

Ageing mechanisms in lithium-ion batteries[☆]

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Abstract

The rechargeable lithium-ion battery has been extensively used in mobile communication and portable instruments due to its many advantages, such as high volumetric and gravimetric energy density and low self-discharge rate. In addition, it is the most promising candidate as the power source for (hybrid) electric vehicles and stationary energy storage. For these applications in durable equipment, the long-term cycling and storage behaviour becomes of increasing interest. In this paper, the mechanisms of lithium-ion battery ageing are reviewed and evaluated.

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1. Introduction

Lithium-ion batteries have been commercially used for a number of years in small portable devices like cell phones, laptop computers, camcorders, and similar electronic devices. Due to short innovation cycles in this field, battery life-time beyond a limited period of time played only a minor role for this kind of applications. But the commencing penetration of lithium-ion batteries in the market of durable consumer and investment goods, like (hybrid) electrical vehicles, temporary storage systems for renewable energy sources, and also in the market of batteries for conventional vehicles, requires a more sophisticated evaluation of battery life-time. The goals of the United States Advanced Battery Council (USABC) in the FreedomCAR research initiative (2002; www.uscar.com),

e.g., demand a calendar life-time of 15 years for 42 V battery systems and hybrid electrical vehicles (HEV's), and 10 years for electrical vehicles (EV's). In terms of cycle life, a life-time of up to 1000 cycles at 80% depth-of-discharge (DOD) is demanded.

Unfortunately, lithium-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.

In this paper, we will give a review on today's knowledge on the mechanisms of ageing in lithium-ion batteries. We will try to identify and evaluate different processes, as far as they are known from the literature, in order to establish a solid basis for further investigations.

Ageing mechanisms occurring at anodes and cathodes differ significantly and are therefore discussed in two separate chapters. The influence of the electrolyte and the ageing of

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the electrolyte itself (and the separator as well) mainly take place at the electrodes and in interaction with them, so they are covered in the corresponding chapters. The article closes with a review on electrochemical impedance spectroscopy as the tool of choice for non-destructively studying ageing processes and determining the state of health of lithium-ion batteries.

2. Ageing of carbonaceous anodes

2.1. General aspects

Carbon, in particular graphite, is the most important anode material in lithium-ion batteries, and thus, the greatest understanding of anode ageing has been accomplished with graphite-based cells [1–3]. Although alternative anode materials like lithium storage metals and alloys have recently found increased attention among researchers, emphasis was mostly laid on the active materials itself and related problems (e.g., nanostructured materials, control of volume changes), whereas ageing effects have found considerably less attention [4–6]. Hardly any literature data exists on ageing mechanisms of hard carbons [7]. Thus, unsurprisingly, the vast majority of references in the literature related to anode ageing concentrates on graphitic carbons. In general, the situation reported in the literature is difficult to analyze as each lithium-ion cell system has its own chemistry and many ageing effects are influenced by the nature of the cell components (e.g., active material and electrode design, electrolyte composition, impurities, etc.). Furthermore, most available literature data concentrates on complete cells without the attribution of certain effects to either anode or cathode. In view of these limitations, this part of the study can summarise and discuss only the dominant ageing mechanisms of graphite anodes.

As for the cathode, ageing effects at the graphite anode lead to a modification of the electrode properties with time and use. Ageing effects that may occur during storage (e.g., self-discharge, impedance rise) will affect the calendar life of the battery, whereas the cycle life is in addition influenced by ageing effects that may occur during use (e.g., mechanical degradation, lithium metal plating) [8]. Ageing during storage can be monitored by electrochemical “values” such as capacity loss, impedance rise, potential change, state of charge (SOC) and state of health (SOH) [9]. However, it is important to point out that anode materials such as graphite may exhibit discharge plateaus, i.e., the electrode potential does not significantly vary with the state of charge [10–12]. During cycling, one can measure the capacity fade, the impedance rise which is closely related to power fade, and overpotentials that influence the potential profile of the charge/discharge curves. For a concise discussion, it should be pointed out that ageing with time and use can lead to—and may be caused by—changes (i) of the electrode/at the electrolyte interface and in the electrolyte, (ii) of the active material, and (iii) of the composite electrode (current collector, active materials, conductive additives, binder, porosity, etc.). Most literature data account changes at the electrode/electrolyte interface for being responsible for the ageing of/at carbon electrodes, and hence, this influence on anode ageing will be discussed in more detail here [13,14]. Changes of the active material and the composite electrode are seldom discussed, but they may have an influence on the ageing process, which will be regarded by short summaries in the corresponding chapters.

2.2. Changes at the electrode/electrolyte interface

Changes at the electrode/electrolyte interface (Fig. 1) due to reactions of the anode with the electrolyte are considered by many researchers to be the major source for ageing of/at the anode [15]. It is well known that lithium-ion

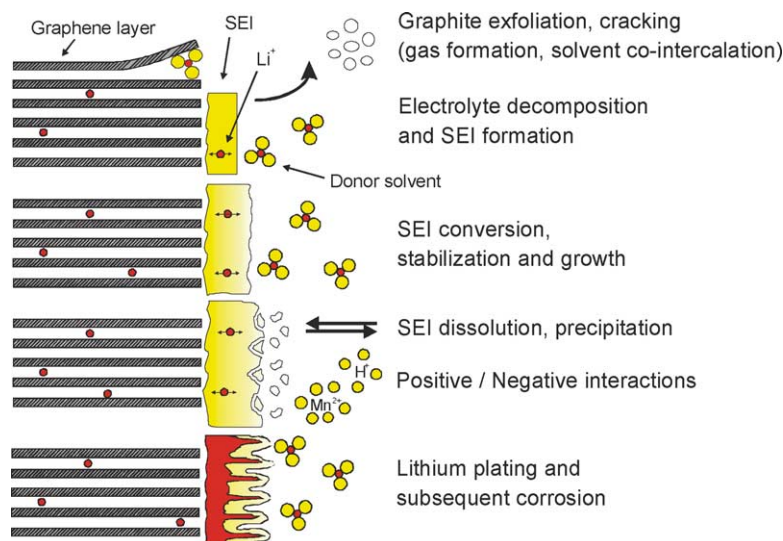


Fig. 1. Changes at the anode/electrolyte interface.

battery anodes operate at voltages that are outside the electrochemical stability window of the electrolyte components. Hence, reductive electrolyte decomposition accompanied by irreversible consumption of lithium ions takes place at the electrode/electrolyte interface when the electrode is in the charged state (polarised to low potentials). The decomposition products build up “protective layers” that cover the electrode’s surface. This process occurs mainly (but not exclusively) at the beginning of cycling, especially during the first cycle. The layers, which form on the surface of graphite, may be principally divided in two types according to their different functions. At certain graphite surface sites (i.e., at the prismatic surfaces and defects in basal planes) lithium ion transport into/from the graphite structure by intercalation/deintercalation takes place. Here, the protective layers have to act as a so-called solid electrolyte interphase, SEI [16]. The properties of the SEI layers are unique since they are in first approximation permeable for lithium cations but rather impermeable for other electrolyte components and electrons. Thus, normally the SEI reasonably protects (i) the electrolyte compounds from further reduction and (ii) the charged electrode from corrosion. Protective layers, which form on graphite surfaces, where no lithium ion transport into/from the graphite structure takes place (i.e., at the basal plane surfaces), have no SEI function in the above-described sense. However, these “non-SEI layers” (as they are called by a few authors) still protect these anode sites from further reduction reactions with the electrolyte. It has been reported that the composition of the SEI layers and non-SEI layers are also very different [17]. Due to these distinct differences in functions and composition, one might expect also different ageing processes at SEI and non-SEI layers. In this study, we will however follow the conventions in the literature to designate the protective layers as SEI independent of their function.

Usually, SEI formation at the anode is accompanied by the release of gaseous electrolyte decomposition products [18]. The amount of irreversible charge capacity that is consumed during the formation of the SEI was found to be dependent on the specific surface area of the graphite as well as on the layer formation conditions [19–21]. Unfortunately, the SEI layers do not have the properties of a true solid electrolyte for lithium cations as the transference number for unsolvated lithium cations is not 1 ($t_{\text{Li}} \neq 1$). Other charged (anions, electrons, solvated cations) and neutral (solvents, impurities) species still seem to diffuse/migrate through the SEI. Moreover, transport of solvated lithium cations and other electrolyte components even seems to occur in the later stages of cycling, as irreversible charge capacities and self-discharge reactions still can be observed after prolonged cycling. As a consequence, corrosion of Li_xC_6 (and thus capacity loss) and electrolyte decomposition (and thus electrolyte loss and further SEI formation) are ongoing throughout the entire battery life; however, compared to the first cycle, to a lower extent and at lower rate. On a long time scale, the SEI penetrates into pores of the electrode and in addition may also penetrate into the pores of the separator. This may result in

a decrease of the accessible active surface area of the electrode. Many authors have measured the impedance rise of the electrodes, which is directly linked to the power fade of the cell [22–32]. The increase in electrode impedance is considered to be caused by the growth of the SEI as well as by changes of the SEI in composition and morphology. In summary, whereas SEI formation at the anode takes place mainly in the first few charge/discharge cycles, SEI conversion, stabilisation and growth will also proceed during further cycling and storage.

As the SEI is composed of electrolyte decomposition products, it is self-suggesting that the SEI properties are extremely dependent on the composition of electrolyte used [33,34]. SEI formation in the presence of electrolyte components with beneficial SEI formation capabilities, i.e., resulting low irreversible capacity, stable SEI, and low self-discharge rate, should also slow down the ageing of the SEI [35,36]. Putting it simply, film forming electrolyte solvents and additives, therefore, should not only have a supporting effect on the SEI formation processes (in the first cycles), but also on the SEI ageing processes (during prolonged cycling and storage).

In view of cell properties like power fade, impedance rise or safety, the impact of the SEI thermal behaviour should be particularly discussed [37–39]. On the one hand, it should be mentioned that elevated temperatures definitely enhance the kinetics of the lithium insertion/removal processes into/from the host lattice. On the other hand, it is widely believed that the morphology and composition of the SEI changes at elevated temperatures [40–48]. In the worst case, thermal runaway may cause the cell to catch fire or to explode. Differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) methods have been used by different groups to study the electrode or cell behaviour at elevated temperatures [49–52]. ARC studies revealed that exothermic side reactions of lithiated carbon can cause self-heating, which starts typically at temperatures of approximately 80 °C in various electrolytes. The onset temperature depends on the electrolyte salt and can be as low as 60 °C for electrolytes containing LiBF_4 [53]. There seems to be an even more dramatic influence of the temperature, as the results of electrochemical cycling studies indicate that Li/graphite half-cells show a significant capacity fade when they are stored at elevated temperatures even below 60 °C [54].

As a rule, the negative impact of elevated temperatures on cell ageing is mainly attributed to an increased degradation rate of the SEI, as the SEI film starts to break down or to dissolve. However, also a restructuring of the damaged SEI or a re-precipitation of dissolved SEI products might take place. It has also been proposed that at elevated temperatures, metastable organic SEI components like lithium alkyl carbonates are converted into more stable inorganic products, e.g., lithium salts like lithium carbonate, lithium fluoride, etc. [51,53]. However, though the inorganic SEI products are more stable and are less easily penetrated by solvent molecules, the growth of inorganic components may result in a lower ionic conductivity of the SEI for lithium.

Based on X-ray photoelectron spectroscopy (XPS) analysis data, it has been reported that semicarbonates indeed are removed from the surface of electrodes that are stored at elevated temperatures [55]. It has been suggested that (i) traces of acidic compounds present in the electrolyte (e.g., HF if LiPF_6 is used) react with Li_2CO_3 forming LiF and H_2CO_3 and (ii) semicarbonates thermally decompose [56,57]. These “stabilisation” reactions are also accompanied by a morphology change of the SEI. During the conversion, parts of the anode surface may be uncovered from the SEI and become exposed to the electrolyte so that redox reactions between the charged electrode and electrolyte components lead to additional SEI formation and capacity loss. However, the above-mentioned mechanisms may not explain that the charge capacity loss due to self-discharge of carbon-based anodes consists of two fractions, a reversible and an irreversible part. Supported by X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS) measurements, it was proposed that this phenomenon has its origin in the formation of metastable electron–ion–electrolyte complexes at the electrode/electrolyte interface [58].

Low temperatures result in different challenges [59–62]. The intercalation potential of carbonaceous anode materials (graphite, hard carbons, soft carbons, doped graphites) is close to the potential of lithium metal. In the case of slow lithium ion diffusion into carbon and/or reduced lithium ion diffusion in the electrolyte, both effects are particularly pronounced at low temperatures, metallic lithium plating and lithium dendrite growth must be considered as parasitic side reactions during charging. Subsequent reactions of the Li metal with the electrolyte induce, or at least accelerate, ageing and, furthermore, deteriorate safety [63,64]. Poor cell balance (e.g., an excess of cathode material) [65], geometric misfits (e.g., large cathodes overlapping anodes at the edges) and mixed potential effects (e.g., locally different polarisation; effect of electrode thickness and porosity) enhance the probability of Li metal plating [66,67].

Interactions of the positive electrode (cathode) with the negative electrode (anode) have also to be taken into consideration. Apart from transport of (soluble) SEI products between the anode and cathode and possible chemical redox reactions at the respective electrodes [68], the main effect of the cathode on the anode properties (including ageing) is transition metal dissolution. Especially the LiMn_2O_4 spinel is considered to release transition metal ions (e.g., Mn^{2+}) that can be incorporated into the anode SEI (in ionic or, after reduction, in metallic form), which leads to accelerated cell ageing [69,70].

Finally, the formation of acidic compounds like HF (e.g., from the reaction of LiPF_6 with trace water) has been reported to have a negative influence on the stability of the SEI [71].

2.3. Changes of the active material

Within the bulk of the active material, only minor ageing effects can be expected to occur. The volume changes of

graphite, during the uptake and removal of lithium ions, are not considered to be drastic (typically in the order of 10% or less, depending on the material) and only a minor negative impact on the reversibility of the material is expected as a consequence. Structural changes (e.g., AB-AA, ABC-AA shifting during lithium uptake) can cause mechanical stress on defects and on C–C bonds, which might result in cracking or related structural damage. At the surface of the active material, ion exchange at surface groups with lithium ions and redox reactions of surface groups are possible but should also have only minor impact on cell ageing. However, graphite exfoliation and graphite particle cracking due to solvent co-intercalation, electrolyte reduction inside graphite, and/or gas evolution inside graphite will certainly lead to a rapid degradation of the electrode [12]. The latter reactions are considered to have the strongest impact on active material changes, which contribute to cell ageing.

2.4. Changes of the composite electrode

In general, contact loss (mechanical or electronic) within the composite electrode results in higher cell impedance, and thus, has to be considered as cause for ageing [72]. One inevitable source for contact loss is the volume changes of the active anode material, which may lead to mechanical disintegration within the composite electrode. Contact loss (i) between carbon particles, (ii) between current collector and carbon, (iii) between binder and carbon, and (iv) between binder and current collector can be the result. Also, the electrode porosity, which is a key feature for good anode performance, since it allows the electrolyte to penetrate into the bulk of the electrode, is certainly affected by the volume changes of the active material (for effects of the SEI on the electrode porosity, see above). In addition, the internal cell pressure has to be taken into consideration [73]. It is widely accepted in the literature that fluorine-containing polymers (e.g., polyvinylidenedifluoride (PVdF)) and copolymers (e.g., poly-hexafluoropropene-vinylidenedifluoride) that are used as binder materials in composite electrodes do react with the (charged) anode to form LiF [74–76]. This reactivity can contribute to degradation in mechanical electrode properties in the long run. Moreover, current collector corrosion can occur by reactions with electrolyte components or if the potential of the anode gets too positive versus Li/Li^+ . It leads to loss of electronic and mechanical contact between the current collector and the other electrode components. Furthermore, corrosion products that exhibit poor electronic conductivity cause overpotentials and favour inhomogeneous current and potential distributions, and thus, lithium plating [77].

2.5. Conclusion on anode ageing

As far as the anode side is concerned, ageing effects may be mainly attributed to changes at the electrode/electrolyte interface. Table 1 provides an overview on the causes and effects of ageing and mentions also measures that enhance or reduce the effects. Bold characters indicate the main con-

Table 1
Lithium-ion anode ageing—causes, effects, and influences

Cause	Effect	Leads to	Reduced by	Enhanced by
Electrolyte decomposition (→SEI) (Continuous side reaction at low rate)	Loss of lithium Impedance rise	Capacity fade Power fade	Stable SEI (additives) Rate decreases with time	High temperatures High SOC (low potential)
Solvent co-intercalation, gas evolution and subsequent cracking formation in particles	Loss of active material (graphite exfoliation) Loss of lithium	Capacity fade	Stable SEI (additives) Carbon pre-treatment	Overcharge
Decrease of accessible surface area due to continuous SEI growth	Impedance rise	Power fade	Stable SEI (additives)	High temperatures High SOC (low potential)
Changes in porosity due to volume changes, SEI formation and growth	Impedance rise Overpotentials	Power fade	External pressure Stable SEI (additives)	High cycling rate High SOC (low potential)
Contact loss of active material particles due to volume changes during cycling	Loss of active material	Capacity fade	External pressure	High cycling rate High DOD
Decomposition of binder	Loss of lithium Loss of mechanical stability	Capacity fade	Proper binder choice	High SOC (low potential) High temperatures
Current collector corrosion	Overpotentials Impedance rise Inhomogeneous distribution of current and potential	Power fade Enhances other ageing mechanisms	Current collector pre-treatment (?)	Overdischarge Low SOC (high potential)
Metallic lithium plating and subsequent electrolyte decomposition by metallic Li	Loss of lithium (Loss of electrolyte)	Capacity fade (power fade)	Narrow potential window	Low temperature High cycling rates Poor cell balance Geometric misfits

tributions. Most of the therein-mentioned effects can be considered as additive, e.g., the storage of an electrode at high state of charge (at the maximum of its reactivity) in combination with high temperatures will result in even more self-discharge and charge capacity loss than the storage at ambient temperatures. We conclude that the dominant ageing mechanisms on carbon-based anodes can be concisely described as follows:

- SEI formation and growth leads to an impedance rise at the anode. Usually, SEI formation takes place mainly at the beginning of cycling. SEI growth proceeds during cycling and storage and is favoured by elevated temperatures. Impedance rise can be directly related to power fade.
- In parallel to SEI growth, corrosion of lithium in the active carbon takes place, leading to self-discharge and capacity fade due to loss of mobile lithium.
- The formation and growth of the SEI leads to gradual contact loss within the composite anode, and thus, increases the impedance in the cell.
- Lithium metal plating might occur at low temperatures, at high rates and for inhomogeneous current and potential distributions. The Li metal reacts with the electrolyte, which may contribute to accelerated ageing.

- A strong influence of the specific cell components on the ageing mechanism can be observed. Although the general mechanisms presented here hold true for most of the lithium-ion systems they may be pronounced differently for each particular system.

3. Ageing of lithium metal oxide cathodes

3.1. General aspects

Cathode materials affect significantly both performance data as well as cycling and calendar life of lithium-ion cells. Lithium manganese oxides (LiMn_2O_4) with spinel structure and lithium nickel cobalt mixed oxides [$\text{Li}(\text{Ni},\text{Co})\text{O}_2$] with layered structures have been extensively studied in the last few years for usage in high energy and high power batteries in order to replace lithium cobalt oxide (LiCoO_2) as cathode material in terms of cost, abundance and performance. In this chapter, we will summarise some basic ageing mechanisms under cycling and different storage conditions for both types of cathode materials and discuss the differences from literature data. The mechanisms of capacity fading and their prevention are still of increasing interest and not completely

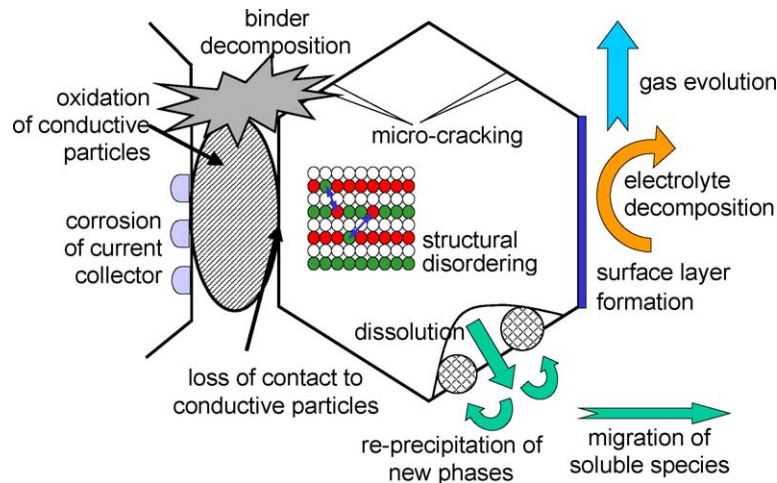


Fig. 2. Overview on basic ageing mechanisms of cathode materials.

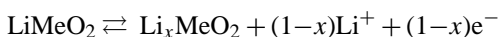
understood at the moment. Some recent publications are focussed on ageing of lithium-ion batteries including cathode materials [1–3,8,78]. A number of changes on the cathode may influence the life-time of a lithium-ion cell:

- ageing of active material;
- degradation or changes of electrode components like conducting agents, binder, corrosion of current collector;
- oxidation of electrolyte components and surface film formation;
- interaction of ageing products with the negative electrode.

These effects do not occur separately and cannot be discussed independently from each other. They are very sensitive to individual electrode composition and are influenced by cycling and storage conditions. In general, charge capacity fading of positive active material can originate from three basic principles:

- structural changes during cycling;
- chemical decomposition/dissolution reaction;
- surface film modification.

Similar to the negative carbon material, degradation of positive active materials depends on state of charge and cycling conditions. The electrochemical reaction of the positive materials proceeds as an insertion reaction of lithium ions in the metal oxide:

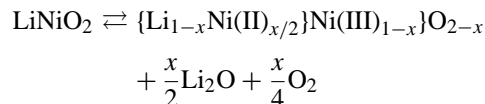


The insertion/extraction of lithium ions leads to changes in the molar volume of the materials, which may induce mechanical stress and strain to the oxide particles and, hence, to the electrode. Also, phase transitions can occur, which lead to distortion of the crystal lattice and further mechanical stress. Figs. 2 and 3 give a schematic overview on ageing mechanisms for lithium-ion cathode materials, which have been described in literature so far.

3.2. Lithium nickel cobalt oxides

3.2.1. Structural aspects

LiNiO_2 and LiCoO_2 are end members of a complete homogeneous solid solution series and are crystallised in the $\alpha\text{-NaFeO}_2$ structure. Nickel and cobalt both are trivalent and in the low-spin state ($\text{Co}^{3+} t_{2g}^6 e_g^0$; $\text{Ni}^{3+} t_{2g}^6 e_g^1$) [79]. It is difficult to synthesise pure stoichiometric LiNiO_2 [80,81]. This is due to a structural disorder reaction, in which divalent nickel ions replace lithium ions on their sites. Simultaneously, trivalent nickel ions on the nickel sites are reduced to the divalent state for charge balance. The complete disorder reaction can be formulated as:



With increasing cobalt content in the mixed oxide, the lithium–nickel-disorder decreases, indicating the stabilisation of the layered structure by cobalt [82]. Pure lithium nickel oxide exhibits a number of reversible phase transitions during electrochemical lithiation/delithiation [83–92]. The transition of the monoclinic phase domain M1 and the formation of the totally delithiated phase H3 lead to large and anisotropic volume jumps and, as a result, to a rapid decrease in capacity. The monoclinic/hexagonal phase transitions can be prevented by cobalt contents of about 20 mole%. Aluminium and magnesium dopants further stabilise the layered structure. The total volume changes of lithium nickel cobalt oxide are rather low [93] and can be minimised by additional doping with aluminium [94,95] or magnesium [96,97]. Therefore, Al or Mg doped lithium nickel cobalt oxides exhibit better cycle life compared to undoped materials [98–100].

Doped $\text{Li}(\text{Ni},\text{Co})\text{O}_2$ with optimised compositions are quite stable in the discharged state even at higher temperatures and exhibit very good cycle life, if the end of charge voltage is controlled carefully and overcharge can be avoided.

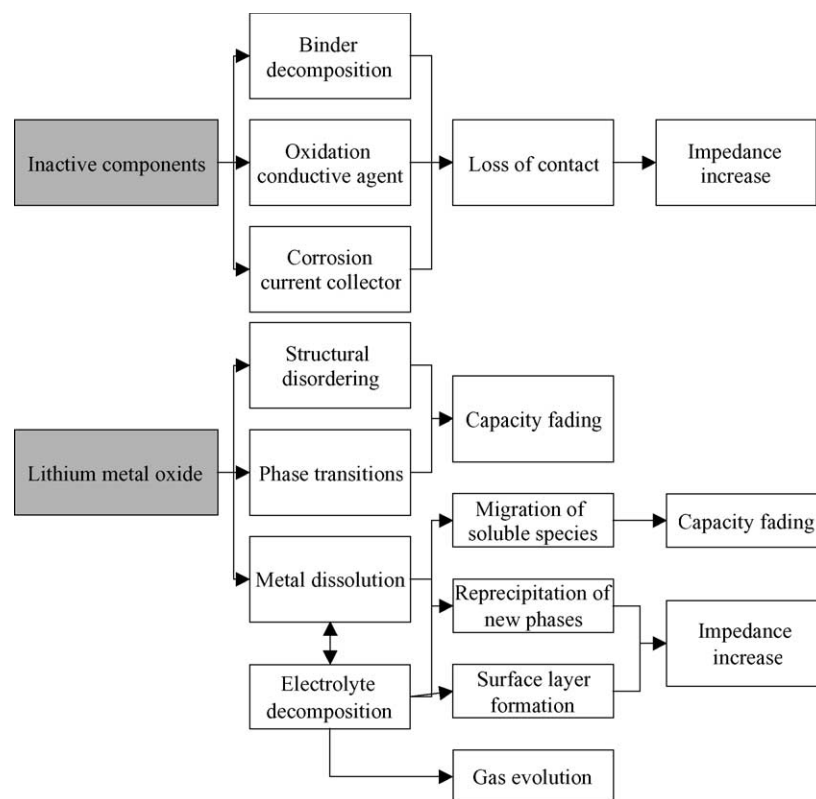


Fig. 3. Cause and effect of ageing mechanisms of cathode materials [169].

Dissolution of lithium nickel cobalt oxides in practical electrolytes seems not to be a problem. When Li_xCoO_2 is charged beyond a potential of 4.2 V versus Li/Li^+ , slight dissolution occurs and small amounts of cobalt can be found on the anode [101,102].

3.2.2. Surface effects

Surface–electrolyte interactions and formation of surface layers (SEI) have been widely investigated and described for anode materials of lithium-ion batteries [14,103]. According to Broussely et al., the increase of interfacial impedance of the carbon anode is responsible for the capacity fading of high-energy batteries [8]. A considerable increase of interfacial impedance was attributed to the lithium nickel cobalt oxide cathode of high power batteries [20,22,28,29,32,38,41,42,45,46,72,104–116] leading to power loss. This increase is accelerated by higher temperature and by high end of charge voltages positive to 4.2 V versus Li/Li^+ . Formation of surface films due to electrolyte oxidation and LiPF_6 decomposition has been reported in the literature. Also, lithium nickel cobalt oxide itself can act as a source of oxygen for these oxidation reactions by formation of a sub-surface layer of a lithium/oxygen deficient oxide phase of rock-salt structure type [104,117]. Fig. 4 summarises the mechanisms of surface film formation at lithium nickel cobalt oxide in the charged state. This rock-salt structure lithium nickel cobalt oxide exhibits low lithium ion conductivity, which leads to an increase of the surface impedance.

In addition to that, some surface electrolyte reactions are accompanied by the evolution of gaseous species [118–120].

3.3. Lithium manganese spinel

The capacity fading mechanisms are more complex if LiMn_2O_4 is used as positive material. Cycle life and calendar life are strongly dependent on both the composition of active material and state of charge. The mechanisms are not yet fully understood but can be roughly classified in:

Changes at low state of charge

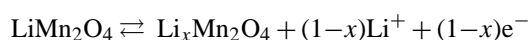
- structural changes due to Jahn–Teller distortion of Mn^{3+} [121,122];
- decomposition reaction and dissolution of Mn^{2+} in the electrolyte.

Changes at high state of charge

- thermodynamic instability of delithiated lithium manganese spinel;
- electrolyte oxidation [123,124];
- formation of an oxygen-rich spinel [125];
- site exchange between Li and Mn [126].

3.3.1. Structural aspects

The reversible electrode reaction of lithium manganese spinel is given by:



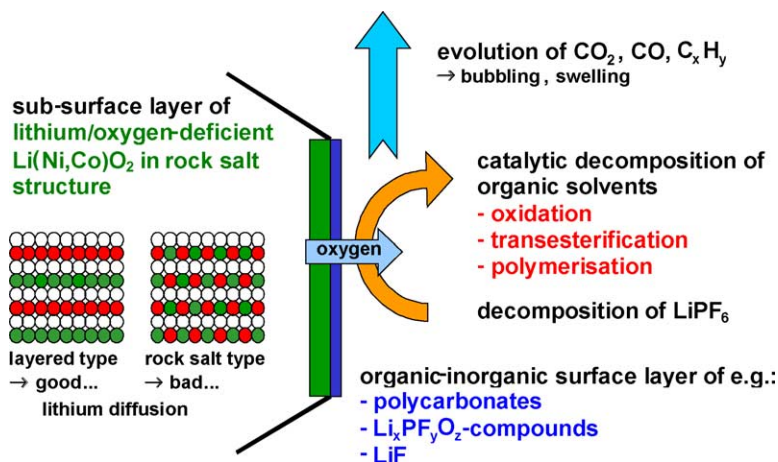


Fig. 4. Mechanisms of surface alteration of lithium nickel cobalt oxide electrodes in LiPF₆-based electrolytes.

At low potentials, lithium manganese spinel can insert additional lithium and a Mn(III) Jahn–Teller distorted tetragonal phase is formed. The correlation between potential plateaus and structural changes has been investigated extensively by X-ray diffraction methods [127–131]. A phase transition occurs at $x=0.5$, which is explained by formation of an ordered lithium superstructure. In recent studies [132–134], further phase transitions have been identified for stoichiometric lithium manganese oxides.

In order to obtain good cycling stability, the formation of the lithium superstructure phase at $x=0.5$ [135] and the formation of the double hexagonal phase [124] have to be prevented.

Improvement of capacity retention has been achieved by two ways:

- partial substitution of manganese ions by trivalent or divalent cations like Co, Cr, Al and Mg [136–140];
- partial substitution of manganese by excess lithium [125,140–145].

Both strategies lead to:

- decrease of Mn(III) content—improved stability in the discharged state;
- fixing of lithium in the host lattice—improved stability in the charged state;
- decrease of volume changes during cycling—improved cycling stability;
- prevention of formation of superstructures—improved cycling stability.

Therefore, optimised lithium manganese spinels can exhibit very good cycle life. For nowadays state-of-the-art lithium manganese spinels, structural changes are no longer the predominant ageing mechanisms, as far as reasonable potential windows are chosen.

3.3.2. Dissolution of manganese in the electrolyte

In contrast to lithium nickel cobalt oxides, chemical dissolution of lithium manganese spinel in electrolytes is a crucial

problem, especially at elevated temperatures [110,146–156]. The manganese dissolution leads to a loss of active material, and therefore, capacity fading. Additionally, the precipitation of electronic isolating manganese species, e.g., MnF₂, MnCO₃ and various oxides on the cathode has been observed, leading to increasing electrode impedance.

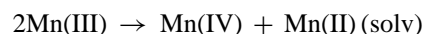
In complete cells capacity fading is strongly accelerated and cannot solely be explained by the loss of positive active material. Obviously, dissolved manganese ions move to the negative electrode and are incorporated in the SEI at the carbon electrode. Manganese can be detected on the negative electrode. This leads to enhanced electrolyte decomposition and promotes the self-discharge of the lithiated carbon. Therefore, even very small amounts of manganese in the electrolyte affect calendar life of the lithium-ion cell.

In general two different mechanisms of manganese dissolution are discussed:

- manganese dissolution at low potentials;
- acid dissolution catalysed by HF.

Both mechanisms are accelerated at higher temperatures.

3.3.2.1. Manganese dissolution at low potentials (manganese disproportionation). Manganese disproportionation is relevant in the discharged state. In this mechanism, trivalent manganese ions disproportionate into tetravalent and divalent ones [121]:



The divalent manganese ions are soluble in the electrolyte, whereas the tetravalent manganese ions remain in the solid phase. There is evidence that the spinel structure is maintained during this dissolution process and that the lost manganese ions on the manganese sites are replaced by lithium ions. In this manner, a disordered lithium-rich spinel of increased manganese oxidation state is formed. So, the com-

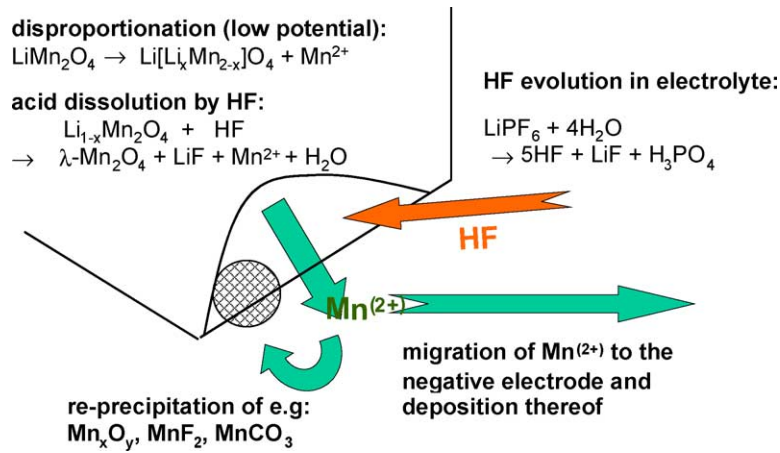
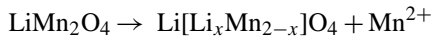


Fig. 5. Dissolution of lithium manganese spinel.

plete dissolution reaction can be qualitatively written as:



A low manganese oxidation state in the spinel structure, which is lowest in the deep-discharged state, is decisive for the disproportionation effect. So, deep-discharges have to be avoided to prevent disproportionation dissolution of lithium manganese spinel.

3.3.2.2. Manganese dissolution at elevated potentials (acid dissolution). In the medium to high charged state of the battery, a considerable dissolution of manganese into the electrolyte also occurs [123,157]. The dissolution mechanism in the elevated potential regions is not yet totally clarified, but is presumed to evolve qualitatively according to a chemical delithiation reaction by HF. Lithium fluoride (LiF) is an insoluble by-product, which can be found on the surface of the lithium manganese spinel particles. Main source of HF is the hydrolysis of the conductive salt LiPF_6 . The hydrolysis reaction is induced by protic impurities and proceeds in different steps, dependent on the amount of accessible water.

Protective surface coatings with lithium cobalt oxide [151] or other oxides [158,159] seem to improve the performance of lithium manganese spinels at elevated temperatures. Electrolyte additives, which neutralise HF and absorb protons [156], and the use of lithium manganese oxides with low specific surface area [160] also lead to decreased capacity fading. Good results were achieved by blending the lithium manganese spinel powder by lithium nickel oxide, lithium cobalt oxide or lithium nickel cobalt oxide [161–163]. Alternative conductive salts like lithium bis(oxalato) borate (LiBOB), which are insensitive versus hydrolysis, are in development and are promising candidates. Fig. 5 gives a schematic drawing of manganese dissolution in electrolyte and its impact on the complete cell.

4. Identification of ageing processes using electrochemical impedance spectroscopy

Impedance spectroscopy is an electrochemical method chiefly employed for investigation of reaction mechanisms. It has been proposed as a fast, non-destructive and reliable technique, able to identify the actual origin of cell degradation processes and bring some ageing effects in light, which are difficult to recognise by traditional test methods.

Fig. 6 displays a typical impedance diagram plotted on a commercial lithium-ion battery in the 6000 to 10^{-3} Hz frequency range, in the Nyquist plane. The significant inductive behaviour observed at frequencies higher than ca. 100 Hz is considered to be related both with the geometry of the cell and porosity of the plates. The intersection of the diagram with the real axis refers to the sum of internal ohmic resistances of the electrolyte and of the other resistive components. The capacitive loops appearing at lower frequencies describe the response of the different electrochemical processes involved in the reactions mechanism.

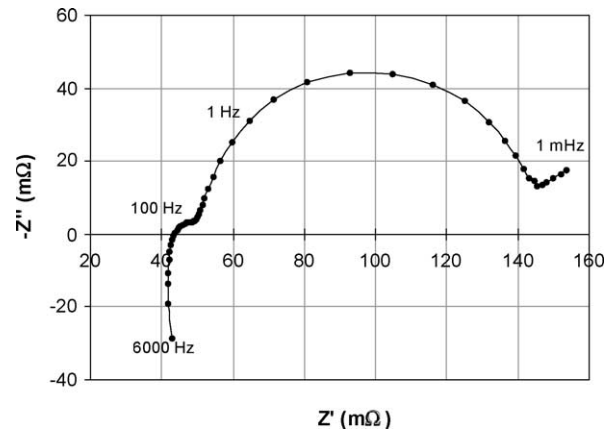


Fig. 6. Typical impedance diagram plotted on a prismatic 5 Ah-SAFT Li-ion cell at intermediate state-of-charge.

Obviously, the low-frequency loops may not be reliably resolved corresponding to the individual electrode parameters when the time constants and magnitudes of the relevant processes do not differ appreciably. For rigorous analysis, a three-electrode setup is required to distinguish the contribution of both of the cathode and anode. In the case of lithium-ion cells, half-cell measurements proved that the frequency ranges of both electrodes overlap, which calls for special care in interpreting impedance results when, for example, investigating ageing effects to identify the involved processes.

Most published data revealed for oxide-based cathodes as well as for carbon-based anodes a pair of capacitive semi-circles, terminating with a low frequency spike corresponding to Li^+ cations diffusion in the host solid-state phase. The first loop was often interpreted by relaxation of charge carriers in the solid electrolyte interphase [164,165]. On the contrary, where this loop did not vary as a function of time after assembling the cell, the process involved was related with the particle-to-particle contacts resistance [23]. The second capacitive loop, strongly depending on the electrode potential, was ascribed to the charge-transfer resistance in parallel with the double-layer capacitance [165–167].

Only few investigations concerning the use of ac impedance spectroscopy, to characterise the effect of accelerated ageing on the performances of lithium-ion cells, have been reported. These measurements are generally made with the cell at open-circuit conditions. A full spectrum complex impedance measurement scan is made at time intervals or at different cycle numbers. Data from the individual electrodes, where available, are compared with that from the complete cell.

It was shown that capacity fade of Sony cells was accompanied by an increase in the internal impedance of the battery upon cycling [29]. Combined half-cell impedance and voltammetric measurements confirmed that LiCoO_2 cathode deteriorated more severely than the carbon electrode over cycling, and hence, contributed more to the capacity decay. The most likely cause was that, after extended cycling, the cathode was heavily passivated resulting in a large interface resistance.

Similar behaviour was observed on commercial LiCoO_2 /graphite cell system from Japan Storage Battery [168]. In addition to cathode degradation during continuous float charging, producing free Co in the solution, electrolyte decomposition also occurred. The latter led to an accompanying substantial increase in the electrolyte ohmic resistance and in the cathode polarization resistance, due to growth of surface passivating film. Either a 15°C increase in test temperature or a 0.1 V increase in charging voltage cut the cell life in half.

Since the end-of-life of the high-power cell is caused by power fade associated with an impedance rise rather than a capacity fade, systematic impedance investigation was achieved within the framework of the Advanced Technology Development Program focusing on high-power lithium-ion batteries, involving different cathode chemistries, for the hy-

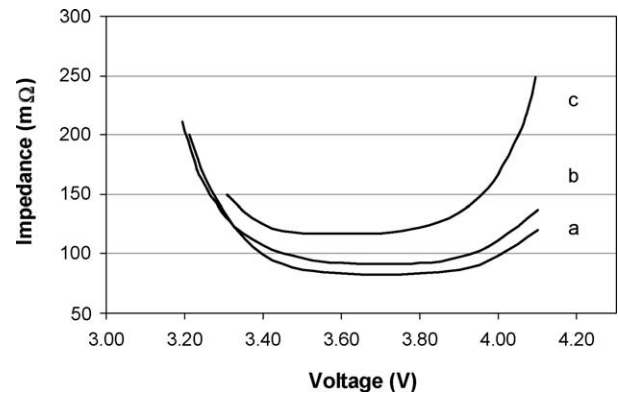


Fig. 7. Effect of accelerated ageing on the impedance of Li-ion cell: (a) before heating, (b) after heating for 1 month at 50°C , and (c) after cycle life test for 1 month at 50°C .

brid electric vehicle [22,38,112]. The correlation between the impedance data and the cell power capability reflected a consistent trend and low variability. The main observations were:

- Tiny change in the high-frequency ohmic resistance during life testing, reflecting the stability of the electrolyte solution.
- The major increase in cell impedance was due to the interfacial processes. By comparing the impedance characteristics of laboratory symmetrical cells assembled with two identical $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrodes, using successively fresh material and material harvested from the aged cell, it was possible to identify the cathode as the principal cause of premature performance fade during accelerated life testing; the anode retained most of its original capacity. Accordingly, partial substitution of Co with Al in the cathode material significantly enhanced the calendar life stability of the whole cell.
- The SOC dependence of the cell impedance showed a U-shape curve revealing a steeper increase, and hence, a more rapid ageing, at voltages both above 3.8 V and below 3.4 V (Fig. 7).

Finally, from these few application examples, electrochemical impedance spectroscopy appears as a specific test method that can be used for non-destructive continuous observation of the effects of cycling and storage under field operating conditions on life-time of Li-ion cells and batteries. Besides, for analysis of ageing mechanisms, this technique could partly substitute the physico-chemical post-mortem analyses, which undoubtedly reduces the technical effort and, therefore, time and costs.

5. Summary

Battery ageing, increasing cell impedance, power fading, and capacity decay origin from multiple and complex mechanisms. Material parameters, as well as storage and cycling

conditions, have an impact on battery life-time and performance. Depending on the cell chemistry, both high and low state of charge may deteriorate performance and shorten battery life. At high temperatures, the decay is accelerated, but low temperatures, especially during charging, also can have a negative impact. Amongst the material parameters, surface chemistry plays a major role for both anode and cathode materials. On the cathode, phase transitions and structural changes in the bulk material strongly influence ageing, while changes in the bulk anode material are considered of minor importance only.

Many of the mechanisms responsible for battery decay and ageing can be monitored and investigated non-destructively by the use of impedance spectroscopy. Although the interpretation of impedance data is challenging and not always unambiguous, impedance spectroscopy, together with the more conventional methods of battery science, electrochemical and other, is a powerful tool for the investigation of ageing processes in lithium-ion batteries.

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