

Bimetallic phosphates AlP/SiP₂ composite as anode material for lithium ion batteries with long cycle life

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Experimental

Material synthesis

The AlP/SiP₂ composite was synthesized by a facile, scalable and low-cost method of high energy ball milling (QM-3C, Nanjing) for 15 h at the speed of 1200 rpm under Argon atmosphere. The mixture of Al (Alfa, 99.8%), Si (Alfa, 99.999%) and P (Alfa, 98%) powder was seal in a stainless steel jar with a molar ratio of 1: 1: 3 and the powder-to-ball weight ratio was 1: 25. The AlP/SiP₂@C composite was synthesized by ball milling the as-prepared AlP/SiP₂ composite and Ketjenblack with the weight ratio of 6: 3 for 4 h at 1200 rpm. For comparison, the materials of AlP, SiP₂, AlP@C and SiP₂@C were also synthesized under the same conditions. The molar ratios are Al: P = 1: 1 and Si: P = 1: 2 in AlP and SiP₂, respectively. The AlP@C and SiP₂@C are synthesized with the same weight ratio as AlP/SiP₂@C.

Material characterization

The crystal structure of AlP/SiP₂ composite was characterized by XRD with a Cu K α radiation at a scan rate of 2° min⁻¹ (Bruker D8 ADVANCE). Raman spectra were obtained on Confocal Raman Microscope (HORIBA Jobin Yvon LabRAM HR Evolution) with 532 nm laser. The morphology and microstructure were observed through a Hitach SU8220 field-emission scanning electron microscope (SEM) and FEI Talos F200S field-emission TEM. The element mappings were conducted via energy dispersive X-ray spectroscopy (EDS) with high-resolution TEM (HRTEM). Notably, the morphology of AlP/SiP₂@C composite was observed by SEM (TESCAN CLARA) coupled with EDS (Oxford Xplore 30) measurements. X-ray photoelectron spectroscopy (XPS) spectra were obtained on Escalab 250Xi (Thermo Fisher) with Al K α radiation.

Electrochemical Characterization

The working electrodes were prepared by mixing the active materials (AlP/SiP₂ and AlP/SiP₂@C composite) and Polyacrylic acid (PAA, binder) at a weight ratio of 9: 1 in N-Methylpyrrolidone (DAMAO, AR) to form a slurry, which was pasted on a

copper foil and vacuum dried at 60 °C for 12 h. All kinds of slurries with various active materials, including AIP, SiP₂, AIP/SiP₂, AIP@C, SiP₂@C and AIP/SiP₂@C, were pasted on the copper foil via coating machine (Heifei Kejing Materials Technology Ltd Co). For fair comparison, all electrodes were selected to control their loading mass around 1.2 mg (corresponding to 1.53 mg cm⁻²). After vacuum drying, the electrodes were pressed with the pressure of 4 MPa and the thickness of electrode is about 7 μm. The counter and reference electrodes in LIBs were Li metal. The electrolyte was 1 M of LiPF₆ in a mixture of ethylene carbonate (EC), diethyl Carbonate (DEC), ethyl methyl carbonate (EMC) (1: 1: 1 in volume) with the addition of 2% vinylene carbonate (VC). The CR2032 coin cells were assembled in an argon-filled glove box (H₂O < 0.1 ppm, O₂ < 0.1 ppm) for electrochemical performance characterizations. The galvanostatic charge-discharge (GCD) measurements were carried on a LAND battery tester between 0.005 and 3.0 V. Cyclic voltammetry (CV) measurements were conducted on Autolab Pgstat 302N electrochemical workstation at a scan rate of 0.1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was performed at the same electrochemical workstation in the frequency range of 0.01 Hz to 100 KHz. For comparison, the GCD tests were performed in the electrolyte of 1 M LiPF₆ in fluoroethylene carbonate (FEC)/diethyl carbonate (DEC) (1:1 in volume) and the electrodes were prepared by the binder of poly(vinylidene fluoride) (PVDF, Alfa Aesar, 99.9%).

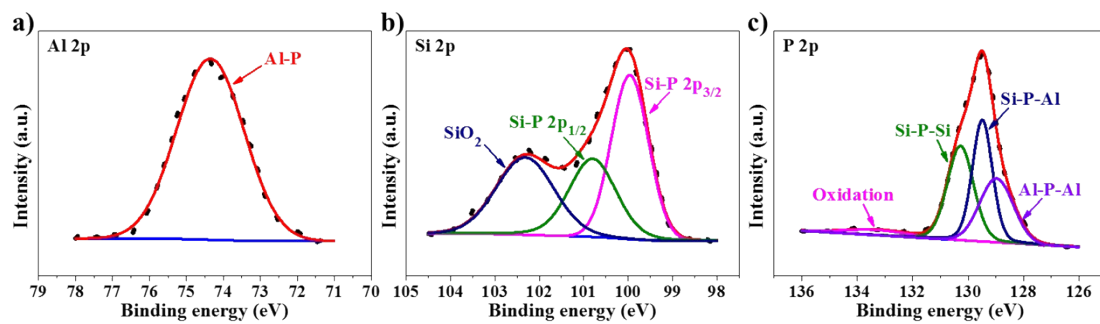


Fig. S1 XPS narrow spectra of (a) Al 2p, (b) Si 2p and (c) P 2p for AlP/SiP₂ composite.

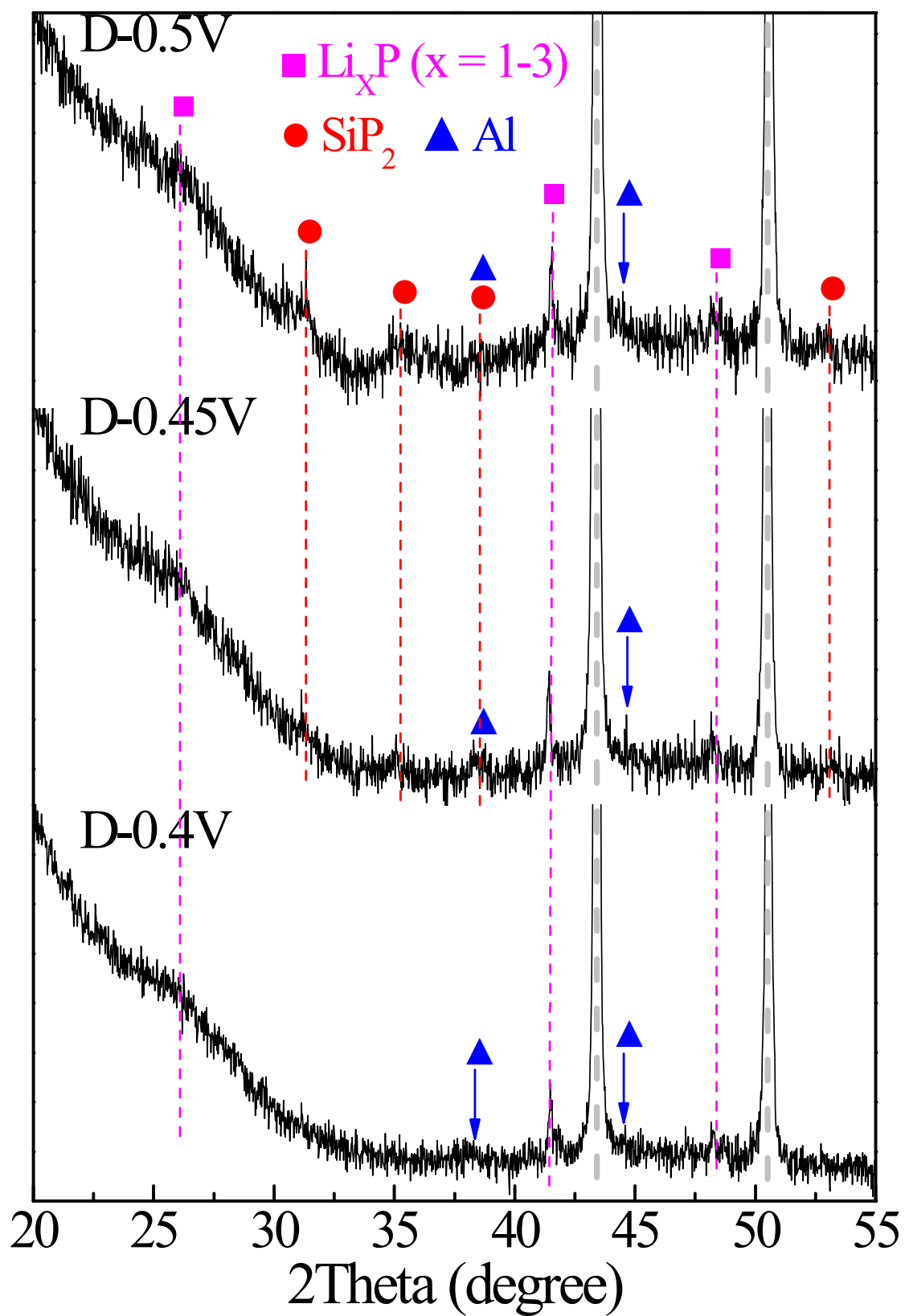


Fig. S2 Ex situ XRD patterns of AlP/SiP₂ electrode obtained at different potential.

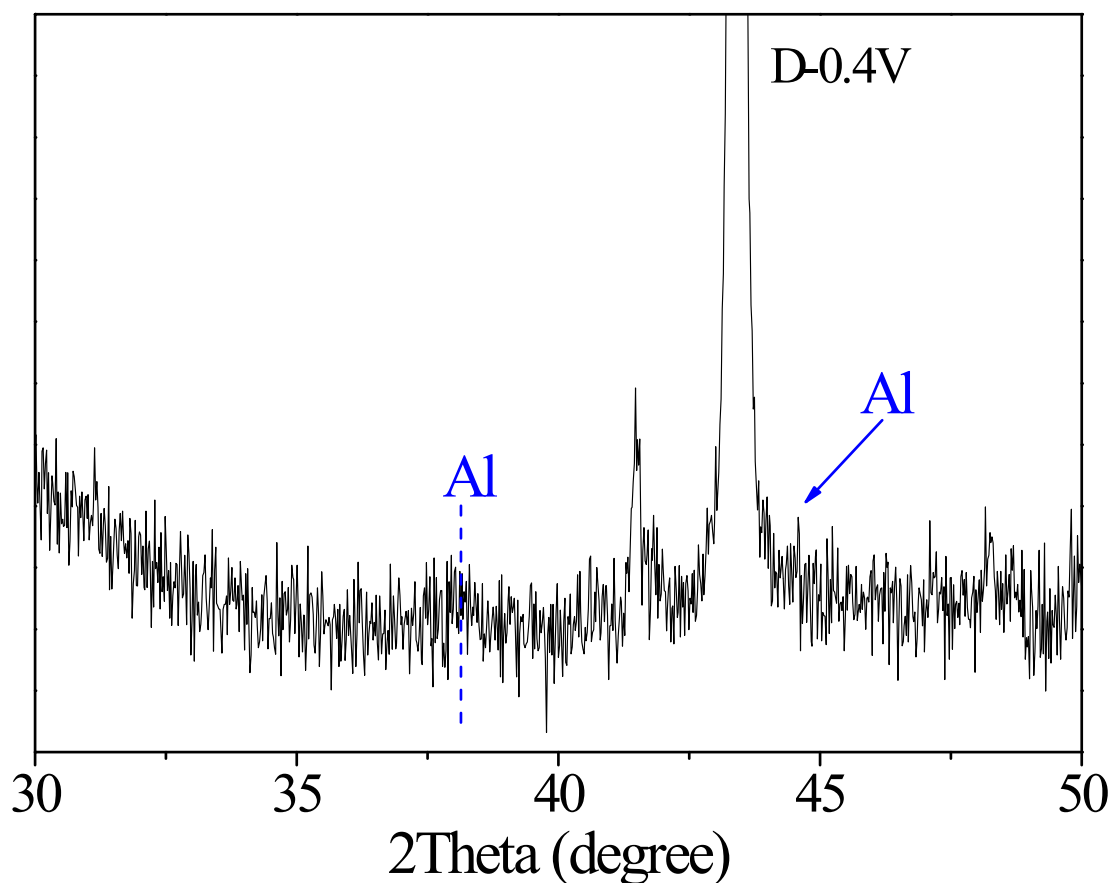
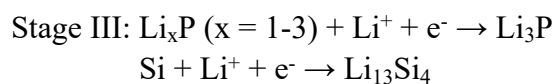
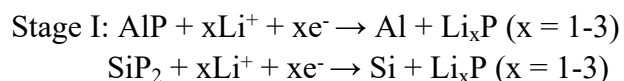


Fig. S3 Enlarged XRD pattern of AIP/SiP₂ electrode collected at the discharged state of 0.4 V.

Combined with the CV curve and ex-situ XRD patterns of AIP/SiP₂, the detail reaction mechanism of AIP/SiP₂ can be concluded at the following section. During the discharging process, the AIP firstly decomposes to Li_xP (x = 1-3) and metal Al (~ 0.7 V). Subsequently, the SiP₂ is also alloyed with Li⁺ to form Li_xP (x = 1-3) and thus the Li_xP (x = 1-3) and metal Al coexist accompanied by the vanished signals of SiP₂ at 0.4 V. At the discharged state of 0.2 V, the Al metal is alloyed with Li⁺ to form LiAl phase. Finally, at almost 0.01 V, the electrochemical products of Li₃P and Li₁₃Si₄ were generated. Based on the above results, the discharging process of AIP/SiP₂ electrode consists of following steps.



It is worth mentioning that the formation of metal Al during electrochemical process can improve the conductivity of electrode. Moreover, compared with AlP and SiP₂, the AlP/SiP₂ electrode possesses multiple reaction steps, which is helpful to mitigate volume expansion for durable cycling life.

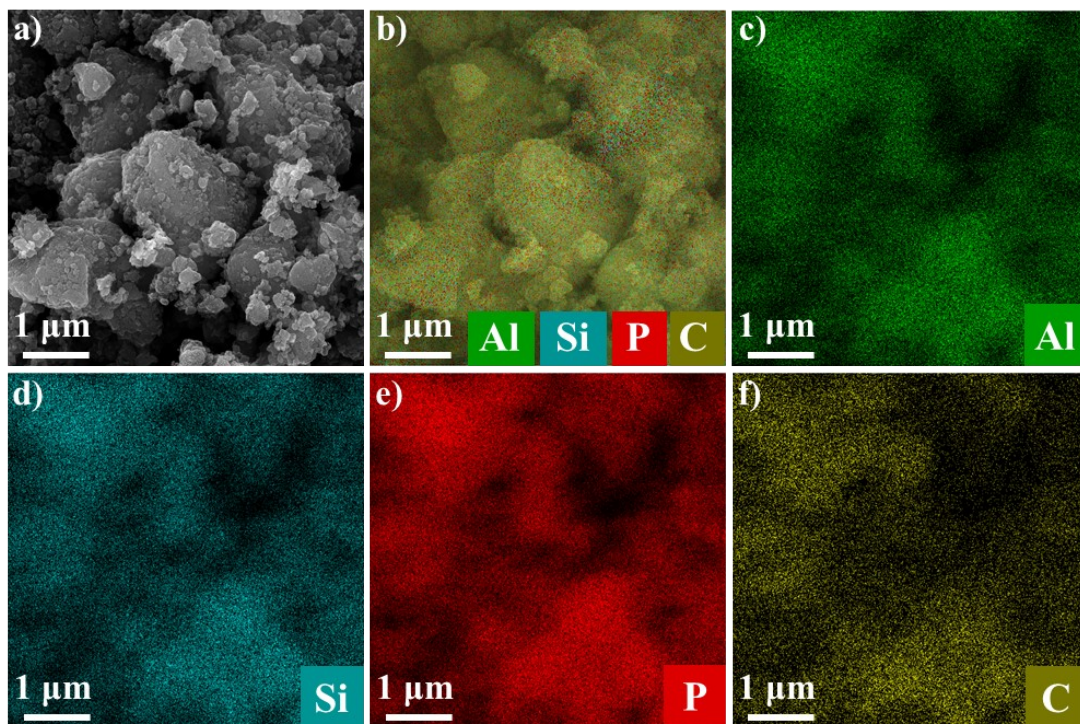


Fig. S4 (a) SEM image and (b-f) the corresponding EDS mapping images of AlP/SiP₂@C composite.

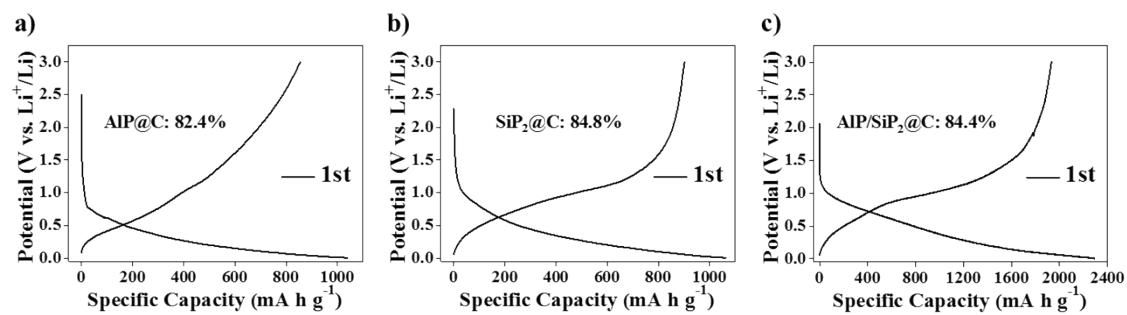


Fig. S5. The initial charge-discharge voltage profile of (a) AIP@C, (b) SiP₂@C and (c) AIP/SiP₂@C at the current density of 0.3 A g⁻¹.

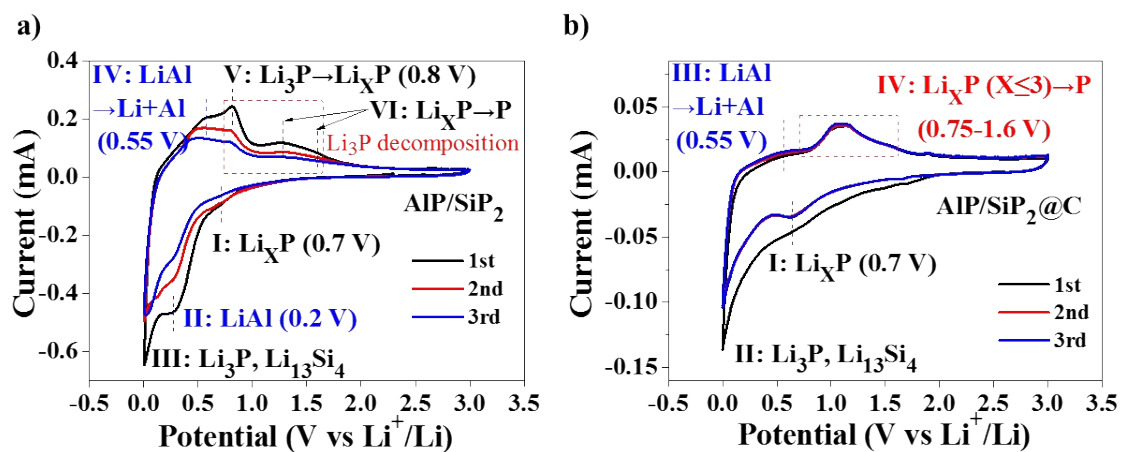


Fig. S6. Initial three CV curves of (a) AIP@C and (b) AIP/SiP₂@C electrode at a scan rate of 0.1 mV s⁻¹.

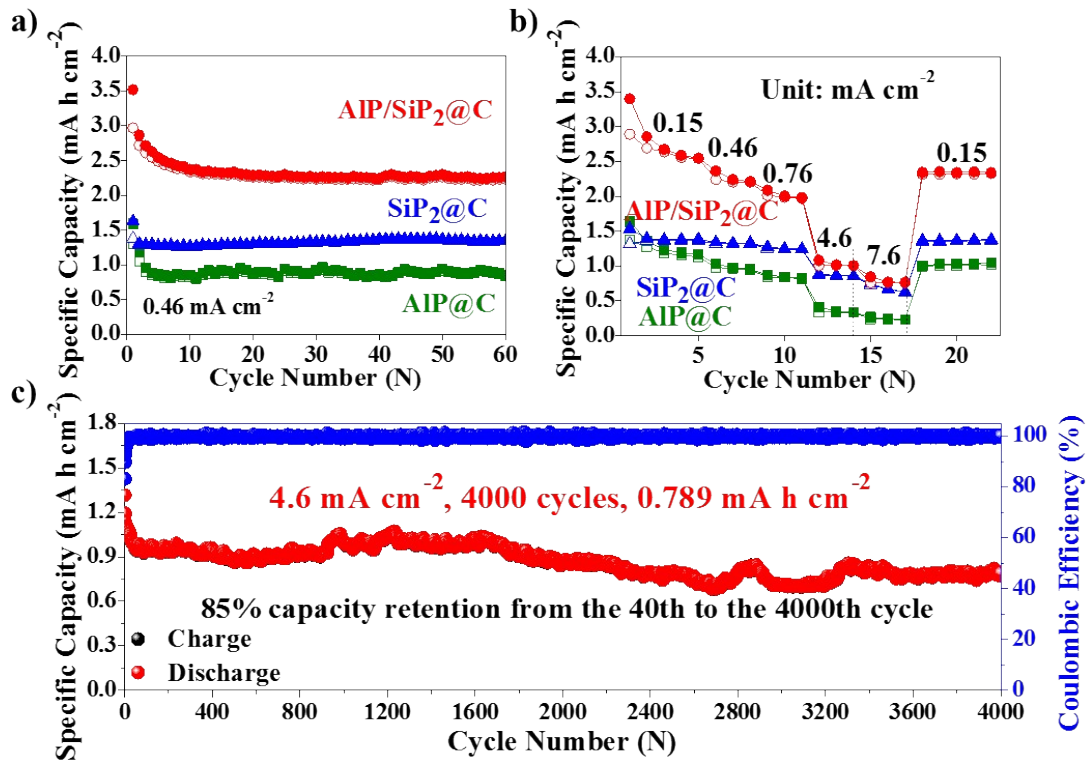


Fig. S7. The comparison of AIP/SiP₂@C, AIP@C and SiP₂@C composite between (a) cycling performance and (b) Rate performance; (c) the long cycle-life of AIP/SiP₂@C composite.