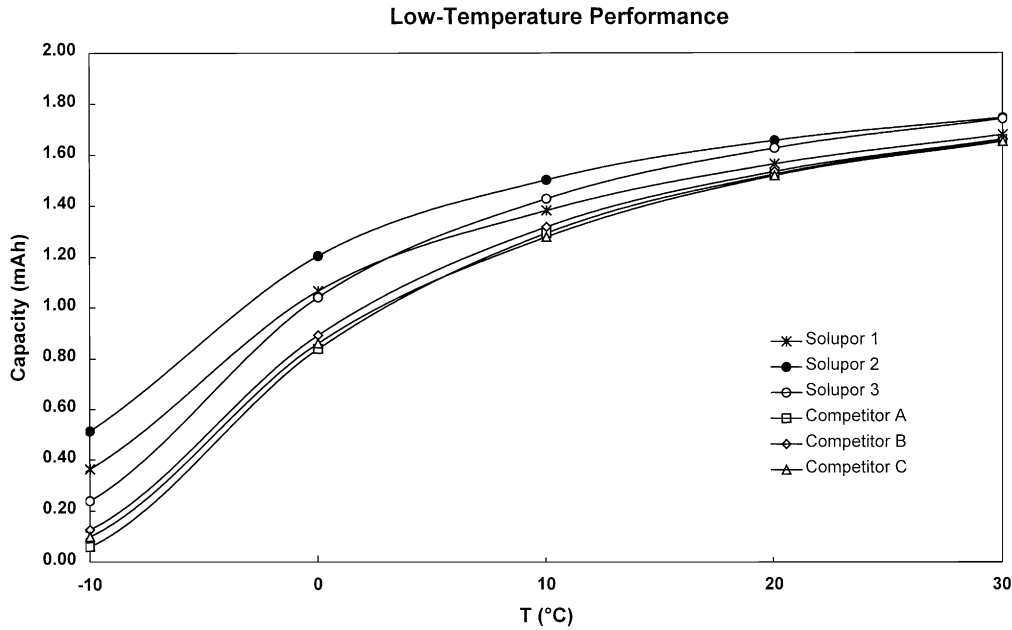


Fig. 3. The temperature performance of cells with different separators. The capacity is determined from the constant-current discharge step.

and higher, the capacities obtained in the cells with Solupor are slightly higher.

Fig. 3 shows the performance of the cells in the temperature range -10 to $+30^{\circ}\text{C}$ in the form of the discharge capacity in the constant current step. It is clear that lowering the temperature has a pronounced negative effect on the performance of the cells. Fig. 3 clearly demonstrates that the Solupor materials perform much better than the competitor materials at temperatures below 10°C . The group of competitor materials, having similar microstructures and porosities, show an almost identical behaviour.

The results of the rate capability test and the temperature test show a decreasing capacity at high rates and at low temperatures, indicating a kinetic or transport-limited effect. Obviously, the resistance of the active materials and the electrolyte increases towards lower temperatures. The only difference in the cells, however, is the separator material, thus the effects can only be attributed to the differences in these materials.

The ‘measured’ capacity is determined by the area under the charge/discharge curve. The boundaries of this area are fixed by the cut-off voltages and the voltage profile. Therefore, an increase of the cell impedance will result in loss of capacity. The differences in the performance (and impedance) of the cells cannot simply be explained by the small variations in the ‘electrolyte’ resistance as measured in the Nyquist plots. The (ohmic) contribution of the IR drop at a maximum current of ~ 4 mA and a resistance of 2.5Ω is only 0.01 V. The effect of this drop on the capacity determining cut-off voltages, especially the high cut-off voltage of 4.2 V, is negligible.

However, the transport of lithium ions through a separator, and therefore the current, will be determined by the

tortuosity or effective path-length through the pores. The ASTM Gurley number is a good indication of the permeability of a membrane. It has been shown for Celgard[®] that the forementioned membrane resistance can be related to the Gurley number (Eq. 15 in [6]),

$$R_m A = \frac{r_{\text{elec}}}{5 \times 18 \times 10^{-3}} t_{\text{Gur}} d \quad (1)$$

where R_m is the membrane resistance (Ω), A the membrane area (cm^2), R_{elec} the specific electrolyte resistance ($\Omega \text{ cm}$), t_{Gur} the Gurley number (10 cm^3 , air, 2.3 mmHg), d the thickness and $5 \times 18 \times 10^{-3}$ a scaling factor. Experiments are in progress to find a similar relationship for the network structure of the Solupor materials.

The Gurley number is proportional to τ^2 , where τ is the tortuosity. Table 1 makes clear that the Solupor materials have much lower Gurley numbers (and tortuosity), and therefore a more ‘open’ microstructure than the competitor materials.

The limiting current through a cell can also be linked to the tortuosity, as has been shown by Abraham et al. [2]. For highly porous Celgard K292, with $\tau = 1.7$ based on porosity, a limiting current I_1 for the cell $\text{Li} // \text{LiCoO}_2$ can be

Table 1
The properties of the Solupor and competitor separator materials

Property	Solupor			Competitor		
	1	2	3	A	B	C
Thickness (μm)	28	29	35	30	25	30
Puncture (g)	510	490	440	600	350	170
Gurley (s/50 ml)	120	100	60	340	270	188
Pore size (μm)	0.07	0.07	0.09	0.06	0.06	0.06

calculated (Eq. 9 in [2]) as follows:

$$I_l = \frac{2nFCDP}{\tau(1-t_+)l} \quad (2)$$

where F is the Faraday constant, C the electrolyte concentration, D the diffusion coefficient of Li^+ in the electrolyte, P the porosity, t_+ the transference number of the electrolyte, and l the inter-electrode distance including the porous electrodes.

A low tortuosity in Solupor therefore allows high limiting currents. Since the Solupor 2 sample performs the best, while the Solupor 3 sample has the lowest Gurley number, there is probably an optimal morphology for the Solupor network structure. The pore-size distribution and the surface structures are important parameters as well.

4. Conclusions

The combined results of the fast wetting with several electrolyte systems, the high rate capability and the high performance at low temperatures have to be attributed to the open, three-dimensional network structure with low tortuosity. The good performance combined with a high puncture resistance and small pore sizes render the Solupor separators interesting for the application in lithium ion batteries.

The experiments are extended to a wider range of Solupor and competitor materials with the goal to relate the experimental results more fundamentally to the morphology of the materials. The industry ‘standard’ thickness of 25 μm can easily be reduced to 20 μm or lower while keeping a strong material and saving volume and expensive electrolyte. Currently, rate-capability tests to higher C-rates and thermal-shutdown experiments with a wider range of electrolyte systems are in progress.

References

- [1] M. Doyle, J. Newman, A.S. Cozdz, C.N. Schmutz, J.-M. Tarascon, J. Electrochem. Soc. 143 (1996) 1890.
- [2] K.M. Abraham, D.M. Pasquariello, E.M. Willstaedt, J. Electrochem. Soc. 145 (1998) 482.
- [3] F.C. Laman, M.A. Gee, J. Denovan, J. Electrochem. Soc. 140 (1993) L51.
- [4] Japanese Patent No. 2642206, Asahi Chemical Industry Co., Ltd.
- [5] G. Venugopal, J. Moore, J. Howard, S. Pandalwar, J. Power Sources 77 (1999) 34.
- [6] R.W. Callahan, K.V. Nguyen, J.G. McLean, J. Propst, D.K. Hoffman, in: Proceedings of the 10th International Seminar on Primary and Secondary Battery Technology and Application, 1–4 March 1993.
- [7] I. Kuribayashi, J. Power Sources 63 (1996) 87.
- [8] K.M. Abraham, M. Alamgir, D.K. Hoffinan, J. Electrochem. Soc. 142 (1995) 683.