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# Critical review of state of health estimation methods of Li-ion batteries for real applications

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Lithium-ion battery packs in hybrid and electric vehicles, as well as in other traction applications, are always equipped with a Battery Management System (BMS). The BMS consists of hardware and software for battery management including, among others, algorithms determining battery states. The accurate and reliable State of Health (SOH) estimation is a challenging issue and it is a core factor of a battery energy storage system.

In this paper, battery SOH monitoring methods are reviewed. To this end, different scientific and technical literature is studied and the respective approaches are classified in specific groups. The groups are organized in terms of the way the method is carried out: Experimental Techniques or Adaptive Models. Not only strengths and weaknesses for the use in online BMS applications are reviewed but also their accuracy and precision is studied. At the end of the document a potential, new and promising via in order to develop a methodology to estimate the SOH in real applications is detailed.

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**Contents**



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## 1. Introduction

The world is facing huge challenges. On the one hand, the world's population has already reached 7 billion and may rise to 10 billion in the coming decades [1]. On the other hand, technology is improving incredibly rapidly. This mixture means that the need for energy is increasing and furthermore, in an unpredictable way. Due to these two aspects, the doubt about the amount of accessible energy in the near future is a global concern. The impact of population growth and technological improvements which have to surely satisfy the needs of people now and in the future is becoming a threat.

Energy is produced by fossil fuels, nuclear energy or by renewable energies. The problem with fossil fuels is that they are limited and they took millions of years to create. Moreover, they affect the atmosphere with the $CO_2$ emissions they produce. Nuclear energy, in contrast, has a very low rate of gas emissions, but it is not easy to deal with the waste products; it produces due to their negative impact on our health and our environment. Regarding renewable energies, their intermittency makes them inefficient. A dependency on them cannot be created due to the impossibility of using them when they are needed.

Via the use of electrical storage, according to the U.S. Energy Department, the efficiency of generation facilities could increase by 40% and in turn would greatly reduce the dependence on polluting and inefficient power plants [2]. It could also drastically reduce the number of brownouts and blackouts thanks to the presence of the energy reserves.

The range of different Energy Storage Systems (ESS) is very wide, taking part different chemistries and cells formats. For many years, nickel–cadmium technology has been the only suitable battery for portable equipment from wireless communications to mobile computing until Nickel Metal Hybrid and Li-ion batteries emerged in the early 1990s. Today, Li-ion is the fastest growing and most promising battery technology. Li-ion technology is widely used in consumer low power products in the field of electronics such as cell phones and laptops and in high power applications such as electric vehicles, trams, bicycles, etc. It has rapidly become a standard power source and battery performance continues to improve so that it is possible its use in applications that demand more power. The main advantages of Li-ion batteries, are the high energy density (23–70 Wh/kg), the very high efficiency (near 90%) and the relatively long cycle life (3000 cycles at 80% depth of discharge) [3,4].

For example in transportation applications, like in electric or hybrid vehicles in order to cover the needs of fuel saving and ecological aspects, new improved functions of the vehicle are required. Including too safety, comfort, reliability and vehicle availability issues. The electric control and the powered systems for accelerating, braking, steering and stabilization need a reliable supply of electrical energy. Furthermore, the planned generation of electrical energy, an adequate storage, and early detection of possible restrictions of reliability must be managed by the battery monitoring system allowing the implementation of actions by the energy management unit well in advance, while the driver does not need to be involved at all [5]. In order to use an ESS covering all these aspects, a BMS must be used. The BMS is an electronic system which manages the operational mode of a battery to ensure and guarantee its safe operation mode. Basically this system is the one which protects the overall system and, based on its diagnostics, provides the optimal performance management of the energy storage.

As part of the diagnostic approach, the battery management system performs the on-board SOH estimation. SOH is a metric to evaluate the ageing level of batteries, which often includes capacity fade and/or power fade. It gives very useful information for predicting when the battery should be removed. If the performance of the battery is not normal it should be reflected in this parameter. It is not easy to estimate this state as it is not possible to perform a direct measurement. So that different estimation methods have been studied in this document in which their advantages and drawbacks are compared. The state-of-art review of literature summarized in this document points out that in general there is a lack of an explicit sensitivity evaluation of the SOH estimation methods. Furthermore, the process of developing a complete SOH estimation model (design, parameterization, implementation and validation) is not exhaustively described.

## 2. SOH estimation methods

The commercialization of electric and hybrid vehicles leads to an increasing demand for long life time batteries. Knowing the SOH can be used to recognize an ongoing or a sudden degradation of the battery cells and to prevent a possible failure of the electric system and, accordingly, the vehicle. Even though the importance of the SOH is really high, still does not exist a consensus in the industry or in the scientific community on what SOH is and how should be determined. It is a parameter that reflects the present condition of the battery cell described in percentage, being the 100% a fresh cell. In one hand when the capacity is decreased until 80% of the initial rated capacity the battery is considered not usable for an electric vehicle and should be removed. On the other hand, the increase of the internal resistance can be in some cases higher than the decrease of the battery capacity. The estimation of the battery SOH has to take into consideration both; battery capacity fade and impedance increase.

Unfortunately, Li-ion batteries are complex systems to understand, and the processes of their ageing are even more complicated. Capacity decrease and power fading do not originate from one single cause, but from a number of various processes and their interactions. Moreover, most of these processes cannot be studied independently and occur at similar timescales, complicating the investigation of ageing mechanisms. Ageing mechanisms occurring at anodes and cathodes differ significantly [6–10]. On the one hand, it is studied that dominant ageing mechanisms on anodes are caused by Solid Electrolyte Interface (SEI) formation which causes a significant increase of the impedance. This effect occurs mainly in the beginning of cycle life. Secondly, when loss of lithium in the active carbon takes place, it leads to self-discharge and capacity fades. Also, lithium metal plating contributes to an accelerated ageing causing capacity fade and power fade. The lithium metal plating may occur when the batteries are charged at low temperatures ($<0\,^{\circ}C$) and/or at high current charge rates, whereby, the process of lithium ion through the negative electrode decreases and typical metal oxide parts take place on the surface of the electrode. Lithium plating results to less active material and thus the battery capacity decreases and the battery impedance increases as a consequence. On the other hand, cathode materials are affected significantly by both performances, cycling and

**Table 1**
Differences between experimental techniques and adaptive methods [11,13,14].

| | SOH estimation | |
|---|---|---|
| | **Experimental techniques** | **Adaptive methods** |
| **Based on** | Storing the lifetime data and the use of the previous knowledge of the operation performance of the cell/battery. | Calculation of the parameters, which are sensitive to the degradation in a cell/battery. |
| **Advantages** | 1. Low computational effort<br>2. Possible implementation in a BMS | 1. High accuracy<br>2. Possible to be used as in situ estimation |
| **Drawbacks** | 1. Low accuracy<br>2. Not suited for situ estimation | 1. High computational effort<br>2. Difficult in BMS implementation |

calendar life of Li-ion cells. In general, charge capacity fading of positive active material can be originated from these three basic principles: structural changes during cycling, chemical decomposition or dissolution reaction and surface film modification. Other effects that occur in batteries can also cause an increment in the impedance, like: loss of contact between the inactive components, metal dissolution or electrolyte decomposition [11].

In order to predict these changes, the determination of the SOH can be done by two different approaches; experimental and adaptive methods. Experimental methods store the cycling data history of the battery. With it and a previously gained knowledge about the influence of the main parameters affecting the battery lifetime, an estimation of the SOH can be performed. This approach requires a good insight in the interrelation of operation and degradation of the battery cell, either gained by physical analysis or the evaluation of large data sets of operation history in connection with SOH tests of the battery cell.

Adaptive methods determine the SOH through calculation from parameters that are sensitive to the degradation of the battery cell. This necessary data must be measurable or should be examined throughout the operation of the battery. This possibility gives the advantage of not needing many tests and simulations of the battery behaviour. It will ensure a better adaptability on different battery types and chemistries but they also play with the drawback of having a high computational load, which complicates the online running of the model on a real application [12]. In order to have a more clear view of the main differences between the experimental and adaptive methods, the next table was developed. In it, the main advantages and drawbacks are clearly detected (Table 1).

Therefore, methods for the determination of the state of health of the battery cells are investigated through the determining of the available capacity and the internal resistance of the battery cells. To understand the performance of each method in a better way, following the just mentioned classification some methods will be explained in a deeper way. These lists of methods, which can be found in literature, are classified in Fig. 1.

Apart from the techniques mentioned in Fig. 1, a deep research on degradation mechanisms detection methods is going to be done in order to study the possibility of its use to estimate the SOH in Li-ion batteries.

## 2.1. Experimental techniques

The most effective and simplest method of monitoring battery behaviour is through the measurement of battery voltage, current and temperature. Experimental techniques may provide the benefits for case study and individual analysis. However, the applicability of the knowledge to other chemistries, cell designs, or operating conditions is limited since they are all empirical results.

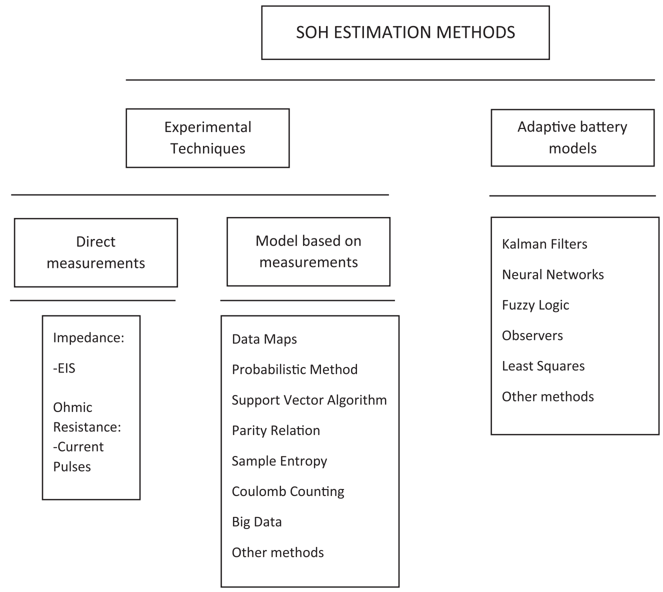


**Fig. 1.** Classification of SOH estimation methods.

### 2.1.1. Direct measurements

A well-known approach for battery fault diagnosis and prognosis is to estimate the battery SOH from the battery impedance or resistance. Apart from this approach, there is also another technique Hybrid Power Pulse Tests (HPPT) method which is capable to determine the dynamic power capability.

*2.1.1.1. Internal resistance measurement.* The life evolution of a battery is determined by its capacity loss and the increment of its internal resistance. Due to this reason several authors have made their research in order to measure the internal resistance of a battery cell [15] These resistance measurements are used to evaluate resistance degradation during subsequent life testing.

When measuring the DC resistance, current pulses are applied. The resistance is described in [16] and shown in Eq. (1) following the Ohm's law,

$$R_i = \frac{\Delta I}{\Delta V} \quad (1)$$

where corresponds to the voltage drop and refers to the applied current pulse at 1C. This way, the current/voltage changes is evaluated and the internal resistance is calculated depending on the SOC and temperature In this same work, there is also explained a way to calculate the polarization resistance of electrical vehicles using discharge curves. Making a comparison between the discharge curves at different currents, and the same curves but recalculated to the 1C discharge curve, an additional voltage drop appears which determines the polarization resistance. A significant number of curves are needed previously to be able to calculate the resistance on board.

The author in [14] uses the same pulses methodology to estimate the internal resistance, but by applying different timing pulses: 10 ms, 2 s and 30 s of the current pulse. Pulses are also used in [17] in order to track the resistance growth. The evolution is also studied when taking into consideration different parameters like Depth of Discharge (DOD), temperature or SOC. It is concluded that the SOC seems to be completely independent from the growth of the resistance. In [18] too, a deep research has been performed studying the internal resistance growth according to different SOC state and different temperatures. On the one hand he same conclusion as before is achieved; the influence of SOC is not notable for the resistance increase. On the other hand, it is affirmed that the temperature highly affects the increase of the resistance, and in consequence the life of the battery cell. Several works uses the current pulses in order to check the evolution of the resistance, applying different timing or current rate pulses [19], [20]. In this last work, the different timing for measuring the open circuit voltage (OCV) is highlighted due to the different obtained results when applying different waiting times.

Another technique to measure the internal resistance is the Joule effect. The losses produced by this effect makes changes in the temperature of the cell. In order to track this evolution a calorimeter needs to be used . A good reference of this can be found too in the manual [21] in which the method is used. In [22] the SOH is estimated through the IR measurement and the use of adaptive methods.

Internal resistance models are also in use for resistance measurement. In [23] an evaluation of large-capacity 40 Ah and 80 Ah Li-ion cells developed for industrial use is done. Their performances show that the cells exhibit reduced voltage characteristics and increased IR in degraded conditions. In order to estimate the cell status from the voltage characteristics a DC power supply system was constructed. The Li-ion batteries in the system are maintained by a floating charge method. During the experimental procedures which took approximately 2 years, the model was developed obtaining a precise model.

In this section must be mentioned too that the HPPT method is capable to determine the dynamic power capability over the device's useable charge and voltage range using a test profile that incorporates both charge and discharge pulses. The minimum voltage can be also determined that can be reached after discharge, and the maximum voltage after charge. This information is of great value as the discharge and charging ranges can be enclosed to values in which the battery will have a longer life, ensuring that it will not suffer from over-charges or over-discharges [24,25].

*2.1.1.2. Impedance measurement.* Other way of determining the SOH is by estimating the actual value of the impedance. For reaching this purpose Electrochemical Impedance Spectroscopy (EIS) is used. For example in several documents like in [26,27] and in [28] they focus on the non-destructive measurement of a battery's internal impedance as a function of frequency.

Due to the fact that battery impedance increases with ageing and different battery dynamics tend to affect different frequency ranges on the EIS measurement, impedance spectroscopy can be used as a diagnostic tool. At high frequencies, inductive effects in the battery wiring and porous structure are prominent. In addition, impedance becomes purely ohmic as frequency decreases. At lower frequencies, capacitive effects become important. Apart from these characteristics, there are several important battery parameters which can be extracted from an EIS measurement. For example, a transition is sometimes visible at very low frequencies where the Nyquist plot's angle changes from 45° to 90°, indicating a switch from semi-infinite diffusion to finite-length diffusion.

Due to this highly valuable information and in order to base the SOH estimation on this EIS measurement, equivalent circuit models have been developed so as to estimate the SOH of a battery in the most simple and accurate way. On one hand, the fact that the large battery currents used in applications such as electrified vehicles, tend to excite complex dynamics that equivalent circuit models typically do not capture, makes this estimation method stronger. On the other hand, even if impedance spectroscopy provides a very promising tool for battery health model identification, for making this usage possible, electrochemical model reduction must be achieved. For example in [29], it is demonstrated that although SOH information inferred from battery impedance (and also resistance) measurement is valuable, experimental results have shown significant variations of battery resistance/impedance among different battery types. Moreover, it is highlighted that because of the cost and complexity of on-board implementations it is not feasible to use a battery identification algorithm combined with a calibration table for each possible battery type. Therefore, in order to achieve accurate and robust battery diagnosis/prognosis, the battery resistance needs to be combined with other features via an integrated algorithm.

Anyway, this characterization has been widely used for SOH estimation, not only for Li-ion batteries but also for nickel metal hydride [30] or Lead-Acid batteries [31] and in applications as aircraft [32], electric vehicles and more [20,33–39].

### 2.1.2. Models based on measurements

*2.1.2.1. Data fitting.* As already seen, resistance measurement is very valuable data in order to estimate the SOH of a battery. With the purpose of having a detailed IR fitting, a characteristic map is proposed for calculating the IR at every SOC and temperature. The data map is needed due to the fact that is essential to perform long-time predictions and also because it may need some time for calculations before delivering a reliable IR value.

The main drawback is that each map must be parameterized for each cell reference. In [40], even if the method is built upon a weighted ampere-hour throughput model of the battery, it is based on the concept of severity factor map. Under the development of this framework, an investigation of two primary factors of battery life reduction is made. These two factors are the DOD and the temperature.

The severity factor represents the relative ageing effect with respect to the baseline given by the nominal operating conditions (e.g., discharge/charge at fixed current rate and fixed DOD) as provided by the battery manufacturer. A severity factor greater than 1, represents conditions which are more severe than the baseline in terms of ageing. Once the factor map is done, the graphic can be interpreted in two ways due to its main interest regions: the fringe spot and the sweet spot. If the battery is operating in the fringe region, the Ah-throughput will be weighted with a severity factor higher than the severity factor used when the battery is operating in the sweet area, which reflects more severe operating conditions. The main advantage of this method is that it is a suitable online tool to estimate battery life in terms of miles per year of the vehicle. Contrary to this, its main drawback is the lengthy and extensive previous experimental data that is required.

In [41], a capacity fade model is proposed. It is composed of three factors: capacity loss, increase of internal resistance and diffusion effects. Depending on how the discharge curve of the cell changes, capacity loss, increase of internal resistance or/and diffusion effects are happening. A linear combination of these three shifts represents the change in discharge curves by capacity fade. In order to make an evaluation, a database is required. For the construction of it, the three capacity fade factors are quantified based on the manipulation of data of fresh and deteriorated battery discharge curves. Once this step is made, a prediction of the capacity fade can be made through the comparison between the predicted and actual state of these three factors of the battery.

In [42,43] a method is proposed in order to estimate battery cycle number using ECE 15 driving cycle. This is of great importance in order to obtain realistic experiments of electric vehicles. Consequently both methods are independent from the battery parameters which are difficult to be obtained during drive. In [42] also another method to obtain SOH of a battery using the cycle number is introduced.

*2.1.2.2. Probabilistic method.* There are methods in which the capacity is estimated by using a probabilistic algorithm. For example, in [44] a probabilistic method is proposed for estimating the SOH by analysing the charge and discharge data of electric storage batteries. The method has its origins in classical probability theory. It consists on calculating the probability of the number of times where the same voltage is measured according to the discharge curves of new and aged batteries. Obtaining this probability, two peaks will be seen in which the ageing tendency is reflected. The peak shows how much the same voltage point has been repeated, as many measurements in a row with the same voltage value, as higher the peak will reach. From this moment on, an algorithm estimates the capacity just comparing the quantity of data which has the same voltage. After this, with a generated look up table it estimates the capacity of the cell based on partial charge or discharge. This way, an important advantage is obtained; the algorithm saves time due to its partial charge and discharge tests. Apart from this, a good benefit is that the algorithm is easy enough so that can be developed in a BMS.

Probabilistic models can be also employed to perform the SOC and SOH estimation. For example in [45], the author combines equivalent circuit models and state transition models with probabilistic methods like Bayesian regression and classification. All this accompanied by ageing processes in order to validate the methodology using experimental results. Other research in which Bayesian statistics have been used is [46] Here also, the statistical method comes together with an equivalent circuit model and a model created using historical data. [47] bases its analysis on statistical distribution of the ambient temperature at battery locations. Despite its simplicity, this new approach does not sacrifice the accuracy of the battery ageing rate estimation since it accounts for temperature fluctuations experienced by batteries in the field.

*2.1.2.3. Coulomb counting.* There is another technique which is based on Ah counting which is very much used for the estimation of the SOH. Through the charging or discharging methods, the number of Ah which are either charged or discharged are counted, this way the transferred amount of Ah are tracked and consequently the remaining capacity is known [48]. The used equation to estimate the SOH Eq. (2) needs as input parameters, the measured capacity and the maximum available capacity.

$$SOH = \frac{Q_{max}}{Q_{nominal}} \cdot 100\% \tag{2}$$

Nevertheless, the method also counts with some drawbacks. Tracking the Ah counting requires a high storing capacity which obliges which sometimes is also a high time consuming. Not only that but also, the precision of the method is highly required due to the accumulative error it carries. Even those disadvantages, the coulomb counting method is the most used method due to its simplicity and its low affecting relation with other parameters like DOD, C-rate or temperature, which usually have a strong effect on other methods. This technique is very well used for SOH and SOC estimation [49–51].

*2.1.2.4. Support vector regression algorithm.* The Support Vector Regression algorithm (SVR) is a nonlinear generalization algorithm that analyses data and recognizes patterns. It is used for classification and regression analysis. The basic SVR takes a set of input data and predicts, for each given input, which of two possible classes forms the output. It adopts the original machine learning algorithm and applies it for non-parametric function estimation. It can be used as a regression algorithm for nonlinear problems and is therefore also suitable for SOH estimation of Li-ion batteries.

Conventional SVR is formulated as a convex quadratic programming, but apart from this formulation way there are more forms such as: Support Vector Parameter Identification (SVPI) which is an SP improved of the conventional SVR in terms of computational efficiency, in which performance of parameter identification is used. This method works based on updating the support vectors [52]. Along this work [52], a comparison of several algorithms to analyse the incremental capacity is developed and evaluated. It is also shown that the usage of SVR gives the most consistent identification results with the less computational load. The support vector is also used in [53] in which with the help of pattern recognition a method for predicting battery SOH is shown. It is also capable of generating a percentage-based prognosis of battery cranking power capability.

In [54] the Support Vector Machine (SVM) is used. As the estimation of SOH is highly influenced by environmental and load conditions, the SVM is combined with a new method for training and testing data processing based on load collectives. For this approach, an intensive measurement investigation was carried out on Li-ion power-cells aged at different degrees ensuring a large amount of data. Other works apply the Bayesian theory for SVM based SOH estimation. This is the case of [45], in this work it is proved that the Bayesian treatment of the support vector machine can be accurately used for SOH estimation. It is used for both; diagnosis and model development. Moreover, a particle filter is used in order to develop statistical estimations of SOC and SOH. For these estimations, the noise of the system and the operational conditions are also considered in order to provide a more accurate estimation. Validation of this approach on experimental data from Li-ion batteries is also presented with high accurate results. On the contrary, a particle filter, a Bayesian treatment and a battery model should be implemented in a battery management system, in order to have an accurate online estimation, which seems to be the most difficult point to reach of the method.

*2.1.2.5. Parity-relation method.* By the use of parity-relation method desired performance of the batteries can be used in order to study and compare the performance of the current battery as shown in [55]. Through analysis based on the presented battery model describing the battery dynamics during cranking, it is shown that the residual integrates the SOH information provided by both battery resistance and voltage loss, hence enhancing diagnostic/prognostic performance. First, through analysis of extensive real vehicle cranking data, battery ohmic behaviour and voltage loss were observed during engine cranking for a battery model development. Secondly, parity-relation based integrated battery SOH monitoring method is developed. The parity relation is designed to characterize the behaviour of good batteries during engine cranking. Extensive evaluation results using real vehicle cranking data have verified the effectiveness of the proposed method, better diagnostic performance than conventional resistance- based methods is achieved. All this comes with the drawback of developing a model for each type of battery/cell due to their different performance. Also, there is a patent in which this parity-relation is used for SOH estimation [56]. The method consists on training offline parity-relation parameters between extracted battery voltage and current signals during offline battery discharge events using at least one new offline battery. Portions of terminal voltage and current signals of an on-board battery corresponding to an on-board engine cranking process are also extracted, and battery voltage of the on-board battery are estimated based on the parity-relation parameters and the already extracted portions of the on-board battery current signals. A diagnostic residual defining a deviation between the battery voltage estimation of the on-board battery and extracted portions of the on-board battery terminal voltage signals is generated. This way a measure of battery SOH based on the diagnostic residual is then provided.

*2.1.2.6. Failure detection.* Other authors keep their attention in measuring the mechanical fatigue or the failures that the cell is suffering. Based on this data, the evaluation of the state of health of Li-ion cells is made. In [57] a physics-based model of a battery experiencing a single source of ageing is employed as a surrogate battery. In fact the model is based on the growth of a Solid Electrolyte Interface at the carbonaceous anode material. Palmgren–Miner rule is used in order to measure the mechanical fatigue of every single cell. Other case is [58] in which the internal structure of the cell is also studied. Basal investigation of a new type Al–Cu–Li alloy is carried out. The peak ageing of the new type Al–Cu–Li alloy is determined through tensile tests and the Transmission Electron Microscopy is used in order to investigate the microstructure of the experimental alloy. The qualitative relationship of mechanical properties and microstructure was established depending on the effect of each parameter.

Identification of the major characteristics of capacity fade is compulsory in order to estimate a good State of Health, which means identifying the impedance growth and capacity loss. Impedance growth is significant at both the positive and negative electrodes, though capacity fade loss due to SEI growth is usually attributed to the negative. In [6] techniques for accelerated life testing are summarized. Simple models are used to describe mechanisms for capacity loss at the negative. Finally, numerical simulations are used to explore the effect of porous electrodes on fade behaviour. In [59] the accelerated calendar and cycle life of Li-ion cells is studied. In calendar life temperature accelerates cell performance degradation. The rates of area specific impedance increase and power fade followed simple laws based on a power of time and Arrhenius kinetics. The data have been modelled using these two concepts and the calculated data agree well with the experimental values.

There are many other works which focus on failure or cracking detection, [31,60–64]. For example, in [64] a first principles-based model is developed to simulate the capacity fade of Li-ion batteries. Incorporation of a continuous occurrence of the solvent reduction reaction during Constant Current and Constant Voltage (CC–CV) charging explains the capacity fade of the battery. The effect of parameters such as end of charge voltage, depth of discharge, film resistance, exchange current density, over voltage of the parasitic reaction on the capacity fade and battery performance are studied qualitatively. The parameters are updated for every cycle as a result of the side reaction were state-of-charge of the electrode materials and the film resistance, both estimated at the end of CC–CV charging. The effect of rate of solvent reduction reaction and the conductivity of the film formed were also added to the study. Several parameters, which have a high effect on the cell performance are evaluated and studied every cycle, which means many time in updating all parameters which are needed for the estimation. It is a fact that impedance measurements give valuable information on the battery state but in order to obtain a reliable and on-board methodology, the studied information needs to be combined with other conventional algorithms or self-learning tools to achieve reliable and stable results for real-world applications.

*2.1.2.7. Sample entropy.* Researchers use this sample entropy in combination with other methods in order to obtain better and more accurate estimations. For example, in the next study, Sample Entropy and a Support vector machine are used [65]. In this paper, an intelligent prognostic for battery health based on sample entropy feature of discharge voltage is proposed. Sample entropy can provide computational means for assessing the predictability of a time series and it can also quantity the regularity of a data sequence. Therefore, when it is applied to discharge voltage battery data, it could serve an indicator for battery health. In this work, the intelligent ability is introduced by utilizing machine learning methods namely support vector machine and relevance vector machine. Sample entropy and estimated SOH are employed as data input and target vector of learning algorithms, respectively. The results show that the proposed method is plausible due to the good performance of both machines in SOH prediction.

Other possible combination which has been already developed is using Sample Entropy with a least square method and a HPPT [66]. In this work the ageing datasets of eight cells with the same chemistry were used. The sample entropy of cell voltage sequence under the well-known HPPT profile is adopted as the input of the health estimator. The calculated sample entropy and capacity of a reference Li-ion cell at three different ambient temperatures are employed as the training data to establish the model by using the least-squares optimization. The other cells were used in order to validate the performance and robustness of the estimation.

*2.1.2.8. Big data.* Big data is based on the processing of large and complex data. There are five domains in which big data can have a big impact. Firstly, big data can unlock significant value by making information transparent and usable at much higher frequency. Secondly, as organizations create and store more transactional data in digital form, they can collect more accurate and detailed performance information, and therefore expose variability and boost performance. Thirdly, big data allows ever-narrower segmentation of customers and therefore much more precisely tailored products or services. Fourthly, sophisticated analytics can substantially improve decision-making. Finally, big data can be used to improve the development of the next generation of products and services. For instance, manufacturers are using data obtained from sensors embedded in products to create innovative after-sales service offerings such as predictive maintenance (preventive measures that take place before a failure occurs or is even noticed) [67].

Even if the filed in which big data has been mostly used is in economics, it can be transferred to all other fields, like estimating and predicting the SOH in any kind of application. Developing a methodology based on the study of so many data could be useful for predicting very accurately the state of health of the battery. It can also be valuable in order to study where the most aggressive degradation comes from and can give lot of information about how to predict or even avoid it. The biggest drawback is how to deal with all the data and how to develop an accurate algorithm, which will guarantee a good performance.

*2.1.2.9. Destructive methods.* Classical methods used to study the SOH may require the destruction of the cell, disabling any further use of the cell.

- Raman spectroscopy [68–77]
- X-ray diffraction [78,79]
- Scanning Electron Microscope (SEM) [80,81]
- X-Ray Photoelectron Spectroscopy [82–86]
- Scanning Transmission Electron Microscope (STEM) [87,88]
- Cyclic Voltammetry [89,90]
- Auger Electron Spectroscopy (AES) [82,91,92]
- Atomic Force Microscopy (AFM) [93–95]

Generally in this methods accurate SOH estimation are obtained due to the exact degradation information that the examination offers. On the contrary, in order to analyse the battery ageing mechanism dismantling of batteries is required, like in methods such as X-ray Diffraction or Scanning Electron Microscopy. Moreover, these methods may permanently damage the battery. Therefore, the methods are considered inappropriate for the battery management system in an industrial application.

### 2.2. Adaptive models

Parameter estimation techniques based on equivalent circuit models have been also developed to quantify the degradation in Li-ion batteries. Some models aim to monitor the state of health of Li-ion batteries in industrial applications using an on-board internal resistance estimation technique. There are several ways with which the estimation of the SOH can be done. For example with the use of Kalman Filters and an equivalent circuit model, or with a dual sliding mode observer with which the capacity fade of Li-ion batteries can be estimated. These kinds of methods will be deeply analysed in the next lines.

#### 2.2.1. Kalman filter

A Kalman Filter (KF) is an adaptive method which is also very used for SOH estimation. Is uses a series of measurements observed over time, and estimates the output variables that tend to be the more precise.There are two steps to follow when using a kalman filter. First, a prediction state is required, in it the filter estimates the current output variable. In the second step, the estimation is updated in order to get a more accurate result giving the estimation a higher certainty. It requires the use of recursive equations that can be implemented when the discrete model of the system is known in state space mode. This happens because the current state of the system is the result of the effect of all the inputs in already past states.

On one hand this method can be run online, and very accurately. On the other hand matrix operations are necessary to perform in order to achieve the results, which requires indeed a big storing data.

The author of [96] uses a kalman filter in order to develop a battery model and to estimate its parameters. Along the work, it is certified that the results obtained through this technique are highly accurate and efficient. It is also confirmed that the size of the matrix it has to be used correspond directly to the number of states of the battery model.

An on-board SOH estimation is made in [97]. In it a model-based monitoring approach is presented. The state of health is dependent of the internal resistance. The model is based on a linear parameter-varying model, which aims to cover the temperature operation range of battery cells in a hybrid electric vehicle. A Kalman filter is also needed for the online estimation of the internal resistance.

*2.2.1.1. Extended Kalman filter.* The kalman filter can only operate with linear systems, which usually don't happen to be battery models. Due to this limitation, variations and extensions have been developed inside the kalman filter. The extended kalman filter is one of them, is the non-linear version of the kalman filter.

The extended kalman filter has been widely used for developing battery models. In [98] using the state of charge as internal state of a nonlinear model of the cell. In [96] the filter is used in order to estimate the SOH of a cell, by calculating through the filter the capacity and internal resistance of a cell.

Many authors use the filter in order to estimate the SOC [99] but in this case an electrochemical model is used. Several advantages come with the extended kalman filter used in this work. It has been proved that the obtained results are very accurate, the algorithm to implement is lighter which means that it can be run in a real application and what is more, the developed model shows a linear correlation with the dynamics of the cell.

The main purpose of the author in [100] is calculating the SOC and estimating the OCV. In this case, the parameter used in the model are the internal states. It is highlighted in this work the effort which is needed to track the states when a constant current is being applied.

In [101], combination of EIS internal impedance method and an extended kalman filter is proposed in order to estimate the SOH. The filter is based on a basic model which is composed by a voltage source and the internal resistance.

The author of [102] proposes an enhanced closed loop estimator based on extended kalman filter. Different SOCs, current profiles and even hysteresis influence are taking into consideration. The proposed model has been validated with different experimental results obtained from different scenarios. It is demonstrated that the enhanced model can reduce the estimation error nearly by half compared to an estimator ignoring the hysteresis effect. It allows an accurate and stable estimation over different conditions.

*2.2.1.2. Unscented Kalman filter.* The unscented kalman filter is an algorithm that uses a series observed over time in order to obtain the most accurate result. It estimates the result from different unknown variables to be more precise than those based on a single measurement. It is also used to estimate the SOC, the capacity and even the internal resistance [103], this work is based on an equivalent circuit model. Due to the different evolution of the capacity decrease and the resistance growth in terms of time, both parameters are calculated separately. This characteristic gives the chance of not estimating always both parameters, which means a less time consuming exercise and a less computing effort.

*2.2.1.3. Dual extended Kalman filter.* A dual kalman filter consists in the use of two kalman filters. This necessity came from the fact that the dimensions and complexity of the formed matrix could be too be in order to compute it. In this case, [104] one of the filters is used for parameter estimation and the other one for state estimation. Due to the fact that the meaning between the resulting convergence and the physical effects is not completely clear, a basic model is used in order to guarantee the convergence.

A dual extended kalman filter is also used in [105], this time for SOC and capacity estimation. Apart from the filter, a OCV-SOC loo-up table and experimental results are needed to run the method. Even though the results are no completely exact, the error is quite reduced though the use of the kalman filter.

#### 2.2.2. Observers

Observers can also be used to perform SOH estimation. In this work [106], not only SOH but also SOC is estimated, both in different timing by different observers. Apart from the observers, a cell electric model is used. As mentioned before, this characteristics gives the alternative of reducing the time consuming and the computational effort, even though there are necessary two observers working. Robustness is shown by the results in terms of different errors and temperature.

#### 2.2.3. Fuzzy logic

Fuzzy Logic technique allows modelling nonlinear and complex systems by processing the measured data using the rules of the Fuzzy Logic theory. It is a non-monotonic logic using true and false statements in all their possible ways. The Fuzzy Logic method allows a certain level of uncertainty in the calculations. The measured data can be categorized by crisp or fuzzy sets. Crisp sets categorize data with certainty, while data sets in fuzzy sets have uncertain values. For example a crisp set could be a set of temperatures between 30 °C and 40 °C, a fuzzy set could be categorized by the expression "warm". The subset categorized by the expression "warm" is defined by its so called membership function and each element in a fuzzy set gets a degree of membership which indicates the degree of belonging to the different subsets. The Fuzzy Logic method is a powerful method, but it requires a big amount of testing data, relatively large computations and a good understanding of the batteries themselves for an accurate SOH prediction.

In [20] a combination of fuzzy logic with impedance spectroscopy is used. This second methodology determines the initial parameters in order to estimate the initial parameters used by the fuzzy logic. The method works simply by measuring the impedance at three frequencies. A combination of least square and Fuzzy Logic is carried out, obtaining accurate results. For running the method, the relation between SOC and the battery open circuit voltage is necessary.Through the methodology capacity and SOC of the cell are determined.

Regarding this method it is confirmed in [107] that the only reliable means of determining battery SOH is through offline discharge testing of the batteries. The patented approach combines a battery interrogation technique, such as impedance measurements, with Fuzzy Logic analysis of the data. From the data obtained by EIS measurements it was observed that the magnitude of the impedance at 10 Hz, the magnitude of the impedance at 5.6 Hz and the phase angle at 3.16 Hz showed monotonic behaviour with the battery SOH. The model has been programmed into a handheld battery tester and preliminary test results are provided.

Many other authors also use this technique in combination with EIS in order to estimate the SOH [108,109]. In the case of [110] impedance measurements, combined with Fuzzy Logic data analysis have been used to estimate the SOH of lead acid batteries used in portable defibrillators. An extended method for SOH estimation in UPS is also proposed. Salkind et al. proposed a method for SOH estimation based on impedance spectroscopy and Fuzzy Logic as well. Also in [111] the combination of these two techniques is used. In this work [109], different conditions of temperature and SOC are studied in lithium ion batteries.

#### 2.2.4. Artificial Neural Networks

An Artificial Neural Network (ANN) tries to imitate the Neural Network of the human brain. It has become a common tool for modelling complex or even unknown systems because of his simplicity in handling data from such systems [112]. The big advantage of ANNs for SOH estimation is its ability to handle data with nonlinear dependencies and its universality due to the fact, that it is not necessary to take into consideration all the details of the battery. The biggest disadvantage is the big computational cost of this method, which may be a problem in order to implement the algorithm in a BMS [12].

A typical ANN is build up of three layers: an input layer, a hidden layer and an output layer. It is composed by points or 'neurons' which are connected to work together and to process the information coming from the input layer. The points are connected by lines simulating the weights, which are in principle functions between the layers. To find appropriate values for these weights it is necessary to train the ANN before using it for estimations. This training phase is the biggest limitation of an ANN because a lot of different data is needed to get an accurately working network [113].

A method in which a Neural Network has been used for SOH estimation is reference [114]. This work describes SOH monitoring of a high-power-density Li-ion cell, using recurrent Neural Networks to predict the deterioration in battery performance. In addition, [115] reports on a pattern recognition method that is primarily engineered to detect the chemistry, number of cells, and state of charge in an unknown package of batteries. It can be used for condition monitoring in a known set of batteries thereby, creating a health monitoring apparatus that can be an integral part of a battery management system in an Electric Vehicle (EV) or Hybrid Electric Vehicle (HEV) using Li-ion batteries. The methodology is based on distinct signatures that one can identify in a relatively straightforward equivalent circuit of a battery. These signatures are extracted using time domain diagnostics and are used in combination with nonlinear mappings such as exponential regression and artificial Neural Networks for pattern recognition purposes. In other works [116,117] this technology is also used.

#### 2.2.5. Least squares

This method is based on an electrochemical model that depends on the cell resistance and the solid phase diffusion time [118]. In order to estimate the SOH, it combines an off line linear least squares algorithm, in which using the voltage measurements as the input, a least squares technique is used to identify the coefficients of the parameters of the model. Then for a real time implementation, a gradient based parameter estimator is used. It continually measures the voltage and current data at a fixed sample time. It must be pointed out that for a more realistic performance of the model, the present methodology should be validated at different C-rates and temperatures.

In [119] a real time estimation of the state of health is made. Based on the online estimation of battery model parameters, firstly, the form that best matches the battery dynamic behaviour is determined by analysing the previous obtained experimental data. A second order battery electric model is presented, in which the output voltage, the temperature of the battery and the current are necessary data for obtaining the dynamic behaviour of the Li-ion cell. With it an online identification of the internal resistance is obtained and therefore an estimation of the SOH is made. Secondly, in order to estimate the electric model parameters, a recursive least squared algorithm with a time variant forgetting factor is used.

Another method which estimates the capacity using least squares is explained in [120]. In this paper, an analytical model driven by experimental data is presented. Based on the data collected during the ageing campaign a model to predict capacity degradation is proposed. The model gives the actual capacity value after a number of cycles, knowing the condition at which the battery is operating. For the identification of the parameters, a least square based optimization study is used. The model can be used for various purposes, it can provide the general usage guideline to minimize battery ageing, can also predict the battery end-of-life and SOH, and can give a general usage guideline for HEV and EV applications. In this work the effect of the temperature must be included in order to have a more realistic and dynamic prediction algorithm.

An estimation algorithm for the study of the state of health is developed in [121]. This study consists of estimating the current SOH of the battery based on voltage characterization when charging, and realizes real-time detection of health status in remote monitoring system. Concretely, a modification of the actual voltage curve fitting is made to make it more applicable for the estimation of the SOH in pure EV batteries. First, the battery charging voltage curves under different numbers of cycles are evaluated according to the area surrounded by voltage curve. Based on this battery charging voltage curve, an adaptive voltage curve model is developed. Changing the original nonlinear problem into linearization, by using the recursive least square method, the estimation of the undetermined coefficients is made. After several recursive calculations, the parameters will ultimately respectively converge to three constants, which will be used in the model.

#### 2.2.6. Other methods

Other kind of SOH estimation methods can be found in literature which are not considered to be inside the determined classification.

In [122] an electrical battery model is proposed in order to track the evolution of the internal resistance growth and capacity decrease in terms of affecting grade of DODs, current rates and temperatures. The model itself estimates from the cell voltage and the current variation the open circuit voltage. Adaptive methods like least squares, kalman filter and neural network are also used in order to adjust and recalculate the parameters of the model.

The method shown in [123] estimates the capacity fade in Li-ion batteries. It combines two algorithms, the principal algorithm and the supplementary algorithm. With both methods the capacity and the IR value are estimated. The principal algorithm is based on an equivalent circuit model, which is appropriate for the dynamic cell model to investigate the phenomena and a parameter estimation methodology. This methodology determines the capacity fading and the power fading by using the least squared method. This is an accurate and robust algorithm for the estimation of capacity fading but it has a significant computational load. The supplementary algorithm on the contrary has a much lower computational load but the precision you get of the obtained parameter is also poorer. In it a linear regression is calculated from the relationship of SOC and OCV. In order to use both algorithms a hybrid algorithm is developed obtaining a balance of both, accuracy and computational weight. The proper estimation algorithm is selected on the basis of a selection criterion that includes the calculation frequency and the degree of capacity fading. Moreover, the principal algorithm is also performed when unexpected fading has occurred. This way, the capacity fades and power increase estimation will be refreshed in order to obtain an accurate estimation in case an error has occurred.

Taking into account real cases, like the one used in Toyota Prius, [124] the method involves plotting battery minimum and maximum block number against battery current in a histogram type plot. Failures such as corroded sensing wires, "bathtub" type capacity fading throughout the battery pack and individual module of block failures are identified using this method. The method consist on a measurement of the discharging slope and a two capacitor model. Moreover, the latest battery monitoring models illustrate how multiple measurement inputs can be configured to guarantee finding potential service-affecting battery faults. Once detected, this information can be sent through embedded alarm communication systems to a designated maintenance response authority [125].

## 3. Degradation mechanism detection

### 3.1. Mechanistic model based on differential voltage curves

In [126], modelling and experimental techniques are combined to provide an universal tool for diagnosis and prognosis. The model consists on a modified equivalent circuit model. It can simulate the different degradation modes via a synthetic approach based on the electrodes behaviour. Each half-cell model is constructed from previously developed laboratory experimental data.

The mechanistic proposed model is composed by two layers: a top layer with cell configuration and inputs from cell operating and degradation modes and a sub-layer with half-cell modules that describe the electrode behaviour. Both modules are described through an equivalent circuit model to handle the electrode chemistry based on voltage and capacity variations. By considering electrode composition and model parameter adjustment that vary depending on the degradation of each electrode, the two electrodes configurations are constructed.

For the detection of battery mechanisms and the quantification of them, the analysis of the incremental capacity curves (IC, $dQ/dV$ $f(V)$) and differential voltage (DV, $dV/dQ$ $f(Q)$) is made. As already seen and explained, from the evolution of these curves, focusing on how the peaks and valleys change, different degradation modes can be distinguished and quantified. Note that for analysing the degradation mechanisms, DV and IC curves must be obtained from a slow and non-stop discharge (C/25) at 25 °C.

The method is interesting as it can be implemented in a BMS just controlling three parameters: voltage, current and temperature. It is also able to classify the different degradation modes, such as: loss of active material, loss of lithium inventory, kinetic degradation or the increase of the polarization resistance and any combination of the degradation modes. The main advantage of this method is the universality that it has. It can be used for different chemistries, cell designs, battery sizes and operating conditions.

Nevertheless, a deep knowledge of degradation mechanisms occurring in a cell is absolutely needed, which means time of checking and researching the degradation of each chemistry cells. Moreover, the mechanistic model needs to be as much precise as possible so as to minimize a possible accumulative error in order to obtain a precise and accurate result.

### 3.2. Comparison of ageing mechanisms of different cell chemistries by the use of differential voltage curves

The next research study which is going to be mentioned [127] uses differential voltage and incremental capacity curves for analysing and quantifying the degradation in different chemistry cells. For developing this work they refer to [126] to explore how to identify the ageing mechanisms and estimate the SOH in an electric vehicle.

Five different types of commercial Li-ion batteries suitable for EV applications were tested: LTO/NMC, C/LFP (two different capacities were tested: 60 Ah, 11 Ah), C/LMO (two different capacities were tested: 35 Ah, 10 Ah). From all this tested batteries, special attention is going to be paid to the developed C/LFP batteries [128].

To develop this study, the batteries were charged at 1/3 C, discharged at 1.5 C, 90 cycles under 5 °C; after every 30 cycles the cells were tested. For the differential voltage curve study, the last charge was used.

The differential voltage curves of new batteries and after being subjected to a number of cycles are plotted and compared in Fig. 2. It is affirmed then that the capacity significantly decreases as the cycle number decreases, indicating there is a loss of internal material. Analysing battery ageing using differential voltage curves has the potential to be applied in a BMS. These curves can be obtained by real-time calculations according to the constant current charge curves in the slow charging process of the battery. The differences in the curves between the fresh cell and the current state can identify the internal ageing mechanisms of batteries in real time and estimate the battery SOH.

Current and voltage of the batteries can be directly measured. In addition, to estimate the difference between the predicted and the actual state, a root mean squared error is calculated through the measured voltage and the predicted battery voltage. The needed parameters can be determined by means of a genetic algorithm so as to minimize the root mean squared error between the predicted voltage and the actual value.

Such methodology based on a genetic algorithm and a root mean squared error of the predicted parameters, may reproduce the battery constant current charge curve of LFP cells, precisely. Furthermore, SOH of the batteries and degradation mechanisms

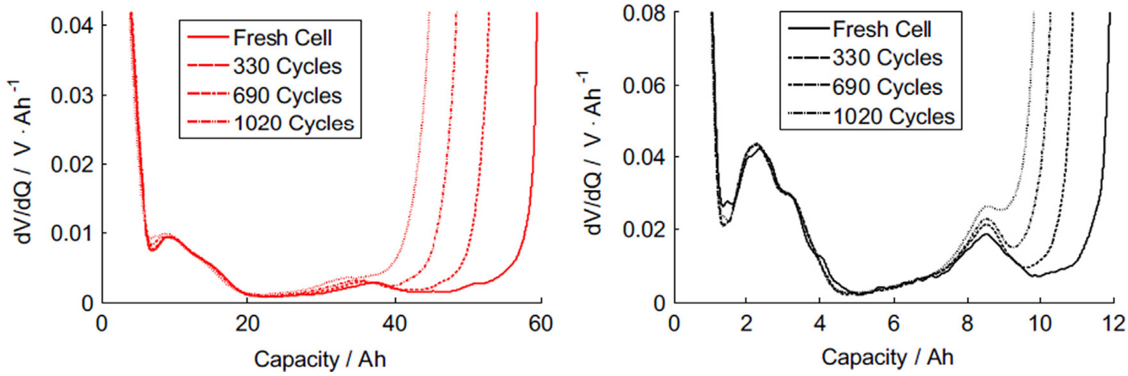


**Fig. 2.** Obtained DV charging curves in two different C/LFP cells [127].

can be also estimated. However, the genetic algorithm is difficult to implement online because of the high computational power required. Although using any other method it is difficult to implement it in an actual BMS. Due to the reason, the incremental capacity curves were studied in order to change the methodology for SOH estimation.

The point counting method is used to obtain the incremental capacity curve, within a resolution and precision enough for on-board BMS development. Obtaining by this way a smooth but precise curve for an accurate response. As seen before in [52], from this curve three peaks can be clearly identified (Fig. 3). The positions of the voltage plateaus in the process of charging can be marked in terms of the voltage positions where the peaks are located in the IC curves. These three areas represent the capacity participating in the related phase transformation process in the battery charging/discharging process. Therefore, so as to measure the capacity participating in each phase but considering too that the three peaks are very close to each other, a Fuzzy Logic [129] function has been used.

By using this method, the analysis can be developed on-board in a BMS. Moreover, ageing of the battery could be conveniently analysed through the constant charge curves during the battery charging process. On the contrary, according to this work [129] in order to obtain accurate results, Fuzzy Logic must be used. This means developing lot of tests for the training this methodology requires.

### 3.3. Other methodologies

Researchers like Bloom illustrated in [130] how capacity loss of cells can be showed based on DV curves. Tests were made for 18,650-sized cells. These high-power Li-ion cells were characterized in terms of performance and cycle- and calendar life at 45 °C. Among other parameters, it was measured the C/25 capacity every 4 weeks during the test. Differentiation of the C/25 voltage versus capacity data with respect to capacity yielded DV curves. Through the analysis of DV curves it was shown that capacity fade in high-power Li-ion cells were primarily caused by two main causes.

It is concluded that capacity fade in Li-ion cells can be a complex and intertwined process. From the curve analysis, the anode material in a significant fraction of the cells showed two types of capacity loss. The loss of accessible material tended to happen early in cell life, either during formation or during the first 4 weeks of testing. Most likely this was caused by a physical rather than chemical process. After 4 weeks, the principal cause of capacity loss was due to occurrence offside reactions. Which process is dominant depends on several factors, some electrochemical and some physical. These phenomena were observed in both the calendar- and cycle-life experiments.

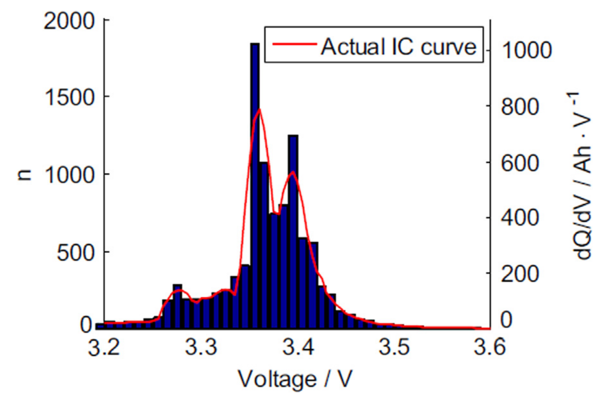


**Fig. 3.** IC curve of a fresh cell derived by point counting method [127].

In addition the paper shows that using DV curves to model the fade processes helps unravel which process is occurring in the life of a cell. Deep examination of degradation mechanisms of high power lithium ion batteries was made through DV curves. It should be mentioned that the curves were obtained through C/25 charge and discharge data, but the tests were noisy due to the very slow charge/discharge rates. Mathematical filtering was used to average out the noise and accentuate the peaks. Note that this work was the base of many others like [126], but no further research was developed in terms of estimation of SOH.

In the next work [131], NMC cells were tested through differential voltage curves. NMC positive electrodes were tested for calendar and cycle life at 60% state of charge. The temperatures used in these tests were 25 and 45 °C (cycle life) and 45 and 55 °C (calendar life). The works analysed the C/25 capacity data, which determines the possible cause of the capacity decrease was occurring. For this case as well, mathematical filtering was used to take out the noise of the C/25 charge/discharge data.

The apparent loss of C/25 capacity can be due to many factors, such as side reactions. These side reactions may lead to solid electrolyte interface layer growth or simply removal of active lithium from the cell. However, the data used during this work do not reveal which electrode is the primary location of observed C/25 capacity loss. The analysis of the DV curves can be used to determine which electrode is the major source of capacity fade and what type of reaction is occurring. It is shown that depending on how the DV curve shifts the cause of capacity fade can be detected. In addition, the analysis indicates that lithium-capacity-consuming side reactions were occurring primarily at the negative electrode.

Even if, this is not exactly the purpose of this work because the cells which are going to be used are LFP cells, can be again demonstrated that DV curves are widely used, even for other cells chemistries like NMC, to analyse degradation mechanisms of the cell.

Finally, in [132] a method for estimating battery pack capacities for LFP cells is proposed. The method studies through the charging cell voltage curves (CCVC) the estimation of the $LiFePO_4$ battery pack capacities in electric vehicles. The estimation of cell capacities is done through overlapping CCVCs using CCVC transformation. CCVCs of two $LiFePO_4$ cells with large capacity difference are used for test and validation.

A comparison of the CCVC curves is made so as to estimate the actual capacity of the battery pack. It is shown that by CCVC transformation, CCVCs of cells with different internal resistances, initial remaining cell capacities and total cell capacities can be overlapped and cell capacities can be calculated. Further, an equivalent simplified approach is also developed using voltage–capacity rate curve and a Genetic Algorithm so as to find the optimum transformation parameter for overlapping the curves.

In addition, a small battery pack with four $LiFePO_4$ cells in series was employed to verify the method [132]. With the proposed method, the battery pack capacity can be precisely estimated which could be used for the driving range prediction. Meanwhile, the estimated cell capacities in battery packs will significantly support the study of cell degradation and cell variations in vehicle driving conditions. So as to mention the main drawbacks of this method cannot be forgotten that more simple algorithms need to be developed for an online estimation of cell capacities and pack capacities in electric vehicles. The Genetic Algorithm presented in this work is still complex in computing for any on-board application.

## 4. Analysis and comparison

### 4.1. Accuracy and computational effort

One of the major issues of a SOH estimation method is to reach high accurate results. In Fig. 4 the accuracy of the studied experimental techniques is shown. The minimum accuracy is represented in black for each method, and the maximum rate in light grey. Moreover in red, the average of all tested experimental techniques is shown.

It should be underlined that the methods with the highest accuracy may not be necessarily the most used ones. Impedance measurement [26–39], sample entropy [65–66] and big data [67] are the techniques with the highest accuracy, but the most used ones are the probabilistic [44–47] and coulomb counting methods [48–51]. This is due to the simplicity of these last methods. Apart from that, failure detection [57–64] and big data [67] methods are getting more used, which means that a lot of research is being developed in order to improve these techniques and use them more frequently.

According to the accuracy obtained through the use of adaptive methods, Fig. 5 is shown. As previously remarked, methods with the highest accuracy (any type of Kalman Filter [96–105], Fuzzy Logic [107–111], Neural Networks [112–117] or methods based on degradation mechanisms detection [126]-[132]) may not be necessarily the most used ones (least squares [118–121], observers [106], basic Kalman Filter techniques [96–102]). The reason of this fact is the combination of accuracy and simplicity.

In addition, it must be underlined that inside the different Kalman Filter methodologies, the most basic ones (Kalman Filter [96–97] and the extended ones [98-102]) are much more used in real applications in comparison with the unscented [103] and Dual Kalman Filters [104,105]. These last two methodologies require a bigger computational effort, which makes them much more complicated in order to implement them in a real controller.

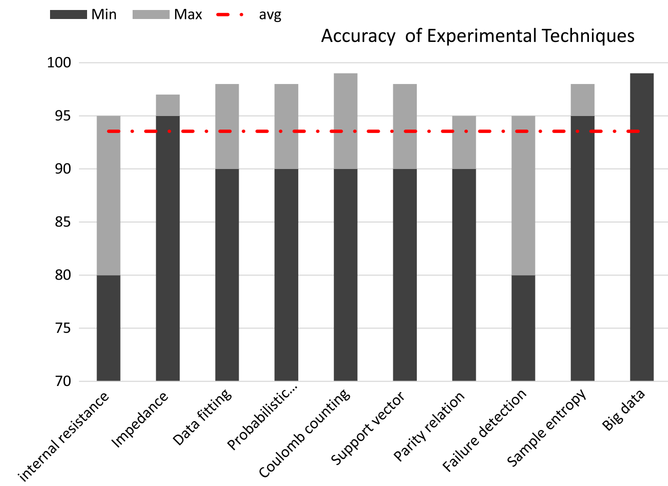


**Fig. 4.** Accuracy of the experimental techniques. In black the lowest obtained accuracy rate, and in grey the highest. In red, the average accuracy of all methods. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

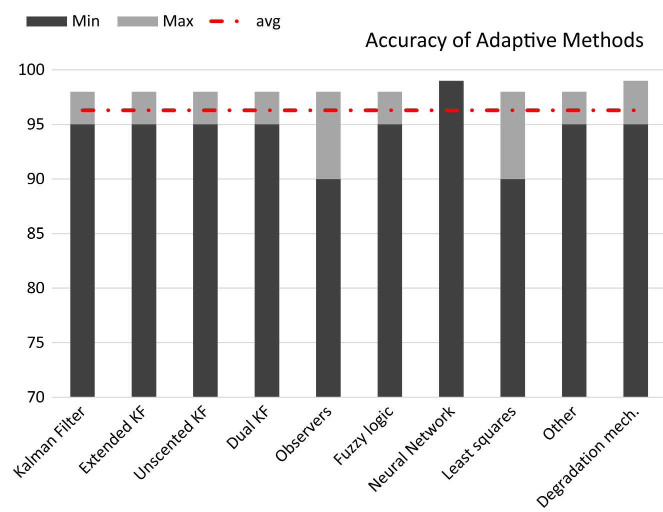


**Fig. 5.** Accuracy of the adaptive methods. In black the lowest obtained accuracy rate, and in grey the highest. In red, the average accuracy of all methods.

According to the rest of adaptive technologies, huge work is being developed in Neural Networks [112–117] and Fuzzy Logic [107–111] techniques in order to make them more computationally affordable so as to use them in an online way. Much progress is being done too in the field of the degradation mechanism detection [126–132] but still no applicable methodology has been developed yet.

In terms of computational effort, in Fig. 6, a comparison in terms of computational complexity and required measurements can be seen for the most existing techniques in literature. One of the most significant findings to emerge from this study is that experimental techniques like OCV or Coulomb Counting methods, require much less measurements and computational effort than an adaptive models such as a Kalman Filtering. Contrary to this, the precision of the methods based on experimental techniques is not as high as in adaptive models.

### 4.2. Current and future methods

In order to elaborate an efficient, precise and applicable SOH estimation methodology, some factors must be taken into consideration. Table 2 details the most common methods in terms of the reason of why are the most used techniques; how can they be improved and finally, which is the effect that this improvements create or require.

It can be detected that extended Kalman Filters, observers and least squares coincide in the improvement they need to achieve. More research is necessary to be developed in order to run an algorithm or methodology in a BMS. For the basic Kalman Filter something similar is happening, but in this case research has to be focused in controlling the performance changes, due to the fact that this filter is not able to contemplate still these changes.

Finally, coulomb counting, which is considered in the most used technology of the moment, has de pros of been simple and practical but on the contrary usually needs other method in order to update the parameters and eliminate any possible error. This handicap should be solved in the easiest, quickest and more efficient way.

Table 3 presents the methods, which seems to be more used in the future and their common issues. It is interesting to detect these common issues because these issues are needed to get reached. By this way, any possible SOH estimation technology, which will be developed should take these points into account. Universality of the methodologies is a very interesting and important issue. Developing an universal tool, which can be used for different technologies is a huge step forwards the SOH estimation methodology development. Another common factor of these methods is that they are becoming of great importance in many fields, not only for battery state investigation but also for sustainability calculation difficulties, economics, engineering problem solving, etc. Apart from this, the accuracy they can offer is very high, but always with the drawback of requiring a high computational effort. That's why, simpler methods must be developed. They offer too, the possibility of not only working with linear problems but also with nonlinear and uncertain calculation. Usually, for using them, they need to be integrated with other methodologies in order to reduce their main drawbacks.

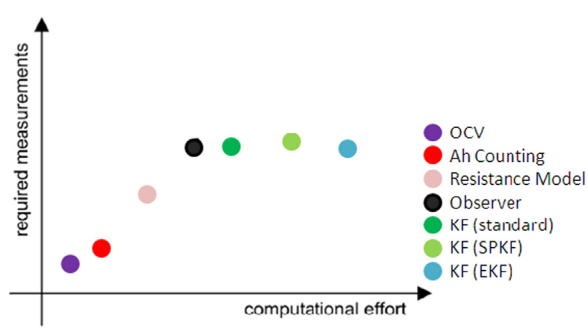


**Fig. 6.** Comparison of some of the investigated methods in terms of computational complexity and required measurements [133].

Following this point, it is thought that using these different technologies in the proper combined way should be a possible solution to develop a novel, accurate, precise, universal, easy and fast methodology. Indeed, works already presented in this paper demonstrate that elaborating a SOH estimation method based on a combination between degradation mechanism detection and an adaptive method seems to be possible. Accurate and precise results could be obtained with the development of an online BMS implementable method. As drawback can be mentioned that all chemistries could differ in the treatment of the degradation mechanisms, which will require deep and extensive knowledge.

### 4.3. *Proposed methods*

This literature research demonstrates that degradation mechanisms detection by incremental capacity curves or differential voltage curves could be very useful in order to predict and estimate the State of Health of a cell or battery pack.

As mentioned, these curves reveal battery degradation mechanisms and they can also quantify the degree of degradation in a cell. Due to this fact, it is highly recommended to use this differential curves in order to reveal why and how degradation mechanisms occur. Through its use, a suitable tool could be developed in order to learn how to prevent very risky and not desirable degradation mechanisms to occur like lithium platting. Detecting and preventing these irreversible degradation mechanisms would be the key for enlarging the useful lifetime of the battery.

In addition, techniques based on Kalman Filters, Neural Networks and other adaptive methods offer a very high accuracy. Moreover, it seems very suitable and possible an improvement of Neural Networks or Fuzzy Logic technologies coming in the next years. In order to have a general idea of the main advantages and drawbacks of the possible combinations of these methodologies, Table 4 was developed. Firstly, the degradation mechanism detection and the possible selected adaptive or big data methodology are described separately. Then, the combination of first the degradation mechanism detection with an adaptive method (Neural Network or Fuzzy Logic technique) is explained.

Secondly degradation mechanism detection is combined with big data. Both combinations are very similar, they offer the benefit of being suitable for all chemistries, and they have a high accuracy. Nevertheless when an adaptive method is used, the method is

**Table 2**
Review of the most used techniques.

| Method | Reason | Improvement | Effect/Requirement |
|---|---|---|---|
| **Coulomb Counting** [48–51] | 1. Simplicity<br>2. Practical<br>3. Fast | 1. With other method supporting for: SOC estimation and updates. | 1. When applying other method, the main advantages are gone: simplicity and response velocity |
| **Kalman Filter** [96–97] | 1. Accurate<br>2. Error bounds | 1. For simple systems, not controlling lot of variables.<br>2. For keeping under control the main problematic parameter. | 1. If the performance changes, it is not contemplated. |
| **Extended Kalman Filter** [98–102] | 1. Accurate<br>2. Error bounds<br>3. Valid for non-linear systems<br>4. Very used | 1. Need powerful controllers.<br>2. For mature technologies in order to adapt the filter for the performance already studied. | 1. Need time for researching the chemistry and improving the controllers. |
| **Observers** [106] | 1. Possible for all chemistries<br>2. Faster than KF | 1. For mature technologies<br>2. Need powerful controllers | 1. Need time for researching the chemistry and improving the controllers. |
| **Least Squares** [118–121] | 1. Precise<br>2. Robust | 1. For mature technologies<br>2. Need powerful controllers | 1. Need time for researching the chemistry and improving the controllers. |

**Table 3**
Review of most used methods.

| Method | Reason | Common issues |
|---|---|---|
| **Neural Network** [112–117] | 1. Ideal for parameter estimation<br>2. No need so many data as Fuzzy Logic, or Failure detection<br>3. For online purposes<br>4. Accurate | 1. Universal techniques, which can be used for any chemistry.<br>2. Lot of research being developed in any field: economics, engineering, sustainability, etc.<br>3. High accuracy.<br>4. Models are becoming more simple.<br>5. Possible to make uncertain calculations.<br>6. These methodologies are usually used with other techniques like: EIS, equivalent circuit models, least squares. |
| **Failure Detection** [57–64] | 1. Deep knowledge on degradation<br>2. Prevention may be possible<br>3. Simple models<br>4. For online purposes<br>5. Accurate | |
| **Fuzzy Logic** [107–111] | 1. Suitable for no linear and complex systems<br>2. Capability of self-learning<br>3. For online purposes<br>4. Accurate | |
| **Big Data** [67] | 1. Huge research on this field<br>2. Treat huge quantities of data in the same way at the same time<br>3. Accurate | 1. Why not use these accurate technologies together and create a new methodology? |
| **Degradation mechanism Detection (* No method)** [126–132] | 1. Seems possible online<br>2. Suitable for any chemistry<br>3. Accurate | |

**Table 4**
Advantages and drawbacks of the proposed methods and their combinations.

| Method | Advantages | Drawbacks |
|---|---|---|
| **Degradation mechanism detection** | 1. Lot of information about the degradation mechanism<br>2. Possible to detect/prevent irreversible degradation<br>3. Useful to learn how to detect extension of the useful life | 1. Computational complexity is large-Difficult to implement it online<br>2. Difficult for implement it in situ |
| **Neural Networks/Fuzzy Logic/Big Data** | 1. Suitable for all chemistries<br>2. Accurate<br>3. Seems to be the most used techniques in the future | 1. Need large amount of data to train.<br>2. The precision depends on the accuracy of the model.<br>3. Computational complexity is large |
| **Degradation mechanism detection + Neural Networks/ Fuzzy Logic** | 1. Suitable for all chemistries<br>2. Capability of self-learning<br>3. Accurate | 1. The precision depends on the accuracy of the model<br>2. Computational complexity is large |
| **Degradation mechanism detection + Big Data** | 1. Suitable for all chemistries<br>2. Online (BMS)<br>3. Accurate | 1. Need large amount of data to train.<br>2. The precision depends on the accuracy of the model.<br>3. Lack of coordination between database systems |

capable of self-learning as new data is available. This is not very possible by using big data, but it gives the opportunity of developing an easier algorithm, which can be applied more easily in a BMS. On the contrary, using big data the amount of needed data must be really huge while with adaptive methods, the algorithm goes getting better results due to the self-learning characteristic. Moreover, the biggest drawback comes from the use of big data due to the lack of coordination between database systems, so the data testing is still not easy.

## 5. Conclusion

For the moment there is no unique perfect solution for SOH estimation. The best combination should be selected depending on what is going to be estimated and the data which is available. For example, in the case of possessing huge amount of data and there is a possible simple algorithm which can be used, the combination of degradation mechanism detection and big data methodology would be the most adequate. In other case, like obtaining data little by little as the tests are being developed, it would be more suitable to use an adaptive model combined with the degradation mechanism detection. In this case, better accuracy would be achieved through the self-learning of the data.

Due to these facts, a new methodology based on a suitable and accurate adaptive model or big data and degradation mechanism detection should to be developed. Though the new methodology, three main objectives could be achieved.

The first one consists on developing the algorithm covering all wished requirements:

- Relatively high precision and accuracy.
- End of Life detection of the cell.
- Possible implementation in a BMS.
- In-situ development (application always available).

All this taking into account that the validation should be developed in a wide set of conditions. This means that the cells to be tested should have been cycled at different temperatures, depths of discharge, current rates and even just in storing conditions at also different temperatures and state of charge.

As a second objective, it can be mentioned that in case the algorithm or methodology is developed, it will cover the requirements at cell level. This may derivate to more research due to the fact that in applications such as electric vehicles, a battery pack must be used, where several cells are connected in series or parallel at each module or system level. Due to this reason, once the algorithm is available and validated at cell level, a deep research must be done so as to implement the algorithm in an effective and efficient way at module level.

Moreover, it cannot be forgotten that variability through the production processes of the cells cause differences in the behaviour of the cells. Furthermore, the temperature is not homogeneous in a battery pack so as a consequence it affects in different way to all the cells. The same happens with the cell balancing, is necessary to use a cell balancing method [135,134]. Nevertheless, even with its use is difficult to control the heterogeneity in the cells ageing. All these characteristics must be taken into account so as to develop a precise methodology to estimate the SOH through differential voltage curves at module level.

The third objective, which will be suitable to reach, is to develop a SOH estimation tool without constraints on chemistry variations, cell designs, battery sizes and geometries, and operating or ageing conditions. Due to this reason, firstly, as mentioned in the first objective wide range of parameter values should be tested in the validation of the developed algorithm. Secondly, other chemistries should be tested with the developed algorithm.

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