

## Supporting Information

Rate-dependent, Li ion insertion/deinsertion behaviour of  $\text{LiFePO}_4$  cathodes in commercial

18650  $\text{LiFePO}_4$  cells

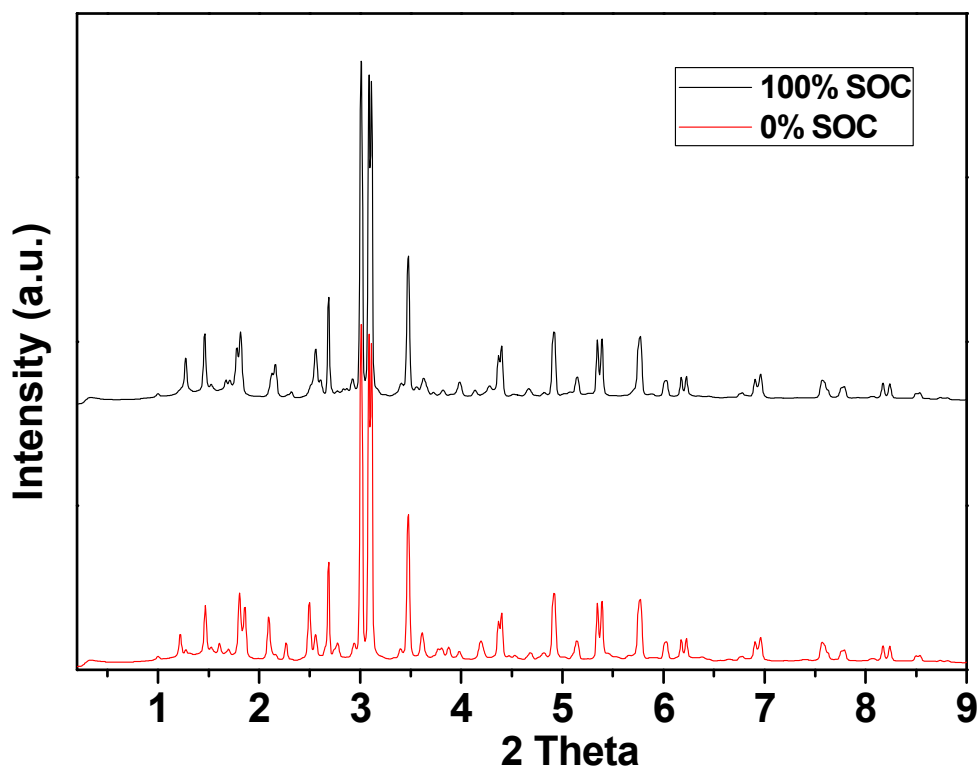
Qi Liu,<sup>1</sup> Hao He<sup>1</sup>, Zhe-Fei Li<sup>1</sup>, Yadong Liu<sup>1</sup>, Yang Ren<sup>\*,2</sup>, Wenquan Lu<sup>3</sup>, Jun Lu<sup>3</sup>, Eric  
A. Stach<sup>4</sup> and Jian Xie<sup>\*,1</sup>

<sup>1</sup>Department of Mechanical Engineering, Purdue School of Engineering and Technology, Indiana  
University-Purdue University, Indianapolis, IN 46202, USA

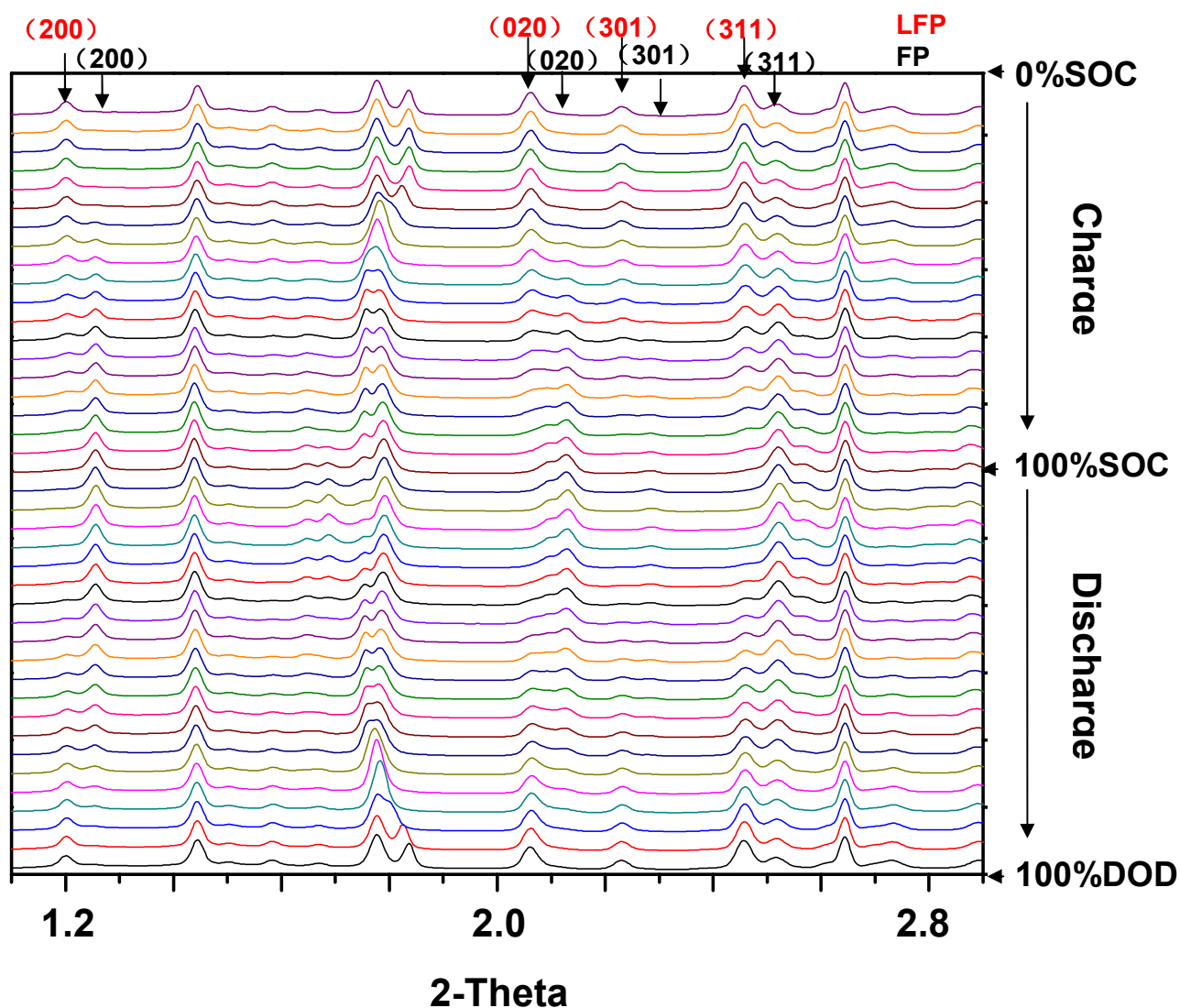
<sup>2</sup>X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South  
Cass Avenue, Lemont, IL, 60439, USA

<sup>3</sup>Chemical Science and Engineering Division, Argonne National Laboratory, 9700 South Cass  
Avenue, Lemont, IL, 60439, USA

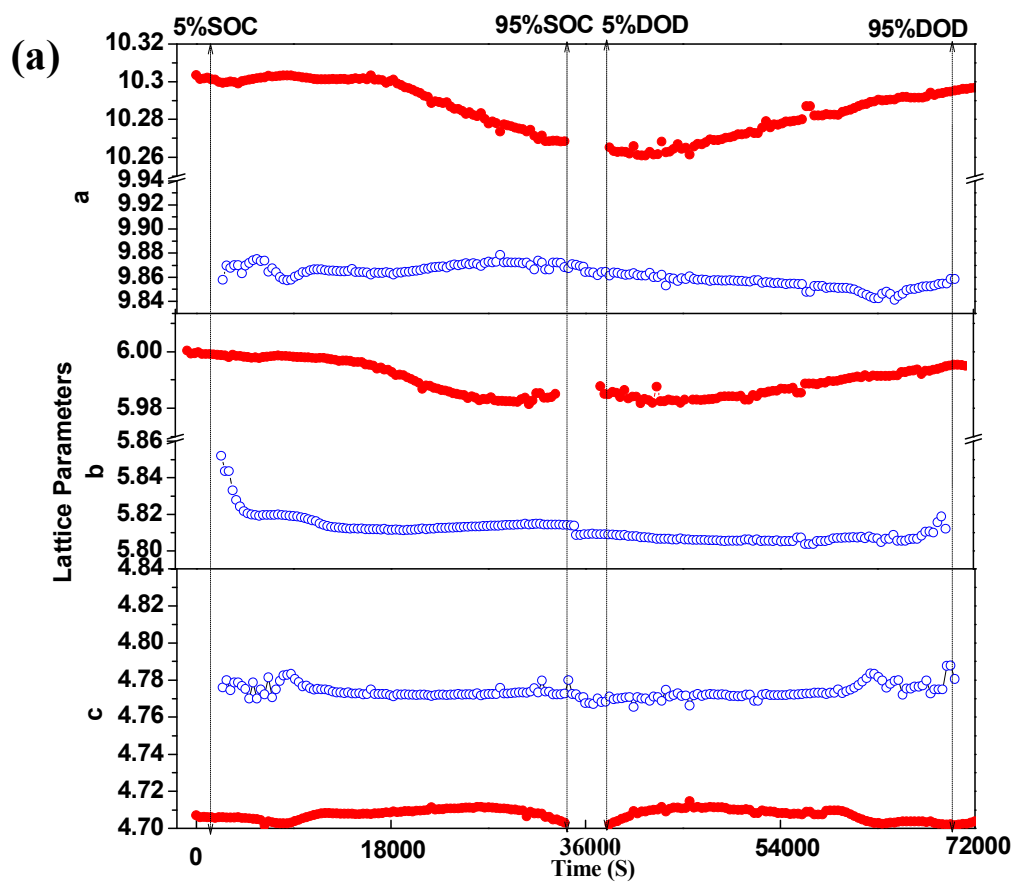
<sup>4</sup>Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

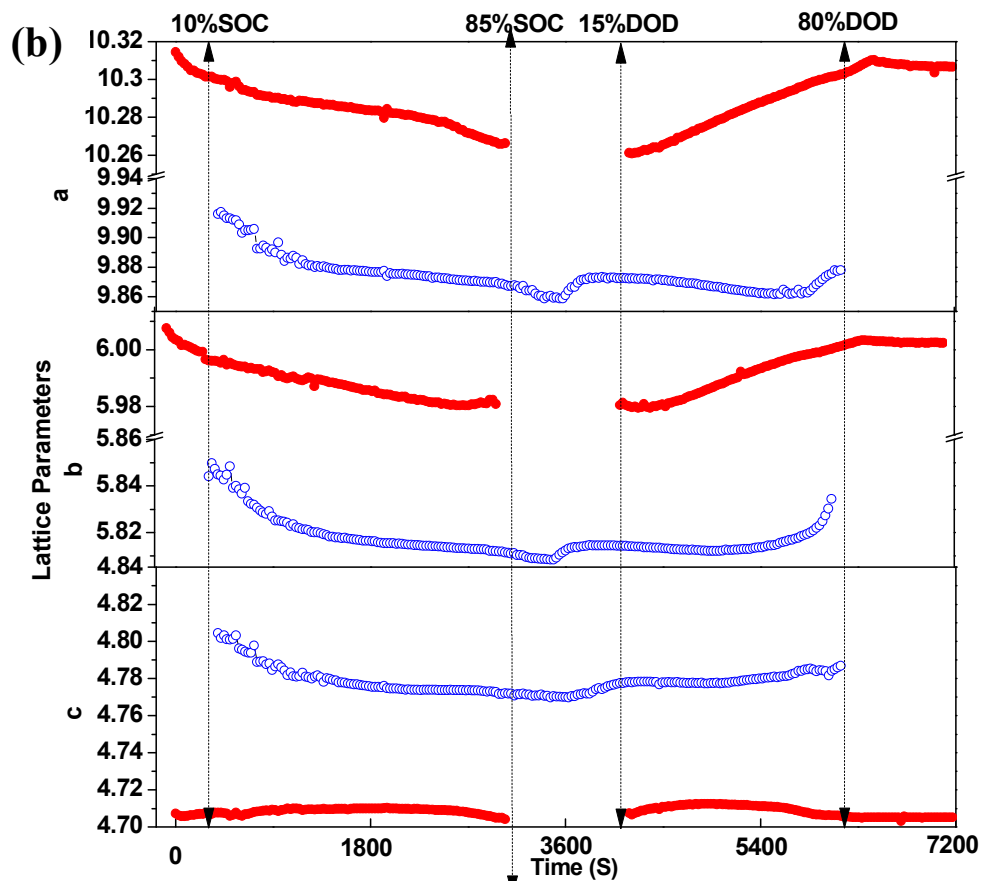


**Figure S1.** *Operando* XRD patterns of the 18650 cell under SOC = 0% and SOC = 100% during the 1<sup>st</sup> cycle at a 1 C rate. All the structure information for the 18650 cell is presented in one diffraction pattern. The broad background contribution starting at  $2\theta = 0.3^\circ$  results from the amorphous carbon black, which was added to improve the electronic conductivity, and the electrolyte. The strongest peaks at  $2\theta = 2.96^\circ$ ,  $3.42^\circ$ , and  $4.84^\circ$  represent the copper that served as the anode current collector. The peaks at  $2\theta = 2.64^\circ$ ,  $3.06^\circ$ ,  $4.32^\circ$  and  $5.07^\circ$  represent the alumina that served as the current collector for cathode. And the peaks at  $2\theta = 3.04^\circ$ ,  $4.29^\circ$  and  $5.29^\circ$  represent the stainless steel case for the cell.



**Figure S2.** Detailed XRD patterns between  $2\theta = 1.0^\circ$  and  $2.9^\circ$  during the 1<sup>st</sup> cycle of the charging process at a 1 C rate. The expected diffraction peaks ( $2\theta$ ) at  $1.21^\circ$ ,  $2.06^\circ$ ,  $2.21^\circ$ , and  $2.47^\circ$  result from the (200), (020), (301), and (311) planes of LiFePO<sub>4</sub>; the peaks ( $2\theta$ ) at  $1.25^\circ$ ,  $2.11^\circ$ ,  $2.27^\circ$  and  $2.53^\circ$  are ascribed to the (200), (020), (301), and (311) planes of FePO<sub>4</sub>.





**Figure S3.** Lattice parameter evolution during the 1<sup>st</sup> cycle of charge-discharge at (a) 0.1 C and (b) 1 C, calculated from the refinement data. Filled circles correspond to  $\text{Li}_{1-x}\text{FePO}_4$ ; empty circles correspond to  $\text{Li}_y\text{FePO}_4$ .