Journal of Energy Storage 1 (2015) 44–53

Contents lists available at ScienceDirect

Journal of Energy Storage

journal homepage: www.elsevier.com/locate/est

Nonlinear aging characteristics of lithium-ion cells under different operational conditions

Simon F. Schuster [a,*], Tobias Bach [b], Elena Fleder [b], Jana Müller [b], Martin Brand [a], Gerhard Sextl [b], Andreas Jossen [a]

[a] *Institute for Electrical Energy Storage Technology, Technische Universität München, Arcisstraße 21, 80333 Munich, Germany*
[b] *Fraunhofer Institute for Silicate Research, Neunerplatz 2, 97082 Würzburg, Germany*

ARTICLE INFO

Article history:
Received 16 March 2015
Received in revised form 27 April 2015
Accepted 6 May 2015
Available online 22 May 2015

Keywords:
cyclic aging
nonlinear
2nd-life
reuse
lithium plating

ABSTRACT

The potential reuse of lithium-ion batteries exhausted upon electric vehicle operation is a broadly discussed topic. However, a profound understanding of battery aging behavior is a prerequisite to assess overall system cost and economic benefit of battery reuse: Whereas the capacity fade under load is commonly reported to show a linear dependency on charge throughput, a turning point to nonlinear aging characteristics is observed at residual capacities of about 80% under different operational conditions. Based on a widespread aging matrix, results indicate an earlier appearance of nonlinear characteristics at high charging rates and operational voltage windows but low temperatures. Scanning electron microscopy images reveal areas of thick surface films at the anode while the cathode stays unmodified. Therefore, a thickening of the solid electrolyte interphase, catalyzed by oxidation products migrating to the anode, is believed to be the dominating aging mechanism before the turning point. Afterwards, lithium plating might even occur at moderate temperatures and charging rates due to deteriorated ionic kinetics and graphite active material loss. As all these mechanisms are dependent on the cell potential, an optimized operational strategy may avoid or retard nonlinear aging characteristics and extend the life of lithium-ion cells.

1. Introduction

Although a global wide introduction of battery electric vehicles (BEV) is regarded as an inevitable next step to lower the emission of greenhouse gases, the product acceptance of potential customers are still rather low. Due to the high price of BEV resulting from the costly battery storages, barely 2% of newly registered cars in Germany in 2013 were pure or hybrid electric [1]. Despite a growing need due to a possible lithium scarcity in the future, a reduction of the price achieved by recycling of disused batteries in not economically feasible for now [2]. Therefore, a potential reuse of lithium-ion batteries exhausted upon BEV operation is a broadly discussed topic, e.g. in the context of 2nd-life-applications like stationary energy storage [3–9]. Using aged batteries to reduce grid-strengthening investments, for frequency sustainment issues or as an interim storage for renewable energies, promises high revenue potentials [5,6]. However, a profound understanding and predictability of battery aging behavior is a prerequisite to assess overall system cost and economic benefit of battery reuse.

In general, the consequences of aging in lithium-ion cells are the loss of capacity, the increase of impedance and the reduction of the maximum power due to a higher polarization. The reasons for aging can be divided into three groups, namely the loss of active materials, the loss of lithium and the deterioration of ionic kinetics [10].

The evolution of passive layers, i.e. the solid electrolyte interphase (SEI) at the anode and the solid permeable interphase at the cathode (SPI), takes on a key role in the aging of lithium-ion cells [11]. Whereas the SEI ideally prevents any further reduction of the electrolyte at the anode after formation, the electrolyte is continuously oxidized at the cathode due to the SPI's incapability of full passivation [12–14]. As the thickening and reconstruction of passive layers consume active lithium, there is a direct correlation to capacity loss [15–20]. Under extreme operational conditions such as a high state of charge (SoC) or high temperatures, these layers can even isolate active material by growing into its porous structure or clog the separator's pores [16,21].

---

* Corresponding author. Tel.: +49 89 289 26969; fax: +49 89 289 26968.
E-mail address: simon.schuster@tum.de (S.F. Schuster).

http://dx.doi.org/10.1016/j.est.2015.05.003
2352-152X/© 2015 Elsevier Ltd. All rights reserved.

At the cathode, a high delithiation degree, e.g. $x < 0.35$ for $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) or $x < 0.5$ for Li_xCoO_2 (LCO), may result in irreversible structural changes, named rock salt structure, leading to an irreversible capacity loss [17,22,23]. Lithium cations move to the anode releasing electrons when charging a lithium-ion cell, which results in an increase of vacancies in the lithium layers. Thereby, repulsion forces between encompassing transition metal layers rise due to the missing virtue of compensation. Due to similar ionic radii, 0.76 Å for Li^+ and 0.67 Å for Ni^{2+}, the latter tend to migrate to the lithium layers and compensate the repulsion forces between transition metal layers by filling these vacancies irreversibly [24]. As a consequence, released oxygen promotes the oxidation of electrolyte leading to a further growth of the SPI. In addition, due to the higher conductivity of the SEI compared to the combination of SPI and rock salt structure, the cathode is assigned the main portion of charge transfer resistance [12,25]. With an increase of oxygen vacancies, the dissolution of the cathode is promoted. As a consequence, oxidation products migrate to the anode where they are reduced and catalyze the growth of the SEI by forming electron conducting tunnel paths [17]. For NMC cells, most of the oxidation products detected at the anode is manganese, but there are also traces of nickel and cobalt [26]. Whereas the anode material is principally not damaged by these deposits, ionic kinetics are deteriorated as a result [27–35]. In addition, cells cycled with high depths of discharge (DoD) seem to be more contaminated with oxidation products than cells stored at high SoC [36].

When lithium cations are inserted into or extracted from active material, the concomitant volumetric change, e.g. 10.2% for graphite anodes [37,38] and 3.4% for NMC transition metal layer cathodes [38,39], can lead to a loss of particles' bonds due to micro cracks or a loss of the contact of particles to the collector. It is assumed for graphite that especially the crossing of phase transitions results in erratic volumetric changes, indicating that also small DoD within an operational voltage window (ΔV) of phase transitions may lead to severe aging effects [33,34]. As the relative variation of graphite's lattice parameters in increased at two-phase reactions between different stages at the almost delithiated state, sliding and buckling of graphite planes must especially be considered when lithium-ion cells are discharged to very low SoC [37]. Such an irreversible structural disordering in the lattice of graphite leads to active material loss and thus, capacity loss of the anode. When the binding agent, typically polyvinylidendifluoride (PVDF), is decomposed, active materials may expand permanently facilitating a contact loss of particle to particle or collector [14,25]. As a consequence, active material gets isolated resulting in a loss of the electrode's capacity. In addition, passive layers may help to compensate volumetric changes but further capacity loss occurs if the layers break and need to be reconstructed [15,36,40].

At a high SoC, the potential of graphite anodes can come close to the critical value of 0 V vs. Li/Li^+. Low temperatures lead to a higher polarization due to slower diffusion processes and a hampered charge transfer. Thus, when charging lithium-ion cells at low temperatures with high currents, the graphite potential may drop below 0 V vs. Li/Li^+ [30,41]. As a consequence, lithium cannot be intercalated and is plated between active material and SEI. In [42], the thickness of a metallic lithium layer in plated lithium iron phosphate (LFP) based cells was measured to be 5 mm, which could even impose mechanical stress onto the cells' components. Facing a thermal runaway, plated lithium may lead to an increase of heat formation and so reduces the safety of a lithium-ion cell [43]. Theoretically, lithium plating is a reversible process as long as a conductive connection to graphite exists. As lithium oxidizes at about 100 mV vs. Li/Li^+, lower than the potential of deintercalation, plated lithium is removed in the subsequent discharge at first being apparent from a specific voltage plateau at the beginning [41,44,45]. This process is called stripping of plated lithium in which the ratio of LiC_6 and LiC_{12} stays constant until the deintercalation process starts [42,46]. In addition, it was spotted that during relaxation processes, plated lithium can oxidize to be chemically intercalated into graphite resulting in an increase of LiC_6 and reduction of LiC_{12} [46]. Although lithium plating is theoretically reversible, it is assumed that porous structures are formed during stripping and chemical intercalation processes, tending to lose the conductive connection to graphite [42,44–47]. In this case, isolated lithium may react with the electrolyte or damage the SEI resulting in a growth or reconstruction under accompanied capacity loss due to lithium consumption. In conclusion, when lithium plating occurs, one has to assume a mixture of stripping, chemical intercalation and isolation [42,44–47]. To avoid plating, a boost charging strategy, i.e. using high charging rates only at the beginning and reducing it at higher SoC is supposed to be a candidate for lowering the risk of this severe aging effect [48–50]. In addition, e.g. carbon black can improve the electrode's conductivity leading to a lower polarization but electrolyte additives used to stabilize the SEI growth as ethylene carbonate (EC) have shown to cause the opposite [16].

Most studies reveal a capacity fade for cells in storage with square root dependency on time [27,34,35,40,51]. The capacity under load is commonly reported to fade with a linear dependency on the charge throughput [34,35,40]. In rejection of these dependencies, enhanced aging upon prolonged cycling for distinct lithium-ion cells is observed in a few studies. Such a behavior for graphite based cells is e.g. described for cathodes comprising nickel, cobalt and aluminum (NCA) [52], LFP [33], NMC [34] and a blend of lithium manganese spinel (LMO) with NMC [36]. Possibly, these nonlinear aging characteristics are independent on the cathode chemistries but related to aging mechanisms of the anode. Instead of just observing enhanced aging upon prolonged cycling, only a handful of studies report about and explicitly address the origins of nonlinear aging characteristics [33,36,53,54].

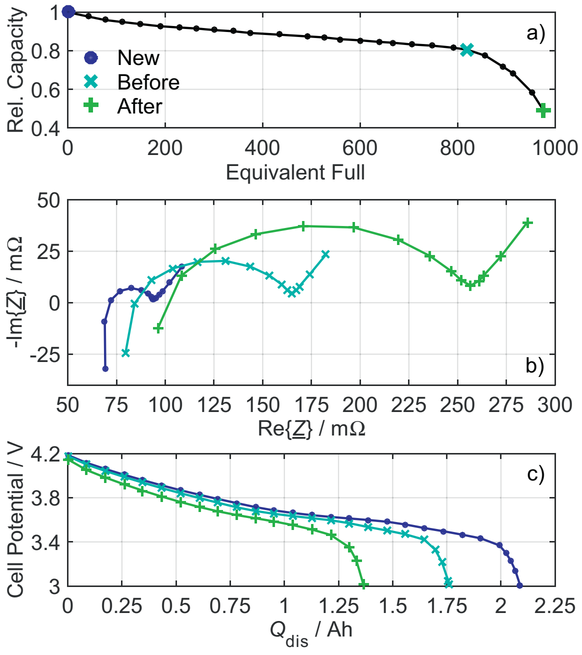

Fig. 1. (a) Development of the relative discharge capacity versus EFC for a graphite// NMC lithium-ion cell; (b) Nyquist plots of the impedance and (c) slow discharge curves referring to the three spots in (a): New cell (blue), before the start of nonlinear aging characteristics (cyan) and after the occurrence of these (green).