

Supplementary information

The fine electrochemical performance of porous Cu₃P/Cu and the high energy density of Cu₃P as anode for Li-ion batteries

Shibing Ni,^{a,b*} Jianjun Ma^a, Xiaohu Lv^a, Xuelin Yang,^{a,b} * Lulu Zhang^{a,b}

^a College of Materials and Chemical Engineering, Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China.

^bHubei Provincial Collaborative Innovation Center for New Energy Microgrid, China Three Gorges University.

E-mail: shibingni07@126.com.

Experiments

Sample preparation

Cu₃P electrode was synthesized by a facile high temperature reaction method. Cu foams (100 PPI pore size, 380 g m⁻² surface density, 1.5 mm thick) was purchased from Changsha Lyrun New Material. Red phosphorus (analytical grade) was purchased from Sinopharm Chemical Reagent Corporation. In a typical procedure, 0.5 g red phosphorus was firstly placed in a ceramic boat, Cu foams were then placed on it. Cu foam scraps were use to separate red phosphorus and Cu foam. The ceramic boat was placed in a tube furnace and then heated to 350 °C for 5h in N₂ atmosphere at a heating rate of 3 °C min⁻¹. The weight of Cu₃P on Cu can be calculated according to the reaction $P + 3Cu \rightarrow Cu_3P$. $m_{Cu_3P} = \Delta m \times 221.5/31$, where Δm is the weight difference of Cu foam before and after reaction.

Structure and morphology characterization

The structure and morphology of the resulting products were characterized by X-Ray powder diffraction (Rigaku Ultima IV, Cu K α radiation, $\lambda=1.5406 \text{ \AA}$) and field-

emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL).

Electrochemical characterization

For fabricating of lithium ion battery, the $\text{Cu}_3\text{P}/\text{Cu}$ was dried at 120 °C for 24 h in vacuum oven. Coin-type cells (2025) of Li/1 M LiPF_6 in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/ $\text{Cu}_3\text{P}/\text{Cu}$ discs with diameter of 14 mm were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, H_2O <1.0 ppm, O_2 <1.0 ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage region between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). The Cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of 0.2 mV s^{-1} between 0 and 3 V.

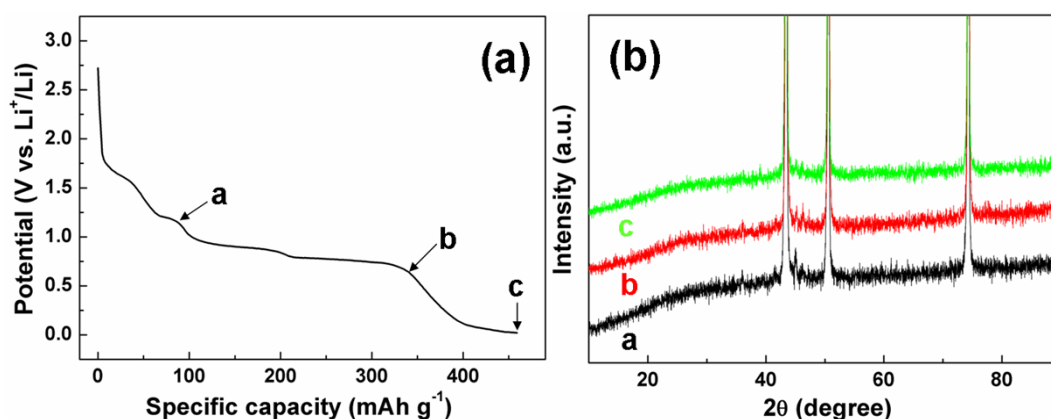


Fig. S1 the initial discharge curve (a) and corresponding XRD patterns of the $\text{Cu}_3\text{P}/\text{Cu}$ electrode.

Fig. S1 shows the XRD patterns of the $\text{Cu}_3\text{P}/\text{Cu}$ electrode under different state in the initial discharge process. It is estimated to be about 0.74, 2.83 and 3.79 mol Li^+ per Cu_3P formula at point a, b and c, respectively. As seen, the diffraction peaks of Cu_3P reduce along with the increasing of discharge degree, and finally disappear when discharging to 0.02 V. The results suggest a phase transition of Cu_3P owing to the formation of $\text{Li}_x\text{Cu}_{3-x}\text{P}$ and Cu in discharging, accompanied by an amorphization

process [1, 2].

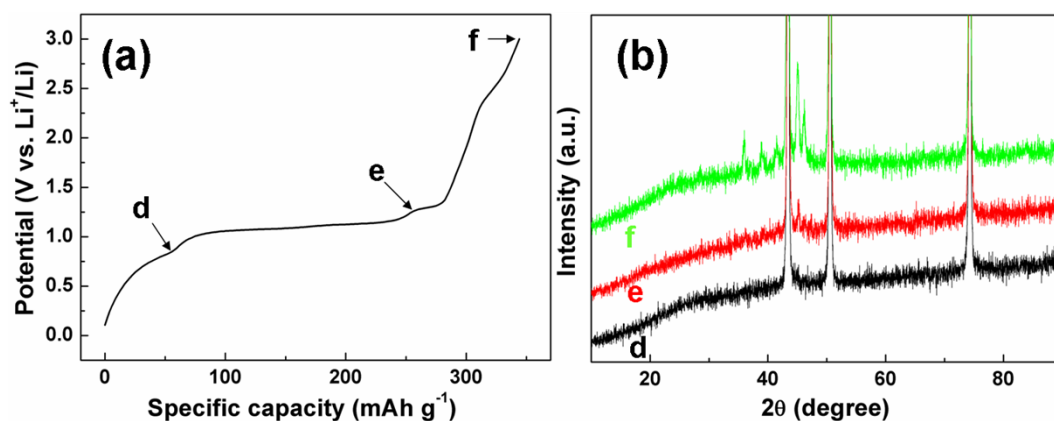


Fig. S2 the initial charge curve (a) and corresponding XRD patterns of the $\text{Cu}_3\text{P}/\text{Cu}$ electrode.

Fig. S2 shows the XRD patterns of the $\text{Cu}_3\text{P}/\text{Cu}$ electrode under different state in the initial charge process. As seen, the diffraction peaks of Cu_3P appear when charging to 3.0 V, suggesting the reversible extraction of lithium ions owing to the formation of $\text{Li}_x\text{Cu}_{3-x}\text{P}$ in charging process, accompanied by a recrystallization process [1, 2].

[1] M.P. Bichat, T. Politova, J.L. Pascal, F. Favier and L. Monconduit, *J. Electrochem. Soc.*, 2004, 151, A2074-A2081.

[2] B. Mauvernay, M.P. Bichat, F. Favier, L. Monconduit, M. Morcrette and M.L. Doublet, *Ionics*, 2005, 11, 36-45.