Supplementary information

Why LiFePO₄ is a Safe Battery Electrode: Coulomb Repulsion Induced Electron-State Reshuffling upon Lithiation

Xiaosong Liu,[a,b†] Yung Jui Wang,[a,c†] Bernardo Barbielllini,[c*] Hasnain Hafiz,[c] Susmita Basak,[c] Jun Liu,[d] Thomas Richardson,[d] Guojiun Shu,[e] Fangcheng Chou,[e] Tsu-Chien Weng,[f] Dennis Nordlund,[f] Dimosthenis Sokaras,[f] Brian Moritz,[g] Thomas Deveraux,[g] Ruimin Qiao,[a] Yi-De Chuang,[a] Arun Bansil,[c] Zahid Hussain[a] and Wanli Yang[a*]

[a.] *Advance Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.*
[b.] *State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, 200050, P.R.China.*
[c.] *Department of Physics, Northeastern University, Boston, MA 02115, USA.*
[d.] *Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA.*
[e.] *Center for Condensed Matter Sciences, National Taiwan University, Taipei, 10617 Taiwan.*
[f.] *Stanford Synchrotron Radiation Light Source, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA.*
[g.] *Stanford Institute for Materials and Energy Sciences, Stanford University and SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA.*
† These authors contribute equally to this work.
* Corresponding Authors: B.Amidei@neu.edu (B.B.) and WLYang@lbl.gov (W.Y.)

Experimental Methods

Soft x-ray absorption (sXAS) and emission (sXES) spectroscopy. The O K-edge and Fe L-edge spectroscopy was performed at the undulator beamline 8.0 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). The spherical grating monochromater (SGM) supply a linearly polarized photon beam with resolving power up to 6000. The sXAS spectra were collected in total electron yield (TEY) mode with the data normalized to the photon flux of incident beam measured by an upstream clean gold mesh. The sXES spectra were collected by a Rowland circle geometry spectrometer perpendicular to the incident beam. The experimental resolution is better than 0.2 eV for sXAS. For sXES measurements, the resolution of incident x-ray photon is about 0.9 eV and resolution of the spectrometer is about 0.7 eV.

Hard x-ray Raman scattering (hXRS). The cross-section of hXRS is dominated by the dipole transitions within the low-momentum transfer regime, thus in principle is analogous to sXAS. Stemming from the long penetration depth of high-energy x-ray photon, the hXRS provides the intrinsic bulk information compared to the surface-sensitive sXAS. The O K-edge and Fe L-edge hXRS measurements were performed at Beamline 6-2 at Stanford Synchrotron Radiation Lightsource (SSRL) with the Si-660 reflection of the XRS spectrometer corresponding to an incident scanning energy of about 10.4 keV. Although the statistics is not as good as the sXAS, the spectral fine structures are still unambiguously shown in the hXRS.

Multi-peak fitting of sXES spectroscopy. The multi-peak fitting of Fe-L XES spectra was performed with software WinXAS. The L_3 and L_2 were fitted with same group of Gaussian functions. Two broad components were used to fit the background. The main emission peaks were fitted with one Gaussian function for $FePO_4$ and three Gaussian functions for $LiFePO_4$. The physics arguments under this analysis were described in the main text.
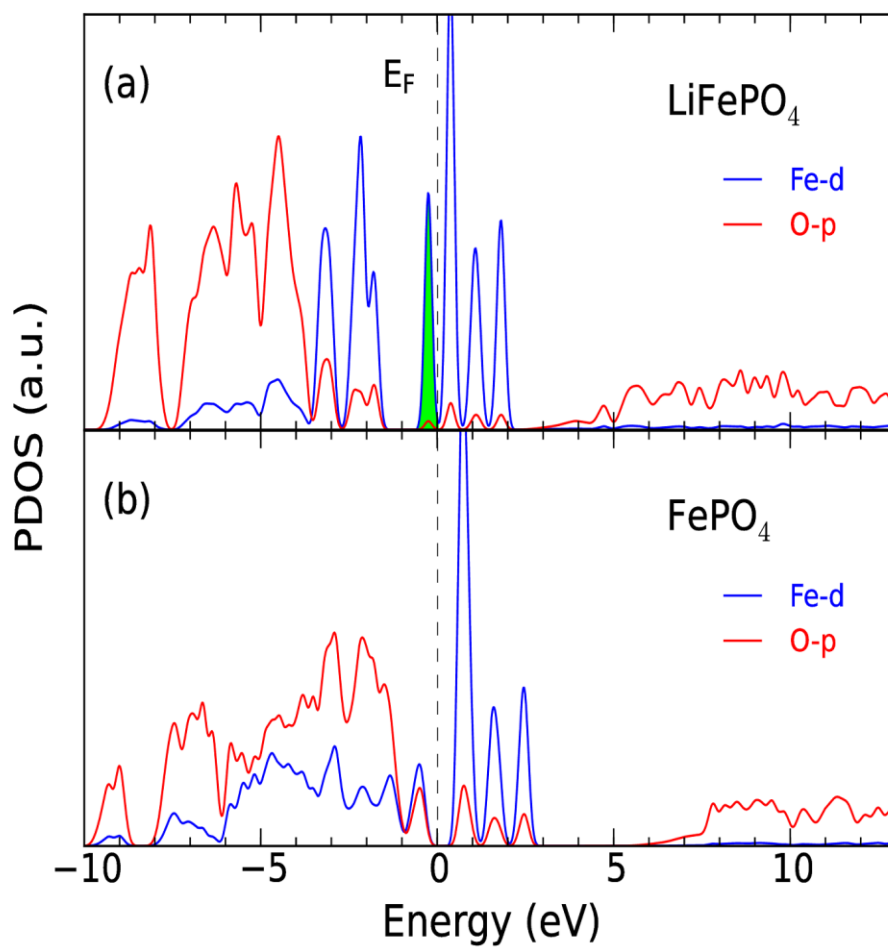
FIG. S1 The GGA (U=0) spin-polarized pDOS of Fe-3d (4 atoms) and O-2p pDOS (16 atoms) of (a) LiFePO$_4$ and (b) FePO$_4$. Blue (red) indicates Fe-d (O-p) states. The distinct occupied Fe-3d state close to the Fermi level (filled with green) is the state of electrons with the minority spin. The Fermi energy is set to be 0 eV. The GGA bandgap of less than 1 eV for both LiFePO$_4$ and FePO$_4$ is clearly underestimated. Although the occupied Fe-d and O-p GGA-pDOS of LiFePO$_4$ shows similar lineshape and distribution compared with MBJGGA+U pDOS shown in Fig. 4, the broad occupied Fe-d states in GGA-pDOS of FePO$_4$ between -6 eV and Fermi energy is inconsistent with the localized Fe-d states in MBJGGA+U pDOS located at 6 eV below the Fermi energy.
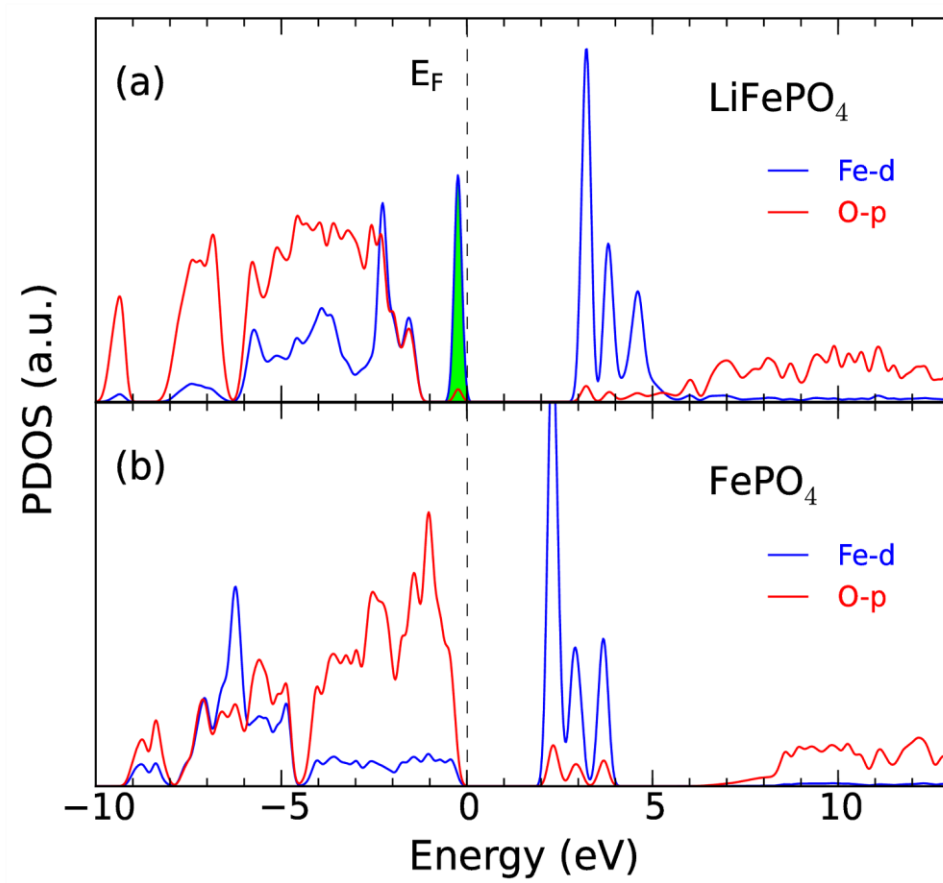
FIG. S2 The GGA+U with U=4 eV spin-polarized pDOS of Fe-3d (4 atoms) and O-2p pDOS (16 atoms) of (a) LiFePO$_4$ and (b) FePO$_4$ with the same layout as Fig. S1. By including Hubbard U = 4 eV in the GGA calculations, the bandgap of 3 eV and 2 eV are opened in LiFePO$_4$ and FePO$_4$ respectively. In contrast to the GGA calculations, the GGA+U and MBJGGA+U calculations show similar occupied pDOS of FePO$_4$. However, for GGA+U pDOS of LiFePO$_4$, the broad Fe-d states at 2 eV below the Fermi energy highly overlap with the O-p states, which feature is not seen in the MBJGGA+U calculations.