Visualizing elemental deposition patterns on carbonaceous anodes from lithium ion batteries: A laser ablation-inductively coupled plasma-mass spectrometry study on factors influencing the deposition of lithium, nickel, manganese and cobalt after dissolution and migration from the $Li_1[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ and $LiMn_{1.5}Ni_{0.5}O_4$ cathode

Timo Schwieters[a], Marco Evertz[a], Alexander Fengler[a], Markus Börner[a], Tim Dagger[a], Yannick Stenzel[a], Patrick Harte[a], Martin Winter[a,b], Sascha Nowak[a,*]

[a] MEET Battery Research Center, University of Münster, Corrensstraße 46, 48149 Münster, Germany
[b] Helmholtz-Institute Münster (HI MS), IEK-12, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany

HIGHLIGHTS

- Investigation of the lithium and metal deposition on anodes.
- Development of self made standards and first LA-ICP-MS application for the analysis.
- Depth analysis of the deposited cations in the anode layer.

ARTICLE INFO

ABSTRACT

In this study, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is applied to previously aged carbonaceous anodes from lithium ion batteries (LIBs). These electrodes are treated by cyclic aging in a lithium ion cell set-up against $Li1[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ = NMC111 to elucidate factors that influence transition metal dissolution (TMD) of the cathode and subsequent deposition on the anode. The investigations are carried out by qualitatively visualizing the 7Li and TM patterns (^{60}Ni, ^{55}Mn and ^{59}Co) of whole coin and pouch-bag electrodes.

The lithium, as well as the TM amount, found on the anode, is directly correlated to the applied upper cut-off voltage (4.6, 4.7, 4.8 and 4.9 V) showing more deposition of Li and TMs at elevated voltages. While 7Li shows a more homogeneous pattern, the TM distribution is inhomogeneous but showing a similar pattern for all TMs of the same sample. An unequal pressure distribution, resulting in a nonparallel electrode alignment, on the electrode stack is identified to be responsible for the inhomogeneous TM deposition pattern. This uneven electrode orientation results in different diffusion pathways for the TM migration with regard to the spatial distances.

1. Introduction

Lithium ion batteries (LIBs) became the most applied energy storage system for power consumer electronics like smartphones, laptops or smartwatches in the last two decades [1,2]. Their high specific energy (Wh kg^{-1}), high energy density (Wh L^{-1}), high energy efficiency and long cycle life are the unique characteristics responsible for this success [3,4]. More recently, LIBs found its way as a power source for electric vehicles (EVs), hybrid EVs (HEVs) or plug-in HEVs (PHEVs) to meet the requirement for a more sustainable way of human transportation compared to the use of combustion engines [5]. Furthermore, new energy storage systems are required that store and feed energy to the grid even in remote areas where wind or solar power plants are installed. LIBs can fill this gap due to its excellent customizability regarding size and implemented chemistries.

In general, LIBs consist of a positive (cathode) and a negative

(anode) electrode, an electrolyte, a separator and a case enclosing the battery parts. The components that are directly involved in the energy storage mechanism upon cell charge and discharge are considered as active materials, whereas components like binder, separator or casing represent the inactive parts. Despite being inactive regarding the energy storage or redox process, these parts can also react and thus be partially responsible for cell degradation.

In order to provide lithium ion conductivity between the electrodes usually a non-aqueous electrolyte is used. It consists of a conducting salt (e.g. lithium hexafluorophosphate ($LiPF_6$)) dissolved in a combination of linear (e.g. dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC) [6–8]) and cyclic carbonates (e.g. ethylene carbonate (EC) or propylene carbonate (PC) [9–11]).

The anode materials of choice for commercially available cells consist of carbonaceous components (e.g. graphite, soft or hard carbon) that exhibit a specific capacity of $372 \, mAh \, g^{-1}$ [12,13]. These layered anode materials can inter- and deintercalate highly reversible lithium ions forming graphite intercalation compounds $Li_{1-x}C_6$ upon charge (= lithiation of graphite).

The most applied cathode active materials are layered transition metal oxides $LiMO_2$ (M = Co, Ni, Mn, etc.), spinel compounds LiM_2O_4 (M = Mn, Ni, etc.) and olivine compounds $LiMPO_4$ (M = Fe, Mn, Ni, Co, etc.) [14]. Excluding the complexity and variety of all possible anode/cathode combinations, this work focuses on a system based on a carbonaceous anode and $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ = NMC111 [15–17]) as cathode material. NMC is a prominent candidate displaying a layered lithium metal oxide with varying contents of nickel, manganese and cobalt. Originating from $LiCoO_2$ (LCO) [18], which was commercialized already 26 years ago [19], the cobalt was substituted partially/entirely by nickel and manganese to customize the intrinsic properties of the material. Not only the toxicity of cobalt but also the structural instability of the delithiated material against decomposition represent a reason for substituting cobalt by more abundant, less expensive and environmentally friendly transition metals (TMs), such as nickel and manganese. On the one hand, nickel enhances the capacity providing the redox couples Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} at the operation voltage between 3.6 and 4.3 V; on the other hand, manganese is known to stabilize the structure by providing the chemically inactive tetravalent Mn^{4+} [20].

However, this technology still needs to be improved in order to eliminate or at least suppress capacity and power fading over time. The processes that contribute to an inferior performance of a LIB are part of the complex phenomenon called aging. One of the most important aspects concerning aging is electrode degradation accompanied by an ongoing reduction of available active lithium for intercalation/insertion reactions. The sources for active lithium in a pristine cell are the cathode material incorporating the lithium in its lattice and the conducting salt. Some parts of the lithium from the cathode will not be available for the use as charge carrier due to several possible reasons, such as high local Ohmic resistances or charge transfer resistance resulting in hindered lithium ion mobility [21]. Another possibility is the so-called lithium loss describing the process of active lithium turning inactive in the course of cyclic aging. This can either happen due to clogging of diffusion pathways or chemical reactions on top and within the anode material forming products like Li_2O, LiF or $LiCO_3$ [22,23]. These lithium-rich degradation products of the electrolyte are known to be the inorganic part of the solid electrolyte interphase (SEI) that is formed mainly during the first lithiation process of the carbonaceous anode [24]. Although these reduction processes inevitably lead to a depletion of active lithium, the SEI formation is mandatory for further electrochemical cycling. The SEI covers the graphite particles at every point of contact between graphite and the electrolyte thus protecting the electrolyte from further reduction. Hence, a uniform formation of a protective film that is permeable to lithium ions is beneficial for long cycle life and less capacity fading. The uniformity can be negatively affected by transition metals (Ni, Mn and/or Co) depositing on the

anode surface after migration through the electrolyte and separator. The degree of transition metal dissolution (TMD) and subsequent reduction and deposition on the anode were reported for $LiMn_2O_4$ and NMC111 to be mainly induced by elevated upper cut-off voltages in lithium ion cells (> 4.3 V vs. Li/Li^+) [25–34]. Despite being favorable in the first place regarding capacity due to more released active lithium, the battery performance will decrease dramatically over time [35,36] accompanied by an impedance rise at the anode [37]. The exact degradation mechanism concerning the TMD is still under debate. Jang et al. and Xia et al. proposed mechanisms that include disproportionation reactions [30,38] whereas others state that formed HF due to present moisture catalyzes the TMD [39–42]. The latter was recently disproven by Evertz et al. by comparing the HF content in the electrolyte before and after cyclic aging [43]. They found less than $5 \, mg \, L^{-1} \, F^-$ in the aged electrolyte. Therefore, in accordance with Börner et al. three reasons for TMD were postulated [44]:

- Impurities within the NMC host lattice (e.g., oxygen vacancy)
- Structural deformation of NMC particles that leads to particle cracking
- Phase transformation from layered to spinel structures on nanoscale level

In this study laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) was applied to aged mesocarbon microbeads/ hard carbon electrodes (MCMB/HC, hereafter graphite) previously aged in a lithium ion cell setup with NMC111. A qualitative proof of principle about spatially resolved elemental information of Li, Ni, Mn and Co in order to visualize the lithium and transition metal distribution pattern on the anode is presented. Furthermore, different factors possibly influencing the deposition pattern were evaluated:

- The washing procedure of the aged electrodes after disassembling
- The amount of applied electrolyte
- Gravity effects on the electrolyte influenced by the orientation during cycling (vertical or horizontal)
- Unequal pressure conditions inside the cells

Additionally, a total depth profiling, which was developed earlier [45], was conducted to evaluate the penetration/diffusion depth of the lithium and deposited TMs.

To obtain an excessive TMD, the upper cut-off voltage was dramatically increased from nominal 4.2 V to 4.6–4.9 V. Enhancing the cut-off voltage to these levels implicates a larger amount of delithiated lithium from the cathode lattice resulting in structural instabilities, which promote TMD.

2. Experimental

2.1. Cell designs

Lithium ion cell experiments were carried out using coin (2032, Hohsen Corporation, Japan) and custom-made pouch-bag cells (see Fig. 1).

A bottom and a top case including a seal ring enclose the remaining parts of the coin cell exhibiting dimensions of 20 × 3.2 mm, in diameter and height, respectively (see Fig. 1a). One spring to maintain a constant pressure inside the cell and two spacers (0.3 and 0.5 mm in thickness) complete the inactive metallic parts of the cell. The MCMB/HC and NMC electrodes with areas of $1.13 \, cm^2$ each (12 mm in diameter) are divided by two separators, each with an area of $2.54 \, cm^2$ (17 mm in diameter). Both materials were provided by an in-house pilot plant battery-line, whereby the capacity of the anode material was provided with an excess capacity of 50% (compared to the cathode capacity) to avoid lithium metal deposition (plating). One polypropylene separator (Celgard 2500, Celgard LLC, USA) was faced directly to the graphite