Investigation of the Mesoscale State-of-Charge Distribution in Lithium Ion Battery Cathode Materials by means of Classification-Single-Particle Inductively Coupled Plasma Optical Emission Spectroscopy

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Introduction

- The **state-of-charge (SOC) distribution is an important indicator for the level of synchronization of the (de)lithiation reactions at the mesoscale** and thus for the macroscale capacity utilization of the battery
  - Under ideal conditions, all particles of the cathode active material are uniformly (de)lithiated during the charging and discharging process
    - Many reasons exist that can lead to contact loss, which inhibits the (de)lithiation of individual particles (see **Figure 1**)

- **Disadvantages of exemplary state-of-the-art diagnostic techniques**
  - Synchrotron-based techniques (*e.g.*, transmission X-ray microscopy)
    - Only indirect investigation of SOC by evaluating the Ni oxidation-state distribution
    - Limited by the highly specialized instrumentation required and the associated low available measurement time

- **Classification-Single-Particle Inductively Coupled Plasma Optical Emission Spectroscopy (CL-SP-ICP-OES)**
  - Measurements directly based on the lithium content of single particles
  - Application of widespread commercial ICP-OES instruments
  - Statistically viable elucidation of the mesoscale SOC distribution

- **Promising first results with CL-SP-ICP-TOF-MS presented**

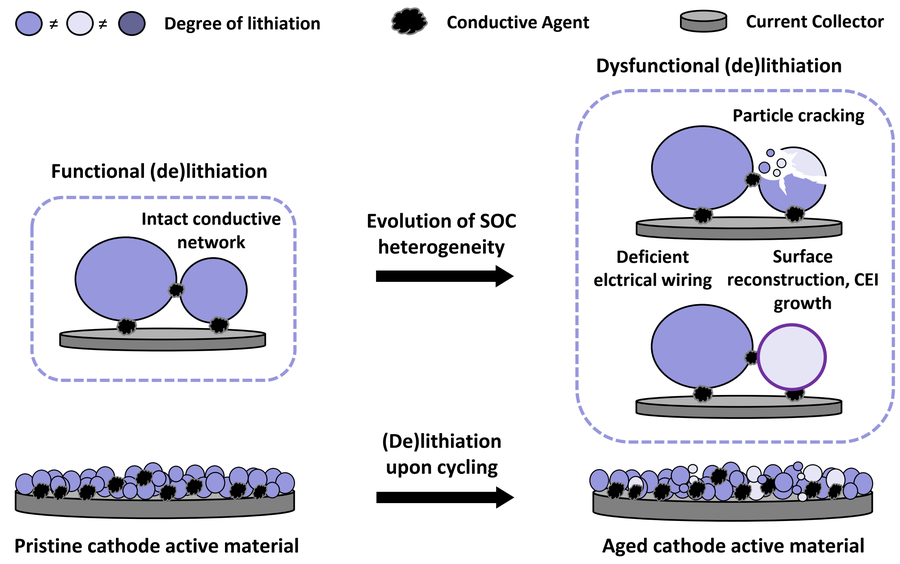


Figure 1: Schematic representation of aging phenomena potentially leading to the evolution of SOC heterogeneity

Method

Matrix-matched external calibration

- Calibration for SP analyses commonly performed with monodisperse particle size standards
  - **No size standards available for cathode active materials**

- Electrochemically delithiated $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ (NMC532) as cathode active material with different SOCs is used as a matrix-matched external calibration
  - The SOCs enable the simulation of different degrees of lithiation (DOLs) on particle level for the investigation of the mesoscale SOC distribution

- After delithiation and thus lower mean DOLs, the mean intensity ratio of Li and, e.g., Mn (I(Li)/I(Mn)) on a single particle level decreases linearly as obtained after acidic microwave digestion with ICP-OES in solution mode and by CL-SP-ICP-OES, respectively (see **Figure 2 a.)**)

- Mean DOLs correlate in a linear relationship to the different SOCs (see **Figure 2 b.)**)

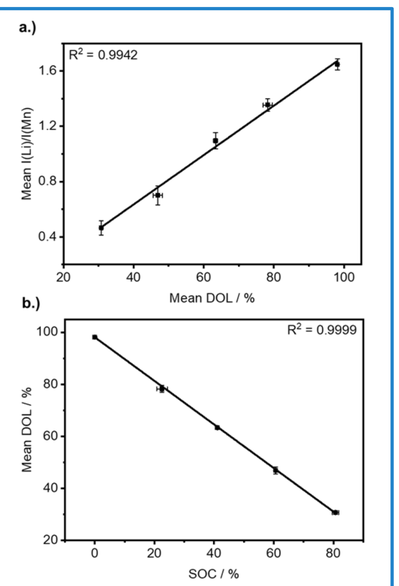
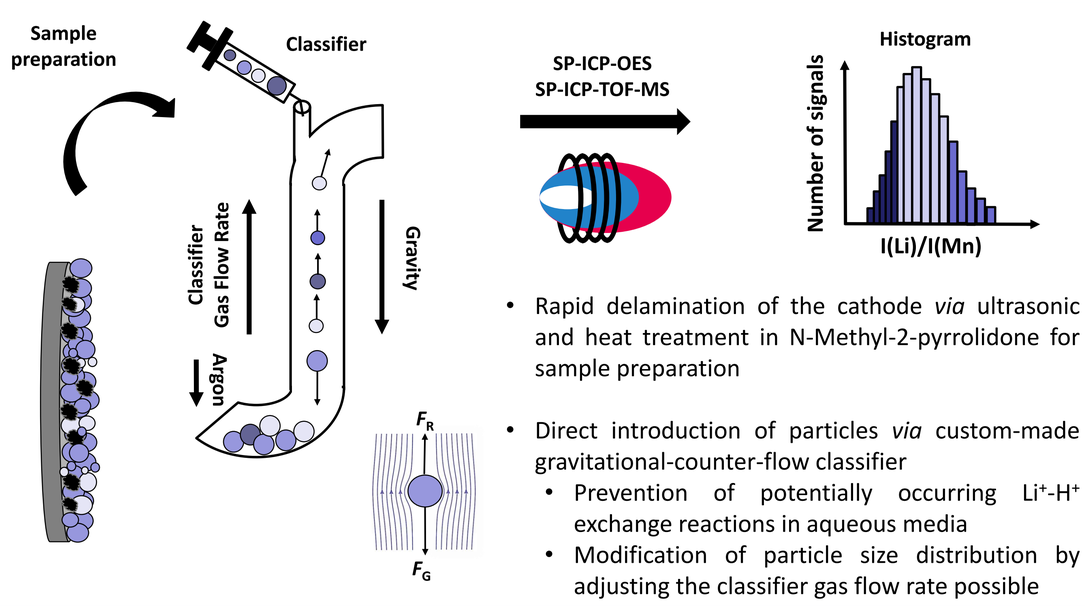


Figure 2: Results of the calibration approach

Sample preparation and single particle analysis



- Rapid delamination of the cathode *via* ultrasonic and heat treatment in N-Methyl-2-pyrrolidone for sample preparation

- Direct introduction of particles *via* custom-made gravitational-counter-flow classifier
  - Prevention of potentially occurring Li^+-H^+ exchange reactions in aqueous media
  - Modification of particle size distribution by adjusting the classifier gas flow rate possible

Results

CL-SP-ICP-OES

- The particles are directly introduced into the plasma as a quasi-continuous flow (see **Figure 3**)

- ICP-OES measurements were performed using the **ARCOS from SPECTRO Analytical Instruments GmbH** with axial plasma viewing and integration times of 100 ms
  - Particle number concentration is monitored online by flow cell particle analysis
    - Evaluation of the possibility to achieve single-particle events by means of Poisson statistics

- The contact loss described above manifests itself in the immobilization of active lithium in isolated particles
  - By determining the intensity ratio of Li and, e.g., Mn (I(Li)/I(Mn)), isolated particles can be identified and counted (**see Figure 4 b.)**)

- Time-of-flight secondary ion mass spectrometry (TOF-SIMS) results confirm the evolved SOC heterogeneity as indicated by CL-SP-ICP-OES (see white arrows in **Figure 5**)

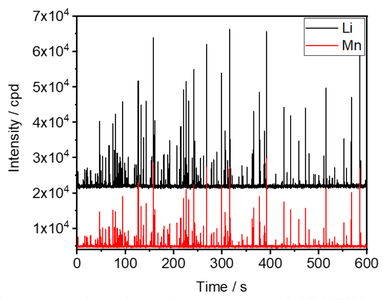


Figure 3: Acquired time scan of Li 670.776 and Mn 257.611 nm by CL-SP-ICP-OES

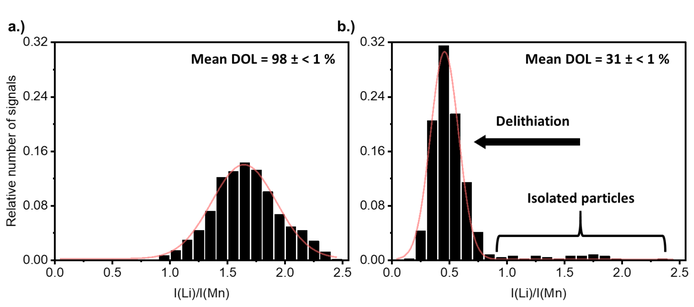


Figure 4: Relative histograms of the particle intensity ratios of Li and Mn of a.) pristine and b.) electrochemically delithiated NMC532

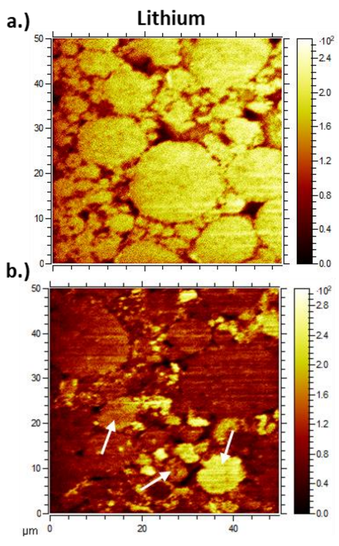


Figure 5: TOF-SIMS mappings of a.) pristine and b.) electrochemically delithiated NMC532

CL-SP-ICP-TOF-MS

- First SP-ICP-TOF-MS measurements were performed using the **Vitesse from Nu Instruments Ltd.** with integration times of 116 µs
  - Quasi-simultaneous event-resolved multi-element detection of single NMC532 particles (see **Figure 6**)
    - Significant reduction of measurement time compared to CL-SP-ICP-OES (> 98 %)
      - > 4500 particle events in 5 min with Vitesse

- In contrast to CL-SP-ICP-OES, the high sensitivity also allows a statistically viable investigation of the particle intensity ratios of ^7Li and ^{60}Ni and ^7Li and ^{59}Co

- Fast and intuitive data evaluation was performed with the Nu Quant software

- Bimodal distribution in the histogram of pristine NMC532 observed (see **Figure 7**)
  - Further research needed for the explanation

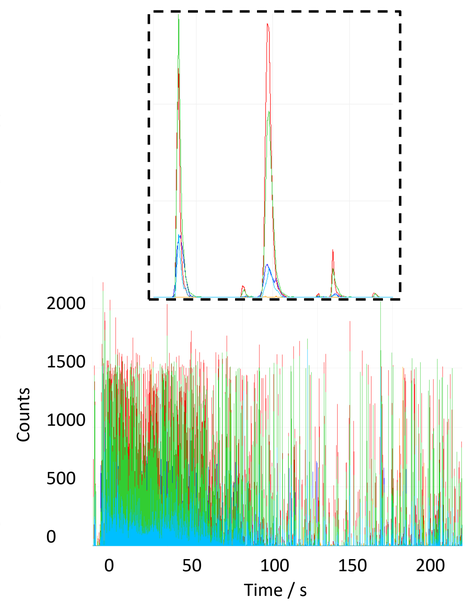


Figure 6: Acquired time scan of ^7Li, ^{60}Ni, ^{55}Mn and ^{59}Co by CL-SP-ICP-TOF-MS with magnified single particle events

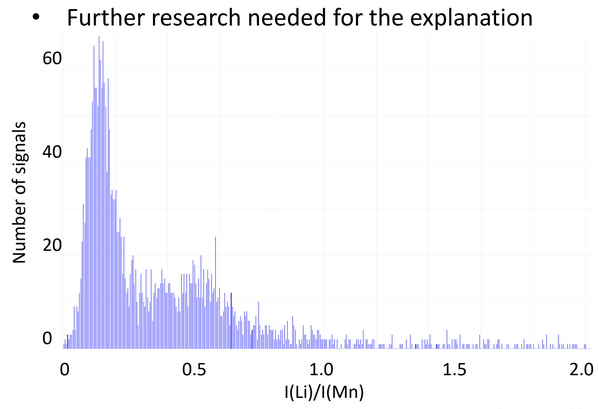


Figure 7: Histogram of the particle intensity ratios of ^7Li and ^{55}Mn of pristine NMC532

Conclusions / Outlook

- The application of CL-SP-ICP-OES enables the investigation of the mesoscale SOC distribution by evaluating the peak intensity ratio of Li and Mn as confirmed by TOF-SIMS
- Promising first results with the Vitesse are presented that can contribute to the mesoscopic research of the SOC distribution
- Further research with CL-SP-ICP-TOF-MS is needed to exploit the potential
- Coupling of laser ablation to SP-ICP-TOF-MS to enable the mapping of the SOC distribution with high lateral resolution throughout the cathode

Literature

Kröger, T.-N., Wiemers-Meyer, S., Harte, P., Winter, M., Nowak, S., Anal. Chem., 2021, 93, 7532 7539.
Kröger, T.-N., Harte, P., Klein, S., Beuse, T., Börner, M., Winter, M., Nowak, S., Wiemers-Meyer, S., J. Power Sources, 2022, 527, 231204

Acknowledgement

The authors would like to acknowledge the German Federal Ministry of Economic Affairs, Innovation, Digitalisation and Energy of North Rhine-Westphalia for funding the project "KWKplus Speicher" (PRO0067D).
The authors would like to acknowledge Lukas Schlatt from Nu Instruments Ltd. for performing the measurements in collaboration with the MEET battery research center.

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