Delineating Local Electromigration for Nanoscale Probing of Lithium Ion Intercalation and Extraction by Electrochemical Strain Microscopy

Supplementary Information

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$LiFePO_4$ precursor was prepared by combining lithium hydroxide monohydrate $LiOH{\cdot}H_2O$ (≥ 99.0%, Fluka), ferric nitrate $Fe(NO_3)_3{\cdot}9H_2O$ (A.C.S. Reagent, Baker Analyzed), phosphoric acid H_3PO_4 (A.C.S. Reagent, min.85% spectrum), and L-ascorbic acid $C_6H_8O_6$ (≥ 99.0%, Sigma) with a molar ratio of Li:Fe:P:ascorbic acid of 1:1:1:1. All ingredients were mixed with distilled water at 1 mol/L concentration and heated at 60 ℃ for 1 hour to fully dissolve ascorbic acid. The solution was further diluted to 0.01 mol/L and 50 μL was drop-cast onto titanium (Ti) foil for electrode preparation. Films were annealed at 600 ℃ for 3 hours in N_2 gas.

Scanning electron microscopy (SEM, FEI Sirion) is used to examine the morphology of the $LiFePO_4$, which exhibits inhomogeneous distribution of micro- and nano-crystalline areas, as shown in Figs. S1(a), (b), and (c). Electrochemical testing of the $LiFePO_4$ electrode was carried out using a test cell with a lithium (Li) metal foil as anode and Celguard 2400 microporous film as separator. The electrolyte was 1.0 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (volume ratio: 1:1). The cell was assembled in a globe box filled with pure argon. Charging and discharging measurements were performed using Arbin BT2000 electrochemical measurement system with a potential range of 4.2 V – 2.0 V (vs. Li/Li^+), as shown in Fig. S1(d).

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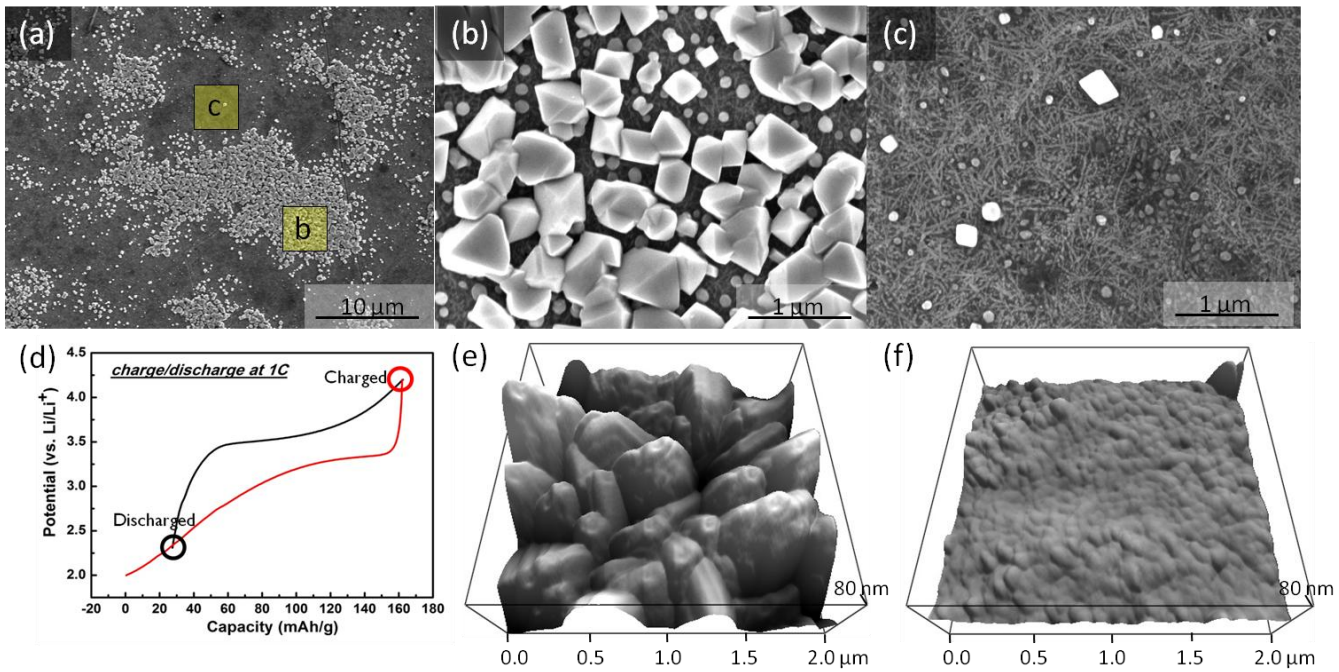

Figure S1: Inhomogeneous $LiFePO_4$ film consisting of both micro- and nano-crystalline areas for Li-ion battery cathode; (a) SEM image of the film; zoom in on (b) micro- and (c) nano-crystalline areas; (d) charging (red) and discharging (black) curves for $LiFePO_4$ film; and AFM topography mapping of (e) micro- and (f) nano-crystalline areas.

Three separate samples, one as-processed, one charged to 4.2 V, and the other discharged to 2 V were used for electrochemical strain microscopy (ESM) testing. All samples were glued to a thin stainless steel disk using epoxy (Tra-bond F113, Emerson and Cuming), and the edges of the Ti foil were painted with silver paint to insure a conductive path between the steel disk and the sample. All of the ESM measurements were taken using an Asylum Research MFP-3D atomic force microscope (AFM) with the piezoresponse force microscopy (PFM) module and ASYELEC-01 cantilever made of a tetrahedral silicon tip coated with iridium for conductivity. During ESM scanning, the topography of film was simultaneously mapped, as shown in Fig. S1(e) and (f) for micro- and nano-crystalline areas. Linear correlation between the ESM response and magnitude of alternating current (AC) voltage as expected from Eq. (2) is observed, as shown in Fig. S2, where the ESM scans were performed repeatedly over the same area while increasing AC voltage, with the responses at each AC voltage averaged over the scanned area. An AC driving voltage of 3 V was applied using dual frequency resonance tracking (DFRT) for ESM mapping, which also generated mappings of quality factor, as shown in Fig. S3.

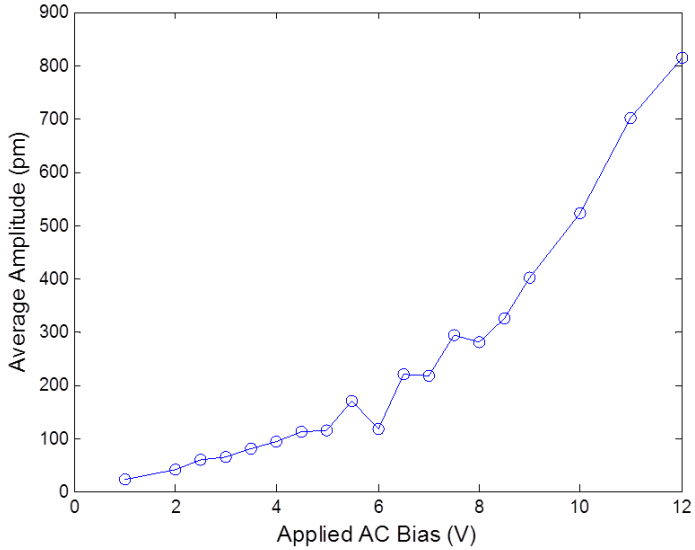

Figure S2 ESM response versus AC voltage.

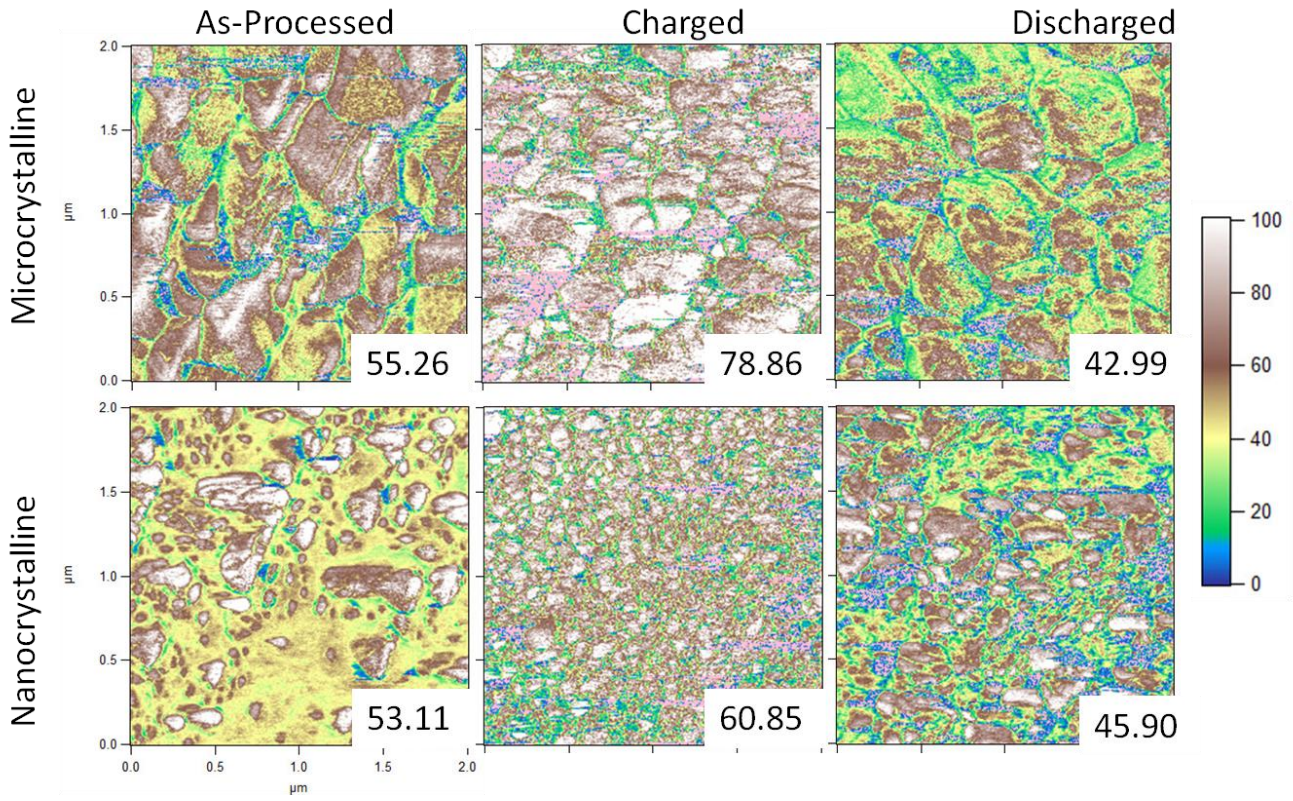

Figure S3 Comparison of ESM quality factor mappings of $LiFePO_4$ nanocrystalline electrode in microcrystalline and nanocrystalline areas at different stages of processing and testing, with the averaged amplitude identified in each mapping.