vitesse

Vitesse Note **NT09**

Very low mass isotope data collection with the Nu Vitesse, using single particle multi-element ICP-MS for lithium battery electrode materials

Keywords:
Lithium ion battery materials
Single particle multielement ICP-MS
Very low mass performance
Nanoparticle composition

Introduction
Time-of-flight ICP-MS is recognised as a simultaneous elemental analysis technique but the intrinsic qualities of a time-of-flight mass spectrum mean that sensitivity for very low masses is much lower than for higher masses. The use of a multipole device in the reaction cell to remove interferences also introduces a mass bias in the instrument response which is somewhat overcome in the Nu Vitesse by the use of an axial field gradient across the reaction cell, but not completely. The pressurising of the cell and required RF field needed to obtain broad band transmission across the mass range generally means that sensitivities below 23Na are too low to be useful in full mass range spectra. This note will show how very low mass data can be obtained with specific tuning conditions and how this benefits certain applications such as the analysis of battery materials.

Nanoparticulate battery electrode materials
Multielement analysis covering from mass 7 to mass 75 is required for the analysis of nanoparticulate electrode materials used in lithium-ion battery technologies after lithiation and de-lithiation from the charge/discharge process. The battery electrode materials degrade in the presence of moisture so two different sample introduction methods were used to examine the nanoparticulate compositions. The first used a gravitational counter-flow classifier device developed at MEET, Munster, Germany, where particles released from the electrode surface by ultrasonicification in N-methyl-2-pyrrolidone were introduced to the ICP (figure 1). Changing the counter-gas flow changed the particle size distribution so the composition of particles relative to size could be examined.

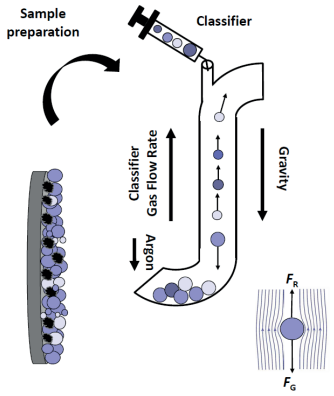

Figure 1: Schematic representation of the sample preparation technique developed at MEET.[1] The nanoparticles are released from the electrode surface into a non-aqueous solvent, aliquots of which are injected into a counter flowing argon stream which can be adjusted to vary the number and size distribution of particles arriving in the plasma.

The second method used low fluence laser ablation to release particles from the electrode surface which could then be measured using the single particle technique. The ablation technique used an 193nm Excimer laser with 10µm spots and 20Hz ablation at <<1J/cm^2 fluence (figure 2).

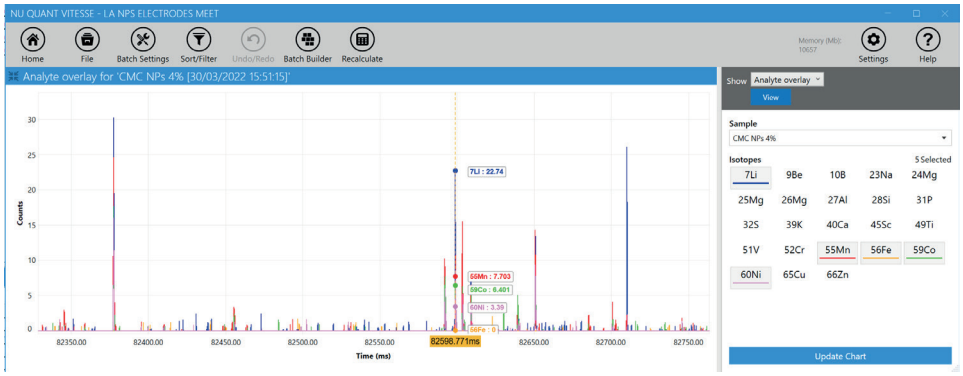

Figure 2: Showing the nanoparticle signals from the release of electrode materials using low fluence laser ablation to sample the surface without the use of a solvent. Data was processed using single particle mode to determine the particle compositions of each electrode.

Tuning for low mass performance
Reducing the gas flows into the reaction cell so only the minimal amount needed is used to remove the argon interferences means that the scattering of very low mass ions is drastically reduced. By also then reducing the RF amplitude of the voltage applied to the reaction cell multipole, the transmission of very low mass ions is increased but with a reduction in the mid and high mass performance.

vitesse

The reaction cell gas flows and axial field can then be tuned to obtain narrow peak widths for nanoparticles and maintain the optimised performance for very low mass ions. This then allows single particle measurements of lithium containing nanoparticles along with elements of the first row transition metals in the same manner as previously seen in SP-ICP-TOF-MS with the Nu Vitesse (figure 3).

Figure 3: Upper figure shows the nanoparticle signals of lithium battery electrode materials captured over 40 seconds using the gravitational counter flow device. The lower image is a zoomed section (14.32s – 14.39s) showing the traces for individual particles collected with 80µs spectra.

Comparing composition of different materials

The elemental content found in each particle can be evaluated in a variety of ways using both the internal Python scripts of Nu Quant or via 3rd party software packages. Graphical representation and principal component analysis can be used to identify distinct stoichiometric differences in samples, filtering then allows the composition to be for the mix of elements for particles associated only with lithium (Figure 4).

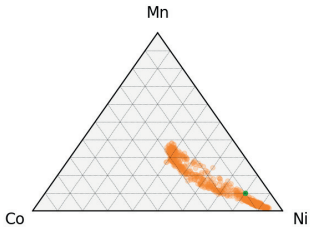

Figure 4: Ternary plot of manganese, cobalt and nickel in particles identified to contain lithium from battery electrode material. The green spot indicates the expected relative composition.

Conclusion

It has been possible to collect data for lithium in the same spectra as the first row transition metals for a range of nanoparticle materials used in lithium ion battery electrodes. The flexibility of tuning and high speed data acquisition of the Nu Vitesse along with the powerful use of nanoparticle detection algorithms and Python scripts for data evaluation makes it easier to undertake high quality research on these critical new technologies for batteries.

References:

1. Kroger, T. N.; Wiemers-Meyer, S.; Harte, P.; Winter, M.; Nowak, S.: Direct Multielement Analysis of Polydisperse Microparticles by Classification-Single-Particle ICP-OES in the Field of Lithium-Ion Battery Electrode Materials. Analytical Chemistry 2021, 93, 7532-7539.

Acknowledgements:

Thanks go to Till Niklas Kröger, Dr. Sascha Nowak and Dr. Simon Wiemers-Meyer from the University of Münster, MEET Battery Research Center, Corrensstraße 46, 48149 Münster, Germany.