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Review

Ageing forecast of lithium-ion batteries for electric and hybrid vehicles

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ABSTRACT

Reliability of energy storage devices is one of the foremost preoccupations in Electric Vehicles development. Battery ageing, i.e. the time dependent degradation of battery energy and power, depends on the in-use solicitations endured by the storage system. The connection between solicitations and battery life must be analyzed and modeled to match battery in-service life with car lifetime. Large variation in pulse duration and amplitude make life prediction an intricate problem. Consequently, the first step of the methodology is the definition of a test protocol able to define a damage notion. In case of Li-ion batteries, impedance rise and capacity fade are clearly involved in damage evaluation. The protocol must estimate this impact and allow a sensitivity study in terms of damage. This paper presents different methods to estimate battery ageing and tries to give, for each, some of the advantages and disadvantages that could appear when modeling.

KEYWORDS: energy storage, electric vehicle, Li-batteries, ageing, modeling

1. INTRODUCTION

During the last few years, Lithium-ion batteries became references for multiple applications, like spatial, communications or portable electronics. In a near future, and already today [1-2], these electrochemical energy storage systems will be used in electric and hybrid vehicles. In these particular types of vehicles (EV, HEV or PHEV), a part of energy is stored in batteries to be used later. The architectures of such transportation allow, partially or totally, decreasing of fuel consumption. It could be a good way to limit both pollution and greenhouse effect gases emissions. Lithium ion batteries, with high energy densities, are particularly adapted for this type of use. Unfortunately, performance of a Li-ion battery declines both with time and use. It is called ageing.

To be able to anticipate this deterioration is very important for multiple reasons. The first one is the correct sizing of the energy storage system. Indeed, to reach vehicle specifications asked at the beginning and at the end of life, the battery, inside a vehicle, is generally oversized. Due to high prices and volume/weight of batteries, to quantify, as precisely as possible, dimensions is a very important point for car makers. A second reason is to understand and to limit the most impacting parameters on ageing. To predict impacts of each parameter is crucial in order to get onboard a more effective energy management strategy. For example, would a coolant system be useful inside the battery pack? For these reasons, and many others (warranty time…), to get a predictive model of battery ageing is important for a car maker.

This paper reviews existing models and possibilities to forecast battery ageing of electric vehicles (EV), hybrid electric vehicles (HEV) or plug-in hybrid electric vehicles (PHEV).

In the particular field of such battery electric vehicles (BEV), both using conditions and ageing mechanisms are very specific:

- Firstly, parameters of battery solicitation are very complex. In particular, current profiles are largely non-linear (with huge and brief power demands or, in the contrary, energy recuperation when braking). Moreover, a wide temperature operating range is also commonly observed, during an entire year of use.
- Secondly, a typical passenger car is parked between 80% and 95% of its time and is not driven. Even if the battery, in this case, is obviously not used, its performance slightly decreases upon time. It is called calendar ageing, opposite to cycling ageing (observed during the aforementioned use of the vehicle).

An accurate battery ageing model has thus to take into account both cycling and calendar degradations. These two particularities make a battery ageing model for BEV not so easy to establish.

2. Battery ageing mechanisms

The decrease of battery properties along life and use is due to a lot of chemical/electrochemical mechanisms. These mechanisms largely depend on the technology used (nature of the active materials, choice of the electrolyte -liquid or polymer-, architecture -prismatic or planar or cylindrical,…) but each component inside the battery is going to be degraded (Figure 1).

Phenomena have been largely described in previous numerous studies [3-4] and, hence, they will not be completely described here. But for a better comprehension of the purpose, a general overview of today's foremost knowledge of components ageing is reported here.

2.1. Electrolyte ageing

Common electrolytes in Lithium-ion batteries are made of a lithium salt (mainly $LiPF_6$) and a mixture of several liquid organic solvents. These solvents are generally chosen among EC (ethylene carbonate), PC (propylene carbonate), DEC (diethyl carbonate) and DMC (dimethyl carbonate). VC (vinyl carbonate) or VEC (vinyl ethyl carbonate) are sometimes used, as additive, to increase battery life [5]. At relative low voltage, and in contact with negative electrodes (i.e., at high state of charge of the battery), partial reduction of the electrolyte can occur with production of gas [6] and/or insoluble species (like Li_2CO_3, LiF, PF_5…) [7]. These chemical products are going to obstruct both the electrode and the separator pores, and will moreover "eat up" a part of the available lithium ions (dissolved in the electrolyte), leading thereby to a decrease of the cell capacity [8-9]. On the contrary, oxidation of electrolyte can also occur, at high voltage, and in contact with positive electrodes and

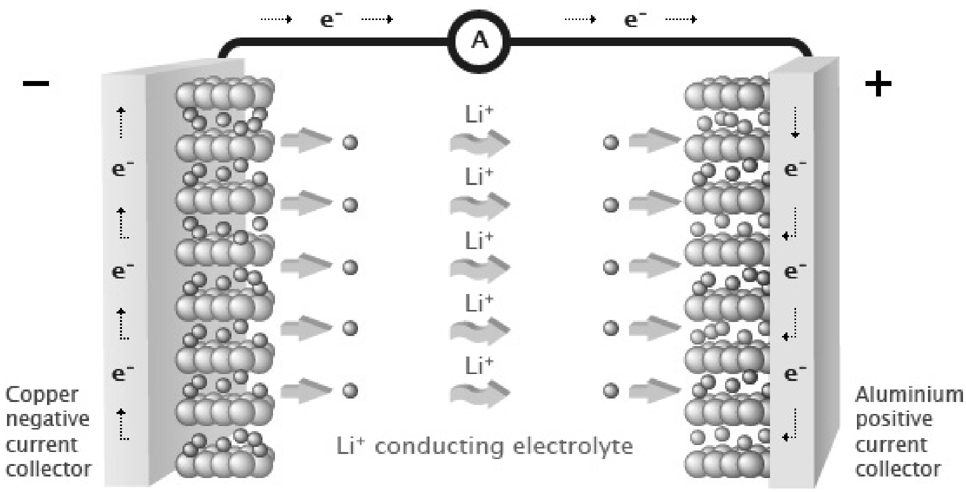

Figure 1. Li-ion battery during a discharge (Li^+ and e^- displace reversely at charging).

consequently make vulnerable the lifespan of the cell [10-12].

2.2. Current collectors ageing

Current collectors are generally made of copper, for negative electrode, and of aluminum, for positive electrode. In function of the voltage where the electrodes are polarized, these collectors can be corroded and then partially dissolved [13-14]. Although risk is minimal if the discharge end is well controlled [15], corrosion could lead to direct impedance increase (higher contact resistance between active material and current collector), or to indirect loss of electro-active material (being no longer electronically linked to collector).

2.3. Negative electrode ageing

Lots of researchers have studied carbon electrode ageing [16-18], and, for most of them, the main ageing phenomenon is a modification of the carbon-based electrode/electrolyte interface [19]. Indeed, at low voltage, graphite is going to react with electrolyte. The decomposition products build up a passivating/oxide layer (that partially covers the electrode surface) named solid electrolyte interphase (SEI). This layer prevents (partially) the graphite surface for being more degraded (which can be regarded as a positive effect) but also lead to use up the lithium salt and the solvent, decreasing conductivity of the cell (which is a negative effect). This process occurs mainly at the beginning of the cell life (i.e. as soon as electrode and electrolyte are in contact), but not only. In fact, formation of the SEI is ongoing throughout the entire battery lifetime. More precise studies have been done, and it seems that SEI layers have a complex structure [20-23], still not completely unrevealed.

2.4. Positive electrode ageing

Several positive electrode materials are now available on the market ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$...), and, for each of them, ageing mechanisms are somehow different and have thus different impacts on the observed performance fading [4]. The positive electrode is actually a hybrid-composite electrode (where inorganic and organic compounds are mixed together), meaning that ageing sources could be multiple (for instance, it could come from the inorganic active material, the polymeric PTFE or PVdF binder and/or the carbon based-conductive additives). However, we will keep in mind that ageing of the active material is, here, the main source of degradation (since the active material is present at more than 80%wgt in the composite electrode), with: structural disordering [24], partial dissolution [3] and/or surface modification [25].

3. Battery ageing forecast

Battery ageing forecast is following one (or several) properties of a cell (power, capacity, resistance...), or a complete battery pack, along its life, according to the conditions of use. This prevision is based on tests (to be performed) or data (already obtained), and there are, obviously, several ways to model the evolutions of a battery. Ageing estimation can be grouped into three main approaches: physics-based, mathematical and fatigue models (Figure 2).

The first approach, called here “physics-based models”, uses physical information inputs, like an empirical curve of voltage *vs* SOC (State Of Charge) or a physical measurement of ionic diffusion, for example. This group contains the electrochemical models, the empirical models and the empirical models + ECM (Equivalent Circuit Model).

The second approach, called here “mathematical models”, is very different from the former one. This method commonly uses electrical data to link inputs and outputs of a battery, during its life. Artificial neural network models (ANN) are somewhat representative of multiple computational models.

The last approach, called here “fatigue models”, is based on a mechanical view of the battery ageing. Actually, this method analyzes the impacts/effects of incremental damages on the battery lifetime, depending on controlled input conditions.

In this paper, we will describe each model and will detail advantages/disadvantages, and also the ability to forecast battery ageing in function of the vehicle use conditions.

4. Physics-based models

4.1. Electrochemical models

Electrochemical models are based on physico-chemical processes. These models need multiple

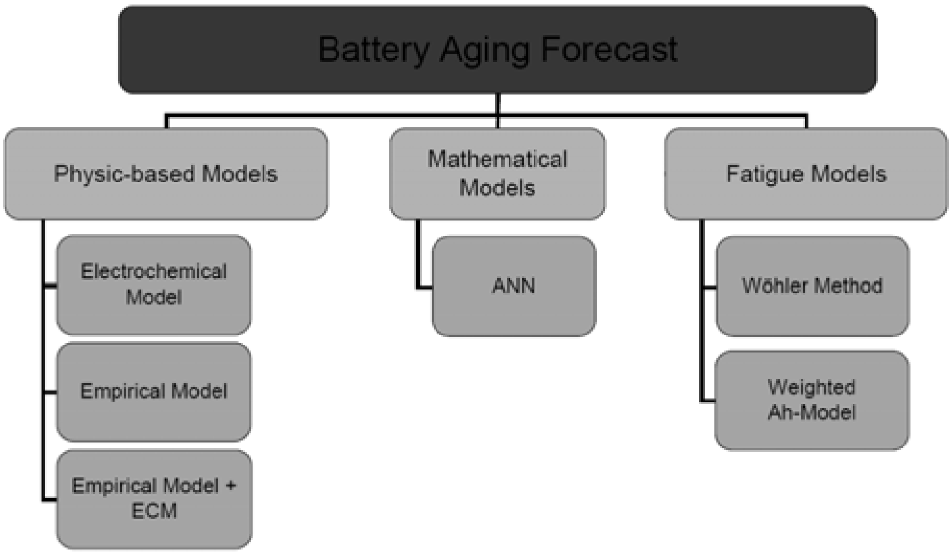

Figure 2. Different approaches of batteries ageing forecast.

equations to link electrical and physical properties of the cell. For example, Nernst equation can be used to link an electrode voltage to a local lithium concentration. The first Fick's law can link diffusion flux of lithium ions and their concentration inside the cell. These models are often complex (see, for example, ref. [26]). They use, indeed, a lot of equations with partial derivatives and become more and more complex if precision in prevision is demanded. Calculation time is, thus, important. Moreover, electro-chemical models can contain up to dozens of independent (or dependent) parameters, each one evolving independently (or dependently) during ageing, with mathematical laws and equations often unknown. Because of complexity of ageing phenomenon modeled and of the lack of knowledge (or calculation solving), in most of cases, these models have to be simplified compared to reality and integrate finally only one physical source of ageing.

Among the electrochemical existing models there are, to begin, very simple ones [27-28] using Tafel's equations, Fick's laws or Butler-Volmer relation. However, these models do not include an evolution upon time and they are only behavioral models. In most electrochemical ageing models developed [29-30], formation and evolution of SEI is the only reaction taken into account. With more development, models can include lithium ions diffusion limitation [18], or a more complex limitation mode (diffusion, solvent decomposition kinetics or a mix of the two) [31]. Decomposition of organic solvent and decrease of porosity can also be added. More complex electrochemical ageing models have been then published [32-34], with even the possibility to distinguish between anodic and cathodic capacity losses. In all of these battery ageing models, electrolyte decomposition on negative electrodes is considered as the predominant source of damage. It is an approximation of real phenomena occurring in the electrochemical complex system, even if it would be difficult/ impossible to have, with this method, an exhaustive model.

Disadvantages

A first problem of this type of model is how to build and determine equations, parameters and physical laws. Aging phenomena are partly known, but are partly still vague. To develop electrochemical ageing equations with correct physical parameters will be thus difficult. Contrary to an electrical signal, here, a lot of parameters have to be measured and each of them evolves during operations but also during ageing. This point could be a stumbling block for a car maker: some battery cells are not yet available commercially and also not allowed to be dismantled. Another problem is the computation time: with a simple 1-dimension model and few partial differential equations, solutions are difficult to obtain and lot of time is needed. Complexity increases exponentially with number of equations and their dimensions. Computer resources and time needed are then very important. It is also a reason why numbers of phenomena, taken into account, are limited.

Advantages

Despite these disadvantages, electrochemical models are the most commonly used for ageing prevision. These types of model, by nature, are able to model a wide variety of solicitations and is not dependant of type of ageing tests made; allowing great flexibility of modeling (both EV and HEV profiles, for example). To be based on electrochemistry is another advantage, foundations are rooted on reality, on chemical reactions, and all parameters are measurable. These two qualities - flexibility and measurable parameters - can also lead to a third quality for a vehicle maker: possibility to transpose a model to another type (technology) of lithium cell. In theory, if the new cell has a similar chemistry and similar ageing processes, the new electrochemical model needs only new physical parameters: diffusion coefficient, particle size, electrode thickness and no need of long and expensive ageing tests. Due to rapid evolution of battery technologies, car makers would be delighted to get such a quick and easy evolving model.

4.2. Empirical models

A rapid technique, easy to establish, is to use ageing tests and to extrapolate results. It is known as empirical methods. It is commonly used, as a first approach, and can give rapid lifetime estimation. For example, Broussely uses this technique for calendar ageing [35-36] and extrapolate the results with a quite good precision of lithium loss, in the cell, upon time (Figure 3).

If all the conditions stay the same upon operation, estimation over 10 years can be done with a simple lecture, providing interesting information impossible to get without any extrapolation. These models consist in a very simple approach [37-39]. Even if there is no explanation of phenomena, empiric models [38-40] show power losses, during calendar and cycling ageing tests, in function of square root of time. Of course, because of errors during tests and also by divergence with time, it is very important to control disparity and precision of measurements. For example, a study [41], on several lithium cells during calendar ageing, analyzes such error and dispersion during time. Lifespan, for a lithium-ion cell, is here estimated between 8 and 18 years,

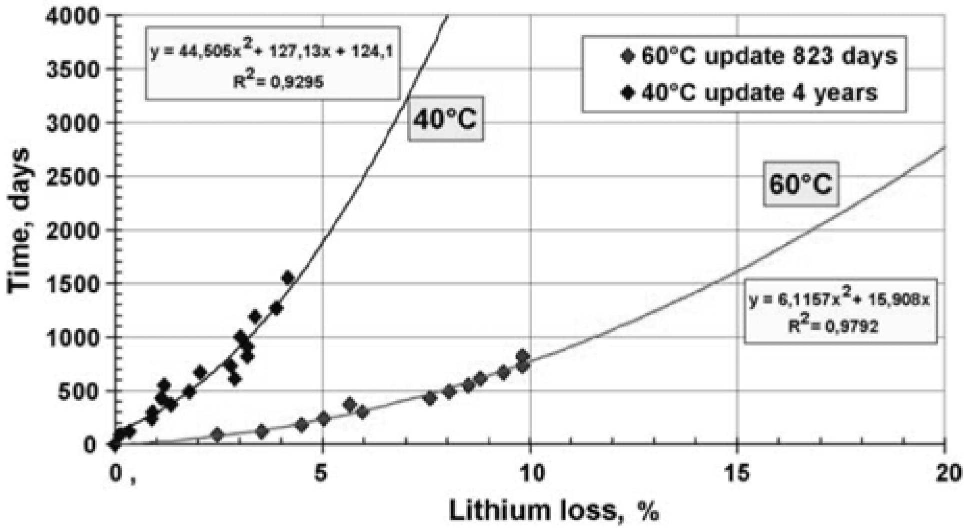

Figure 3. Example of an empirical approach: Extrapolation of lithium loss over time for different calendar conditions [36].

including dispersion due to cell fabrication but also extrapolation errors of this empirical model used.

Advantages and disadvantages

The empirical models are easy to perform and are thus very often used, particularly as a first approach. But, because there is no explanation of the ageing phenomena, here, ageing tests have to be closed of a final use. If test conditions are slightly different, a new ageing test with extrapolation is needed. There is no flexibility. It is, however, possible to use this approach for a vehicle lifespan prediction with an ageing solicitation, a specific vehicle profile, corresponding to a large majority of vehicle use and users. Unfortunately, this type of profile is very difficult to develop due to large variety of uses (road, highway, valley, mountain…) and users. Independently, to be able to extrapolate, from 1 year of test, to 10 or 15 years of ageing, could be risky: ageing phenomena can indeed change (more or less rapidly) with time. Extrapolation, based on finally few data, may lead to a prevision error of 40% [42]. Thus, empirical models will be used for a limited time of extrapolation.

For these reasons, it seems impossible to use this approach for electric vehicle applications. Complexity and variety of vehicle solicitations are too important.

4.3. Empirical models & equivalent circuit model

A lithium-ion cell can be considered as an electrical dipole and thus be modeled with an ECM (Equivalent Circuit Model). It is also possible to model the behavior of a cell, in response to a specific solicitation. For example, voltage under a CCCV charge (Constant Current - Constant Voltage). These ECM are commonly used for capacity measurement or simple electrochemical characterizations [43-44]. They consist in an equivalent electrical circuit, made of various electrical components (mainly resistors, capacitors...) and organized in a (more or less) realistic way. For example, a simple ECM, modeling charge and discharge curves, is represented in Figure 4.

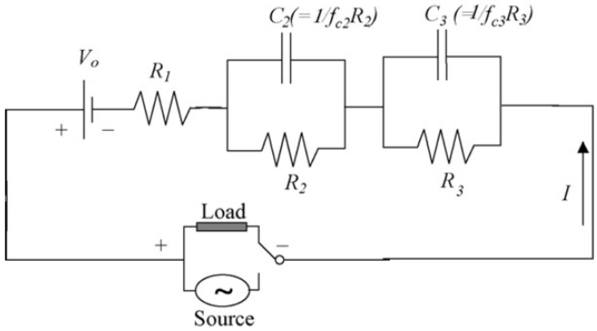

Figure 4. ECM for behavior simulation of lithium cell [47].

More complex equivalent circuits have been created [45-46] to simulate, more precisely, the cell behavior, including more electrical components. Sometimes, components are totally unreal (i.e. with no particular real physical signification). But, in most of the cases (and as it should be), components are linked to reality, and values come essentially from EIS (Electrochemical Impedance Spectroscopy) measurements [47-48]. In that way, these models are physics-based: for example, in Figure 4, R_1 represents internal resistance of the cell and connector, R_2 and R_3 represent faradaic processes (at both electrodes).

These equivalent circuit models can also be used to predict ageing. Each single component of these (more or less complex) electric circuits can be linked to internal or external parameters, like temperature, current, state of charge... Thanks to ageing tests and EIS experiments, it is then possible to establish evolution laws of each electric parameter that composes the ECM. For example, EIS spectra evolve directly with number of cycle [49]. A very complete empirical + ECM model was described by Liaw [50], who reports evolution of each parameter of his dedicated ECM. For instance, in his paper, resistance is function of two parameters (*d* & *e*) and state of charge. For a solicitation, both *d* and *e* coefficients are measured upon ageing and extrapolated empirically [51]. Parameters can be extrapolated to predict future evolution of the lithium cell.

Advantages and disadvantages

Equivalent circuits are very well-known in the scientific community and to establish an electrical circuit is quite easy. In most of the cases, it is possible to set it up without any physicochemical experiment but only impedance measurements (EIS). Depending on user needs complexity, models can be adapted with a more or less advanced electrical circuit. This approach has the following advantage, compared to other solutions, for ageing forecasting: a behavior model is included and works directly, in parallel, with the ageing model. Parameters are updated continuously, all along the modeling process, to reflect evolutions of the battery, and it is thus possible to get the predicted discharge curve after 800 cycles, for example. Most of the time, based on physics reality, the electric elements of the ECM are extrapolated in function of the operating conditions and ageing. But this extrapolation is also based on empirical tests. Quality of ageing modeling, for this technique, is the same as empirical ones: a mathematical extrapolation of a curve. Empirical ECM seems not to be enough complex to take into account all parameters and complexity inherent to electric vehicle solicitations. In fact, it is just a better way to model a battery (in comparison with the empirical way used alone) but it still exhibits the same limitations due to multiple influences (occurring inside the battery) that are not supported.

5. Mathematical models

5.1. Artificial neural network

Mathematical models are different from other models because they are using numerical resolution methods. We describe here only artificial neural network (ANN) models, although a large number of other methods can also be used (fuzzy neural network, fuzzy logic model, neuro-fuzzy based modeling, adaptive algorithm...) working, generally, in a very similar way.

ANN is a computational model with a biological inspired conception. Based on neuronal network, this statistical approach works with input and output data and has also capacity to learn from experiences (Figure 5). Multiple ANN models were already used for lead-acid batteries estimators [52-53]. To paraphrase Parthiban [54], ANN modeling is essentially a "black box" operation, linking input to output data, using a particular set of non linear basis functions. For users, important steps to be followed to develop an ANN model are:

(1) Data collection. Users collect a maximum of input/output data in function of what they desire to model. For example, in the battery field, input can be either temperature or current and output capacity.

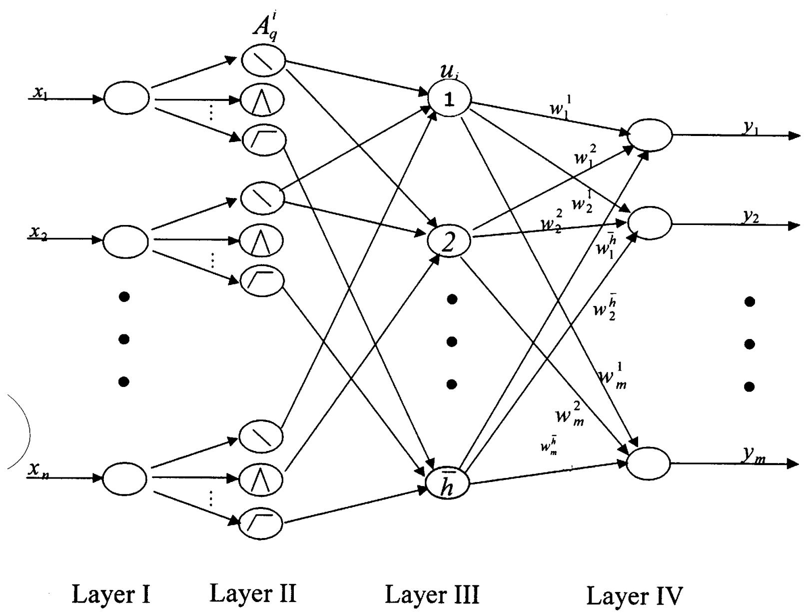

Figure 5. Scheme of fuzzy neural network, similar to ANN [54].

(2) Analysis and pre-processing of the data. Data are transformed to be analyzable by the network.

(3) Training of the ANN. Formation of the artificial neural network, based on collected input/output data. Network is statistically built to match inputs and outputs in a way to minimize error.

(4) Test of the trained network. During confirmation phase, the network trained has to be tested in order to be sure of its validity. Extrapolation (of the beginning of a second data series) made by the network is tested with real data (end of the second data series).

(5) The ANN model is ready for simulation and, for instance, to predict ageing of battery according to inputs provided.

For a battery, this statistical approach is used, in most of the cases, for SOC (State Of Charge) [55] or SOH (State Of Health) estimators [52, 56-57]. In fact, the data quantity to be collected is so important that the user needs a structure able to "learn" and process all information received. Several authors have developed ANN to model battery ageing [58-59] and studied error between prevision and empirical points (after the formation of the network). It appears that this method can be accurate. Unfortunately, few numbers of ageing simulations, for a long period (no more than 50 cycles for Parthiban [54]), leads several authors to skepticism. In fact, only one publication, made by Mellit [60], shows a long term ageing forecast, using an artificial neural network. With 4 years of data collection, they succeeded in training an ANN able to extrapolate voltage and intensity for one year prediction.

Advantages and disadvantages

To sum up, there is, here, an algorithmic method for equations resolution, able to establish links between inputs and outputs. An artificial neural network can be trained to predict ageing of a battery, but needs a large quantity of data in order to be as precise as possible. At this time, there are not enough proofs to confirm the ability of ANN to accurately forecast battery ageing, even if few publications seem promising. An important specificity of ANN models, which could be actually a problem, is its "black box" approach. There is no link with physics/electrochemistry of the system and there is absolutely no understanding of what really happens in the battery upon ageing. Hence, one only has to trust the mathematical algorithms, trying to link (with arithmetic) inputs and outputs together.

Nevertheless, mathematical models can be used by the electric vehicle industry. But it means, for a car maker, having a large fleet of vehicles (EV, PHEV...) with onboard data loggers, being used to capture real-world fleet operations data (charge profile, temperature...). With few vehicles (but how many?) and few running years (but how long?), data collected will be used to train an ANN model and to model future battery ageing during the forthcoming uses. There are obviously three major problems for a vehicle maker: the first one is to build a car and a battery pack entirely before estimation of the battery ageing. It makes the model very expensive to develop and moreover difficult to integrate in the development of a vehicle. The second hard task is time. Collecting data will need a lot of time, and if a first battery pack is not satisfying, all the work has to be restarted. Moreover, ANN did not provide extrapolated data for a long term (for Mellit [60], 4 years of colleted data lead to only 1 year of ageing forecast). The third problem is the complete opacity of the model. If after several years (and lots of money spent), a huge ageing mechanism is established, it will be without any intrinsic understanding and it will be thus impossible to generalize this observed behavior to any other battery pack.

6. Fatigue models

Fatigue models come from the mechanics domain, developed over hundreds of years. They are based on a totally different vision of the battery degradation with time: events are impacting in an incremental way, step by step. It is thus a heuristic approach; the model does not really represent ageing effects on a physical or chemical basis.

6.1. Wöhler method

The Wöhler method is also known as the cycle counting model or the SN method. Both of them are basic methods, based on a fatigue approach.

August Wöhler worked on rail tracks and was investing metal fatigue during the 19th century.

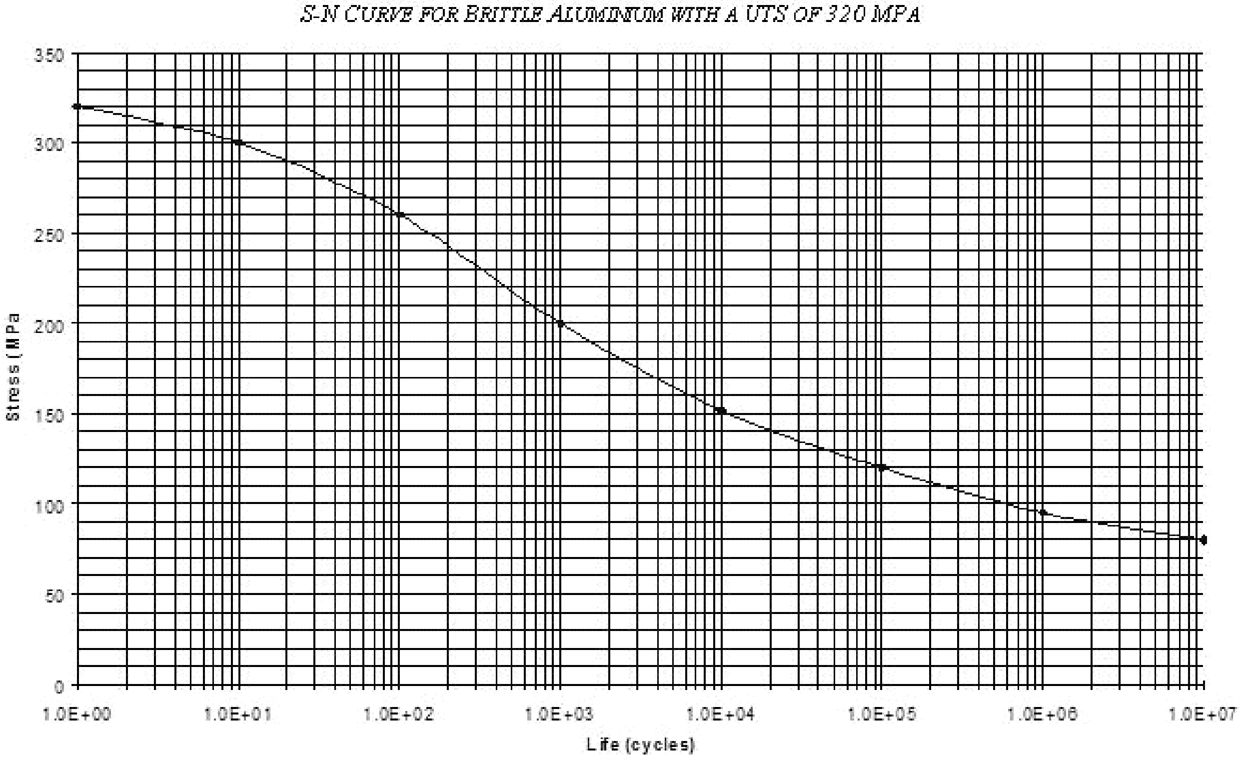

Figure 6. A typical Wöhler curve.

He concluded that metal failure results from cyclic stress accumulation during use, and not only static stress. Fatigue is then defined by the progressive damage that occurs when a material is subjected to cyclic loads. The Wöhler method comes from direct mechanical stress domain. August Wöhler lets his name to the well-known Wöhler curve (or SN-curve) representing number of cycles before rupture, in function of applied cyclic stress to the material (Figure 6).

In a theoretical vision of the Wöhler curve, the curve is associated with an accumulation of energy which is dissipated within the material and leads to incremental structural changes. This method is still used today: lifespan of a component is estimated by progressive losses upon time and use. Transposition to battery ageing is relatively simple and an example is given by Wenzl [61]: a battery, operated in floating condition for which lifetime tests predict a lifetime of 10 years, i.e. 3650 days, is considered to lose 10% of its lifetime each year. Lifetime prediction can be formulated mathematically as "proportion of lifetime which has been used up = n×1/3650" with n being the number of days that has already passed. There are two types of equivalent SN-curve already used to estimate battery lifetime:

- The curve showing the number of cycles of a battery as a function of depth of discharge (DOD) until the end of lifetime (Figure 7).
- The curve showing the lifetime of a battery as a function of its charging voltage or temperature.

In case of non-monotone solicitation, the direct use of S-N curves is impossible because they are developed and built for constant-stress-amplitude operating conditions. That is why Palmgren [62] and, then, Miner [63] have developed a theory, known today as the Palmgren-Miner rule: according to this rule, the damage accumulated during one cycle (or one event) would cumulate with the previous damage. In practice, solicitation is divided into elemental cycles; each cycle is isolated and grouped with equivalent amplitude or period cycle. Each group of cycles is then impacting the lifetime in function of its frequency/occurrence.

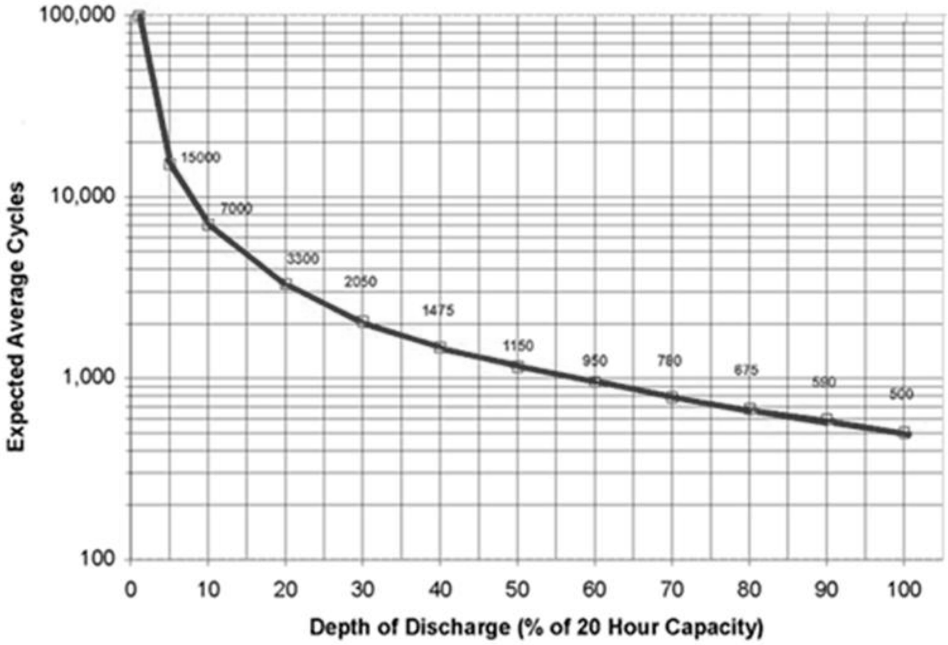

Figure 7. SN-curve applied to battery lifetime estimation. Number of cycles in function of depth of discharge before the end of lifetime [www.mpoweruk.com/life.html].

This method of ageing evaluation, for lead-acid batteries, was firstly introduced in 1983 by Facinelli [64]. Described, with more details by Sauer [46], the Wöhler method is mathematically very simple: if $NE^{max}{}_i$ is the number of events i that can occur during the lifetime of a battery until its failure (under the assumptions that only events of type i occurs) and NE_i is the number of events that occurred during the period of observation, then the loss of lifetime associated with event i is:

$$LL_i = \frac{NE_i}{NE_i^{\max}} \qquad (1)$$

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

$$LL = \sum_i LL_i \qquad (2)$$

The end of lifetime is reached when LL is equal to 1. Events are defined as a simple cycle in the Wöhler method, and depth of discharge for this cycle is the impacting parameter for lithium-ion batteries. Each moment has to be associated to one event (and only one) for which a Wöhler curve exists.

Advantages and disadvantages

Several authors noticed [45] that this method is simple and quick to implement. In most of the cases, battery supplier provides directly a typical Wöhler curve and, if no curve is provided, few simple ageing tests in laboratory can be performed. However, hypothesis made in the Wöhler method are, at least, questionable: there is no interaction between several ageing events, or an event will impact lifetime equally at the beginning or at the end of life of the system. Each SN-curve uses only one parameter (in general, depth of discharge of the battery). There is another limitation for using a Wöhler method for BEV: the vehicle use implies complicated and diverse solicitations. Firstly, it is quite impossible to discern a DOD in this type of solicitation and, secondly, more than one parameter is impacting (temperature, current, DOD...). All these reasons make this first fatigue model not convenient for battery ageing estimation.

6.2. Weighted Ah model

The weighted Ah model (or weighted Ah-throughput approach) is an evolution of the aforementioned Wöhler method. It is also a fatigue model since it is based on a damage addition hypothesis. Here, lifetime is reduced, in function of the charge throughput during use and not in function of number of cycles. Moreover, this approach takes into account multiple parameters. An example, showing the general idea of this approach (for lead acid batteries) is given by Sauer [46]:

- Cycling a lead-acid battery, at low SOC, stresses the battery more than cycling at high SOC. Any Ah that is charged or discharged to the battery needs to be weighted with a factor.

- Cycling of a battery, while acid stratification is present is known to result in inhomogeneous current distribution all along the electrode. As a result, certain parts of the electrodes are more stressed than others. Again, the Ah throughput needs to be weighted with a factor, which depends on the degree of acid stratification.

- 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 electrode sulphation and battery capacity loss. Therefore, the Ah throughput also needs to be weighted with a factor depending on the time since the last full charge was performed.

All these parameters are included via a weighting factor, indicating if an event is more or less impacting to lifetime, comparatively to a reference (w_i, in Equation 3). Several versions of ageing models using this approach for lead acid [65-66] and NiCd batteries [67] have been developed. Definition of an elemental event is important and users can choose among many possibilities: an event can be defined by a period (30 seconds...), by a property (one event by temperature, end of cycle...) or anything else (time between two moments with zero current...). Whatever the classification made, each moment has to be associated to one event (and only one) for which a Wöhler curve exists. Equation (1) from the Wöhler method is thus adapted and includes several parameters with adequate weighting factor [61].

$$Ah_{eff} = \sum_i w_i \times NE_i \times Ah_i \qquad (3)$$

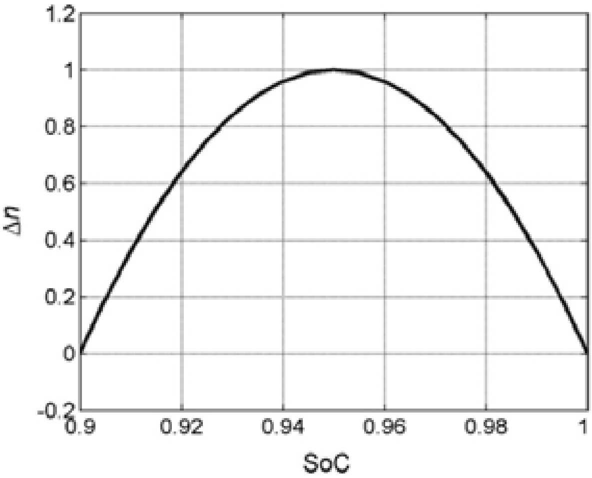

Figure 8. Weighting factor for bad charging counts [69].

With Ah_{eff} being the effective Ah-throughput of an event *i*, NE_i the number of events *i* and w_i the weight (or severity) associated with the event *i*. The battery is considered to fail once the effective Ah-throughput exceeds the total Ah-throughput of the battery. For example, in the model developed by Puls [68], the weighting factors chosen are temperature, time between two charges and one parameter associated to lower state of charge. These weighting factors, which represents the most difficult task to do in this type of model, could be then calculated mathematically [69] or in an empirical way (Figure 8).

In general, fatigue models, are published with an End Of Life (EOL) criteria, for a better comprehension, because it represents how model operates (accumulation of different small losses of lifetime upon use). But it is also possible to directly model the properties and performances (like capacity, energy, peak power...) during use and life of the battery.

Advantages and disadvantages

Weighted Ah-throughput model is a large improvement of the first fatigue approach, the Wöhler method. By including several parameters, it takes into account all the multiple specificities of a vehicle solicitation (temperature, SOC, current...). Ah-throughput is also a better parameter than the number of cycles, because no real (driving profile) cycles are made during a laboratory test. It could be a good choice for modeling battery pack ageing of a vehicle because it needs no destructive measurement. However, a disadvantage, noticed by Kaiser [45], is that the parameters values are not updated during simulation and do not completely reflect the damage encountered by the battery (contrary to Electrochemical or Empirical + MCE models, for example), leading thus to a less precise model. Another problem, for this approach, is the calendar ageing: by definition, there is no charge throughput, so obviously no ageing. Another model has to be chosen, at least for this part, complicating the modeling task.

To conclude, it should be pointed out that none of these fatigue models has so far been yet validated. Existing models are based on the lead acid technology and, for now, the only weighted Ah-throughput models for Lithium ion batteries were made by Marano [70] and Di Filippi [71], and are still under development. Confirmation of the subtended hypothesis has to be made before any practical use of the weighted Ah-throughput.

CONCLUSIONS

This review outlined different ways to predict Lithium-ion battery ageing for a vehicle use (meaning large variety of complex solicitations). Six separate approaches were described here and analyzed, from our knowledge. To sum up:

- There are a lot of electrochemical models able to predict battery ageing, more or less sophisticated. They seem difficult to establish (equations and parameters), and need an important calculation time. However, operations are much closer to reality and could provide a good prevision.

- Empirical models are very useful, for a quick estimation. A simple extrapolation can be useful, but not enough precise and complex to model vehicle solicitations.

- Empirical models, linked with an equivalent circuit model, are more precise, since it includes a kind of behaviour model. However, this approach is dependant of empirical ageing tests and, do not exhibit an important flexibility.

- Artificial neural networks (ANN) can be used for battery ageing prediction. This black box approach needs however a lot of ageing data to work properly, and consequently a long time of tests. Quality of ANN is still not demonstrated.

- A simple fatigue (Wöhler) approach is relatively easy to establish. But modelling is limited by a single impacting parameter and a solicitation able to be divided into elemental cycles. That is why it cannot be convenient in the case of various vehicle solicitations.

- The weighted Ah approach corrects these latter problems by including several parameters through some weighting factors. Charge throughput is also a better criteria than cycle, especially for a complex solicitation, but not possible for specific calendar ageing.

All these models have obviously qualities and defaults. In the particular case of complex vehicle solicitations, few of them seem relevant. Electrochemical models are enough complex, but to identify ageing phenomena, to be able to measure all the physical and chemical parameters needed is arduous. Weighted Ah models are a second possibility. This fatigue approach does not need any chemical/physical measurements and is relatively simple to establish. Nevertheless, inherent hypothesis have to be checked before implementation in a predictive model. Question of calendar ageing, without any charge throughput, is also an important question.

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