



Cubic Prussian blue crystals from a facile one-step synthesis as positive electrode material for superior potassium-ion capacitors



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ABSTRACT

Cubic Prussian blue (PB) crystals are prepared by a facile one-step synthesis. The structure and morphology of the as-prepared samples are characterized by X-ray power diffraction, inductively coupled plasma, scanning electron microscopy and electrochemical measurement. The PB electrode exhibits superior electrochemical behavior in K₂SO₄ aqueous solution including high reversible capacity (80 mAh g⁻¹ at the current density of 0.5 A g⁻¹), outstanding rate capability and good cycling stability. The K-ion capacitor (KIC) is also fabricated by using PB as a positive electrode and commercial activated carbon as a negative electrode, and it presents a maximum energy density of 28 Wh kg⁻¹ at the current density of 1 A g⁻¹ (corresponding to 7.5 mA cm⁻²). Furthermore, the KIC also exhibits excellent cycling stability at the current density of 2 A g⁻¹ with capacity retention of nearly 98% over 1200 cycles. Our synthesized electrode material provides a new way for fabricating high performance electrode materials for superior KIC.

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1. Introduction

Due to global climatic warming and energy shortage, human beings have started to use renewable energy sources (such as tide, wind and solar energy) to replace diminishing fossil fuels (such as coal, petroleum and gas) [1,2]. These clean energy sources are intermittent in nature while the mankind needs relatively constant electric power supply to maintain social functions in order [3]. To solve this conflict, the human not only needs to develop smart grids and novel energy storage devices but also utilizes these energy sources more efficiently [4,5]. Compared to other energy storage technologies such as lithium ion batteries, lithium-air batteries, lithium-sulfur batteries, sodium ion batteries, sodium-sulfur batteries, electrochemical capacitors et al. [6–16], aqueous capacitors have some huge advantages in terms of cycling life and power delivery. So it is becoming a more and more promising energy storage device for hybrid electric vehicles and other devices such as cranes, forklifts and buses in recent years [17–20]. Unfortunately, such energy storage system possesses insufficiently low energy density.

Hybrid capacitor has attracted a great deal of attentions owing to much higher energy density since it was firstly introduced in 2001 [21]. This hybrid system is usually assembled by a Faradaic ion-intercalation electrode (redox electrode) with an electric double-layer electrode (typically carbon materials) in an organic or aqueous electrolyte. In this system, both battery redox reactions and adsorption/desorption of electrical double-layer capacitance occur simultaneously. The redox electrode offers large energy density when the non-Faradaic capacitive electrode provides excellent cycling stability and high power density for the hybrid system [22]. Although lithium ion capacitors have got much progress, the source of lithium is limited and lithium is expensive [23–26]. Considering these reasons, it is very necessary to search both less expensive and more abundant electrode materials for novel energy storage systems by using new working metal ions such as K⁺, Na⁺, Mg²⁺, Al³⁺ and so on.

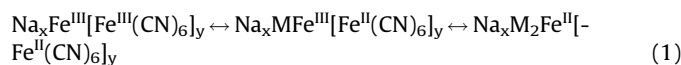
Potassium element is not only more widespread but also more abundant than lithium element in natural resources, and its inorganic salts are readily available and much cheaper than those based on lithium element [27]. Moreover, some potassium-based energy storage devices have been widely investigated such as organic potassium-ion battery, potassium-sulfur battery and potassium-ion oxygen battery owing to their more suitability for

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large-scale stationary energy storage [28–35]. Consequently, the potassium-based energy storage devices are becoming more and more promising among many candidates. Some research groups have shown interest in replacing lithium with potassium to build a novel potassium ion battery in recent years [36–40]. For instance, Cui's group from Stanford University explored electrochemical behavior of copper hexacyanoferrate electrode in KNO_3 electrolyte solution for a potassium ion battery, but their reversible specific capacity is small, only 59 mAh g^{-1} [41]. Another example is that a K-ion capacitor ($\text{K}_{0.19}\text{MnO}_2//\text{AC}$) shows superior cycling stability with capacity retention of 90% over 2000 cycles in K_2SO_4 electrolyte, but it is still unsatisfied with the specific capacity [39]. Recently, there were several reports about Prussian blue or its analogues for Li, Na, Mg, Al, and Zn batteries or capacitors [42–52]. However, to the best of our knowledge, there is rare report on Prussian blue as aqueous KIC with excellent performance. Thus, searching suitable electrode materials for aqueous KIC for large-scale energy storage is still a huge challenge.

Prussian blue (PB) is classified as a part of transition metal hexacyanometallates, which consist of mixed valence compounds. It has been used as a pigment for hundreds of years due to its non-toxicity, low cost and easy accessibility. Until Neff and Itaya firstly reported the electrochemical performance of PB in the 1980's [44], more scientific and technical staffs started to study it as positive electrode materials for batteries and electrodes for sensors [53–59]. For instance, R. W. Murray et al. explored the electrochemistry property of Prussian blue film grown on Pt and SnO electrodes in 1988, which verified two different kinds of ferric sites in their framework structure [53]. Subsequently, R. Marassi et al investigated influence of conditions on electrochemical behavior of Prussian blue films, which shown that electrochemical properties was strongly dependent on the method of their preparation [54]. Another example is that F. Scholz et al. firstly fabricated a solid-state secondary cell with Prussian blue as the active material of both the anode and cathode, which exhibited 60 cycles with capacity retention of nearly 99% [55]. However, these researches are very slow about its application as battery materials in the past decades. Significantly, Cui's group revived the research interest of Prussian blue in 2011, and they reported it as an excellent positive electrode material in aqueous rechargeable batteries [41]. PB has the perovskite-type structure that facilitates reversible intercalation processes for alkali ions. The general formula of PB is $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]_y\text{V}_{1-y}$ ($0 < x < 2$, $y < 1$), where V denotes a $[\text{Fe}(\text{CN})_6]^{4-}$ vacancy occupied by coordinating water [48]. The Prussian blue would take place a two-electron redox reaction in theory during alkali metal ion (M) insertion/extraction process [56,60]:



Moreover, the open-framework contains large octahedral interstitial sites and open channels for ionic diffusion, which allow ion insertion/extraction without collapse of the crystal framework [61].

In this work, we report a kind of cubic PB by using a facile and scalable one-step method, which has perfect cubic crystal with fewer vacancies. The PB electrode exhibits high reversible capacity (80 mAh g^{-1} at the current density of 0.5 A g^{-1}), superior rate capability and excellent cycling stability due to better potassium-ion storage capability and structure stability, thus showing to be a promising intercalation positive electrode material for KIC. Furthermore, a KIC is fabricated by using a PB positive electrode and an activated carbon negative electrode in K_2SO_4 electrolyte solution. It exhibits good cycling stability at the current density of 2 A g^{-1} over 1200 cycles, and gives an energy density as high as 28 Wh kg^{-1} based on the total mass of active material.

2. Experimental

2.1. Materials synthesis

All chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd (China) and were used without further treatment. High-quality PB crystals were synthesized according to a facile strategy. In a typical procedure, $0.58 \text{ g Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and 1 g poly(vinylpyrrolidone) (PVP) were added into 100 ml sodium chloride solution under ultrasonic stirring. Next, 2 ml hydrochloric acid was added into the above mixed solutions. A clear blue solution was obtained at room temperature after vigorous stirring for 1 h . Then, this system was mixed at 80°C for 10 h . The sample was collected by centrifugation (8000 rpm , 10 min) and washed with distilled water and ethanol for three times, respectively. Finally, the PB cubes were obtained through drying at 80°C in a vacuum oven for 12 h .

2.2. Materials characterizations

The crystalline structure was confirmed via utilizing a Bruker D4 X-ray diffractometer (Bruker, Germany) with Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV , 40 mA). Scanning electron microscopy (SEM) was tested by a Philips XL30 microscope (Philips, Netherlands) operated at 25 kV . Inductively coupled plasma (ICP) was conducted by Thermo E.IRIS Duo. The elemental analysis for C and N elements were conducted on a Vario EL Elemental Analyzer.

2.3. Electrochemical measurements

The as-prepared PB cubes were mixed with PTFE (water dispersion: 10 wt. \%) and acetylene black in a weight ratio of $8:1:1$ with the help of ethanol to make electrodes. Later, the mixture was pressed into film and then dried at 80°C for 12 h in a vacuum oven. After drying, the film was cut into disks of approximately 1.5 mg . Finally, these disks were pressed onto Ni mesh to be used as the working electrode. The cyclic voltammetric (CV) testing and charge-discharge measurements of the PB electrodes were carried out in $0.5 \text{ mol l}^{-1} \text{ K}_2\text{SO}_4$ aqueous solution by using a three-electrode system. The system consisting of the above working electrode, Ni mesh as the counter electrode and saturated calomel electrode (SCE), was used for the test of their electrochemical performance. SCE was used as the reference electrode, which is a reference or comparison during measuring electrode potentials, its potential is 0.24 V vs. standard hydrogen electrode (SHE). The CV curves were obtained on an electrochemical working station of CHI660C (Chenhua, China). The EIS testing was performed with initialized potential of 0.25 V (vs. SCE) and the potential amplitude of 5 mV over the frequency range from 10^5 to 10^{-2} Hz . An activated carbon (AC) with a specific surface area of about $2000 \text{ m}^2 \text{ g}^{-1}$ was purchased from Ningde Chemical Industrial Co. Ltd. (China). The AC electrode was prepared in the same way as the above PB electrode. A two-electrode cell, which consisted of the PB positive electrode and the AC negative electrode in $0.5 \text{ mol l}^{-1} \text{ K}_2\text{SO}_4$ aqueous solution, was used to test the cycling behavior on a Land cell tester (Wuhan, China). All the measurements were performed at room temperature.

In the two-electrode cell, energy density (E) and power density (P) of electrode materials are calculated according to the following equations:

$$E = (I \cdot t \cdot \Delta U) / m \quad (2)$$

$$P = (I \cdot \Delta U) / m \quad (3)$$

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