

Supporting Information For

Direct regeneration of spent LiFePO_4 by graphite prelithiation strategy

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Experimental

LiFePO₄ battery cycling

LiFePO₄||graphite batteries have a rated capacity of 2160 mA h and a nominal voltage of 3.2 V. Individual LFP battery were cycled galvanostatically using a LAND Battery Test System from 2.5 V to 4.0 V at 216 mA g⁻¹ charge rate and discharged at 216 mA g⁻¹ rate under 25 °C. Electrochemical performances are shown in Figure S1. The charge capacity and discharge capacity of LiFePO₄ battery is 2077.6 mA h and 2066.4 mA h, respectively. The initial Coulombic efficiency is up to 99.46%. After 2000 cycles, the capacity retention is 70.82%, which is lower than 80% of the original capacity. So we used these spent LFP batteries as modeling sample to investigate their fail mechanism and regeneration method.

The battery dismantling and electrode fabrication

In order to compare the morphology and chemical composition of LFP cathodes before and after cycling, we disassembled the spent battery and the original battery and the obtained anode and cathode were put into the glove box filled with argon gas for later use.

The LFP electrodes were fabricated by mixing the active materials (spent LiFePO₄, original LiFePO₄), Super P, and polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) in a weight ratio of 8:1:1. The mixed slurry was coated onto aluminum foil and then dried at 80 °C under vacuum for 20 h to evaporate solvent. Electrodes with a diameter of 10 mm were punched and weighed. 1 M LiPF₆ solution in EC: DEC: DMC mixture (1:1:1 in volume) was utilized as electrolyte. The

graphite anode was made in the same way except that the slurry was coated onto copper foil.

Coin cell assembly and testing

2032-type coin cells were assembled in an Ar filled glove box (oxygen and moisture less than 0.1 ppm) using Celgard 2400 film as separator. Lithium foil were utilized as the counter electrode either to evaluate the performance of LFP cathode or to electrochemically lithiate the graphite anode. Prelithiated graphite anodes were prepared with graphite electrode as the working electrode and Li foil as the counter electrode. The electrochemical properties of the regenerated cathode will be affected if the amount of lithium ion in the prelithiated graphite is too much or too little. On the one hand, if the amount of lithium ion is too much, metal lithium is tended to precipitate on the surface of graphite during the process of charging, the resulted lithium dendrites will significantly reduce the safety of batteries. On the other hand, if the amount of lithium ion is too small, the electrochemical performance of the regenerated cathode will be affected. Therefore, ICP-MS was used to confirm the deficiency of lithium ion in spent cathode in the first step, and then the degree of prelithiation for the graphite was determined by controlling the cutoff voltage in our experimental design. The cutoff voltage was 0.1 V and the current density was 37.2 mA g⁻¹ according to the mass of graphite. After the prelithiated process, the graphite half cell was disassembled in an argon filled glove box and the prelithiated graphite anode was washed by dimethyl carbonate (DMC) for several times and then paired with the spent LFP cathode. The galvanostatic charge and discharge measurements

were carried out on a Land BT2000 battery test system over a voltage range of 2.5 to 4.0 V for both LFP cathode and LFP||graphite full cell.

Detailed dismantling process: (1) Fully discharge under LAND Cell Test System (2001A, Wuhan, China), discharge cut-off voltage is 2.5 V, in the form of multiple discharges, 2C discharge → standing for 1min→1C discharge → standing for 1min→ 0.5c discharge → standing for 1min→ 0.1c discharge → end. The use of multiple discharge is to migrate lithium ions as far as possible to the cathode, to avoid the lithium precipitation on the surface of graphite. (2) Cut the side of battery without tabs. (3) Cut the symmetrical side in the same way. (4) Cut the aluminum-plastic film on both sides of the battery. (5) Cut off the electrode ears on both sides together with the aluminum-plastic film, and remove the cell completely. (6) Separate positive electrode LFP plate, negative electrode graphite plate and diaphragm in the cell. (7) Wash and dry the positive electrode piece with DMC and put it into the glove box for later use. Recycle the negative electrode piece, diaphragm and shell.

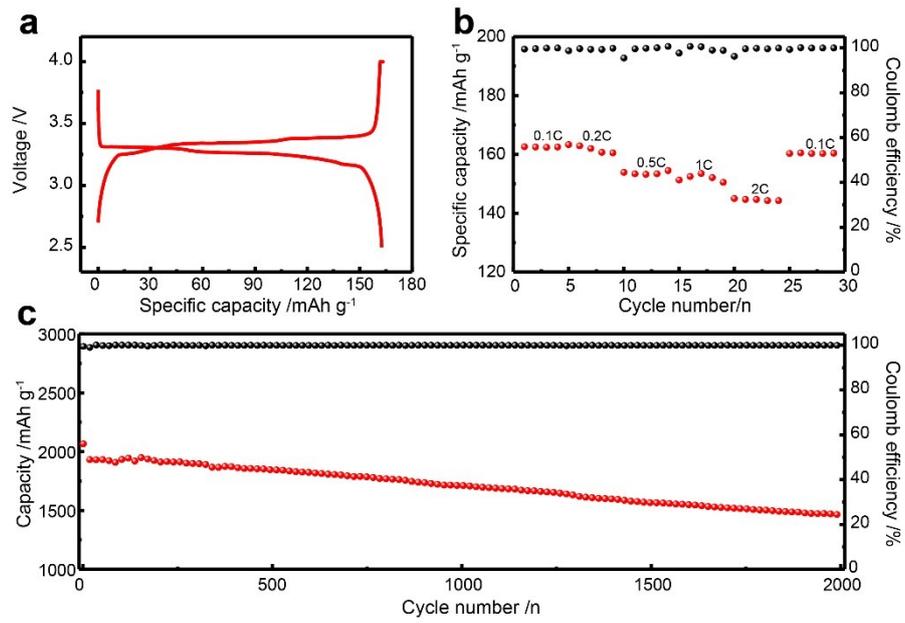


Figure S1. The electrochemical performance of the LiFePO₄||graphite battery (a) The typical charge/discharge profiles. (b) Rate performance. (c) Cycling performance at a current density of 216 mA g⁻¹

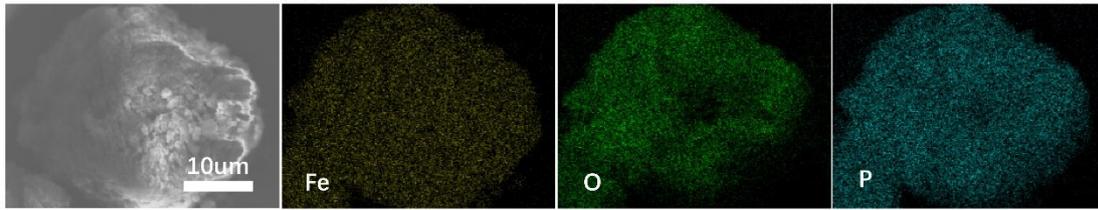


Figure S2. EDS elemental mapping: Fe (orange), P (blue), O (green) of original
LiFePO₄ powder

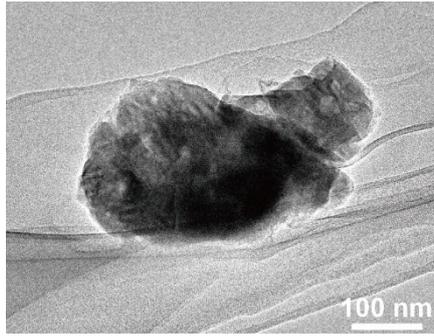


Figure S3. The TEM images of spent LiFePO₄

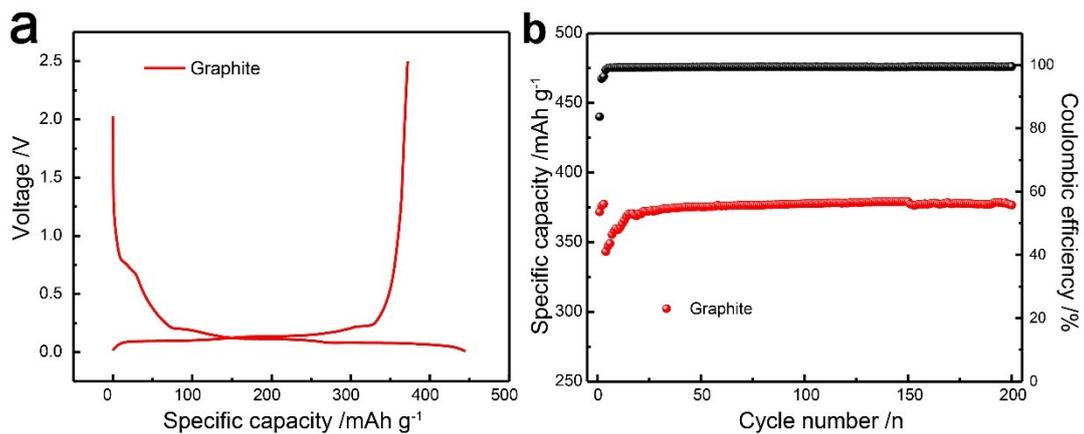


Figure S4. The electrochemical performance of the graphite based half cells. (a) The typical charge/discharge profiles. (b) Cycling performance at a current density of 0.5C.

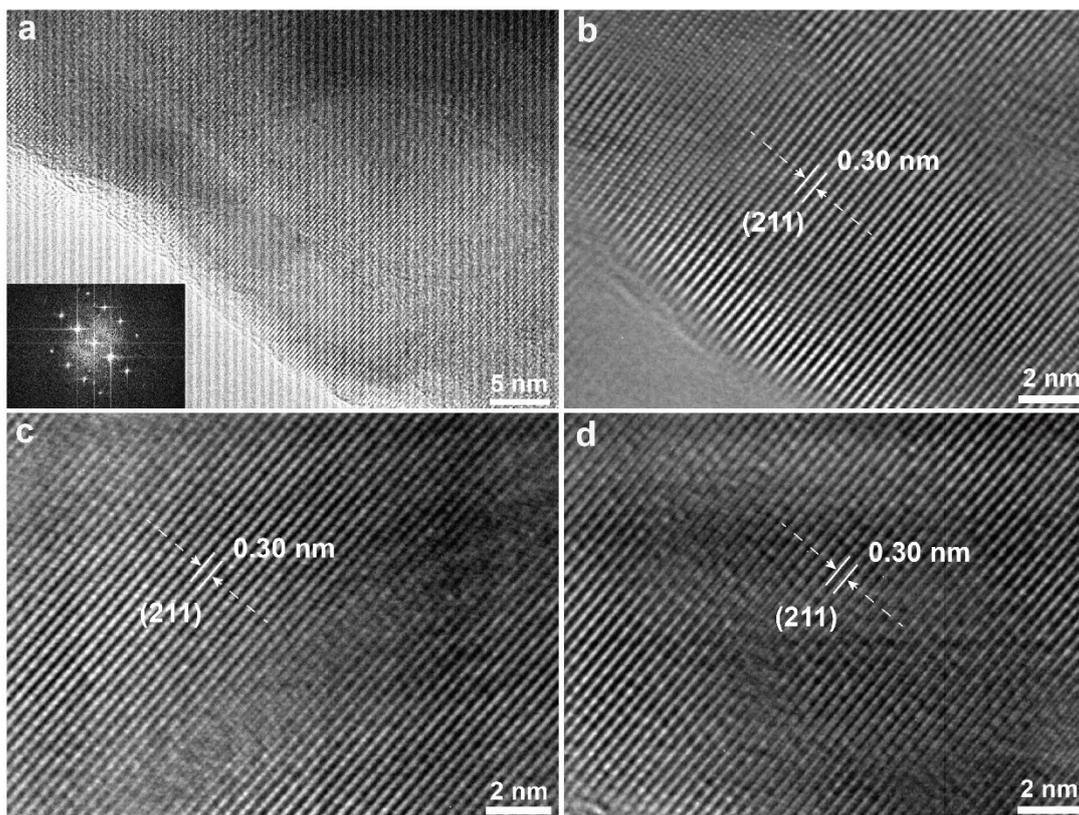


Figure S5. (a) TEM image of regeneration LiFePO_4 . The lattice fringe spacing on the (b) surface and (c) middle and (d) inside of this LFP nanoparticle.