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## SECONDARY LITHIUM CELL: SEPARATORS COMPATIBLE WITH ELECTROLYTE SOLUTION BASED ON CYCLIC ESTERS

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*Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.*

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To overcome the incompatibility between microporous polypropylene separator and electrolyte solutions based on cyclic esters, three methods of preliminary impregnation of the separator with electrolyte solution, without using surface active agents, are investigated. Values of the specific resistance of the separator, measured in 1M solutions of lithium salts in propylene carbonate, depending on the method of preliminary treatment, are obtained. Experimental data from the tests of secondary lithium button cells supplied with pretreated separators are presented. It is concluded that the pretreatment methods discussed can be used successfully. The best results are obtained by thermal pretreatment with the basic solvent.

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In the last decade a number of authors have shown the excellent properties of the microporous polypropylene separator for secondary lithium cells<sup>1,2</sup>. Its high resistivity to lithium dendrites combines well with a good ionic conductivity. It is also known that the lithium electrode displays high reversibility when the electrolyte solution is based on cyclic esters, such as propylene carbonate and ethylene carbonate<sup>2-6</sup>. The use of such solutions, however, usually requires a glass separator, since the interaction of the microporous polypropylene separator with the solvents of the cyclic esters group causes an inadmissibly high resistance of the cell. Our preliminary investigations showed that the main reason for this is the liophobic behavior of the polypropylene separator with respect to the cyclic esters, whereby the electrolyte solutions based on them practically cannot penetrate into the separator pores.

A classic solution in this case is the preliminary treatment of the separator with surface active substances. A separator for alkaline cells, pretreated with surface active agents which can be soaked well by the cyclic esters, is available from the Celanese Corporation. Unfortunately the lithium electrode is very sensitive even to traces of impurities in the electrolyte. The introduction of surface active components

in the system may have either a positive or a negative effect on the lithium electrode and cell cycling ability. However, this effect can be cleared up after a comparison with cells supplied with well soaked separators which are not pretreated with surface active agents.

The aim of the present work is to look for methods of preliminary treatment of the microporous polypropylene separator, which will make it compatible with the cyclic esters without using surface active substances. The following approaches were used: (i) preliminary deposition of a thin layer of the lithium salt, used in the cell electrolyte solution, on the surface of the separator pores; (ii) preliminary deposition of a thin layer of the basic electrolyte solvent on the surface of the separator pores; (iii) preliminary thermal treatment of the separator with the basic electrolyte solvent.

### EXPERIMENTAL

Samples of the Celgard 2400 microporous polypropylene separator with a 25 mm diameter, produced by the Celanese Corporation, were preliminary treated by one of the methods described below:

(i) The separator sample was treated with a solution of the lithium salt, used in the electrolyte of the designed electrochemical cell, in a suitable volatile nonaqueous solvent. Solvents towards which the polypropylene separator is lyophilic can be a matter of choice. The separator was preliminary impregnated with this solution. Then the volatile solvent was evaporated under vacuum at a suitable temperature, whereby the salt precipitated on the surface of the separator pores. The volatile solvent was selected since most salts appropriate for lithium cells have unsatisfactory thermal stability. Furtheron the pretreated sample was kept for 24 h in a standard electrolyte which was a 1M solution of the same salt dissolved in propylene carbonate. Then the sample was transferred either to a conductometric cell for measuring its specific resistance or to a button cell for testing its electrochemical behavior. Two systems were tested:  $\text{LiAsF}_6$  in tetrahydrofuran (THF), whereafter the solvent was evaporated from the separator under vacuum at  $60^\circ\text{C}$  and  $\text{LiClO}_4$  in acetonitrile (AN) with evaporation of the solvent at  $80^\circ\text{C}$ .

(ii) The separator sample was treated with a mixture of propylene carbonate and a volatile nonaqueous solvent to which the polypropylene separator is lyophilic. Then the volatile fraction was evaporated under vacuum at a suitable temperature. Due to the great difference in the evaporation temperatures of the two components (up to  $174^\circ\text{C}$ ), the main amount of the propylene carbonate was deposited on the surface of the separator pores. Further on the procedure was similar to the one described above. The sample was kept for 24 h in a 1M solution of a suitable lithium salt, whereafter its properties were established. The system THF-PC was investigated.

(iii) The separator sample was treated for 15 min in PC preliminary heated to various temperatures. Then it was transferred to the standard electrolyte and kept there for 24 h.  $\text{LiClO}_4$  and  $\text{LiAsF}_6$  were used for the preparation of the standard electrolyte. After that the sample was tested as in the previous two cases.

The conductometric cell (Fig. 1) consisted of a plastic container (4, 4') and two polished stainless steel electrodes (2, 2') pressing the separator (3) tightly on both sides. After the corresponding pretreatment the separator samples were placed symmetrically between the two electrodes to measure the change of their resistance due to the electrolyte penetration into their pores. The inner space of the cell was a gas phase. The resistance was measured by using the

autobalance universal bridge technique at 1 kHz with automatic compensation of the cell capacity.

The electrochemical button cell (1), shown in Fig. 2, with an electrode working area of  $2.5 \text{ cm}^2$ , comprised a lithium electrode (2) of 0.2 mm thickness, a separator (3) and a 0.25 mm thick cathode (4). The anode was a lithium foil pressed onto an expanded nickel net. The cathode was a mixture of 70% lithium vanadate and 30% teflonized carbon black pressed onto a knitted nickel net. The technology of lithium vanadate synthesis and the cathode preparation have been described earlier<sup>7,8</sup>. Due to the high reversibility of the positive lithium vanadate electrode, the number of cell cycles was determined by the behavior of the lithium electrode under the test conditions.

The solvents obtained from Merck were distilled after drying under a molecular sieve for 48 h. The lithium salts produced by Fluka were used after prolonged (48 h) drying under vacuum at a suitable temperature, 80°C for  $\text{LiAsF}_6$  and 220°C for  $\text{LiClO}_4$ . The procedures were carried out in a glove box with a moisture content maintained below 10 ppm. The moisture content of the prepared electrolytes was below 50 ppm.

## RESULTS AND DISCUSSION

Figure 3 presents the dependence of the separator resistivity on the lithium salt concentration in the solution with which the separator is pretreated. The results for the following cases are demonstrated: upper curve — pretreatment with a solution of  $\text{LiClO}_4$  in AN and measurement of the sample resistivity after 24 h storage in 1M solution of  $\text{LiClO}_4$  in PC; lower curve — pretreatment with a solution of  $\text{LiAsF}_6$  in THF and measurement of the sample resistivity after 24 h storage in 1M solution of  $\text{LiAsF}_6$  in PC. It can be seen that due to the separator pretreatment the resistivity decreases by several orders in comparison with that of the untreated sample. It is also evident that the separator treated with  $\text{LiClO}_4$  in AN has a higher resistivity than that treated with  $\text{LiAsF}_6$  in THF, in spite that the conductivity of  $\text{LiClO}_4$  in PC is higher than that of  $\text{LiAsF}_6$  in PC. A possible explanation of this effect is that THF soaks the polypropylene separator much better than AN, which leads to a considerably better distribution of the lithium salt in the separator pores. Later when the separator is put in the electrolyte, this salt acts as a lyophilic agent.

Figure 4 shows the dependence of the separator resistivity after 24 h storage in 1M solution of  $\text{LiClO}_4$  in PC on the PC concentration in the PC-THF mixture used for the separator pretreatment. This dependence displays a wide minimum, as a result of which at a variation of the PC concentration from 15% to 70% the separator resistivity remains practically unchanged.

The change of the separator resistivity after 24 h storage in 1M- $\text{LiClO}_4$  in PC as a function of temperature of the thermal pretreatment with PC is presented in Fig. 5. It can be seen that when the pretreatment temperature rises above 90°C, the separator resistivity decreases sharply, reaching its steady minimum value over 110°C. These results indicate that at temperatures above 90°C propylene carbonate starts acting as a lyophilic agent with respect to propylene, which effect reaches its

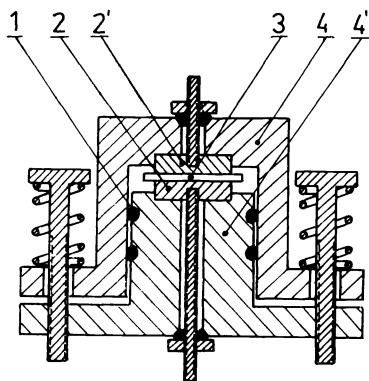


FIG. 1

Schematic diagram of a conductometric cell:  
1 O-rings; 2,2' stainless steel electrodes; 3 separator; 4, 4' plastic container

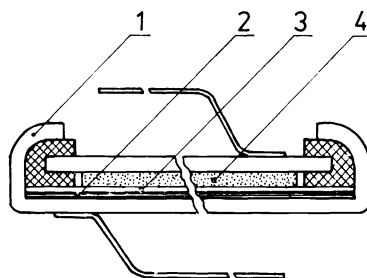


FIG. 2

Secondary lithium button cell design. 1 Cell casing; 2 Li-electrode; 3 separator; 4 cathode

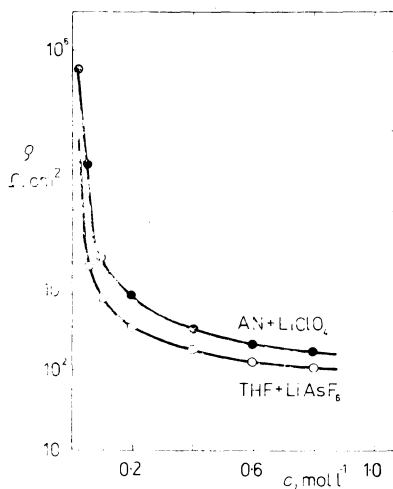


FIG. 3

Dependence of the resistivity of separators pretreated with solutions of  $\text{LiAsF}_6$  in THF and  $\text{LiClO}_4$  in AN on the lithium salt concentration in them

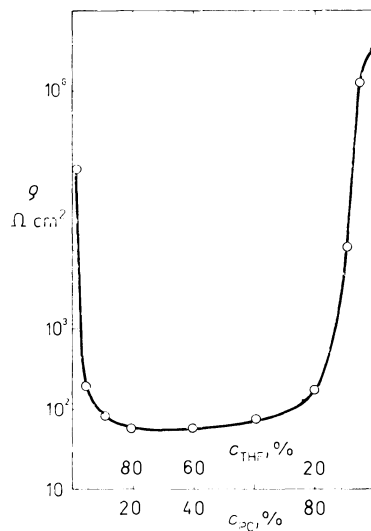


FIG. 4.

Dependence of the resistivity of a separator pretreated with a mixture of PC-THF on the PC concentration in it.  $1\text{M-LiClO}_4$  in PC-THF mixture

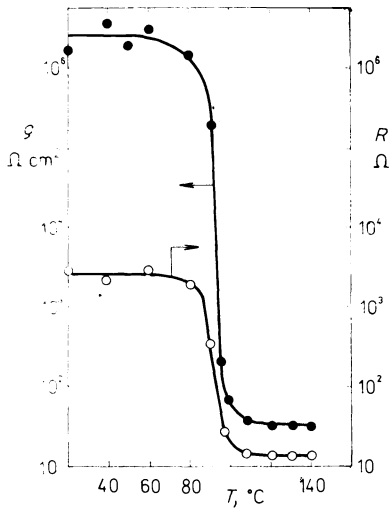


FIG. 5

Effect of the temperature of thermal pretreatment on the separator resistivity,  $\rho$ , and the corresponding button cell resistance,  $R$

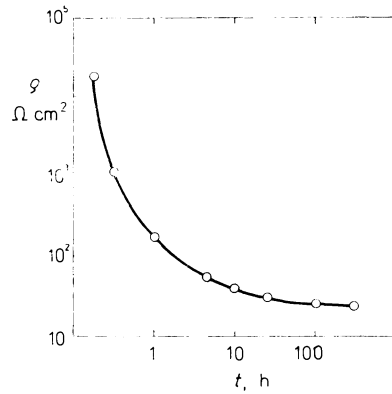


FIG. 6

Dependence of the resistivity of a separator pretreated at  $110^{\circ}\text{C}$  on the duration of its storage in the standard electrolyte solution.  $1\text{M-LiClO}_4$  in PC

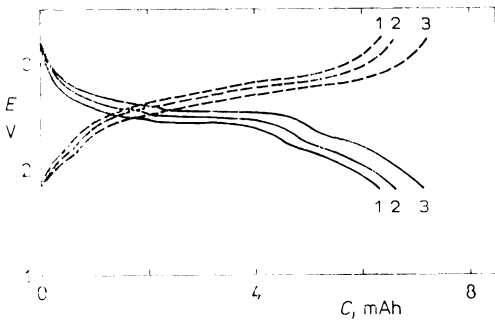


FIG. 7

Charge-discharge curves of lithium-lithium vanadate button cells supplied with separators pretreated by the three methods described: 1 LST; 2 ST; 3 TT. 5th cycle,  $i_{\text{Ch}}$   $0.25 \text{ mA cm}^{-2}$ ,  $i_{\text{DCh}}$   $1 \text{ mA cm}^{-2}$ ;  $1\text{M-LiAsF}_6$  in PC

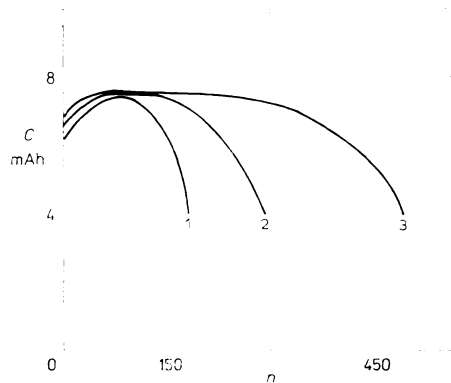


FIG. 8

Influence of the methods of separator pretreatment on the cycling performance (number of cycles  $n$ ) of lithium-lithium vanadate button cells. 1 LST; 2 ST; 3 TT. Otherwise as in Fig. 7

optimum over 110°C. The dependence of the active resistance of a lithium–lithium vanadate button cell on the temperature of the thermal pretreatment with PC, measured by the bridge technique at 1 kHz, is given for comparison in Fig. 5. It can be seen that the two dependences are similar in character, but the change of the cell resistance is remarkably lower, which is probably due to the leakages surrounding the separator and connecting the anodic and cathodic space.

Figure 6 gives the dependence of the resistivity of a separator pretreated at 110°C on the duration of its storage in the standard electrolyte. It can be seen that after 24 h the separator resistivity reaches nearly its steady state value. In practice, the separator in the real cell can obtain the necessary amount of lithium salt from the cell electrolyte, since the separator pore volume is by one order of magnitude lower than that of the electrolyte. Therefore in terms of the above result the cycling of the cell should not be started earlier than 24 h after its assembling.

The fifth cycle was selected for comparison of the charge–discharge curves of cells produced with separators pretreated by the methods described, since during the first several cycles a process of stabilization normally takes place. The effect of the lithium salt treatment (LST), the solvent treatment (ST) and the thermal treatment (TT) on the button cell charge–discharge curves is compared in Fig. 7. The curves are for 1M-LiAsF<sub>6</sub> in THF (LST), a mixture of 30% PC in THF (ST) and thermal treatment at 110°C (TT). As can be seen, in spite of the considerable differences between the separator resistivity in these cases, the corresponding cell capacities differ only by 10–15%.

It was interesting to find out whether the method of separator pretreatment affects the cell cycling ability. The data obtained from the long term cycling of cells supplied with separators pretreated by the three methods described are shown in Fig. 8. It can be seen that while the cell capacities are insignificantly affected by the pretreatment method, the cycling performance of the cell is strongly dependent on it. In the light of these results it can be concluded that the lower reversibility of the cells with separators pretreated by the first two methods is due to the uneven distribution of comparatively stable gas spaces formed in the separator pores or between the electrodes and the separator. The presence of these gas spaces probably leads to irregular current distribution on the electrodes and thus affects significantly the cell cycling ability. Furthermore, these results demonstrate the remarkable effect which the insufficient soaking of the cell components may have on the cycling performance of lithium batteries.

It can be concluded from these findings that the pretreatment methods discussed can be used successfully to make the microporous polypropylene separator compatible with electrolytes based on cyclic esters, without using surface active agents. The best results, however, are obtained by thermal pretreatment with the basic solvent.

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