Aging Mechanisms of Anode Materials in Lithium-ion Batteries for Electric Vehicles

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ABSTRACT

Electrode material aging leads to a decrease in capacity and/or a rise in resistance of the whole cell and thus can dramatically affect the performance of lithium-ion batteries. In this paper, we give an interpretation of capacity/power fading of anode-oriented aging mechanisms under cycling and various storage conditions for carbon-based anodes. For the anode, the main aging mechanisms are the loss of recyclable lithium ions caused by the formation and increasing growth of a Solid Electrolyte Interphase (SEI) and the mechanical fatigue caused by the diffusion-induced stress on the carbon anode particles. Additionally, anode aging largely depends on the electrochemical behaviour under cycling and storage conditions and results from both structural/morphological changes and side reactions aggravated by decomposition products and protic impurities in the electrolyte. Please keep this in mind when designing your figures and tables etc.

INTRODUCTION

Lithium-ion cells are attractive candidates for power storage owing to their high power and energy-density and low self-discharge rate. Unfortunately, the life span of a lithium-ion cell, as is generally known, is restricted by side reactions that may be detrimental to the cell’s component parts, which include the active lithium, binder, current collectors, the separator, conducting salt and solvents, etc., and these reactions result in a capacity decrease/resistance rise of the cell [1-3]. Understanding the anode aging mechanisms in lithium-ion batteries is of great importance to address the life time and safety challenges, to make precise lifetime predictions and to improve the battery performance [4]. This paper attempts to study and summarize the present research regarding the predominant aging mechanisms of the negative electrode (carbon anode) of lithium-ion cells applied to EVs.
EVOLUTION OF THE PASSIVATED SURFACE LAYER AT THE ANODE/ELECTROLYTE INTERFACE

Generally, the most critical part of the cell is the anode/electrolyte interface because of the high reactivity of the organic electrolyte with any type of electrode material and lithium ions. Graphite, carbon, amorphous silicon and lithium titanium oxide are the main candidates for the anode materials [5]. Figure 1 from Ref. [6] shows a flowchart of the aging mechanisms for anode materials of a lithium-ion battery. To further the discussion, the anode aging under the conditions of storage and use will be summarized in terms of the following: (i) SEI formation, stable growth, dissolution and precipitation at the interface between the anodes and electrolytes; (ii) Anode mechanical failure; and (iii) Anode electrochemical aging.

![Figure 1. Aging mechanisms of the anode materials—causes, effects, and results.](image)

Graphite is commonly adopted as the anode material for lithium-ion batteries with organic electrolytes, such as LiPF6, with co-solvents like ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (EMC)) [7]. When the anode operates at a potential that exceeds the electrochemically stable window of the electrolyte components, some major reactions in a LiPF6 salt system with EC and DMC are supposed to take place with the consumption of lithium ions [8-12].

As the reactions continue, the consumption of lithium ions and the electrolyte solvents are inevitable as the electrode is in a state of charge; then, the electrolyte decomposes and produces deposits. This process subsequently results in the formation of a protective, ionically conductive but electrically insulating passivation...
layer on the surface of the anode during the first charge cycle, the so-called SEI (e.g., LiCO3, (CH2OCO2Li)2, CH3OCO2Li, Li2O, LiF, etc.), and the SEI evolution is illustrated in Figure 2, which is from Ref. [6]. Furthermore, the ROCO2Li can undergo a reduction reaction with traces of H2O and CO2 in the electrolyte to form LiCO3 [13-19], which further reacts with EC to form transesterification products [6,9-13]. Additionally, anion contaminants, such as F- from LiPF6, readily react with lithium ions to form insoluble reaction products LiF, which are non-uniform, electrically insulating, and unstable on the surface of the graphite particles. When the side reactions continue during prolonged cycling, the produced deposits accumulate in the SEI and consequently lead to stable growth of the SEI, which, in turn, leads to the loss of active lithium and further decomposition of the electrolyte [20,21]. Subsequently, a restructuring of the damaged SEI or a re-precipitation of the dissolved SEI products might occur as the SEI membrane begins to dissolve or to decompose [12,22].

In addition, interactions of the anode with the cathode must also be taken into account. For instance, metal is present on the anode surface. Dissolution of the cathode electrode metal from the lattice into the electrolyte can be caused by two main reaction mechanisms in the cell [6]. These reactions can be due to the disproportionation of Mn3+ to Mn2+ and Mn4+ ions at low states of charge, or due to traces of HF within the LiPF6 electrolyte. Because manganese ions do not change their oxidation state to Mn3+ during storage within the NMC and the spinel phase, manganese dissolution caused by HF is more likely. Dissolved transition metals are transported through the electrolyte to the surface of the anode, resulting in the deposition of cation contaminants, such as Mn, Co and Fe, which are incorporated into the SEI layer [1,2,7,12].

Moreover, the graphite electrode materials are susceptible to lithium plating and lithium dendrite growth because of the close proximity of its reversible potential to that of Li+/Li. Both effects are especially aggravated when the unmodified graphite anode operates at low temperatures (below 25°C) [23] and/or a high charging rate. Thus, the lithium plates on the SEI surface of the anode rather than intercalating into the lattice of the carbon. If these moss-like metallic deposits and dendrites continue to grow between the polymer separator and the anode, a short circuit is created, which then can lead to thermal runaway and battery failure [6,7].
SUMMARY

This paper presented the aging mechanisms of anode materials in lithium-ion batteries, elaborating on the causes, effects and their results, taking place during a battery’s life as well as the methods adopted to mitigate the aging phenomena in lithium-ion batteries. Additionally, the anode aging effect is probably not caused by itself aging alone, but may be caused by the interface changes between the electrodes and the electrolyte. In short, the main anode aging mechanism can be summarized as follows:

- Changes at the anode/electrolyte interface. The SEI membrane is fabricated during the first electrochemical charge and then further evolves with precipitation on the anode during cycling and storage. Moreover, interactions of the anode with the cathode and metallic lithium plating must be considered as significant factors in the anode aging.
- Mechanical failure, such as graphite exfoliation and particle cracking lead to isolation of active materials, which subsequently aggravates electrode aging.
- Anode electrochemical aging characteristics. Some side reactions at the electrode/solution interface or the SEI and electrolytes, together with the contact loss within the composite anode materials, consequently result in a resistance rise of electrode.

REFERENCES


