Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A new, cheap, productive FeP anode material for sodium-ion batteries - Understanding the Na storage mechanism

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Experimental Section

Synthesis of FeP phosphide: Fe (>99.5%, Sigma) and red P (>99 %, Sigma) were used as the starting materials without further purifying. FeP was prepared by the simple ball-milling method using the corresponding stoichiometric molar ratio of the metal (Fe) to P. The starting materials were put into a hardened steel vial with milling balls 2 mm in diameter. The weight ratio of milling balls to powder was 20:1. The vial was assembled in an argon-filled glove-box, and then mounted on the ball mill. The rotation speed of the mill was set to 300 rpm for 20 h.

Characterization: The crystalline structure of the active powder was characterized by powder X-ray diffraction (XRD) on a GBC MMA diffractometer with a Cu K_α source. The morphology of the sample was investigated by field emission scanning electron microscopy (FESEM; JEOL JSM-7500FA) and transmission electron microscopy (TEM, JEOL 2011, 200 keV). X-ray photoelectron spectroscopy (XPS) was conducted using a SPECS PHOIBOS 100 Analyser installed in a high-vacuum chamber with base pressure below 10^{-8} mbar. X-ray excitation was provided by Al Kα radiation with photon energy hν = 1486.6 eV at the high voltage of 12 kV and power of 120 W. Ex- situ XRD data were collected by powder X-ray diffraction (XRD) on a GBC MMA diffractometer with a Cu K_α source. The cell used for the data collection was charged at a current density of 100 mA g^{-1} between 0 V and 1.5 V.

Electrochemical measurements: The FeP electrodes were prepared by mixing 70% active materials, 10% carbon black, and 20% binder by weight to form an electrode slurry, which then was coated on copper foil, followed by drying in a vacuum oven overnight at 80 °C, and then pressing at 30 MPa. The electrode was punched into a round area with 5 mg cm^{-2}. Three kinds of FeP electrodes were prepared by changing the binders: carboxymethyl cellulose (CMC)), Poly(vinylidene fluoride) (PVDF), carboxymethyl cellulose (CMC))/Poly(acrylic acid) (PAA). The sodium foil was cut by the doctor blade technique from a sodium bulk stored in mineral oil, which then was employed as both reference and counter electrode. The electrolyte was 1.0 mol/L

$NaClO_4$ in an ethylene carbonate (EC) - diethyl carbonate (DEC) solution (1:1 v/v), with or without 5 vol.% addition of fluoroethylene carbonate (FEC). The cells were assembled in an argon-filled glove box. The electrochemical performances were tested by a Land Test System at current density of 50 mA g^{-1} in the voltage range of 0–1.5 V (vs. Na^+/Na).

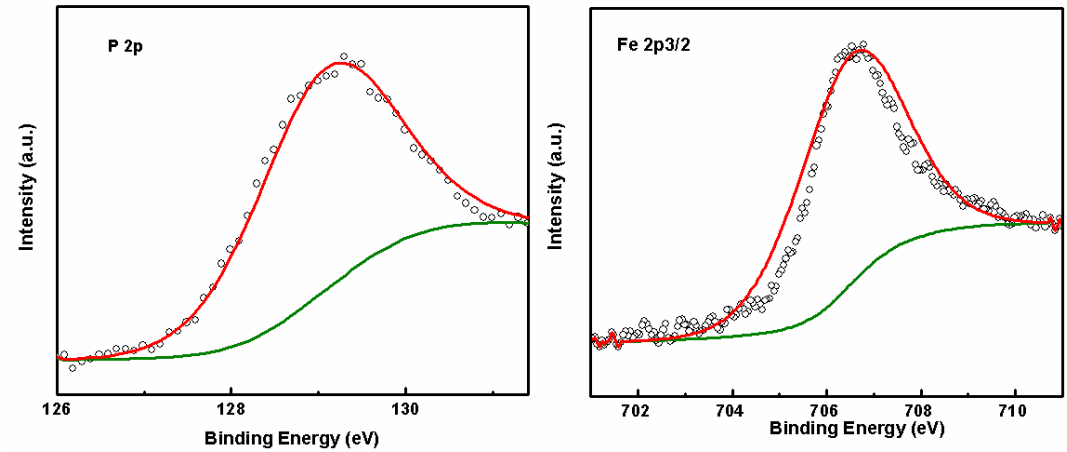

Figure S1 X-ray photoelectron spectroscopy (XPS) of the as-prepared FeP.

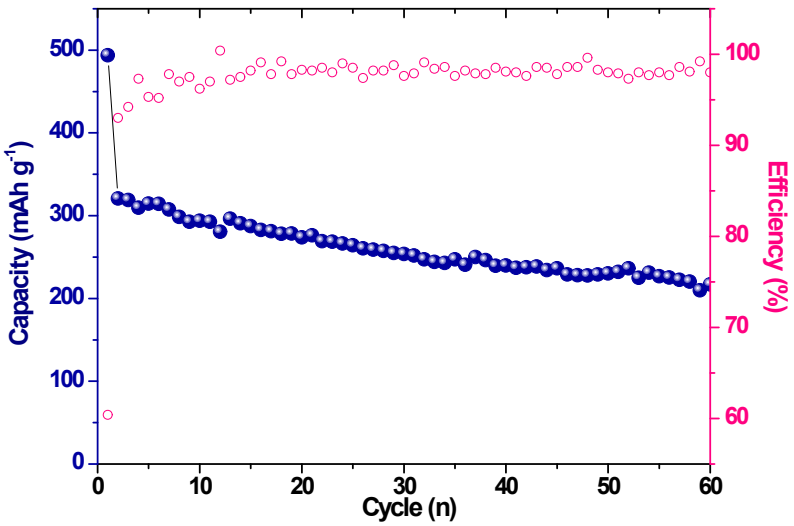

Figure S2. The cycling performance of FeP with CMC/PAA binder in the electrolyte of 1M NaClO4/EC:DEC with 5% FEC additive.

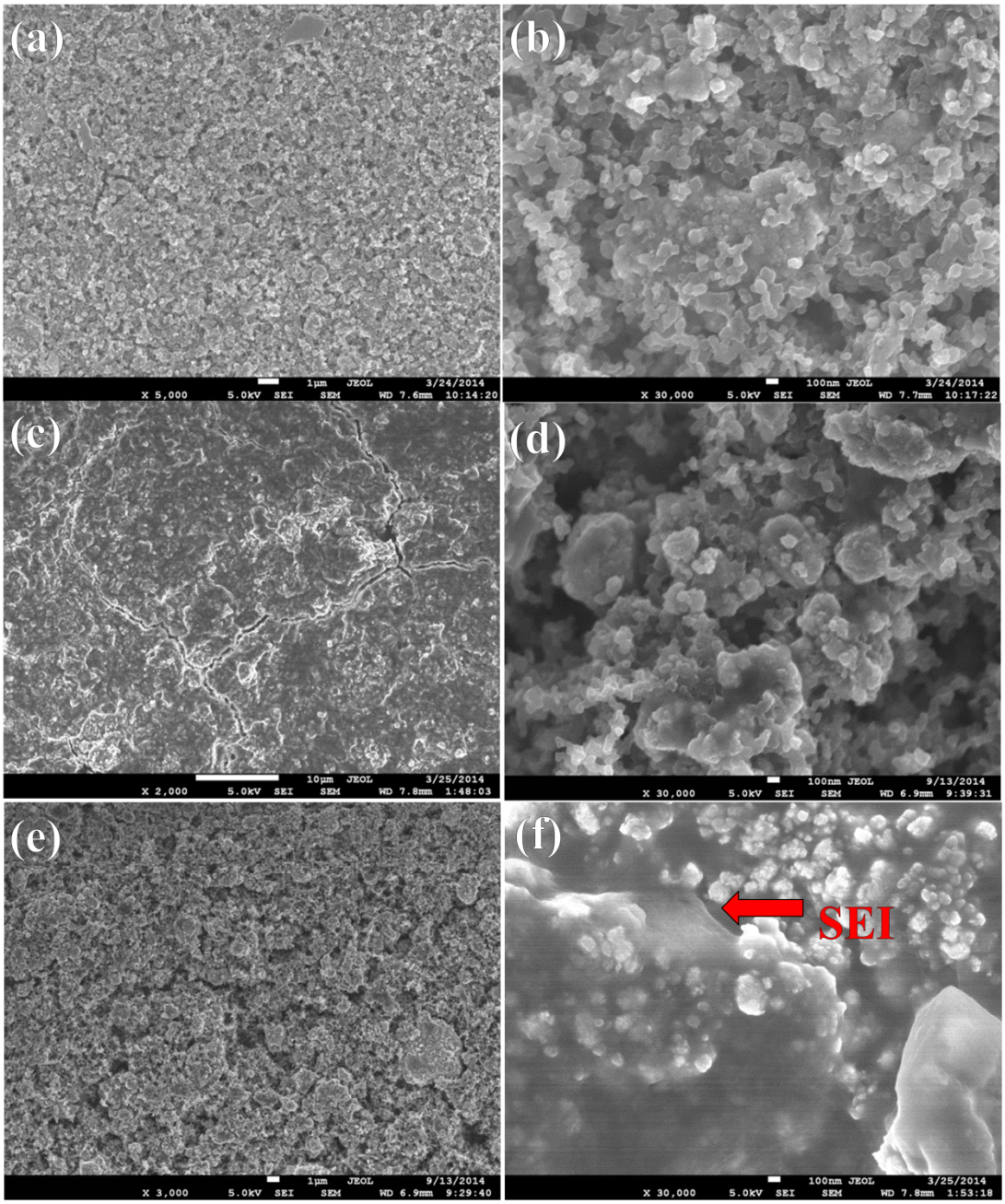

Figure S3. SEM images of FeP Electrodes with CMC/PAA binder (a, b) before and (c - f) after 5 cycles in the electrolyte (c, d) without FEC and (e, f) with FEC additive.

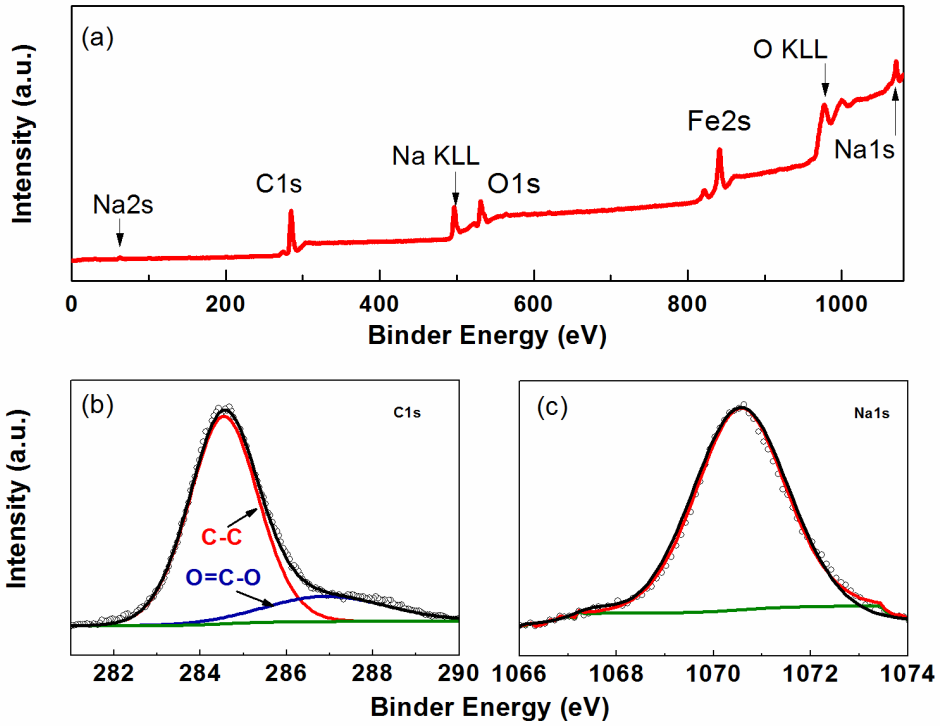

Figure S4. X-ray photoelectron spectroscopy (XPS) of the FeP electrode after 1 cycle in the electrolyte with FEC additive: (a) survey spectrum; (b) C1s; (c) Na1s.

The C1s spectra and its fitting curves are presented in Figure S4(b). The peaks at the bonding energy of 284.6 and 287.2 eV are corresponding to the group of C-C and O=C-O, respectively. Moreover, the signal of Na 1s can be detected, but the signal from the elements of P and Fe 2p cannot be detected by XPS, suggesting a thick SEI layer covering on the surface of the electrode and its composition is $NaCO_3$.

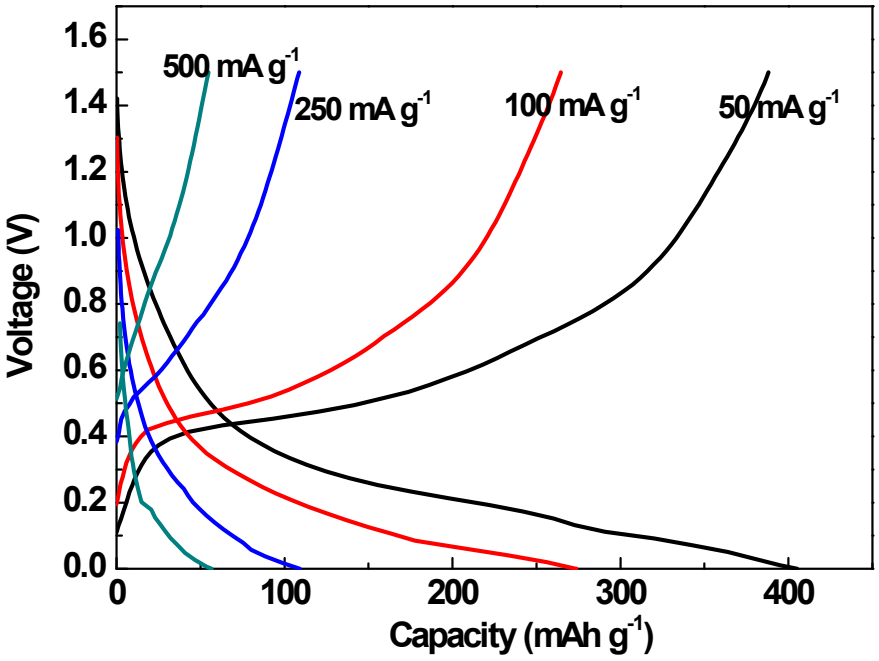

Figure S5. The rate capability of FeP tested at different current density.