## **Supporting Information**

## Atomic Scale Insight on the Fundamental Mechanism of Mn Doped LiFePO<sub>4</sub>

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**Figure S1** Cycling stabilities of LiFePO<sub>4</sub> (LFP) and Mn doped LiFePO<sub>4</sub> (Mn-LFP) with different Mn doping amount of 0.1%, 0.5% and 1.0% (weight percentage) cycled at 1C after 3 formations at C/10.



Figure S2 SEM images of the pristine LFP (a) and pristine Mn-LFP (b).



Figure S3 XRD patterns of the pristine LFP and the pristine Mn-LFP.



**Figure S4** XPS survey spectra of the pristine LFP (**a**) and pristine Mn-LFP (**b**) powder samples.



Figure S5(a) - (b) Cyclic voltammetry (CV) curves of the LFP and Mn-LFP, between 2.5 - 4.2 V, with scan rates of 0.1, 0.2, 0.5, 0.8 and 1 mV s<sup>-1</sup>.



**Figure S6(a)** – (b) Relationship between the  $Z_{re}$  and the frequency of the pristine LFP versus Mn-LFP at the 1<sup>st</sup>, 50<sup>th</sup>, 100<sup>th</sup>, 200<sup>th</sup>, 400<sup>th</sup>, and 500<sup>th</sup> cycle. The slope, which is the Warburg impedance coefficient, was used to calculate the lithium-ion diffusion coefficient.



**Figure S7(a)** HAADF-STEM image of cycled LFP, **(b)** - **(d)** and the corresponding EDS mapping of Fe, P and O. **(e)** - **(h)** Analogous HAADF-STEM image and the corresponding EDS mapping of Fe, P and O but for cycled Mn-LFP.



Figure S8 XPS survey spectra of the cycled LFP (a) and cycled Mn-LFP (b) cathodes.



Figure S9 XPS survey spectra of the SEI formed on the post 500 cycled Li metal anodes, tested against LFP (a), and tested against Mn-LFP (b).



**Figure S10(a) - (b)** XPS high resolution spectra of F 1s and O 1s in the SEI formed on the post 500 cycled Li metal anode tested against LFP. (c) - (d) The corresponding XPS high resolution spectra tested against Mn-LFP.



**Figure S11 (a) - (b)** SEM image and EDS elemental mapping of O, F, P and Fe for the SEI formed on the post 500 cycled Li metal anode tested against LFP. (c) - (d) The corresponding SEM image and EDS elemental mapping of O, F, P and Fe for the SEI tested against Mn-LFP.