Electronic Supplementary Information (ESI)

A Stable Filamentous Coaxial Microelectrode for Li-ion Batteries: A Case of Olivine $LiFePO_4$

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Supplementary Information including Experimental Section, Figure S1 and Table S1.

Experimental Section

1. Preparation of $LiFePO_4$ microelectrode by spray drying method

The 0.036 mol LiH_2PO_4 (Aladdin 99.9%), 0.036 mol $FeCl_2 \cdot 4H_2O$ (Aladdin 99.9%), 0.00108 mol $LiOH \cdot H_2O$ (Aladdin 99.9%), 15 ml hydrochloric acid (36%-38%), and 0.85188 g or no sucrose were successively added to 50 ml deionized water, which was diluted to 200 ml and thoroughly stirred to obtain a precursor solution. Then, the precursor solution was atomized by an ultrasonic nebulizer (402AI, yuewell company) at a frequency of 1.7 MHz, and the sprayed droplets were blown to a 50 μm diameter platinum wire by a hot air gun at 550 °C (560C, DES). Finally, the precursors were heat-treated with or without sucrose at 600 °C for 8 h in a tube furnace under an Ar + 5% H_2 atmosphere.

2. Characterization of materials

The crystal structures and morphology of as-prepared $LiFePO_4$ microelectrodes were characterized by powder X-ray diffraction (XRD, Bruker D2 PHASER diffractometer with Cu kα radiation) and scanning electron microscopy (SEM, Phenom ProX), respectively. The vibrational, rotational and other low frequency modes were measured by a Raman Imaging Microscope (Thermo Fisher Scientific DXRxi). And the optical microscope images were also acquired by this Raman Imaging Microscope.

3. Electrochemical Characterization

The as-prepared $LiFePO_4$ microelectrode was cut into a number of short pieces, and one end of each piece was firmly pressed between an aluminum mesh, in order to fix the microelectrode and enhance the electrical conductivity. In the conventional coin cells (CR2025), the counter electrode of lithium metal was separated from the microelectrode by a Celgard 2400 porous polypropylene film, and the electrolyte was 1 M $LiClO_4$ in ethylene carbonate/diethyl carbonate (EC/DEC with a volume ratio of 1:1). Galvanostatic charge/discharge tests were performed in a voltage range from 2.8 V to 4.0 V vs. Li^+/Li at room temperature by using Hokuto Denko battery testing system.

4. Weighment of Microelectrodes

The mass loading of active materials were measured for cycled microelectrodes by using Inductively Coupled Plasma mass spectrometry (ICP, Optima 7000). Because the microelectrodes are too small, it is difficult to accurately measure the mass of active material with an electronic balance. By using an Inductive Coupled Plasma Emission Spectrometer, we measured the iron content to calculate the $LiFePO_4$ mass of cycled microelectrodes. During the dissolution process, the microelectrode was taken out immediately when it showed the luster of a platinum wire, so little platinum was dissolved in aqua regia and it will not affect the ICP results of other elements. As shown in Table S1, the mass loading of ME-1, ME-2, ME-3 and ME-4 is 60.2μg, 60.5 μg, 36.8 μg and 43.8 μg, respectively, for the

galvanostatic measurements with a current of 5 μA in Fig. 3a and b. And the mass loading is 59.5 μg of ME-4 cycled at 25 μA in Fig. 3c and d.

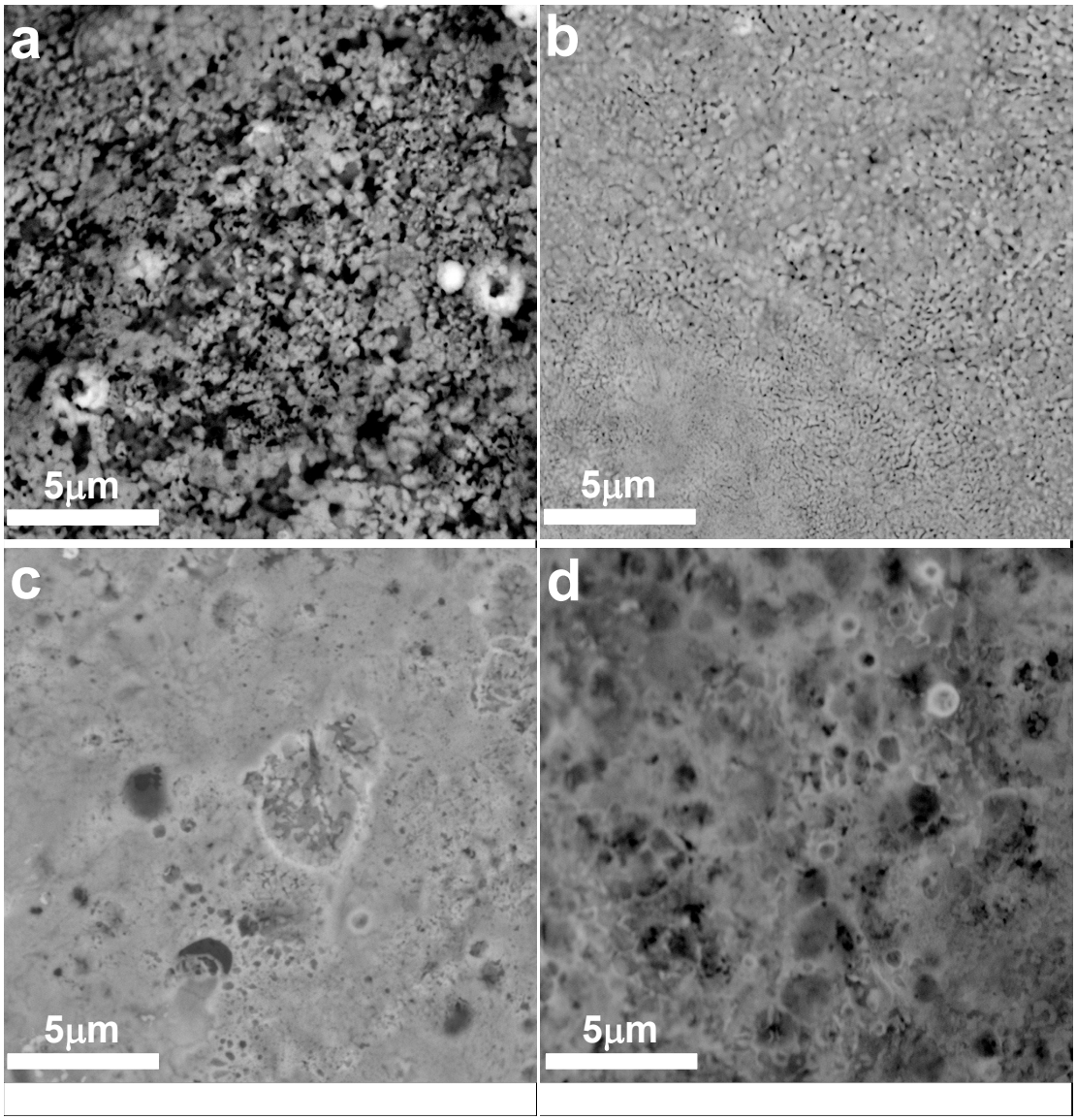

Figure S1. SEM images of pristine microelectrodes (a) ME-1, (b) ME-2, (c) ME-3 and (d) ME-4.

Table S1. The mass loading of microelectrodes calculated from ICP results.

Sample	**Active materials**
ME-1	60.2μg
ME-2	60.5 μg
ME-3	36.8 μg
ME-4, cycled at 5 μA	43.8 μg
ME-4, cycled at 25 μA	59.5 μg