The effect of 1,2-dimethoxyethane on the storage and performance of lithium cells with MnO_2 and $(CF)_n$ cathodes

E. Frąckowiak [a,*], S. Kuksenko [b]

[a] Institute of Chemistry and Technical Electrochemistry, Poznań University of Technology, ul. Piotrowo 3, 60-965 Poznań, Poland
[b] Institute of Chemistry and Inorganic Chemistry, Ukrainian Academy of Sciences, 32-34 Pr. Palladina, 252142 Kiev, Ukraine

Abstract

The characteristics of lithium cells with MnO_2 and $(CF)_n$ cathodes were investigated for two different electrolyte compositions, i.e., $LiClO_4$/PC + DME and $LiClO_4$/PC. For such lithium cells, the greater loss of long-term storage capacity was found in the case of cells using mixed PC + DME electrolyte. The oxidation process of DME by the cathode elements during the storage period is assumed to be the cause of the capacity loss. In the case of cells using MnO_2 as a cathode, the polymerisation process of the oxidation products of DME on the cathode surface can be also considered. After storage at 45°C, the smaller loss of capacity was found for the cells using MnO_2 as a cathode. The different behaviour of these two kinds of cells during a pulse discharge was also confirmed. © 1998 Elsevier Science S.A.

1. Introduction

One of the basic requirements for lithium cells in view of full scale production is their good ability for the charge retention during a long-term storage. Such a capability can be influenced by three factors, i.e.:

–the chemical stability of the cathode and anode material in aprotic solution;

–the chemical reactivity of the solvent in the presence of the electrode materials;

–the degree of hermetic closing of the cell.

An aggravation of the electrical characteristics at the beginning of storage is connected with a certain chemical degradation of the electrolyte and of the active electrode materials.

The criterion for selection of an electrolyte for lithium cells should be based on various requirements, such as: high conductivity, low viscosity, high permittivity and anticorrosive properties. The most popular electrolyte for lithium cells consists of lithium perchlorate dissolved in the mixture of propylene carbonate and 1,2-dimethoxyethane [1,2]. The two solvents, i.e., 1,2-dimethoxyethane (DME) and propylene carbonate (PC), have quite different properties. DME has a low dielectric constant ($\varepsilon = 7.2$)

and a low viscosity ($\eta = 0.455$ cP), whereas for PC these values are $\varepsilon = 64.4$ and $\eta = 2.503$ cP, respectively. Therefore, the mixture of the two solvents should assure optimum properties.

The effect of this mixed PC + DME organic electrolyte on the electrical characteristics of lithium cells with MnO_2 and $(CF)_n$ cathodes respectively, was investigated during long-term storage. The results are reported in this work.

2. Experimental

Carbon fluoride (type ITG-0-1, Russia) and manganese dioxide (type EDM-2, Georgia) were used for the preparation of cathodes. The cathodes were prepared following the standard technology, i.e., by mixing and pressing the active material together with acetylene black, colloidal graphite and polytetrafluoroethylene suspension. The $(CF)_n$- and MnO_2-based cathodes were thermally treated at 180°C and at 370°C, respectively. Lithium anodes were prepared in disk shape using lithium ribbon (LE-1, Russia). Stainless steel current collectors were used both for positive and negative terminals. Non-woven polypropylene was used as a separator. A quantity of 1.5 M solutions of $LiClO_4$ in either pure propylene carbonate (PC) or in a mixture of propylene carbonate and 1,2-dimethoxyethane

* Corresponding author.

(PC + DME) in the volume ratio 25:75%, were the organic electrolytes. The content of water was less than 70 ppm. PC was preliminarily dried over molecular sieves and then twice distilled under pressure of 2 mmHg and at 72–75°C taking only the middle fraction. DME was distilled under low pressure over metallic lithium and then kept for a few hours in the presence of a liquid Na–K alloy. $LiClO_4$ salt was recrystallised and dried under vacuum using a Fischer gun at 180°C for 40 h.

After assembly, the cells were short-circuited for 1 min to remove the traces of contamination from the electrolyte and to clean the surface of the lithium electrode.

The results discussed in this work refer to cells of type CR 2016 (system Li/MnO_2) and BR 2016 (system $Li/(CF)_n$), having 20 mm diameter and 1.6 mm height.

3. Results and discussion

The electrical characteristics of both freshly assembled cells (after 1 month of technical storage at room temperature) and of cells stored at 45°C, were tested to determine the capacity delivery at a constant load of 30 kΩ and simultaneously at a pulse load of 300 Ω for 3 s. The pulse frequency was 1 pulse per 10 h. Figs. 1 and 2 present discharge curves of the freshly assembled (a) and of stored at 45°C (b) CR 2016 and BR 2016 cells, respectively, both having a 1.5 M $LiClO_4$/PC + DME electrolyte. After an initial storage period and a discharge to 25% depth, the cells were again stored for 30 days, discharged to 50% depth, stored again for 30 days, and finally discharged to
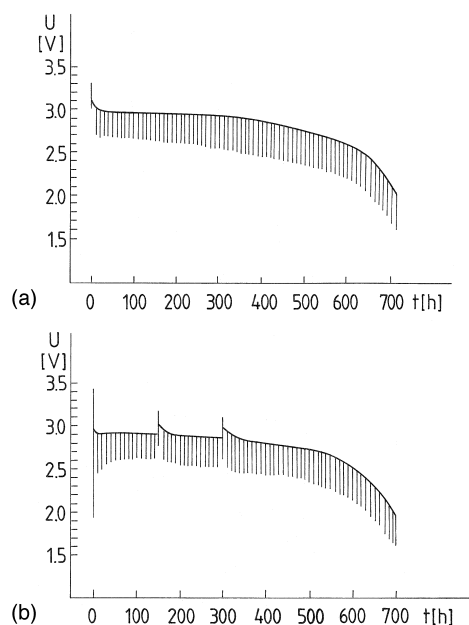

Fig. 1. Discharge characteristics of CR 2016 cells having 1.5 M $LiClO_4$/PC + DME electrolyte. (a) freshly assembled; (b) stored three times for 30 days at 45°C. Constant load of 30 kΩ and pulse load of 300 Ω during 3 s.

Fig. 2. Discharge characteristics of BR 2016 cells having 1.5 M $LiClO_4$/PC + DME electrolyte. (a) freshly assembled; (b) stored three times for 30 days at 45°C. Constant load of 30 kΩ and pulse load of 300 Ω during 3 s.

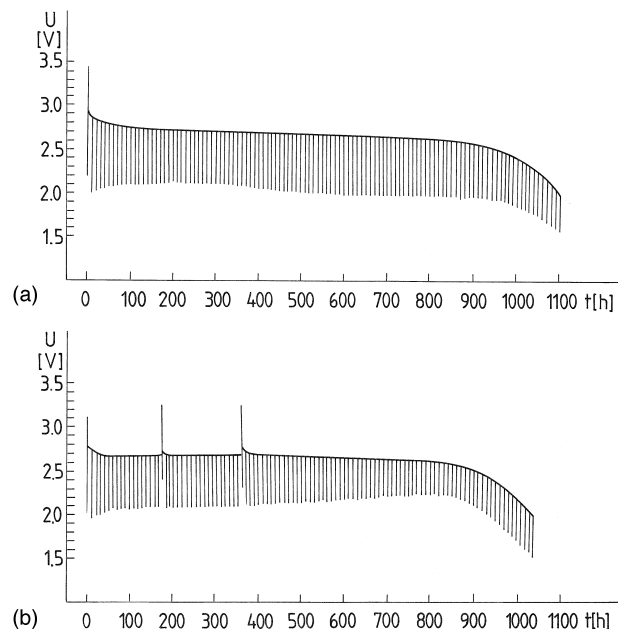2.0 V. According to our experience, a storage period of 30 days at 45°C is equivalent to 1 yr storage at 20°C.

After three storage periods, the weight of the cells remained unchanged, this suggesting that they were closed hermetically and hence, that a loss of the more volatile DME solvent through the seal may be excluded. After each storage period and before discharge, the open circuit voltage (OCV) of the cells was registered. The higher value of OCV, i.e., 3.45 ± 0.03 V, was observed for the freshly assembled BR 2016 cells, while the OCV of the CR 2016 cells was 3.30 ± 0.03 V. After an initial period of storage at 45°C, the OCV of BR 2016 cells reached the value of 3.11 ± 0.02 V (Fig. 2b). Such a value of OCV is related to the decrease of the cathode potential due to lithium insertion into the layered $(CF)_n$ cathode from the electrolyte. In the same conditions, the OCV of the CR 2016 cells increased to the value of 3.43 ± 0.03 V (Fig. 1b). This different behaviour is tentatively associated to the transport of structural water from MnO_2 to the electrolyte caused by the ionic exchange and by the formation of overoxidated compounds.

The OCV of BR 2016 cells increased to 3.26 V following the first discharge and the second storage. Such a behaviour could be explained assuming the formation of an intermediate fluoride intercalation compound $(CLi_xF)_n$ on the cathode surface which is subsequently decomposed to LiF and carbon [3]. The presence of solvent molecules accompanying the intercalation process accelerates the decomposition of the intercalate. After the second discharge and the third storage period, the OCV of BR 2016 cells

was the same as that measured after the second storage, i.e., 3.26 V (Fig. 2b). This fact is consistent with the above mentioned discharge mechanism.

After the first discharge and the second storage period, the OCV of CR 2016 cells decreased to the value of 3.14 V and then decreased again to 3.05 V after the second discharge and the third storage period, according to the higher degree of lithium intercalation into MnO_2.

Fig. 1 shows that, after the first storage, the plateau of the discharge curve for CR 2016 cells decreases of 70–80 mV. Accordingly, the discharge capacity of CR 2016 cells decreased from 66 mA h to 64 mA h after three storage periods (three times per 30 days at 45°C).

Fig. 2a and b shows that, after the first storage period, the discharge characteristics of BR 2016 cells differ from each other in terms of both curvature and slope. For stored cells, the flat profile is reached more quickly (Fig. 2b). The discharge capacity of BR 2016 cells decreased from 96 mA h to 90 mA h after three storage periods of 30 days at 45°C.

Figs. 3 and 4 show the discharge characteristics of CR 2016 and BR 2016 cells, respectively, with 1 M $LiClO_4$/PC electrolyte. After three storage periods (30 days at 45°C), the discharge capacity of CR 2016 cells was equal to 65 mA h, while that of BR 2016 cells was 94 mA h.

Generally, the characteristics of the lithium cells here investigated confirm a high operating voltage. However, BR cells have definitely a flatter discharge profile, this being explained thermodynamically by the reduction process in which the amount of conducting carbon gradually increases. The values of the cell voltage under pulses depend on the polarisation of cathodes which are lower for BR cells. The CR cells deliver higher voltage at the pulse load. However, in the case of $(CF)_n$ electrodes, the surface of the cathode continuously increases during discharge; hence, the decrease of the pulse voltage is smaller at the end of the discharge.

Table 1 presents the percentage of capacity loss for the CR 2016 and the BR 2016 cells with a different composition of electrolyte, determined at the end of a long-term storage. The test discharge was performed at 30 kΩ load until reaching 2.0 V, and at the same time, the cells were
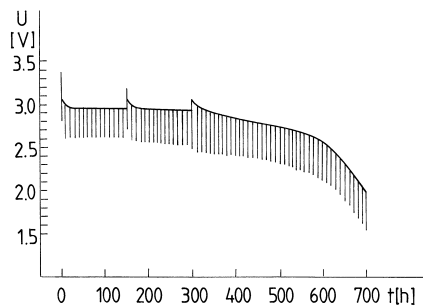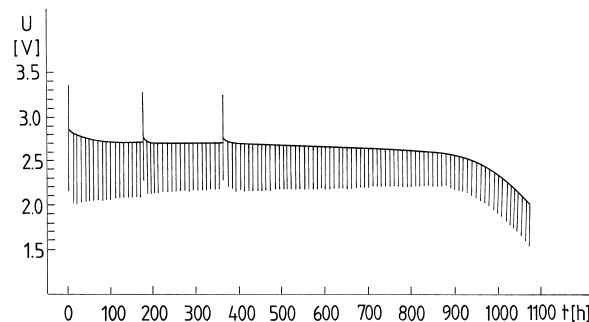

Fig. 4. Discharge characteristics of BR 2016 cells having 1.5 M $LiClO_4$/PC electrolyte, stored three times for 30 days at 45°C. Constant load of 30 kΩ and pulse load of 300 Ω during 3 s.

pulse loaded (300 Ω during 3 s). 16 cells of CR type and 16 cells of BR type were chosen for the test, and average data are given in Table 1.

From the results presented in Table 1, the loss of capacity for lithium cells is definitively higher for those cells using DME in the electrolyte. Literature data obtained on the 1.5 V Li/FeS cell having a similar 1.2 M $LiClO_4$/PC + DME (50:50% by weight) electrolyte, report that practically no loss of capacity was observed after storage for 60 days at 60°C [4]. The comparison of these results with those obtained in our work allows us to draw the following assumptions. Without load, DME, being an electron donor, can be electrochemically oxidised on the MnO_2 and $(CF)_n$ cathode materials, which have a high oxidation potential. The oxidation of DME is a concurring process during the reduction of the active cathode material. As a consequence, the OCV of the lithium cells decreases, especially for BR 2016 cells, and the first discharge time at a load of 30 kΩ also diminishes.

We can assume that the polymerisation of DME oxidation products occurs on the MnO_2 cathode which has a catalytic active surface due to the presence of acidic surface groups, with some consequent blockage of the porous cathode.

After a partial discharge followed by a storage at higher temperature, the BR 2016 cells present a smaller decrease of potential during pulses in the discharge process as compared to CR 2016 cells (Figs. 2b and 4). This phenomenon can be related to a process of recrystallisation of LiF through the electrolyte and to the increase of the cathode surface during the electrochemical reduction.

Fig. 3. Discharge characteristics of CR 2016 cells having 1.5 M. $LiClO_4$/PC electrolyte, stored three times for 30 days at 45°C. Constant load of 30 kΩ and pulse load of 300 Ω during 3 s.

Table 1
Loss of capacity (%) for CR 2016 and BR 2016 lithium cells having 1 M $LiClO_4$ in different organic solvents (PC + DME or PC) after three storage periods of 30 days at 45°C

Cells	Loss of capacity, % (±0.5%)	
	PC + DME	PC
CR 2016	3	2
BR 2016	6	2

Considering the physicochemical properties of our two solutions of electrolyte and the mutual interaction between the conducting supporting salt and the organic solvents, it should be mentioned that the conductivity of a mixed composition, i.e., 1.5 M LiClO$_4$/PC + DME is higher than that of 1.5 M LiClO$_4$/PC. On the contrary, the Walden product, i.e., the conductivity multiplied by the viscosity, has a lower value for the mixed PC + DME composition. However, taking into account the ionic association constant K_s of the LiClO$_4$ salt in our two investigated electrolytes, this value is almost the same in the two cases [2]. This means that the contact distance of the ions (0.3 nm for the Li$^+$ ClO$_4^-$ ion-pair) is not changed for the solvent separated Li$^+$/solvent/ClO$_4^-$ ion-pair (0.8 nm) when passing from our mixed composition PC + DME to pure PC. Hence, the amount of available Li$^+$ cations for the electrode reactions is comparable in our two electrolyte solutions.

Therefore, the different behaviour observed for cells with two kinds of cathodes and various electrolyte compositions could be explained assuming the oxidation of DME which has stronger donor properties than PC. The observed loss of capacity is influenced by the oxidising properties of the cathode materials and by the composition of the electrolyte. The higher the OCV of the cell, the higher the loss of capacity during storage.

4. Conclusions

The DME component of the organic electrolyte in lithium cells with MnO$_2$ and (CF)$_n$ cathodes can be electrochemically oxidised on the cathode materials.

The polymerisation of the oxidation products of DME on the MnO$_2$ cathode material and the immobilisation of the electrolyte in the cathode pores, cause the restriction of Li$^+$ diffusion to the electrode surface.

The loss of capacity during three storage periods of 30 days at 45°C is definitely greater for cells with (CF)$_n$ cathode (6%) than for the cells with MnO$_2$ cathode (3%).

For the cells with (CF)$_n$ cathode, after a partial discharge followed by a storage at elevated temperature (45°C), the values of potential during pulses are definitely higher than those of cells using MnO$_2$ cathodes.

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