Supplementary Information

S1. Set-up used for operando X-ray imaging of 18650 cell failure

The experiments performed at the ESRF beamline ID19 and Diamond Light Source beamline I12 involved high-speed radiography only, and not computed tomography. Therefore, rotational compatibility was not needed. A commercial battery nail penetration system (MTI Nail Penetration Tester, MSK-800-TE9002, MTI, Richmond, CA, USA) was modified to provide X-ray and infrared transparent windows for simultaneous thermal and high-speed X-ray imaging (Figure S1). The front and rear doors of the nail penetration system were replaced with 2 mm thick aluminium panels that had integrated infra-red transparent sapphire windows (2 mm thick), and X-ray transparent Kapton windows for simultaneous thermal imaging and radiography. The entire penetration system was mounted onto a heavy duty electronically controlled sample stage that, while under load (*ca.* 120 kg), could move in the vertical direction only at ESRF, and both the vertical and horizontal planes in Diamond Light Source. To extract the harmful gases generated during thermal runaway, the nail penetration system was connected to the beamline ventilation system via flexi-piping, and an additional wider ventilation pipe was placed over the top of the system to help exhaust escaping gases (Figure S1a,b).

During imaging, the lithium-ion batteries were held firmly in place by hydraulic clamps, which along with the penetration piston, was connected to a 3 bar air supply (Figure S1b,c). The thermal camera was mounted directly above the field of view of the beam, at a slight angle facing down at the cell being tested and was shielded against the high energy X-ray by a lead cover (Figure S1a). Electrical connections for voltage monitoring and heating were passed through a side porthole (Figure S1b), and all electrical equipment (penetration system, thermal camera, heating elements and power supplies) were extended and controlled from outside the hutch in the user control room.

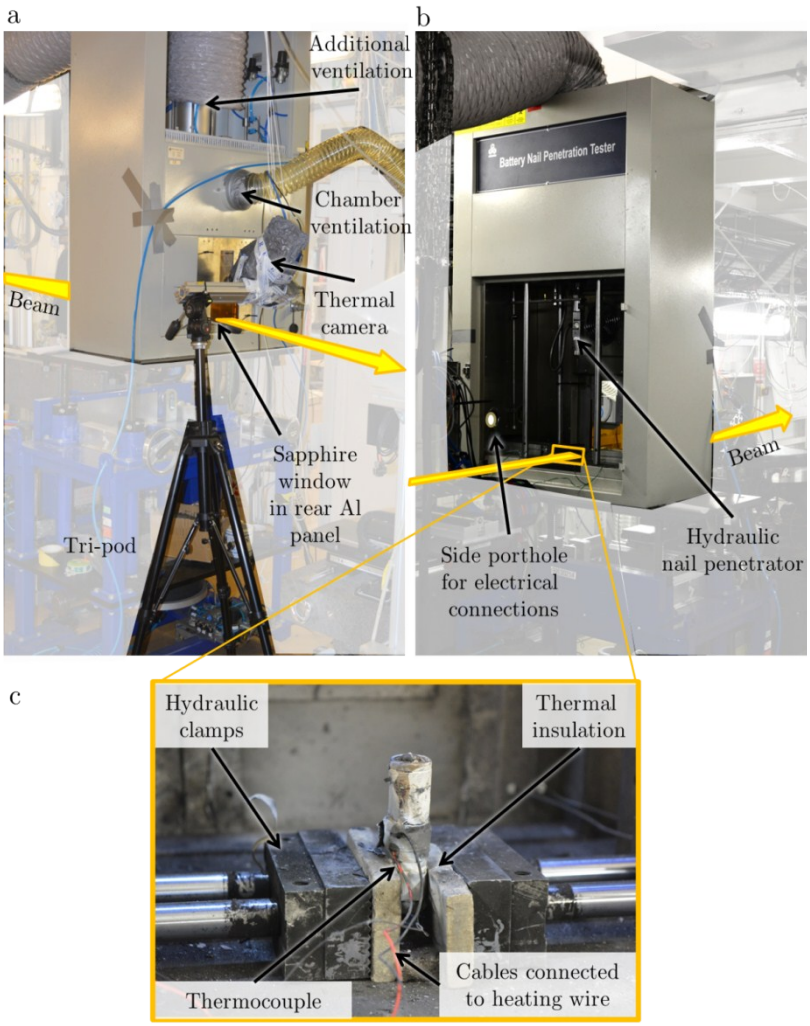

Figure S1. (a) Rear view of the nail penetration system showing the placement of the rear Al panel with an integrated sapphire window, the thermal camera, and ventilation pipes. (b) Front view of the nail penetration system (without the X-ray transparent Al front panel), showing the location of the battery being tested and hydraulic penetration piston. (c) Magnified view of inside of the penetration system showing a failed 18650 battery secured in place by hydraulic clamps and insulation plates.