



Spatial lithium quantification by backscattered electron microscopy coupled with energy-dispersive X-ray spectroscopy[☆]

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ABSTRACT

The quantification of lithium in electron microscopes by energy-dispersive X-ray spectroscopy (EDS) is highly challenging due to the low energy of the characteristic X-rays. Only special windowless detectors can detect Li, yet the sensitivity is suboptimal (i.e., ~20 wt. %). We introduce the use of quantitative backscattered electron microscopy in combination with measurements using a standard EDS sensor to achieve spatially resolved quantification of Li. The method is demonstrated using two Mg-Li alloys with 4 and 20 wt. % Li and good accuracy with a deviation of only ~1.2 wt. % and ~2.5 wt. %, respectively, is achieved.

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In the wake of the ever-increasing technological significance of Li-ion batteries, Li detection has become the holy grail of energy-dispersive X-ray spectroscopy (EDS). The characteristic X-rays emitted by Li under the electron beam are low-energetic (~55 eV) and thus absorbed by EDS detector windows. Although windowless detectors capable of detecting Li are available, they are expensive and very delicate. Furthermore, most of the generated X-rays are absorbed by the sample itself. Therefore, despite higher depth of penetration by the electron beam, the information depth is much lower than for heavier elements. To make matters worse, the intensity of X-rays is dependent on the bonding state and the mechanisms of X-ray generation are not well-understood [1]. Due to these fundamental physical constraints, the available EDS detectors for Li have limits for detection and quantification of ~20 wt. % [1,2]. Keeping in mind the low atomic number of Li, this can account for 50 at. % and more of a sample. As alternatives to EDS, techniques such as electron energy-loss spectroscopy (EELS) [3], high-resolution X-ray diffraction-computed tomography [4], or focused ion beam (FIB) milling coupled with time-of-flight mass spectroscopy (TOF-MS) [2] have been used but the experimental effort of any of these approaches is high.

Here we present a method for spatially resolved Li quantification that can be performed in a standard scanning electron micro-

scope. This is accomplished by coupling quantitative backscattered electron imaging (qBEI) with conventional EDS.

The grey value S (typically expressed as an eight bit value, i.e., a dimensionless value between 0 and 255) of an element in backscattered electron (BSE) microscopy is directly related to backscattered coefficient η which is a function of the atomic number Z . For mixtures of elements, the following simple relationship can be used for the mean backscattered coefficient [5]:

$$\bar{\eta} = \sum_{i=1}^n c_i \eta_i$$

where c_i is the weight fraction and η_i is the backscattered coefficient of element i . qBEI takes these relationships into account and allows for the determination of the mean atomic number Z of a region of interest (ROI) if the grey values of some standards with known composition in the relevant Z range have been recorded for calibration under the chosen imaging conditions. If the ROI is composed of light elements and a heavier element, the concentration of the heavier element can be estimated. Such is the case in bone where the Ca mineralization can be measured using qBEI [6,7].

A similar approach would be promising for Li detection in binary compounds or compounds of Li with elements of very similar backscattered coefficient (that can be averaged as a single value), such as Mg and Al. For more complex mixtures, however, direct quantification of the Li content only is possible if the proportions of the other elements are known. This information can be obtained using EDS, even if Li itself cannot be detected.

[☆] Dedicated to Professor Peter J. Uggowitzer on the occasion of his 70th birthday.

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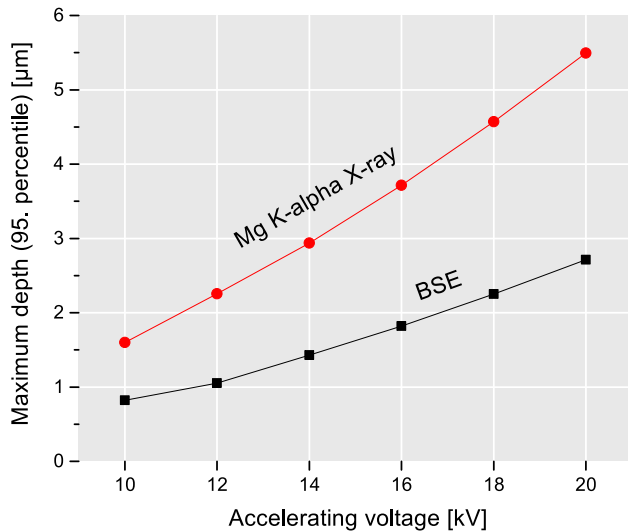


Fig. 1. Maximum escape depth for the 95. percentile of non-absorbed Mg K-alpha X-ray and BSE, respectively, in a Mg alloy with 20 wt. % Li.

For practical implementation, the method can be described as follows:

- 1 Calibration of various grey values using elemental standards or standards of known composition
- 2 Measurement of the grey value \bar{S}_{ROI} and EDS spectrum of a ROI
- 3 Calculation of the mean grey value \bar{S}_{others} of the other elements using their proportions obtained by EDS
- 4 Calculation of the Li content $x = \frac{\bar{S}_{ROI} - \bar{S}_{others}}{\bar{S}_{Li} - \bar{S}_{others}}$ where \bar{S}_{Li} is the grey value produced by Li which can be calculated from the calibration (1.), derived by Monte Carlo simulation of electron backscattering, or approximated as 0.

Several practical aspects should be considered when performing such measurements. First, we obtained better results when the contrast and brightness (gain and offset) of the detector were set such that the grey values of the calibration standards produced mid-range grey values. Furthermore, no extreme values (0 or 255) should be present in the areas of interest.

Secondly, the interaction volume of characteristic X-rays is larger than that of BSE (except for Li and possibly other very light elements). Therefore, we performed BSE imaging with a higher voltage (20 keV) than EDS (14 keV) so that the interaction depth of the 95. percentile of BSE and X-rays, respectively, is roughly the same. The voltages that fulfil these conditions were obtained by Monte Carlo-simulation of several combinations of the light elements Li, Mg, and Al using CASINO 2.5.1.0 [8]. The results for a hypothetical MgLi20 alloy are given in Fig. 1. Alternatively, equal voltages could be used when the features to be measured are larger than the interaction volume of characteristic X-rays.

S may increase at a greater than linear range with Z as the signal of the solid-state detector depends both on the number of BSE and on their energy [5]. Heavier elements backscatter more energetic electrons. To account for this effect, we used S/η over Z instead of S over Z for the calibration. The backscattered coefficients were obtained by simulation with CASINO 3.3 [9].

The alloys were cast as billets with a diameter of 28 mm and a height of 112 and 122 mm (LAX410 and LSX2021, respectively) using an electric induction furnace and Ar shielding gas.

A Tescan Mira 3 field-emission scanning electron microscope equipped with a Ametek EDAX Octane elect super (70 mm²) silicon drift detector for EDS was used. EDS was performed at 14 kV. EDAX TEAM software, version 4.5.1, was used for EDS quantifica-

Table 1

Nominal alloy compositions (wt. %).

	Mg	Li	Al	Si	Ca
LAX410	Base	4	0.8	–	0.3
LSX2021	Base	20	–	2	1

Table 2

Mg, Al, Si, and Ca concentrations measured by EDS, grey values S measured by qBEI, and calculated Li contents.

	LSX2021		LAX410		
	ROI1	ROI2	ROI1	ROI2	ROI3
Mg (wt. %)	98.5	69.8	99.3	84.1	60.6
Al (wt. %)	–	–	0.6	8.2	18.1
Si (wt. %)	0.5	13.1	–	–	–
Ca (wt. %)	0.9	17.2	0.2	7.7	21.3
Calculated \bar{S}_{others}	140	167	139	151	171
Measured \bar{S}_{ROI}	119	169	136	148	178
⇒ x Li (wt. %)	17.5	–	2.8	2.2	–

tion by calculating atomic number (Z), absorbance (A), and fluorescence (F) correction factors (ZAF corrections). A four-quadrant solid-state BSE detector was used for imaging at 20 kV. The gain of the individual segments was set to an average value of 23% and the offset was set to an average of 96%. The output gain (“contrast”) was set to 0% and the output offset (“brightness”) was set to 48%.

As qBEI standards, technically pure Mg, Al foil, and a Si single crystal were used. For calibration, we zoomed in at the matrix to avoid possible inhomogeneities.

Li alloys were mechanically grinded/polished using standard metallographic techniques and water-free diamond suspension as a last step (Struers DP-Suspension P, 1 μm). They were transferred to the microscopy laboratory covered with isopropanol to avoid oxidation, dried, and brought into vacuum as quickly as possible.

Glow-discharge optical emission spectroscopy (GDOES) of MgLi20Ca1Y0.5, MgLi20Ca5Y0.5, MgLi20Ca5Y1, and MgLi20Ca5Y2 was carried out using a Spectruma Analytik GDA750 device by an external accredited testing laboratory.

In the following, we demonstrate the technique using two Mg-Li-based alloys LAX410 and LSX2021, the nominal compositions of which are given in Table 1. Mg-Li are the lightest structural alloys and can exhibit exceptional specific strength [10]. Fig. 2 gives BSE micrographs of the two alloys with contrast and brightness optimized for qBEI (0%/48%) with marked linescans over ROIs. As qBEI standards, Al, Mg and Si were used. The qBEI calibration is given in Fig. 3. It should be noted that calculated S values greater than 255 can be used in the calibration while experimentally, this would lead to overexposure.

CALPHAD calculations (ThermoCalc 2020a, TCMG5 database) show that the Li concentrations in the HCP Mg matrix for LAX410 and in the BCC Mg matrix for LSX2021 are expected to be near the nominal composition of the alloys (see supplementary materials). Using the calibration shown in Fig. 3 and EDS quantifications of Mg, Al, Si, and Ca, we obtained values of 2.8 and 17.5 wt. % for the matrix (ROI1) of the two alloys (Table 2); these values are indeed near the nominal compositions of 4 and 20 wt. %, respectively. ROI2 in LSX2021 and ROI3 in LAX410 produced slightly higher \bar{S}_{ROI} values than calculated from EDS (\bar{S}_{others}), indicating the absence of Li in these phases. ROI2 in LAX410 resulted in a Li content 2.2 wt. %. The particle in ROI2 appears to have an internal dendritic structure. Therefore, we suggest that the Li content is due to intergrowth of dendrites of Li-free intermetallics (e.g., Al₂Ca or Mg₂Ca Laves phase particles) with Li-containing matrix.

As a comparison, glow-discharge optical emission spectroscopy (GDOES) of four other Mg alloys with 20 wt. % Li (similar to

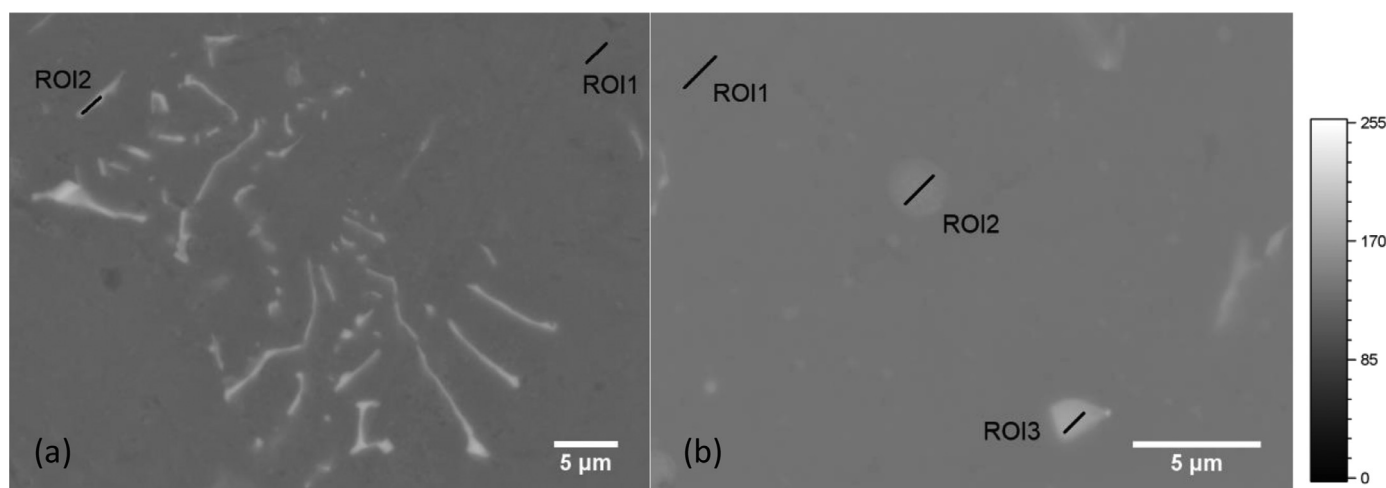


Fig. 2. qBEI micrographs with marked linescans over ROIs of (a) LSX2021 and (b) LAX410.

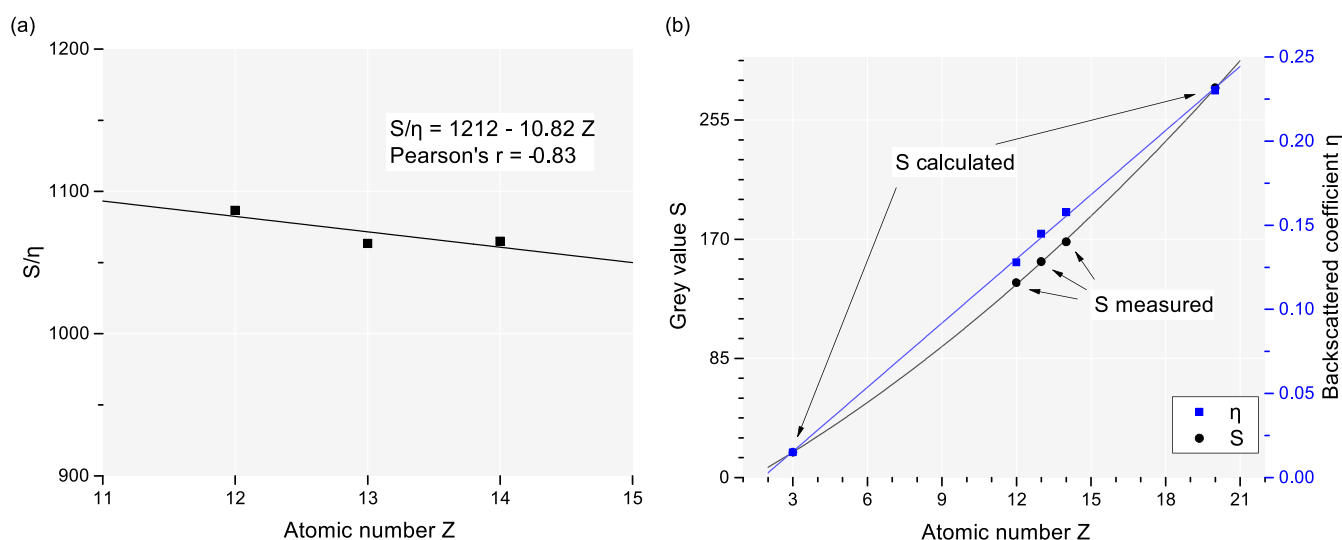


Fig. 3. (a). qBEI calibration using measured S and simulated η values (b) measured and calculated S and simulated η .

LSX2021) was performed by an external accredited testing laboratory and the nominal Li composition was found to be present in our alloys, i.e., Li contents of wt. %.

The results show that even single-digit mass percentages of Li (as are typical in Li-ion battery electrodes) can be quantified using qBEI coupled with EDS with acceptable accuracy. Thus, the sensitivity of windowless EDS detectors is exceeded. The bonding state of Li is of no concern since electron backscattering is governed by the nucleus. Additionally, the information depth of BSE is much larger than for Li characteristic X-rays. Further research could use a wider range of qBEI standards to improve accuracy and focus on automating the method.

Limitations of the method could be posed by surface roughness influencing the BSE signal as well as by the presence of unknown quantities of other light elements undetectable by EDS, such as H.

Although we demonstrated the method for scanning electron microscopy (SEM), similar approaches could be followed in transmission electron imaging (TEM) using Z-contrast techniques such as high-angle annular dark-field (HAADF).

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Declaration of Competing Interest

An Austrian patent application (A 50783/2020) for the method has been filed by LKR Light Metals Technologies, a subsidiary of Austrian Institute of Technology. Besides this, the authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.scriptamat.2020.113664](https://doi.org/10.1016/j.scriptamat.2020.113664).

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