Bifunctional porous iron phosphide/carbon nanostructure enabled high-performance sodium-ion battery and hydrogen evolution reaction

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1. Introduction

Recently, there is an increasing emphasis on developing cheaper and sustainable energy technologies to reduce the reliance on fossil fuels [1–5]. Among them, sodium-ion batteries (SIBs) and water electrolysis through hydrogen evolution reaction (HER) are two promising alternatives due to their high energy storage and conversion capabilities. To achieve long cycle lifetime, high rate sodium storage performance and stable HER reactivity, porous FeP/C nanostructures have been designed and synthesized through low temperature phosphorization of the Metal-Organic Framework (MOF) nanostructure. The resulting FeP/C composite consists of highly porous nanocubic structure with FeP nanoparticles distributing the carbon scaffolding, showing high surface area and small pore size distribution. This unique nanostructure enables fast and efficient electrons/ions transportation, and provides abundant reactive sites uniformly distributing the highly-ordered MOF-derived nanocubes. Benefitting from the unique porous structure, the FeP/C nanocubes exhibit remarkable sodium storage performance in terms of high capacity (410 mA h g\(^{-1}\), 100 mA g\(^{-1}\)), excellent rate capacity (up to 1 A g\(^{-1}\)) and long cycle life (> 200 cycles). The electrochemical reaction mechanisms of the FeP/C composite upon sodiation/desodiation are investigated in detail via ex-situ XRD, SEM and TEM methods, which show that the sodium storage in FeP is based on both the intercalation/conversion reactions and a low onset overpotential of 80 mV and a low Tafel slope of 40 mV dec\(^{-1}\). These results reveal the sodiation mechanism of FeP and suggest that the MOF-derived FeP/C composite is a promising candidate for high-performance SIBs and HER electrode material.

Transition metal phosphides, such as iron phosphate (FeP), have recently been studied as promising high performance active materials for sodium-ion batteries (SIBs) and hydrogen evolution reaction (HER) due to their excellent energy storage and conversion capabilities. To achieve long cycle lifetime, high rate sodium storage performance and stable HER reactivity, porous FeP/C nanostructures have been designed and synthesized through low temperature phosphorization of the Metal-Organic Framework (MOF) nanostructure. The resulting FeP/C composite consists of highly porous nanocubic structure with FeP nanoparticles distributing the carbon scaffolding, showing high surface area and small pore size distribution. This unique nanostructure enables fast and efficient electrons/ions transportation, and provides abundant reactive sites uniformly distributing the highly-ordered MOF-derived nanocubes. Benefitting from the unique porous structure, the FeP/C nanocubes exhibit remarkable sodium storage performance in terms of high capacity (410 mA h g\(^{-1}\), 100 mA g\(^{-1}\)), excellent rate capacity (up to 1 A g\(^{-1}\)) and long cycle life (> 200 cycles). The electrochemical reaction mechanisms of the FeP/C composite upon sodiation/desodiation are investigated in detail via ex-situ XRD, SEM and TEM methods, which show that the sodium storage in FeP is based on both the intercalation/conversion reactions. In addition, FeP/C as HER electrodes maintain its reactivity for at least 40 h and exhibit an low onset overpotential of 80 mV and a low Tafel slope of 40 mV dec\(^{-1}\). These results reveal the sodium storage mechanism of FeP and suggest that the MOF-derived FeP/C composite is a promising candidate for high-performance SIBs and HER electrode material.

**Keywords:**
- Metal-Organic Framework
- Porous FeP/C nanocomposites
- Sodium-ion batteries
- Hydrogen evolution reaction

**ABSTRACT**

Transition metal phosphides, such as iron phosphate (FeP), have recently been studied as promising high performance active materials for sodium-ion batteries (SIBs) and hydrogen evolution reaction (HER) due to their excellent energy storage and conversion capabilities. To achieve long cycle lifetime, high rate sodium storage performance and stable HER reactivity, porous FeP/C nanostructures have been designed and synthesized through low temperature phosphorization of the Metal-Organic Framework (MOF) nanostructure. The resulting FeP/C composite consists of highly porous nanocubic structure with FeP nanoparticles distributing the carbon scaffolding, showing high surface area and small pore size distribution. This unique nanostructure enables fast and efficient electrons/ions transportation, and provides abundant reactive sites uniformly distributing the highly-ordered MOF-derived nanocubes. Benefitting from the unique porous structure, the FeP/C nanocubes exhibit remarkable sodium storage performance in terms of high capacity (410 mA h g\(^{-1}\), 100 mA g\(^{-1}\)), excellent rate capacity (up to 1 A g\(^{-1}\)) and long cycle life (> 200 cycles). The electrochemical reaction mechanisms of the FeP/C composite upon sodiation/desodiation are investigated in detail via ex-situ XRD, SEM and TEM methods, which show that the sodium storage in FeP is based on both the intercalation/conversion reactions. In addition, FeP/C as HER electrodes maintain its reactivity for at least 40 h and exhibit an low onset overpotential of 80 mV and a low Tafel slope of 40 mV dec\(^{-1}\). These results reveal the sodium storage mechanism of FeP and suggest that the MOF-derived FeP/C composite is a promising candidate for high-performance SIBs and HER electrode material.
charge/discharge processes and poor reaction kinetics due to its low electrical conductivity [39,48–50].

To enhance the above-mentioned electrochemical properties and remedy these shortcomings, an effective strategy by phosphorization of Metal-Organic Framework (MOF) is adopted in this work to form a three-dimensional, highly-ordered and carbon-modified porous nanostructure (FePNC) [51,52]. Pyrolysis of the MOF structures are achieved via annealing in inert environment, of which the organic complexes are transformed into interconnected carbon scaffold [53–56]. The structure contraction and reconstruction lead to the formation of cubic shaped three-dimensional porous nanostructures, providing large surface area and short ionic pathways, enabling fast charge/discharge [57,58]. The high porosity can also effectively accommodate large volume changes upon sodiation/desodiation, as well as allowing better electrolyte permeation [59]. Apart from the uniform morphology and abundant porosity that provides large surface area, the incorporation of the carbonaceous elements from the MOF derivatives also rightly ensures facilitation of electronic transport for conductivity improvement [60,61]. Evaluated as the electrodes for SIBs and HER, FePNC exhibits significant improvement in SIBs and HER performances in contrast to the commercial MOF derived FeP/C composite (FePCM). As SIBs anode materials, FePNC delivers a high specific capacity of 410 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) and excellent rate capability with a specific capacity of 110 mA h g\(^{-1}\) at high current density of 1 A g\(^{-1}\). To understand and to reveal the underlying mechanisms of the sodiation/desodiation mechanisms of the FeP-based materials, ex-situ XRD and microscopy methods are adopted on electrochemically cycled electrodes. As HER catalysts, FePNC display early onset of the kinetic reactions with a lower onset overpotential as compared to FePCM, with performance on par to recent reports of FeP-based HER catalysts [33,55,62–66].

2. Experimental details

2.1. Synthesis of prussian blue analogue (PBA)

Prussian blue analogues (PBA), one of the MOF materials, were synthesized as sacrificial template using the methods as follows. 12.0 g of PVP (polyvinylpyrrolidone, MW = 40,000) and 0.60 g of potassium (III) hexacyanoferrate (K\(_3\)Fe(CN)\(_6\)) were added to a flask of 0.1 M hydrochloric acid solution (200 ml) with magnetic stirring. Stirring was continued until the solution was clear and free of any visible suspension. The mixture was then moved to a programmable oven for heating at 80 °C for 12–24 h. After the process, the solution is centrifuged and dried to obtain PBA powders.

2.2. Synthesis of FePNC and FePCM

Sodium hypophosphite monobasic (Na\(_2\)H\(_2\)PO\(_2\)H\(_2\)O) was utilized as the phosphorization precursor and were placed, with as-prepared PBA powders, in an alumina crucible at two separate ends with the PBA at the downstream part of the crucible (in w/w ratio of 5:1, respectively). The process was carried out in pure argon-filled tube furnace controlled by a mass flow controller at 10 scm. Heating was carried out with rate of 2 °C min\(^{-1}\) to a target temperature of 200 °C and dwell for 3 h. Subsequently, the temperature is increased to 350 °C at a rate of 1 °C min\(^{-1}\) and dwell for another 3 h. To synthesize FePCM, identical experimental process is adopted with the as-prepared PBA replaced by commercially acquired Prussian blue powders.

2.3. Materials characterization methods

Field emission scanning electron microscope (FESEM, JEOL JSM-7600F) were used to study the morphological as well as energy dispersive X-ray spectroscopy (EDS) studies. In-depth microstructure analysis were conducted via high resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) analysis (JEOL JEM-2010, accelerating voltage of 200.0 kV). Crystal structure and phase identification were performed using X-ray diffraction techniques (XRD, Bruker D8 Advance, Cu Kα lines λ = 0.154 nm). The bonding states were studied via X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Al Kα source at 1486.6 eV) at a base pressure of 10\(^{-7}\) Pa. Raman spectroscopy was performed on a confocal Raman system (WT Tec, c300R). Thermogravimetric analysis were performed to analyse the content of all composite samples (TGA, Shimadzu DTG-60). N\(_2\) adsorption/desorption isotherms was measured on an automated gas sorption analyser (Autolab-iQ, Quantachrome Instruments). The surface area analysis were determined by multipoint Brunauer-Emmett-Teller (BET) method. The pore size distribution were determined by Barrett-Joyner-Halenda (BJH) method.

2.4. Sodium-ion batteries characterization and performance tests

All samples were assembled into 2032 coin cell via half-cell, two-electrode configuration in pure argon-filled glove box enclosure with the moisture and oxygen concentration controlled at <1 ppm. To prepare for the electrode materials, active materials were mixed with super-P conductive carbon black and carboxymethyl cellulose (CMC, MW = 700,000) in ratio of 8:1:1 w/w respectively. The stated powders were mixed uniformly for at least 30 min using a mortar agate with a few drops of DI-water as solvent. The resultant homogeneous mixture were then applied onto nickel (Ni) foam substrates manually by hand and baked in a vacuum oven at 120 °C for at least 12 h. Ni foam were chosen as current collector predominantly due to its porous nature which allows effective electrolyte permeation. The three-dimensional structure also accommodate larger active material mass loadings as compared to flat-surfaced alternative, i.e. copper foil. Typically, the mass loading of each electrode is around 1.5–2.0 mg, with the specific capacity considers only the active materials, i.e. FeP/C. As reference/counter electrodes, pure sodium flakes were tailored into 1 cm\(^2\) squarish shaped and used directly in assembly. The electrolyte were prepared using mixture of 1 M of sodium hexafluorophosphate (NaPF\(_6\)) with ethylene carbonate/diethyl carbonate (EC/DEC, 1:1, v/v), and 2% (v/v) of fluoroethylene carbonate (FEC) as stabilizer. Glass fibre filters (GB-100R Advance) were used as separators. Ex-situ analysis were prepared by extracting electrode materials and seal-proof via the use Kapton tape in glove-box environment. Electrochemical characterization such as cyclic-voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were investigated on a VMP3 Biologic potentiostat. Galvanostatic charge/discharge performance tests were conducted using a battery analysing workstation (Neware) in a voltage range of 0.01–2.50 V.

2.5. Hydrogen evolution reaction characterization and performance tests

All electrochemical characterization and performance testing were conducted on VMP3 Biologic potentiostat using three-electrode configuration in an electrolyte of 0.5 M H\(_2\)SO\(_4\) solution. Platinum wire and Ag/AgCl in saturated KCl electrode were used as counter and reference electrodes respectively. The working electrodes were prepared by dissolving 5 mg of active materials into 2 ml solution, consist of 9:1 (v/v) ratio of absolute ethanol and Nafton (5 wt%) respectively. After adding in the active materials, the solution is sonicated for at least 1 h to achieve homogeneous slurry. 5 µl of the content was then loaded onto a glassy carbon electrode of 3 mm in diameter as working electrode. Linear sweep voltammetry (LSV) were conducted with a scan rate of 5 mV s\(^{-1}\). Electrochemical impedance spectroscopy (EIS) were conducted in a frequency range of 100 kHz to 0.1 Hz. Potentials were converted from Ag/AgCl to reversible hydrogen electrode (vs. RHE) via + (0.197 + 0.0592 pH) V.
3. Results and discussions

3.1. Materials characterization

The typical synthesis process of the FePNC is shown in Fig. 1a. Firstly, PBA nanocubes were synthesized by hydrothermal method at 80 °C for more than 12 hours. The as-prepared PBA shows uniform nanocubic structure with average size of 500–700 nm in length (Fig. S1, Supporting information). The synthesized PBA nanocubes were then subjected to phosphorization in an inert, argon-filled environment via chemical vapour deposition method at 350 °C for 3 h. After full phosphorization, FePNC was obtained with well-retained morphology but much rougher surface (Fig. 1b and c), suggesting the formation of porous structure due to the nanoparticles growth under the carbonization/phosphorization processes [67,68]. Energy-dispersive X-ray spectroscopy (EDS) was conducted to investigate the element components of the FePNC nanostructure (Fig. 1d). The spectrum indicates the existence of Fe, P and C elements in the FePNC composite with Fe:P atom ratio close to 1:1. The elemental mapping images (Fig. 1e) show the overlapping positions of the Fe and P signals, suggesting the formation of the iron phosphide structure. The mapping image of C signal suggests the formation of carbon after phosphorization. As a comparison, FePCM derived from commercial Prussian blue powders (Fig. S2, Supporting information) with the same synthesis conditions shows random morphologies with much larger size as shown in SEM micrographs depicted in Fig. S3 (Supporting information). The EDS results of FePCM show similar observations to FePNC (Fig. S4, Supporting information), suggesting the formation of FeP structure. TEM and HR-TEM studies were conducted to study the in-depth microstructure of FePNC (Fig. 1f–h). The FePNC exhibits uniform nanocubic structure with an average size of 600 nm, consistent with SEM micrographs. Higher magnification TEM image (Fig. 1g) reveals the FePNC is highly porous. The corresponding selected area diffraction pattern (SAED) image consists of two concentric diffraction rings that belong to FeP (211) and (011) diffraction planes (inset of Fig. 1g). HRTEM image displays distinct lattice spacings of 0.273 and 0.188 nm, corresponding to the FeP crystal planes of (011) and (211) respectively (Fig. 1h). The results indicate the successful formation of the FeP nanostructure of FePNC.

The X-ray diffraction (XRD) patterns of FePNC and FePCM samples are shown in Fig. 2a. The diffraction patterns of FePNC and FePCM samples show several diffraction peaks which belong to orthorhombic FeP (JCPDS no. 65-2595), indicating identical FeP crystal structure of FePNC and FePCM. To further elaborate the chemical structure of the FeP structure, X-ray photoelectron spectroscopy (XPS) was performed as shown in Fig. 2b and c. The peak features of both the FePNC and FePCM are almost the same, suggesting the chemical similarities of both samples. As shown in Fig. 2b, the Fe
2P3/2 peak at 707.0 eV corresponds to the Fe-P bonding [69]. The weak and broad contribution at around 711.5 eV is assigned to the Fe-O bonding [69], and is resulted from the superficial oxidation of the FeP nanostructures [69,70]. As compared to the stated works, the superficial oxidation for both samples is not severe considering the relative intensities of Fe-P and Fe-O band. The P 2p bands for both samples show two distinctive peaks at around 129.5 and 134.0 eV (Fig. 2c), corresponding to the P-Fe and P-O bondings, respectively [69,70].

The Raman spectra of FePNC and FePCM are shown in Fig. S5a (Supporting information). The two strong peaks at 1340 and 1590 cm$^{-1}$ are observed corresponding to the D and G bands of the carbonaceous materials [71]. The carbon content in the FePNC composite was further determined by the thermogravimetric analysis (TGA), as shown in Fig. 2d. TGA curve of FePNC exhibits a decrease in weight about 3% within 100 °C, which is ascribed to the water removal process. Afterwards, there is a continuous weight increase until 590 °C, corresponds to carbon combustion accompanied with the oxidation of FeP [72]. According to the previous report, the oxidation process is as follows [72]:

$$\text{FeP} + 2\text{O}_2 \rightarrow \text{FePO}_2$$

The weight decrease from 600 °C is ascribed to further combustion of carbon. From the above analysis, the carbon content in FePNC composite is determined to be 33 wt%. Similarly, the carbon content in FePCM composite is calculated to be 24 wt%, lower than that in FePNC (Fig. S5b, Supporting information). From the results, the difference in quality of the Prussian blue precursor prepared by different synthetic methods have influence structural formation of which resulted in difference in carbon content, i.e. defects and vacancies formation [73].

Fig. 2e shows the $N_2$ adsorption/desorption isotherm recorded on FePNC, which resembles a type IV with H3 type hysteresis loop [74]. FePNC exhibits a large surface area around 133.35 m$^2$ g$^{-1}$, which is much higher than FePCM (73.84 m$^2$ g$^{-1}$, Fig. S5e, Supporting information). The well-defined morphology of FePNC framework also yields a narrow and mesoporous pore size distribution, centred at 5.70 nm, as shown in Fig. 2f. In contrast, FePCM has non-uniform pore size distribution as shown in Fig. S5d (Supporting information). The narrow pore size distribution ensures large surface area and shortened ions diffusion pathway, playing an important role for the improvement of electrochemical performance due to the larger amount of reactive sites, better electrolyte absorption and effective charge/discharge kinetics.

3.2. Sodium-ion batteries performance

The electrochemical properties of FePNC as SIBs anode material are characterized by cyclic-voltammetry (CV) technique in the voltage window of 0.01–2.50 V, shown in Fig. 3a. At the first cathodic scan, two distinct broad bands at around 0.23 and 0.67 V are observed, which are ascribed to the sodiation process and the solid-electrolyte interphase (SEI) formation [37]. In the following cycles, structural stabilization after the first cycle causes the cathodic peaks to shift to 0.56 and 0.92 V respectively [37]. The anodic scan of all cycles shows identical features, with peaks centred at 0.87 and 1.70 V due to the sodium removal from the FeP structure [37]. Comparing the intensity of the anodic peaks in all cycles, the 0.87 V reaction is more retainable than that of the reaction of 1.70 V. In contrast, the CV curves of the FePCM are shown in Fig. S6a (Supporting information). The intensity of the reaction peaks is much weaker and exhibits larger decay in current intensities with increasing cycles, suggesting poor reaction kinetics and reversibility. In view of the fact there are few works reported on the detailed electrochemical mechanism of FeP anode [37–39], the in-depth investigation of the sodiation/desodiation mechanism of the FeP electrode will be reported in later section of this report. Fig. 3b shows the first two cycles of galvanostatic charge/discharge profiles measured at 100 mA g$^{-1}$. The reaction plateaus are consistent to the CV profiles. FePNC exhibits first discharge capacity of 740 mAh g$^{-1}$ and charge capacity of 506 mAh g$^{-1}$, corresponding to an initial Coulombic efficiency (CE) of 68.4%. The large decrease of capacity from the 1st cycle is ascribed to the irreversible SEI formation [37,75–77]. In contrast, the specific capacity of FePCM shows a larger capacity decay from the first cycle which rapidly drop to 145.0 mA h g$^{-1}$ after 10 cycles, as shown in Fig. S6b (Supporting information). In comparison, FePNC exhibits far superior stability of specific capacity of
410.0 mA h g\(^{-1}\) after 10 cycles (Fig. 3C). The first cycle of FePCM displays CE of 38.9%, significantly lower than that of FePNC.

Fig. 3c shows the rate capability of FePNC and FePCM. For FePNC, specific capacities of 410.6, 314.8, 239.4, 179.6 and 122.8 mA h g\(^{-1}\) are achieved at 100, 200, 500, 800 and 1000 mA g\(^{-1}\), respectively. As the current density returns to 100 mA g\(^{-1}\), the specific capacity recovers to a highly reversible capacity of 358.9 mA h g\(^{-1}\). In contrast, the FePCM exhibits lower capacities of 147.8, 84.1, 57.5, 39.9 and 27.0 mA h g\(^{-1}\) at the same current densities. Fig. 3d compares the long-term cycling stability of the FePNC and FePCM at 200 mA g\(^{-1}\). The specific capacity of FePNC is able to maintain at around 274.7 mA h g\(^{-1}\) after 200 cycles with high CE of ~100%. In contrast, FePCM exhibits rapid decrease in specific capacities. The improved rate capability and long-term cycling stability of FePNC are attributed to the larger surface area (smaller and uniform pore size distribution) and uniform hybrid nanostructure, which accommodates large volume changes and enables fast and efficient ionic diffusion during the rapid electrochemical reaction. The carbonaceous framework also ensures longer cycling lifetime (due to increase of electronic conductivity) with higher CE, indicating low energy lost during SIBs charge/discharge processes.

Charge transfer kinetics of the FePNC and FePCM anode materials are investigated by the electrochemical impedance spectroscopy (EIS). Based on a fitted equivalent circuit (inset of Fig. 3e), the charge-transfer resistances (R\(_{ct}\)) at different cycles are obtained. The fresh
FePNC electrode exhibits small $R_{ct}$ at 105.3 $\Omega$, which further decreases to 34.5 $\Omega$ after 100 cycles. In comparison, $R_{ct}$ of FePCM after 100th cycle is much higher (169.4 $\Omega$), indicating lower electrical conductivity of FePCM. The significant decrease of $R_{ct}$ at stable cycling of 100th cycle of FePNC indicates the further enhancement and stabilization of the electronic transport which is not available in FePCM (Fig. S7, Supporting Information). The ionic diffusion is also investigated further via the Warburg coefficient $\sigma$, which is inversely proportional to diffusion coefficient $D (D=\sigma^2)$. $\sigma$ can be evaluated via the linear regression of $E(Z)$ and $\omega^{-1/2}$. The results are shown in Fig. 3f, in which the slope of FePNC is significantly smaller than FePCM at the 100th cycle. The results indicate that FePNC has a definitive advantage for facilitation of sodium diffusion kinetics as compared to FePCM.

3.3. Ex-situ FePNC SIBs electrode materials characterization

Ex-situ studies have been conducted on the FePNC electrodes to reveal the electrochemical mechanisms during the sodiation/desodiation processes. Several cycling states were selected to perform the ex-situ studies, as shown in Fig. 4a. As shown in Fig. 4b, the XRD patterns of the fresh anode materials consist of the FeP and nickel (Ni) signals due to the use of Ni foam as current collector. After cathodic scan to 0.48 V, the FeP diffraction peaks shift to lower Bragg angles (20), indicating an increase in lattice spacing ascribed to Na ions insertion to the FeP crystal structure. After scanning to 0.01 V, two new peaks at 36.1 and 37.0° emerged, ascribing to the (110) and (013) diffraction peaks of hexagonal trisodium phosphide (Na$_3$P) (ICSD no. 01-073-3917). The formation of Na$_3$P reveals that the cathodic peak at 0.23 V is based on conversion reaction [76–78]. Therefore the overall sodiation processes of the FeP may be described as follows [76–78]:

FeP + $x$ Na$^+$ + $x$ e$^-$ $\rightarrow$ Na$_x$FeP

(2)

Na$_{x}$FeP + (3–$x$) Na$^+$ + (3–$x$) e$^-$ $\rightarrow$ Na$_3$P + Fe

(3)

After the full sodiation, there are no Fe diffraction patterns observed, indicating the obtained Fe particles is amorphous. After the subsequent anodic scan to 0.58 V, the two diffraction peaks of Na$_3$P are still visible. Subsequent desodiation to 1.54 V, after the first anodic peak at 0.87 V, shows the re-emergence of FeP (202) and (211) diffraction peaks. Meanwhile, the Na$_3$P diffraction peaks diminish completely at this cycling state, corresponding to the reverse of the reaction (2) and (3). Extending the desodiation to 2.50 V, the FeP diffraction peaks at (202) and (211) is maintained, but with weaker intensity than the fresh cell. The emergence of the FeP diffraction peak at these two desodiation states exhibits lower Bragg angles than the fresh cell, indicating incomplete desodiation i.e. NaxFeP. The loss of crystallinity after the first sodiation/lithiation cycle is a common attribute in conversion-reaction based anode materials upon sodiation/desodiation, which recent reports have ascribed to the amorphisation, decrease in crystallite sizes upon desodiation or irreversibility of transition metals formation [39,75–81]. To further explore the structural changes, ex-situ SEM investigations were conducted as shown in Fig. 5a. For all sodiation/desodiation states indicated, the initial nanocube framework of FePNC is well-retained (Fig. S8, Supporting information). Except for the sodiation state at 0.48 V, micrographs for all cycling states indeed display subtle differences in surface morphology indicate slight structural changes upon the commencement of the conversion reaction at sodiation/desodiation. EDS was conducted to investigate the variation of insertion of the Na ions in the FeP nanobox structure at indicated cycling states. The atomic ratios of Na: Fe were determined as 1.80:1, 3.88:1, 1.21:1 and 0.45:1 at discharge voltage of 0.48, 0.01 and recharge potential of 1.54 and 2.50 V respectively. The results are consistent with the sodiation/desodiation process as discussed. TEM micrographs of FePNC discharged to 0.01 and charged to 2.50 V are shown in Fig. 5b and c. The morphology and porous nature of the FePNC nanocubes are well-preserved under sodiation/desodiation. SAED analysis of the fully sodiated electrode (0.01 V) exhibits diffraction ring patterns that are
ascribed to the (110) of Na$_3$P and (011) of Fe (inset of Fig. 5b). The weak/broad profile Fe diffraction pattern is detected on the contrary to the ex-situ XRD results due to the higher applied voltage of the SAED process (200.0 vs 40.0 kV). SAED image of the FePNC electrode charged to 2.50 V are shown in Fig. 5c. Two weak but distinctive diffraction rings are detected and ascribed to the re-emergence of (211) and (013) plane of FeP after the desodiation. The results are consistent with the ex-situ XRD studies.

To investigate the structural robustness after long cycling effect, SEM analysis were conducted on the electrode materials after cycling lifetime of 100th cycle. The results are shown in Fig. S9 (Supporting information). The cubic-morphology framework of the FePNC remains intact with little change in structural integrity. Apart from the SEI formation on top of the individual FeP nanostructures, there is very little structural expansion as well as agglomeration on each FeP nanocubes indicating that the FePNC nanostructure framework is well-preserved during long cycling lifetime.

3.4. Hydrogen evolution reaction performance

The HER performance of the FePNC and FePCM is investigated and corrected for iR losses (Fig. S10, details in Supporting information) in 0.5 M H$_2$SO$_4$ solution, as shown in Fig. 6. The catalytic activity for all samples is confirmed through the linear sweep voltammetry (LSV) curve (Fig. 6a). By determining the voltage value from the deviation of linearity of the Tafel plot, the onset overpotential (\(\eta\)) can be calculated. FePNC exhibits \(\eta\) at around 80 mV, significantly lower than FePCM (~600 mV). \(\eta\) values at 10 and 20 mA cm$^{-2}$ are 180 and 210 mV, respectively. In addition, FePNC is able to display a large cathodic current density at > 90 mA cm$^{-2}$, larger than FePCM and Pt/C electrode materials. The Tafel plots of all samples are shown in Fig. 6b. The Tafel slope of FePNC, FePCM and Pt/C electrodes are evaluated as 40.3, 120.0 and 22.3 mV dec$^{-1}$ respectively. The Tafel slope of the Pt/C is close to the reported values and is of a Volmer-Tafel mechanism with Tafel step as the rate determining step (Volmer: $2H^+ + 2e^- \rightarrow 2H_{ads}$.
Tafel: \( \text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \). The FePNC undergoes a Volmer-Heyrovsky mechanism with the Heyrovsky step as the rate-determining step, i.e. the adsorption of an extra proton and electron to produce hydrogen (Heyrovsky: \( \text{H}_{\text{ads}} + \text{H}^+ + e^- \rightarrow \text{H}_2 \)) \(^{[82,83]}\).

To gain insight into the transport kinetics of the catalysts, the samples were subjected to EIS analysis with the Nyquist impedance plot shown in Fig. 6c. The charge-transfer resistance (\( R_{\text{ct}} \)) were attributed to the charge transfer kinetics of the \( \text{H}^+ \) reduction process at the electrode-electrolyte interface. The \( R_{\text{ct}} \) value is determined as 18.64 \( \Omega \) for FePNC and 257.0 \( \Omega \) for FePCM. The much smaller \( R_{\text{ct}} \) of FePNC shows, again, the beneficial advantage of the nanostructured carbonaceous structure of FePNC in facilitating the charge transport properties. The sustainability of the HER reactivity of FePNC in the acidic environment is also tested and shown in Fig. 6d. Chronoamperometric electrolysis (CA) demonstrates stable HER activity for more than 40 h, indicating the stable lifetime of the FePNC HER catalysts. As shown, the HER performance of MOF derived-FePNC is comparable with recent reports of FeP-based catalysts (Table S2, Supporting information).

4. Conclusions

In summary, we have successfully designed and synthesized highly porous FeP/C nanocomposites with a highly-ordered nanocubic structure derived from the as-synthesized MOF, or FePNC. FePNC have demonstrated enhanced performance as SIBs anode materials at high rate capability and long cycling stability in comparison to the FeP/C derived from commercially-acquired, irregular MOF materials (FePCM). Through ex-situ investigations, we attribute SIBs charge/discharge processes to the combination of intercalation/conversion reactions. FePNC deployed as HER electrodes have also demonstrated much improved performance in comparison with FePCM. The improvement of the SIBs and HER performance of FePNC is attributed to the uniform morphology, larger surface area as well as the conductive carbonaceous framework in enhancing the capacity/stability at all rates of cycling. Through improvement via the use of MOF-derivative framework, our results have demonstrated the potential of FeP-based materials as economical options for SIBs and HER electrode materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2018.03.009.

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