



# Total reflection X-ray fluorescence in the field of lithium ion batteries – Elemental detection in Lithium containing electrolytes using nanoliter droplets<sup>☆</sup>



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## ABSTRACT

In this work, an approach for the measurement of transition metal dissolution from the respective cathode active material  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  is presented. Furthermore, undiluted lithium ion battery electrolyte solutions with practical (=high) salt concentration are used. It is demonstrated, that nanoliter dispensers are capable to compensate the formation of an excessive salt crust compared to conventionally prepared total reflection X-ray fluorescence (TXRF) carriers ( $\mu\text{L}$  droplet application), resulting in improved recovery rates. The quantification is conducted by application of an internal standard solution placed between the sample dots composed of highly concentrated salts.

The application procedures are compared to inductively coupled plasma-optical emission spectroscopy. The recovery rates of the new TXRF sample preparation vary between 98% and 105%, compared to 85% to 90% obtained with the conventional application procedure.

The concentration of transition metals (TMs) in real cells does not exceed a few  $\text{mg L}^{-1}$ . To demonstrate the applicability of the nanoliter droplet approach, components from cells aged by charge/discharge cycling were analyzed. Noteworthy, though the TMs are present in the cathode material in the same amounts, the concentration of nickel in the electrolyte was three times higher than that of manganese ( $1.4 \text{ mg L}^{-1}$  to  $0.4 \text{ mg L}^{-1}$ ). Cobalt could not even be quantified as it did not exceed the limit of quantification ( $\text{LOQ} > 0.3 \text{ mg L}^{-1}$ ). This was further confirmed by the deposition of the TMs on the other cell parts (anode and separator), where nickel showed always the highest value.

## 1. Introduction

As the global energy demand and consumption are constantly rising due to the increasing world-wide population, current and future generations are confronted by challenging tasks. Therefore, renewable energies - like solar and wind power - are used, but suffer from their natural fluctuation in energy production, thus, secondary energy storage facilities are necessary [1,2].

As state-of-the-art technique to address these challenging demands, the lithium ion battery (LIB) is capable of offering high energy and power densities as well as excellent cycle life, energy efficiency and sufficient safety [3]. The LIB was already introduced in the early 1990's by Sony [4]. Nowadays, this technique is widely used in portable electronics, like tablets and smartphones. The working principle is based on redox reactions of the two battery cell electrodes often

referred to as anode and cathode, which serve as hosts for the lithium ion transfer between them [5].

A separator is present acting as physical barrier – to circumvent an internal short circuit – which is soaked with electrolyte, the lithium ion transport media [6–12]. The electrolyte consists of a mixture of linear and cyclic carbonates, like ethylene carbonate (EC) and ethyl methyl carbonate (EMC); several others were reported as well [13–17]. Furthermore, a conductive salt is added to this mixture, widely reported is the use of lithium hexafluorophosphate ( $\text{LiPF}_6$ ) [18]. In general, the LIB concept offers a variety of different electrode materials as well as electrolyte compositions, which is an excellent basis for an interdisciplinary research approach.

State-of-the-art lithium ion batteries suffer from capacity and energy fading especially at extreme operation conditions (e.g. elevated charge cut-off voltages or temperatures), which is referred to as aging in

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literature. The origin of this can be assigned to reactions at the respective electrodes (either carbonaceous anodes or lithium transition metal oxide cathodes), the carbonate based electrolyte of the cell or to reactions of the electrolyte with the electrodes [19–21]. Focusing on aging mechanism of the electrolyte, the main degradation is assigned to the decomposition of the lithium conducting salt  $\text{LiPF}_6$ , which was excessively studied using gas-, ion- and liquid-chromatographic techniques [22–33]. As aging mechanisms referring to the alteration of electrode materials, transition metal dissolution (TMD), particle cracking, phase transformation, lithium plating as well as several other mechanisms were reported [20,34–40].

When the *post-mortem* elemental analysis of the respective electrolyte solution is conducted by plasma-based techniques (ICP-OES/MS), excessive dilution factors are necessary to dilute the high salt and solvent concentrations of the electrolyte. Additionally, the low sample volume that can be extracted from aged battery cells are another limiting factor using plasma-based techniques. However, the high lithium and solvent concentration is not interfering when using X-ray based techniques like total reflection X-ray fluorescence (TXRF) as commercial devices are not capable to detect lithium. Nonetheless, other matrix effects like shading can still occur [41]. The suitability of TXRF analysis in the field of battery research was already shown in previous publications [38,42], focusing on TM detection on carbonaceous anodes. The adaption of elemental analysis to electrolyte solutions was only reported by Terada et al. who performed *in-situ* TXRF of electrolyte solutions [43].

However, there are several issues with the application of high salt and solvent fractions, like in homogeneously dried sample droplets (“doughnut effect”), handling errors during the pipetting process or extended sample heights exceeding the criteria of total reflection. Fittschen et al. already reported the possibility to compensate the above-mentioned effects by application of picoliter and/or nanoliter droplets using inkjet printers [41,44–46].

Here, a new approach for the elemental analysis of LIB electrolytes is presented using nanoliter droplets without prior dilution of the electrolyte with an internal standard, thus, printing the internal standard in between the undiluted electrolyte. First, suitable patterns for the quantification of LIB electrolytes are developed and validated with respect to recovery rates and relative standard deviations of a TM enriched LIB electrolyte. Here, the terms patterns refer to the geometrical array which was applied *via* the nanoliter droplet approach on the quartz glass carriers. Afterwards, the application of the method on components from cells aged by charge/discharge is presented.

## 2. Experimental

### 2.1. Sample preparation

The validation of the respective patterns was conducted using a TM enriched electrolyte solution based on 1 M  $\text{LiPF}_6$  in ethylene carbonate/ethyl methyl carbonate (EC/EMC; 50/50 wt%; LP50, BASF, Ludwigshafen, Germany). The soluble salt species were composed of the bis(trifluoromethane)sulfonimide (TFSI) anion with manganese, nickel or cobalt as cation. All TFSI salts were purchased from Sigma Aldrich (purity 99%, St. Louis, USA) and the standard concentration was set to  $50 \text{ mg L}^{-1}$  by weighting the corresponding amounts of the respective salts using a high precision balance (Cubis QStat, Sartorius, Göttingen, Germany).

### 2.2. Cell assembly and charge/discharge aging procedure

A MesoCarbon MicroBead (MCMB) graphite/hard carbon composite (MTI Corporation, Richmond, USA) served as active anode material and lithium nickel cobalt manganese oxide ( $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ; NCM111, Toda Kogyo Corp., Hiroshima, Japan) as active cathode material. Electrodes based on these materials were prepared in-house. The slurry

preparation process used polyvinylidene difluoride (PVdF, KynarFlex® 761, La Garenne-Colombes Cedex, France) as binder dissolved in *N*-Methyl-2-pyrrolidone (NMP) (99.5%, Acros Organics, New Jersey, USA) as processing solvent. The active mass loadings for the cathode and anode were set at 93% and 95% for NCM and MCMB, respectively. Additionally, carbon black (99.7%, SuperP®, Timcal, Bironico, Switzerland) was added as conductive agent.

For constant current cycling charge/discharge investigations, coin cells were assembled using electrode areas of  $1.13 \text{ cm}^2$  for cathodes and anodes. As separator a hybrid non-woven fiber/polypropylene foil (Freudenberg 2190/Celgard 2500) was used with an area of  $2.67 \text{ cm}^2$  and 1 M  $\text{LiPF}_6$  in ethylene carbonate/ethyl methyl carbonate (EC/EMC, (50/50 wt%) (LP 50, Selectilyte®, BASF, Ludwigshafen, Germany)) acted as electrolyte. Cycling was performed using a Maccor series 4000 battery test system (Maccor Inc., Tulsa, USA) in a voltage window from 3.0 V–4.6 V using a specific current of 160 mA corresponding to charge rates of 1C using  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM111) as cathode active material.

### 2.3. Post-mortem sample pretreatment

*Post-mortem* analysis of the cells was performed by opening the coin cells and placing the electrolyte soaked separator in reaction vials and subsequent centrifugation (8000 rpm, 10 min, Galaxy 5D, VWR, Radnor, USA) of it. The residue electrolytes at the bottom of the reaction vial (20–30  $\mu\text{L}$ ), of which 10  $\mu\text{L}$  was applied for the analysis *via* the nanoliter dispenser. The other residues were used for the comparison with the ICP-OES. The quantification was performed with  $10 \text{ mg L}^{-1}$  gallium ICP standard solution for all nanoliter droplet experiments ( $1000 \text{ mg L}^{-1}$ , Cetripur®, Merck, Darmstadt, Germany).

The centrifuged separator was placed in 2 mL of concentrated nitric acid (65 vol%, Suprapur®, Merck, Darmstadt, Germany) to dissolve residues at the cathode/separator contact area. The collected anodes were washed with 1 mL EMC to rinse off residues of the conducting salt, afterwards the anode was treated by ball-milling and preparing a suspension of the anode. A detailed description is given in [42].

### 2.4. Analytical equipment

#### 2.4.1. TXRF

A Picofox S2 system (Bruker Corporation, Billerica, USA) was used for determining the TM contents in electrolyte solutions. All measurements were carried out on 30 mm quartz glass carriers from Bruker Corporation, which were pre-treated with a silicon solution (SERVA Electrophoresis GmbH, Heidelberg, Germany) for introducing hydrophobic surface properties. The measurement conditions were set to 1000 s irradiation per sample and each sample was measured three times. A molybdenum source served as anode material and generated the X-rays at voltages of 50 kV and currents of 600  $\mu\text{A}$  corresponding to excitation energies of 17.5 keV.

#### 2.4.2. Nanoliter dispenser

The iTWO-TXRF Nanoliter Dispenser (M2 Automation, Berlin, Germany) was used in order to ensure undiluted sample preparation of cycled battery electrolytes. Therefore, the non-woven/polymeric hybrid separator were centrifuged as described above and then different patterns (geometrical array on the quartz glass carrier, see Fig. 1) were applied to transfer the spiked electrolyte solution onto the quartz glass carrier. After the application of the electrolyte and the internal standard, the droplets were dried at  $55^\circ\text{C}$  directly in the device. The total volume which was applied in one droplet varied between  $14.8 \pm 1.0 \text{ nL}$  and  $15.4 \pm 0.3 \text{ nL}$  depending on the liquid and was determined gravimetrically ( $n = 3$ ). The total area of all developed deposition patterns was  $49 \text{ mm}^2$  to match the dimension of the TXRF beam of the Picofox S2. Furthermore, all patterns were applied to a field of  $23 * 23$  separated grids (529 pixel) in order to obtain accurate

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