



$K_{1-x}Fe_{2+x/3}(CN)_6 \cdot yH_2O$, Prussian Blue as a displacement anode for lithium ion batteries



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HIGHLIGHTS

- Prussian Blue, $K_{0.88}Fe^{III}_{1.04}[Fe^{II}(CN)_6] \cdot yH_2O$, is used as anode in lithium ion batteries.
- It can deliver 450 mAh g^{-1} at 8.75 mA g^{-1} in the low voltage window from 0.005 to 1.6 V vs Li⁺/Li.
- For the first time, a conversion or displacement reaction is proposed for this kind of systems.

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ABSTRACT

Nanosized Prussian Blue, $K_{0.88}Fe_{2.04}(CN)_6 \cdot yH_2O$, prepared in aqueous solution at room temperature, is shown to be active as anode for lithium ion batteries after mild dehydration. It exhibits reversible capacities of up to 400 mAh g^{-1} at 8.75 mA g^{-1} and 150 mAh g^{-1} at 1750 mA g^{-1} , with relatively low hysteresis and long cycle life in the low voltage range 0.005–1.6 V vs lithium. Ex-situ XRD, FTIR as well as SEM and TEM studies on pristine and cycled electrodes suggest that the reversible insertion of about $\sim 5 \text{ Li}^+/\text{f.u.}$ is associated with a displacement (or conversion) reaction on the Prussian Blue structure along with the reduction of all iron atoms, reported for the first time in this kind of systems. The products of re-oxidation do not recover the crystal structure of Prussian Blue.

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1. Introduction

Lithium ion batteries are the most widely used electrochemical energy storage (EES) devices for portable electronics due to their high energy density [1]. Nevertheless, their applicability to electric vehicle is hindered by the inability to increase the energy density beyond the intercalation of one lithium ion per transition metal or anodes alternative to graphite with appropriate redox voltages. Electrode materials based on alloying [2] as well as those based on displacement or conversion reactions [3] have opened new possibilities, but so far high power and stable cycling has not been achieved. While emerging battery technologies can benefit from the knowledge on Li-ion batteries, novel materials, purposely

studied initially for other chemistries such as Mg or Na-ion batteries are also being tested back for Li-ion batteries, the benefit being mutual. Specifically, metal organic frameworks, as those of the Prussian Blue family have emerged as interesting intercalation based high power electrode materials [4].

Prussian Blue (PB), ideally $KFe_2(CN)_6 \cdot xH_2O$, is a well-known synthetic blue pigment [5]. It has a cubic lattice with $a = 10.1780 \text{ \AA}$ (space group $Fm\bar{3}m$). In this structure, the iron atoms, Fe(II) and Fe(III), coexist on alternate corners of a small cube of 5.1 \AA along the three directions of space connected by linear cyanide anions. Alkali atoms alternately occupy half of the centres of these small cubes (see Fig. 1a) [6]. Interstitial Fe^{3+} and CN vacancies are the usual defects [7].

Based on the oxidation state of the transition metal ions, PB and its transition metal substituted analogues, $KM^II Fe^III(CN)_6 \cdot xH_2O$ (PBA) [8,9] have been studied for many different properties including charge-transfer phase transitions or magnetic ordering. [10,11] Because of their large channels, they have also been tested for H_2

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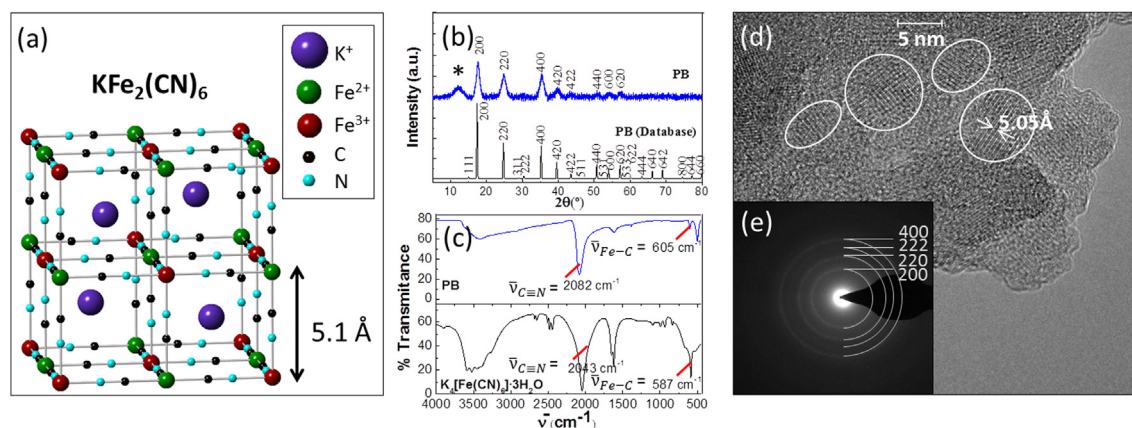


Fig. 1. a) PB structure b) XRD patterns of the PB synthesized and the PB listed in ICSD Karlsruhe Database (n° 162081). The Kapton[®] film peak has been marked with an *. c) IR spectra of PB and the starting reagent, $K_4[Fe(CN)_6] \cdot 3H_2O$, labelling the characteristic $C \equiv N$ and $Fe-C \equiv N$ absorption bands of both. d) TEM image of PB domains and e) electron diffraction pattern of PB nanocrystals with crystallographic planes indexed.

and CO_2 storage and separation [12–14] in their dehydrated state as well as for ^{137}Cs decontamination [15,16]. Interestingly, with the combination of the transition metals redox properties along with the large available tunnels for ion diffusion, PBA also display an attractive electrochemical behaviour, [17–21] which has been recently exploited in the field of electrochemical energy storage. In this sense, $KMFe(CN)_6 \cdot xH_2O$ ($M = Ni, Cu$) have shown reversible capacities of $\sim 50 \text{ mAh g}^{-1}$ with the insertion of Li^+ , Na^+ , NH_4^+ or K^+ in aqueous electrolyte, at very high charge and discharge rates of 1 A g^{-1} at $\sim 1 \text{ V}$ vs NHE. [2,9,22,23] Divalent cations, such as Mg^{2+} , Ca^{2+} , Si^{2+} and Ba^{2+} , have also been inserted into the Ni based PBA. [24] Moreover, a 0.95 V full PBA based cell, with Cu-PBA as positive- and Mn-PBA as negative-electrode materials, has recently demonstrated to deliver 28 mAh g^{-1} at 1C with no capacity loss for 1000 cycles [25].

Additionally, $KMFe(CN)_6 \cdot xH_2O$ ($M = Mn, Fe, Co, Ni$ and Zn) are also active as cathodes for Na^+ and Li^+ insertion/de-insertion in organic electrolyte. Reversible capacities of $\sim 100 \text{ mAh g}^{-1}$ were exhibited for $M = Fe$ when tested versus Na^+ , [26] and good performance was also observed when $AMn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$ ($A = Li^+, Na^+$) is cycled both versus sodium and lithium. [27] Recently high quality crystals of $NaFe_2(CN)_6$ have shown capacities above 150 mAh g^{-1} vs Na [28].

In alkali-ion batteries, PBAs have been mainly studied as positives. Interestingly, Sung Y-E and coworkers, as well as Zhang et al., have recently reported the electrochemical properties of PBA based on Co and Mn as negative for Li-ion batteries. Their experiments with Co-based PBA showed that this material can deliver reversible capacities of 400 mAh g^{-1} in the $0.01\text{--}3.0 \text{ V}$ range [29,30].

In this paper we report on the electrochemical performance of nanosized Prussian Blue, $K_{0.88}Fe_{2.04}(CN)_6 \cdot yH_2O$, as negative (indifferently called anode hereafter) for Li-ion batteries in organic electrolytes in the low voltage $0.005\text{--}1.6 \text{ V}$ range, which enables high voltage full cells to be prepared. Iron being the only transition metal in the compound it represents the lower cost member of the PBA family. We also present insights on the possible mechanism of the alkali ion storage in this compound.

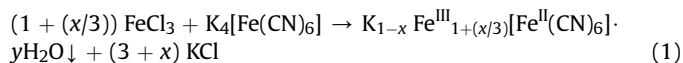
2. Experimental

2.1. Synthesis

2.1.1. PB synthesis

All chemicals were of analytical reagent and ACS grade and were used without further purification. The preparation of PB is

straightforward: 100 mL of a freshly prepared pale yellow $K_4[Fe(CN)_6] \cdot 3H_2O$ 40 mM aqueous solution was mixed with 100 mL of a yellow–orange $FeCl_3 \cdot 6H_2O$ 40 mM aqueous solution, using deionized water in both cases. [31] As soon as the two solutions came in contact, a blue ink colour suspension containing PB was formed in excess of potassium ions according to the reaction of Equation (1). The small PB particles resisted centrifugation at 4000 rpm during 10 min and it was necessary to force its precipitation by adding ethanol. Then, after 48 h filtering, washing with ethanol ($3 \times 10 \text{ mL}$), and drying, dark blue crystal-like aggregates of “soluble” [21] PB, actually $K_{0.88}Fe_{2.04}(CN)_6 \cdot yH_2O$, were formed.



2.1.2. PW synthesis

Prussian White was synthesized via solvothermal method, following the recipe described by Jiang. [32] In brief, $K_4[Fe(CN)_6]$ (1.05 mmol) added into deaerated distilled water (25 mL), was transferred into a Teflon-lined stainless autoclave, sealed in an Argon filled glove bag and then maintained at $160 \text{ }^{\circ}C$ for 48 h. After the reaction was completed, the precipitate was collected by filtration, washed several times with distilled water and acetone, and finally dried in a vacuum oven at $60 \text{ }^{\circ}C$ for 12 h.

2.2. Structural characterization

PXRD data were collected in a Bruker D8 Advance X-Ray diffractometer, with $\lambda_{CuK\alpha} = 1.54056 \text{ \AA}$. The measured data range extends from 5° to 80° , 2θ , with a step width of 0.0194° . IR spectra were recorded in the range of $\bar{\nu} = 4000\text{--}450 \text{ cm}^{-1}$ in transmission mode in a Perkin Elmer FTIR Spectrum 400 DTGS spectrophotometer by preparing KBr pellets. High Resolution Transmission Electron Microscopy (HRTEM) images, EDX spectra and electron diffraction patterns were recorded using a FEI Tecnai F20 S-TWIN electron microscope operated at an accelerating voltage of 200 kV equipped with an EDX spectrometer. Scanning Electron Microscopy (SEM) was utilized to study the morphology and contrast of pristine and cycled material. SEM was performed in a FEI Quanta 200F SEM operated at 30 kV and equipped with an Apollo 10 SSD Energy Dispersive X-ray (EDX) and Scanning Transmission Electron Microscopy (STEM) STEM-II detectors. Elemental analysis (H, C, N) has been performed in a Euro Elemental Analyser (CHNS), to check the

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