Si/C composite anodes are of great interest for increasing the energy density of Li-ion cells. We report the applicability of the glow discharge optical emission spectroscopy (GD-OES) technique to detect and quantify the Si distribution in Si/C composite anodes. The calibration was developed in the range of 0−100 wt.-% Si by lab coated samples, which are similar to real anodes. The method was verified by pristine real Si/C composite anodes with known compositions (11 wt.-% and 67 wt.-% Si) before being built into cells. Finally, a first attempt of analyzing the Si/C composite anode from a commercial 18650-type cell is presented.

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The increasing need for efficient stationary and mobile high-energy storage systems, throughout human induced climate change, have motivated the further development of lithium-ion (Li-ion) batteries. Since this battery technology was first brought to the market in 1991 by Sony,1 energy density has continuously been improved. Within the development effort, elemental Si has become a prominent candidate to replace graphite as the material used in the negative electrode (anode), due to the higher theoretical specific capacity (3579 mAh g−1 for Si vs. 372 mAh g−1 for graphite).2 On the other hand, pure Si induces high mechanical stress to the anode, which can be reduced by using Si/C composite materials.

However, to best of our knowledge, there is no fast method available to measure depth profiles of Si in composite anodes, which is highly important for quality assurance, electrode development, and post-mortem studies. Using the known methods, one intrinsically will face several problems with the depth resolved quantification of Si; e.g. energy dispersive X-ray analysis (EDX) is neither capable quantifying nor providing a depth profile of Li. In inductively coupled plasma mass spectrometry (ICP-MS), Si is not easily accessible (hazardous conditions e.g. working with HF) and no depth-profile can be obtained. In X-ray photoelectron spectroscopy (XPS), the removal rates in the sputtering process are very low and therefore depth profiles are only possible if the surface of the topmost electrode is well distinguished. Glow discharge optical emission spectroscopy (GD-OES) is a promising technique to access both, depth profiles across the whole depth of electrodes and a variety of elements including Si and Li. Saito and Rahman and Takahara et al.,3 firstly developed GD-OES methods for Li-ion electrodes. Later on, our group developed a GD-OES based method to distinguish between different aging mechanisms on graphite anodes.4 In the present study, we present a new promising method to measure depth profiles of Si/C composite anodes in Li-ion batteries. The method was calibrated by samples with known compositions, verified by lab coated anodes, and a first attempt to analyze the Si/C composite anode from a commercial 18650-type cell is presented.

**Experimental**

The GD-OES analysis was carried out using a GDA750 device (Spectruma, rf mode, 550V discharge voltage, 2hPa). A gas mixture of 1 vol.-% of H2 in Ar (both 6.0 purity) was used. The following emission lines were used: O (130.2 nm), C (156.1 nm), P (178.3 nm), Si (288.1 nm), Li (670.7 nm). The samples have an area of ~5 mm2 and the resulting crater depth was measured mechanically using a profilometer (Taylor Hobson, Form Talysurf 50). The calibration of the GD-OES method was achieved by samples with known composition (see Figure 1). These Si/C coatings simulate real anode materials by variation of Li, P, O and Si in graphite matrices. To avoid matrix effects, the Si/C composite coatings have similar chemical compositions and porosities like real electrodes and were prepared under ambient conditions. The two anodes contained Si/C composite materials consisting of 11 wt.-% Si within the composite, 6 wt.-% CMC/SBR binder mixture, and 6 wt.-% conductive additive as well as 67 wt.-% Si, 10 wt.-% LiPAA binder and 20 wt.-% graphite, respectively.

Cell opening of the commercial 18650 cell was performed under Ar atmosphere (glove box, MBraun, O2 < 0.1 ppm, H2O < 0.1 ppm) at the lower cut of potential (2.5 V). The sample from the commercially available cell was prepared under Ar atmosphere and transferred to the GD-OES using an airtight sample holder.

**Results and Discussion**

Figure 1 shows the correlation of known Si wt.-% for all calibration samples and the respective wt.-% measured by GD-OES. An excellent correlation coefficient R2 = 0.999 proves the accuracy of the method and allows for application to unknown samples. A similar approach was previously done for graphite based anodes,4,5 which usually contain elements like C, Li, O, however no Si. In research cells, the amount of Si in Si/C composite anodes can vary from 0 to 100 wt.-%.6−8 To cover this range we used SiO2 as Si source (resulting in up to ~35 wt.-% Si) and Si powder (up to 67 wt.-%) in the graphite based coatings. Both SiO2 and Si used in the graphite based coatings make sure that the reference samples mimic the Si/C composite matrix of real anode materials. To complete the calibration curve we used a carbon based anode without containing any Si (0 wt.-%) and a pure Si wafer (100 wt.-%).

Figure 2a shows the quantitative depth profiles measured on a Si/C composite anode (11 wt.-% Si) which was coated and calcined

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with a pilot line coater in our lab. One can see the nearly constant Si wt.-% within the coating depth. On the first few micrometers, a higher amount of O (∼1 wt.-%) is visible most probably due to oxidation during storage of the electrode at ambient atmosphere before the GD-OES measurements. The broken line shows the reproduced measurement. Both samples were taken from the same homogeneous electrode. Good reproducibility and homogeneity of the electrode within the coated area and depth can be seen. The results show that the electrodes have a high quality and are suitable for tests in electrochemical cells, which will be carried out later. We note that due to the high coating thickness (∼60 μm), the whole electrode depth was not measured.

Figure 2b shows the GD-OES depth profile of the pristine anode containing 67 wt.-% Si. The higher O and the lower Si wt.-% on the anode surface also indicates slight surface oxidation similar to the anode above. Within the bulk of the anode the elemental distribution is nearly constant, showing a slight inhomogeneity of the carbon distribution, which is likely due to the distribution of conductive additives or the carbon based binder.

Figure 3a shows the discharge of curves of the first 50 cycles of a commercial 18650 type cell. To the best of our knowledge, these are one of the first commercially available cells containing a Si/C composite as anode. The discharge curve of cycle 1 shows a deviation from the other cycles. The reduced capacity in the first discharge curve could be explained considering an incomplete formation, which persists through the first cycles. Figure 3b shows a GD-OES depth profile of the first 15 μm of the unwashed anode taken from the commercial cell. Within the first 100 nm a higher content of O (16 wt.-%) and Li (3 wt.-%) is visible, which is due to well-known SEI compounds like Li2O, Li2O2, Li2O3 and SiO2 were reported as key species in the SEI on Si/C composite electrodes,10,11 which contribute to the high O content within the SEI. Also within the SEI layer, a higher amount of Si (5 wt.-%), P (4 wt.-%), and a lower C (71 wt.-%) amount could be detected, compared to the bulk concentration, while Si (14 wt.-%) and P (8 wt-%) reach a maximum at roughly 500 nm.

However, we emphasize that the results on the Si surface peak of the anode from the commercial cell are preliminary at the moment and will be compared with complimentary methods in detail in a later paper. Nevertheless, the total Si amount of the commercial anode can be estimated as explained in the following.

The mean total Si contents c_{Si} of the measured electrodes were calculated using Equation 1.

$$c_{Si} = \frac{1}{z_i} \int_{z_i}^{z_L} c_{Si}(z) \, dz$$ [1]

The integration was performed over the measurement time starting with the depth $z = 0$ until the element intensity of interest crosses with the main element of the next layer $z_L$ resulting in the mathematical area under the GD-OES depth profile curve. This area is divided by the integration depth resulting in the overall mean value of the element of interest. In our case, $z_L$ was defined by the Cu current collector, since the matrix changes at this point, and preferential sputtering occurs. The integration according to Equation 1 resulted in the following values: 10.43 and 11.06 wt.-% Si (11.00 wt.-%) for the pristine anode in Figure 2a and 66.89 wt.-% (67 wt.-%) for the pristine anode in Figures 2b and 2c (set point values in brackets). All three calculated values for the Si wt.-% are additionally plotted in Figure 1 as red triangles. One can clearly see that these data fit very well, confirming the calibration. More quantitatively, the data points from the pristine real anodes do not change the $R^2$ value of 0.999. Integration according to Equation 1 of the anode from the commercial cell results in a mean value of 4.15 wt.-% Si. This is in the same range an EDX area analysis (0.36 μm²) which yielded ~3 wt.-%, though this is no real quantitative analysis.

Conclusions

We have shown that GD-OES is not only capable of measuring pure graphite anode materials, it is also a very powerful technique for obtaining depth profiles and detecting Si concentrations of Si/C composite anodes.

In particular:

1. We calibrated a GD-OES method based on the Si 288.1 nm line with Si containing samples in the range of 0–100 wt.-% Si.
2) Quantitative depth-resolved analysis of the Si concentration was obtained in pristine Si/C composite anodes with 11 wt.-% and 67 wt.-% Si.

3) First preliminary results on the anode from a commercial 18650 cell were obtained and an overall Si amount of ~4 wt.-% was determined.

Further investigations over the whole depth of Si/C composite anodes and with aged-cells are underway in our lab.

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