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ScienceDirect
Journal of Power Sources 176 (2008) 534–546
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Comparison of different approaches for lifetime prediction of electrochemical systems—Using lead-acid batteries as example

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Available online 26 August 2007

Abstract

Different approaches for lifetime prediction for electrochemical energy storage devices are discussed with respect to their general concepts. Examples for their implementation and advantages and disadvantages are given. The models are based on: (a) physical and chemical processes and their interaction as regards ageing effects; (b) weighting of the Ah throughput whenever the operating conditions deviate from the standard conditions used for determining the lifetime under laboratory conditions; (c) an event-oriented concept from mechanical engineering (Wöhler curves) which is based on a pattern recognition approach to identify severe operating conditions.

Examples and details are explained for lead-acid batteries. The approaches can be applied to other electrochemical technologies including fuel cells. However, it is beyond the scope of this paper, to describe the models in all mathematical details. The models are used in system design and identification of appropriate operating strategies and therefore they must have high computational speed to allow for a comparison of a large number of system variations.

Keywords: Ageing; Lifetime prediction; Degradation; Batteries; Simulation; Modelling

1. Introduction

Lifetime prediction of electrochemical systems obviously requires a detailed understanding of ageing processes and their causes [1]. However, lifetime prediction on the basis of such detailed understanding is only possible in the few applications where one ageing process dominates and where test procedures and methods are available which allow investigation of this dominant ageing process without the influence of other ageing processes. A typical application where this is true is uninterruptible power supply systems which are operated at float charge conditions. For lead-acid batteries, corrosion and drying out are the major ageing effects.

However, where a number of ageing processes take place in parallel due to complex operation conditions such as a combination of cycling, partial state of charge cycling, incomplete or rare full charging or operation in a wide range of temperatures, the complex interaction between the various ageing processes and the operating conditions must be analysed. It is very difficult to develop appropriate laboratory ageing tests to analyse the interaction between the ageing processes and link them to lifetime expectancy on an experimental basis. In lead-acid batteries, Malbranche et al. [2] have tried to define test procedures which accentuate individual ageing effects. Their work shows, that this is possible only up to a certain point. These difficulties become obvious when looking at the following

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doi:10.1016/j.jpowsour.2007.08.057

examples:

1. Small currents or even rest periods have a significant impact on lead-acid battery lifetime, but to measure their effect in laboratory tests costs a lot of time, which is typically either not available or too expensive due to the large number of test circuits required. Accelerated tests to investigate small currents and rest periods are a contradiction in terms. Also, the effect will depend on SOC and electrolyte stratification and may depend on the microstructure of the active material which in turn depends on the conditions under investigation.
2. High temperature accelerates certain ageing effects like drying out and corrosion. On the other hand other effects like dissolution of sulphate crystals are supported by high temperatures. Therefore, desulphation is better at higher temperatures and the ageing effect of sulphation will be significantly smaller at high temperature operation compared with lower temperatures. To show the complexity even more pronounced: the statement made in the last sentence is true, if the battery is cycled. If the battery is at rest or in open circuit conditions, high temperatures accelerate sulphation by enhancing the recrystallisation process of lead-sulphate crystals resulting in larger crystals with reduced active surface.

To achieve a credible lifetime prediction, it is necessary to take these effects and their interactions into account properly.

A clear distinction must be made between "on-board" diagnosis of the remaining lifetime of an individual product and lifetime prediction for planning purposes which requires a comparison between different, well-characterised average products, system designs or operating strategies [3].

This paper concentrates on the lifetime prediction for planning purposes which is a tool for estimating the effect of changes in operating conditions and battery characteristics on the expected lifetime and for detecting operating conditions which are particularly severe, e.g. length of time until full state of charge is reached as a function of accumulated Ah throughput and state of charge. All of the models discussed below can be used for this purpose. However, it is necessary to state that the precision of all lifetime prediction models is limited with respect to a precise prediction of the lifetime in years. This does not reduce their usefulness in any way. The models are intended to determine the impact of operating conditions and strategies, system sizing or the choice of competing products on the lifetime and to provide a ranking between the different options. A precise lifetime prediction is difficult, because typically not all factors can be taken into account, such as high frequency ripples, and the exact operating conditions cannot be predicted accurately. Lifetime prediction can be made in a first order approach only for a well-defined product with mean properties. Statistical variations in the product quality also result in statistical variations of the lifetime. Nevertheless, quantitative lifetime models are a necessary tool for the design of systems taking into account lifetime cost and reliability issues.

In this paper we will use a number of terms in a specific manner:

Operating strategy	Parameters and settings of the overall electrical systems which influences voltage, current and state of charge
Operating conditions	Combination of all state variables of the battery as they are
Stress factors	Parameters which can be calculated from the time series of current, voltage, state of charge and temperature and describe the severity of the operating conditions and the rate with which ageing processes proceed
Ageing processes	Processes which lead to irreversible changes of the structure of components and materials
Effect of ageing processes	Impact of ageing processes on the performance of the battery such as capacity, high rate power capability, charge acceptance, etc.

It is not within the scope of this paper to describe the models in technical details, but to discuss the general concept of the models, their advantages and disadvantages, means to verify them, their limitations, the necessary input data and parameters, and the possibility to transfer the models to different battery technologies and fuel cells.

2. Three different approaches

Three different approaches will be discussed and compared within this paper:

1. *Physico-chemical ageing model*: A detailed chemical and physical model of the ageing processes of the electrochemical system for time step simulation is used. It provides detailed information on local conditions such as temperature, potential, current, SOC, electrolyte concentration, etc. (state variables) which are the result of the operating conditions. Each single ageing effect is examined according to its dependency on the state variables and quantified, e.g. loss of active mass surface due to recrystallisation processes, or loss of grid conductivity due to corrosion. Based on knowledge of the relationships between ageing effects and state variables, the effect of the ageing processes at any place in the system can be evaluated. The resulting changes in the performance are directly incorporated into the model and therefore the state variables adapt accordingly, for example changes in grid resistance lead to changes in current distribution along the electrode and therefore also to changes of the electrolyte density at different heights of the battery, even if identical current profiles and power requirements exist.
2. *Weighted Ah ageing model*: A weighted Ah ageing model is based on the assumption that the impact of a given Ah throughput on the lifetime depends on the details of the conditions during the Ah throughput. It is assumed that, under standard conditions, a battery can achieve an overall Ah throughput until the end of the lifetime is reached. Deviations from the standard conditions result in a virtual increase (or decrease) of the physical Ah throughput, e.g. cycling at

low states of charge is known to be detrimental in lead-acid batteries resulting in lifetime reduction.

3. *Event-oriented ageing model*: Adding up the incremental loss of lifetime caused by different events is a standard approach for lifetime prediction in many areas of engineering and is referred to as Wöhler or SN curve. This approach is frequently used for planning purposes and for designing and estimating the lifetime of components. For electrochemical systems this approach can also be used provided that several conditions are fulfilled. "Events" must be identified whose impact on lifetime can either be determined experimentally or can be evaluated based on expert knowledge. Events must be described clearly and must be distinguishable from all other events. The order of occurrence of the events, if properly defined, is of no relevance which simplifies the analysis.

The weighted Ah ageing model and the event-oriented ageing model share a number of similarities, in particular the concept of incremental loss of lifetime as a result of the operating conditions. However, there are important differences as regards the parametrisation of the two models and limitations of their use. Under certain operating conditions, for instance, it will be difficult to define the end of an event.

Lifetime prediction models must provide credible results to be useful. Credibility is achieved by comparing predictions of a model with lifetime tests where the test conditions differ from those used for extracting parameters for the model. There are significant differences between the three models as regards this.

The authors have developed models using each of the three approaches discussed above for lead-acid batteries. The approaches will be discussed in the following sections in more detail.

3. Physico-chemical ageing model

The physico-chemical ageing model is based on a two-step approach (Fig. 1). In the first step a battery model based on the fundamental equations of the chemical and electrochemical reactions, Ohm's law and the diffusion processes of reactants in the battery is used. This model provides the most important state variables for any point in the battery at any time, such as: local potential, local current density, local state of charge, local microstructure of active material (porosity, size of active mass crystals (electrochemical active surface), size of sulphate crystals (chemical active surface)), local acid concentration and local Pb^{2+}-ion concentration, local temperature, local gassing current, local oxygen reduction current, local corrosion current, gas pressure in the battery cell.

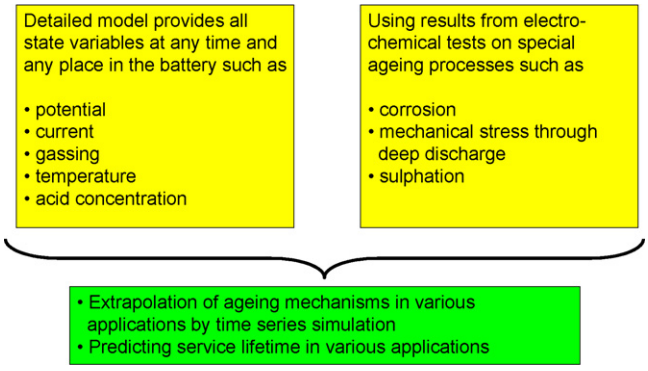

Fig. 1. General approach for the physico-chemical ageing model.

In the second step the information is used to quantify ageing processes and their impact on the performance of the battery. As all boundary conditions are well-known, information from laboratory experiments on the ageing effects can be used. This allows for a prediction of the lifetime for any type of battery for any operating conditions. This approach has been investigated in detail in Ref. [4].

3.1. Modelling of state variables

The simulation is based on a resistance network, also called the equivalent circuit diagram (see Fig. 2, only positive electrode is shown), which is solved in each time step. Kirchhof's laws are used to get a full set of linear equations. All voltage sources and resistors are calculated in each time step according to the actual conditions such as temperature, current, acid concentration and level of degradations which have already occurred as a result of ageing effects. The equilibrium voltages of the voltage sources are calculated from the local acid concentration. For the resistors of the main charging/discharging reaction, the full Butler–Volmer relationship is used. This also includes a calculation of the available inner surface, which depends on state of charge, the coverage by lead-sulphate crystals and the size distribution of the crystals. Hence, the overvoltage of reactions and current pathways depend on the current which flows through them. As the electrochemical processes are highly non-linear (described by the Butler–Volmer-equation), the resistance value of the resistor which represents this process must be calculated in an iterative manner until the error is below the defined limits.

The electrolyte concentration is calculated on the basis of Fick's law of diffusion, generation and use of sulphate ions during charging and discharging, gravity and electrolyte mixing by gassing in a separate model. The acid concentration at any point in the battery is returned to the main model to calculate the resistance of the electrolyte, the rates for the charge/discharge reaction, the electro-chemical equilibrium voltage and the equilibrium concentration of Pb^{2+} ions in the electrolyte. Therefore, there is continuous and direct interaction between the electrical model and the acid concentration distribution.

The spatial resolution in this model is three elements in the vertical and three elements in the horizontal direction in each electrode. More elements are possible, but compromises between resolution and calculation speed must be made [5–7].

In fact the model is a two-dimensional model and the geometry of the cell is reduced to one single pair of positive and negative plates facing each other. It is assumed that all other pairs of electrodes have similar conditions due to symmetry reasons.

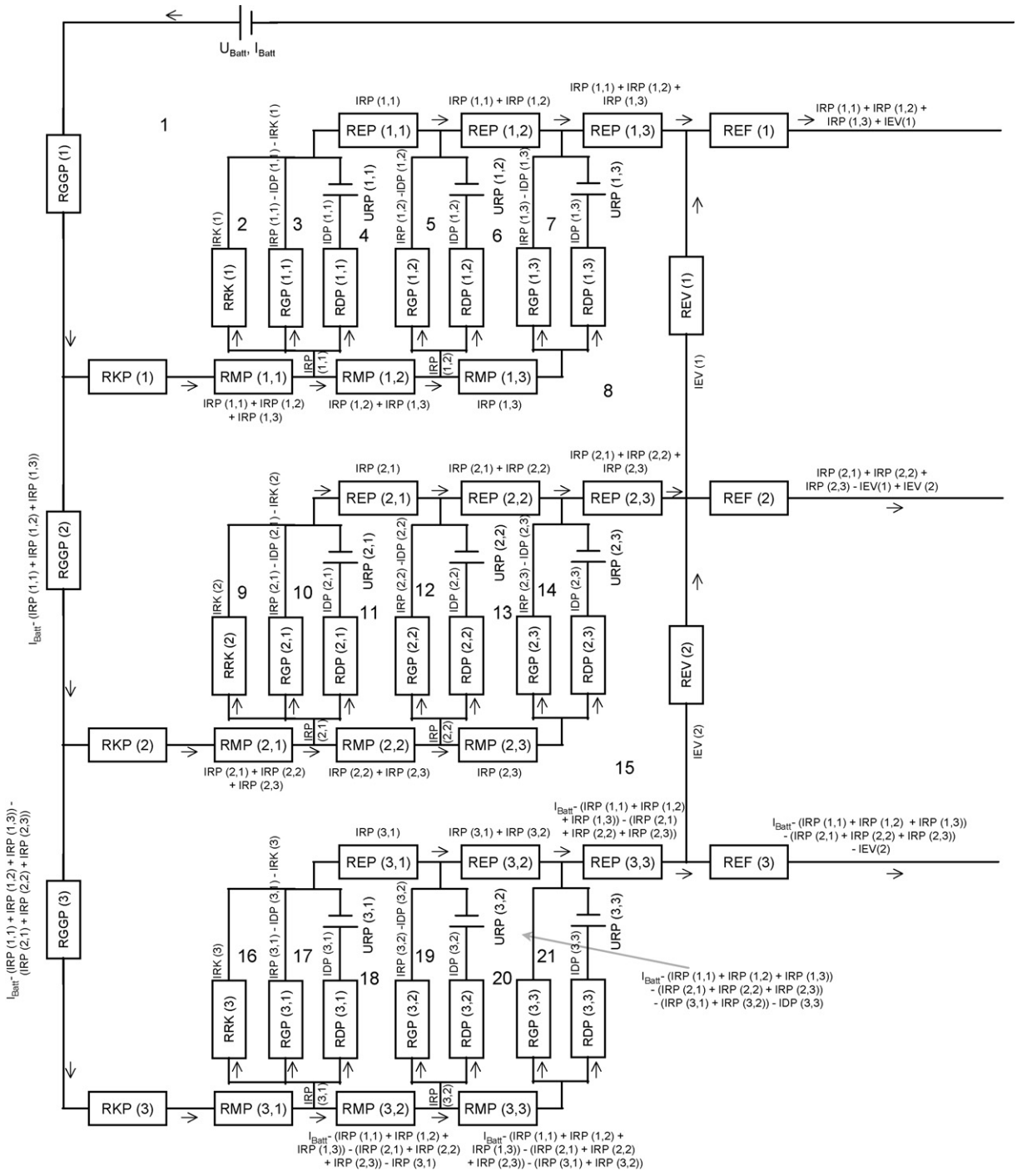

Fig. 2. Equivalent circuit diagram of the positive electrode (left-hand side of the figure: grid; right-hand side: electrical path way through the electrolyte to the negative electrode). Electrode is split into three vertical levels and three horizontal levels within the active mass. Explanation of elements: UBatt: battery terminal voltage; I_{Battery}: battery terminal current; RGGP: resistance of the positive grid along the height of the electrode (depending on the remaining grid thickness taking into account grid corrosion); RKP: resistance of the corrosion layer of the positive electrode (depending on the corrosion process); RMP: resistance of active material of the positive active mass (depending on porosity, state of charge and temperature); RRK: pathway for corrosion current, resistance calculated accordingly; RGP: pathway for gassing current at the positive electrode, resistance calculated according to gassing reaction (depending on local electrode potential, temperature, active surface and acid concentration); RDP: pathway for main reaction current at positive electrode, leading to a charge or discharge of the electrode, resistance calculated from the Butler–Volmer equation (depending on potential, temperature, active surface, and acid and Pb^{2+} concentration); URP: electrochemical voltage source of positive electrode, depending on acid concentration and temperature; REP: resistance of the electrolyte within the porous positive electrode (depending on porosity, acid concentration and temperature); REF: resistance of the electrolyte in the free electrolyte volume between the positive and the negative electrode (depending on acid concentration and temperature); RES: resistance of the electrolyte in the separator between the positive and the negative electrode (depending on acid concentration, porosity of the separator and temperature); REV: vertical resistance of the electrolyte in the free electrolyte volume between the electrodes (depending on acid concentration and temperature). The currents through the elements are described in the same way with an *I* for current instead an *R* for resistance.

Furthermore, it is assume that the current distribution is homogenous along the width of the electrodes.[1] Capacitors which are required to model changes of voltage and current correctly are omitted here as they would increase the complexity of the model considerably and are not relevant when simulating the behaviour of a battery using long time steps with constant current conditions during each time step. However, dynamic effects are taken into account by a detailed simulation of the concentration of the relevant ions in the electrolyte (HSO_4^- and Pb^{2+}). The minimum time step is 1 s.

The equivalent electric circuit diagram is used instead of solving a set of inhomogeneous, non-linear and coupled differential equations. It turned out that solving the model is much more robust when using the equivalent electric circuit diagram compared to solving the differential equations. The use of equivalent circuit diagrams of this complexity including the non-linearity of the resistors and voltage sources is standard in electrical engineering and tools for solving them are available.

3.2. Ageing processes

With the above-described model, the conditions at each point of time and every point in the electrodes and the electrolyte are well known. Therefore it is relatively simple to analyse the impact on different ageing effects.

In the laboratory, the analysis of ageing effects is done always under well-controlled conditions. This situation now exists for each point in the battery as well. The transfer of knowledge of the local conditions in the battery to a quantified impact on the ageing processes and battery performance is carried out in a two-step approach.

Firstly, from literature the general dependencies of most ageing mechanism on the state variables are known. Corrosion is used here as an example. Corrosion depends on temperature, potential and acid concentration. The general dependencies have been described already by Lander [8]. They are taken into account by using the exact values of the state variables from the models. However, the speed of corrosion depends also very much on the alloy, the active mass coverage, or even the casting conditions. It is impossible to calculate the corrosion resistance from first principles. In a second step therefore, specific corrosion tests on grids are performed under well-defined operating conditions in the laboratory. This information is used as the base variable in the model and adjusts the "Lander curve" to the correct value. Together it is now possible to calculate the local degree of corrosion of a grid under the given operating conditions. Obviously, a number of assumptions are made, e.g. that the general shape of the Lander curve is independent of alloy composition and production processes and that the influence of active mass coverage on corrosion is accounted for by using local potential and acid concentration values [7].

[1] This is true in first-order approximation. In reality there might be inhomogeneities along the electrode due to asymmetrical grids and the position of the current collector. However, it is assumed that these effects are only of secondary importance due to the very good conductivity of the grids.

Based on the same general concept, the impact of all major ageing effects can be analysed. As the ageing effects change the performance of the battery locally or for the complete cell, their effects are taken into account directly, e.g. by adapting the resistance of the grid, the inner surface of the active masses, etc. To be able to do this requires knowledge of some of the design parameters of the battery, e.g. thickness of the grid.

Consequently, the degree of ageing of the battery and the impact on the battery performance can be analysed at any point in time. "Measurements" of the inner resistance or "capacity tests" can be made regularly with the model to determine the current state of health.

3.3. Advantages and disadvantages of physico-chemical ageing models

Compared with the two other approaches described in the following sections of this paper, the physico-chemical ageing model is the most complex and most sophisticated approach. This model approach not only provides an ageing model, but also a model for the electrical performance. This is an additional although not strictly speaking necessary feature of the model as it addresses the increase of stress factors when an aged battery is subjected to the same power and performance requirements as a new battery.

However, the model approach requires several input information. This is on the one hand geometric data for the battery cell including the porosity of the active materials and on the other hand data of laboratory experiments on the major ageing effects. The model for the state variables requires mainly detailed geometrical data on the size, thickness and porosity of the electrodes, the case and the electrolyte volume and density. These are typical non-confidential data and can be measured by many laboratories very simply. The tests concerning ageing effects are more complex. The duration of the tests is typically in the range of 3 months and several tests must be performed in parallel. This is already out of the scope of what a "normal" end-user of batteries can do. In addition, the design of the experiments to limit the interaction between parallel ageing effects must be carried out with great care. Because of the complexity of the model the computational speed of simulation is significantly smaller compared with the other models. The limited resolution of the model is a compromise between computing speed (increases more than linear with number of simulation points) and resolution of the model. Currently, the calculation is 200 times faster than real time, e.g. runs approximately 40 h for 1 year of operation.

Part of the complexity of this approach is that the model has to be parameterised in such a way that the model output is consistent with the measured data. Measured current and temperature data are used as input to the model and the voltage as calculated from the model has to be similar to the measured voltage values. Once major differences occur especially in the state of charge, the model parameters have to be changed or a reset of the model parameters, i.e. when full charge has been reached, has to be made. Otherwise the model calculation might show a nearly fully charged battery and therefore a strongly increasing voltage and limiting charging current whereas the battery in the

field might be at a medium state of charge and therefore accepts all charge at relatively low charging voltage.

The approach can be transferred to any other battery technology. This requires on the one hand the representation of the technology-specific processes in the model of the state variables and on the other hand the identification of the relevant ageing processes and appropriate laboratory tests to characterise the specific material or technology. The adaptation of this ageing model to other battery technologies therefore can be done only with a significant time effort and by highly specialised scientists and engineers. This is a disadvantage compared to the other models.

As major advantages of the model three aspects need to be recognised. Once the parameters are determined for a certain battery, the model allows for an analysis of a wide variety of operating conditions and control strategies. There are no limitations because the model approach does not use simplifications which limit the validity of the model. The second advantage is that the model provides a very detailed understanding of the ageing processes in the battery and the interactions between operating strategies and battery ageing. This can be used by battery manufacturers for improving the battery design to meet the requirements of certain operating conditions better. Furthermore, due to the detailed modelling of the ageing effects combined with the electrical performance simulation, it is possible to analyse control strategies (max. depth of discharge, end of charging voltages, duration of charging periods, etc.) in more detail compared to the other models.

4. Weighted Ah ageing model

Lifetime data by manufacturers are based on well-defined test conditions. Cycle lifetime is simply determined by discharging the battery with a constant current to a certain depth of discharge and a subsequent full charge with a given charging regime. From these standard cycles the overall Ah throughput until the capacity has fallen below a pre-set level is measured. For lifetime prediction purposes, the lifetime of the battery is simply given as the time until the total Ah throughput is identical to the Ah throughput measured under such constant conditions.

However, in real application the operating conditions typically deviate from these standard operating conditions and the Ah throughput of the battery may be more or less damaging than during the standard operating conditions. The weighted Ah ageing model takes these deviations into account and makes the assumption that the battery is at the end of its lifetime once the weighted Ah throughput has exceeded the expected unweighted Ah throughput which has been measured under nominal operating conditions.

Per definition, the end of lifetime is reached once the capacity of the battery under standard test conditions (e.g. 10 h discharge current, 25 °C) is below 80% of the nominal capacity.

The following example shows the general idea of the approach for lead-acid batteries:

1. Cycling a lead-acid battery at low states of charge stresses the battery more than cycling at high states of charge. Therefore, any Ah which is charged or discharged to the battery needs to be weighted with a factor which is the higher the lower the state of charge.
2. Cycling of a battery while acid stratification is present is known to result in inhomogeneous current distribution along the electrode. As a result parts of the electrodes are stressed very much. Again, the Ah throughput needs to be weighted with a factor which depends on the degree of acid stratification.
3. Long periods without a full charge of the battery are known to be detrimental as well because the sulphate crystals grow. This finally results in sulphation (active mass which cannot be reconverted under normal charging conditions) and capacity loss. Therefore the Ah throughput also needs to be weighted with a factor depending on the time since the last full charge.

For lead-acid batteries a very detailed Ah throughput model has been developed. The first version of the model was published in Refs. [7,9], a newly revised and extended version is under preparation for publication. It takes into account acid stratification, current density, voltage, temperature, state of charge, time and the quality of a full charge, i.e. the degree to which homogeneity of the state variables in the cell has been achieved. In this advanced model weighting factors for acid stratification, bad full charges, SOC weight and current amplitude are taken into account.

Fig. 3 shows an operation profile, which has been taken from a laboratory bench test for the characterisation of lead-acid batteries with special respect to operation in photovoltaic power supply systems [10]. Fig. 3 shows the state of charge of a flat plate battery with liquid electrolyte. The SOC is scaled to nominal capacity ($C_{10} = 54$ Ah), the initial C_{10} capacity of the battery was approximately 160% of the nominal capacity. In addition the figure shows the voltage and the battery current. Together with the calculated state of charge the measured capacity is shown (stars) and the capacity curve calculated by the model. For the calculation of the capacity curve, a standard curve of capacity against Ah throughput is used so that the effect of the current profile on voltage can be modelled properly.

Fig. 4 shows more details of the model. All data are calculated from the operational data shown in Fig. 3. The upper graph shows the accumulated Ah throughput as it occurs (unweighted Ah throughput) and the weighted Ah throughput according to the model. While the real Ah throughput is approximately 320× the nominal capacity until the capacity dropped below its set value after a test period of 210 days, the weighted Ah throughput is by a factor of 5 higher. The middle graph and the lower graph show selected weighting factors. The lower graph shows the acid stratification factor which, in this example, is mostly close to 1 (i.e. no additional stress). The reason is, that the battery is frequently at a voltage of 2.4 V, resulting in gassing and therefore a natural mixing of the electrolyte. Therefore, acid stratification is assumed to be small. The middle graph shows the weighting factor for the current rate (green). This factor is 1 if the current is I_{10} (current for which the lifetime has been defined). Filter functions are used to calculate the average current. The blue curve shows the weighting factor taking into account the state

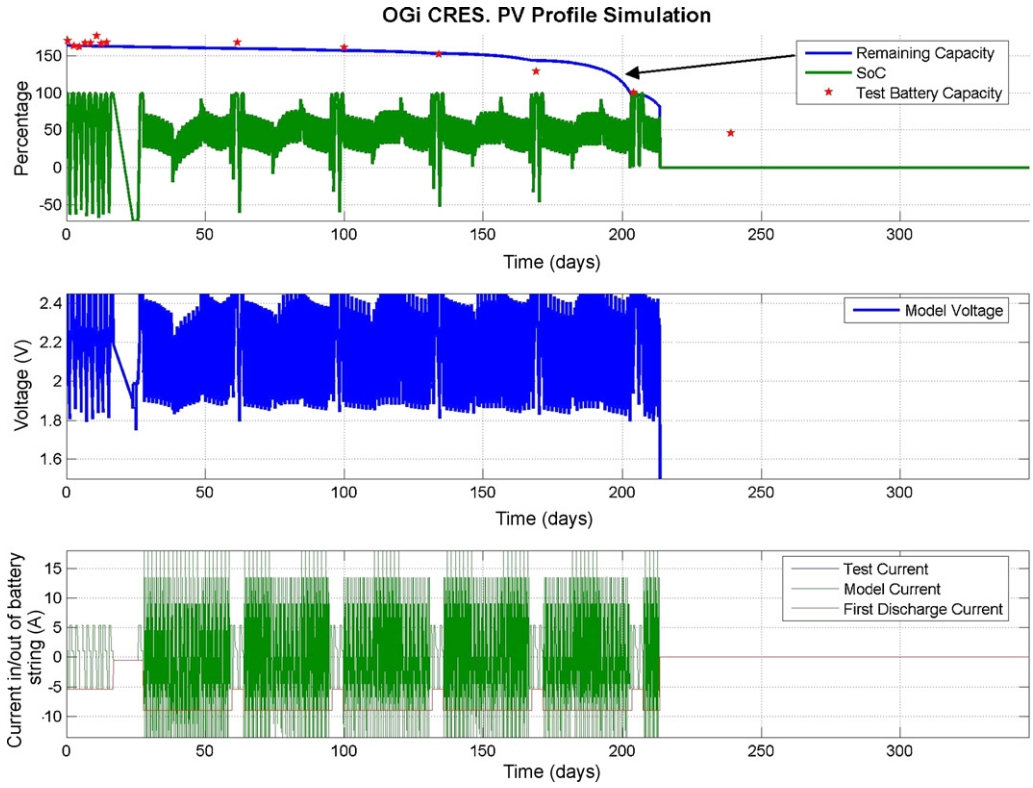

Fig. 3. Remaining capacity calculated by the model, measured capacity and SOC (upper graph), voltage (middle graph) and current (lower graph) for an OGi (flat plate) lead-acid battery with flooded electrolyte during a laboratory test with test profile representing typical operating conditions in photovoltaic power supply systems.

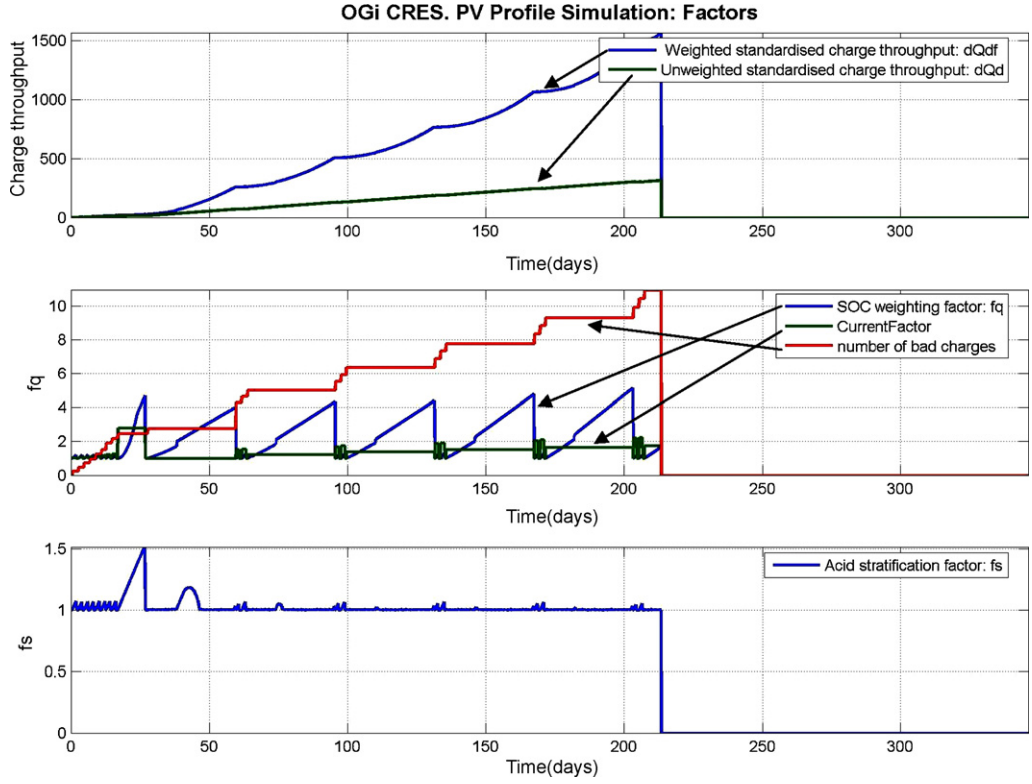

Fig. 4. Details from the weighted Ah ageing model for the operating conditions shown in Fig. 3. The upper graph shows the unweighted charge throughput (green) and the weighted Ah throughout (blue). In the middle graph weighting factors for the current (green) and the factor "SOC and time since last full charge" (blue) are shown. The lower graph shows the weighting factor for acid stratification. After 210 days the test is over, therefore all curves are set to zero after 210 days. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of charge and the time since the last full charge of the battery. It increases between two full charges and is reset to 1 once the battery has been fully charged and all inhomogeneities are removed. In addition a counter for the number of incomplete full charges (red curve) is shown. Incomplete charging has an impact on the distribution of the size of the sulphate crystals and therefore charge efficiency.

The current value of the factors is multiplied with the Ah throughput at any time step and finally results in the weighted Ah throughput.

For the parameterisation of the model first of all standard lifetime data provided by the manufacturers are necessary. In addition, the parameters for the weighting factors are needed. There are two different approaches to determine the parameters: expert estimates or parameter identification from measured data. If measured data are available as those which have been presented in Fig. 3, the parameter identification is an efficient and appropriate way. The benefit of the model is that the parameters need to be identified only once. Any other operating conditions can then be analysed with the model without any further modifications assuming no interaction between the weighting factors have to be taken into account. The same set of parameters can be used for high rate or low rate cycling regimes or for different applications. This allows analysing system designs (sizing of components) and operation strategies.

The weighting factors can be design specific as well. A paper is currently under preparation by the authors which provides a quantitative description of acid stratification and shows that the speed and magnitude with which acid stratification develops is a design feature of batteries.

The advantage of the model is a very high computational speed and therefore it is very useful for system design tools where a large number of systems must be analysed in a short time. Furthermore, the basic structure of the model is easy to understand and therefore it can be adapted to different battery technologies by taking into account the relevant stress factors and their quantitative impact on ageing for each technology.

However, the model is a heuristic approach. The model does not represent ageing effects on a physical or chemical basis. Therefore, the model does not provide direct feed-back to the manufacturers of the batteries to improve the technology. This would require a link between the weighting actors and the specific design features.

5. Event-oriented ageing model

5.1. General concept

In many fields of mechanical engineering an event-oriented ageing model is used which is often referred to as SN or Wöhler curve after the German railway engineer who first introduced the principle as a means to determine the lifetime of railway components. The lifetime of a component, in mechanical engineering simply the lifetime before breaking in a catastrophic failure mode, is estimated by assigning the incremental loss of lifetime associated with well-defined events and adding up the loss of lifetime per event. Usually, each event is described by one scalar value, e.g. the force of bending or the amplitude of vibration. We will refer to this scalar value as “stress factor”. When varying the magnitude of the stress factor, the number of events before breaking changes in a characteristic fashion: the greater the damage induced in the component by a certain value of the stress factor, the fewer events can take place before breaking. In a theoretical treatise of the Wöhler curve [11], the curve is associated with an accumulation of energy which is dissipated within the material and leads to incremental structural changes. Two types of Wöhler curves are used already today to estimate the battery lifetime:

1. The curve showing the number of cycles of a battery as a function of depth of discharge until the end of lifetime. This curve is given by most battery manufacturers in data sheets.
2. The curve showing the lifetime of a battery in days as a function of its float charging voltage or temperature.

However, both of these Wöhler curves as well as a lot of Wöhler curves in mechanical engineering are one-dimensional curves using only one stress factor as parameter and leaving all other parameters of the operating conditions constant. For batteries and fuel cells, such one-dimensional curves do not provide a realistic description of the operating conditions because there is a complex combination of stress factors in real applications.

The mathematics of event-oriented ageing models is simple: if NE_i^{max} is the number of events i which can occur during the lifetime of a battery until the failure occurs (under the assumptions that only events of type i occur) and NE_i is the number of events that have occurred during the period of observation, then the loss of lifetime associated with event i is

$$LL_i = \frac{NE_i}{NE_i^{max}}.$$

The portion of lifetime lost during a period of observation is then the sum over all types of events during this period:

$$LL = \sum_i LL_i$$

The end of lifetime is reached when LL is equal to 1. As every event is associated with a length of time, then the lifetime is the sum over the duration of all events i which have taken place.

Obviously the use of this model is based on the following assumptions:

1. The loss of lifetime per event is very small.
2. The loss of lifetime for a given event does not depend on the order of events, i.e. is independent of the events which took place previously.
3. The loss of lifetime associated with an event does not depend on the accumulated loss of lifetime. The incremental loss of lifetime caused by a particular event for a new battery is assumed to be identical to the loss of lifetime for a battery at the very end of its life.
4. Every point of time must be assigned to exactly one event for which data from a Wöhler curve exist. The simultaneous assignment to several types of events is not allowed.

The first assumption is true for batteries under normal operation. It does not hold for severe operating conditions capable of destroying a battery after a few repetitions (e.g. discharging to 0 V and remaining at 0 V for some time before recharging).

The second assumption is fulfilled in battery practice only, if the battery at the end of the event has returned to an appropriate condition. For lead-acid batteries this requirement means being fully charged with conversion of all discharged active material and removal of acid stratification. An event, therefore, must start with a fully charged battery and finish with a fully charged battery. In applications, where this is not assured, it is necessary to analyse whether the approach is appropriate and can be used at all. However, the number of applications, where such defined conditions are fulfilled is large. The assumption as formulated here also means that different events must be statistically distributed. Otherwise, it would be necessary to discuss whether a battery which will be subjected to float operation for the first half of its life and cycling operation for the second half will have a different life expectancy than a battery with a statistical mixture of these two types of events.

The third assumption is the most difficult one. When defining an event using parameters which already incorporate ageing (e.g. depth of discharge based on the actual capacity of the battery during the event), then ageing effects are at least partially incorporated. However, such definitions may not always be possible. Obviously, if the performance characteristics of a battery do not change significantly during the lifetime, e.g. battery capacity is only reduced by ca. 20% from its nominal value, then this assumption probably holds. Furthermore, it is possible to put the capacity throughput at the discharge current of the event into relation to the remaining capacity. The remaining capacity is always known by summing up the stress events that happened so far if a capacity curve over lifetime is used.

As regards the last assumption, Fig. 5 shows an example of the voltage, current and temperature of a battery in a railway application. It is immediately obvious that a simple one-dimensional Wöhler curve cannot be used and the definition of an event must be made carefully so that every point in time will be assigned to only one type of event.

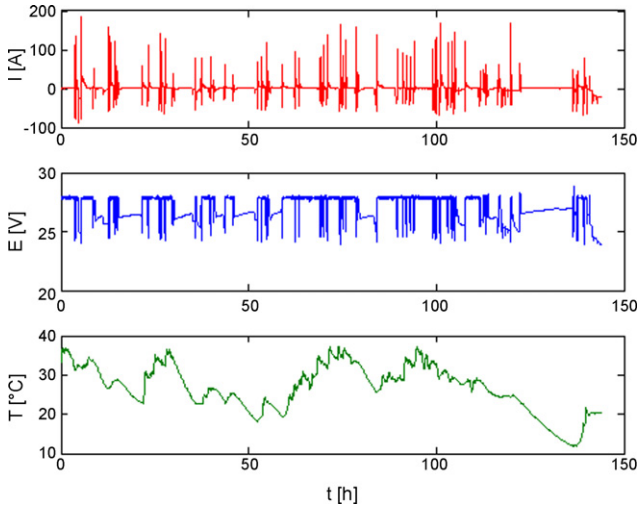

Fig. 5. Measured data of current, voltage and temperature for a period of 90 h from a battery system in a railway (24 V system).

5.2. Definition of events

Batteries in many applications can be considered to be subject to a combination of three different types of events: float operation, cyclic operation and cycling at a partial state of charge. The exact definition of "event" is application and technology specific and, as an example, is given here for lead-acid batteries for railway applications. The main classes of events are listed below. Each main class is subdivided into several sub-classes of events, which are discussed in more detail after the definition of the main classes.

5.2.1. Float operation

Batteries in railway applications may remain at a full state of charge for a long time, however, during that time may undergo severe temperature changes and may undergo changes in the charging voltage as the availability of electrical power on board a train changes. Float operation may also be interrupted for very short time by short, low rate discharges. In addition, the batteries may have to provide high rate discharge currents for starting the internal combustion engine of a train. Approximately 0.25% of the capacity is removed and float voltage is reached immediately after starting the motor. Neither of these occurrences is considered to be a discharge cycle.

5.2.2. Cyclic operation

Train batteries are occasionally discharged as part of their normal operation, e.g. shunting operations. For safety reasons, certain consumers are never switched off even if this leads to a damaging deep discharge of the battery and the battery may remain at a very low SOC for a few hours. Recharging the battery always occurs via a constant current/constant voltage charging regime with I_5 and usually up to a voltage of 2.35–2.4 V cell^{-1}. During discharging the battery current will tend to fluctuate as loads will be switched on and off, and during charging the charging current may sometimes fall below the set value as the availability of electrical power on board a train is limited.

5.2.3. Cycling at partial state of charge

Occasionally, a battery has not reached its full state of charge before another discharge starts. Damaging conditions like sulphation and acid stratification are then allowed to exercise their effect longer than in a normal discharge followed by a full charge. The duration of such an event, starting and ending with a fully charged battery, may last up to a week and the total Ah throughput and the lowest depth of discharge that is reached during this time may vary within a wide range.

The distinction between a cyclic operation and cycling at partial state of charge is conceptually simple. In a cyclic operation there is a continuous discharge followed by a continuous charging process which is finished when the battery has reached its full state of charge. Interruptions of the discharge or charge ($I_{\text{battery}} = 0$) are permitted. If the discharging process is interrupted by charging currents, even if the charging process takes

only a very short time, or the recharging process is interrupted by a period of discharging before the battery is fully charged, then cycling at partial state of charge exists. When analysing data in detail, a more differentiated definition has to be used, e.g. one where regenerative breaking is still considered to be a cyclic operation and opportunity charging is cycling at partial state of charge.

Based on these considerations, events were accurately defined and battery experts asked to provide estimates by how much the total number of events during the lifetime of a battery would change if well-defined stress factors would change.

For float operation, the stress factors to be considered were voltage (eight groups of float voltages between 2.23 and 2.4 V cell^{-1}) and number of short, high rate discharges (no discharges, 1–5 discharges per 24 h, 6–11 discharges per 24 h, 12–24 discharges per 24 h).

For cycling operation, the stress factors were depth of discharge (DOD) and amplitude of discharge current. The stress factor "depth of discharge" was grouped in categories according to Table 1 as follows. The percentage value given here are for an average discharge current in the range of I_2–I_5 for flooded tubular batteries.

It is necessary to take into consideration, that the identification of the events is the result of a detailed analysis of typical events that occur in this specific application. Currents of approximately I_{200} correspond to the current requirement of some safety features of railway systems which are never switched off and very deep discharges with waiting times before recharging starts may therefore occur. Concepts used in pattern recognition or expert systems may be used for identifying events that may occur in an application of interest.

In all cases, the recharge was assumed to be a constant current/constant voltage charging regime. The discharge currents were grouped into currents above I_2, I_2–I_5, I_5–I_{10}, I_{10}–I_{20}, I_{20}–I_{100} and less than I_{100}. This is a second dimension of Table 1.

The stress factors in cycling at partial state of charge are: (a) length of time before reaching again full state of charge; (b) Ah-throughput during this time. The stress factor "length of time" was grouped into duration of up to 1 day, 1–2 days, 2–3 days, 3–4 days and up to 7 days, and the stress factor "Ah-throughput" into up to 0.5 nominal capacity throughput (C_N), 0.5–1C_N, 1–1.5C_N, 1.5–2C_N, 2–4C_N and 4–6C_N.

Table 1
Example for the rating of stress factors for current rates between I_2 and I_5

Max. DOD 0–10% followed immediately by a full recharge	887%
Max. DOD 0–20% followed immediately by a full recharge	452%
Max. DOD 20–40% followed immediately by a full recharge	247%
Max. DOD 40–60% followed immediately by a full recharge	157%
Max. DOD 60–80% followed immediately by a full recharge	100%
Max. DOD 80–100% followed immediately by a full recharge	68%
DOD 100% followed by a waiting period of up to 24 h before a full recharge is started	58%
DOD 100% followed by a further discharge with approximately I_{200} for up to 24 h followed by a full recharge	37%

Lifetime defined for cycling with 80% DOD.

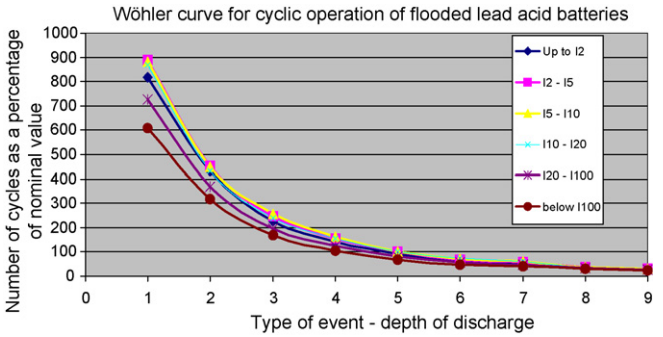

Fig. 6. Example for Wöhler curves for different events (compare Table 1) for different current rates.

Fig. 6 shows Wöhler curves as an example for the above discussed case of cyclic operation. The data must be taken as a general example.

For the parameterisation of the model first of all standard lifetime data provided by the manufacturers are necessary. The data of all Wöhler curves are given as a percentage so that the transfer to other battery systems is straightforward.

The parameters "Ah throughput" and "length of time" form additional sets of curves for the "cycling at partial state of charge" class of events and the parameters "charging voltage" and "number of high rate discharge events per 24 h" form a set of curves for the "float operation" class of events. For each event, an increase of 10 °C above 20 °C was assumed to half the number of events. The task of estimating lifetime is then reduced to a computational program which identifies events from measured or simulated current, voltage and temperature curves. Very strict assignment criteria were used so far but methods based on fuzzy logic or pattern recognition might offer advantages. The program identifies the events defined above from the current and voltage profile of measured data or data from simulations and assigns the loss of lifetime per event taking the effect of temperature into account. Computational speed is very high.

Data as shown in Fig. 5 were used to analyse the stress events and to predict the lifetime. The analysis of a 7-day period from which the data in Fig. 5 were taken showed a loss of battery lifetime of 1%, i.e. the battery under these conditions would have had a lifetime of about 2 years.

The weighted Ah model assumes a certain loss-of-capacity curve and the event-oriented model does not assume any change in the performance throughout the battery lifetime. However, when real data are used, the event-oriented model can have the change of performance as input. Consequently, the degree of ageing of the battery and the impact on the battery performance can be analysed at any point in time.

6. Comparison of the different approaches

The information requirement for the three approaches discussed above and the methods to verify them differ greatly. In

a paper by Wenzl et al. [1] the reasons why verification of lifetime prediction is so difficult and time consuming are discussed in detail. In summary, lifetime prediction models can only be verified for a battery which is well characterised when it is new and for which the complete data sets of voltage, current and temperature are available from installation to decommissioning including a capacity test and possibly other tests at the time of decommissioning. There are hardly any such data sets available. If lifetime prediction models need to be parameterised, then the validity of the model cannot be checked by using the same data set that has been used for the parameterisation. Additional data sets are required for verification.

Method 1 requires knowledge of the interaction between electrochemical and physical measurements (state variables: resistance and voltages as a function of state of charge; temperature; microstructure of the active material) and ageing processes which are usually not accessible to non-destructive measurements. Only the loss of performance as a result of the combination of ageing processes that have taken place can be measured when putting the complete cell into the test. But the detailed modelling approach allows separating the ageing effects within the models and this is unique within the different approaches presented in this paper. The calibration of the models for the different ageing effects can be done most efficiently if parts of the cell are subjected to ageing tests, e.g. grids only to corrosion tests. However, once this has been accomplished and the model describes correctly the changes of performance during the lifetime of a battery and thus correctly predicts the lifetime of the battery, then the model has achieved a considerable step towards verification. A single set of lifetime tests in the laboratory which confirms the lifetime prediction model will be sufficient. The model can then be considered to predict the lifetime of the battery sufficiently well, even if changes of operating conditions lead to a different combination of ageing effects. When analysing measured data, the current, voltage and temperature values have to be recreated by the model first. Good agreement between measurement and model will immediately qualify the model and provide credibility to the lifetime prediction.

The transfer to other types of lead-acid batteries is very simple and requires only adequate design parameters and results from the specific ageing tests on components of the cell. Transfer to other battery technologies and fuel cells is straightforward and significant parts of the mathematical algorithms can be reused, but the description of the specific electrochemical reactions and the general knowledge on the dependence of ageing effects on the state variables must be worked out newly.

The situation is different for the weighted Ah model. The weighting factors cannot be derived from first principles and need to be obtained differently. Expert expertise or fitting the parameters are two options to correctly predict the lifetime of a battery for which lifetime measurements are available. Supporting expert estimates by calculations using physico-chemical models or a first principle approach is possible. When analysing measured data, the current, voltage and temperature values have to be recreated by the model first. Good agreement between measurement and model will not in itself qualify the model and provide credibility to the lifetime prediction, unless the agreement extends over the whole of the lifetime.

The use of this approach requires the availability of measurements to fit the parameters, respectively verify that the combination of expert estimates does in fact lead to the lifetime which has been measured. Subsequently another set of measurements is required, sufficiently different not to be a repeat of the parameterisation process but sufficiently close to be similar. An extension beyond “similar” data sets offers less and less credibility, as does the transfer of the model to other battery types. A paper by the authors is under preparation which shows that the development of acid stratification in different batteries differs considerably and therefore, obviously, a factor describing the weight of Ah throughput when using a battery with electrolyte stratification depends on the battery type.

The Ah weighted approach uses a curve which models the capacity over the lifetime of the battery. In lead-acid batteries, this curve shows a small increase of capacity at the beginning, then a very constant phase and then a fast decrease of capacity. The increase of capacity is not represented by the model capacity curve. However, this is not critical because the model should predict the end of lifetime and small deviations at the beginning of the life have no impact on the lifetime result itself.

The event-oriented approach is the approach used today for lifetime prediction but is extended to variations in the operating conditions which are at present not accounted for properly. It requires an application-oriented definition and classification of events and information concerning the number of these events until the end of lifetime is reached. For some events, measurements are available, e.g. number of cycles at a certain temperature and depth of discharge or days at float charging. In principle, of course, it is possible to determine all the required data in the laboratory correctly without any doubts concerning their validity, but this process takes very long and is exceedingly expensive. However, interpolation by expert opinion can be used as long as measurements for a few types of events exist. This approach therefore is simple and depends on the assumption that the loss of lifetime caused by an event does not depend on the previous event or on the age of the battery. Verification of the model is therefore simply a question of analysing one single set of measurements which extends over the lifetime of the battery. A detailed characterisation of the battery at the beginning is not necessary, but the end of lifetime criteria need to be chosen suitably. In applications where the degradation process is very slow, both the event oriented and weighted Ah throughput model face difficulties.

In contrast to the other models, measured data can be taken as they are and need not be recalculated before applying the lifetime prediction models.

A transfer of results to other batteries is straightforward as the model is independent of battery technologies and design specifics and requires only the adjustment of the input matrices to other battery types or fuel cells.

Table 2 sums up advantages and disadvantages of the different models.

Table 2
Comparison of the different model approaches with regard to parameter identification, model complexity and transfer to other applications, battery designs and battery technologies (electrochemical systems)

	Parameter identification	Preciseness and quality of information	Model complexity and calculation speed	Transfer of model to other applications and battery designs	Transfer of model to other electrochemical systems
Physico-chemical ageing model	Through lab experiments and literature study	High, can give very detailed information	High/slow	Only battery design parameters needed	Same structure, but new models required
Weighted Ah ageing model	Expert expertise and data from lifetime tests (field or lab)	Medium, allows optimisation of operating conditions	Medium/medium	Deviating ageing effects must be identified and included	Same structure, but new weighting factors needed
Event-oriented ageing model	Expert expertise	Low, does not allow extrapolations to other conditions	Low/high	New expert expertise needed if other stress events occur	Same structure, new expert expertise needed

All approaches allow an optimisation of the operating strategy of an application. However, only the weighted Ah throughput model and the event-oriented model are applicable for an online optimisation of the operating strategy. If the various weighting factors increase more and more or the battery is classified to be in an event which uses up a significant portion of the lifetime, then a cost-benefit analysis can be made concerning changes in the operating strategy. In renewable energy systems, for instance, the cost of providing a full charge can then be easily compared to the cost of not doing so.

7. Application of the model for different battery technologies and fuel cells

The three types of models have been explained using lead-acid batteries as examples. However, they clearly apply to other electrochemical systems as well, including fuel cells. Generally, for fuel cells the application of the concepts is easier than for batteries. The reason is the fact that fuel cells can be operated in steady state conditions. No changes in "state of charge" occur and therefore the complexity is reduced by at least one-dimension.

To adapt the models to other electrochemical technologies, the specific ageing conditions and their stress factors must be identified.

As an example, the following effects, among others, should be taken into account for lithium batteries:

- Cycle depth—due to breathing of the active mass during cycling the lifetime depends significantly on the cycle depth.
- Operational state of charge (some materials show better lifetimes if the batteries are cycled at medium states of charge rather than at high state of charge due to increased side reactions at high state of charge) and its impact on cycle lifetime.
- Charging voltage—the electrolyte will be irreversibly decomposed at too high charging voltages.
- Formation of solid electrolyte interface.
- Temperature (typical lifetime reduction as for all electrochemical systems).
- Lithium plating in case of too high current rates (depending on the temperature).

It is necessary to take into account that lithium-based batteries are a class of batteries with a very wide range of different technologies. Therefore, the weighting factors, stress factors or events are different for different materials. For lead-acid batteries or nickel-metal hydride batteries the situation is simpler, because the materials used are always the same.

If interactions between the various stress factors and ageing effects are described in principle and the knowledge of what causes loss of lifetime has been quantified, each of the three modelling approaches can be applied.

Experimental investigation on the current and temperature distribution with a fuel cell show clearly, that the approach with the physico-chemical ageing model can be transferred to fuel cells as well [12,13]. State variables within a cell can deviate significantly from what is expected from the mean values measured on the outside of the cell. Therefore, corrosion processes or any other detrimental effects which depend on potential, current rates, temperature and concentration of fuels can be modelled and linked to ageing effects.

But also the event-oriented model can be applied. Different operating temperatures, start and shut down of the cells, or normal operation at different current levels are different events with unequal impact on the overall lifetime.

8. Summary

Three different general approaches for lifetime models for electrochemical energy storage systems have been presented. They all aim at the support of system designers in the selection of the appropriate product, optimum battery sizing and the definition of the best operating strategy so that minimum lifetime costs can be achieved as the ultimate objective.

To be an efficient tool for these purposes the models must be fast with respect to the calculation speed and the parameterisation must be simple. The parameterisation of the models presented here follows different concepts, but it is possible to analyse different operating conditions with one set of data. The transfer from one battery type to another and the transfer to other battery technologies and to fuel cells is possible in all three cases but follows different requirements.

It is highly recommended that battery manufacturers and representatives from large user groups of electrochemical storage systems identify a modelling approach for which the model parameters are delivered directly by the manufacturers. This would allow the users to achieve reliable information on the expected lifetimes in certain applications and can be also a basis for the handling of warranty issues. The concepts presented in this paper are a basis for this discussion.

Acknowledgements

The work presented here was funded in part by the Deutsche Bahn AG and the European Union ("Benchmarking", ENK6-CT2001-80576 and "ACTUS", ENK6-CT2000-00069).

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