Supporting Information for

Exploring the Kinetic Limitations Causing Unusual Low-Voltage Li Reinsertion in either Layered or Tri-Dimensional Li_2IrO_3 Cathode Materials

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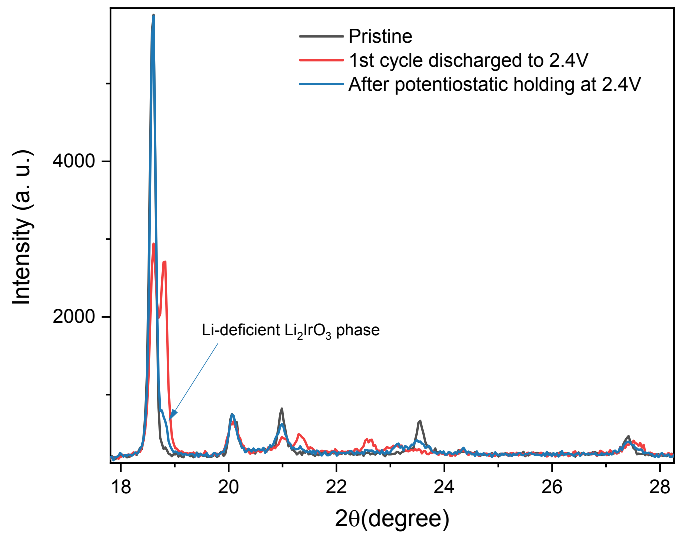

Figure S1. *Ex situ* XRD patterns for pristine α-Li_2IrO_3 (in black), and the phases discharged to 2.4V at 1st cycle (in red) and after potentiostatic holding at 2.4V (in blue) with a C/50 current cutoff.

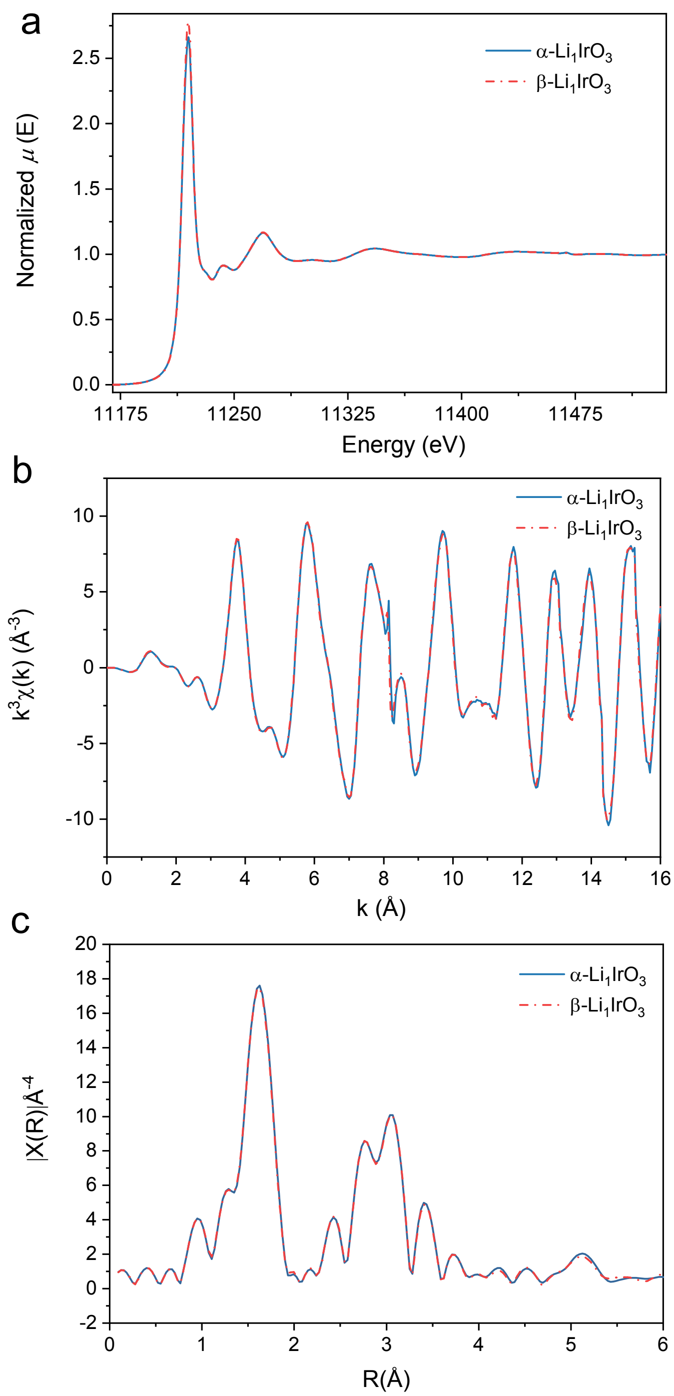

Figure S2. (a) The L_3-edge XANES of Ir collected on delithiated α- and β-Li_1IrO_3. (b) The corresponding k_3-weighted EXAFS oscillations. (c) Magnitude of Fourier Transform of k^3-weighted EXAFS of α- and β-Li_1IrO_3.

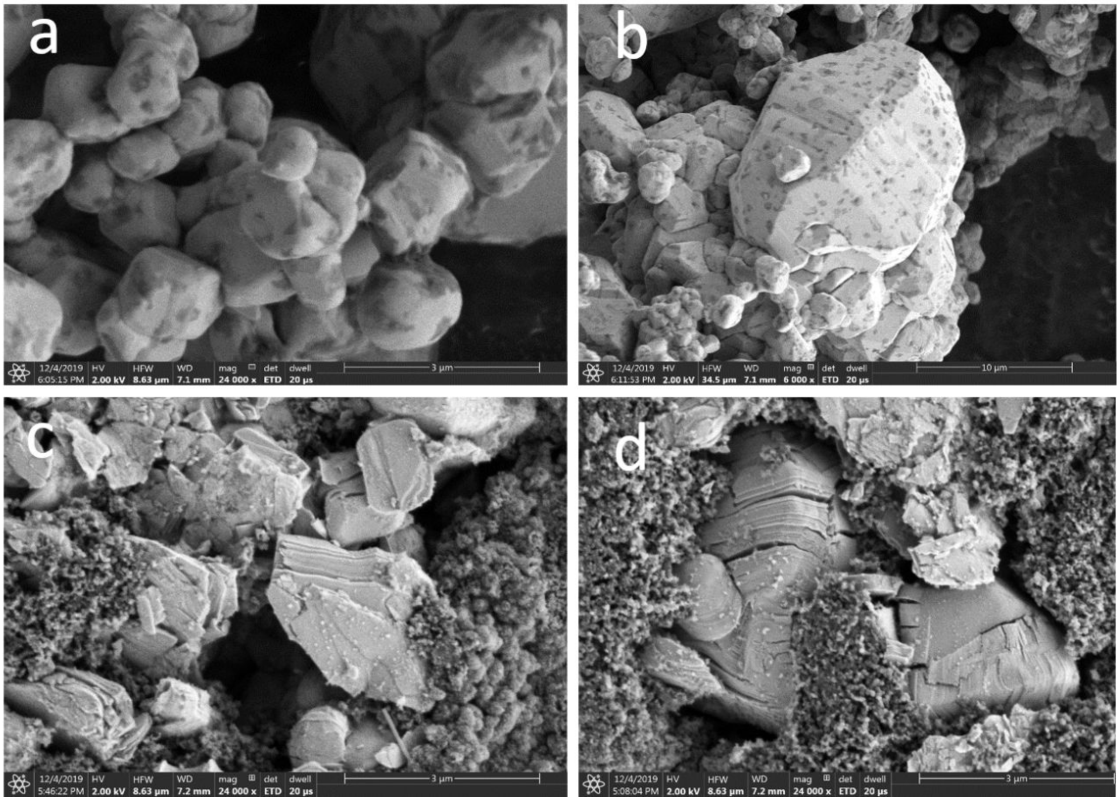

Figure S3. (a) and (b) show the SEM images of α-Li_2IrO_3 powder. (c) and (d) show the SEM images of α-Li_2IrO_3 electrode after cycling in the potential interval 1.65 – 3.9 V (5 cycles). The exfoliation of the particles after cycling demonstrates there should be a very large strain during charge and discharge.

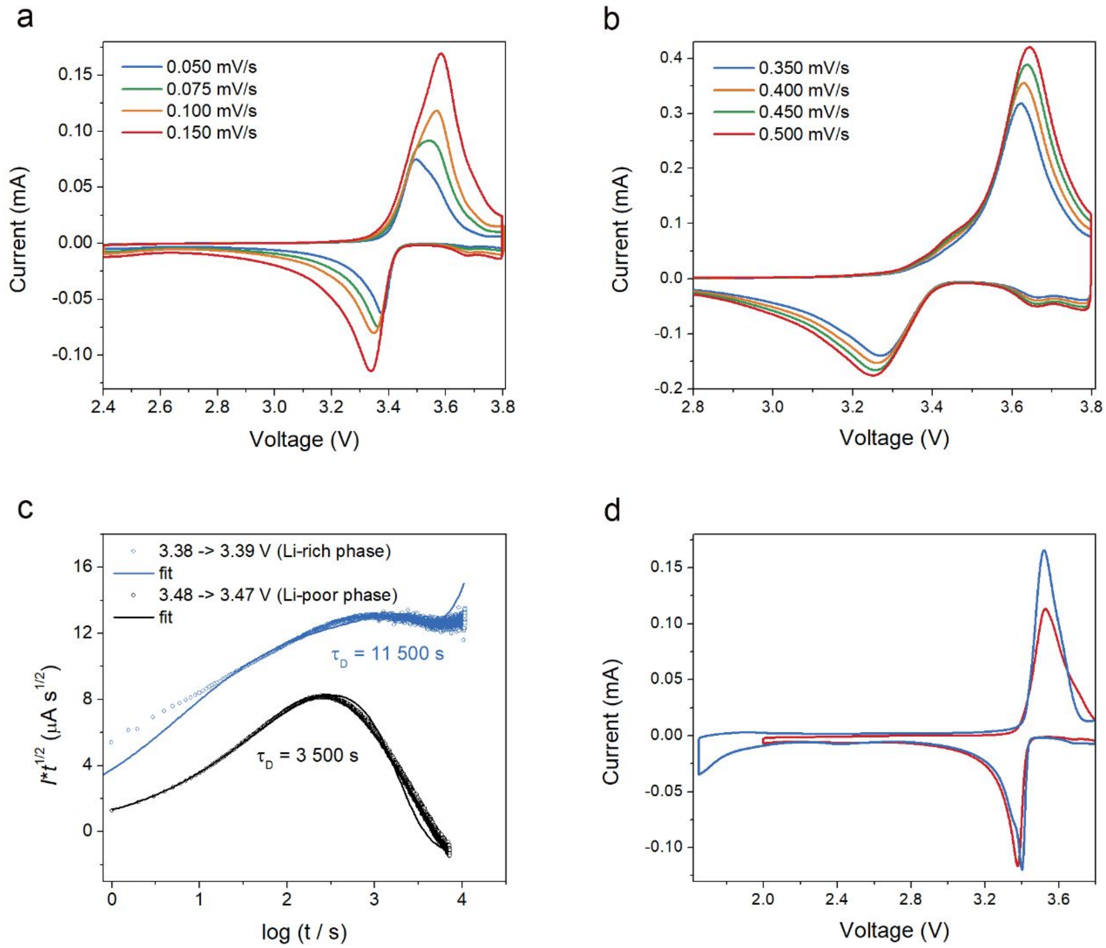

Figure S4. CVs of β-Li_2IrO_3 electrodes at low (a) and high (b) scan rates. (c) Current transients registered upon delithiation for the potential step from 3.380 to 3.390 V (diffusion in the Li-rich phase) and upon lithiation for the potential step from 3.480 to 3.470 V (diffusion in the Li-poor phase). (d) CVs with 2.0 and 1.65 V cathodic potential limits at 0.1 $mV\cdot s^{-1}$.

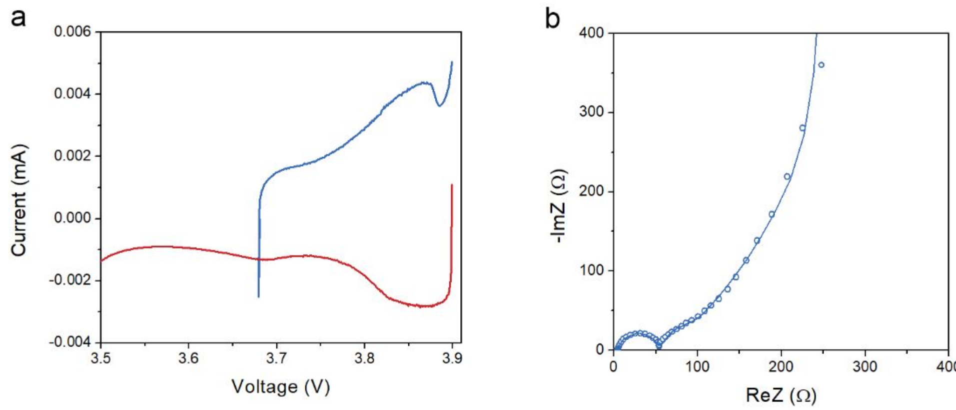

Figure S5. (a) shows the single-phase region at 3.7 – 3.9 V for β-Li_2IrO_3 and (b) shows the impedance spectrum registered at 3.7 V (symbols) and the fit to the equivalent circuit (solid line). The equivalent circuit comprises two RC elements, R_{SEI}/C_{SEI} and R_{ct}/C_{dl}, which account for the resistance and capacitance of surface layers (SEI) and for the charge transfer resistance and the double-layer capacitance, correspondingly. Diffusion is modelled by a spherical Warburg element (resistance and capacitance of diffusion - R_d and C_d). Parameter values: R_{SEI} = 46.8 Ω, C_{SEI} = 7 μF, R_{ct} = 151 Ω, C_{dl} = 40 μF, R_d = 946 Ω, C_d = 0.37 mF.