Supporting Information

Operando Electrochemical Atomic Force Microscopy of Solid-Electrolyte Interphase Formation on Graphite Anodes: The Evolution of SEI Morphology and Mechanical Properties

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Explanation of DMT modulus by PeakForce QNM method:

(1) By PeakForce tapping with the probe, the force-distance curves are obtained from the detected sample surface due to the deformation of the material. The force curve is converted to a force versus separation plot for fitting and further analysis, where the separation is calculated from the Z piezo position and the cantilever deflection.

(2) To obtain the Young's Modulus, the retract curve is fit using the Derjaguin-Muller-Toporov (DMT) model.

$$F - F_{adh} = \frac{4}{3}E^*\sqrt{R(d-d_0)^3}$$

Where F-F_{adh} is the force on the cantilever relative to the adhesion force, R is the tip end radius, and d-d_0 is the deformation of the sample. The result of the fit is the reduced modulus E^*. The software can calculate the Young' Modulus of the sample E_s by the equation:

$$E^* = \left[\frac{1-v_s^2}{E_s} + \frac{1-v_{tip}^2}{E_{tip}}\right]^{-1}$$

Where E_{tip} is the Young's modulus of silicon tip,v_s and v_{tip} are Poisson's ratio of graphite and silicon probe, respectively.

(3) RTESPA-300 silicon probes with reflective Al coating (Bruker Corp., k = 40 N m^{-1}, f_0 = 300 kHz) was used in this work. Before each experiment, the probe was calibrated by using a standard HOPG (modulus = 18 GPa) sample in Ar atmosphere for a precise measurement of mechanical properties. Through which, the deflection sensitivity, tip radius and spring constant values were recorded. Nano-indentation mechanical measurements were conducted at the same time as the morphology was mapped. By recording the load and displacement of the specialized tips and cantilevers when being pressed into the surface, a force-distance curve is generated, which is further used to calculate the hardness, elastic modulus and various viscoelastic properties of the materials. All the results obtained by EC-AFM were analysed by Nanoscope Analysis software.

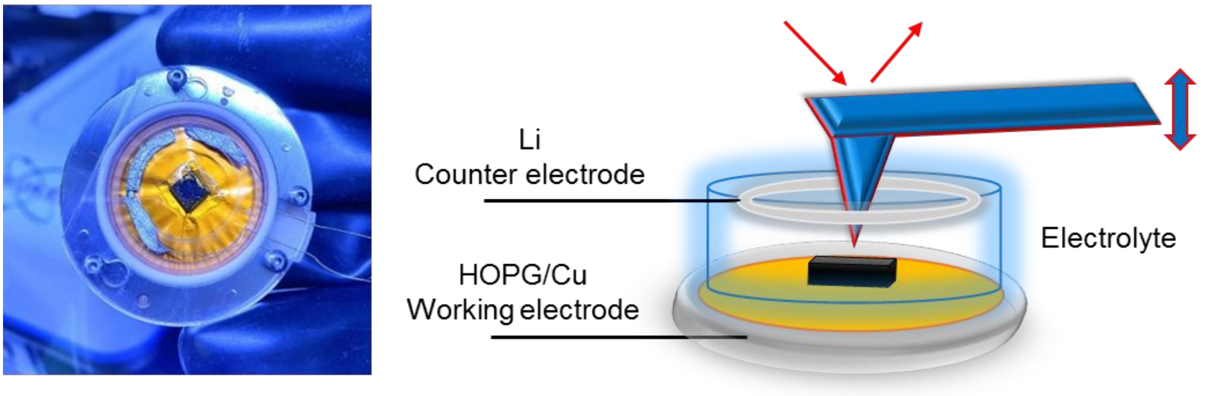

Figure S1. The photo and schematic diagram of the electrochemical cell configuration.

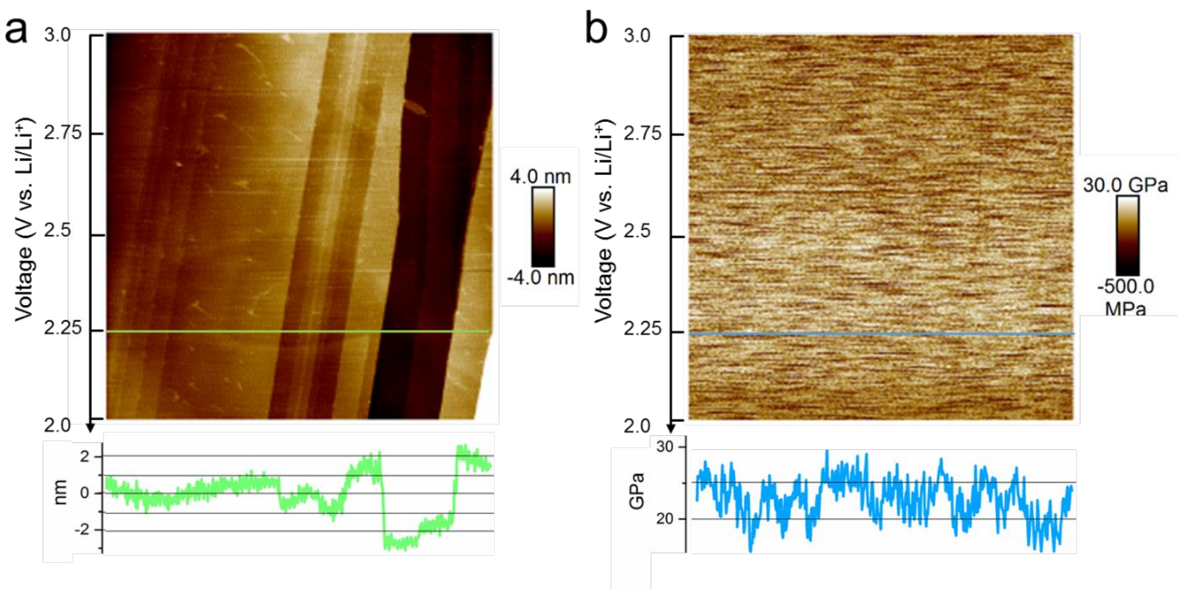

Figure S2. Enlarged figure 2 column 1 (3.0-2.0 V, *vs*. Li/Li$^+$), and section line data from the height and DMT modulus.

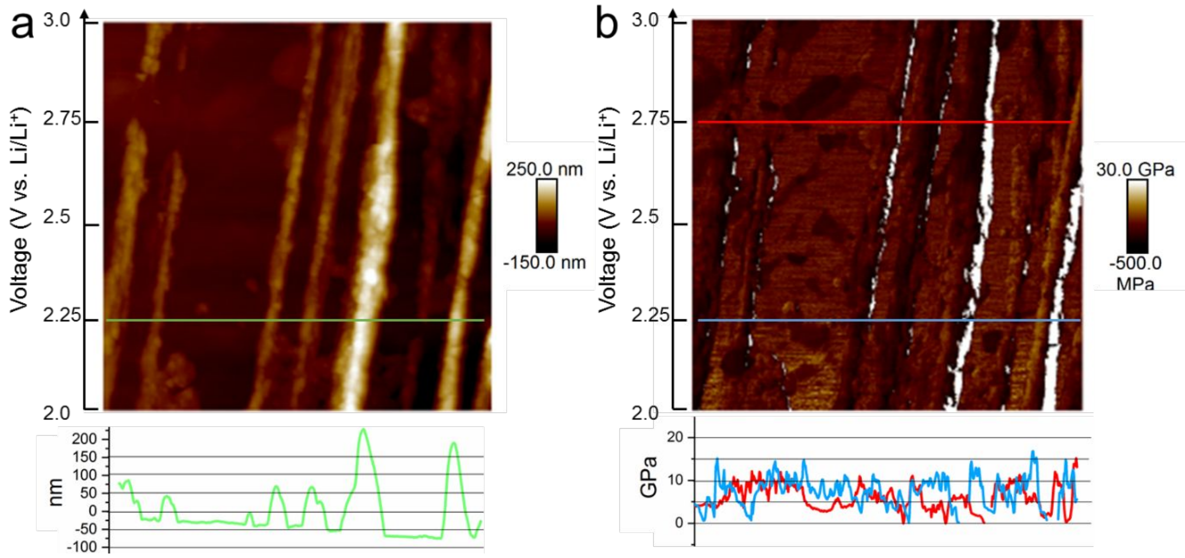

Figure S3. Enlarged figure 2 column 6 (2.0-3.0 V, *vs*. Li/Li$^+$), and section line data from the height and DMT modulus. It should be noted that the white areas among the black areas in the modulus image of 1.0-2.0 and 2.0-3.0 V in **Figure 2** are caused by sensing error of the probe, which might be attributed to the incompatibility of high spring constant of probe to low hardness of the SEI material.

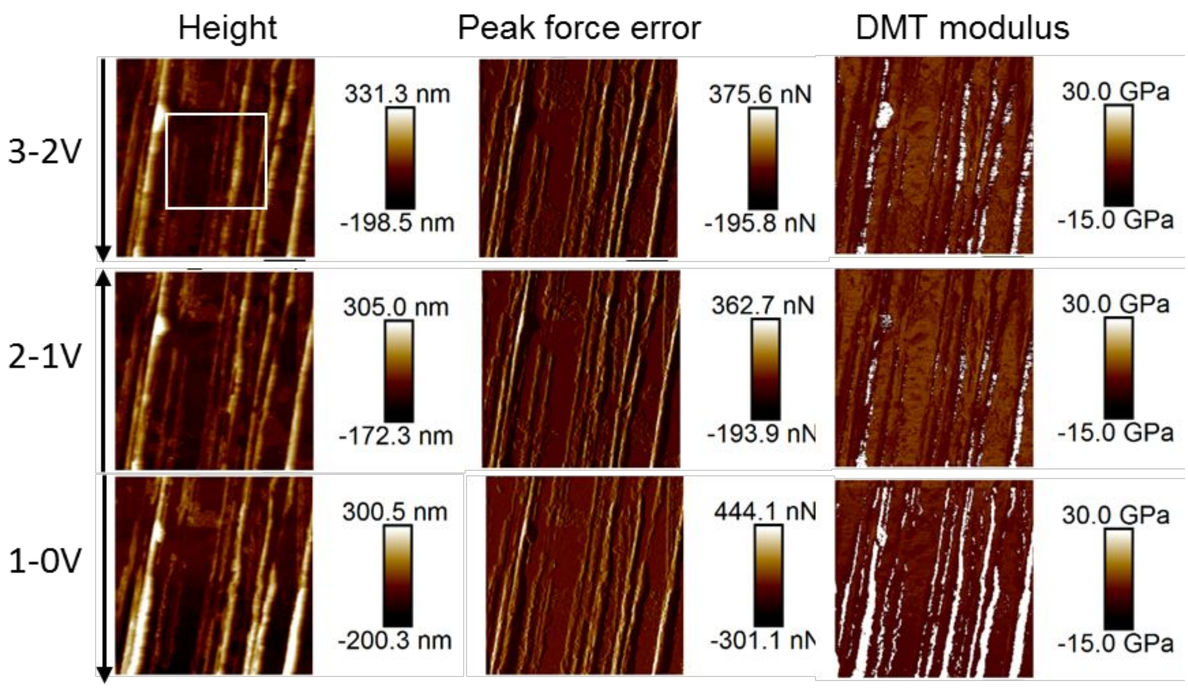

Figure S4. Second discharge in a zoomed out 20 µm area, the white square area is the 10 µm area scanned in the first cycle in the electrolyte of EC/EMC (3.0-0.0 V, *vs*. Li/Li^+).

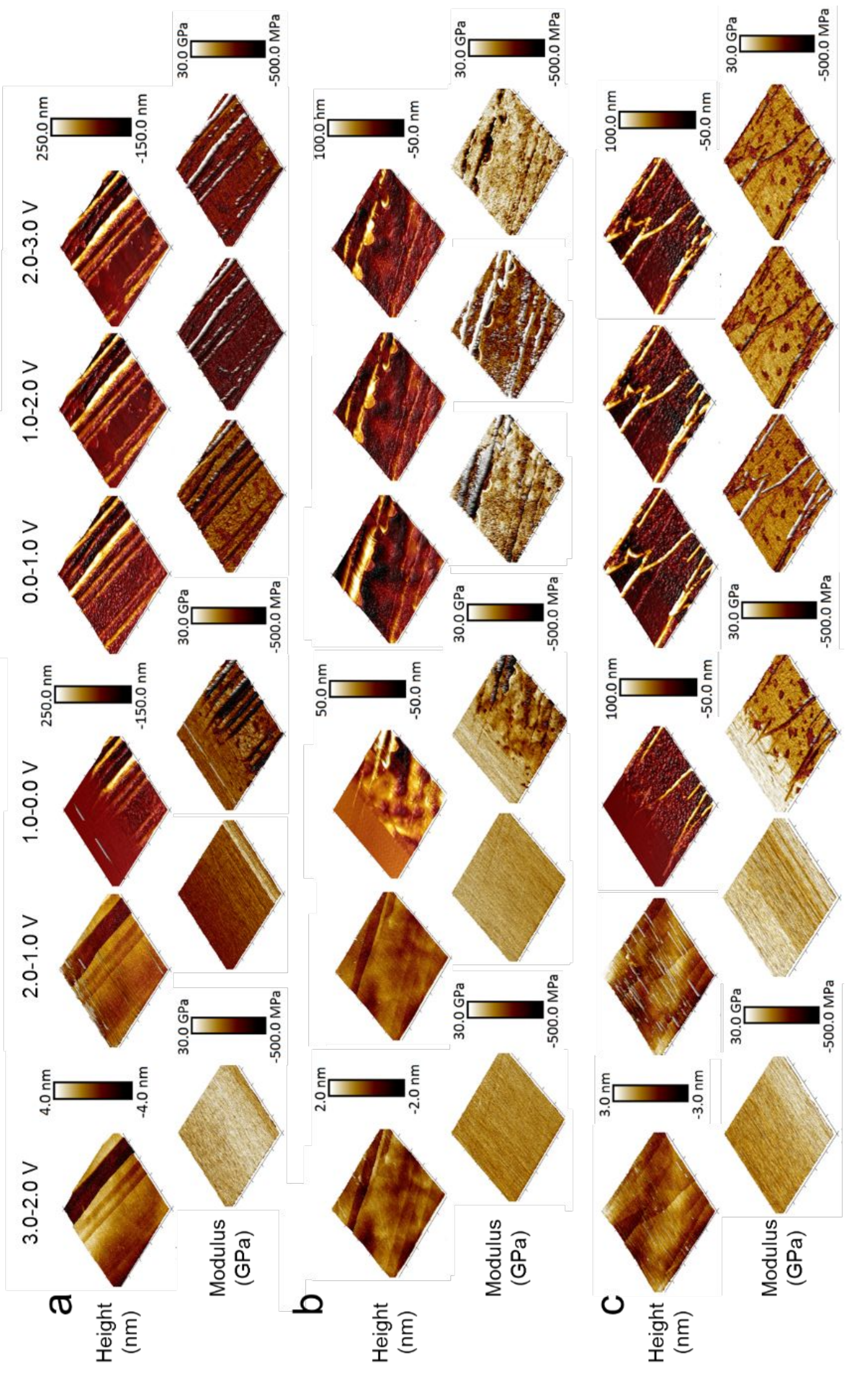
a
b
c
Height (nm)
Modulus (GPa)
3.0-2.0 V
2.0-1.0 V
1.0-0.0 V
0.0-1.0 V
1.0-2.0 V
2.0-3.0 V
4.0 nm
-4.0 nm
2.0 nm
-2.0 nm
3.0 nm
-3.0 nm
250.0 nm
-150.0 nm
50.0 nm
-50.0 nm
100.0 nm
-50.0 nm
30.0 GPa
-500.0 MPa

Figure S5. The whole processes of six columns of 3D images of height and modulus obtained in the different electrolytes ((a) EC/EMC, (b) EC/EMC/VC and (c) EC/EMC/VC/FEC) at the stages of 3.0-2.0 V (column 1), 2.0-1.0 V (column 2), 1.0-0.0 V (column 3), 0.0-1.0 V (column 4), 1.0-2.0 V (column 5) and 2.0-3.0 V (column 6). All voltages quoted *vs*. Li/Li^+

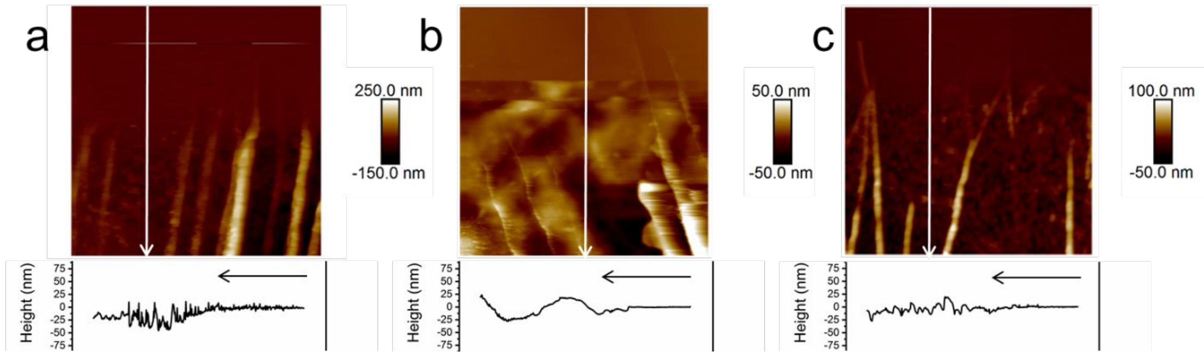

Figure S6. The magnified images of 1.0-0.0 V (*vs*. Li/Li^+) in the three electrolytes of (a) EC/EMC, (b) EC/EMC/VC, and (c) EC/EMC/VC/FEC, and corresponding height data of the section lines across only the particle SEI at the basal planes.

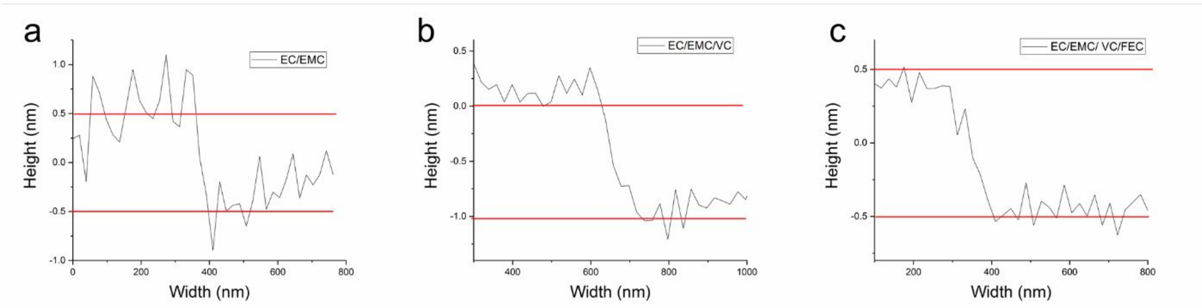

Figure S7. The height across the section line in Figure 4 column 1, indicating the similar terrace thickness of about 1 nm.

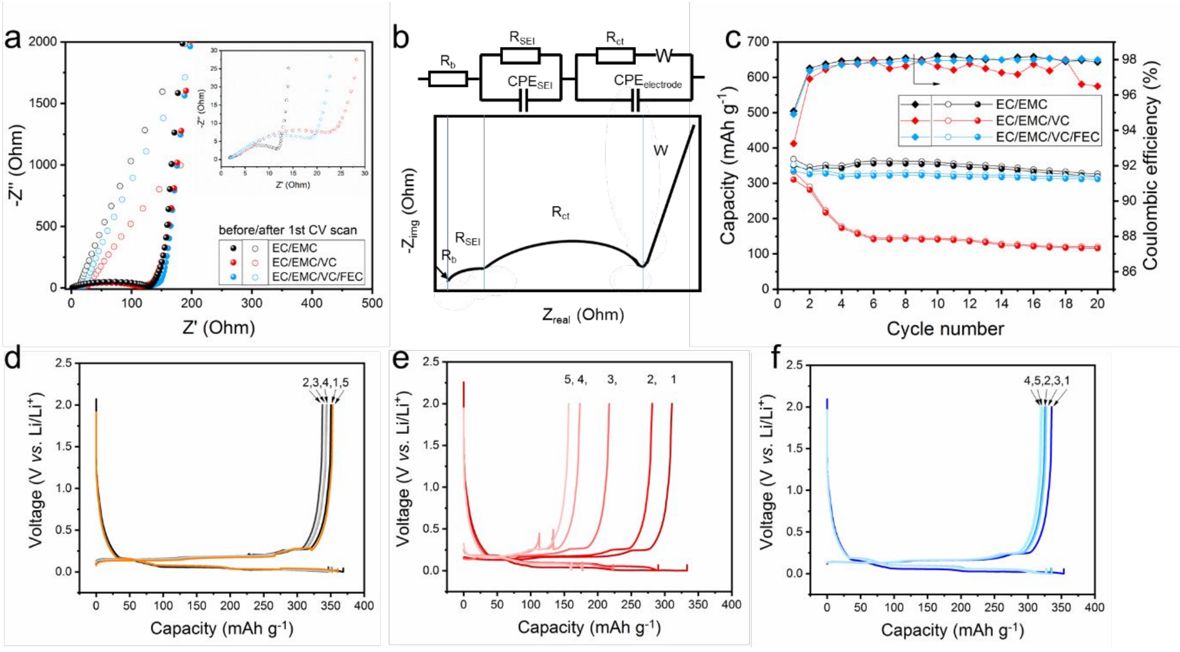

Figure S8. (a) Nyquist plots of the three coin cells before and after the 1st discharge/charge process, inset is the magnified image. (b) Simplified equivalent circuit and corresponding resistance parts. (c) Cycling performance in 10 cycles of the three coin cells at a current rate of 0.2C. The first five discharge-charge voltage profiles of the cells with (d) EC/EMC, (e) EC/EMC/VC and (f) EC/EMC/VC/FEC.

Table S1. The resistance fitting data of the Nyquist plot of three coin cells after first CV scan.

	R_b (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	W (Ω)
EC/EMC	1.58	1.44	9.57	535.5×10^{-3}
EC/EMC/VC	2.03	1.49	19.30	33.81×10^{-3}
EC/EMC/VC/FEC	1.64	2.10	16.33	194.7×10^{-3}

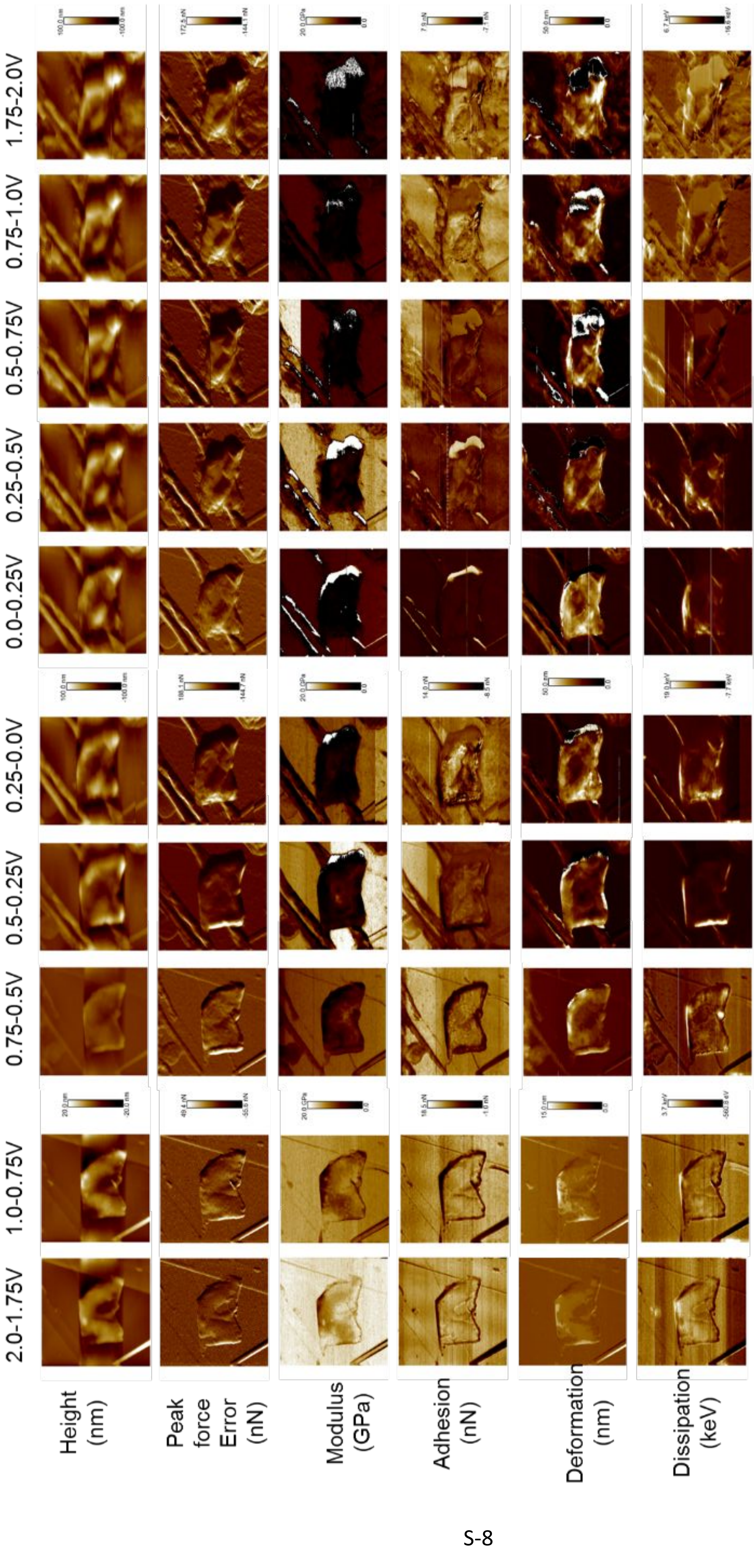
1.75-2.0V
0.75-1.0V
0.5-0.75V
0.25-0.5V
0.0-0.25V
0.25-0.0V
0.5-0.25V
0.75-0.5V
1.0-0.75V
2.0-1.75V
Height (nm)
Peak force Error (nN)
Modulus (GPa)
Adhesion (nN)
Deformation (nm)
Dissipation (keV)

Figure S9. The series of images for the whole process of operando EC-AFM monitoring of an individual graphite sheet on HOPG substrate is further carried out in the EC/EMC electrolyte by discharging/charging at a scan rate of 1 mV s^{-1}. A 4×4 μm^2 area is presented. All voltages quoted *vs*. Li/Li^+.

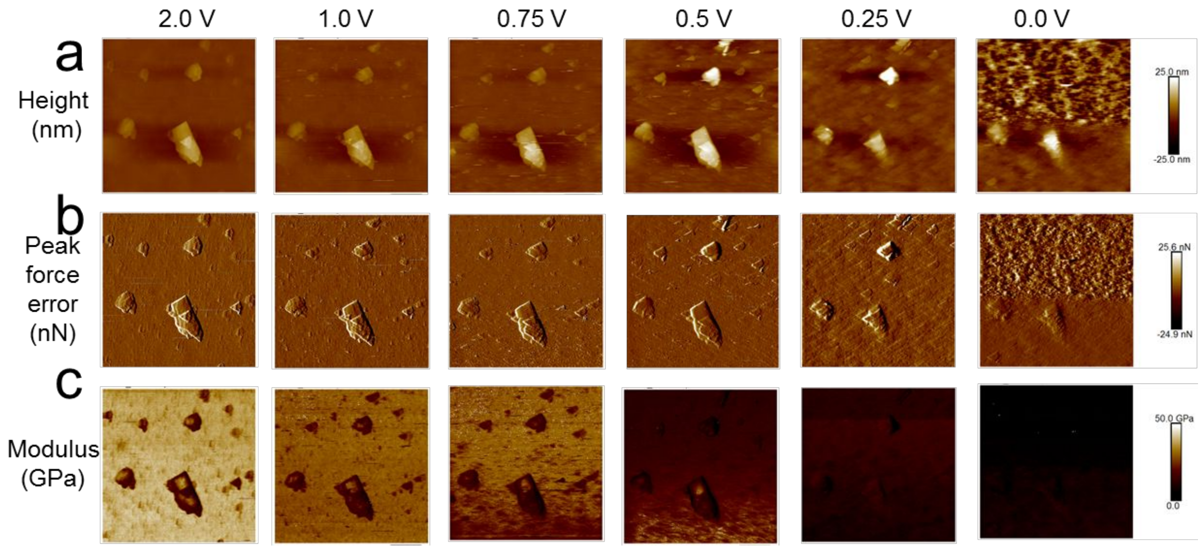

Figure S10. A discharge process of *in situ* EC-AFM for graphite sheets on a silicon substrate with an area of 4×4 μm^2, in the EC/EMC electrolyte by discharging/charging at a scan rate of 1 mV s^{-1}. A similar process is demonstrated despite silicon exhibiting a more influenced surface near 0.0 V due to its electrochemical activity in the electrolyte. All voltages quoted *vs*. Li/Li^+.