A review on lithium-ion battery ageing mechanisms and estimations for automotive applications

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Abstract

Lithium-ion batteries have become the focus of research interest, thanks to their numerous benefits for vehicle applications. One main limitation of these technologies resides in the battery ageing. The effects of battery ageing limit its performance and occur throughout its whole life, even if the battery is used or not, which is a major drawback on real usage. Furthermore, degradations take place in every condition, but in different proportions as usage and external conditions interact to provoke degradations. The ageing phenomena are highly complicated to characterize due to the factors cross-dependence. This paper reviews various aspects of recent research and developments, from different fields, on Lithium-ion battery ageing mechanisms and estimations. A summary of techniques, models and algorithms used for battery ageing estimation (SOH, RUL), going from a detailed electrochemical approach to statistical methods based on data, are presented.

Keywords: Ageing, Lithium-ion battery, Estimation, State Of Health, Remaining Useful Life, Modeling

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1. Introduction

Lithium-ion batteries have been commercialized since 1991, initially concerning mobile devices such as cell phones and laptops [1]. Interest on this technology has considerably increased and generated a lot of researches in order to improve the performances of those batteries [2]. Recently, Lithium-ion batteries penetrated the market of hybrid and electrical vehicles thanks to the high Lithium's density, the weak weight of the Lithium batteries making them the most promising candidate for this field of applications [3].

Different organizations converged to estimate Electric Vehicles (EV) representing $\sim 60\%$ of the total market of passenger cars through 2050 [4, 5], with a presence on all major regions of the world. Supposed evolution of EV sales is the result of petroleum prices increasing and is highly sensitive to the battery development [6]. As an example, Renault demonstrates the profitability of its Fluence ZE from 15000km/year [7]. Considering prices evolution, this benefit is predicted to decrease with time, which will induce more interesting EV costs [8].

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Such market evolution induces important coming step for batteries as roadmaps consider the long term goals of battery evolution to be : augmentation of maximal capacity, acquiring a battery lifetime equivalent to the car lifetime, reducing costs in order to be the same as those of an Internal Combustion Engine (ICE) vehicle, operating in all climates [9, 10, 11].

Preliminary uses of this battery technology had a low lifetime need. With the new applications, interests are now focused on ageing phenomena considering manufacturers requirements. In terms of battery design, beyond all performances constraints, some objectives are clearly defined for service life (10-15 years or 20000-30000 discharges [4]). So, battery ageing phenomena are commonly used to evoke both main consequences of time and use on a battery. The resistance growth and the capacity fade, will be discussed in the following parts. The aims of increasing batteries performances stoke the requirement of a better understood battery ageing [12, 13].

Identifying ageing and degradation mechanisms in a battery is the main and most challenging goal. Such processes are complicated as many factors from environment or from utilization mode interact to generate different ageing effects. Hence, the capacity fade and the resistance growth do not depend on the same variables. This made the ageing comprehension a difficult task, and through the years, many studies tried to explore the battery ageing.

This review intends to summarize today's results on mechanisms, factors and estimation methods of Lithium-ion batteries ageing on automotive applications. The first aspect presented here is the notion of battery ageing in an electrochemical description, with explanation of known battery ageing phenomena. Based on these ageing characteristics, many studies investigated Lithium-ion battery ageing factors, effects, and tried to estimate the battery state of health (SOH) by several methods. These ageing studies and methodologies come from many various fields such as electrochemical models, performances models or statistical methods. The diversity and the multitude of existing studies dealing with battery ageing provides a large amount of informations. This paper presents all of these approaches along with their respective performances. Finally, a discussion on the methods advantages and drawbacks is proposed. This debate illustrates the current methods disadvantages, we finally suggest a new methodology for battery ageing estimation.

2. Electrochemical ageing

Ageing initially takes place in the chemical composition of the battery's electrolyte. The degradation mechanisms from the positive and negative electrode are different [14, 15]. The origin of ageing mechanisms can be either chemical or mechanical and are strongly dependent of electrodes composition. Ageing provokes throughout time the degradation of the electrode [16], which can induce a loss of active material by the dissolution of material in the electrolyte, manganese for example [14]. Thus, the main phenomena come from electrodes degradation.

2.1. Ageing effects on negative electrode

Most negative electrodes are composed of graphite but it also can be carbon, titanate or silicone [17]. The choice of the graphite material is important in ageing and safety properties of a battery [15]. The main ageing factor on graphite electrode is the development with the time on the electrolyte/electrode interface of a solid interface named Solid Electrolyte Interphase (SEI) [18]. This solid interphase is naturally created during the first charge. Its role is to protect the negative electrode from possible corrosions and the electrolyte from reductions [19]. This phenomenon predominately occurs during the beginning of a cycle. Its a natural barrier between the negative electrode and the electrolyte and consequently provides a guarantee of security [20, 21]. The SEI is not stable as Lithium-ion battery operates in tension outside the electrochemical stability window of the electrolyte [22]. Thus, the SEI develops over time which induces loss of continuous Lithiums ions and an electrolyte decomposition [23]. Moreover, loss of available Lithium due to side reactions at the graphite negative electrode have been reported as the main source of ageing during storage periods [24]. That is, the SEI is relatively stable over time, inside the stability window, and the capacity loss is not significant in short terms, permitting Li-ion batteries utilization over long periods.

Furthermore, the SEI is permeable to the Lithium ions and to other charged elements (anion, electrons) or neutral elements (solvent) [14, 25]. Thereby, the solvent interacts with the graphite after diffusion through the SEI, which induces graphite exfoliation [26] and creates gas which can crack the SEI and therefore allows its expansion [19, 27]. Nevertheless, the gas formation is low and it seems to happen only during storage periods and with high voltage [28]. With time, there is a loss of active surface, increasing electrode's impedance. Figure 1 illustrates all these phenomena occurring at the SEI. This phenomenon may take place during utilization of the battery as well as during storages.

A high SOC (State Of Charge >80%) should provoke an acceleration of these phenomena as the potential difference between electrodes interfaces and electrolyte is important [29]. Moreover, inadequate conditions can accelerate the process, such as high temperature, overcharge, short circuit [30]. Thus, under high temperatures, the SEI may dissolve and create Lithium salts less permeable to the Lithium ions and therefore increase the negative electrode impedance [31]. On the contrary, low temperatures lead to a decrease of the diffusion of Lithium within the SEI and graphite [32, 33], which can overlay the electrode with a Lithium plating. It is important to note that the SEI formation, its development, and the Lithium plating is all responsible to the loss of cyclable Lithium, under utilization transportation's conditions [34].

2.2. Ageing effects on positive electrode

Bourlot et al. [28] shows, from positive electrode observations, that there is no evident modification of the positive electrode's morphology, for all levels of battery utilization [35]. This is the confirmation of the primordial importance of the negative electrode in the battery ageing [36].

However, the positive electrode is subject to a low alteration within time, depending on the chosen material [37]. There is also a SEI creation on the positive electrode/electrolyte interface, that is more difficult to detect [38, 39], due to high voltages on this electrode [40]. To sum up, the principal consequences observed on an aged positive electrode are : wear of active mass, electrolyte degradation, electrolyte oxidation and formation of a SEI, interaction of positive electrode element dissolved within the electrolyte at the negative electrode [35, 41, 42].

These effects are not independent and their respective interaction differs as follows to the used positive electrode material [43]. As for the negative one, statements highly depend on the SOC and the temperature.

2.3. Consequences of ageing phenomena

In this part, two principal effects of battery ageing are identified : capacity fade and impedance raise. Both phenomena differ from chemical causes, thus have different uses origins. This imply a non-linear dependency of these ageing impacts.

The performance loss is caused by various physical-based mechanisms, which depend on the electrode materials. They can either be of mechanical or chemical origin. The consequences of theses mechanisms on the Lithium-ion cells are :

- The (primary) loss of cyclable lithium which increases the cell imbalance. Loss of cyclable lithium is related to side reactions which can occur at both electrodes, as the SEI grows at carbon anode due to electrolyte decomposition [44].
- The (secondary) loss of electrode active materials, possibly a material dissolution, structural degradation, particle isolation, and electrode delamination [45].
- Resistance increase of the cell, due to passive films at the active particle surface and loss of electrical contact within the porous electrode [46].

In term of battery performances, both loss of cyclable and loss of active materials lead to the battery capacity fade. Secondly, the battery resistance growth is engendered by the passive films. On vehicle utilization, the capacity loss induces an autonomy reduction. On the other hand the resistance augmentation reduces the maximum of power available.

3. Ageing origins

Battery ageing can be dissociated into two parts : the calendar ageing and the cycle one [47]. Each term defines the alterations caused by different uses of the battery. Thus, the calendar ageing corresponds to the phenomena and the consequences of battery storages. On the contrary, cycle ageing is associated with the impact of battery utilization periods named cycles (both charge or discharge).

3.1. Calendar ageing

Calendar ageing is the irreversible proportion of lost capacity during a storage. In other terms, it is the degradation caused by the battery storage [48, 49]. Self discharge rate vary highly according to storage conditions. Hence, effects occurring within the battery can be accelerated or slowed depending on the storage conditions [50]. Numerous experimental studies showed the impact of storage conditions on this ageing. For example, studies test cells over several temperatures, SOC (sixty cells for Bloom et al. [51] and three hundred for Wright et al. [52]) and Ramasamy et al. [53] deals with cells under different end-of-charge voltages and temperatures.

The main conditions considering the calendar ageing and the self discharge is the storage temperature [54]. When the temperature is high, secondary reactions such as corrosion are facilitated and the Lithium loss is more important than in moderate temperature conditions, which induces capacity fade [51, 52, 55]. Low temperatures enable to limit the development of these phenomena but these conditions engender some problems due to the loss of material diffusion and alter the battery chemistry [56].

The other principal variable of calendar studies is the SOC level during storage [57]. Thus, for an equal temperature but for different SOC, cells do not age in the same manner. This illustrates a higher battery degradation for elevated SOC [36]. By definition, the SOC represents the ions proportion present on electrodes, which implies, for high SOC, a huge potential disequilibrium on the electrode/electrolyte interface. This promotes precedent chemical reactions.

Only a few studies explore SOC as the unique condition caused by calendar ageing but as a combination with the temperature. Indeed, each of these variables alter together the capacity and the resistance with a non linear effect with time. Studies results [58, 59] evocate the more restrictive effect of a high SOC than of a high temperature. Such results are just an interpretation from few experiences and it remains to understand the complete effect of the combination of those two variables on the calendar ageing.

Temperature and SOC impact directly on battery calendar ageing. Furthermore, capacity fade and resistance augmentation are not linear with time, which implies a strong interaction of ageing behavior with time.

3.2. Cycle ageing

The cycle ageing happens when the battery is either in charge or in discharge. This is a direct consequence of the level, the utilization mode, the temperature conditions and the current solicitations of the battery. Consequently many factors are involved on this kind of ageing. Firstly, all factors previously described impact the calendar ageing and are also included in studies of the cycle ageing, because ageing phenomena previously cited, appear whether the battery is used or not. In most cases, a battery in use is prone to exothermic effects [60, 61] and those reactions can be facilitated under high temperatures and provoke battery ageing. However, it is important to take into account the effects of very low temperatures [59]. Studies report direct impact of ambient temperature but none of them deal with direct battery temperature. This notion remains a misunderstood knowledge.

Except such variables, cycling ageing's factors are function of the battery utilization mode. A recurrent factor on literature is the ΔSOC, which represents the state of charge variation during a cycle. This is a main factor considering the amount of charge taken (resp. given) to the battery during a discharge (resp. charge) [35, 62]. Bloom et al.'s experience [51] consists in testing same Lithium-ion cells with similar temperatures and initial SOC but for different ΔSOC. Results show loss of battery power as ΔSOC's value is high and this for all other possible conditions. This was later confirmed by other experiments [63]. Such phenomenon is mainly due to the positive electrode degradation and to the SEI development, engendered by high discharge, or charge.

Another variable impacting the Lithium-ion battery ageing and function of the utilization mode is the charging/discharging voltage during its life. Thus, high charging voltage implies accelerated ageing phenomenon [64]. To illustrate this, Asakura et al. [65] show that a battery life halved for an 0.1V augmentation of the charging voltage, the EOL is considered here as 70% of initial capacity. Discharge voltage influences the battery ageing through the impedance augmentation [66, 42].

Finally, current peak seems to be a notion involved on ageing phenomenon. Indeed, an important current peak induces a high level of given energy, or released, to the battery.

3.3. Conclusion on ageing characteristics

Previously presented factors influencing battery ageing interact to generate both capacity loss, resistance augmentation and loss of available peak power [67, 68]. Note that all factors are dependent on other external conditions. For transport application, temperature depends on climate, ΔSOC depends on the driving cycle... Thus, utilization mode is widely concerned by ageing studies. Depending on utilizations mode, such as successive accelerations or constant velocity, the battery temperature will not evolve the same way. On the other hand, peak current are not identical within road profile and conductor aggressiveness.

These characteristics make of ageing comprehension and estimation a huge challenge due to the multiple interactions between all factors, coming from utilization mode or environment [69, 70].

4. Ageing estimation

To evaluate ageing, several indicators or notions are created in order to quantify the health level of the battery. The most used indicator in the literature is the State Of Health (SOH) which is generally defined by [71, 72]: $\mathrm{SOH}(t) = \frac{\text{nominal capacity at } t}{\text{intial capacity}}(\%)$

Other SOH definitions can be made through the End Of Life criterion (EOL) [73] but it is still a proportion of battery remaining capacity. This indicator represents the battery capacity fade [74, 75]. As the "ageing" term is not precisely defined, other indicators such as State Of Function (SOF) [73] or Remaining Useful Life (RUL) [76] are introduced. All these notions are deducted from the capacity state of the battery and therefore do not consider all parts of ageing as the resistance is omitted. However, resistance development is specially impactful in high power applications. Thus, Ecker et al. [77] define the EOL criterion as the moment when the initial inner resistance doubles.

Different methods are used to estimate these notions of battery age level, they are divided into several parts :

- Electrochemical models : detail and model the phenomena occurring into the battery
- Equivalent circuit based models : the battery is reduces as an equivalent circuit model
- Performances based models : battery ageing is model by physical equations
- Analytical models with empirical fitting : estimation of ageing parameters through measurements
- Statistical approach : approaches mainly based on data, without a-priori knowledge

4.1. Electrochemical models

Battery ageing can be determined from physical models. Such models seek to quantify factors impact and therefore obtain the description of battery performances evolution. As said previously, several factors interact to generate battery ageing phenomena, which causes the complexity of making a reliable and precise model. The goal of these approaches is to give a sharp understanding of the specific physical and chemical phenomena occurring during battery utilizations.

The physical models can be distinguished into two separate parts. The phenomenological approaches which give a dynamic description of the cell which could be independent of the electrodes materials. The other part consists in atomistic/molecular models which allows access to thermodynamics quantities related to electrodes structures, surfaces or electrolytes such as thermodynamic energies, activation barriers or reaction mechanisms.

Degradation mechanisms related to the materials properties can be deduced from both these approaches. On one side the impact of an ageing process on the cell performance, can be translated into physical equations by fitting the parameters using the macroscopic observations. On the other side, it is possible to identify the prominent occurring physico-chemical processes depending on the employed materials, and evaluate with atomistic calculations, their effect on the battery [78, 79].

4.1.1. Phenomenological approaches

The development of these models starts about twenty years ago, with the work of the Newman's group [80, 81], in order to estimate battery performances based on Butler-Volmer equations and porous electrodes theory [82]. The first attempt of simulation ageing process in a physical model was done by Darling and Newman [83] with the implementation of a simple solvent oxidation reaction within their model. The results were very encouraging and gave good conclusions about choice of solvents. Based on the same approach, Christensen et al. [84] explained the capacity fade by the augmentation of resistance on the negative electrode surface and they developed a model to represent the SEI [85].

Most of the mechanisms incorporated in physical models are related to the negative electrode but they have investigated the impact of the stress occurring during the lithium intercalation process in Lithium Manganese Oxyde batteries [86, 87] and they managed to predict for which electric current and SOC, fractures will appear in the active material particles. The SEI raise and its relation with the capacity loss, has also been studied [88] with a solvent diffusion model. More recently, studies [89, 90] have estimated the effective diffusion coefficient in the electrolyte with the cycle number. They could simulate the evolution of the electrolyte composition and the consequences on the cell performances. Safari et al. [91, 92] also developed a phenomenological model in order to estimate the performance of a commercial LFP/graphite cell and they tried to estimate the impact of the ageing on the battery performances in terms of capacity loss and impedance raise. This study permits to evaluate that cycling is more determinant than storage on the degradation. The loss of active material is less important than loss of active lithium for these batteries for temperature conditions between 25°C and 45°C [93].

4.1.2. Atomistic and molecular approaches

In the approaches listed above, the intrinsic properties related to the electrode and electrolyte materials are not precisely taken account. In order to understand at a nanoscale level the phenomena appearing during the battery ageing, few models have been developed using atomic and molecular methods.

Density functional theory (DFT) is already used to describe the different phenomena occurring during the lithiation / delithiation of the electrodes. Depending on the materials nature, these processes can follow very different mechanisms from monophasic conversion in the case of $LiCoO_2$ batteries to the biphasic domino-cascade process for $LiFePO_4$. Theoretical methods have been developed to investigate these phase transition processes. Dalverny et al. [94] performed ab initio calculations to determine the morphology of the $LiCoO_2$ electrode and theoretical studies have been done to understand the phase transition process within LFP active particles [95]. Furthermore, ab initio calculations can contribute to the degradation phenomenon comprehension by estimating the energies related to solvent decomposition or to lithium salts dissolution. Tasaki et al. [96, 97] have already linked the lithium salts dissolution near to the negative electrode's SEI with the calendar capacity fading.

Molecular dynamic represents also a good way for the comprehension of degradation mechanisms. Indeed, a study [98] have investigated the decomposition of the Ethyl Carbonate (EC) solvent and the consequences on the SEI raise. This could be a key point for understanding ageing problems related to graphite electrodes. Moreover, SEI evolution has been examined by another recent study [30] using Kinetic Monte Carlo (KMC) method. They focus their work on the diminution of the electrode active surface related to SEI formation during cycling.

One of the greatest challenges of the physical models is to link results from atomistic approaches (DFT, molecular dynamics...) with macroscopic models. The aim is to obtain a detailed description of all the phenomena occurring at a nanoscopic scale and thus to estimate directly their impact on the battery performance. This objective is reachable but the remaining problem is to associate top-down models, going from macroscopic observation to a nanoscopic description of the battery, to bottom-up models.

4.2. Equivalent circuit based models

Other methods permit the ageing estimation through models. The model-based methods commonly model battery by an equivalent circuit model and use different techniques in order to estimate these model parameters [99, 100]. However, the equivalent circuit is defined differently on studies.

In order to estimate the battery ageing, parameters can be internal battery parameters as well as resistance ageing parameters. Parameters identification can be directly made from measurements or from more complex approaches through equivalent circuit models [101, 102, 103]. Such methods require a large and diverse data set from time consuming tests. For example, the Relevance Vector Machine (RVM), a machine learning method, is used in battery ageing estimation through this parameters identification. This method is a Bayesian form representing a generalized linear expression of Support Vector Machine (SVM) introduced by Vapnik [104], currently the state-of-the-art in regression and classification algorithms [105, 106]. This method deals with different parameters from large data sets and estimates and predicts the battery degradation. Saha et al. [107, 108] used this method in order to learn a dependency model of internal battery parameters model to estimate and predict the SOH. These studies also use Particle Filter (PF) and later the Rao–Blackwellized PF (RBPF) to obtain a distribution of the RUL prediction.

4.3. Performances based models

This approach uses simple correlations between stress factors and capacity fade / impedance raise. These correlations are induced from ageing tests conducted under several conditions. These methods intend to quantify the impact of ageing factors and to obtain a descriptive expression of the battery level of performances over lifetime. Most of times studies deal independently with both ageing : calendar and cycle [77, 109]. Furthermore, ageing studies are not only focused on capacity and resistance evolutions but also on equivalent circuit parameters in both cycling [110] and calendar part [77, 111].

4.3.1. Calendar ageing

In calendar ageing modeling, the main variables are time and temperature. Furthermore, some studies consider another parameter : the storage SOC [112, 113]. As seen in the part 3.1, the SOC influence can not be neglected in certain conditions. The calendar ageing appears to follow Arrhenius-like kinetic (1), as this law is typically used in order to consider storage temperatures [24, 51, 114]. Thus, capacity fade and resistance increase may be mainly caused by thermal processes which are linear with time [112].

$$t = A\ exp\Big(\frac{-E_a}{RT}\Big), \tag{1}$$

with t a lifetime, A constant, R gas constant, T temperature and E_a the activation energy.

The storage SOC is introduced by using the Tafel equation relating the rate of an electrochemical reaction to the over-potential (2), as in a modeling study [109].

$$\Delta V = A \ln\Big(\frac{i}{i_0}\Big), \tag{2}$$

with ΔV the over-potential, A constant : "Tafel slope", i the current density of the electrochemical reaction and i_0 the exchange current density.

In most studies, the capacity fade due to storage has been observed to be linear dependent on time$^{1/2}$ [51, 109, 115]. For example, Ecker et al. [77] proposed a calendar lifetime prediction model describing capacity and resistance evolutions over time as shown in (3) :

$$\frac{L(T,V,t)}{L(T_0,V_0,t_0)} = 1 + B(T,V) \cdot c_a \cdot t^{1/2} \quad (3)$$

with c_a coefficient of the degradation rate (capacity fade or resistance increase) under reference conditions T_0, t_0 and V_0. $L(T,V,t)$ stands either for resistance or capacity estimated at time t, with a temperature T and voltage V. Moreover, the impacts of temperature and storage voltage are calculated according to an exponential dependence (4) :

$$B(T,V) = c_T^{\frac{T-T_0}{\Delta T}} \cdot c_V^{\frac{V-V0}{\Delta V}} \quad (4)$$

where T_0 and V_0 are reference temperature and voltage. ΔT and ΔV have been set arbitrarily to 10°C and 0.1 V. Parameters c_T and c_V of the proposed law (4) are based on accelerated calendar ageing test data. Considering these data, a time$^{1/2}$ dependence of the degradation rates have been assumed.

Numerical coefficients values are only obtained based on accelerated calendar ageing data. According to experimental data, the hypothesis of the minor contribution of cycle part on ageing is made. Simulation results are in good agreement with the capacity fade evolution during cycling but overestimates substantially the resistance over time.

4.3.2. Cycle ageing

The cycle ageing is more complex to predict as it involves more variables which are interdependent such as temperature and current voltage. Furthermore, these variables are related to external conditions as well as battery utilization. The main factors considered are typically the temperature, the cycle number, ΔSOC, voltage. Note that most studies agreed to deal with cycle number as main time notion. Thus, Wenzl et al. [116] evoke a simple cycle counting method, but the choice of other factors is subject to discussion.

For example, on one hand a study proposes a typical cycle number dependency model for cycle ageing [109] and another one founds that each model parameters follow a cycle$^{1/2}$ trend [117] . On the other hand, Wang et al. [118] develop a cycle life model of $LiFePO_4$ cells considers ΔSOC, temperature and C-rate. This study finds a $Ah^{0.55}$ dependence of the capacity fade, where Ah is the cumulative charge throughput delivered by the battery over its life. According to the author, this parameter is directly proportional to ageing time but allows correlating degradation for different C-rate.

In the case of separate models, both ageing models can be added to each other to represent a general ageing expression.

4.3.3. Global performance models

Another method consists in estimating ageing directly without considering a cycle or a calendar point of view. It can be the same kind of model explained previously but considering the ageing in a general way [119, 120] as well as a damage-accumulation model (fatigue approach). Damage models use a stress factors / capacity fade correlation in order to fix a relationship for capacity loss over time. The Palmgren-Miner rule model is an example of damage accumulation model [121, 122].

In order to use this method, a profile-decomposition method needs to be proposed that divides the load profile into pieces that are compatible with the stated empirical correlations. Safari et al. [123] provides a detailed description of using this method but results were compared against with a theoretical graphite/$LiCoCO_2$ battery model subjected to only one ageing process (SEI formation at the negative electrode).

The main drawback of these models is that they do not provide any insight into the process that contribute to capacity fade and impedance raise. As a consequence, impact of each stress factors has to be investigated independently resulting in heavy sets of experiments. Moreover evaluating battery life by extrapolating accelerated test results can lead to large error as illustrated by Takei et al. [124].

4.4. Analytical model with empirical data fitting

An empirical method is based on data, as large as possible, from experiments in order to evaluate or predict estimator values. Such methods are used to determine model parameters as well as a direct ageing estimator. The main troubles of these methods are the lack of data and the accuracy of the measurements [125].

The most popular method is the "coulomb counting" which allows estimation of SOH by a simple integration of current over time [126]. The major inconvenient of this method is the necessity of doing this counting every time under same conditions, external temperature for example. It requires a recalibration at regular intervals and it can not be done in real time [127].

Fuzzy logic is also used to admit a low noisy level on the data sets [128]. Thus, based on the data a fuzzy logic fix an input-output relationship based on expertise and can estimate an ageing parameter directly or through a model [129, 130]. Salkind et al. [131] utilizes this method to estimate NiMH battery's SOH. Furthermore, Singh et al. [132] used data from Electrochemical Impedance Spectroscopy (EIS) in order to find two entry parameters: the magnitude of impedance and the phase angles. This method predicts the number of remaining cycles available to the battery use. This last method is extremely hard to implement due to the EIS requirement. It is important to note that fuzzy logic method requirements can add significant errors by the expertises assumptions.

A method based on state observations model the ageing estimation problem by an equation system (5), with an input u (state vector) and an output y (voltage), depending of variables x.

$$\begin{cases} \hat{x} = Ax + Bu \\ y = Cx \end{cases} \tag{5}$$

The goal is consequently to adjust a model from observations in order to minimize the error between $\hat{x}$ and y through a gain K. This correction gain K is then fixed by an algorithm, most generally a Particle Filter (PF) [133], and precisely an Extended Kalman Filter (EKF) [74, 134]. The main problem of this method comes from the possible fast divergence under unsuitable conditions, because it is necessary to preset initial matrix [135].

Artificial Neural Networks (ANN) or Neural Networks (NN) are mainly used for battery's SOC prediction [136] but this method can also measure the battery SOH [137, 138], as it was done for lead-acid battery [139, 140]. Such studies take as entry variables simple parameters : voltage, discharge current, discharged capacity, regenerative capacity and temperature. The main advantages of this method are that it requires only easily obtainable values. NN performs despite multi-dependences and affirms the easy adaptivity of the method to other battery technology [141]. As any learning mechanism, NN requires a large number of diverse data to be effective.

4.5. Statistical methods

As analytical models, statistical methods require a large data set to be effective. These methods do not need any a-priori knowledge on the ageing mechanisms and there are not any hypothesis made on factors and does not use any chemical or physical formulation.

A simple method is the use of time series process, mostly Autoregressive Moving Average (ARMA) [142]. These studies consider the ageing level data as a chronological series and the ARMA methods can deduce the following value of this ageing level [143]. Such a method only works for one battery as each ageing will be different because it depends on the battery usage. Moreover the accuracy depends on data : it requires many full battery characterizations to obtain these data. These inconveniences make this method an unrealizable solution on board applications.

Another approach can considers the battery's end of life criteria as a failure and model this end of life by a Weibull law [144, 145]. However, this method consider all different uses and conditions as a unique way which considerably reduce the result accuracy.

The methods previously stated as NN, Fuzzy Logic and RVM can also perform by directly estimated an ageing parameter without considering an a-priori model.

5. Discussion

5.1. Assessment of estimation methods

Through measurements to statistical estimations, many different kinds of empirical methods exist to estimate the level of battery ageing, each of them has pros and cons characteristics.

Direct measurements do not need battery hypothesis as it is a direct estimation. Furthermore, the only bias introduced is the measurement incertitude. However, this method performs for all kind of battery usages. Due to the procedure duration, it is impossible to do such measurements in real time, and to predict the ageing evolution (part 4.4). Especially for an automotive approach, it is unrealistic to do complete battery measurements in order to estimate its degradation level.

Methods like electrochemical models and equivalent circuit models perform well but cannot be directly extended to other batteries (technology, design, materials). This is the first drawback of these methods as technologies are constantly improving which produce new different batteries. Moreover, these two approaches do not perform to models all degradations mechanisms occurring during the battery life, but only the ageing trend in the best cases (parts 4.1, 4.2). This is caused by the initial assumptions. However, electrochemical and physical models are powerful tools to understand the different interactions between different physical phenomena and the trends about operating conditions effect on ageing.

The same statements can be made on the performance models as ageing is a complex and a multi-dependent phenomenon. This method is also dependent on the battery technology. It performs well to estimate ageing under controlled situation, but are rarely tested on real vehicles data because a lot of environmental variables interacts (part 4.3), which make the problem difficult to model.

On the contrary, statistical methods are easily adjustable to different batteries, can perform to give an ageing diagnosis in real time. But, this kind of method requires a large amount of data to be effective. This data collection process is a complex task due to the battery life time in real usages ($>$ 5 years on the manufacturer guarantees). The battery lifetime implies a very long data collection time. Furthermore, in order to be efficient in all situation, statistical methods must to be constructed from various experiments such as different usages mode (driving style, road, climate...) (part 4.5). Hence, the disadvantage of this approach is clearly the data collection process.

As it is explained here, none of the actual methods performs to obtain an ageing estimation able to be included in a real electric vehicle diagnosis experiment. In the Figure 2 is represented the battery ageing estimation methods performances, for different criteria such as their predictions capacities, their abilities to perform in real time context,or their accuracies. This abstract of existing methods clearly illustrates that none of current method could solve all constraints caused by battery ageing estimation. From these criteria, the worst method appears to be the analytical models and the best one is not easily identifiable between the others. That is, the Figure 2 clearly illustrates the actual compromise we faced with the battery ageing estimation.

5.2. Battery ageing summary

The current EV development induces high expectation on future batteries performances and longevity. This requires a good battery ageing comprehension and estimation, which is still a challenging problem.

The battery ageing is hard to identify and to quantify due to the diversity and the complexity of the phenomena which take place into a battery during its whole life. The two different ageing, capacity fade and resistance augmentation, are distinct as degradations provoked during storage and utilization have different influence on the battery characteristics [47].

Many variables are involved in the ageing process, having more or less directly a role [68]. The more recurrent factors are for the calendar ageing : temperature, storage SOC and time. Cycle ageing concerns temperature, ΔSOC, cycle number, charge/discharge voltage and factors coming from the utilization mode but not clearly identify yet, peak current demand for example. These variables come from internal and external conditions and interacts with each other. All these interactions are the main complexity of ageing comprehension, the result of these interactions are difficult to understand and to quantify (part 3).

Studies based on test bench misunderstand the real impact of all variables due to the controlled conditions. For example, Bögel et al. [54] try to reproduce a real EV use on a test bench, but results of this study illustrate the limits of such approaches. These simulations can lead to results such as a complete linear dependence between an ageing phenomena and a variable. Such conclusions usually permit these studies to build various models based on these observations. Hence, it is important to remember the bias initially introduced in a study when it concerns data from a test bench.

5.3. Methods summary

Every presented method tries to solve this problem by different manners but each one has its own disadvantages. Current studies focused on models are not able to consider all the existent phenomena to estimate battery ageing. Furthermore, most studies consider only one of the battery ageing phenomena at a time : the capacity fade [146] or the resistance [147] raise. However, it is well known that both have a significant impact on the electric vehicle use (part 4).

Each of the presented methods can perform well under its own particular conditions : going from a unique detailed battery to a very large and diverse data sets coming from a vehicle fleet. Moreover, chemical studies are not reproducible as it is directly dependent on the battery design and its technology. Statistical methods do not need sophisticated measures but large and various data sets in order to find all existing interactions. The main inconvenient is here the complexity to obtain large data due to the time needed to significantly age batteries.

Many studies solve this time problem with accelerated life tests [77, 124, 148], but this methodology has two main drawbacks. First, an accelerated life test is usually done with a test bench. Hence, the impact of all environmental variables occurring in real life conditions are not taken into account, which produces some errors. Furthermore, these methods can not perform to obtain the same battery ageing as in real life, due to the lower total storage time but also because of the complex interaction between each variable, which was not considered here.

This diversity of methods induces huge compromises to obtain a generic method performing well for an electric vehicle utilization, especially with the aim of a real time result, the Figure 2 also illustrates this idea.

The adaptation to electric vehicles requires an easily flexible method, and thus rejects complicated measurements. Thus, an ideal method would perform quickly from few and easily obtainable variables. Considering the real time calculus criteria, only two of the presented methods are acceptable : equivalent circuit model and statistical methods. Moreover, the precision level is important for a vehicle use and the best method is direct measurements which are hardly realizable.

5.4. Proposed method

A method that answers to all of this criteria does not currently exist, but it seems that the most promising candidate would be a mix between the measurements precision, the statistical methods adaptability and the understanding of physico-chemical process interactions by modeling. Thus, such method will be accurate for all batteries of the same technology. Furthermore, it will avoid complex measures and permit possible on-line methods for automotive applications. This method could be based on an electrochemical, or on a performance model, with complete and non-linear relationships. Such a method can be updated with data from bench tests and from a vehicle fleet under real usages. This would enable us to obtain many informations from various uses and different data acquisition process which provide a guarantee of the model robustness.

In order to be adaptable on a vehicle context, a method requires to be efficient for all kind of usages. In other words, it means a method built from real tests and not from specific bench tests. Furthermore, it is still uncertain if a method without historical update can performed in a battery diagnosis goal. Hence, very few methods deal with the possibility of a battery diagnosis directly done from obtained signals but most consider all the battery history. A proposed idea is to consider the battery performances degradations with an on-line diagnosis approach, hence without a conservation of its full utilization history. Such method will be only based on the immediate recorded data which is a remarkable advantage.

6. Final conclusion

The Lithium-ion battery as the main energy storage solution to the transportation sector is part and parcel of current research. Furthermore, ageing effects occur at each moment of the battery life and is one of the most binding criteria of this technology. In the context of EV, the battery ageing engenders a significant degradation of its performances. These degradations are reflected by an autonomy fade along with a diminution of the acceleration power. These points are particularly constraining for the expansion of the EV market.

This paper presented a review of the battery ageing mechanisms, and their consequences, occurring during a battery life. Different methods tried to understand these phenomena going from an electrochemical point to a more data analysis study. Nevertheless, the ageing processes of Lithium-ion batteries are complex and strongly dependent on operating conditions. In addition, it is still difficult to quantify the different mechanisms and the different ageing mechanisms are correlated and cross-dependent.

These methods coming from a very large set of fields are exposed in this paper. Furthermore, their respective characteristics are discussed and possible new approaches are evoked. Thus, each presented method has advantages and drawbacks, as none of them permit to explore the entire dependencies and correlations of ageing battery factors. There is currently no study considering ageing as a consequence of all the existent interactions between environment and utilization mode. Most of the time, studies only take into consideration the capacity fade in order to define ageing indicators and just a few interpret ageing as a combination of capacity fade and resistance raise. The ageing battery estimation engenders a large set of area, this make the problematic really interesting and very challenging.

Thus, obtaining a complete battery diagnosis based on every ageing factor and compatible with a vehicle use, is still a major remaining challenge. The current focus needs to be on finding the ideal compromise between ageing estimation methods development, in order to be accurate combine with a real time compatibility. Hence, the final goal of an ageing battery estimation, running in real time for electric vehicles, for all kind of uses, requires various compromises.

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List of Figures

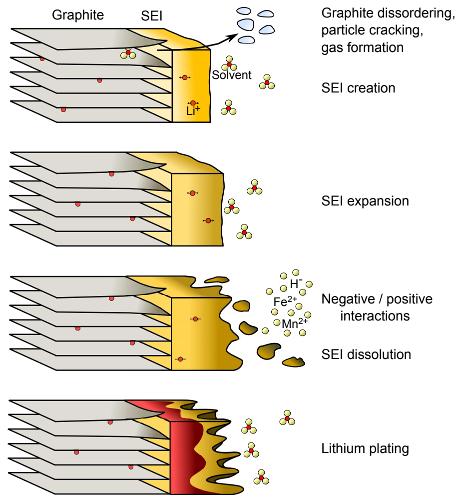

Figure 1: Illustration of ageing effects on battery negative electrode : the capacity fade and the SEI growth

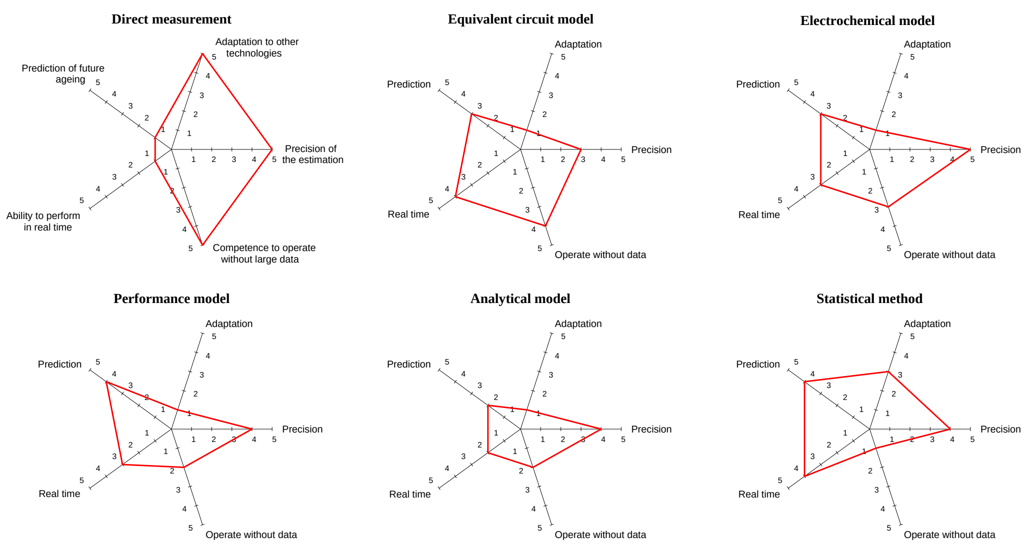

Figure 2: Battery ageing estimation methods performances comparison for five principal aspects