Prussian white analogues as promising cathode for non-aqueous potassium-ion batteries

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ABSTRACT

We prepared Prussian white analogues—$K_xMFe(CN)_6 \cdot mH_2O$ (M = Fe, Co, Ni, or Cu). These compounds are investigated as cathode materials for potassium-ion batteries with a non-aqueous electrolyte. Each of these materials exhibits different K-ion storage properties with reversible capacity values ranging from 35 to 110 mAh g^{-1} at high potentials above 3.2 V *vs.* K^+/K. Among them, FeFe-Prussian white, $K_{1.68}Fe_{1.09}Fe(CN)_6 \cdot 2.1H_2O$, exhibits the highest reversible capacity of 110 mAh g^{-1} and stable cycling performance in contrast to rapid capacity fading of other analogues. Our results demonstrate a remarkable potential of this family of cathode materials for the emerging potassium-ion batteries.

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1. Introduction

Batteries employing inexpensive Earth-abundant elements have recently received considerable attention [1,2]. Shadowed by the worldwide effort on sodium-ion batteries (NIBs), potassium-ion batteries (KIBs) have received little attention, which is seemingly due to the higher mass of K-ion as well as its large size [3]. However, when considering a full-cell scale, the mass burden of K-ions renders KIBs only 5 to 10% heavier than NIBs if the electrodes of the two types of devices exhibit similar capacity values [3]. Indeed, indiscriminate to all emerging batteries, the challenge comes from identifying suitable electrode materials, where KIBs represent no exception.

The recent interests on KIBs have been stimulated by the progress made on the anode side [4–14]. However, further progress of KIBs faces the hurdle on the cathode side, where there have been very few choices of cathode materials. Eftekhari reported a Prussian blue KIB cathode, $K_xFe_2(CN)_6$, which exhibited a reversible capacity of ~78 mAh g^{-1} and impressive cycling life [15]. Cui et al. investigated various Prussian blue analogues as electrodes in KIBs that contain aqueous electrolytes [16, 17]. Recently, a few more cathode candidates were reported, including layered oxides, such as $K_{0.3}MnO_2$ [18] and $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ [19], as well as a couple of organic solids, such as perylenetetracarboxylic dianhydride (PTCDA) [20] and poly(anthraquinonyl sulfide) (PAQS) [21]. Yet, these cathode materials often do not contain sufficient K-ions to extract, which fundamentally limits the choice of anodes. As another issue, the operation potentials of these materials are modest, which on average are at

2.0–2.5 V *vs.* K^+/K, thus restricting the energy density of full cell devices. Therefore, it is highly desirable to identify potassium-containing, high-potential cathode materials. Very recently, Xu et al. reported $K_3V_2(PO_4)_3$ as a KIB cathode with a high reaction potential above 3.6 V and a capacity of 54 mAh g^{-1} [22].

The primary challenge of identifying cathode materials for KIBs might be the much larger radius of K-ion (1.38 Å) *vs.* Li-ion (0.76 Å) and Na-ion (1.02 Å) [23], which is fortunately not an issue for Prussian blue analogues. In 2016, Zhang et al. reported that a $K_{0.22}Fe[Fe(CN)_6]_{0.805} \cdot 4.01H_2O$ cathode could deliver a reversible capacity of 76.7 mAh g^{-1} at 3.2 V with capacity retention of 95.4% after 50 cycles [24]. Note that this Prussian blue electrode still does not contain a good stoichiometry of removable K-ions. It is well known that Prussian white theoretically contains one more extractable K-ion than Prussian blue in the open framework, which renders double capacity during the initial charge of a full cell [25–29]. Most recently, Goodenough et al. reported a Prussian white analogue of $K_{1.89}Mn[Fe(CN)_6]_{0.92} \cdot 0.75H_2O$ as a low cost and high energy potassium-ion cathode, which realized a high capacity of 142 mAh g^{-1} and a high reaction potential of 3.6 V [25]. This pioneering study indicates the feasibility of utilizing Prussian white analogues as low-cost and high-performing cathode materials for KIBs.

In this communication, we, for the first time, report the performance of several Prussian white analogues as cathode in nonaqueous KIBs—$K_xMFe(CN)_6 \cdot mH_2O$ (M = Fe, Co, Ni, or Cu), which were prepared by a simple precipitation method.

2. Experimental

We aim to synthesize four Prussian white analogues: $K_2FeFe(CN)_6$, $K_2CoFe(CN)_6$, $K_2NiFe(CN)_6$, and $K_2CuFe(CN)_6$ by a simple precipitation

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method. Typically, 0.1 mol L^{-1} MCl_2 (M = Fe, Co, Ni, and Cu) solution was dropwise added into 0.1 mol L^{-1} $K_4Fe(CN)_6$ solution under stirring. After four hours of reaction, the precipitate was centrifuged, rinsed, and dried in an oven at 80 °C overnight. Due to the presence of structural defects, common in room-temperature precipitation reactions, the actual chemical formula of Prussian white analogues may deviate from the stoichiometry of $K_2MFe(CN)_6$, which can be analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer 2100 DV) on K, M, and Fe elements. We also conducted thermogravimetric analysis (TGA, SDT Q600) on water content. We determined their formula to be $K_{1.68}Fe_{1.09}Fe(CN)_6 \cdot 2.1H_2O$, $K_{1.55}Co_{0.88}Fe(CN)_6 \cdot 3.2H_2O$, $K_{1.51}Ni_{1.05}Fe(CN)_6 \cdot 3.3H_2O$, and $K_{1.40}Cu_{0.93}Fe(CN)_6 \cdot 4.5H_2O$, respectively. Interestingly, the content of crystal water in these Prussian white analogues increases along the atomic number: Fe < Co < Ni < Cu. We refer to the four obtained Prussian white samples as FeFe-PW, CoFe-PW, NiFe-PW, and CuFe-PW, respectively. The theoretical capacities of FeFe-PW, CoFe-PW, NiFe-PW, and CuFe-PW are 119.7, 108.2, 70.7, and 59.1 mAh g^{-1}, respectively, based on the content of K-ions in the structures, if we assume that the transition metal redox couples, M^{3+}/M^{2+} (M = Fe and Co), are active, but Ni^{3+}/Ni^{2+} and Cu^{3+}/Cu^{2+} are inactive. It is known that Ni^{3+}/Ni^{2+} is inactive in both Li and Na analogues of Prussian blue [27,30].

We collected powder X-ray diffraction (XRD) patterns on a Rigaku Ultima IV Diffractometer with Cu Ka irradiation (λ = 1.5406 Å). The electrodes of Prussian white materials were composed of 70 wt% of Prussian white active mass, 20 wt% Super P, and 10 wt% polyvinylidene fluoride (PVdF). The electrode slurry was cast on Al foil, where the typical loading of active mass is ~2 mg/cm². Coin cells (2032) were assembled in an argon-filled glovebox, which contains Prussian white working electrode, potassium metal counter/reference electrode, glass fiber membrane as a separator, and an electrolyte of 0.8 mol L^{-1} KPF_6 in propylene carbonate (PC) with 4 wt% fluoroethylene carbonate (FEC) additive. Cyclic voltammetry (CV) tests were performed on a VMP-3 multi-channel workstation at a scan rate of 0.1 mV s^{-1}. The galvanostatic charge/discharge tests were carried out on a Maccor system at room temperature. The voltage range for electrochemical tests is 2.0–4.5 V vs. K^+/K.

3. Results and discussion

Prussian white samples were prepared by a conventional precipitation reaction between MCl_2 (M = Fe, Co, Ni, Cu) and $K_4Fe(CN)_6$ in an aqueous solution. As the filtered precipitates were only heated at 80 °C, they still contain crystal water. In this study, we choose to reveal the intrinsic electrochemical behavior of these as-obtained Prussian white materials. The XRD results (Fig. 1a) suggest that all the obtained samples exhibit typical Prussian white patterns, which can be assigned to a face-centered cubic structure (FCC, space group Fm-$3m$). In such a

structure, Fe^{2+} and M^{2+} ions are alternately six-fold coordinated to the carbon and nitrogen end of the cyanide ligands, respectively, which constitutes a three-dimensional open framework with large interstitial cavities to accommodate K-ions and possibly water molecules (Fig. 1b) [27]. For FeFe-PW, there is minor phase transformation, as indicated by the peak-split around ~40° and ~45° [25,26]. Such phase transformation has also been observed in other studies, where high K-ion content in Prussian white structure will induce the cubic lattice to transform to a monoclinic one [25,26].

In principle, $K_2MFe(CN)_6$ can undergo a two-electron-transfer reaction, which converts Prussian white (PW) to Berlin green (BG), based on the M^{3+}/M^{2+} (M = Fe, Co) and Fe^{3+}/Fe^{2+} redox couples by the following reaction:

$$K_2M^{II}Fe^{II}(CN)_6 \, (PW) \leftrightarrow M^{III}Fe^{III}(CN)_6 \, (BG) + 2K^+ + 2e^-$$

This corresponds to a very high theoretical capacity of ~150 mAh g^{-1} for compounds, i.e., $K_2FeFe(CN)_6$ and $K_2CoFe(CN)_6$. We tested the as-obtained Prussian white electrodes by CV measurements at a scan rate of 0.1 mV s^{-1} in the potential range of 2–4.5 V vs. K^+/K. As shown, FeFe-PW electrode demonstrates a typical two K-ion extraction/insertion behavior, whereas CoFe-PW, NiFe-PW and CuFe-PW electrodes seem to operate by a one-electron reaction mechanism (Fig. 2 inset).

As depicted in Fig. 2a, FeFe-PW displays two distinct charge/discharge plateaus at 4.1/3.9 V and 3.6/3.2 V, which can be attributed to the Fe^{3+}/Fe^{2+} redox couples on the carbon side and on the nitrogen side, respectively [27–29]. It is noteworthy that the discharge potentials of 3.9 and 3.2 V of K_xFeFe-PW are higher than those of Na_xFeFe-PW, 3.3 and 3.0 V, in Na-ion batteries [29]. This may have to do with the facts that the standard potential of K^+/K is ~0.3 V lower than that of Na^+/Na in PC solvent [31] and that the energy may be more negative when K-ions are incorporated into the $FeFe(CN)_6$ framework [32]. The first-cycle charge/discharge capacity of 105.1/110.5 mAh g^{-1} for FeFe-PW gives rise to an initial coulombic efficiency of 105.1%, which is likely due to the mixed oxidation states of Fe (II) and Fe (III) of the iron site coordinated to nitrogen end of cyanide, thus resulting in a shorter low-potential plateau during the first depotassiation [29]. However, the following discharge (potassiation) may form a Prussian white structure with more K-ions inserted than its pristine form, which would give rise to a coulombic efficiency more than 100%. In the third cycle, the discharge capacity is still of 105 mAh g^{-1}, indicating good K-insertion reversibility of FeFe-PW. Importantly, the initial discharge capacity of FeFe-PW compound is as high as 110.5 mAh g^{-1}, which corresponds to 92% utilization of its theoretical capacity of 119.7 mAh g^{-1} when assuming intercalation/deintercalation of 1.68 potassium ions. If more potassium ions are present in the FeFe-PW lattice and all crystal water molecules can be eliminated, higher K-storage capacity can be expected.
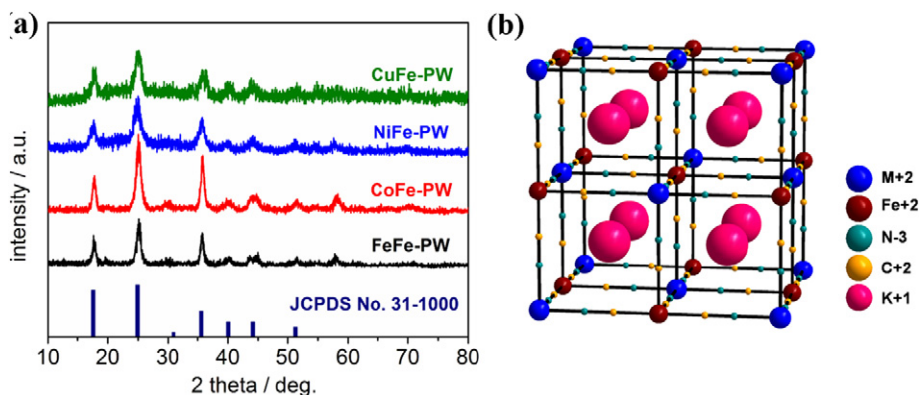

Fig. 1. (a) XRD patterns of the four Prussian white analogues in comparison with the standard diffraction pattern of $K_2CoFe(CN)_6$ (JCPDS No. 31-1000), (b) A schematic of the crystal structure of $K_2MFe(CN)_6$, M = Fe, Co, Ni, and Cu.