Support information

Imaging state of charge and its correlation to strong interaction variety in LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ nanorods-graphene hybrid

J.G. Zhou[1,2*], J. Wang[1*], Y. Hu[1], T. Regier [1], H. Wang[3], Y. Yang[4], Yi Cui[4], H. Dai[3]

[1] Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Canada S7N 2V3

[2] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, China

[3] Department of Chemistry, Stanford University, Stanford, USA

[4] Department of Materials Science and Engineering, Stanford University, Stanford, USA

1. Experimental

1.1 Synthesis of LMFP/graphene

LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ nanorods were grown onto graphene (LMFP/graphene) by a two-step solution method[1]. Briefly, hydrolysis of Mn and Fe salts is the first step to make Fe-doped Mn$_3$O$_4$ nanoparticles being deposited on graphene oxide (GO). Following this the second step transformed the nanoparticles on GO into LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ nanorods by reacting with LiOH and H$_3$PO$_4$. The GO is also reduced to graphene in this step to obtain LMFP/graphene.

1.2 Delithiation

Delithiation of LMFP/graphene to the different states of charge was achieved through electrochemical charging a coin cell in which the LMFP/graphene active material powder was mixed with Super P carbon black, binder, and polyvinyldifluoride (PVDF, Kynar HSV 900) with a weight ratio of 80:10:10 on an aluminum foil as the working electrode. The 2032 type coin cells also include separator, Li metal foil as the counter electrode, and 1.0 M LiPF$_6$ in 1:1 w/w ethylene carbonate (diethyl carbonate, Novolyte) as the electrolyte. Figure S1 showed the typical charge curve of LMFP/graphene at a rate of C/2 (where a 1C rate corresponded to a current

density of 170mA/g of LMFP)[1]. There are two voltage plateaus in the charge curve showed at ~3.6 and ~4.2 V. The coin cells were disassembled inside an Ar-filled glovebox after being charged to the first and second plateaus, respectively. The obtained electrodes were washed by EC:DEC and dried inside the glovebox and then sealed in a alumina bag. The final samples were denoted as partial charge and full charge, respectively. The corresponding molecular formula calculated from the charging curve is $Li_{0.75}Mn_{0.75}Fe_{0.25}PO_4$ and $Mn_{0.75}Fe_{0.25}PO_4$, respectively for those two samples.
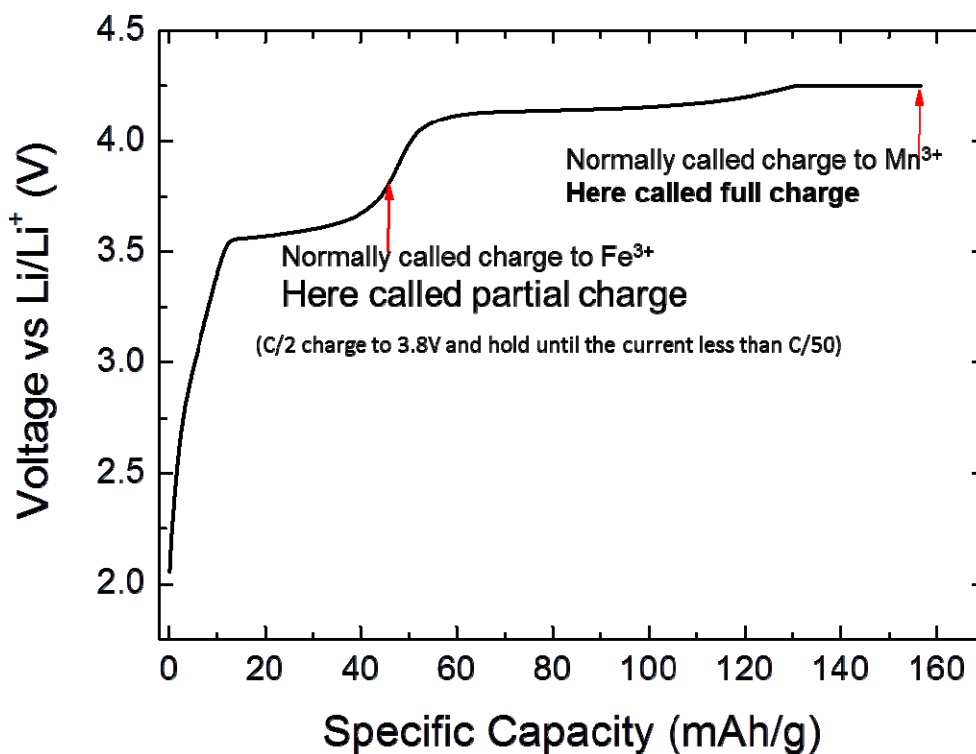

Fig. S1 Typical charge curve of LMFP-C.[1]

1.3 XANES

The XANES spectrocopy of delithiated electrodes was performed on the SGM beamline for Fe L-edge at the Canadian Light Source (CLS). All L-edge XANES were

recorded in the surface sensitive total electron yield (TEY) with use of specimen current and bulk sensitive inverse partial fluorescence yield (IPFY) using a silicon drift detector (SDD) to monitor the X-ray emission from oxygen. Data were first normalized to the incident photon flux I_0 measured with a gold mesh at SGM prior to the measurement. After background correction, the XANES were then normalized to their edge jump (the difference in absorption coefficient just below and at a flat region above the edge). Mn L-edge XANES of pristine and partially charged LMFP-C are displayed in Fig. S2. It presents the same oxidation state for Mn in both samples.
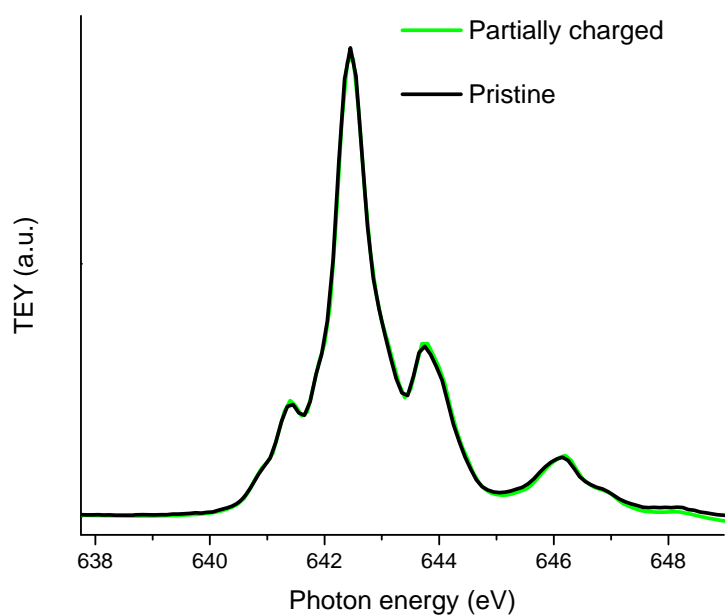
Fig. S2 Mn L-edge XANES of partially charged and pristine LMFP-C.

1.4 STXM

LMFP/graphene was released from a small piece of electrode which was cut from the center of the electrode. This small piece was put in a vial filled with methanol. After a short

period of sonication, LMFP/grapheme can be released into methanol. A drop of the dispensation was deposited onto a Si_3N_4 window and allowed it to dry in the air. STXM measurements were conducted using the STXM at the SM beamline of CLS. The SM STXM is equipped with a 25 nm outermost-zone zone plate (CXRO, Berkeley Lab), and the diffraction-limited spatial resolution for this zone plate is 30 nm. A plane grating monochromator (PGM) was used for C K-edge and Fe L-edge measurements. The image pixel size was 25 nm with 1 ms dwell time per pixel. X-ray photon energy was calibrated using the gas phase XANES of CO_2 reported in the literature. Circularly polarized soft X-ray beam generated from the SM EPU was used, which also averaged out the in-plane polarization dependence of the absorption when the photon beam is incident normal onto the sample surface so that the electric polarization lies on the surface of graphene basal plane.

STXM data was analyzed by aXis2000 (available free for non-commercial applications at http://unicorn.mcmaster.ca/aXis2000.html). The C and Fe L-edge image stacks were appended together to form one whole stack, and then aligned and converted to absorbance (i.e. optical density). Such process assures the identical sample region to be chemically mapped at different absorption edges. Fe L-edge reference spectrum of Fe^{2+} was obtained from the original LMFP/graphene while the reference spectrum of Fe^{3+} was from LMFP/graphene with full charge. Reference spectra at the Fe L-edge were quantitatively scaled to represent 1 nm thick XANES by fitting the spectra to their calculated elemental X-ray absorption profiles of 1 nm thick material. Chemical imaging was conducted for the Fe L-edge stack of the partially charged LMFP-graphene to generate the quantitative maps of Fe with different valance by fitting the stack with the reference spectra, and for the C K-edge stack to obtain the interaction distribution between LMFP and graphene. Color composite images were created by combining individual

component maps with the image intensity rescaled for the best contrast. The C K-edge XANES

from interesting locations were extracted from the image stack at the C K-edge.
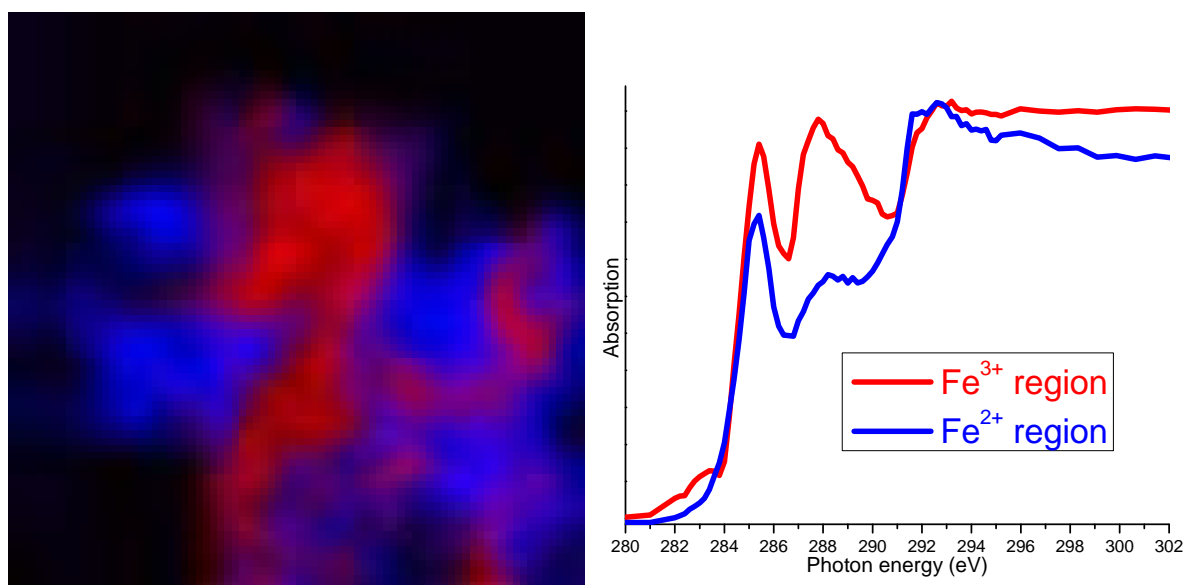

Fig. S3 C K-edge colour composite map of two types of interaction, i.e. stronger interaction

(corresponds to higher Fe^{3+}) and relatively weak interaction (corresponds to higher Fe^{2+}).

1.   H. L. Wang, Y. Yang, Y. Y. Liang, L. F. Cui, H. S. Casalongue, Y. G. Li, G. S. Hong, Y.

Cui and H. J. Dai, *Angew. Chem. Int. Ed.*, 2011, **50**, 7364-7368.