Experimental Investigation on the Internal Resistance of Lithium Iron Phosphate Battery Cells during Calendar Ageing

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***Abstract*—Lithium-ion batteries are increasingly considered for a wide area of applications because of their superior characteristics in comparisons to other energy storage technologies. However, at present, Lithium-ion batteries are expensive storage devices and consequently their ageing behavior must be known in order to estimate their economic viability in different application. The ageing behavior of Lithium-ion batteries is described by the fade of their discharge capacity and by the decrease of their power capability. The capability of a Lithium-ion battery to deliver or to absorb a certain power is directly related to its internal resistance. This work aims to investigate the dependency of the internal resistance of lithium-ion batteries on the storage temperature and on the storage time. For this purpose, accelerated ageing calendar lifetime tests were carried out over a period of one year. Based on the obtained laboratory results, an empirical ageing model was developed; the model is able to predict with accurately the increase of the internal resistance of Lithium-ion batteries during calendar (storage) ageing. Based on the proposed ageing model, it was found out that the internal resistance of the studied Lithium-ion battery cell will double after approximately eleven years if stored at 25°C.**

***Keywords*—Lithium-ion battery, internal resistance, experimental investigation, ageing model, ageing behaviour**

I. Introduction

At present, Lithium-ion (Li-ion) batteries are increasingly considered in different sectors such as automotive industry, renewable energy storage systems, and back-up power applications [1]–[3]. The characteristics of Li-ion batteries which make them suitable for this wide applications' area are their fast response, high energy density, long calendar and cycle lifetime, and low self-discharge rate [3], [4]. In all the aforementioned applications, the Li-ion batteries are used as power sources and therefore, it is critical to have precise information about their power capability at each operating point.

The capability of a battery to deliver a certain power is directly related to its internal resistance; the internal resistance of a battery determines the battery's voltage change (rise or drop) when a certain current (charging or discharging) is applied to it. Thus, in order to meet the desired power capability, the voltage change, and subsequently the internal resistance of the battery cell, has to remain into a certain range. However, this range is changing depending on the operating conditions and on the state-of-health of the battery cell. The internal resistance of Li-ion batteries is dependent on state-of-charge (SOC), temperature and current [5], [6]; moreover, the internal resistance of Li-ion batteries is changing with ageing [6], [7]. Consequently, to predict the internal resistance of a Li-ion battery over its life represent a difficult process.

In recent years, a lot of efforts were focused on the development of models that are able to predict the lifetime of different Li-ion battery chemistries in terms of power capability (internal resistance increase). These models can be divided mainly into two groups depending on the approach that is followed to measure the internal resistance. The first group uses the electrochemical impedance spectroscopy (EIS) to determine the internal resistance of Li-ion battery cells. By performing EIS measurements at beginning-of-life (BOL) and periodically thereafter, at certain time intervals during ageing lifetime tests, lifetime models that are able to predict the internal resistance increase can be developed [8]–[10].

The second group of models uses current pulses to determine the internal resistance of the Li-ion batteries, and subsequently their power capability, during ageing of the battery at different conditions. In most cases, the changes in the internal resistance are investigated during accelerated cycling lifetime tests, under different testing conditions and for different Li-ion battery cells types [5], [8], [11], [12]. Nevertheless, the changes in the internal resistance, using the current pulses technique, are also analyzed during calendar lifetime tests; this approach was used for determining the internal resistance of Li-ion batteries based on Nickel Manganese Cobalt [13] and Nickel Cobalt Aluminum [14], [15] cathodes. Up to the knowledge of the authors, there are no studies published, which investigate the changes of the internal resistance of Lithium Iron Phosphate-based Li-ion battery cells (LFP) during calendar ageing, using the current pulses technique.

Li-ion battery cells based on $LiFePO_4$ (lithium iron phosphate) cathodes and graphite anodes, further referred in this paper as LFP battery cells, are considered suitable for being used in automotive, stationary storage, and back-up power applications because of their characteristics which include high intrinsic safety, good thermal stability, and long lifetime [16]. However, the LFP chemistry is relatively new, hence the ageing mechanisms and lifetime modeling of LFP-battery

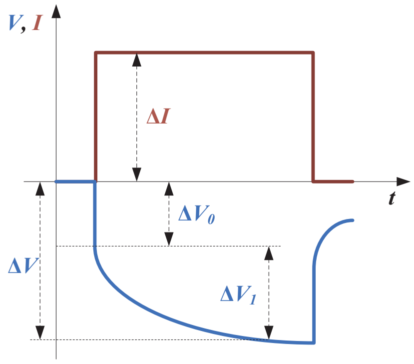

Fig. 1. Battery cell's voltage response due to a discharging current pulse

cells are not well established yet [17]; moreover, the majority of the available studies are focused on capacity fade and internal resistance modeling during cycling lifetime tests and not during calendar lifetime tests [17]–[19].

This work focuses on the development of an empirical lifetime model for predicting the internal resistance of a LFP-based battery cell during calendar ageing. In order to develop the model, the current pulses technique was used. The storage temperature and storage time are the main ageing factors that were considered in this research and their effect on the internal resistance increase was investigated. The dependence of the LFP battery cells' internal resistance on the current and state-of-charge (SOC) during calendar ageing was analyzed as well.

II. Internal Resistance Measurement using Current Pulses

The internal resistance represents a key parameter for Li-ion batteries since it can provide valuable information about the battery power capability and its degradation during ageing. There are different approaches, presented in literature, which can be followed in order to determine the internal resistance of Li-ion batteries [20].

The most widely used method to determine the internal resistance of Li-ion battery cells is to apply a charge or discharge current pulse to the battery cell and to measure the voltage rise or drop, respectively. In Fig. 1 the voltage drop response due to a discharge current pulse is illustrated. As it can be observed, the voltage drop caused by the current pulse is not linear but it evolves in steps governed by processes with different time constants.

After the current pulse is applied, the voltage of the cell drops immediately due to its ohmic resistance (ΔV_0 in Fig. 1); the ohmic resistance represents the resistivity of the active materials of the anode and cathode, the current collectors and the electrolyte [20]. Following the initial voltage decrease, the voltage continues to drop, however less steeper, due to the charge transfer reaction that takes place inside the battery cell (ΔV_1 in Fig. 1). According to [6], the voltage drop caused by the ohmic resistance and the charge transfer reaction has a time constant of less than twenty seconds and is usually used for power capability calculations and power capability predictions.

TABLE I. Basic Characteristics of the LFP Battery Cell

Parameter	Value
Capacity	2.5 Ah
Nominal Voltage	3.3 V
Max. Continuous Charge/Discharge Current	10/70 A
Operating temperature	-30°C to 55°C
Storage temperature	-40°C to 60°C

The internal resistance of the battery cell during discharging is computed by dividing the change in the voltage by the change in the current as given in (1). Furthermore, the internal resistance is generally regarded as the sum of the ohmic resistance and the resistance caused by the charge transfer (polarization resistance). The internal resistance of the battery cell during charging can be defined in a similar manner.

$$R_i = \Delta V/\Delta I = (\Delta V_0 + \Delta V_1)/\Delta I \quad (1)$$

Because the internal resistance of Li-ion battery cells is dependent on many parameters (i.e. age, SOC, current, and temperature), extensive laboratory tests have to be performed in order to investigate its dependence on these parameters and to build a reliable battery cell ageing model.

III. Experimental

A. Accelerated Calendar Ageing

In the present research, the change in the internal resistance of a LFP battery cell during calendar ageing is investigated. In order to accelerate the ageing process of the battery cells, accelerated ageing tests were performed.

The stress factors which are influencing the degradation of Li-ion battery cells, independent on the chemistry, during calendar ageing are the storage temperature and the storage voltage [13]. However, in this paper only the effect of the temperature on the internal resistance of the LFP battery cells is investigated. Due to the non-linear influence of the temperature stress factor on the lifetime of the battery cells (see Fig.2), at least three stress levels should be considered during the accelerated ageing tests. This will allow for a reliable extrapolation and the changes of the cells' internal resistance at desired operation stress (in this case, desired operation temperature) can be obtained.

For the tested LFP cells, whose basic electrical characteristics are summarized in Table I, three different temperatures (40°C, 47.5°C, 55°C) were considered for the accelerated calendar ageing test; thus, three test cases were considered and three LFP battery cells were considered for each of the test cases. The extrapolation was performed for a temperature of 25°C that corresponds to the typical operational temperature of these cells in stationary energy storage applications.

B. Characterization

Before starting the accelerated calendar ageing tests and periodically thereafter, at time intervals of one month, the performance of the battery cells were verified by performing reference performance tests (RPTs).

The RPTs were performed at 25°C and were composed of capacity measurements, internal resistance measurements and

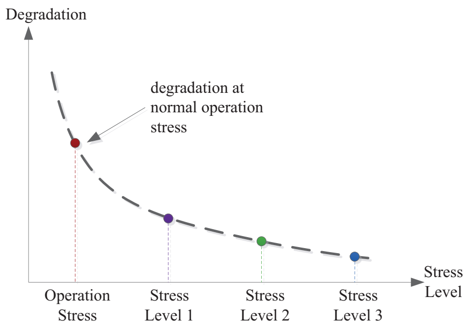

Fig. 2. Extrapolation to normal operation condition of the degradation obtained during accelerated ageing tests

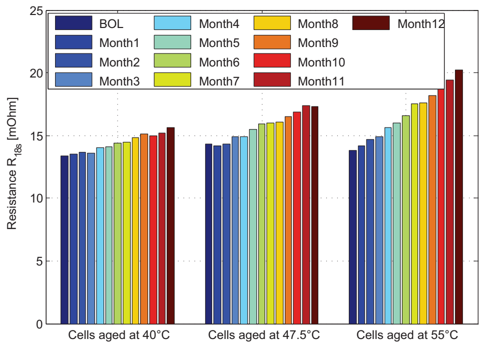

Fig. 3. Internal resistance of the LFP battery cells stored at 50% SOC and different temperatures during one year (measurement performed during a 4C discharging current pulse at 25°C and 50% SOC)

EIS measurements. Since this work focuses on the changes in the internal resistance of LFP cells, only the procedure used to measure this parameter is presented below; nevertheless, the whole RPT procedure is summarized in [21].

The internal resistance was measured based on the current pulses approach, for three SOCs (20%, 50%, and 80%) and for four C-rates (4C, 2C, 1C and 0.5C) by following the below procedure:

0. At the end of the capacity measurements the battery cell is totally discharged and 15 minutes pause is applied for temperature stabilization;
1. Charge the battery cell with 1C current until 20% SOC level is reached;
2. Pause for 15 minutes for temperature stabilization and stabilization of the concentration gradients of the ionic charge carriers;
3. Charge the cells for 18 seconds with the given C-rate;
4. Pause for 15 minutes for temperature stabilization and stabilization of the concentration gradients of the ionic charge carriers;
5. Discharge the cell for 18 seconds with the given C-rate;
6. Repeat steps 2-5 for the remaining C-rates;
7. Repeat steps 1-6 for the remaining SOCs;

IV. Results

In this section the results, obtained during one year of accelerated calendar lifetime tests, concerning the changes in the internal resistance of the tested LFP battery cells, are presented and discussed. The obtained data were used to develop an ageing model able to predict the values of the internal resistance at different ages, temperatures and SOCs.

A. *Effect of the storage temperature on internal resistance*

The changes in the internal resistance of the LFP battery cells measured during the ageing process are presented in Fig. 3 for the discharging case. As it can be observed for both cases, the values of the internal resistance of the LFP battery cells are increasing with the storage time and are strongly dependent on the storage temperature. The increase of the internal resistance during storage is caused in the majority of carbon-based anode Li-ion battery cells by the growth of the solide-electrolyte interface (SEI) layer [7], [13]. Moreover, the rate of the internal resistance increase is accelerated by the increasing the storage temperature.

The percentage of internal resistance (resistance normalized to its BOL values) increase during the accelerated ageing test at elevated temperatures are presented in Fig. 4.

In order to build an empirical ageing model able to predict the changes into the internal resistance of the battery cells during storage, the relative resistances increase (see dots in Fig. 4) were fitted using different mathematical functions (polynomial, square-root, logarithmic etc.). The quality of the fitting was assessed by analyzing the returned values of the correlation coefficient R^2. A power law was found to predict the best the internal resistance increase of the tested LFP cells since it has returned the highest values of R^2. Consequently, this function, generally expressed in (2) was selected for the further development of the ageing model.

$$R_{i\_increase}(t)[\%] = a_T \cdot t^{b_T} \tag{2}$$

The parameters a_T and b_T obtained by fitting the internal resistance increase for all the considered temperatures are summarized in Table II, together with the R^2 coefficients.

The obtained R^2 coefficients results indicate that the power law is able to predict accurately the increase of the battery cells' resistance for different ageing temperatures. However, it was of great interest to develop a more general ageing model, able to describe the changes of the internal resistance of the LFP cells for different calendar ageing temperatures. By examining the values of the coefficients a_T and b_T it was found that they are increasing with increasing the storage temperature. Thus, a_T and b_T, were fitted as function of temperature. As illustrated in Fig. 5 and Fig. 6, it was found that they vary exponentially and linearly with temperature, respectively.

TABLE II. Fitting parameters for internal resistance increase and corresponding correlation coefficient

Temperature	a_T	b_T	R^2
40°C	0.5094	1.4060	0.9705
47.5°C	0.9415	1.2790	0.9728
55°C	2.5730	1.1540	0.9953

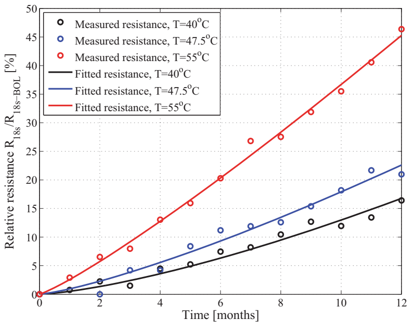

Fig. 4. Internal resistance normalized to its BOL value for LFP battery cells stored at 50% SOC and different temperatures (measurement performed during a 4C discharging current pulse at 25°C and 50% SOC)

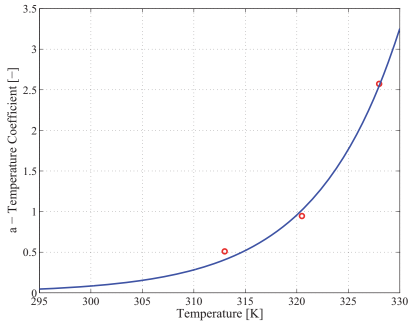

Fig. 5. Variation of the coefficient a_T with temperature

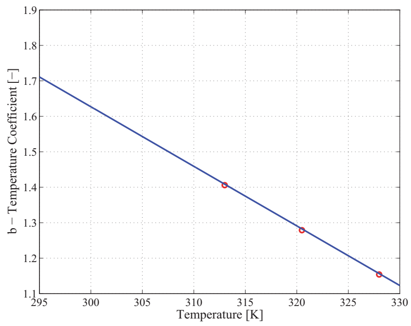

Fig. 6. Variation of the coefficient b_T with temperature

The dependeces on temperature of both temperature fitting coefficients were expressed as:

$$a_T = 9.654 \cdot 10^{-18} \cdot e^{0.1223T} \quad (3)$$

$$b_T = -0.0168 \cdot T + 6.667 \quad (4)$$

By introducing (3) and (4) into the power law (2), the internal resistance ageing model of the LFP battery cells was obtained as:

$$R_{i\_increase}(t,T)[\%] = (9.654 \cdot 10^{-18} \cdot e^{0.1223T}) \cdot \cdot t^{-0.0168 \cdot T + 6.667} \quad (5)$$

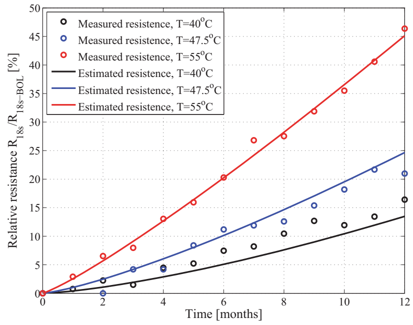

Fig. 7. Estimated internal resistance increase based on the proposed ageing model (5)

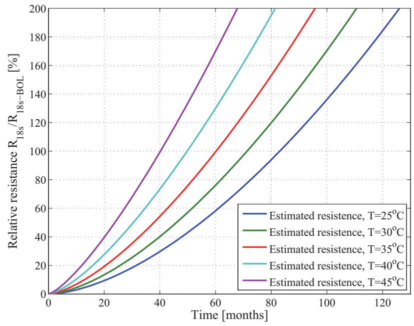

Fig. 8. Estimated resistance increase during storage at different temperatures

The accuracy of the proposed internal resistance ageing model (5) was verified by comparing the measurements obtained in the laboratory during the accelerated ageing tests with the estimated internal resistance increase given by the model; the results are shown in Fig. 7 and they confirm the ability of the model to predict accurately the increase of the LFP battery cell's internal resistance for different temperatures. Based on the proposed ageing model, the ageing behavior of the internal resistance of the tested LFP battery cells can be obtained for different storage temperatures as it is shown in Fig. 8.

Depending on applications' requirements where the Li-ion batteries are used, their EOL can be associated either with the decrease of capacity or with the increase of the internal resistance. As mentioned in [13], the EOL criterion is fulfilled when the internal resistance of the cell doubles. According to this definition and analyzing the results presented in Fig. 8 it was found that the calendar lifetime of the tested LFP battery cell if stored at 25°C is approximately eleven years.

The data used for developing the ageing model given in (5) are based on internal resistance measurements at 50% SOC. However, according to the measurement procedure presented in Section III, internal resistance measurements were performed at two additional SOCs (i.e. 20% and 80%). Utilizing these measurements and following the proposed methodology, ageing models for the cases when the internal resistance of the LFP battery cells was measured at 25°C and 20% and 80% SOC were built. The parameters of the ageing models that are able to estimate the resistance increase when the battery cells

TABLE III. PARAMETERS OF THE RESISTANCE INCREASE AGEING MODELS

SOC	a_T	b_T
20%	$1.845 \cdot 10^{-18} \cdot e^{0.1277T}$	$-0.0319 \cdot T + 11.48$
50%	$9.654 \cdot 10^{-18} \cdot e^{0.1223T}$	$-0.0168 \cdot T + 6.667$
80%	$8.513 \cdot 10^{-18} \cdot e^{0.1581T}$	$-0.0533 \cdot T + 18.45$

are stored at different temperatures are summarize in Table III.

B. Dependence of the internal resistance on the current

In order to investigate the effect of calendar ageing on the dependence of the internal resistance on the current, current pulses with different C-rates were applied, as described in Section III. For a better visualization of the ageing effect, the values of the internal resistance have been normalized to the value measured during a 1C discharging current pulse for each age of the battery cells. As shown in Fig. 9 - 11, the dependence of the internal resistance on the current is changing during the cells' ageing process. However, the variations are small and no obvious trend was observed during the ageing process for none of the considered storage temperatures.

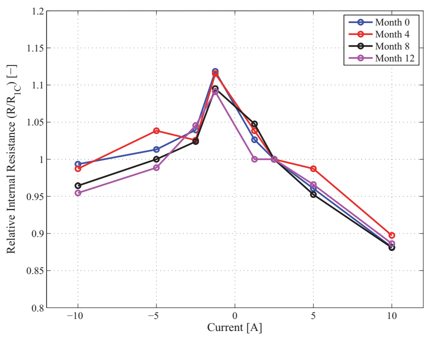

Fig. 9. Dependence of the internal resistance on the current during calendar ageing at 40°C (measurement performed at 25°C and SOC=50%)

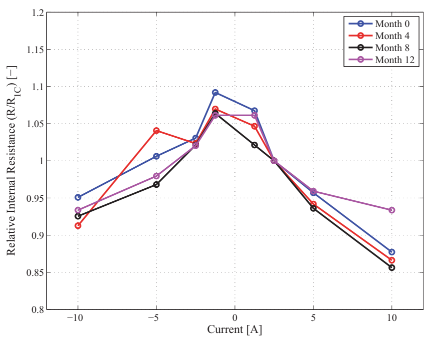

Fig. 10. Dependence of the internal resistance on the current during calendar ageing at 47.5°C (measurement performed at 25°C and SOC=50%)

C. Dependence of the internal resistance on the SOC

In this subsection, the effect of the calendar ageing on the dependence of the internal resistance on SOC is investigated.

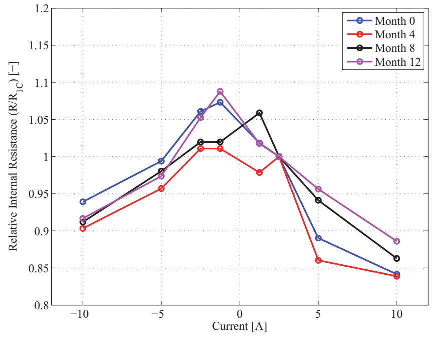

Fig. 11. Dependence of the internal resistance on the current during calendar ageing at 55°C (measurement performed at 25°C and SOC=50%)

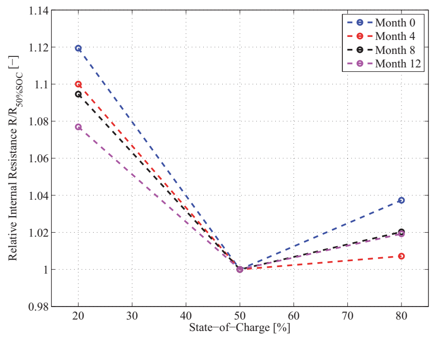

Fig. 12. Dependence of the internal resistance on the SOC during calendar ageing at 40°C (measurement performed at 25°C)

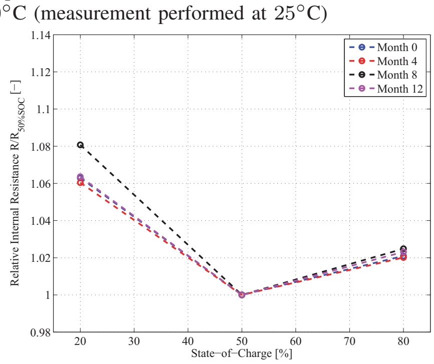

Fig. 13. Dependence of the internal resistance on the SOC during calendar ageing at 47.5°C (measurement performed at 25°C)

The values of the LFP cells' internal resistance have been normalized to the value measured at 50% SOC for each age of the battery cells. As presented in Fig. 12 - 14, independent on the storage temperature and storage time, the internal resistance of the LFP cells shows a parabolic shape that is in good agreement with previous researches focused on different Li-ion cell chemistries [7], [11].

For the cells aged at 40°C (Fig. 12) and 55°C (Fig. 14), the internal resistance dependence on the SOC changes over the cells' lifetime. However, only for the cells aged at the highest temperature a clear trend can be observed for both low and high SOCs: the internal resistance dependence on SOC is reducing with increasing ageing time. For the cells aged at the lowest temperature, the dependence of the internal resistance

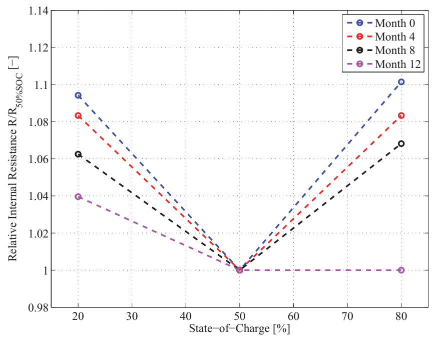

Fig. 14. Dependence of the internal resistance on the SOC during calendar ageing at 55°C (measurement performed at 25°C)

on SOC is reducing with ageing only for low SOCs (i.e. 20%). On the contrary, for the LFP battery cells aged at 47.5°C (Fig. 13), the internal resistance dependence on the SOC does not change with the calendar ageing.

Similar to the internal resistance dependence on the current, no general trend was found concerning the internal resistance dependence on SOC during the calendar ageing of the tested LFP cells. Unfortunately, these results could not be verified due to lack of similar studies on LFP battery cells.

V. Conclusion

In this work the ageing behaviour of the internal resistance of LFP battery cells was investigated during calendar ageing. For this purpose, accelerated calendar ageing tests were performed at three different temperatures (40°C, 47°C, and 55°C) during a period of one year. The values of the internal resistance were deteremined by applying the current pulses technique (measuring the voltage response of the LFP battery cells to the applied charging/discharging current pulses). For all three storage temperatures, a power law was used to express the internal resistance increase with storage time during the calendar ageing. Based on the power laws obtained for the three considered temperatures, an ageing model was developed, which is able to predict accurately the internal resistance increase during storage at different temperatures. Moreover, based on this model it was found that the internal resistance of the tested LFP battery cell will double after eleven years if stored at 25°C. In the final part of the paper, the internal resistance dependence on the SOC and current was investigated; however no clear patterns were observed for this dependencies, during one year of accelerated calendar ageing.

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