Supporting Information

Lithium Acetylide: A Spectroscopic Marker for Lithium Deposition During Fast Charging of Li-Ion Cells

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Supporting Figures.

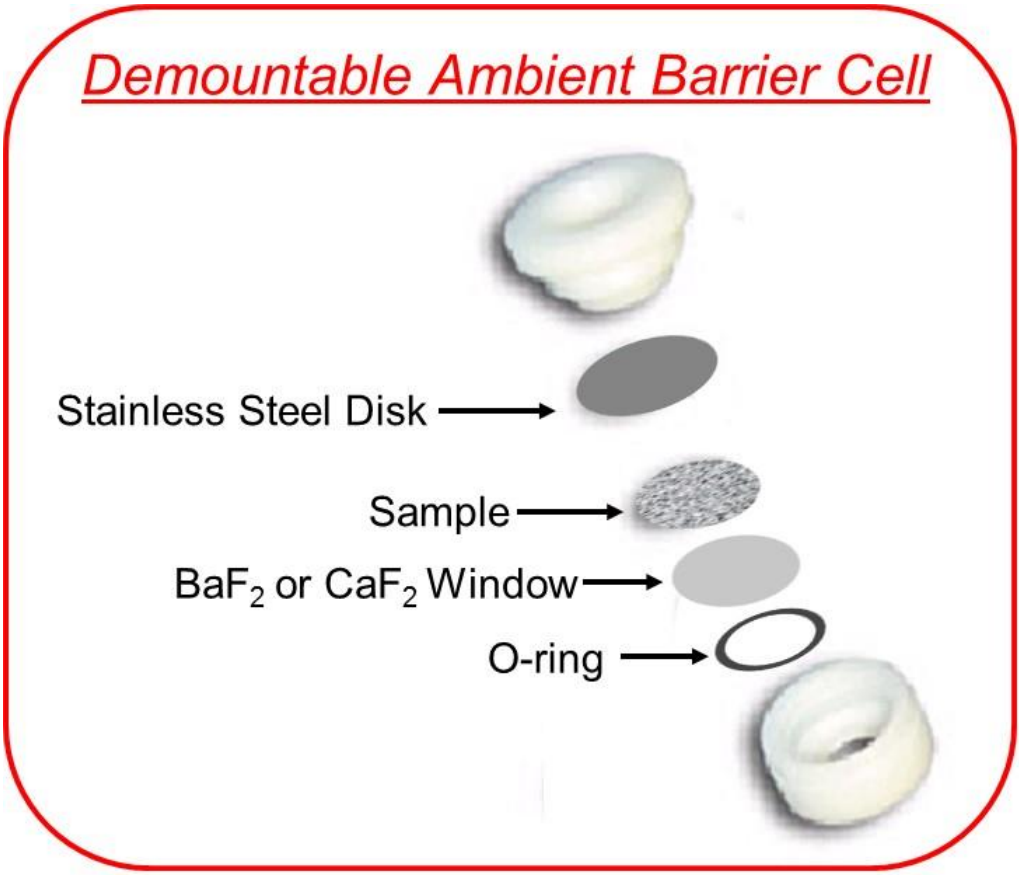

Figure S1. An optical cell for Raman spectroscopy of harvested Gr electrodes. The cell is loaded in an inert-atmosphere glovebox before being transported to the Raman instrument. The BaF_2 window employed in this cell yields a single narrow phonon mode at 241 cm^{-1} used for frequency calibration and as a pseudo intensity standard for all spectra.

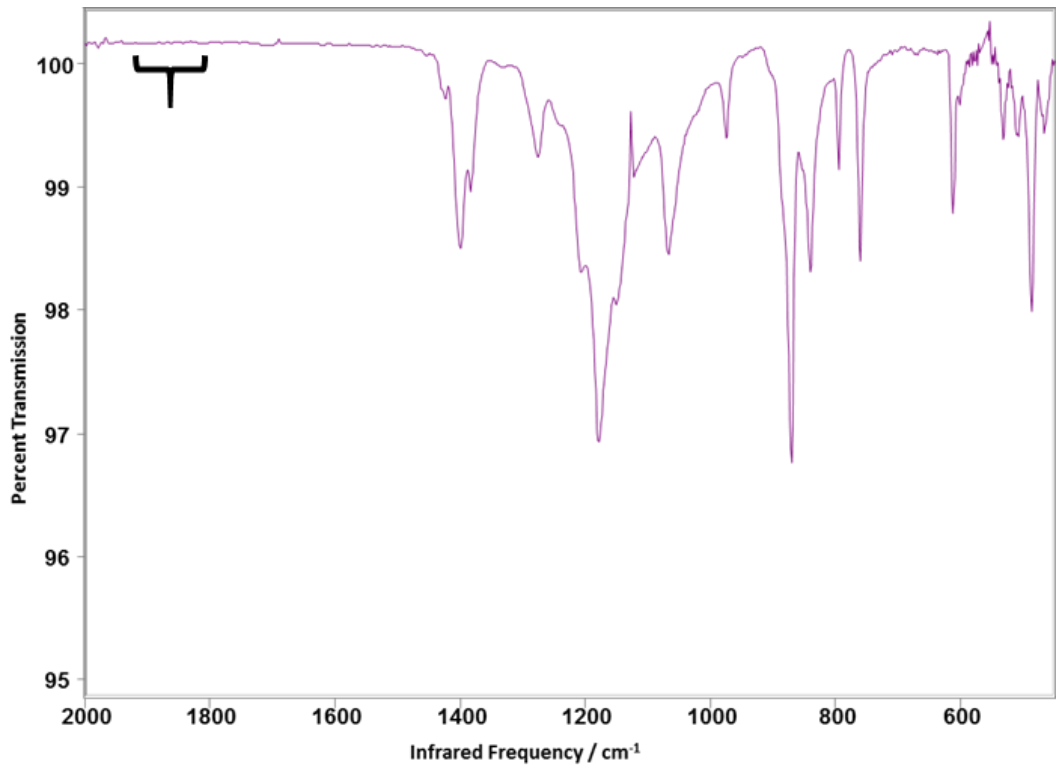

Figure S2. Fourier-transform infrared spectroscopy (FTIR) of a Gr electrode exposed to fast charge and containing visible evidence of Li deposition (same sample as in Figure 2c). The spectrum was collected using a PerkinElmer FTIR 100 spectrometer located inside an argon-filled glovebox, so the sample was never exposed to moisture and oxygen contents >0.4 ppm. The bracket indicates the spectral region in which modes from asymmetric acetylides are expected to appear.

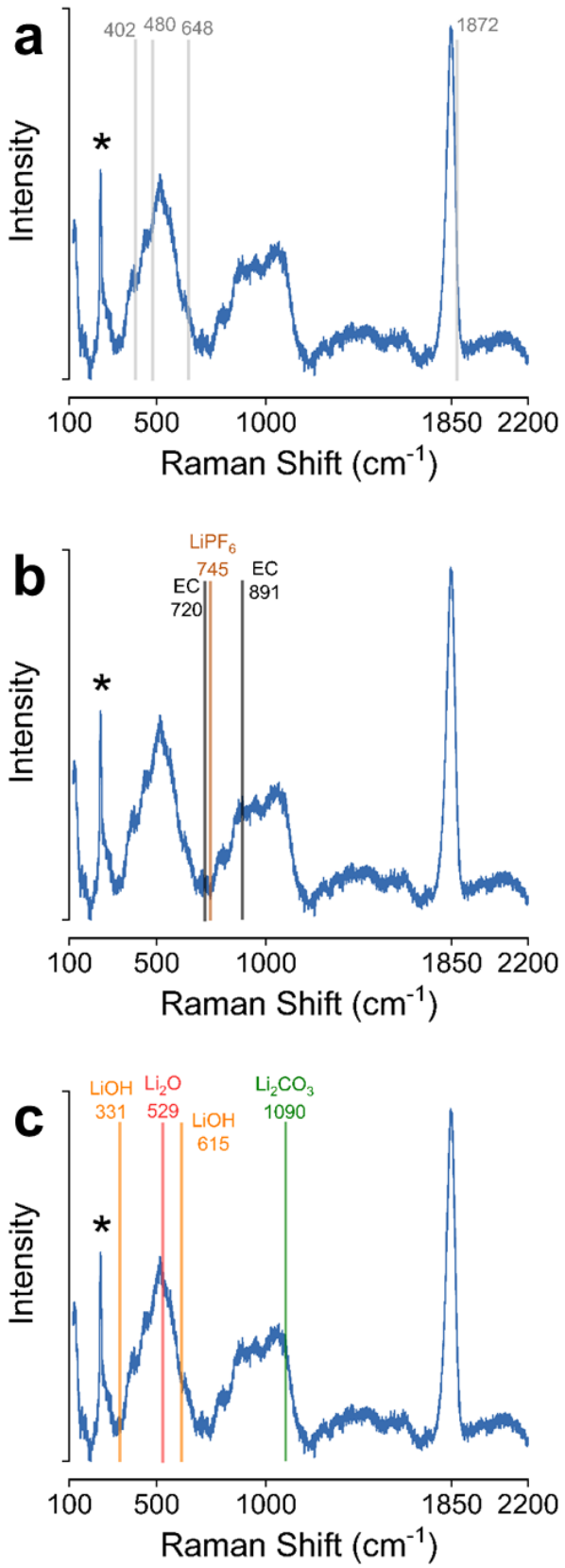

Figure S3. Locations of expected frequencies for Raman-active modes of compounds present at lithiated graphite surfaces in a Li-ion battery: a) Li_2C_2 (ref. [1]); b) dried electrolyte species (refs. [2-4]); c) Li-containing SEI components (ref. [5]). The spectrum shown here is the same as the one shown in Figure 2c. The star indicates the location of the BaF_2 band.

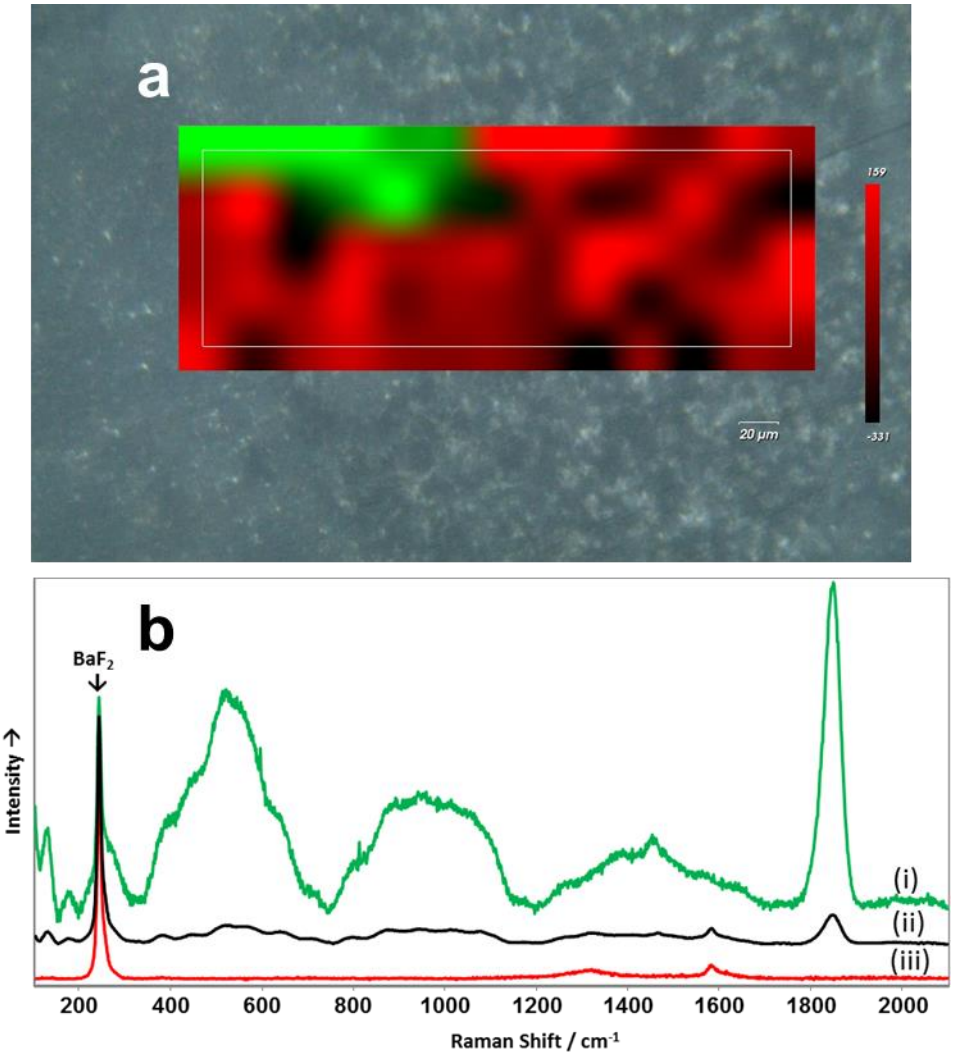

Figure S4. False-color Raman map from a Gr electrode exposed to seven fast-charge steps at 6C: a) spatial distribution of the spectra in panel *b*; b) representative Raman spectra of (i) acetylide-rich regions (green in the map), (ii) regions with modest acetylide band intensity, and (iii) regions presenting Gr-only D and G band signals (red in the map). The spectra in panel b serve as a color code for the interpretation of the map shown in panel *a*.

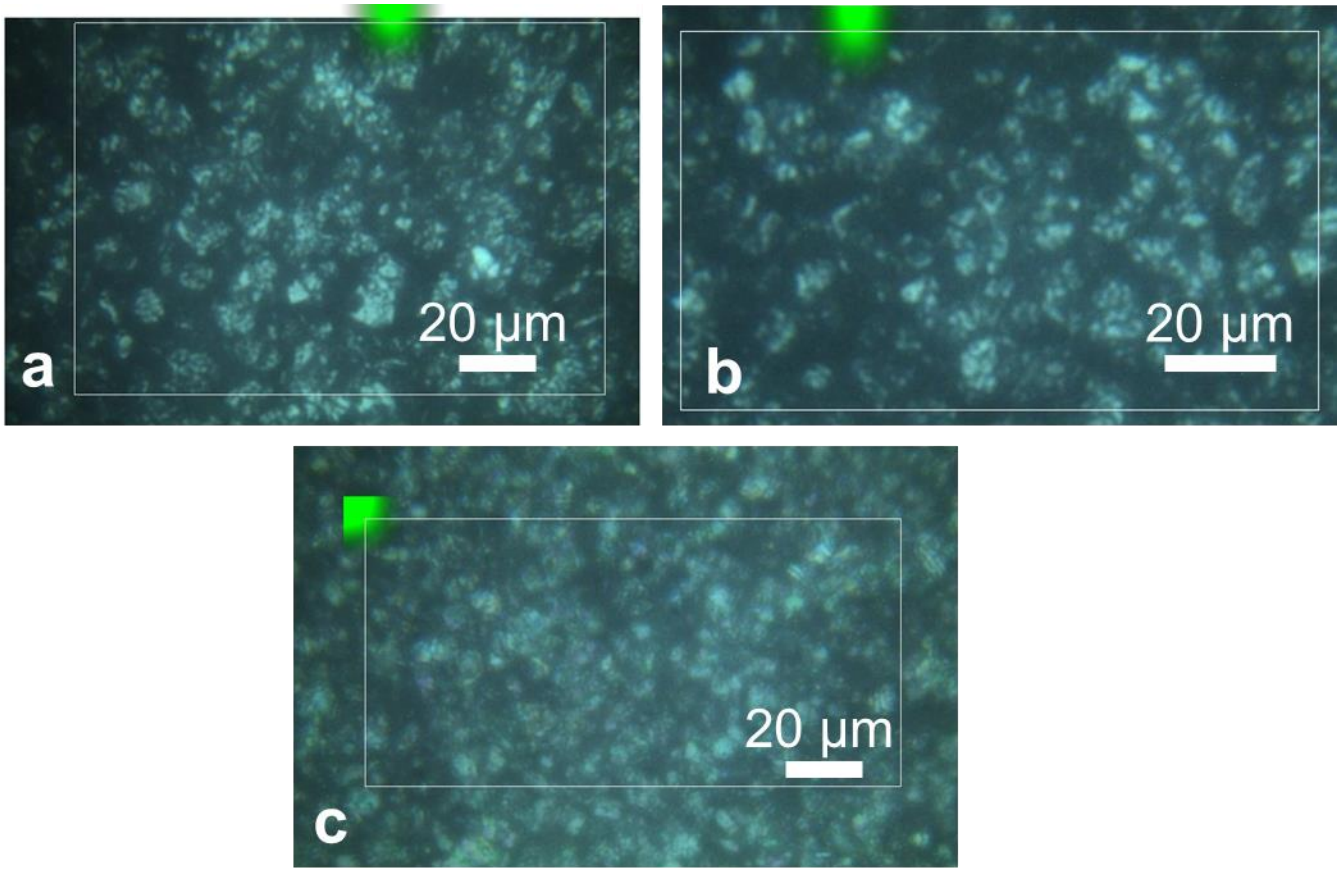

Figure S5. Intensity distribution of the acetylide band on Gr electrodes exposed to different fast-charge regimes: a) a single 3C charge; b) a single 4C charge; c) two charge cycles at 6C. Discharge steps were always carried out at C/5, and cells were fully discharged before analysis. The Raman map is overlaid onto an optical image of the entire analyzed region, and the bright green spots indicate the location of detectable acetylide species. As discussed in the text, charging at 3C does not lead to extensive Li plating. Although at 6C the likelihood of plating is higher, two charge steps do not appear to produce a significant amount of *detectable* Li deposition.

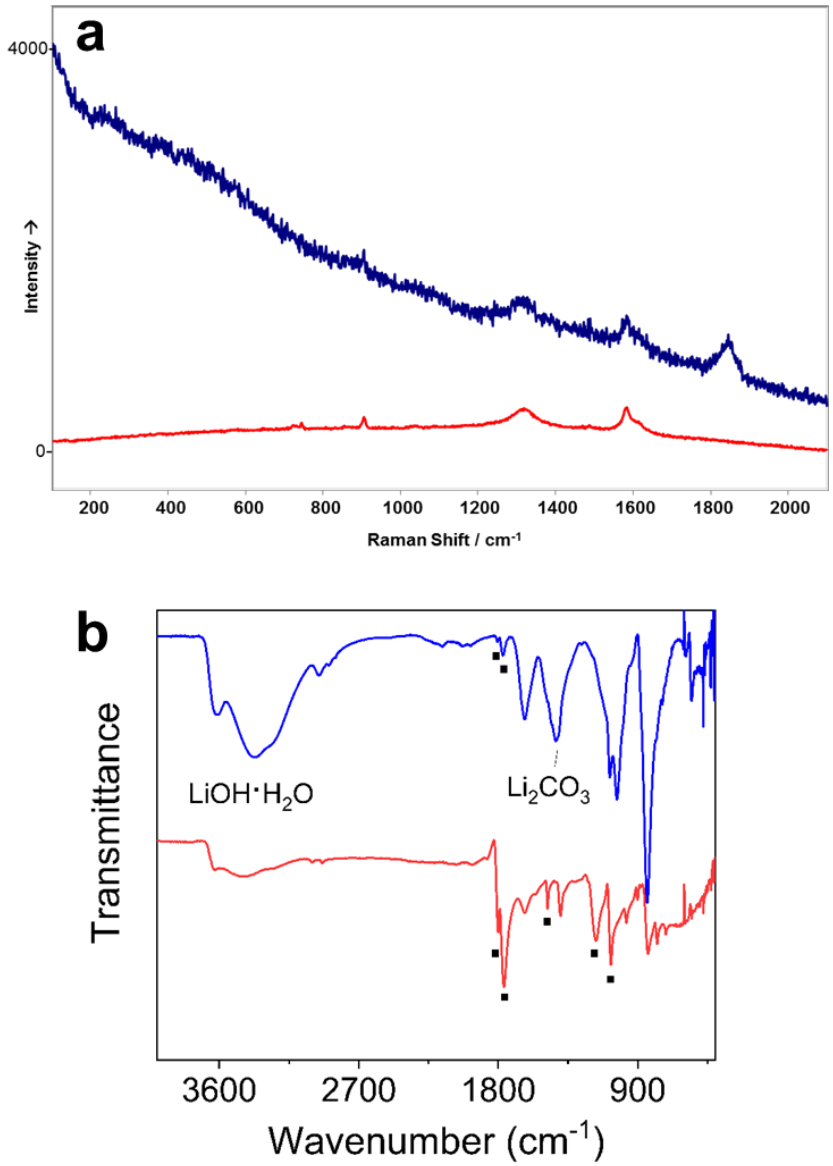

Figure S6. Effects of air exposure on Li plated electrodes: a) Raman spectra of Li plated Gr electrodes (cf. Figure 2c) immediately after exposure to air (*dark blue*) and 2.5 h later (*red*). The blue spectrum presents a single acquisition, and the red spectrum the average of 25 acquisitions. (Total counts for the red spectrum were divided by 25 to normalize the intensity of the red spectrum to that of the blue spectrum.) Note the reduced background and the disappearance of the acetylide band over time; b) FTIR spectra of a Li plated Gr electrode (*blue*, cf. Figure 2c) and of cycled Gr (*red*, no plating) after exposure to lab air. Black squares indicates bands assigned to ethylene carbonate (ref. [6]). Bands from residual solvent are overshadowed by other components in the Li-plated sample. Assignments for Li_2CO_3 and hydrated LiOH are from refs. [7] and [8], respectively.

Supporting References

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