Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information (ESI) for

"Hierarchically Porous and Conductive $LiFePO_4$ Bulk Electrode: Binder-Free and Ultrahigh-Volumetric-Capacity Li-Ion Cathode"

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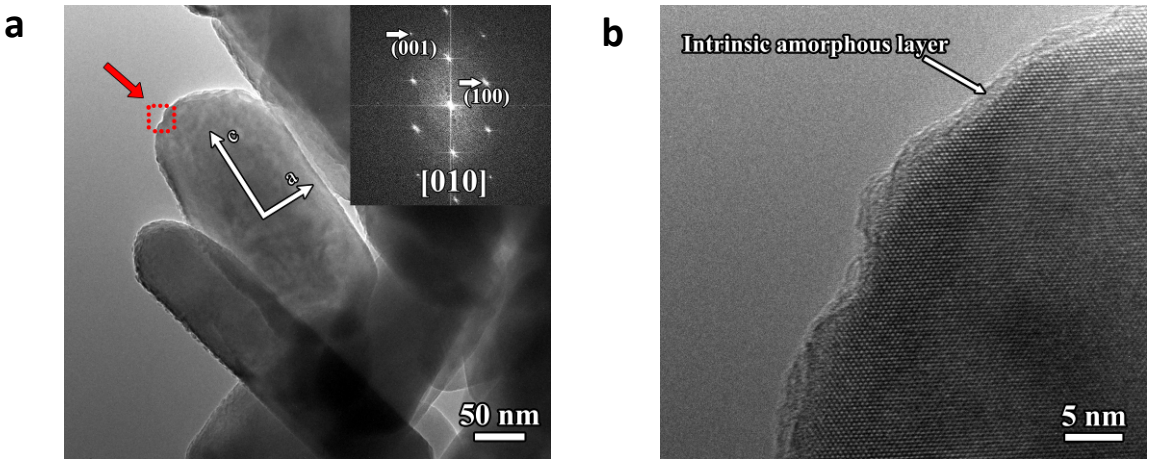

Fig. S1. (a) Typical TEM image of hydrothermally synthesized $LiFePO_4$ particles synthesized in a polyethylene-glycol/water medium (inset: the fast Fourier transform (FFT) pattern of (b), which denotes the beam direction), showing the orientation of the crystallite. (b) High resolution transmission electron microscope (HRTEM) image of the red zone in (a), showing an intrinsic amorphous layer on the surface of hydrothermally synthesized $LiFePO_4$ particles before sintering treatment.

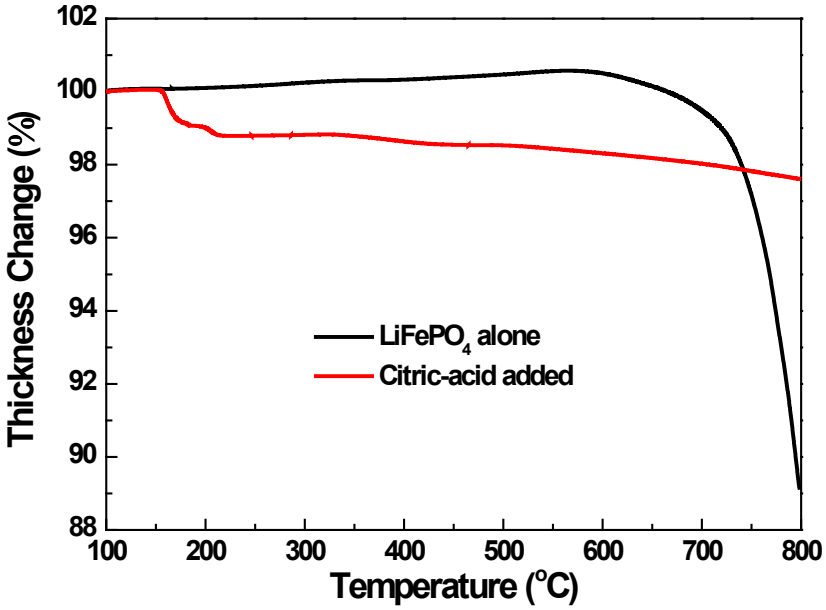

Fig. S2. TMA curves of two pellets made of $LiFePO_4$ alone and citric-acid added, recorded in high-purity argon atmosphere at a heating rate of 5 °C min^{-1} from 100 to 800 °C.

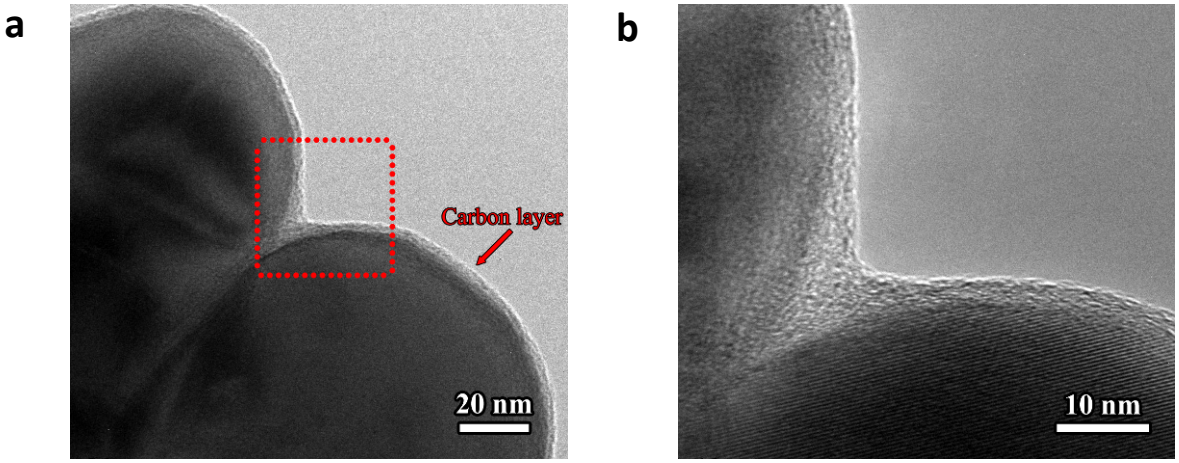

Fig. S3. (a) TEM image of $LiFePO_4$ particles coated with uniform electro-conductive carbon, which is attributed to chemical vapor deposition done at 700 °C for 30 min. (b) High-magnification image of the red zone in (a), showing uniform, interconnected and continuous conductive carbon.

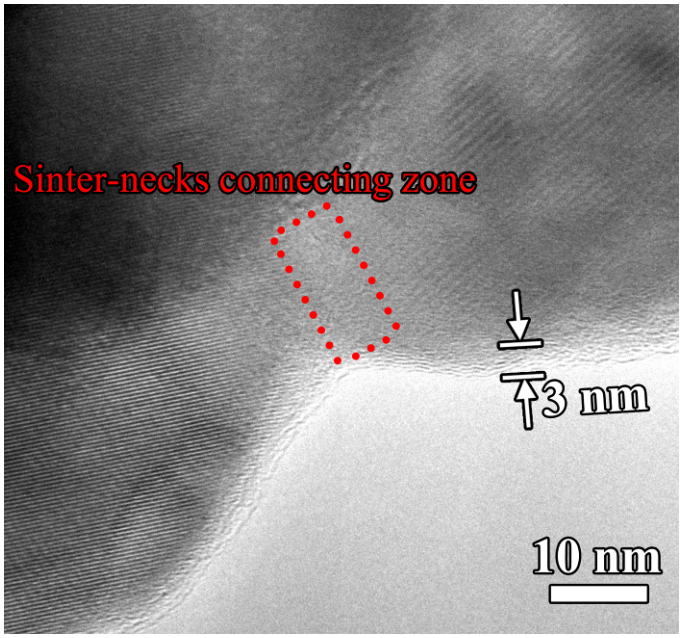

Fig. S4. TEM image of $LiFePO_4$ particles coated with uniform, interconnected and continuous conductive carbon with thickness of 3 nm. Red zone marks sinter-necks connecting zone between two particles.

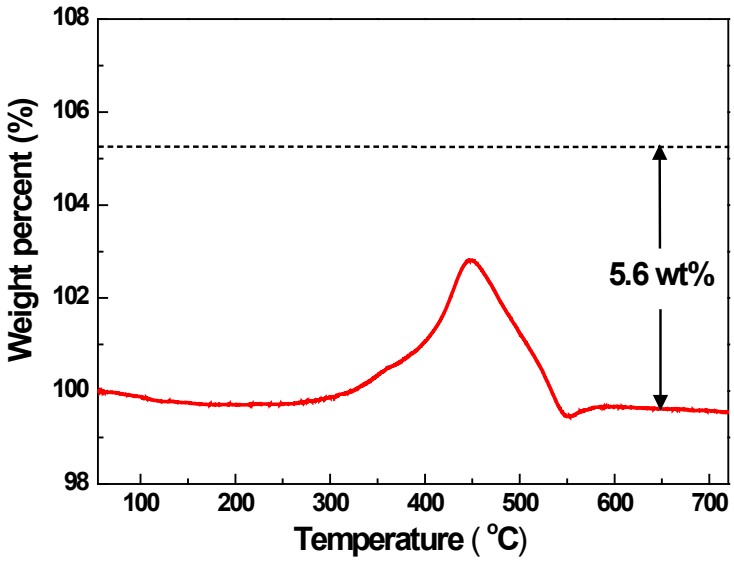

Fig. S5. TG curve of $LiFePO_4$/C bulk electrode tested in air at a heating rate of 5 °C min^{-1}. Considering the theoretical weight gain (5.07 wt%) of pure $LiFePO_4$ during TG measurement in air, the amount of conductive carbon in the $LiFePO_4$-based bulk electrode was calculated to be ~5.6 wt%.

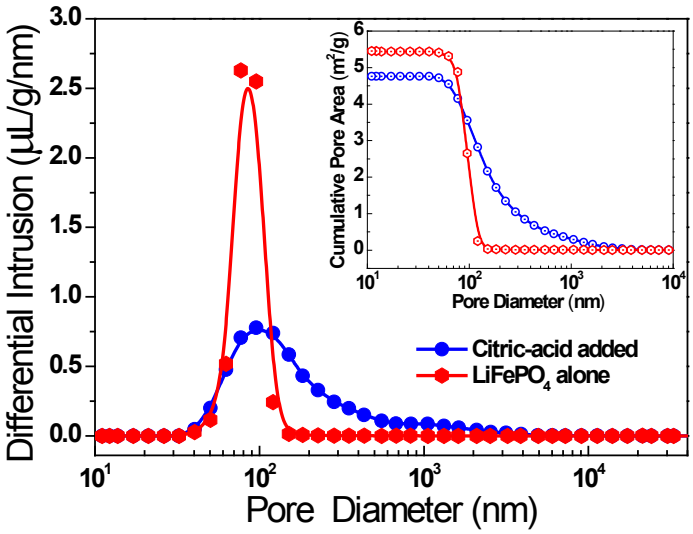

Fig. S6. Pore size distribution of two pellets made of $LiFePO_4$ alone and citric-acid added , determined by mercury porosimetry. Inset shows dependence of cumulative pore area on pore diameter.

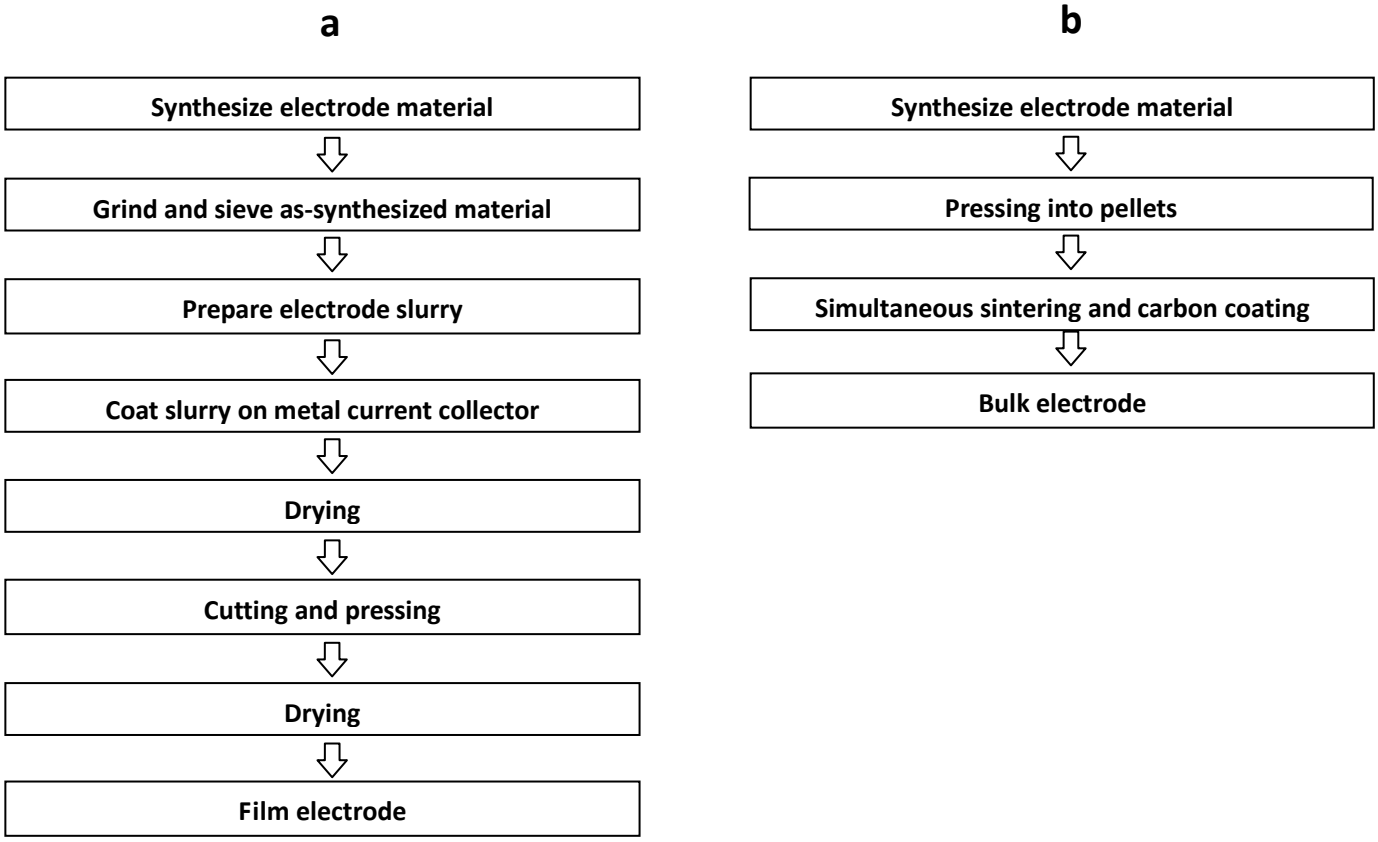

Fig. S7. Flow chart of electrode preparation. (a) Conventional film electrode. (b) Bulk electrode, showing a very simple process for preparing bulk electrode.

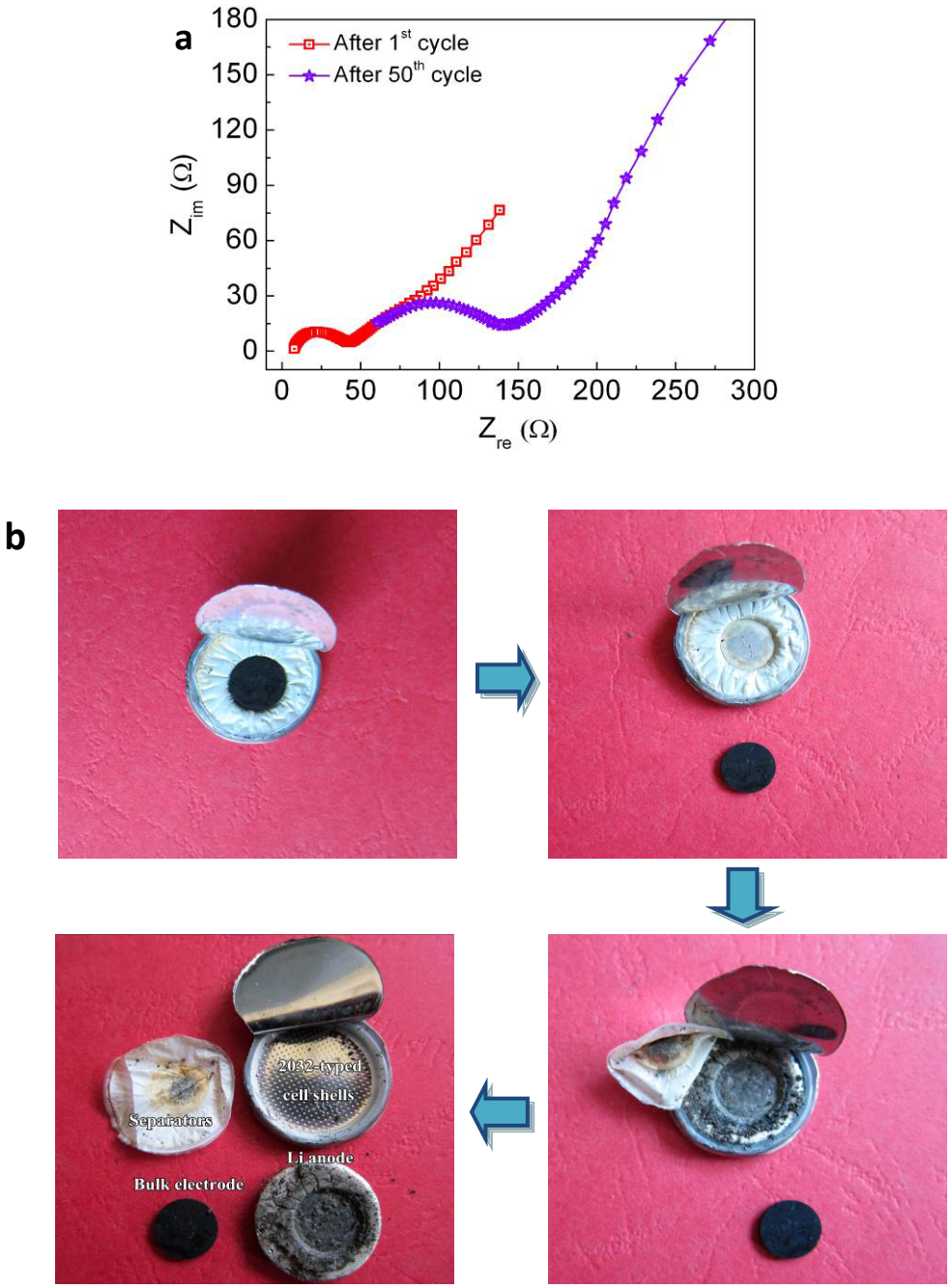

Fig. S8. (a) Nyquist plot of bulk electrode cycled galvanostatically after 1st and 50th cycle. The intercept at the Z_{re} axis in high frequency corresponds to the ohmic resistance of the electrolyte. Apparently, the resistances of the charge transfer and electrolyte both increase during the cell cycling, implying that the electrolyte seems to be reacted with electrode materials. (b) Photographs of the dissembled coin cell after 50 cycles. It is clearly shown that the post-cycling $LiFePO_4$-based bulk electrode has no observable mechanical damage. Flammable greyish substance was observed only on the side of Li metal anode.

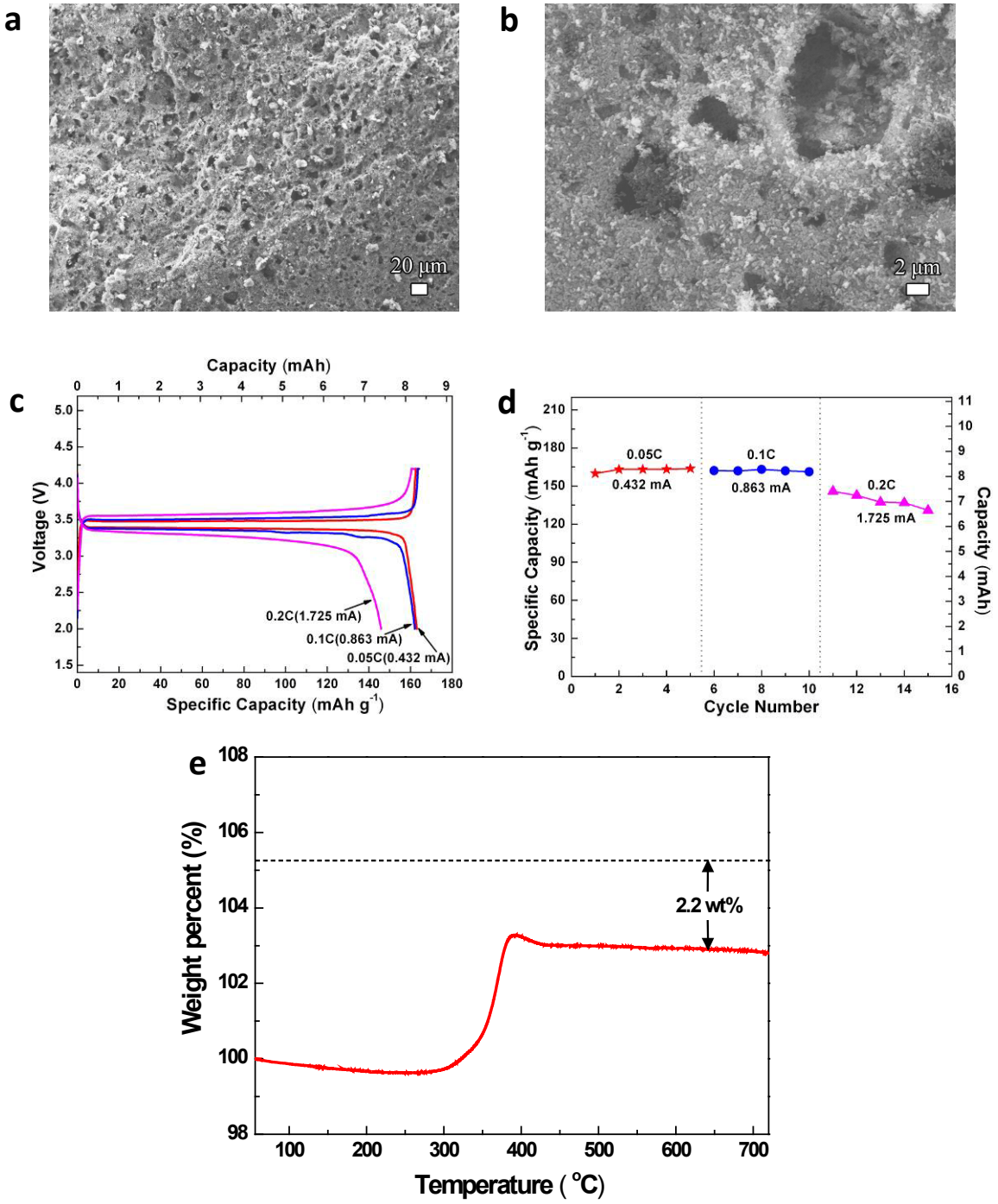

Fig. S9. (a) Typical SEM image of the $LiFePO_4$-based bulk electrode assisted by melamine as pore-forming agent. (b) SEM image with higher magnification. (c) Discharge and charge profiles. (d) Rate performance of the bulk electrode, showing improved capacity at 0.2C (compared with **Fig. 3d**) through optimizing the pore structure. (e) TG curve of the bulk electrode assisted by melamine tested in oxygen atmosphere at a heating rate of 5 °C min^{-1}. The amount of conductive carbon was calculated to be ~2.2 wt%.