Experiment Brief

OnPoint Detector and Octane Elite Super EDS System

Title

Lithium quantification using the composition-by-difference method

Instruments Used

Gatan's OnPoint™ detector and EDAX's Octane Elite Super EDS system were used in combination to determine the lithium concentration in a stoichiometric lithium oxide sample.

Background

Lithium (Li)-ion based batteries have been adopted in electrochemical cells due to their capacity for energy storage at high-energy densities and lighter mass compared to other technologies. However, there remains a significant requirement for a characterization technique that allows the microscale distribution of Li to be determined. Commonly used microanalysis techniques in the scanning electron microscope (SEM) such as energy- or wavelength-dispersive x-ray spectroscopies (EDS or WDS) cannot be applied to low atomic number elements ($Z \leq 3$), including lithium due to the dependence of the fluorescence yield on bonding state and likelihood of x-ray re-absorption [P. Hovington et al., Scanning 38 (2016) p571–578]. However, recent work on metallic alloys demonstrated quantitative analysis of Li in the SEM with ~1 wt. % accuracy using the lithium by composition-by-difference method (Li-CDM) [JA. Österreicher et al., Scripta Materialia 194 (2021) 113664]. In the Li-CDM, the EDS and backscattered electron (BSE) signals are recorded quantitatively, allowing the lithium content to be determined through computation. Here, we extend this approach to materials of known stoichiometry, determining the Li content of lithium aluminate ($LiAlO_2$) with an accuracy better than 1.0 wt. %.

Materials and Methods

A high purity (99.99 %) $LiAlO_2$ (100) crystal substrate was analyzed by Li-CDM after planar-polishing using a Gatan PECS™ II system. qBSE analysis of 56 materials was performed using the OnPoint BSE detector, and an excellent correlation was observed between the measured qBSE and the mean atomic number, $\bar{Z}$ (Figure 1). EDS analysis using the Octane Elite Super EDS detector revealed the Al and O content but, as expected no Li peak was observed. Li-CDM analysis was then performed using DigitalMicrograph® software. The nominal and experimentally derived composition of the $LiAlO_2$ sample is summarized in Table I.

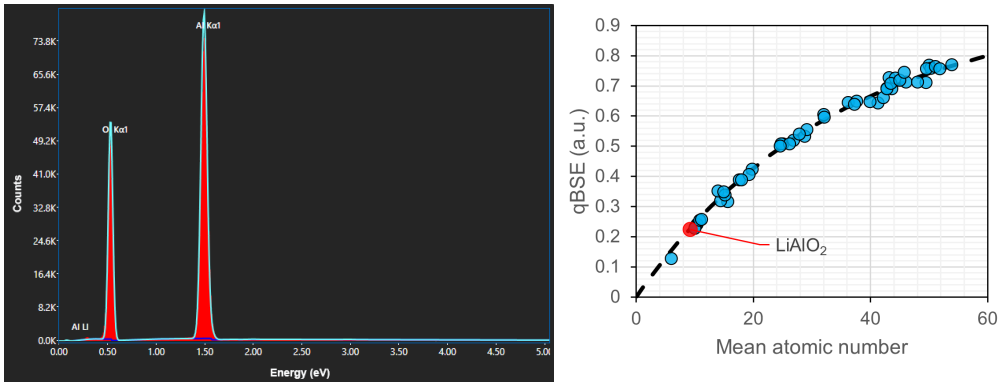

Figure 1. (left) EDS spectrum from $LiAlO_2$ sample. Captured at an accelerating voltage of 20 kV with 50 s exposure time. (right) Quantitative backscattered electron signal (qBSE) plotted against mean atomic number.

Elemental Composition

	Li	Al	O
Stoichiometry			
at. %	25.0	25.0	50.0
Standard dev.	–	–	–
EDS			
at. %	–	29.6	70.4
Standard dev.	–	1.6	5.1
Composition by difference			
at. %	22.5	22.9	54.6
Standard dev.	3.50	1.03	3.95

Table I. Elemental quantification results of $LiAlO_2$ sample.

Summary

Li-CDM determined the Li content of an $LiAlO_2$ stoichiometric sample to be 22.5 ± 3.50 at. % (9.48 ± 1.71 wt. %), within 2.5 at. % and only 1.0 wt. % of the nominal composition 25.0 at. % (10.5 wt. %). These results validate the Li-CDM for a wider range of materials opening exciting characterization possibilities in lithiated battery materials.

Credit(s)

A special thanks to Dr. Johannes Österreicher and the Austrian Institute of Technology for the invention of the Li-CDM.

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