

RELIABILITY OF COMMERCIAL LITHIUM BUTTON CELLS I. EFFECT OF THE ENVIRONMENT ON THE PASSIVATION RESISTANCE

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(Received March 4, 1988; in revised form August 11, 1988)

Summary

The passivation resistance of commercial Li/MnO₂ and Li/CF button cells (20 mm dia., 1.6 mm thick) was measured, after storage under several environments, in an attempt to assess the reliability of such power sources under very low drain discharge. The activation resistance and the series resistance were measured by an a.c. impedance technique as a function of the storage time at 20 °C, 40 °C/93% RH and 55 °C. The weight change was also determined.

The permeation of the solvent from the electrolyte out of, and of water into the cell occurred simultaneously at different rates depending on the environment and the type of cell. The plastic crimp seal of the Li/MnO₂ cell exhibited high solvent permeation and low water permeation, whereas the opposite was observed for the Li/CF cell. The main contribution to the increase in the activation resistance is water permeation. After 720 days of storage, the permeation of the solvent did not significantly raise the series resistance of the cell.

1. Introduction

The presence of a protective surface film on lithium in organic electrolytes is generally recognized and has been the subject of numerous investigations [1]. An increase in the activation resistance in commercial lithium/carbon monofluoride (CF) batteries was reported as a function of storage time at several states-of-discharge, and was attributed to film formation on the lithium electrode [2].

The aim of the present study was to characterize the passivation resistance of commercial Li/MnO₂ and Li/CF button cells under several environments in an attempt to assess the reliability of such power sources under very low drain discharge. A general description of these cells, in particular their construction and main characteristics, is available [3, 4]. One

application, among many others, is as low power consumption devices such as watches. The lithium button cells currently used employ a plastic crimp seal and the main question is the long term reliability of such cells while driving devices to the maximum capacity of the power source. Under very low drain, the current is too low to break down the passivating layer on the lithium electrode. To accelerate the passivation phenomenon further, the cells used in the present study were measured after storage, *i.e.*, without drawing any current.

The internal resistance and the weight change were measured as a function of storage time under three experimental conditions: 20 °C, 40 °C/93% RH and 55 °C. The increase in the internal impedance is shown to be mainly controlled by water permeation into the cell through the plastic crimp seal.

2. Experimental

Fifty CR 2016 (20 mm dia., 1.6 mm thick) Li/MnO₂ cells from Sanyo Electric Trading Co., Osaka, Japan (January 1985), and fifty BR 2016 Li/CF cells from Matsushita Battery Industrial Co., Osaka, Japan (November 1984), were used. The initial capacities were 92 ± 2 and 78 ± 2 mA h, respectively, at a cut-off voltage of 2.0 when discharging into 30 k Ω at 20 °C with mean voltages of 2.9 and 2.8. In a button cell configuration the anode, the separator, and the cathode are parallel planes perpendicular to the axis of symmetry of the cell. The seal is usually a crimped polypropylene plastic and a polymeric sealant [3, 4].

Two cells of each type were stored under each of the following conditions, defined in international standards [5]:

- (a) 20 ± 2 °C, $60 \pm 15\%$ relative humidity (RH);
- (b) 40 ± 2 °C, $93 \pm 2 - 3\%$ RH using a CO₂ incubator;
- (c) 55 ± 2 °C using a constant temperature cabinet in a 20 °C/60% RH room.

The internal resistance of the cells was measured at regular time intervals. After 720 days of storage, resistive discharges were performed to determine the self-discharge.

Two techniques were used to measure the cell impedance. First the a.c. impedance was determined using a frequency response analyzer and an electrochemical interface controlled with a (Hewlett Packard 9825 A) calculator. The alternating voltage was 2.5 mV rms. Five measurements per frequency decade were performed between 0.1 Hz and 100 kHz at the open circuit potential. Analysis in the complex plane gives the series resistance, R_s , and the activation resistance, R_{act} , to within $\pm 2\%$, assuming a simple Randles equivalent circuit.

The second method involved the measurement of the ohmic drop after 10 ms following a current pulse ranging from 0.1 to 2 mA. This galvanostatic method was applied to study the effect of current density and to examine the possibility of using a simple, inexpensive, and fast method to determine the passivation resistance of lithium cells. The results on several types of

cells, especially those with a high internal resistance, have shown that the best correlation with the R_{act} value obtained by the a.c. impedance method was obtained from the ohmic drop determined at a current value of 0.1 mA. The resolution of the digital voltmeter was 1.0 mV. The ohmic drop cannot, therefore, be determined with a resolution better than 10 Ω .

The measurements were performed at 20 °C: the reported values are the average of two cells for each experimental condition, and therefore no statistical data can be given.

In addition to the impedance measurements, five undischarged cells of each type were stored at 40 °C/93% RH, and 55 °C and regularly weighed with an accuracy of ± 0.02 mg.

3. Results

The impedance data given by both the a.c. and the galvanostatic pulse techniques are reported in Figs. 1 and 2 for the Li/MnO₂ and Li/CF cells, respectively. The "as-received" Li/CF cells showed a fairly well defined semi-circle at high frequencies (Fig. 2). As the storage time increased, the diameter of the semi-circle, R_{act} , increased and its centre moved below the real axis. The impedance locus for the Li/MnO₂ cells showed a depressed semi-circle (Fig. 1). The activation resistance is given by the diameter of the semi-circle, but for simplification it has been taken here as the intersect of the semi-circle with the real axis, irrespective of the position of its centre.

The results reported in Figs. 1 and 2 for the fresh, undischarged cells are in agreement with published data [2, 6, 7]. The increase of activation resistance with time after storage has also been reported and attributed to the growth of a passivating film on the lithium electrode [2, 8].

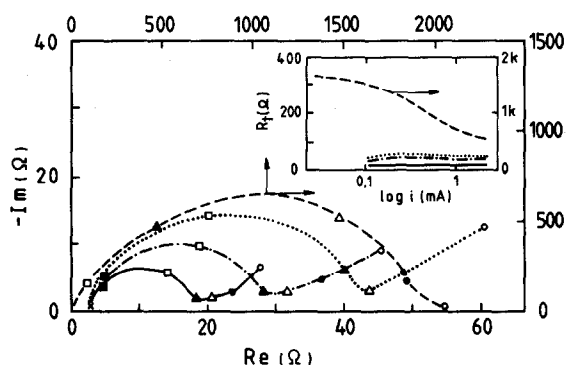


Fig. 1. Complex plane impedance data for the undischarged Li/MnO₂ cell at the open circuit potential: freshly received from the manufacturer, —; after 360 days of storage at 20 °C, - · - ·; 40 °C/93% RH, — — —; 55 °C, · · · · ·. The decades of frequency are shown as follows: 10⁻¹, ○; 1, ●; 10, △; 10², ▲; 10³, □; 10⁴, ■; 10⁵, × Hz. The insert shows the total cell impedance, R_t , determined from the galvanostatic pulse method under various currents.

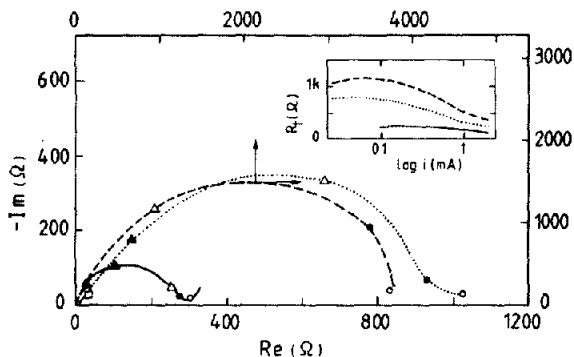


Fig. 2. As Fig. 1 for the Li/CF cell. The response after 360 days of storage at 20 °C is roughly the same as that in the fresh state.

The double layer capacity can be calculated from the frequency at the maximum of the semi-circle and the activation resistance ($C_{dl} = 1/\omega R_{act}$). As R_{act} increased during storage, ω decreased and C_{dl} stayed roughly constant at 4 and 10 μF for the undischarged Li/MnO₂ and Li/CF cells, respectively.

For the Li/MnO₂ cells stored under normal or dry conditions, the galvanostatic pulse method gave impedance values independent of the current used and in agreement with the a.c. impedance method (Fig. 1). For the Li/MnO₂ cells stored at 40 °C/93% RH (Fig. 1) and all of the Li/CF cells (Fig. 2), impedance values measured by the galvanostatic pulse method decreased with increasing current. The data at low current, *i.e.*, at 0.1 mA, were in reasonable agreement with those given by the a.c. impedance technique. The results of the total cell impedance measured by the galvanostatic pulse method will be discussed in a further publication [9].

3.1. Li/MnO₂ cells

The variation of the activation resistance, R_{act} , as a function of the storage time under three environments is shown in Fig. 3. After storage at 20 °C and 55 °C, the activation resistance increased almost linearly with time up to about 540 days, then increased more rapidly. It started at about 10 Ω and reached 40 and 90 Ω after 720 days at 20 °C and 55 °C, respectively. At 40 °C/93% RH, the activation resistance increased exponentially with storage time to reach 1 k Ω after less than 300 days. The increase in resistance was much larger at 40 °C/93% RH than at 55 °C.

The series resistance, R_s , defined as the high-frequency intercept with the real axis, remained constant throughout storage at 20 °C (Fig. 4). At 40 °C/93% RH and 55 °C, a small increase from 2.3 to 3.5 Ω and 3.0 Ω , respectively, was observed.

The weight loss was 4 to 6 times larger at 55 °C than at 40 °C/93% RH (Fig. 5).

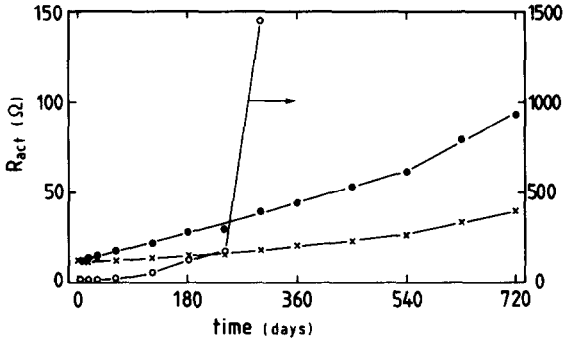


Fig. 3. Dependence of R_{act} on storage time for the undischarged Li/MnO_2 cell stored at 20 °C (x), 40 °C/93% RH (o), and 55 °C (●).

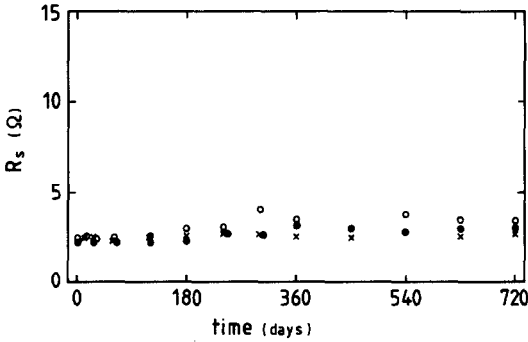


Fig. 4. Dependence of R_s on storage time for the undischarged Li/MnO_2 cell stored at 20 °C (x), 40 °C/93% RH (o), and 55 °C (●).

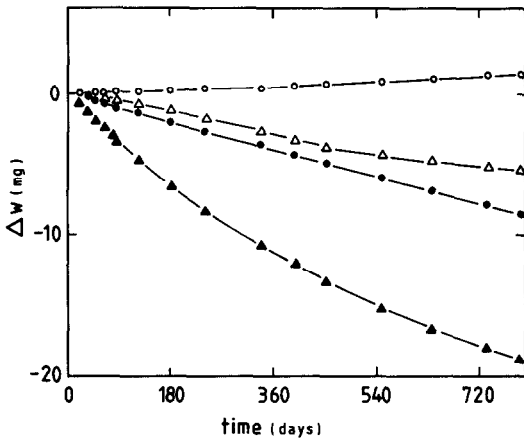


Fig. 5. Change in weight as a function of storage time at 40 °C/93% RH (open symbols) and 55 °C (solid symbols) for the undischarged Li/MnO_2 (triangles) and Li/CF (circles) cells. Average value of five cells for each experimental condition.

The resistive discharges performed after 720 days of storage indicated that the self-discharge increased with increasing temperature (Table 1). The thickness of the cell after discharge was higher after storage in humid environment than at 20 °C and 55 °C (Table 1).

3.2. Li/CF cells

The activation resistances were significantly higher than those of the Li/MnO₂ cells (Fig. 6). During storage at 20 °C, R_{act} remained between 230 and 330 Ω with a maximum value after 30 days and a minimum after about 300 days. At 40 °C/93% RH the activation resistance increased steeply at the beginning of the storage, then less rapidly, and finally rose sharply after more than 300 days. At 55 °C, a sharp increase was again recorded for short times, followed by a decrease to a minimum value around 180 days, and a sharp increase for longer storage times.

The increase of the series resistance, R_s , was very small at 20 °C and 40 °C/93% RH, whereas it was significantly larger at 55 °C. In all cases R_s was negligibly small with respect to R_{act} (Fig. 7).

TABLE 1

Self-discharge, final thickness after discharge following 720 days of storage in the undischarged state, and final activation resistance after 720 days of storage

	Self-discharge (% C_{nom})	Thickness (mm)	R_{act} (Ω)
Li/MnO ₂			
20 °C	1	1.62	40
40 °C/93% RH	17	1.72	3000
55 °C	21	1.61	90
Li/CF			
20 °C	1	1.48	280
40 °C/93% RH	23	1.82	6000
55 °C	12	1.64	4500

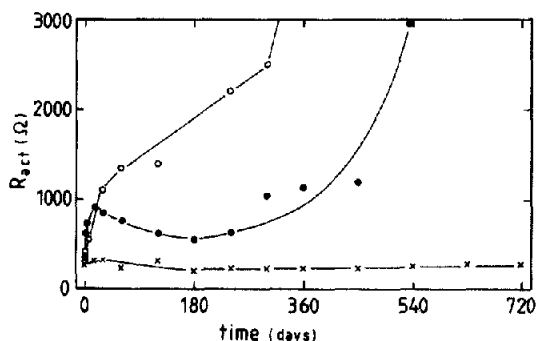


Fig. 6. As Fig. 3 for the Li/CF cell.

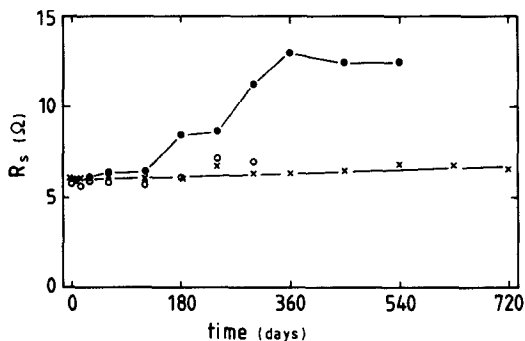


Fig. 7. As Fig. 4 for the Li/CF cell.

A weight loss was measured after storage at 55 °C, while a slight weight increase was recorded at 40 °C/93% RH (Fig. 5).

The resistive discharges performed after 720 days of storage indicated a total self-discharge at 40 °C/93% RH twice that at 55 °C (Table 1). The thickness of the cells after discharge was higher after 720 days at 40 °C/93% RH than at 55 °C, and higher at 55 °C than at 20 °C (Table 1).

4. Discussion

The increase in the internal impedance is expected to arise mainly from gas permeation through the plastic crimp seal. The permeation of the solvent from the electrolyte out of the cell should increase the series resistance, R_s , and lead to the drying out of the cell. The permeation of water inwards should increase the activation resistance because of the reaction of H_2O with the lithium electrode to form a passivating film.

4.1. Weight change

A weight loss was measured other than for the Li/CF cells stored at 40 °C/93% RH, where a slight weight gain was recorded. The weight loss indicates that the permeation of the solvent out of the cell is larger than that of water inwards. The very small increase of the series resistance, R_s , indicates that the solvent permeation occurring over the time investigated was not sufficient to significantly decrease the conductivity of the electrolyte (Figs. 4 and 7).

Comparison of the weight change under the various experimental conditions is best done at the time when the cell impedance reaches a critical value, *e.g.*, 1 k Ω (see Table 2). At 55 °C, the Li/CF cells lose a great deal less weight than the Li/MnO₂ cells. Assuming the same seal geometry, this may be explained by a much lower permeability of the solvent/plastic seal pair in the Li/CF cell than in the Li/MnO₂ cell, or by a larger permeability of the water/polymer pair in the Li/CF cell, despite the low RH

TABLE 2

Storage time at which the total cell impedance reaches $1 \text{ k}\Omega$ and weight change at that storage time for undischarged cells

	Storage time for $R_t = 1 \text{ k}\Omega$ (days)	ΔW at $R_t = 1 \text{ k}\Omega$ (mg)
Li/MnO ₂ cells		
40 °C/93% RH	270	-2
55 °C	> 720	< -20
Li/CF cells		
40 °C/93% RH	30	+0.1
55 °C	360	-4

at 55 °C, or by both actions. Despite the much lower weight loss of the Li/CF cell at 55 °C, these cells exhibit a much larger internal resistance than the Li/MnO₂ cells. It may therefore be suggested that this behaviour arises from the larger water permeability of the seal used in the Li/CF cells. At 40 °C/93% RH, the permeation of water into the Li/CF cell is so high that it over-compensates for the permeation of solvent out of the cell and a weight gain is measured.

4.2. Activation resistances

Activation energies will be calculated from R_{act} and assumed to represent the activation energies of permeation, although a linear correlation between R_{act} and the permeation rate has not been demonstrated. Equilibrium permeation rates follow the classical Arrhenius relationship with temperature

$$P = P_0 \exp(-E_p/RT)$$

where P_0 is a constant for the given permeant/polymer pair, E_p the activation energy of permeation, R the gas constant, and T the temperature in °K [10]. The "rule-of-thumb" saying that the permeation doubles for every 10 °C rise is correct only at ambient temperature for $E_p = 55 \text{ kJ mol}^{-1}$.

The data of Figs. 3 and 6 indicate that after more than 15 days of storage the R_{act} values are always higher at 40 °C/93% RH than at 55 °C. This result shows that the temperature alone cannot account for the increase in the activation resistance. The high humidity is most likely responsible for this behaviour.

The estimation of the activation energies between the R_{act} values at 20 °C and 40 °C/93% RH show that E_p increases with increasing storage time for both types of cells (Fig. 8 and Table 3). The E_p values estimated between 20 °C and 55 °C are much lower than between 20 °C and 40 °C/93% RH and not so much dependent on the storage time. These trends might indicate that: (i) the equilibrium for water permeation is not reached below 360

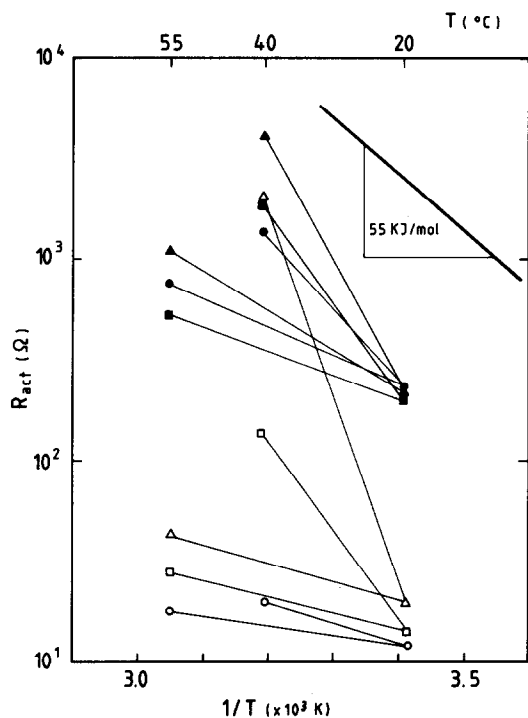


Fig. 8. Temperature dependence of R_{act} for the undischarged Li/MnO₂ (open symbols) and Li/CF (solid symbols) cells after 60 (circles), 180 (squares) and 360 (triangles) days of storage.

TABLE 3

Activation energies estimated from the differences in R_{act} between (i) 20 °C and 40 °C/93% RH and (ii) 20 °C and 55 °C, undischarged cells

Cells	Storage time (days)	E_p (kJ mol ⁻¹)	
		20 - 40 °C/93% RH	20 - 55 °C
Li/MnO ₂	60	19	9
	180	83	15
	360	177	17
Li/CF	60	67	27
	180	81	22
	360	113	31

days of storage; (ii) the activation energies of permeation of water depend on the RH value of the environment.

The analysis does not take into account the presence of other impurities in the electrolyte and the thermal instability of the solvent which might also contribute to the observed increase of R_{act} .

4.3. Self-discharge and thickness change

The self-discharge of lithium cells comes mainly from the reaction of the lithium electrode with impurities, especially water, oxygen, and other impurities in the electrolytes. Although water vapour permeation may be the main contributor to both the self-discharge and the activation resistance, self-discharge is expected to be in relation to the amount of lithium which has reacted with water, while R_{act} may not be directly related to the thickness of the passivating layer [1]. Thus, the self-discharge does not necessarily relate to the R_{act} value after 720 days of storage, as shown in Table 1.

The increased thickness of the cells is apparently related to the humidity and temperature of the storage environment. The greater the thickness, the higher the activation resistance (Table 1). At a given state-of-discharge, the water vapour might increase the volume of the cell by swelling the plastic seal. This will decrease its mechanical strength and thus contribute to the thickness increase during discharge, due to the net volume increase of the electrodes. The swelling of the seal increases its gas permeability and contributes to the increase in the internal resistance.

5. Conclusions

The permeation of solvent from the electrolyte out of, and of water into, the cell occurs simultaneously but at different rates depending on the temperature and humidity of the environment and on the type of cell. The plastic crimp seal of the Li/MnO₂ cell exhibits high permeability for the solvent and a low permeability for water, whereas the opposite is observed for the Li/CF cell. The main contribution to the increase of the activation resistance is the water permeation. After the storage times investigated, the permeation of the solvent does not raise the series resistance of the cell significantly.

The consequences of water permeation on the useful life of lithium cells will be investigated as a function of the state-of-discharge in Part II of this series [9].

Acknowledgements

The author is pleased to thank F. Züllig for his skillful assistance in the experimental work, R. Jeanmonod for discharge measurements, and ETA Inc., Grenchen, member of the SMH Group, for its interest and support. A summary of this work was presented at the 174th Meeting of the Electrochemical Society, Chicago, IL, Oct. 11, 1988, and will be published in a proceedings volume of this society.

List of symbols

R_s	Series resistance (electrolyte, separator, current collectors and leads' resistance) defined in the complex plane as the high-frequency intercept of the real axis
R_{act}	Activation resistance defined in the complex plane as the diameter of the semi-circle
R_t	Total cell impedance ($R_t = R_s + R_{act}$)
Re	Real part of the impedance
Im	Imaginary part of the impedance
C_{dl}	Double layer capacity
f	Frequency
ω	Angular frequency ($\omega = 2\pi f$)
W	Weight
E_p	Activation energy of permeation

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