



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



Yew Von Lim^a, Shaozhan Huang^a, Yingmeng Zhang^b, Dezhi Kong^a, Ye Wang^a, Lu Guo^a, Jun Zhang^c, Yumeng Shi^b, Tu Pei Chen^c, Lay Kee Ang^a, Hui Ying Yang^{a,*}

^a Pillar of Engineering Product Development, Singapore University of Technology and Design, 8 Somapah Road, Singapore 487372, Singapore

^b International Collaborative Laboratory of 2D Materials for Optoelectronic Science & Technology of Ministry of Education, Engineering Technology Research Center for 2D Materials Information Function Devices and Systems of Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

^c School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

ARTICLE INFO

Keywords:

Metal-Organic Framework
Porous FeP/C nanocomposites
Sodium-ion batteries
hydrogen evolution reaction

ABSTRACT

Transition metal phosphides, such as iron phosphide (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 a 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.

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 conversion efficiency and environmental friendliness [6–9]. However, great challenges for the further development of SIBs still persist owing to its poor rate capability and cycling stability, as well as the HER due to the expensive electrocatalysts (commonly using platinum, or Pt) [10–14]. To enhance sodium storage performances and develop affordable electrocatalysts, the most straightforward way is to design nanostructured, inexpensive active materials with improved electrical conductivity to achieve

commercially acceptable electrochemical performances. Indeed, recent reports have shown that nano-structuring of active materials benefitted the improvement in electrochemical performance particularly on SIBs, HER and other alternative energy technologies [15–25].

Transition metal phosphides (TMPs) have recently been considered as an economical replacement for Pt catalyst due to its reactivity in acidic environment and affordability [9,26,27]. By synthesizing low-dimensional TMPs nanostructures, including nanoarrays [28–30], nanowires [31,32] and nanoparticles [33–35], excellent HER activity close to Pt electrode has been reported. TMPs have also been widely employed as potential anode candidates for high-performance SIBs owing to their low intercalation potential and high theoretical capacity [26,36–44]. However, similar to the transition metal oxides and sulfides [45–47], TMPs exhibits large volumetric changes during

* Corresponding author.

E-mail address: yanghuiying@sutd.edu.sg (H.Y. Yang).

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 [33,35,62–66].

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 (K₃Fe(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 move 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 (Na₂H₂PO₂·H₂O) 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 sccm. 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 (WITec, α300R). Thermogravimetric analysis were performed to analyse the content of all composite samples (TGA, Shimadzu DTG-60). N₂ 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 homogenous 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 cm² squarish shaped and used directly in assembly. The electrolyte were prepared using mixture of 1 M of sodium hexafluorophosphate (NaPF₆) 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 Advantec) 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 H₂SO₄ 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 Nafion (5 wt%) respectively. After adding in the active materials, the solution is sonicated for at least 1 hr 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.

Download English Version:

<https://daneshyari.com/en/article/7962387>

Download Persian Version:

<https://daneshyari.com/article/7962387>

[Daneshyari.com](https://daneshyari.com)