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Aging phenomena for Lithium-Ion batteries

Joris de Hoog¹, Karel Fleurbaey¹, Alexandros Nikolian¹, Jean-Marc Timmermans¹, Noshin Omar¹, Joeri Van Mierlo¹, Peter Van den Bossche¹

¹*Vrije Universiteit Brussel, Pleinlaan 2, 1050, Brussels, Belgium, jdehoog@vub.ac.be*

Abstract

This paper will present an overview of the current knowledge on the ageing phenomena inside a Lithium-ion cell during operation and stationary/storage conditions. It starts with an overview of the affecting phenomena on the negative electrode, followed by the effects on the positive electrode. Then, the degradation of the properties of the electrode/electrolyte interface is investigated, after which metal dissolution, electrolyte decomposition and changes to the electrode are assessed. Also, the influence of both cycling and rest periods on the cell are investigated, together with the impact of temperature, (storage) voltage and mechanical stress are examined. The paper concludes with an overview on the state-of-the-art in measurement techniques.

Keywords: Lithium-Ion Batteries, aging, measurement techniques

1 Introduction

As the need for battery-powered vehicles continues to grow, the task of creating ever more efficient drivelines and lightweight storage solutions with viable lifetime becomes increasingly difficult. One of the main challenges in this field is the understanding of the aging phenomena occurring inside the cell on a physical and chemical level. Some of these reactions and phenomena are still poorly grasped, which is mainly due to the fact that lithium ion battery (LIB) technology is still very recent (the first step to develop a practical LIB was made in 1980 by Goodenough et al [1], [2] by adopting LiCoO₂ as cathode material). Right now the industry needs long-lasting high-energy battery cells, and this can only be achieved by better understanding the processes inside the cell on a material level. Another very important factor, and the main subject of this paper is the collection of the different processes and side-reactions that contribute to ageing, such as the formation of a SEI layer, the decomposition of the electrolyte and so on. These phenomena all contribute to degradation of battery performances over time, both in active state (charge, discharge) as in storage/rest stage. The effects of ageing can be

found in the analysis of two important parameters: (1) capacity fade, and (2) impedance change. These two parameters change over time due to the described ageing effects.

2 Phenomena affecting battery performance change

2.1 Negative electrode crystal structure degradation

The negative electrode is often called the ‘anode’ in literature. As the batteries in question are rechargeable, we cannot unambiguously distinguish between anode and cathode, or distinguish the positive and negative electrode. This electrode is usually composed out of graphite, carbon, titanate or silicon [3]. As can be anticipated, the choice of this material will influence the battery ageing. As graphite is the most used negative electrode material, the most profound knowledge has been accomplished with graphite-based electrodes.

Two processes have been identified as cause for mild oxidation of the negative electrode: the production of nanochannels and/or micropores, and the formation of a dense layer of oxides [3]. The production of nanochannels enhances the intercalations, removes some active sites and/or defects in the graphitic materials resulting in an

improvement of the surface structure. The (dense) layer of oxides inhibits the decomposition of the electrolyte and acts as an efficient passivating film. This layer is known as the Solid Electrolyte Interface (SEI). As a result, the reversible capacity and coulomb efficiency increase in the first cycle. When however the oxidation becomes too drastic, an opposite effect is observed.

During the cyclelife of a Lithium-Ion Battery (LIB), the graphite particles of the negative electrode crack into smaller pieces that are less oriented than the original platelets, with the possible filling of the cracks by the reduction products of the electrolyte solution [4]. This will again cause a loss of cyclable active material.

The commonly accepted cause of capacity fading of composite graphite electrodes is attributed to [4]:

1. Growth of electronically insulating surface films, which cause a slow-down of the kinetics, and eventually leads to the electrical disconnection of an increasing fraction of the graphite particles from the current collector.
2. Depletion of the electrolyte solution due to continuous surface reactions, which relates to prolonged cycling and elevated temperatures
3. The exfoliation of graphene plates. This is a process that can happen with extreme intercalation, and it means that complete layers are separated from the material.

2.2 Cathode (positive electrode) crystal structure degradation

Measuring the representative Area Specific Impedance (ASI) of fresh and aged cells reveals that the ASI of the positive electrode increases faster and to a higher end-value after cycling compared to the negative electrode [5]. This suggests that the positive electrode is an important contributor to the increase of overall impedance of a Lithium-ion battery. Also, the impedance at frequencies that correspond to lithium-ion transfer and charge-transfer kinetics increases significantly after ageing.

SEM images show that the positive electrode is coated with a mixture of electrolyte residue and electrode-electrolyte interaction products. This is true for both fresh and aged cells. In addition, oxide particles from aged cells show additional particulate-type features (see Figure 1), which appear to have resulted from localized reactions at the oxide surface.

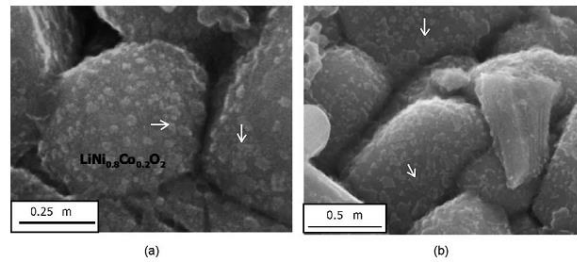


Figure 1: Particulate-type features are marked with the arrows. They are found on the surfaces of oxide particles in positive electrodes from (a) 40°C calendar-life cell and (b) 70°C cycle-life cell [5]

XPS peak profiles are very similar for both fresh and aged cells, and also for cells that aged at elevated temperatures. This means that the surface film develops at the positive electrode and is always composed with the same materials, independent from the cycling temperature. Also, the peaks in the XPS images remain unaffected by the duration of calendar-life testing and cell voltage during ageing. The peaks in the XPS image show lower intensities for aged cells, which indicated that the surface film grows for aged cells. This thicker surface film could explain the increase of impedance for aged cells.

Also, the positive electrode showed structural changes on the oxide particle surfaces. [5] used a High-Resolution Electron Microscope (HREM) to examine the modified oxide surface layers, which are reported to grow significantly after ageing. This increase in thickness could result from occupation of Li layers by Co and Ni, and/or oxygen loss from the surface regions by reactions with the electrolyte. Bourlot et al. [6] concluded that the morphology of the positive electrode does not change significantly over time, for all levels of utilization. Their tests were performed from a capacity fade point of view, and are compatible with the results discussed above. Barré et al. [7] conclude that the main ageing phenomena at the positive electrode are: wear of active mass, electrolyte degradation, electrolyte oxidation and formation of a SEI layer, interaction between positive electrode element dissolved within the electrolyte and the negative electrode.

J. Vetter et al. in [8] come to a similar conclusion. They state the main influences of the cell cathode to the lifetime of the cell to be the ageing of active material, degradation or changes of electrode components (conducting agents, binder, corrosion of current collector and more), the oxidation of electrolyte components and the formation of the SEI layer and the interaction of the ageing products with the negative electrode. Again, the insertion of lithium ions in the positive electrode changes the

molecular volume of the electrode, and can cause mechanical stress to occur.

2.3 Electrode/electrolyte interface properties degradation

In [9] the authors concluded that the changes at electrode/electrolyte interface are a major contributor to ageing for lithium-ion batteries. This reaction takes place mainly at the negative electrode. The reason for this reaction is to be found in the fact that negative electrodes in practice operate outside their electrochemical stability window. This means that reductive electrolyte decomposition takes place at the electrode/electrolyte interface when the negative electrode is in a charged state. This is accompanied by the irreversible consumption of lithium ions at the interface. The decomposition elements build up layers that cover the electrode's surface, and can be considered to be protective (see below). This process occurs mainly in the beginning of the lifespan of the cell, and keeps continuing during its life.

Vetter et.al. [8] characterise these layers into two categories, depending on their function. At specific graphite surface sites (at the prismatic surfaces and defects in the basal planes) lithium-ion transport into and from the graphite structure by intercalation and deintercalation takes place. This means that the protective layers act as a Solid Electrolyte Interface (SEI). The SEI has the property to be conductive for lithium cations, but relatively impermeable for other electrolyte components and electrons. In theory, the SEI layer protects the electrolyte compounds from further reduction, and avoids that the charged electrode corrodes. How the SEI layer is formed is summarized in Figure 2.

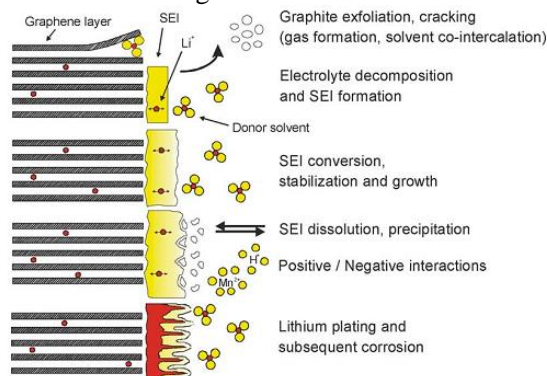


Figure 2: Schematical overview of the changes of the anode/electrode interface [8]

Protective layers also exist at surfaces where there is no lithium-ion transport at the graphite surfaces

(more specifically at the basal plane surfaces), and have no protective function as described above. However, it does protect these sites from further reduction reactions with the electrolyte. These layers are sometimes called Non-SEI layers. The composition of SEI and Non-SEI layers are reported to be very different [10]. Vetter et. Al. however consider the SEI layers uniformly, independently from their function.

The amount of capacity that is irreversibly lost during the formation of the SEI layer is dependent on the specific surface area of the graphite, as well as on the layer formation conditions.

The SEI does not have the same properties as a real solid electrolyte, as other charged elements, such as anions, electrodes, and neutral elements such as solvents and impurities are still able to diffuse or migrate through the SEI. Even worse, transport of solvated lithium seems to keep taking place during cycling of the battery, as irreversible charge capacities and self-discharge reactions can still be observed. This means that corrosion at the graphene electrode and electrolyte decomposition increasing the SEI-layer thickness are still ongoing. When we take the whole lifetime of the battery into account, one can see that the SEI penetrates into the pores of the electrode, and can also penetrate the pores of the separator, which could result in a decrease of the accessible active surface area of the electrode. This could explain the impedance rise of the electrode, together with the fact that the SEI-layer also changes in composition and morphology [8].

2.4 Metal dissolution

Interactions between the positive and negative electrode also cause transition metal dissolution [11]. It was found that mainly the LiMn_2O_4 spinel is considered to release transition metal ions, which can incorporate in the anode SEI, which in turn causes accelerated ageing. The ions can be incorporated into the SEI in ionic or in metallic form after reduction.

2.5 Changes of the composite electrode

Generally, contact loss, both mechanical as electronic, at the composite electrode results in higher cell impedance, and must therefore also be taken into account when considering ageing [12] (electrical contact means the ability for electron transfer between the current collector and the tab of the cell. Mechanical contact is the physical contact between all components of a cell). The main contributor for contact loss is the volume changes

of the active anode material, which can lead to mechanical disconnection within the composite electrode. Contact loss can occur between carbon particles, current collector and carbon, binder and carbon and between binder and current collector. Binder materials and electrode porosity are also affected by volume changes. Also, reactions with electrolyte components or over-potentials (due to overcharging for example) at the negative electrode with regards to Li/Li⁺ can cause current collector corrosion, which leads to a loss of contact, electronic or mechanical, between the current collector and the other electrode components. In addition, internal cell pressure must be taken into account [13]. Research has proven that fluorine-containing polymers and copolymers that are used as binder materials in the composite electrodes will react with the anode, which causes a contribution to the mechanical electrode degradation [14], [15]. Lastly, over-potentials and inhomogeneous current and voltage distributions can be caused by poorly conduction corrosion products, which lead to lithium plating [16].

2.6 Consequences of ageing phenomena

The abovementioned phenomena all contribute to the process called ageing, which in itself denotes the fact that the battery performance decreases over time. Battery deterioration is caused by two different parameters: capacity fade and impedance rise. Both are caused by different chemical reactions.

The decline in performance is caused by a variety of processes, both chemical and mechanical, and the consequences can be divided as follows [7]:

1. The loss of cyclable lithium. This increases the imbalance of the cell, and is related to the side reactions. This phenomenon is verified to occur at both electrodes.
2. The secondary loss of electrode active materials.
3. Resistance increase of the cell, which can be caused by the formation of passive films at the active particle surface, as well as by a loss of electrical contact inside the porous electrode.

3 Variables influencing battery ageing

3.1 Cycle ageing

Assessing the remaining capacity of a battery during its lifetime is a complex and challenging process. The phenomena causing cell degradation as described above need to be understood in order to make a valid conclusion. During cycling, all abovementioned phenomena take place.

In order to assess the remaining lifetime, typically normalized test procedures are followed, where the battery is charged and discharged with specified rates and depths of charge and discharge. Predicting remaining lifetime is however not a trivial task, as the test regime should be very comparable with the actual real-life cycle regime that the battery will be subjected to. To be able to perform high fidelity simulations, the need for an analytical tool used to derive a correct quantitative correlation of battery degradation rate with the SOC is prevalent.

It is very likely that results obtained performing life cycle tests are not applicable for a battery with a different chemistry, as the aging phenomena are highly dependent on the choice of materials for the electrodes, electrolytes, separator, and so on.

In [17], the researchers tested several batteries on their cyclability, with different optimized cells: high-energy, high power and medium power/energy (Typical PHEV cells). High-energy cells are typically used in Electric Vehicles, and showed negligible loss of energy and about 3% loss of power after 1000 cycles from full charge to 80% depth of discharge, as specified in the DST profile [18]. The high-power cells are used in hybrid vehicles, and showed stable power and energy levels after 350,000 cycles, specified by the PNGV-recommendations. This result however is very optimistic, and it remains to be seen if these results are reproducible elsewhere.

In [6], an investigation was performed on the ageing of lithium-ion batteries (7Ah, NCA-type cells with NCA-type cathode and graphite anode), and the difference between cells aged by calendar and cycle life compared to fresh cells. The main conclusion drawn was that aged cells contain more active lithium in the negative electrode after ageing, which can indicate that the effect of ageing is the limitation of the positive electrode. Also, no gas generation inside the cell, no hydrofluoric acid creation, no large degradation of positive or negative electrode material, the passivating layer of the negative electrode remains stable and the ageing process was uniformly distributed in the cell. The main ageing

phenomena discovered in the cells are a slight degradation of the positive material of the cell. Also, a smaller ratio active Li/Metal in the positive electrode of the cell subjected to accelerated cycle life tests was shown.

3.2 Temperature

The operating temperature of a battery significantly influences the ageing rate of a battery. In [19], cells were cycled in a temperature range between -20°C and $+70^{\circ}\text{C}$, until the SoH reached 80% (The SoH was calculated as the ratio of the discharge capacity of an aged cell and the discharge capacity of the same cell when it was new). The researchers used the Arrhenius plot to identify the ageing mechanisms, as defined in the formula (1) below:

$$r = A \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

With the ageing rate r , the pre-exponential factor A , the activation barrier E_a and the Boltzmann constant k_B . This formula has been used in the field of lithium-ion batteries to determine activation barriers for ageing and other processes. A change in the slope of the Arrhenius plot indicates an ageing mechanism change. From the results of the cycling tests, they found that there exist two different ageing mechanisms, for the ranges from -20°C to 25°C , and from 25°C to 70°C . Using different techniques, these mechanisms were investigated. Below 25°C , the main ageing phenomenon was identified to be plating of metallic lithium on the negative electrode (referenced as anode in the source), which leads to a reaction with the electrolyte, which in turn leads to loss of cyclable lithium, which in turn results in capacity fade. Above 25°C , the elevated temperatures accelerate the degradation of the positive electrode and SEI film growth, which leads to capacity fade and internal resistance increase. Also interactions between positive and negative electrode are observed. The measurements further confirm that the ideal operating temperature for cells with a NMC or LMO blend cathode is around 25°C .

In [20], more accelerated tests were performed, with the goal of quantifying the impedance rise and capacity loss influenced by temperature and State Of Charge. The batteries used during testing were 6Ah NMC based lithium batteries, with the anode made from hard carbon. The test consisted of storing the batteries at a certain voltage at different temperatures (25°C , 35°C , 50°C and

65°C) and different levels of SoC (20%, 50%, 80% and 100%). Some cells were stored at float conditions (constant voltage applied) and others at storage conditions (open circuit). Even though there are different theoretical derivations explaining the growth of the SEI layer ([21] vs [22]), all theories conclude that the formation process evolves with the square root of time dependency. A short mathematical explanation will be given here, based on [20] with the following assumptions:

- The cycle of the battery exceeds by far the requirements of the application and ageing is thus neglected in the following
- Different definitions of resistances have been evaluated over ageing, and it is found that all evolve in a similar way over ageing. The authors chose to use the total discharge resistance for the parameterization of the ageing model.
- The authors assume a square root time dependency for the calendar ageing rate. This is also confirmed by the fitting results, where multiple dependencies are investigated for their fit.
- The calendar ageing degeneration rate accelerates exponentially with temperature and voltage, with the exception of impedance parameter R_{ser} .
- The ageing of the OCV can be accounted for using the actual instead of the nominal capacity for the definition of the DoD
- The variation of some impedance parameters is very small and show no significant correlation over time. They are taken constant over time because of this.

The authors of [20] derived following equation (2) to fit their measured calendar ageing data according the assumptions defined above:

$$L_{cal}(t, T, V) = L_{cal}(t_0, T, V) \quad (2) \\ * [1 + B(T, V)] \\ * F(t)]$$

Where L_{cal} is the parameter used for the evolution of capacity, inner resistance or impedance parameters. $B(T, V)$ describes the impact of temperature and potential on the calendar degradation rate. The function $F(t)$ describes the time dependency, which relates to the dominant ageing phenomenon or a combination of ageing phenomena in equation (3):

$$F(t) = c_a * t^{\beta} \quad (3)$$

c_a is the coefficient that describes the rate of ageing at reference conditions (T_0 and V_0) and depends on the specific process. Considering the assumptions mentioned above where the SEI becomes the dominant ageing factor, β becomes 0.5 [23].

The authors find a similar conclusion for the ageing behavior of the capacity loss and internal resistance growth. It is proven that the square root is the best fitting plot for the experimental results. This result is important, as it allows for the usage of the Arrhenius law (4), which describes the exponential dependency of the reaction rate on the temperature. The tested cells contained either LiCoO_2 or $\text{LiNi}_x\text{M}_y\text{O}_2$ positives versus a graphite negative electrode.

$$k = Ae^{-E_a/(k_B T)} \quad (4)$$

Where A is the pre-exponential factor, k is the rate constant of a chemical reaction, T is the absolute temperature (kelvin), E_a is the activation energy and k_B is Boltzmann Constant.

As a result, usually only 3 or 4 different temperature points in the test matrix are sufficient to parameterize an ageing model. The data however deviates from the exponential behavior when the temperature surpasses 60°C , when additional and very harmful chemical reactions occur, often leading to the formation of gasses and a failure of the cell. The impact of the temperature on the cell impedance was also measured, and concluded to have an exponential impact. This is to be expected, considering the theory of SEI formation. The researchers found that internal resistance is influenced more by calendar ageing than by cycling. This is a surprising result, and leads to the conclusion that a cell needs to be cycled to enhance the resistive life.

Another study [24] investigated the battery ageing mechanisms, by comparing the performances of LFP cells at room temperature and at 60°C . The researchers used a technique called Incremental Capacity Analysis (ICA) and other electrochemical techniques. One of the results showed that when the batteries were cycled at 60°C , a significant change in polarization voltage can be found. The polarization resistance increased for one cell up to five times the original value, which is in contradiction with the traditional Arrhenius law. The researchers assumed that this is due to the increased SEI layer growth. They also found that batteries can still provide capacity in accordance to the remaining active material at higher temperatures, provided that the current drawn is low ($C/10$).

In [25], a study was performed on lithium iron phosphate based (LFP) lithium ion batteries. The cells are investigated to evaluate ageing at different current rates, working temperatures and depths of discharge. The performance of the battery at higher temperature (40°C) is compared to the performance at room temperature (25°C), and a mathematical expression of the cycle life in function of the working temperature is derived. The equation reveals that the Arrhenius-law to derive the battery lifetime from one working temperature to another is not viable, due to the non-exponential behaviour of the chemistry in question.

3.3 Storage voltage

The initial voltage of the battery at the start of the storage cycle also has an important influence on ageing. This voltage influence depends heavily on the used materials in the cell, together with the phase transitions during intercalation [20]. The researchers of [20] found a minimal ageing rate for NMC based cells with an SOC of around 80%. Also, the electrolyte material and additives can influence the ideal storage voltage.

An elaborate study on the storage of Lithium-Ion batteries has been performed in [26]. The studied cells are 15 Ah graphite/iron phosphate cells (LFP), and these cells were subjected to a storage time of at least 450 days at 9 different conditions. In general, the temperature was found to be more detrimental than SoC. However, fully lithiated graphite is considered to be unstable since the intercalated lithium tends to diffuse to the graphite edged where it may interact with the solvent components.

Li. et. al. performed a study on the storage performance of lithium ion cells with a LiCoO_2 cathode and a graphite anode at elevated temperatures, while also taking the safety issues into account [27]. They found that all cells with SoC $> 0\%$ exhibit capacity fade and cycling performance decline after storage at 55°C , and that this decline gets worse with higher SoC values. Cells stored with a SoC greater than 50% were unable to pass the 3C/5V overvoltage test, while this test was easy to pass for fresh cells and the cells stored at 0% SoC. This indicates a serious safety issue with these cells, with some cells reaching temperatures above 180°C and bursting into flames in a very short amount of time. Therefore the researchers concluded that the storage of cells is preferably performed in a fully discharged state. After several measurements were performed on stored cells, the conclusion was drawn that the main ageing of the batteries was not

due to bulk structure changes of the electrode materials, but more due to the microstructure variation of the positive electrode (cathode). This includes the decrease in crystallite dimensions, the change of the micro-stress and the precipitation of the surface films over the electrodes. They assume the increase of the cathode impedance to be the main contributor to the overall degradation of the cells after storage.

3.4 Influence of mechanical stress on capacity fade

The mechanical stress caused by the stack casing also has an influence on the capabilities of the battery system. In [28], this influence is investigated by monitoring the stack pressure and capacity of constrained pouch cells during cycling. They found that the pressure is dynamic in nature, fluctuating with charge and discharge, and gradually increases during its lifetime. The initial stack pressure, which is controlled by the manufacturer, is also found to be an important factor for the development of pressure during the lifetime of the stack. High initial pressure causes a more rapid decrease of capacity, while small amounts of pressure can increase the capacity retention in unconstrained cells.

Another study on mechanical stress on battery stacks was performed in [29], where the link between mechanical stress and the change in physical properties of the separator was investigated. More specifically, mechanical stress resulted in a viscoelastic creep in the separator, which reduces the ion transport via a pore closure mechanism. This results ultimately in a capacity fade of the cell, and can climb up to a loss of 70% of the original discharge capacity when objected to very high pressures (30MPa).

4 Measurements of Aging Phenomena

4.1 Raman Spectroscopy

This is a spectroscopy method used to observe vibrational, rotational and other low-frequency modes in a system. A sample is hit with a laser beam, and the reflected light is collected with a lens and sent through a monochromator. It is an appropriate technique for studying the microstructure of carbonaceous materials, including graphite. It is used in [4] to observe the effects of long-term repeated lithium intercalation-deintercalation processes on the

graphite. Some kind of defects and disorders in the crystal structure of the graphite is found, which result in the decrease of the average crystallite size. Also, it is used to observe structural changes of the graphite electrode under mechanical stress, irradiation, doping and others. Raman spectroscopy is used in the field of battery technology to for example investigate the changes in the graphite electrode after cycling [4]. A typical output plot is shown in Figure 3 and shows the result from a new graphite electrode together with the result from the same electrode after 140 cycles.

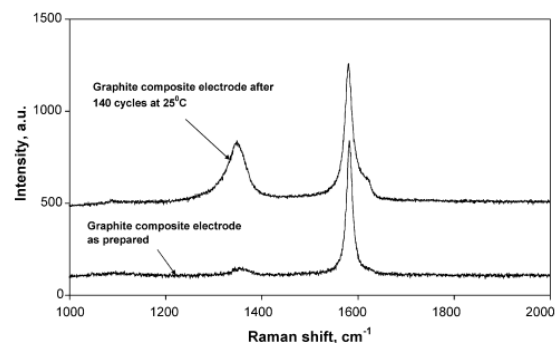


Figure 3: Raman spectra of a new graphite electrode and the same electrode after 140 cycles [4]

The plot reveals a Raman active vibration peak at 1580 cm^{-1} (E_{2g2} mode, called the G-band), which is the main feature of the pristine electrode spectrum. We can see a weak peak at 1350 cm^{-1} (A_{1g} mode), which is an indication of the degree of disorder associated with the finite crystallites size. The ratio of the intensity of the D-band to the G-band is used to characterize the degree of disorder in carbon materials.

4.2 X-Ray Diffraction (XRD)

This spectroscopy method relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. The primary use of the technique is the identification and characterization of compounds based on their diffraction pattern [30].

X-ray analysis is non-destructive, and are widely used in the fields of metallurgy, geology, mineralogy, ceramics and chemistry [31]. It gives information on the structure and chemical composition of the studied sample.

XRD plots are used in the battery technology to do a variety of measurement tasks. In [32], an XRD plot is developed, showing the diffractograms of the graphite electrode before and after 1000 cycles (Figure 4). The “002 peak” corresponds with the

graphite peak, which is shifted and narrower, suggests the presence of residual lithium in the graphite structure. Residual lithium in the discharged anode should be caused by kinetic reasons as the development and growth of the SEI layer, which hinders the lithium from complete transfer to the electrolyte. The narrower peak suggests that the graphite crystal structure is enhanced during cycling.

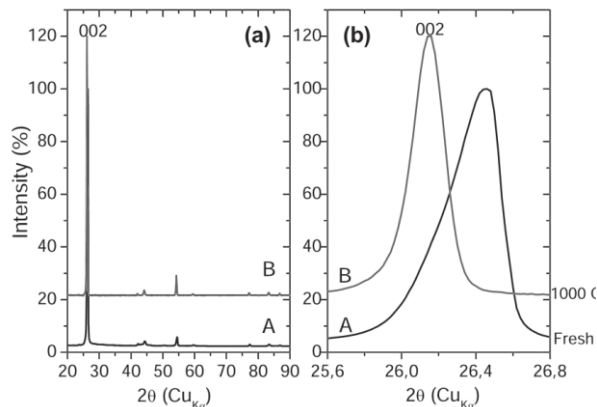


Figure 4: XRD of graphite anode material from a fresh cell (A) and a 1000 cycle cell (B); full spectrum (a) and in the 002 area (b) [32]

4.3 Scanning Electron Microscope (SEM)

This type of electron microscope uses a focused beam of electrons to provide an image of the studied sample. The electrons react with the surface of the sample, and produce a variety of signals that can be picked up by the microscope, and that contain information on the surface, such as the topology and composition. Typical spatial resolution is better than 5 nanometer ($5.0 \times 10^{-9} \text{m}$). The environment can be high vacuum, low vacuum and even wet conditions [33]. This technique is used for example in [27], to examine the changes in the structure of the graphite electrode after prolonged cycling periods.

The preparation of the samples depends on the type of SEM that is being used. Usually, scans are performed in a high-vacuum, which means the sample must be prepared to undergo this vacuum [34]. For battery electrodes, the donor cells must be completely discharged (SoC of 0%), and the electrodes must be rinsed (for example with dimethyl carbonate) and left drying until they are completely dry [35].

4.4 Energy-Dispersive X-Ray Spectroscopy (EDX, EDS, XEDS)

This is used for the elemental analysis or chemical characterization of a sample. The mechanism used is interaction of X-Ray excitation with the sample. Each element has a specific atomic structure, which allows for a unique set of peaks in the x-ray spectrum.

EDS uses the X-ray spectrum that is emitted by a solid sample, which is bombarded with a focused beam of electrons. This provides us with a local chemical analysis. In theory, all elements from number 4 (Be) up to 92 (U) can be detected. Once the spectrum is available, the analysis is straightforward, since it involves the identification of the lines in the spectrum due to the simplicity of X-ray spectra. When quantitative analysis is performed, the line intensities are measured for each element in the sample, and for the same elements in the calibration standards of known composition.

4.5 X-Ray photoelectron Spectroscopy (XPS)

This spectroscopy method measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist in the material. The technique uses X-ray irradiating the material, while also measuring the kinetic energy and the amount of electrons that escape from the material. It requires a vacuum, although recent advances make measurements in ambient pressures possible [36].

XPS is also known as *electron spectroscopy for chemical analysis* (ESCA), which implies its usage as a semi-quantitative technique for determining the composition of a sample, based on the photoelectric effect [37]. An in-depth overview of current and future XPS technologies and advances is given in [38].

In the battery industry, XPS is used for example to evaluate the composition of the deposit layer [39] of the anode of an aged cell. It is used as a tool to collect information on the exact composition of the anode after the cell was aged, but not to quantify ageing in itself.

4.6 Scanning Transmission Electron Microscopy (STEM)

This is a type of transmission electron microscopy (TEM), where a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. This technique allows for ultra-high resolution images of the specimen, up to a single column of atoms. STEM

focuses on a narrow spot on the specimen, which is scanned over a raster. This allows for analysis techniques such as mapping by EDX spectroscopy, electron energy loss spectroscopy (EELS) and annular dark-field imaging. [40] uses STEM to obtain very-high resolution images of the electrodes of a cell in real-time, which allows for observation of the electrodes during lithium intake and release. This platform is then used to gain information on chemical reaction paths, monitor phase changes in the electrodes, or to investigate degradation effects in lithium-ion cells.

4.7 Electrochemical Impedance Spectroscopy (EIS)

During a measurement, a frequency response analyzer (FRA) is used to impose an AC signal to the cell, via a load. The AC voltage and current response are then analyzed by the FRA to determine the resistive, capacitive and inductive behavior, which are the elements that make out the impedance of a cell, at a specific frequency. All the physical reactions in the cell have different time-constants and are therefore exhibited at different frequencies. This means that if a spectroscopy is conducted over a wide frequency range, it is possible to identify and quantify the impedance associated with these various physical/chemical processes. It has many advantages, one of which being that a cell can be tested under real-world conditions (under load, open circuit, during charging, ...). It is also possible to determine multiple parameters with one measurement. It is also useful during the verification process of a battery model. One of the disadvantages however is that the experiment itself can take a long time. The time needed for the experiment is directly related to the lowest frequency tested [41]. The frequency range applied during the measurement depends on the application. The frequency range used for testing batteries is usually from 10 kHz to 50 mHz (high to low). In the field of battery technology, EIS is used for the analysis of a plethora of phenomena. It is used to measure the impedance at different levels of SoC (State of Charge), and it is very useful for characterizing ageing phenomena of battery cells. EIS allows for impedance measurements for a range of frequencies, which also allows for the determination of ageing effects at low frequencies (something which is not possible with simple single frequency impedance measurements, which only provides information for higher frequencies).

4.8 Cyclic Voltammetry (CV)

This is a type of potentiodynamic electrochemical measurement, and a very versatile electroanalytical technique for the study of electroactive species [42]. The main process is cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of the working electrode is always controlled versus a reference electrode. The excitation signal is a linear potential scan with a triangular waveform. In other words, the process is a potential-controlled reversible experiment, which scans the electric potential before turning the direction, and scanning back to the original potential. To obtain a cyclic voltammogram of a battery cell, the cell must be dismantled, and both electrodes must be separated and isolated from each other, and submersed in a solution, as described above. Cyclic Voltammetry in battery research is used to obtain very specific information. In [43] it is used to evaluate the redox potential of the transition-metal ions during cycling.

4.9 Auger Electron Spectroscopy (AES)

This is a commonly used analytical technique that is used in the study of surfaces, and more generally in the area of materials science. The driving force of this technique is the Auger Effect, which is based on the analysis of energetic electrons emitted from an excited atom after a series of relaxation events. The Auger effect is a physical phenomenon in which filling a vacancy of an inner-shell of an atom is accompanied with the emission of an electron from the same atom [44]. In battery measurements, AES can be used for example to measure the SEI film thickness [45], where it is one of three different analysis techniques of the SEI layer, together with surface observation by SEM and composition detection by XPS.

4.10 Atomic Force Microscopy (AFM)

This is a technique often used to gather images and other information of a wide variety of samples, at a very high resolution (nanometer level). AFM works by scanning the surface of the sample with an extremely sharp probe, while maintaining the force between the probe and the surface at a set level. The vertical bending of the probe caused by the topology of the sample is detected with a laser, which is focused on the back of the cantilever. The laser is reflected on the back of the probe, and projected on a photodetector. The movement of the laser spot on

the photodetector gives an exaggerated measurement of the movement [46].

In [47], the surface of lithium on an organic electrolyte has been investigated. It shows that the lithium surface consists of grain boundaries, ridge-lines and a flat area. The samples have to be prepared carefully in order to provide the best quality image possible. Even the slightest contamination layer can cause that nothing of the sample can be seen. If the sample is a solid material, it has to be as clean and flat as possible. Also, it must be fixed on a stable platform, so that it will not move during the scan. It provides information on how the topology and surface roughness changes throughout the aging process, in both long and short term.

Conclusions

This paper gives a literature overview of the main ageing phenomena of lithium ion battery cells.

The main ageing phenomena that have been identified are the formation of an SEI layer on the negative electrode, and the impedance increase on the negative electrode, degradation and dissolution of the active material and the oxidation of the electrolyte.

Further, an overview of different electrochemical characterisation techniques for batteries has been given. The use of these different techniques for evaluating ageing of lithium ion batteries has been discussed based on a literature review.

This overview of both ageing phenomena and characterisation techniques can be used as a starting point for electrochemical modelling of long term behaviour of lithium ion batteries.

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Authors



Eng. Joris de Hoog

Email: jdehoog@vub.ac.be
 Joris de Hoog obtained his M.S. degree in Electronics and ICT in 2013 at the Vrije Universiteit Brussel. He is currently pursuing a PhD degree in the department of Electrical Engineering and Energy Technology (ETEC) at VUB. His current research deals with the aging of Lithium-Ion batteries, and modelling of aging phenomena during the lifetime of a Lithium-Ion battery.



ir. Karel Fleurbaey

Vrije Universiteit Brussel
 Email: kfleurba@vub.ac.be
 Karel Fleurbaey obtained his M.S degree in electromechanical engineering in 2013 at the Vrije Universiteit Brussel (VUB). He is currently pursuing the PhD degree in the department of Electrical Engineering and Energy Technology (ETEC) at VUB. His current research focusses on the characterization and modelling of lithium ion batteries and lithium ion capacitors.



M.Sc. Alexandros Nikolian

Vrije Universiteit Brussel
 Email: Alexandros.Nikolian@vub.ac.be
 Alexandros Nikolian graduated at the Reading University in the UK as Renewable Energy Engineer. He has experience in vehicle simulation & emissions, developed during his activities in the Joint Research Center of the European Union and Hexagon Studio in Turkey. He started as a PhD student in January 2014 at VUB mainly working on IWT BATTLE project and battery modelling.



dr. ir. Jean-Marc Timmermans

Vrije Universiteit Brussel

Email: jptimmer@vub.ac.be

Jean-Marc Timmermans graduated in 2003 as an Electromechanical Engineer at the Vrije Universiteit Brussel. As an academic assistant of the department of Electrical Engineering and Energy Technology (ETEC), he was involved in several projects related to clean vehicle technologies. In 2010 he obtained a PhD at the Vrije Universiteit Brussel. Currently he is a post-doctoral researcher in the field of electrical energy storage systems and project manager in the Battery Innovation center of the MOBI research group at the Vrije Universiteit Brussel.

Prof. Dr. Eng. Omar Noshin

Vrije Universiteit Brussel

Email: noshomar@vub.ac.be

Noshin Omar was born in Kurdistan, in 1982. He obtained the M.S. degree in Electronics and Mechanics from Erasmus University College Brussels. He is currently the head of Battery Innovation Center of MOBI research group at Vrije Universiteit Brussel, Belgium. His research interests include applications of supercapacitors and batteries in BEV's, HEV's and PHEV's. He is also active in several international standardization committees such as IEC TC21/22.

He is the author of more than 60 scientific publications.

Prof. Dr. ir. Peter Van den Bossche

Vrije Universiteit Brussel

Email: pvdbos@vub.ac.be

Peter Van den Bossche graduated as civil mechanical - electrotechnical engineer from the Vrije Universiteit Brussel and defended his PhD at the same institution with the thesis "The Electric Vehicle: raising the standards". He is currently lecturer at the engineering faculties of the Vrije Universiteit Brussel, and in charge of coordinating research and demonstration projects for

electric vehicles in collaboration with the international associations CITELEC and AVERE. His main research interest is electric vehicle standardization, in which quality he is involved in international standards committees such as IEC TC69, of which he is Secretary, and ISO TC22 SC21.



Prof. Dr. ir. Joeri Van Mierlo

Vrije Universiteit Brussel

Email:

joeri.van.mierlo@vub.ac.be

Prof. Dr. ir. Joeri Van Mierlo is a full-time professor at the Vrije Universiteit Brussel, where he leads the MOBI – Mobility, Logistics and automotive technology research centre (<http://mobi.vub.ac.be>). A multidisciplinary and growing team of 60 staff members.

He is expert in the field of Electric and Hybrid vehicles (batteries, power converters, energy management simulations) as well as to the environmental and economical comparison of vehicles with different drive trains and fuels (LCA, TCO).