## **Supporting Information**

## Temperature–dependent Insertion and Adsorption of Lithium on Spinel $Li_4Ti_5O_{12}(111)$ Thin Films as Model Electrode – An Angle-resolved XPS Study

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Fig. S1 XP spectra of the O 1s spectral range after successive Li vapor deposition up to 7.8 MLE on a  $Li_4Ti_5O_{12}(111)$  thin film substrate at 80 K, recorded at grazing emission ( $\theta = 80^\circ$ ). All O 1s spectra are plotted at the same intensity scale.



Fig. S2 XP spectra of the Ti 2p spectral range before (black dots) and after (red dots) 1.2 MLE of Li vapor deposition on a  $Li_4Ti_5O_{12}(111)$  thin film substrate at 300 K, recorded at grazing emission ( $\theta = 80^\circ$ ).



Fig. S3 XP spectra of the Ti 2p spectral range after successive Li vapor deposition up to 7.8 MLE on a  $Li_4Ti_5O_{12}(111)$  thin film substrate at 80 K, recorded at normal emission ( $\theta = 0^\circ$ ). All Ti 2p spectra are plotted at the same intensity scale.



**Fig. S4.** (a) XP spectra of the Ti 2p spectral range (emission 80°) obtained for pristine  $Li_4Ti_5O_{12}(111)$  without vapor-deposited Li during slow heating (~ 100 K h<sup>-1</sup>) from 80 to 260 K, recorded at grazing emission ( $\theta = 80^\circ$ ). (b) Temperature dependence of the FWHM of Ti 2p peak. Red solid dot and gray square symbols correspond to Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$ , respectively.