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Supporting Information

Design and synthesis of high performance $LiFePO_4$/C nanomaterial for lithium ion batteries assisted by a facile H^+/Li^+ ion exchange

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Supplementary Figures

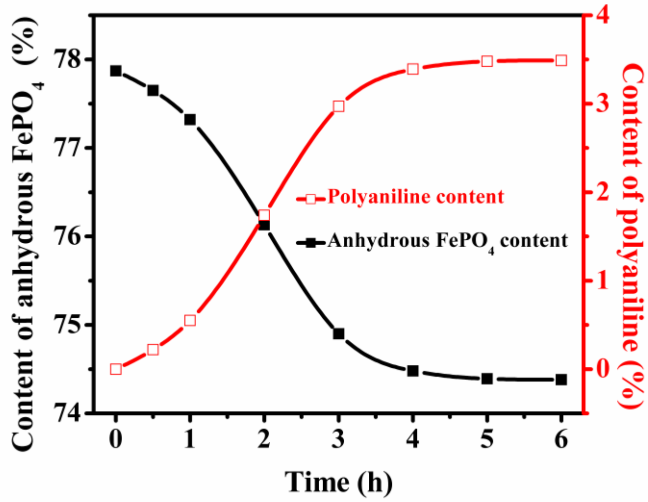

Figure S1. The mass content curves of time-consumed test for anhydrous $FePO_4$ and polyaniline in $FePO_4$-PANI nanocomposites aging for different times (0-6 h).

In the beginning (aging for 0 h), the visible precipitate could be totally regarded as hydrated $FePO_4$, as polyaniline barely appeared at this moment. According to result of TG test, the content of anhydrous $FePO_4$ in the hydrated $FePO_4$ is 77.87 wt. %, indicating that the chemical formula of hydrated $FePO_4$ should be accurately described as $FePO_4 \cdot 2.384H_2O$. After aging for 5 h, the content of anhydrous $FePO_4$ fell to 74.39 wt. %. Assuming that one proton per hydrated $FePO_4$ formula unit has been replaced by Li^+, the thermal decomposition procedures of as-synthesized $FePO_4$-PANI and Li-$FePO_4$-PANI nanocomposites can be theoretically described as follows:

$$FePO_4 \cdot 2.384\ H_2O\text{-PANI} \xrightarrow{\triangle} FePO_4 + 2.384\ H_2O\ (g) + Q\ (g) \quad (1)$$

$$FePO_4 \cdot 0.5\ Li_2O \cdot 1.884\ H_2O\text{-PANI} \xrightarrow{\triangle} 1/3\ Li_3Fe_2(PO_4)_3 + 1/6\ Fe_2O_3 + 1.884\ H_2O\ (g) + Q\ (g) \quad (2)$$

Here, Q represents the gas decomposition products of polyaniline. According to the Equation (1), the content (x) of polyaniline can be calculated by the following formula:

$$\frac{M(FePO_4)}{M(FePO_4)+2.384\ M(H_2O)} \times (1-x) = 74.39\ \%$$

where M (A) represents the molar mass of A. Thus the newly formed polyaniline accounts for 4.47 wt. % of $FePO_4$-PANI. Analogously, based on Equation (2), theoretical weight loss (y) of Li-$FePO_4$-PANI was calculated to be 20.68 wt. % by the following formula:

$$\frac{1/3\ M(Li_3Fe_2(PO_4)_3)+1/6\ M(Fe_2O_3)}{1/3\ M(Li_3Fe_2(PO_4)_3)+1/6\ M(Fe_2O_3)+1.884\ M(H_2O)}\times(1-4.47\ \%)=(1-y)$$

Hence, considering known total weight loss (25.61 wt. %) of $FePO_4$-PANI, the theoretical weight loss of Li-$FePO_4$-PANI should be 4.93 wt. % lower than that of $FePO_4$-PANI.

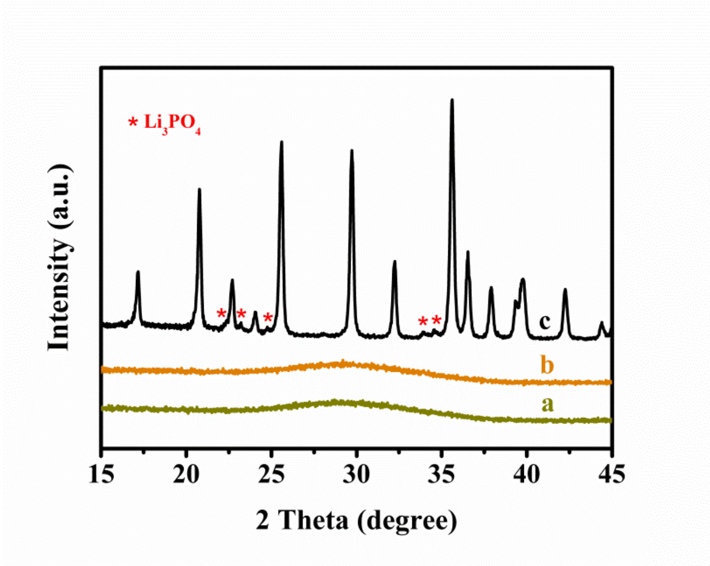

Figure S2. XRD patterns of a) pure hydrated $FePO_4$ (lack of PANI), b) Li-$FePO_4$ (H^+/Li^+ ion exchange for 2 h), c) $LiFePO_4$/C material containing Li_3PO_4 impurity synthesized from Li-$FePO_4$ intermediate.

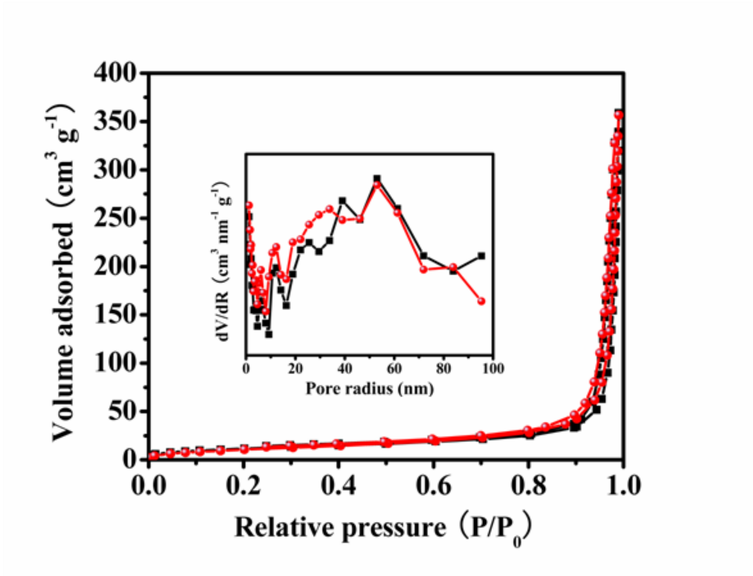

Figure S3. N_2 absorption-desorption isotherms of (dark) $FePO_4$-PANI and (red) Li-$FePO_4$-PANI nanocomposites. Inset shows corresponding pore size distributions.

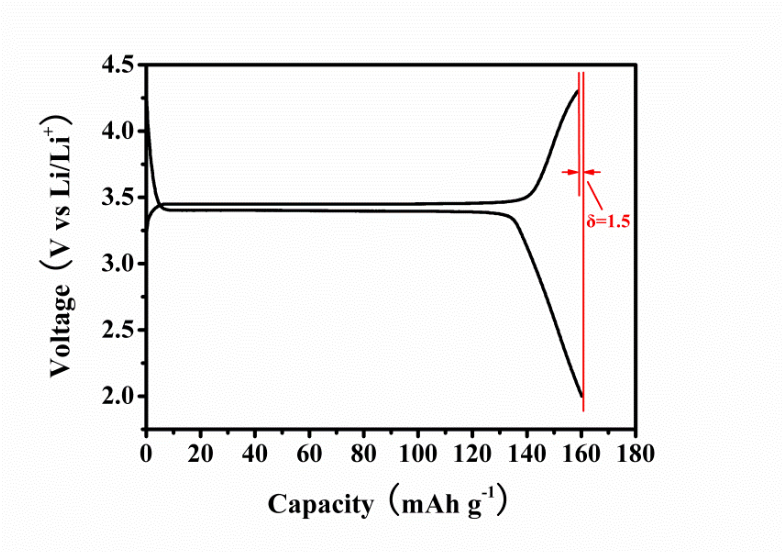

Figure S4. First charge and discharge curves of $LiFePO_4$/C nanomaterial tested at 0.2 C rate. The capacity in initial charge is found to be 1.5 mAh g^{-1} lower than that of discharge, reflecting a slight deficiency of Li in $LiFePO_4$/C nanomaterial, which can be interpreted as thermal evaporation of Li_2O during sintering at elevated temperature.

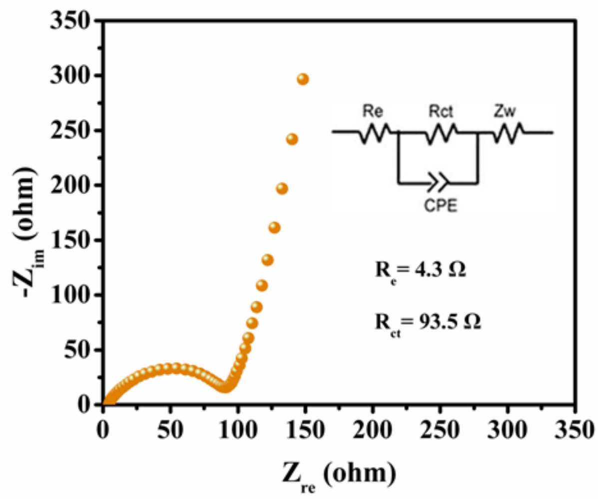

Figure S5. Nyquist plots of commercial $LiFePO_4$/C nanomaterial performed at open circuit voltage (OCV) after three cycles of activation. Inset shows the equivalent circuit and corresponding fitted values of ohmic resistance (R_e) and charge transfer resistance (R_{ct}).

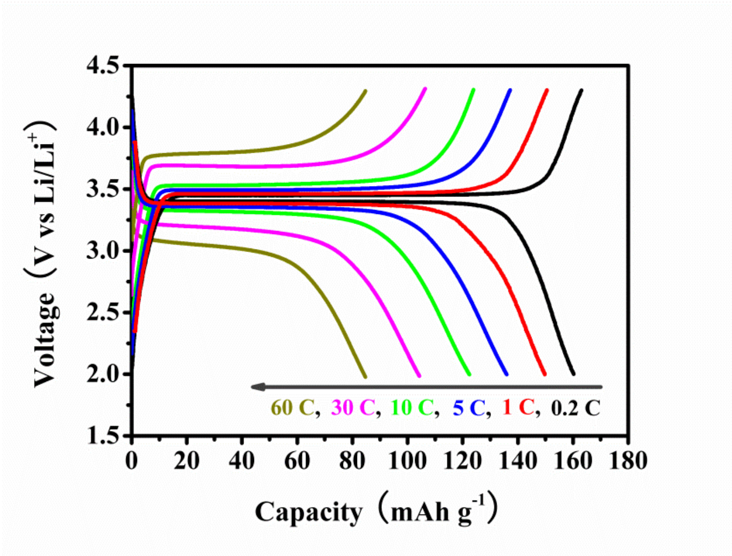

Figure S6. Galvanostatic charge-discharge curves of $LiFePO_4$/C nanomaterial at various rates tested with a relatively higher mass loading of ~5 mg cm^{-2}. Accordingly, the capacities are determined to be 160.2, 149.7, 135.9, 122.4, 104.3 and 84.7 mAh g^{-1} when discharging at 0.2 C, 1 C, 5 C, 10 C, 30 C and 60 C respectively.