Figure S1:

Evolution with sputter time of the AES intensities for Li KLL, Si LVV, O KLL, and C KLL and the ratio I_{Li} / I_{Si} obtained at Li_7Si_3 surface

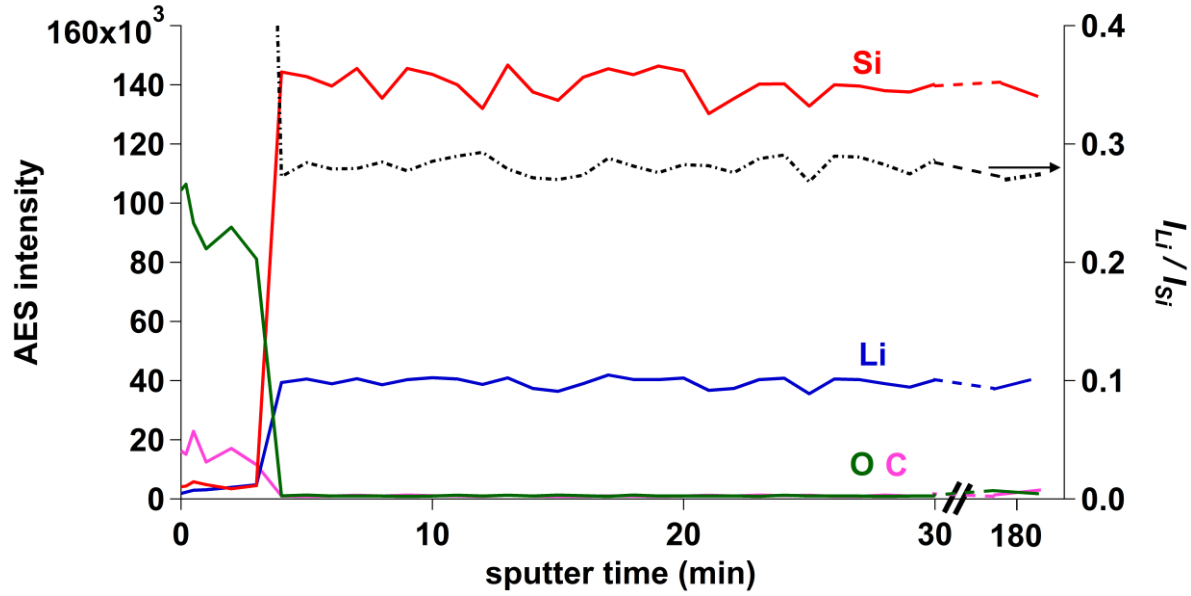


Figure S2:

Evolution with sputter time of the AES intensities for Li KLL, Si LVV, O KLL, and C KLL and the ratio I_{Li} / I_{Si} obtained at $Li_{15}Si_4$ surface

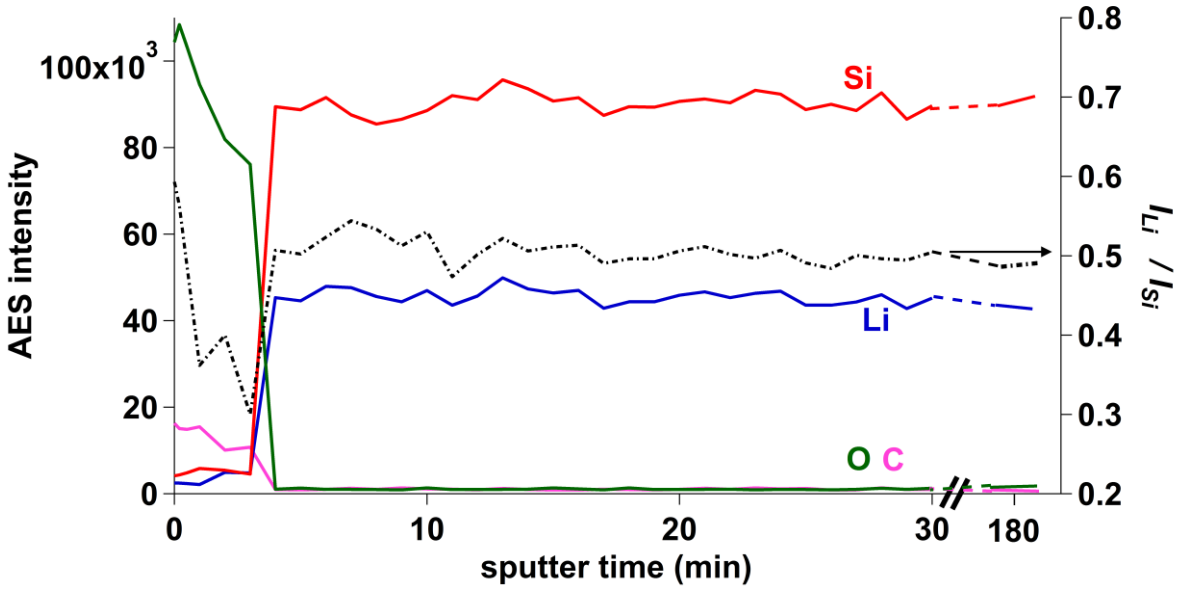


Figure S3:

SEM images of one particle investigated from electrode IV (50% lithiated) a) before sputtering and b) after 90 min of sputtering. In addition, the AES derivative spectra of Li KLL and Si LVV and the corresponding quantification have been reported in different regions (represented by blue squares) of the particle after sputtering.

The composition of the analyzed area corresponding to the shell of the sputtered particle is found to be $Li_{2.5}Si$. This analyzed area is probably located in the gradient region (see Fig. 11 and main text) between the inner core of pure silicon and the outer shell of $Li_{3.1}Si$.

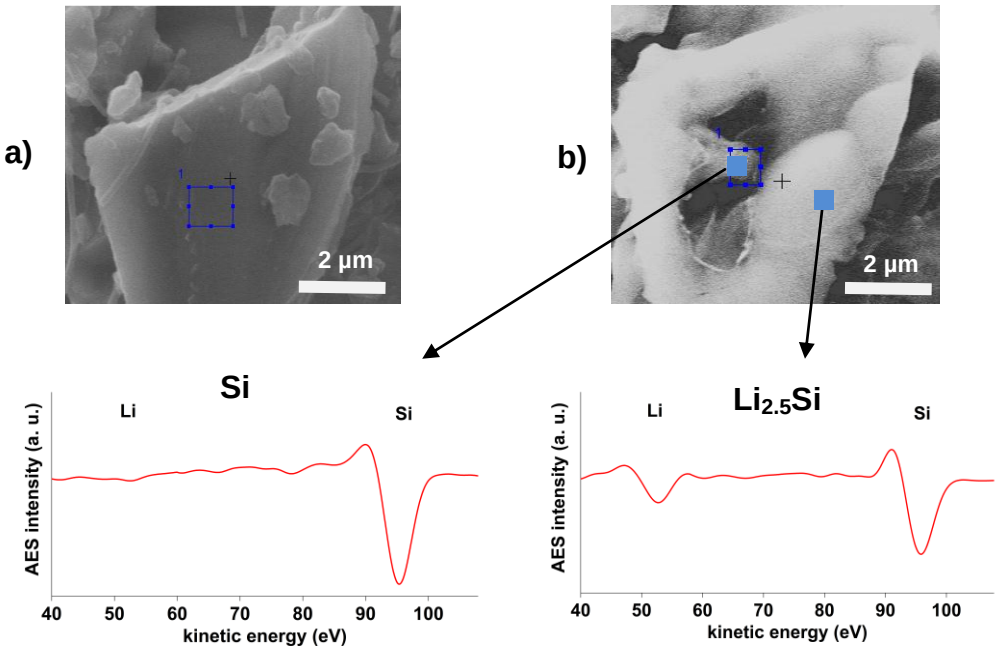
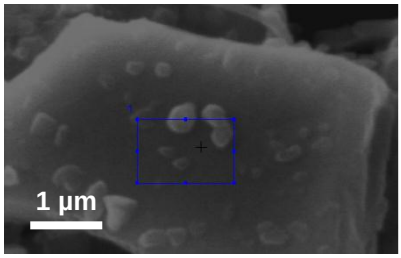


Figure S4:

SEM images of one particle investigated from electrode IV (50% lithiated) a) before sputtering and b) after 70 min of sputtering.

The particle has completely lost its initial morphology.

a)



b)