



# Development of a method for direct elemental analysis of lithium ion battery degradation products by means of total reflection X-ray fluorescence



Marco Evertz, Constantin Lürenbaum, Britta Vortmann, Martin Winter, Sascha Nowak\*

MEET Battery Research Center, Institute of Physical Chemistry, University of Münster, Corrensstraße 46, 48149 Münster, Germany

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## ABSTRACT

A new method using the total reflection X-ray fluorescence (TXRF) technique for the elemental analysis of lithium ion battery (LIB) degradation products is presented. Here we investigate transition metals that have electro-deposited on a graphite electrode, which is the typical LIB anode. For this, the developed non-digestive method is validated against the common methods in elemental analysis of battery degradation, i.e., inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). The results obtained with the TXRF method are compared with those of the standard method with respect to their recovery rate and detection limits.

The TXRF is a well-known quantitative and qualitative analysis technique with very low detection limits and therefore suitable for the adaption in the field of battery aging products.

By avoiding the time consuming dissolution of the solid battery components – performed via microwave assisted acid digestion – recovery rates of 90 to 110% could be observed, thus showing the great applicability of the alternative TXRF method. Furthermore, it could be shown that elevating the C-discharge rates of the cathode material as well as elevating the charging cut-off voltages increases the transition metal deposition on the graphite anode and even at low contents of transition metals, the TXRF delivers excellent results.

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## 1. Introduction

The lithium ion battery (LIB) technology, introduced in the early 90s, opened a whole new market for high power and high energy portable devices. Recent applications in the electromotive industry as well as in the field of stationary storage systems for a more efficient use of renewable energies attracted the LIB technology [1,2].

The common lithium ion batteries are set up with graphitic type anodes offering a capacity of  $372 \text{ mAh g}^{-1}$  and lithium metal oxide type cathodes [3,4]. The limiting factors in capacity of the LIB are strictly depending on the type of cathode, of which basically three different types of lithium metal oxides and phosphates are widely used. Those materials are classified by their tendency of lithium ion transport, marking them 1-dimensional, 2-dimensional and 3-dimensional lithium ion conducting materials [5–9].

Nevertheless, depending on the application LIBs still show severe drawbacks, especially the limited storage lifetime (= calendar life) and cycling lifetime (= cycle life). These criteria are closely related to the degradation of the battery cell components, which is known as cell aging. Furthermore, due to the complexity of lithium ion cells numerous

different aging mechanisms are proposed and can be related to different battery materials and components [10–14].

The dissolution of transition metals from the cathode is proposed to have a major influence on the cycle life due to the deposition of those metals on the graphitic anode (Fig. 1). It has been shown for lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) spinel type cathodes that the deposition of manganese leads to cracking and contamination of the solid electrolyte interphase (SEI) [15,16]. The SEI is a lithium ion conductive, but electronically insulating protective layer and prevents the electrolyte from further decomposition on the anode [17,18]. The deterioration of the SEI and the deposition of the transition metal are then resulting in further electrolyte decomposition and also in the loss of available active lithium leading to decreasing discharge capacity values [19].

The failure mechanisms depend on the cathode material of which the  $\text{LiMn}_2\text{O}_4$  spinel type electrode degradation mechanism is well known, where a disproportionation ( $2 \text{ Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$ ) and acid dissolution by HF are assumed [15]. In here we analyze the degradation products of the layered lithium metal oxide  $\text{Li}_1\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) [20,21].

To understand and quantify the phenomenon of transition metal dissolution on the cathode, a quick and simple analysis technique is desirable in order to examine the transition metal deposition on anodic electrodes, at different cycling regimes as well as different materials.

\* Corresponding author. Tel.: +49 251 83 36735; fax: +49 251 83 36032.  
E-mail address: [sascha.nowak@uni-muenster.de](mailto:sascha.nowak@uni-muenster.de) (S. Nowak).

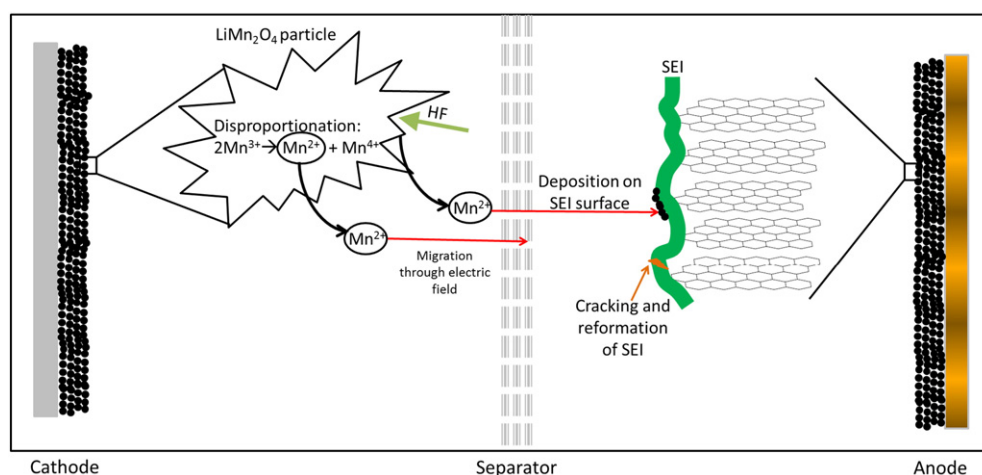


Fig. 1. Scheme of the transition metal dissolution in batteries by the example of lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) spinel electrodes.

Thus, mechanism studies can be performed more easily with a wide range of variable components. The common analysis is based on inductively coupled plasma equipped either with an optical emission or mass spectrometer [16,22] or by combination of X-ray methods [37]. For this analysis several time consuming pretreatment steps are necessary, e.g., the dissolution of the solid samples. In comparison, total reflection X-ray fluorescence (TXRF) spectroscopy is able to determine specific transition metals in the low ppb ranges and offers the possibilities to analyze solid materials and particles in a non-destructive way [23–26]. Therefore, TXRF promises to be a powerful tool in the determination of these deposited transition metals of battery materials in comparison to common existing methods with less sample preparation.

## 2. Experimental

### 2.1. Cell assembly and cycling procedures

The electrodes were prepared in-house using a MesoCarbon MicroBeads (MCMB) graphite/hard carbon composite (MTI Corporation, Richmond, CA) as anode and lithium nickel cobalt manganese oxide (NCM) (Toda Kogyo Corp., Hiroshima, Japan) as cathode material, respectively. The slurries were prepared using N-methyl-2-pyrrolidone (NMP) (99.5%, Acros Organics, New Jersey, NJ) and active mass loadings of 93% and 95% for NCM and MCMB, respectively. Furthermore conductive carbon (99.7%, SuperP®, Timcal, Bironico, Switzerland) and polyvinylidene difluoride, PVdF (KynarFlex® 761, Arkema, La Garenne-Colombes Cedex, France) binder were added to the slurry. The slurries were coated on thin aluminum (cathode) and copper foils (anode) with an active mass thickness of 93  $\mu\text{m}$  and 79  $\mu\text{m}$  for cathode and anode, respectively. The full cells were capacity-balanced with 40% oversized anodes.

For the constant current cycling test, pouch-bag-type cells were assembled using electrode sizes of 3 \* 3 cm for cathodes and 10% area-oversized anodes. As separator Celgard 2500 (Celgard LLC, Charlotte, NC) was used in 4 \* 4 cm dimensions and as electrolyte LP50 (1 M  $\text{LiPF}_6$  in ethylene carbonate/ethyl methyl carbonate) (EC/EMC, (50/50 wt.%) Selectilyte, BASF, Iselin, NJ) was selected. The cycling was performed using a Maccor series 4000 battery test system (Maccor Inc., Tulsa, OK) with charging voltages up to 4.3 V and 4.6 V using a cycling regime of 200 cycles and a charge rate of 1 °C which corresponds to 136  $\text{mAh g}^{-1}$  and 160  $\text{mAh g}^{-1}$  for the charge cut-off voltages of 4.3 V and 4.6 V, respectively. Additionally, similar pouch bag type cells, but with 5 \* 5 cm cathode dimension were assembled in-house and cycled applying a specific C-rate test. The cells were charged and discharged with increasing C-rates rising from 0.1 C up to 10 C with charge cut-off voltages of 4.3 V.

### 2.2. Sample preparation

After cycling, the cells were opened in an argon atmosphere and each electrode was carefully washed with dimethyl carbonate (DMC) (99%, VWR Chemicals, Radnor, PA) to rinse electrolyte residues from the electrode surface. The washing solution was collected and analyzed via TXRF, where no transition metals could be detected, implying that the SEI was not affected. An uncycled pristine electrode functioned as reference cell and was not exhibited to galvanostatic cycling. Nevertheless, it was assembled in the same manner as the cycled cells.

Hence, the sample amount is limited by the performance of the microwave assisted acid digestion, the electrodes were cut into nine pieces of the same size (1 \* 1 cm) using a ceramic scissor (Kyocera Corporation, Kyoto, Japan). Furthermore, this provides additional information as spatial resolution of the deposited transition metals, since the size can be compared with other cell types with same sample sizes.

For the TXRF measurements, the graphitic anode snips were ball-milled in 2 mL reaction vials (Eppendorf AG, Hamburg, Germany) with the use of glass micro beads ( $\varnothing$  1.5 mm, Retsch Technology, Haan, Germany). Furthermore, 1 mL of a 0.01 vol.% solution of the non-ionic surfactant Triton X-100 (99.8%, Merck, Darmstadt, Germany), was added, which serves as tenside. The electrodes were ball-milled for 90 min at 30 Hz using the swing mill MM 400 (Retsch Technology, Haan, Germany) in order to scrape off the graphite from the copper current collector. The aim of this procedure is to suppress the presence of copper in the TXRF analysis as it would result in a copper K- $\alpha$  peak and a corresponding Si-escape peak, which can complicate the quantification. Nevertheless, the copper foil was not completely separated from the active material, but the K- $\alpha$  signal of copper could be drastically reduced using this procedure. With the use of the adapter rack for the MM 400, twenty reaction vials can be ball milled simultaneously which offers the possibility of high throughput analysis. Furthermore, the ball milling leads to a homogeneous suspension as well as a homogeneous particle size distribution. The active material sizes are in the nanometer range and after the milling procedure, the agglomerates are in a range of 15  $\mu\text{m}$  in size. Afterwards, a portion of 100  $\mu\text{L}$  was transferred and further diluted using 0.01 vol.% TX-100 and arsenic standard solution (1000 mg/L, Certipur®, Merck, Darmstadt, Germany), which was used as internal standard (see Fig. 2). The total end concentration of the internal standard was 1 ppm. All dilutions were carried out using deionized water (18.2  $\text{m}\Omega/\text{cm}^2$ , 5 ppb TOC, Millipore Corporation, Darmstadt, Germany).

For analysis a small portion of 5  $\mu\text{L}$  was transferred onto a siliconized quartz glass carrier (Bruker Corporation, Billerica, MA) and dried by heat at 55 °C.

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