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Ageing effects on batteries of high discharge current rate

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Summary

Among the various stress factors determining the ageing of the battery when cycled at high discharge currents, the temperature increase was identified as the main operating mechanism. In order to quantify the improvement of the battery pack cycle life with load levelling, a model was developed to calculate the temperature inside the battery. A curve correlating the battery cycle number with the internal temperature of the battery was designed. As a result, it was calculated that the differential temperature decreased from 11°C in the high stressed battery down to 1.5 °C in the load-levelled system.

Keywords: battery model, cycle life, discharge rate, lead-acid battery.

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1 Introduction

When the first hybrid and pure electric vehicles were commercialized in the early ‘90, traction lead-acid batteries were used as on board storage system, and their limits in this application were soon complained from users and recognized by manufacturers. In those years ENEA, acting as an independent testing institute, investigated a large number of high power lead-acid batteries of various technologies (i.e. flat plate electrodes, spiral wound etc.) for both EV and HEV applications. Among these, two commercial high power lead-acid batteries, of the same type and manufacturer but different in size, were tested. Both the batteries showed a similar relation between cycle life (CL) and the maximum specific power of the duty cycle, (A), that can be expressed by a functional relationship of exponential form $CL= Be^{-kA}$, compatible with a highly non-linear behaviour [1][2].

Maximum specific power is linked to maximum current density, therefore this second parameter has been used to investigate the influence of the battery design on CL, since it is well known that charging and discharging rate has a great influence on the battery life cycle.

In literature it has been established that high recharge rate has a beneficial effect on battery life [3]. Pavlov et al. [4] found high charging currents increase cycle life, whereas Lam et al. [5] claimed that the increasing in cycle life can be obtained only using a pulsed current. The authors assumed that this positive effect can be related to a modification of the positive active mass (PAM) properties.

On the other hand, the effect of discharge current on life cycle was investigated in a less extent. In fact, the literature is missing in the description of the impact of high discharge rates on the life time of the battery. Generally it is possible to state that the cycle life of the cell is decreased whenever the cell is discharged at a rate faster than the rated rate. Furthermore, the reduction in life has a close functional relationship to the observed reduction in ampere-hour capacity with increasing discharge rate. It is possible to find a functional relationship between cycle life and rate of discharge on the basis of the physical processes that occur during the discharge of the battery.

In this report the temperature increase as a function of the discharge current was evaluated. A model was developed to calculate the difference between the environmental temperature and the battery temperature when operated at various discharged rates. Finally, a cycle-life curve was drawn using the differential temperature. It was found that a strict correlation was found between the so obtained curved and the experimental results

2 Ageing effects on batteries

In lead–acid batteries, major ageing processes, leading to gradual loss of performance, are: i) anodic corrosion, ii) PAM degradation, iii) irreversible formation of lead sulphate, iv) detachment of active material from the plates, v) loss of water, and vi) electrolyte stratification [6]. Ageing mechanisms are often inter-dependent. For example, corrosion of the grids will lead to increased resistance to current flow, which will in turn impede proper charge of certain parts of the active mass, resulting in sulphation [7]. Among the above mentioned stress factors, the irreversible formation of lead sulphate and the temperature increase can be identified as the main operating mechanism determining the ageing of the battery when cycled at high discharge currents.

A way to allow the increase of the battery cycle life by reducing the discharge rate consists in load levelling the battery power by introducing a further auxiliary power device, a super-capacitor (SC) obtaining a “hybrid electric storage system”, HSS [8]. This HSS can efficiently store energy during deceleration and supply high power during accelerations and, in both cases, can reduce peak power requirements for the battery.

Notwithstanding this positive result, up to now HSS have been successfully proposed only in the case of forklifts [9], where SCs are conveniently used to increase availability and lead-acid battery cycle-life. Only recently, the introduction of fast charge procedures for EV is changing the outlook [10], because it allows to greatly reduce the size of the battery and, in some cases, the power supplied by the HSS. In this cases, the extra-power offered by SCs can be a chance to support acceleration and to maximize braking energy recovery.

In the following the results of an intensive series of comparative tests are reported, which were performed on two battery packs (3 modules each), cycled in urban cycles to simulate the pack behaviour with and without load levelling.

2.1 Experimental

The batteries used for the experimentation are the HAZE HZY-EV12-65, with a capacity of 60 Ah at C/5 rate. The tests were related to the battery capacity degradation in load-levelled vs. non load-levelled cycles. Figure 1 shows the experimental set-up.

Figure 1: Experimental set-up used for the experimentation. In the foreground is possible to observe the battery packs used for cycle life evaluation

Test procedure was derived from the power cycle of an EV subject to an urban cycle, where charge and discharge phases are presented. In particular, the urban characteristics of the *New European Driving Cycle* (NEDC) were implemented. According to the EUCAR procedure, each test lasted 80 minutes using a sequence of 25 micro-cycles, each of 195 s. To reduce the test duration, the maximal power density used in the experimentation was doubled with respect the EUCAR procedure for "pure electric" vehicles (70 W kg^{-1} vs. 35 W kg^{-1}). The test was continued until the delivered capacity was 75% of the useful capacity for 5 cycles in a row.

2.2 Results

Figure 2 reports the power applied to the battery pack, simulating the load-levelled battery.

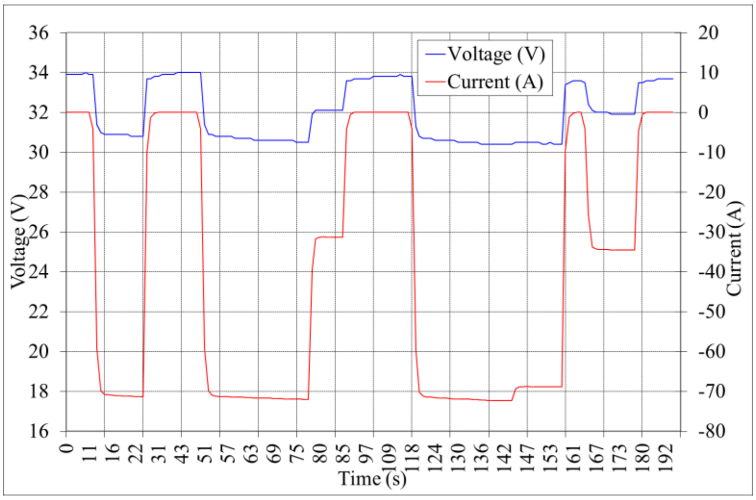

Figure 2: Voltage and Current behavior during the load-leveled battery test.

To simulate the assistance of SCs, the maximum discharge current (70 A) was lowered with respect to the maximum current (160 A) used as reference and reported in Figure 3.

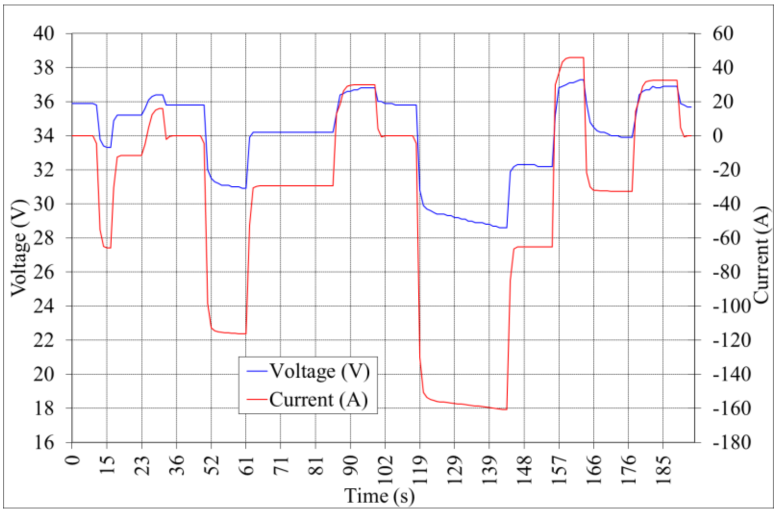

Figure 3: Voltage and Current behavior during the non-load-leveled battery test.

The results of the experimentation are reported in Figure 4: the less stressed battery pack shows, as expected, an increase of cycle life. In particular, the less stressed battery pack was able to operate at the imposed conditions (i.e. the delivered capacity should be greater than the 75% of the useful capacity) for a higher number of cycles (200 charge-discharge cycles vs. only 75 cycles).

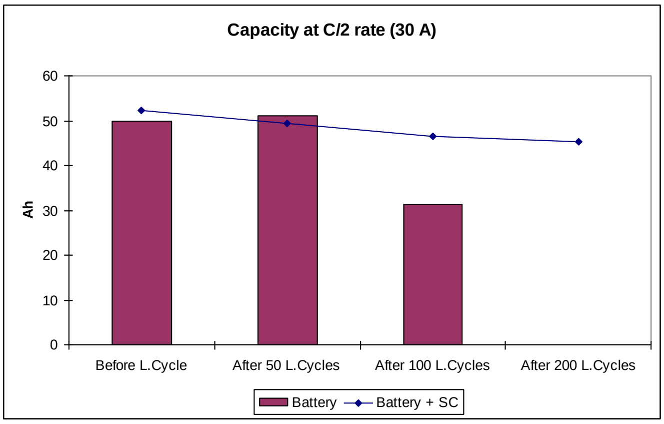

Figure 4: Capacity variation as a function of the cycle life. The test was stopped when the the delivered capacity was 75% of the useful capacity.

On the basis of the test results, it is possible to relate the battery life-time to the operative current peaks (maximum discharge currents), as shown in Figure 5, in which the number of cycles, i.e. the cycle life CL is expressed as a function of the maximum current A. Among the various models fitting the points, the previous found log-linear relation was in good agreement with the experimental data: CL= Be^{-kA} with B = 451.21 and k = -0.011. In Figure 5 one more point (12 A, 400 cycles) was added to the experimental results, to take into account the cycle life certificated by the manufacture (400 cycles) for a module discharged at C/5 rate.

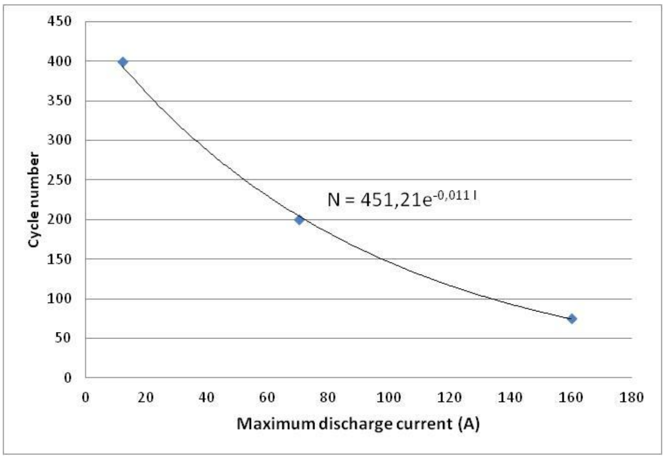

Figure 5: Battery Cycle Life as a function of the maximum discharge current.

3 Simulation model

A model to simulate the battery behaviour has been developed using MATLAB/SIMULINK software. The model was designed to represent the module object of the study and the correspondent electrical circuit is reported in Figure 6: a series of resistances and a parallel of a capacitor with a resistance has been used to represent the battery behaviour.

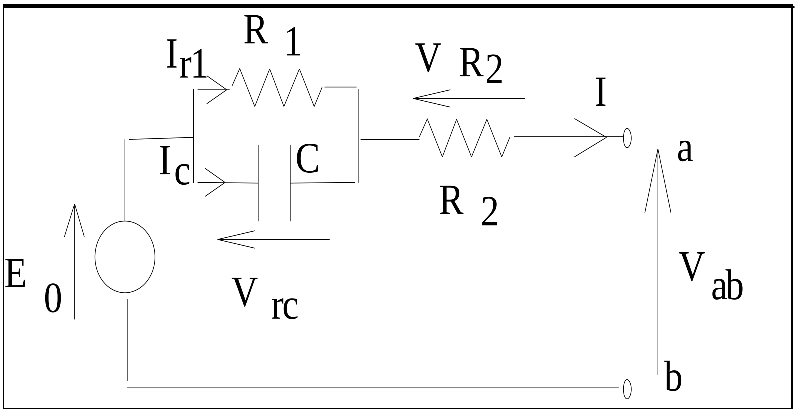

Figure 6: Electrical circuit of the battery used to model the battery parameters.

The unknowns of the system are the battery voltage (V_{ab}) and the value of internal current (I_{R1}). The equations used to calculate them are:

$$V_{ab} = E_0 - I_{R1} \cdot R_1 - I \cdot R_2 \qquad (1)$$

$$\frac{dI_{R1}}{dt} = \frac{1}{\tau} \cdot \left(I - I_{R1}\right) \qquad (2)$$

where $\tau = R_1 \cdot C$, E_0 is the OCV, I is the current used to charge or discharge the battery, R_1 is the ohmic resistance (OR) and R_2 is the internal resistance (IR). The input data are the OCV (E_0), the values of the internal resistances (R1 and R2), and the time constant (τ). The values of the resistances and E_0 have been measured and are reported in Figure 7 as a function of the DOD. The resistance were evaluated during discharge and during charge: the battery was galvanostatically discharged to reach the desiderated DOD value. In that moment the current was set null and after 3 seconds the OR value R_1 was measured. The IR value R_2 was measured after 180 seconds from the current interruption. The same procedure was carried out during the charge process.

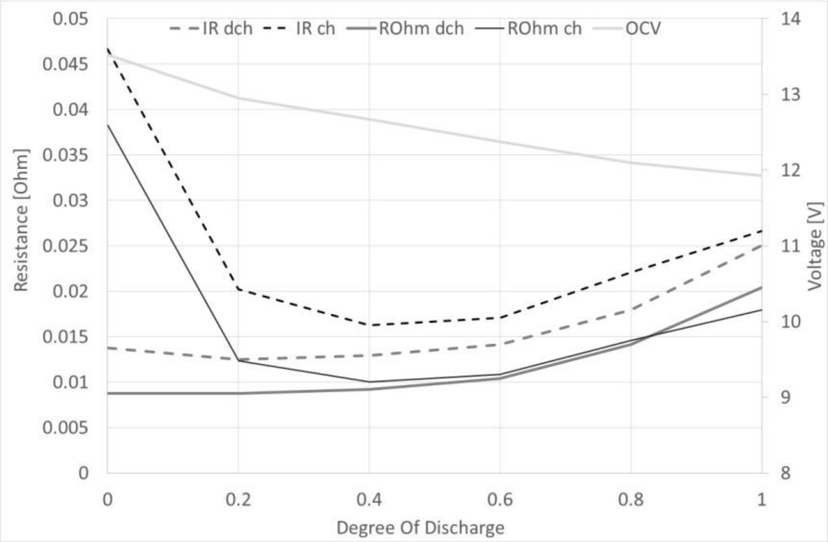

Figure 7: Open Circuit Voltage and internal Resistances (charge and discharge) for the selected battery.

The OCV was found to vary linearly with the DOD and, consequently, it reaches its maximum when the battery is fully charged.

The parameter τ was chosen to best fit the experimental data (in the present work (τ=180 s). The model was validated on the “non-load-levelled battery” cycle defined above and the results are reported in Figure. 8. A good agreement was found between the measured and calculated data especially at high values of the discharge current.

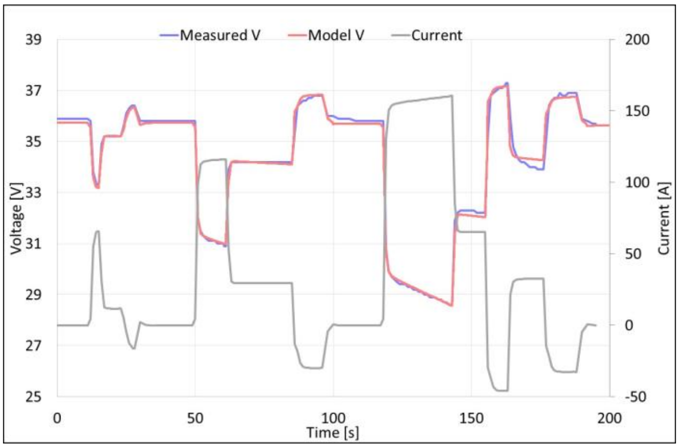

Figure 8: Comparison between the measured and calculated Voltages for the non-load-leveled battery cycle.

The battery temperature has been calculated using the model and the correspondent equation is reported below:

$$C_\theta \frac{d\theta}{dt} = P_{Loss} + \frac{(\theta - \theta_a)}{R_\theta} \qquad (3)$$

In which:

C_θ : Thermal capacity;

θ : The electrolyte temperature;

P_{Loss} : Internal heat generated in the battery;

R_θ : Thermal resistance.

The temperature values reached during the dynamic cycles were not available so the model has been calibrated during a constant discharge test.

In Figure 9 a discharge test conducted at rate C (60 A of current) is reported: the measured temperatures and calculated showed a good agreement between them during the discharge process with the exception of the last seconds in which the measured temperature increased in intensity compared to that calculated. However, this difference is recorded under conditions that are not usually reached during actual use of the battery. In addition, the error is less than a centigrade.

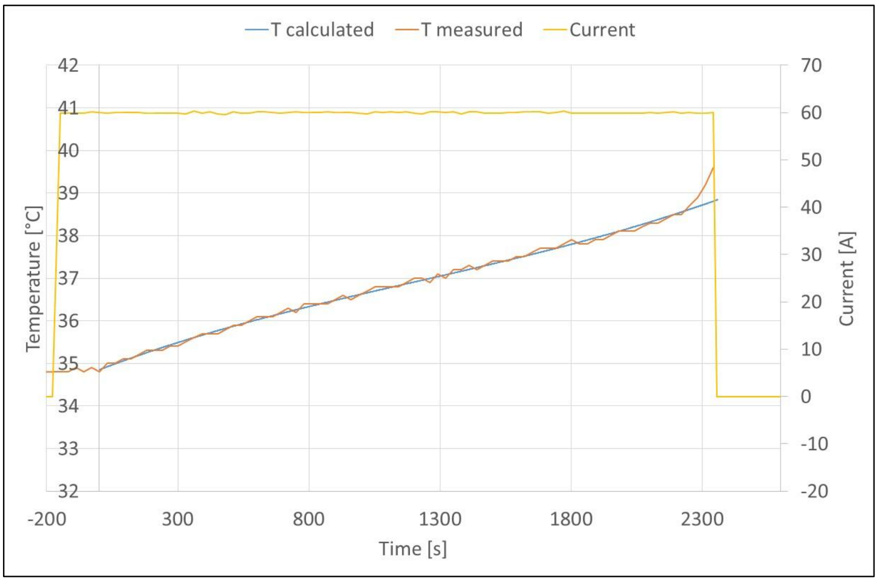

Figure 9: Comparison between measured and calculated temperature (60 A constant discharge).

The coefficients used to calibrate the battery temperature were: $C_\theta = 11.000$ J and $R_\theta = 0.6\ \frac{{}^\circ K}{W}$.

Once the model was calibrated the same points of cycle-life of fig. 5 have been recalculated in function of the battery temperature, Figure 10.

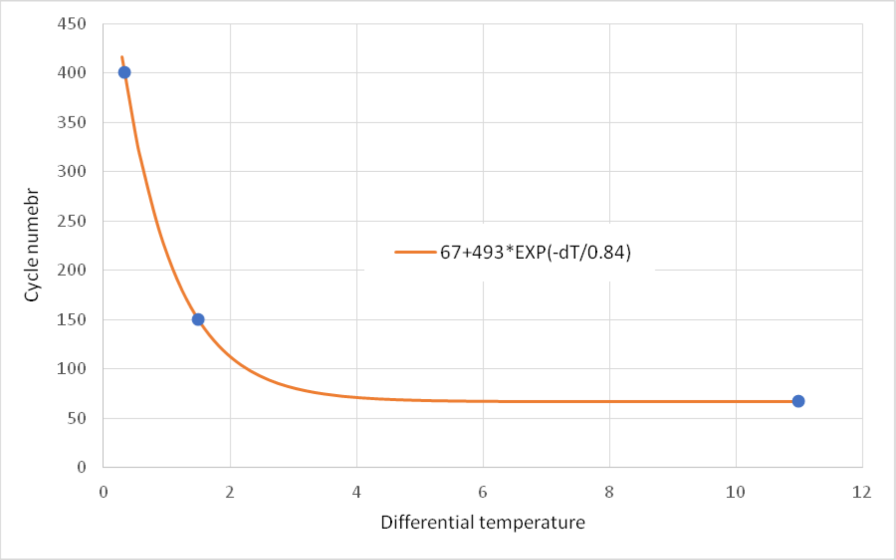

Figure 10: . Life cycle of the battery in function of the electrolyte differential temperature.

Such temperatures have been calculated using the above reported model: the point at left is calculated using a constant discharge with 6 A of current (C/10) and the cycle-life is the factory cycle-life. The mid-point is that calculated with the load-levelled cycle (representative of the adoption of the SC) and the worst point is calculated running the non-load-levelled cycle (without assistance of SC).

The cycle-life curve was designed using as abscissa the difference between the environmental temperature and the battery temperature in order to appreciate the temperature increase due to the battery internal resistance. For the non-load-levelled cycle the temperature increased of about 11 degrees, while for the load-levelled system there is an increase of only 1.5 degrees. At the lower discharge current (6 A), the temperature increased of only 0.33 degree.

4 Discussion

As previously said, two mechanism are particularly important for battery ageing, namely the irreversible formation of lead sulphate and the temperature increase. Other mechanisms concurring to ageing of the battery are the detachment of active material from the plates, PAM degradation and electrolyte stratification. On the other hand, the effect due to corrosion of positive plate is less important while the effect on water loss is practically negligible. As observed in this article there is a strict correlation between the discharge currents, the increase of internal temperature and battery ageing. In fact, during high discharge rates, the imposed currents which flow through the system generate the heat which increases the battery internal temperature. The increase of temperature plays a key role in battery ageing by affecting corrosion, irreversible formation of lead sulphate, PAM degradation, and water loss. Elevated temperature has a strong impact on corrosion: the higher the temperature, the faster the corrosion process. Due to the direct effect of corrosion on battery ageing a positive correlation between temperature and battery life cycle can be found. As part of the fundamental chemical reaction of the battery, sulphate crystals are formed at both electrodes when the battery is discharged. When the battery is charged the crystals dissolve and are converted to PbO_2 and Pb on the positive and negative electrode, respectively. However, if the battery is not properly operated, such as left over at a high DOD for a long period of time, the sulphate crystals grow in size and large sulphate crystals are created. Since these large crystals do not dissolve easily when the battery is charged this leads to a hard and irreversible electrode sulphation. On the other hand, smaller sulphate crystals are formed when the battery is subjected at high discharge rates. The small sulphate crystals are not conductive and can lead to inhomogeneous current distribution and, consequently, to inhomogeneous state of charge SOC can be reached on the electrode surface. The portions of the electrode with the lower SOC will be subjected to harder and irreversible sulphation. The higher the discharge rate, the smaller the crystal size and greater the loss in conductivity between adjacent particles in the active material matrix. Drawing the same amount of charge through a plate structure that is generally less conductive will lead to uneven current distributions and higher stress on the cell. This increased stress will likely lead to shorter life, in a manner analogous to mechanical fatigue. Furthermore, the sulphate crystals will leave part of the active material insulated from the current collector, leading to an electrochemical inactivation of these parts. Temperature has two opposite effects on sulphation process. On one hand high temperature has a positive effect on life cycle since it helps to better fully recharge the battery (more sulphate can be recharged). On the other hand high temperature leads to more hard sulphate build up at a low SOC, contributing to decrease the battery life. Finally, the increase of temperature reduces the battery life by increasing both the rate of water evaporation and the kinetics of PAM degradation.

5 Conclusion

Among the various parameters that can lead to the deterioration of the battery when operated at high discharged currents, the increase of the internal temperature seems to play a major role. From the experimental data it is clear that the internal temperature of the battery increases linearly along with the discharge process. A simple model that mimics the electrical system of the battery has allowed to simulate the cell voltage when the battery is discharged at variable currents. The model also allowed to assess with reasonable accuracy the variation of the internal temperature when the battery was discharged at constant currents. Using this model it was possible to predict that the temperature inside the battery was extremely sensitive to the current used to discharge the battery. As a consequence a correlation between the cycle life exhibited by the batteries discharged at high currents with the temperature increase that occurred within the battery was found. The correlation followed an exponential decay with the increase of temperature inside the battery, compatible with the concept of a highly non-linear threshold type functional behaviour.

Although the mechanisms that contribute to the ageing of lead-acid batteries differ from the one of lithium-ion batteries, it would be interesting to extend this model to the latter, in order to verify the correlation of lithium-ion batteries ageing with temperature.

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