Supplementary Information for

In Situ Formation of Aluminum-Silicon-Lithium Active Materials in Aluminum Matrices for Lithium-Ion Batteries

Mohammad Hossein Tahmasebi,‡[a] Dominik Kramer,[bc] Holger Geßwein,[bc] Tianye Zheng,[a] Kwan-Chee Leung,[d] Benedict Tsz Woon Lo,[d] Reiner Mönig [bc] and Steven T. Boles*[a]

[a] *Department of Electrical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

[b] *Institute for Applied Materials, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany*

[c] *Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), 89069 Ulm, Germany*

[d] *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

‡Present address: Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4R2, Canada

** First author: Mohammad.Tahmasebi@dal.ca; Corresponding author: steven.t.boles@polyu.edu.hk*

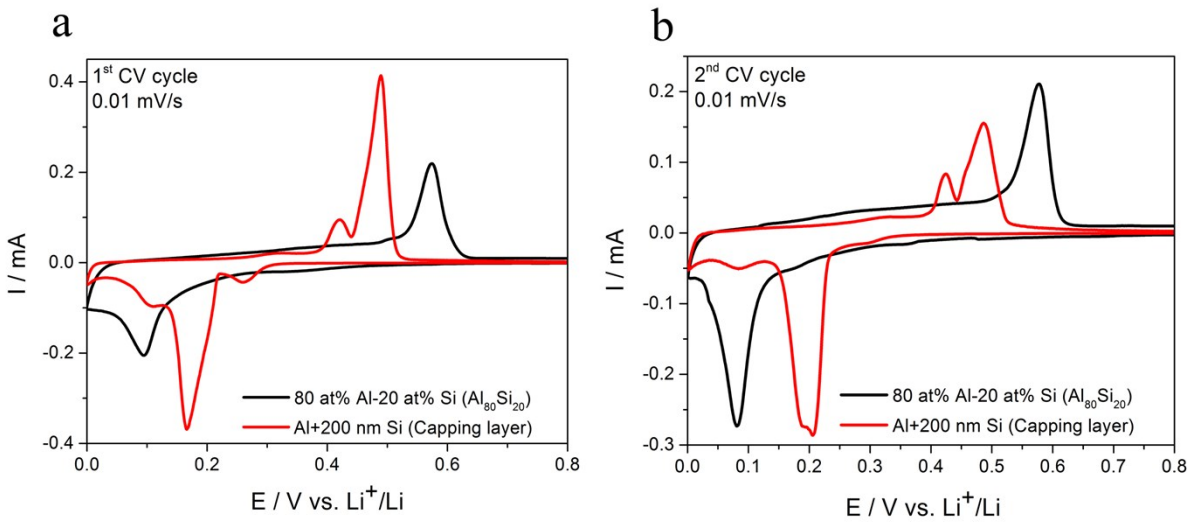

Fig. S1 The CV curves of (a) the first cycle. (b) the second cycle for the sputtered $Al_{80}Si_{20}$ thin-film electrode and Al thin-film with 200 nm sputtered Si-capping layer over the potential range from 0 to 1.5 V, at scan rate of 0.01 mV s^{-1}.

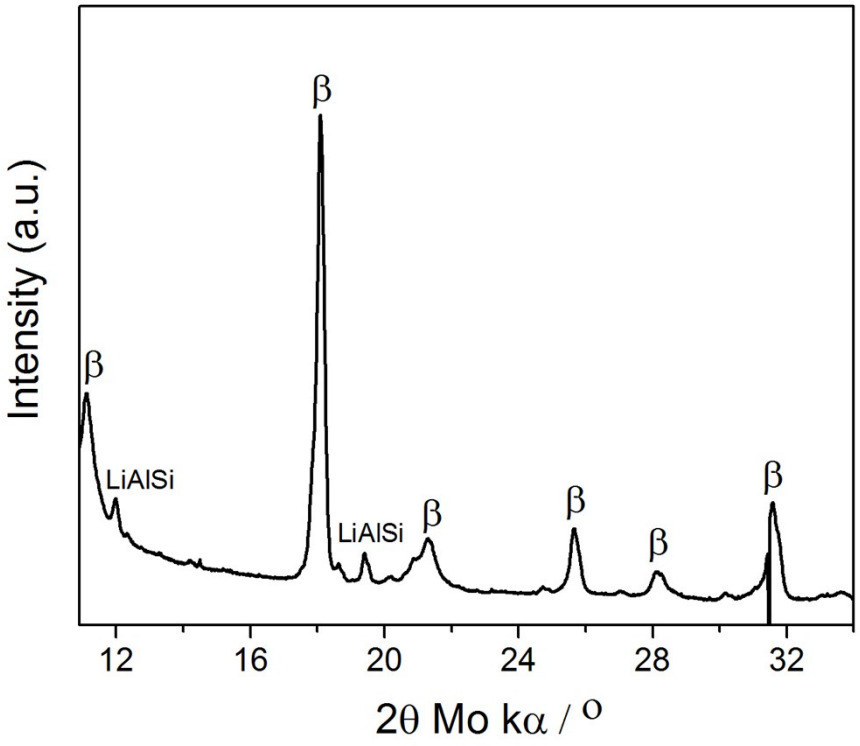

Fig. S2 XRD pattern of an inhomogeneous 88 at% Al-12 at% Si ($Al_{88}Si_{12}$) foil (50 µm-thick) after a potentiostatic lithiation at 5 mV vs. Li/Li^+ for 5 days.

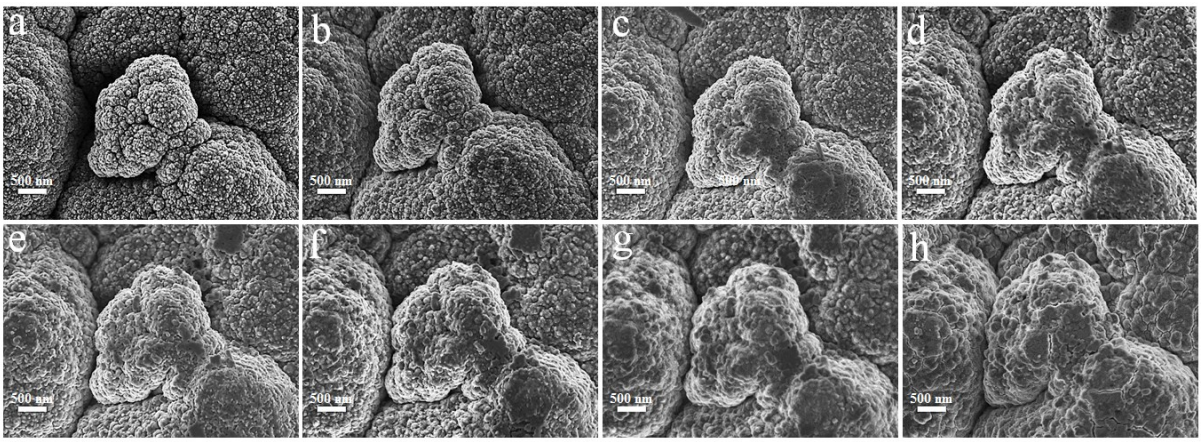

Fig. S3 SEM micrographs (13 kV) of the same region of the surface of $Al_{70}Si_{30}$ thin-film electrode (sputtered on TiN-coated Cu foil) captured by the following steps: (a) Before CV test. After CV scan (0.01 mV s^{-1}) to: (b) 300 mV. (c) 250 mV. (d) 200 mV. (e) 130 mV. (f) 80 mV. (g) 30 mV. (h) 0 V vs. Li/Li^+.

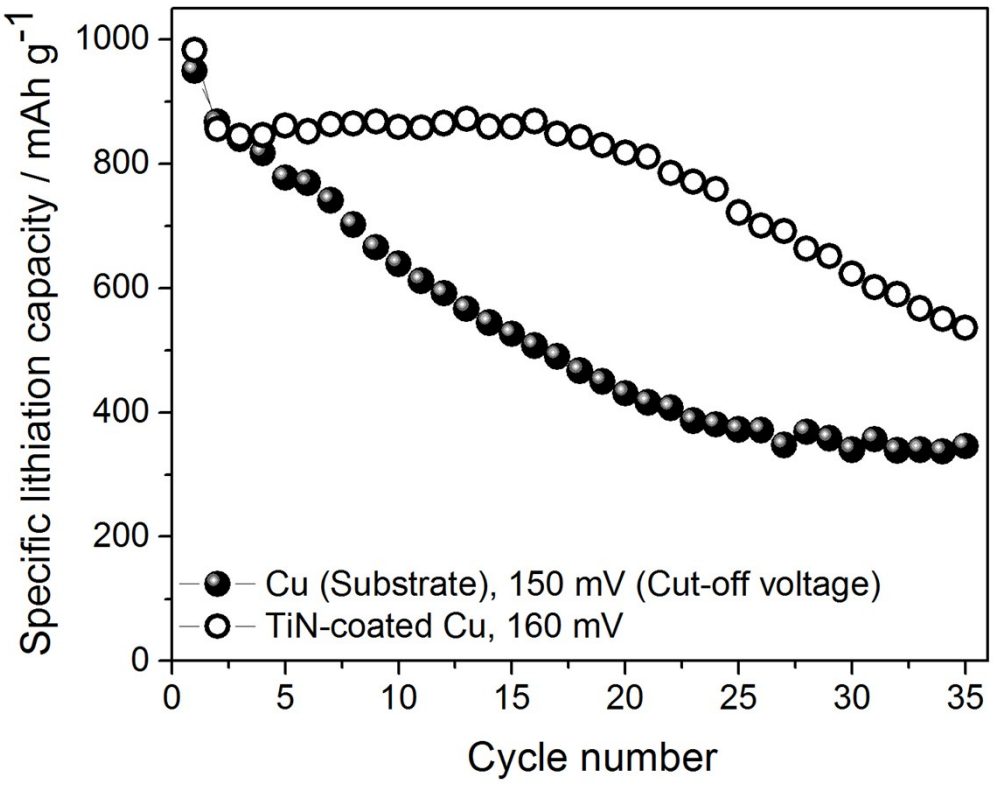

Fig. S4 Cycling performance of the $Al_{55}Si_{45}$ films sputtered on Cu and TiN-coated Cu foil at a rate of C/20 in different cut-off voltages vs. cycle number.

Supplemental note 1. XRD measurements on pristine and lithiated $Al_{70}Si_{30}$ films sputtered onto TiN-coated Cu foil

XRD measurements were performed using a high-energy Rigaku SmartLab diffractometer, equipped with Mo anode tube. The X-ray generated using the Mo anode has a wavelength of 0.71073 Å. The notably shorter wavelength when compared with Cu anode (cf. 1.5406 Å) allows more Bragg's peaks to be observed in the standard 2theta window (up to 90°). A Zr kβ-filter was used to greatly reduce the Mo kβ radiation. Specifically designed parallel beam optics was employed to study the samples. To achieve signal-to-noise ratio and angular resolution, diffraction data of around 2 hours was collection.

Prior to the XRD experiment, the $Al_{70}Si_{30}$ film was galvanostatically lithiated to 130 mV vs. Li/Li^+ at a rate of C/20 in a coin-type cell. The coin-type cell was disassembled and the lithiated film was then washed by dimethyl carbonate (DMC) solution to remove residual electrolyte. Finally, the lithiated and pristine $Al_{70}Si_{30}$ films were covered by a layer of Kapton tape on the XRD sample holders. As it can be seen, the Cu Bragg's peaks are shifted to the right consistently upon lithiation, which is due to sample displacement (Figure S5B). For both pristine and lithiated $Al_{70}Si_{30}$ films, strong copper peaks were observed at 19.558°, 22.625°, 32.223°, 37.976°, 50.637° and 52.050°, also with a board Kapton peak at around 8.5°. A small (111) Al peak could also be found in both samples at 17.450° (Figures S5A and S5C).

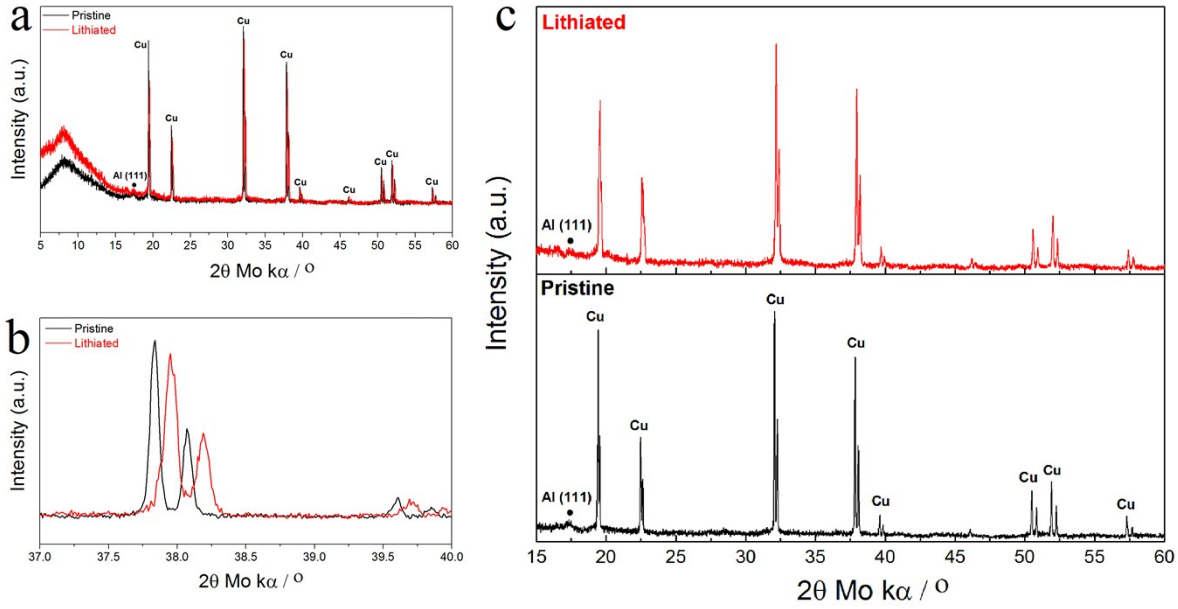

Fig. S5 (a) XRD patterns of the pristine and lithiated $Al_{70}Si_{30}$ film sputtered on TiN-coated Cu foil. (b) Shift in XRD peaks of Cu. (c) XRD patterns of the pristine and lithiated $Al_{70}Si_{30}$ film sputtered on TiN-coated Cu foil normalized to the intensity of the highest XRD peak of Cu.

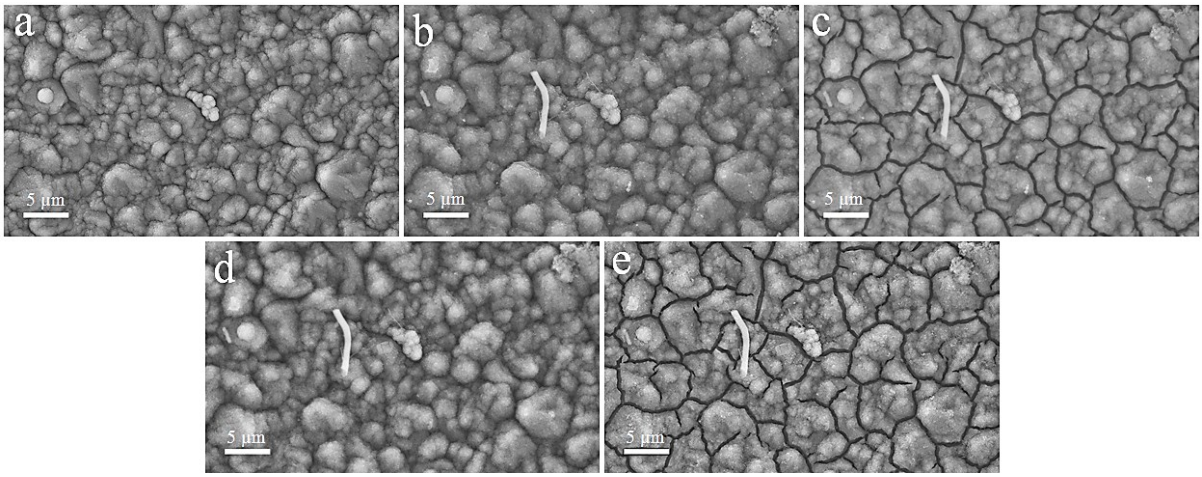

Fig. S6 SEM micrographs (13 kV) of the same region of the surface of $Al_{70}Si_{30}$ thin-film electrode captured by the following steps: (a) Before electrochemical lithiation/delithiation test. (b) After the first lithiation to 130 mV. (c) After the first delithiation to 1.5 V. (d) After the second lithiation to 130 mV. (e) After the second delithiation to 1.5 V at a rate of C/20.

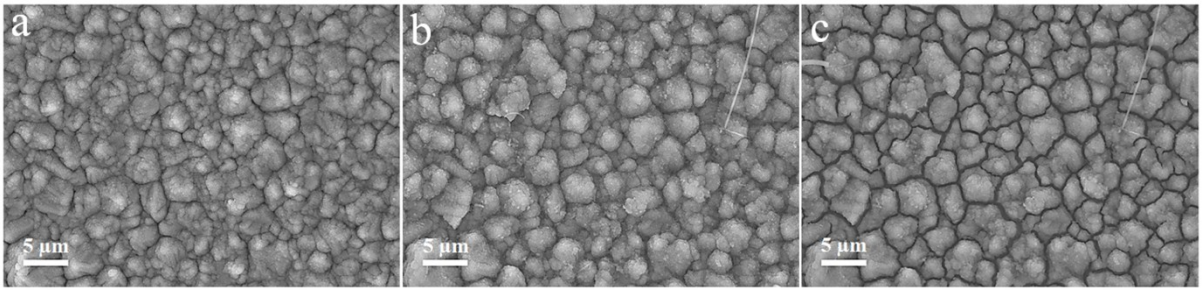

Fig. S7 SEM images of the same region of the surface of $Al_{70}Si_{30}$ thin-film (sputtered on TiN-coated Cu foil) electrode captured by the following steps: (a) Before electrochemical lithiation/delithiation test. (b) After 50th lithiation. (c) After 50th delithiation.

Table S1 Calculations details for specific capacities of the electrodes based on the model presented (Li_9AlSi_3 and LiAl (β) phases) in Figure 5b.

Composition	at% Al	at% Si	S.C of Al (mAh g^{-1})	S.C of Li_9AlSi_3 (mAh g^{-1})	at% Al in Li_9AlSi_3	S.C of Electrode (mAh g^{-1}) (Equation S1)	Vol% Al matrix
Al	100	0	993	2173.4	0	993	100
$Al_{95}Si_5$	95	5	993	2173.4	1.67	1072	92.4
$Al_{90}Si_{10}$	90	10	993	2173.4	3.33	1150	85
$Al_{85}Si_{15}$	85	15	993	2173.4	5	1228	77.7
$Al_{80}Si_{20}$	80	20	993	2173.4	6.67	13071	70.5
$Al_{70}Si_{30}$	70	30	993	2173.4	10	1465	56.6
$Al_{55}Si_{45}$	55	45	993	2173.4	15	1701	36.7
$Al_{50}Si_{50}$	50	50	993	2173.4	16.67	1780	30.3
$Al_{25}Si_{75}$	25	75	993	2173.4	25	2173	0

Equation S1.

$$\text{Specific capacity of the electrode} = \frac{(\text{at\%Al} - \frac{\text{at\%Si}}{3}) \times \text{theoretical S.C. of the Al} + (\frac{4}{3} \times \text{at\%Si}) \times \text{theoretical S.C. of the } Li_9AlSi_3}{100}$$

Assumption S1.

$$M_{Al} \approx M_{Si}$$