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 macroscopic 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 reactions 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
  - Synchrontron-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-ES)
  - Measurements directly based on the lithium content of single particles
  - Application of widespread commercial ICP-ES instruments
  - Statistically viable elucidation of the mesoscale SOC distribution
- Promising first results with CL-SP-ICP-TOF-MS presented

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[Ni0.5Mn0.35Co0.15]O2 (NMC532) as cathode active material with different SOC is used as a matrix-matched external calibration
- The SOC's enable the simulation of different degrees of delithiation (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 after acidic microwave digestion with ICP-ES in solution mode and by CL-SP-ICP-ES, respectively (see Figure 2 a, b)
- Mean DOLs correlate in a linear relationship to the different SOCs (see Figure 2 b, c)

Results

- The particles are directly introduced into the plasma as a quasi-continuous flow (see Figure 3)
- ICP-ES 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 a, b)
  - Time-of-flight secondary ion mass spectrometry (TOF-SIMS) results confirm the evoked SOC heterogeneity as indicated by CL-SP-ICP-ES (see white arrows in Figure 5)

Conclusions / Outlook

- The application of CL-SP-ICP-ES 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 Vitessa 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

Method

- 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 Li¹⁻H⁻ exchange reactions in aqueous media
  - Modification of particle size distribution by adjusting the classifier gas flow rate possible

Acknowledgement

Literature