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On the Accuracy of the Composition-by-difference Method for Determining Lithium Content in Oxides

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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 [1]. However, recent work on metallic alloys demonstrated quantitative Li mapping in the SEM with ~1 wt. % accuracy using the composition-by-difference method [2] (CDM). In the CDM method, quantitative EDS is combined with the quantitative backscattered electron (qBSE) signal to calculate the 'missing' lithium content. Here, we extend this approach to other materials of known stoichiometry, determining the Li content of lithium aluminate with an accuracy better than 2.5 at. % (1.0 wt. %).

A high purity (99.99 %) lithium aluminate, $LiAlO_2$, (100) crystal substrate (MSE Supplies) was analyzed. The sample was planar-polished, and a 2 nm carbon coat applied using a PECS™ II system (Gatan Inc.). CDM analysis was performed in a field emission SEM using an OnPoint™ detector (Gatan Inc.) to collect the qBSE signal and an Octane Elite Super detector (EDAX LLC) to capture EDS spectra (Fig. 1). The OnPoint detector was calibrated for $6 < Z < 61$ using 56 polished mineral standards (Electron Microscopy Sciences). Elemental quantities were determined from the EDS spectrum using APEX software (EDAX LLC), the qBSE calibration and Li content were evaluated using DigitalMicrograph® software (Gatan Inc.).

The qBSE signal as a function of mean atomic number, $\bar{Z}$, is plotted in Fig. 2 with $\bar{Z}$ calculated using the mass average (1) and modified electron fraction (2) approaches (after [3]):

$$\bar{Z} = \sum_{i=1}^{n} c_i Z_i \quad \ldots (1), \qquad \bar{Z} = \frac{\sum_{i=1}^{n} a_i Z_i^{(x+1)}}{\sum_{i=1}^{n} a_i Z_i^{x}} \quad \ldots (2)$$

where c_i and a_i represent the mass and atomic fractions of element i respectively and x is an exponent typically close to unity (here $x = 0.8$) and accounts for screening effects. In line with other publications (e.g., [4]), the qBSE signal was fit to the function:

$$qBSE(\bar{Z}) = C\left(1 - \mathrm{e}^{-\bar{Z}/q}\right) \quad \ldots (3)$$

where C and q are constants related to the SEM and detector settings. For compounds with $\bar{Z} < 25$, excellent fit was observed for the mass average and modified electron approaches, however, for $\bar{Z} > 25$, the modified electron approach showed closer adherence to the fit.

The nominal and experimentally derived composition of the $LiAlO_2$ sample is summarized in Table I. The Li content was determined 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 CDM method for a wider range of materials opening exciting characterization possibilities in lithiated battery materials.

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

	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

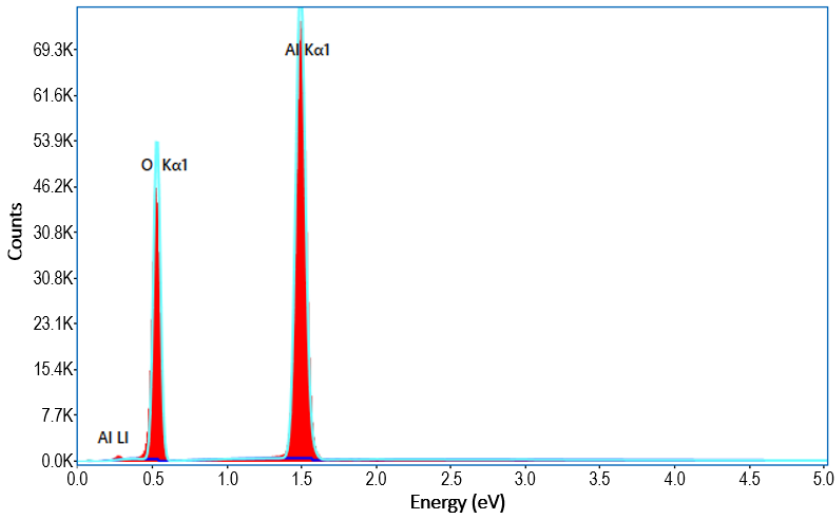

Figure 1. EDS spectrum from $LiAlO_2$ sample. Captured at 20 kV with 50 s exposure time.

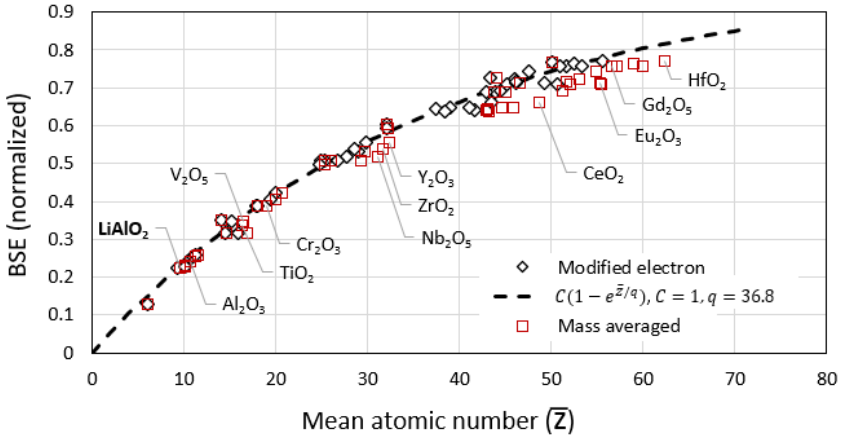

Figure 2. Normalized BSE signal against mean atomic number. Mean atomic number calculated using modified electron (◇) and mass fraction (□) approaches.

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