

Realizing Superior Prussian Blue Positive Electrode for Potassium Storage via Ultrathin Nanosheet Assembly

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Supporting Information

ABSTRACT: Prussian blue analogues have attracted growing attention as the positive electrode materials in rechargeable potassium-ion batteries (KIBs) due to the intrinsic open frameworks and high theoretical capacities. However, the bulk synthesized Prussian blue which is accompanied by aggregation inevitably results in the limited K⁺ ion mobility and suppressed potassium storage performance. In this work, ultrathin nanosheet-assembled hierarchical Prussian blue materials $(K_{1,4}Fe_4[Fe(CN)_6]_3)$ are synthesized via a facile dissolution-recrystallization strategy. On the strength of this architecture, the positive electrode displays both high rate (71 and 24.9 mAh g^{-1} at 50 and 600 mA g^{-1}) and long life-span properties (75.2% of the primal capacity retained after 100 cycles) for potassium storage. The enhanced diffusion kinetics and structural stability are further demonstrated through the galvanostatic intermittent titration technique analysis and ex-situ X-ray diffraction. Our work provides a new nanostructuring strategy for improving the potassium storage in intercalation electrodes.



KEYWORDS: hierarchical structure, Prussian blue analogues, dissolution-recrystallization strategy, potassium ion batteries, solid-state diffusion

INTRODUCTION

The increasing consumption of nonrenewable energy resources has caused many social problems such as energy crisis and environmental pollution. To solve these problems, the exploration of clean and renewable energy sources is highly demanded, which in turn also promotes the development of high efficiency energy storage systems.¹⁻⁶ Li-ion batteries (LIBs) as one of the promising energy storage systems have been commercialized by virtue of their high energy density.⁴ Nevertheless, the scarcity of lithium (Li) reserves and the rising cost of lithium hamper the further popularization of LIBs.7 Other alternative sustainable systems as the promising candidates for post-LIBs such as sodium/potassium ion batteries and multivalent metal ion batteries have appeared in recent years.^{8–10} Among them, K-ion batteries (KIBs) and Na-ion batteries (NIBs) as the low-cost alternatives have attracted much attention on account of the abundant resources of potassium and sodium.^{11–13} K^+ ions with the weaker Lewis acidity are capable of forming smaller solvated ions compared to Li⁺ and Na⁺ ions, indicating the superior ion-conductivity and more efficient ion transport.¹⁴ Moreover, the K⁺/K couples possess lower redox potential (-2.94 V vs SHE), which is similar to Li^+/Li (-3.04 V vs SHE), and even more negative than Na^+/Na (-2.71 V vs SHE), enabling a suitable

electrochemical voltage window for KIBs.¹⁵ However, the large ionic radius of K⁺ (Li⁺ (0.76) < Na⁺ (1.02) < K⁺ (1.38) Å) not only limits the solid-state diffusion but also causes the larger lattice distortion for intercalation positive electrodes.^{16,17} In order to tackle the problem, development of suitable electrodes with high-efficiency potassium storage is of great importance.

To date, different types of advanced materials have been investigated as K-ion positive electrode materials, such as layered metal oxides, polyanionic compounds, organic crystals, and Prussian blue analogues (PBAs). Layered metal oxides theoretically demonstrate high volumetric density and high capacity. However, the accommodation of the large K⁺ ions is inevitably accompanied by complicated phase transitions and structure degradation.¹⁷ Although organic positive materials show good performances in KIBs, they do not possess K-ions initially, which hinders their practical applications in full-cell design. Polyanionic compounds are promising positive materials for KIBs but typically suffer from low specific capacity.¹⁵ Notably, Prussian blue (PB) and its analogues serve as the most promising positive materials for KIBs on account

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of their intrinsic large interstitial cavities, low cost, and facile preparation. $^{18-20}\,$ The open framework formed by cyanide groups and transition metals enables the free diffusion of alkali metal ions (Li⁺, Na⁺, and K⁺), which was proved by Imanishi et al. and Wessells et al.²¹⁻²³ Recently, He et al. clarified the relationship between the crystallite size and the potassium storage performance for Prussian white, demonstrating that the ultrasmall $K_{1.7}Fe[Fe(CN)_6]_{0.9}$ crystallites deliver the highest discharge capacity.²⁴ Potassium PB nanoparticles were also synthesized by Zhang et al. via a facile precipitation method, exhibiting excellent potassium storage performance in both half-cells and full-cells.²⁵ However, the bulk synthesized PBs are usually accompanied by aggregation, which inevitably results in limited electrochemical performance due to the suppressed K⁺ mobility. To further improve the efficiency of potassium storage, the effective construction of hierarchical structure with more exposed active sites and a shorter ion diffusion path is one of the most attractive strategies.²⁶⁻²⁹ In this regard, PBAs with an ultrathin nanosheet-assembled hierarchical structure are expected to exhibit enhanced potassium storage and have not been investigated previously to the best of our knowledge.

Herein, we report an ultrathin nanosheet-assembled hierarchical Prussian blue (PB-NSs) as the efficient KIB positive electrode material. The PB-NSs exhibit excellent cycle life (75.2% capacity retention after 100 cycles) and greatly enhanced rate performance for KIBs compared to the PBs with a bulk structure. The promoted solid-state diffusion kinetics is confirmed by galvanostatic intermittent titration technique (GITT). Furthermore, its structural evolution upon potassium storage is in-depth investigated by ex situ X-ray diffraction (ex situ XRD).

EXPERIMENTAL SECTION

Material Synthesis. The PB-NSs were prepared by a low temperature solvothermal method. Briefly, 1 mmol $K_3Fe(CN)_6$ was dissolved in the mixed solution composed of 10 mL of 36% hydrochloric acid (HCl), 10 mL of deionized water, and 50 mL of *N*,*N*-dimethylformamide (DMF). A yellow transparent solution was obtained after magnetic stirring for 10 min. Then, the yellow solution was injected into a Teflon-lined autoclave with a volume of 100 mL, aged at 70 °C for 48 h. After that, a dark blue precipitate was collected by centrifugation, washed by DI water and alcohol, and then desiccated overnight in a vacuum oven at 80 °C. In order to obtain the optimal structure, different periods of aging time were studied while other parameters were kept the same as PB-NSs, and the sample being aged for 3 h was denoted as PB-NBs.

Material Characterization. The as-synthesized sample was identified by D8 Advance X-ray diffractometer with $K\alpha$ rays radiated from Cu. The field emission scanning electron microscopy (FESEM) pictures were captured by the JEOL JSM-7100F. TEM images were recorded using a Titan G2 60-300 transmission electron microscope. Specific surface areas (BET) of samples were obtained by the Tristar II 3020 instrument. Micro-Raman spectroscopy system was used to measure the Raman spectra at ambient temperature. The elemental contents and chemical bonding information were obtained by Optima 4300DV (Inductively coupled plasma, ICP) and 60-SXB IR spectrometer (FT-IR). X-ray photoelectron spectroscopy (XPS) tests were further carried out by the VG Multi Lab 2000.

Electrochemical Measurements. 2016 coin cells were used to test the K-ion batteries, which were assembled in a glovebox full of pure argon. The positive electrode was fabricated with 60 wt % PB-NSs (or PB-NBs), 30 wt % ketjen carbon, and poly-(tetrauoroethylene) (10 wt %, PTFE). A typical loading of the PB-NSs electroactive material is about 1.5–2.0 mg cm⁻², and potassium foil was served as the negative electrode. The electrolyte was 0.5 M

solution of KPF₆ in mixed diethyl carbonate–ethylene carbon (DEC–EC; 1:1 v/v), and 5 wt % FEC was employed as an additive to stabilize the electrode during cycling. The Glass Microfibre Filter (Whatman: grade GF/A) was employed as the separator. Before testing, the coin cell was aged overnight to reach a normal operation state. Galvanostatic charge/discharge experiments were proceeded in a multichannel batteries measurement system (LAND CT2001A) at room temperature. Cyclic voltammetry (CV) was carried out on an electrochemical workstation (Autolab PGSTAT302N) at 0.1 mV s⁻¹ between 2.0 and 4.0 V.

Calculation for the Apparent Diffusion Coefficients. Calculation for the apparent diffusion coefficients of K⁺ ions through GITT results: The D^{GITT} can be obtained through the potential variation to an intermittent invariable current pulse (10 mA g⁻¹). The detailed calculation was carried out from eq 1:²⁷

$$D^{\text{GITT}} = \frac{4}{\pi \tau} \left(\frac{n_{\text{m}} V_{\text{m}}}{S} \right)^2 \left(\frac{\Delta E_{\text{s}}}{\Delta E_{\text{t}}} \right)^2 \tag{1}$$

where τ represents the time for an individual constant current pulse and $n_{m\nu}$ $V_{m\nu}$ and S indicate the molar number, molar volumes, and electrode–electrolyte contact area, respectively. ΔE_t is the integral difference of cell voltage for charging or discharging, and the voltage variation during the individual open-circuit period can be denoted as ΔE_s .

RESULTS AND DISCUSSION

The PB-NSs were obtained through a facile hydrothermal reaction. The SEM images of PB-NSs show the flower-like hierarchical structure. Ultrathin nanosheets with exposed active sites were entirely assembled on the surface, and the size of PB-NSs ranges from 400 to 600 nm (Figure 1a,b). A closer



Figure 1. Morphological characterizations and evolution of PB-NSs with (a, b) SEM and (c) TEM images for PB-NSs. (d) Schematic diagram and the corresponding SEM images of the as-synthesized Prussian blue materials aged for (d-1) 3, (d-2) 6, and (d-3) 48 h.

observation reveals that these nanosheets are randomly stacked with multidimensional open channels (Figure 1b). As confirmed by TEM (Figure 1c), the thickness of ultrathin nanosheets is about 10 nm. To identify the formation mechanism of PB-NSs, time-dependent experiments were employed. The Prussian blue nanoballs (PB-NBs) with a rough and uneven surface were initially formed (Figure 1d-1). Then, a number of nanoflakes appeared on the surface (Figure 1d-2). As time prolonged, these nanoflakes gradually extended along



Figure 2. Characterizations of the as-synthesized Prussian blue materials with (a) XRD patterns, (b) Fe 2p spectra, (c) Raman spectra, and (d) nitrogen adsorption-desorption isotherms of PB-NSs and PB-NBs. Inset of panel d shows the pore size distribution.

their basal planes, and transformed to ultrathin nanosheets. Finally, the nanosheets reassembled and a flower-like hierarchical structure was formed when the aging time spans over 48 h (Figure 1d-3). The morphology evolution follows an outside-in reaction process. The original solid nanoballs were first formed (Figure S1) due to the rapid reaction between $[Fe(CN)_6]^{4-}$ and Fe^{2+}/Fe^{3+} at the initial stage, and then the newly formed PB-NBs with metastable surface went through a dissolution-recrystallization process with numerous nanoflakes appearing.³⁰ As the reaction proceeded, ultrathin nanosheets extended and assembled on the surface in the recrystallization process (Figure S2).²⁷ Modulating the structure at nanoscale is an effective strategy for achieving enhanced electrochemical performance, and hence the unique ultrathin nanosheetassembled three-dimensional structure is expected to be favorable for obtaining more efficient potassium storage.³¹ As a comparison, the PB-NBs with a bulk structure were also isolated and investigated on the structure and electrochemical properties.

The XRD measurement was carried out to identify the crystalline structure of the synthesized PB-NSs and PB-NBs (Figure 2a). The diffraction patterns of these two samples are similar and consistent with the standard card of Fe₄[Fe- $(CN)_6$]₃ (JCPD card No. 52-1907), indicating the formation of three-dimensional crystalline structure composed of cyanide-bridging and transition metal nodes.²⁵ The stronger peak of PB-NSs demonstrates the more crystalline feature due to the prolonged recrystallization period.²³ To determine the accurate chemical formula, ICP analysis was carried out (Table S1), which deduces the compositions of K_{1.4}Fe₄[Fe(CN)₆]₃ and KFe₄[Fe(CN)₆]₃ for PB-NSs and PB-NBs, respectively. The X-ray photoelectron spectroscopy (XPS) result indicates

the presence of C, N, O, Fe, and K and the elemental mapping shows their uniform distribution (Figure S3 and S4). Thermogravimetric analyses (TGA) were conducted for PB-NSs and PB-NBs (Figure S5), with a weight loss below 250 °C being ascribed to the removal of adsorbed water and interstitial water, and that above 250 °C arising from the decomposition of the PB framework, indicating a small amount of water being present in PB-NSs.³² Also, the FT-IR spectra confirm the existence of water in the open framework (Figure S6). The sharp absorption at around 1648 cm⁻¹ can be associated with the $\delta H_2 O$ bending modes.³³ According to previous reports, crystal water molecules compete with K-ions to occupy the interstitial sites and inhibit K-ions diffusion. They also deteriorate the integrity of crystal structure upon cycling.^{27,32} Therefore, PB-NSs which have a lower water content (according to TGA) are expected to exhibit better electrochemical performance.

The valence states of the obtained materials were further investigated. Figure 2b shows the Fe 2p spectra with two distinct peaks observed at 707.45 and 720.20 eV which can be ascribed to the Fe²⁺ within the $[Fe(CN)_6]^{4-}$ units. Moreover, the higher binding energy peaks situated at around 711.44 and 722.88 eV manifest the presence of Fe³⁺ in the PB-NSs.³⁴ The valence states of Fe in PB-NBs are much the same as PB-NSs, regardless of the shorter reaction time. The previous reports have shown that CN[¬] coordinated to Fe³⁺ shows higherwavenumber peaks than that with Fe²⁺ in Raman spectrum.³⁵ Thus, the two Raman peaks located at 2100 and 2158 cm⁻¹ in Figure 2c strongly confirm the coexistence of Fe²⁺ and Fe³⁺, which is in accordance with the XPS results.³⁶ Moreover, the relatively stronger vibration at 2100 cm⁻¹ in PB-NSs than in PB-NBs manifests a higher content of Fe²⁺ due to the insertion



Figure 3. Electrochemical performances for potassium storage. (a) The third-scan CV profiles at 0.1 mV s⁻¹, (b) rate performances, and (c) cycling performances at 200 mA g⁻¹ for PB-NSs and PB-NBs.

of additional K⁺ ions, which is consistent with the ICP results. The prolonged reaction time leads to sufficient nucleation, which facilitates the preferable crystallization and elimination of defects, resulting in the different chemical compositions between PB-NSs and PB-NBs.^{30,37} Nitrogen adsorption–desorption isotherm shows an increased surface area from 24.1 to 111.8 m² g⁻¹ after the formation of ultrathin nanosheets (Figure 2d), leading to the shortened ion diffusion distance and hence promoted K⁺ ion transport. A hysteresis loop is observed in the range of $P/P_0 = 0.5-1.0$ for PB-NSs, demonstrating numerous mesopores generated in the formation of nanosheets.³⁸ Pore-size distribution curves demonstrate a dominant pore diameter situated at around 10 nm, further verifying the mesoporous structure.

Further, the electrochemical performances of PB-NSs and PB-NBs as positive electrode materials for KIBs were investigated. CV was first conducted at 0.1 mV s⁻¹ in the potential range of 2.0-4.0 V to study the redox properties (Figure 3a). A pair of redox peaks situated at around $\sim 3.05/$ 3.58 V can be observed. The larger integral area of PB-NSs compared to PB-NBs indicates a higher specific capacity, and the higher peak current density suggests the faster kinetics for K⁺ insertion/extraction.³⁹ The first three cycles of CV curves are presented (Figure S7), and the more distinct anodic peak in the first scan indicates a more K⁺ ion extraction in PB-NSs than PB-NBs. This result agrees well with the ICP result (Table S1). The high initial K⁺ content in PB demonstrates preferable recrystallization, which is of great importance for achieving excellent electrochemical performances.^{19,40,41} The initial galvanostatic charge-discharge curves of the electrodes at 50 mA g^{-1} are presented (Figure S8). The initial Coulombic efficiency for PB-NBs is below 100%, which is attributed to the decomposition of interstitial water and the instability of low crystallization. Crystal water decomposes during the charging process and deteriorates the battery performance with cycling,

which can also lead to severe capacity decay.⁴² However, PB-NSs show an initial Coulombic efficiency over 100%, suggesting that the unsaturated content of initial K⁺ in PB-NSs results in low capacity during charging, while the structure can accommodate more K⁺ ions during the following discharge, resulting in a higher discharge capacity. What's more, the higher Coulombic efficiency also implies the lower content of interstitial water and the stability of PB-NSs.^{27,30} Benefiting from the ultrathin nanosheet-assembled hierarchical structure, more active sites are exposed and the diffusion path is shortened, which results in lower polarization and higher specific capacity, as confirmed by the third charge-discharge curve (Figure S9).

The rate capabilities were also evaluated as the current densities altered from 50 to 600 mA g^{-1} (Figure 3b). PB-NSs deliver a discharge capacity of 71 mAh g^{-1} at 50 mA g^{-1} , and even at a high current density of 600 mA g^{-1} , a reversible capacity of 24.9 mAh g^{-1} can still be delivered. When the current density is back to 50 mA g^{-1} , a specific capacity of 60 mAh g^{-1} is recovered. For comparison, the discharge capacities of PB-NBs are only 59 mAh g^{-1} at 50 mA g^{-1} and 1.8 mAh g^{-1} at 600 mA g^{-1} , with a capacity of 40 mAh g^{-1} retained when the current density returns to 50 mA g^{-1} . The charge/ discharge profiles at different rates for PB-NSs and PB-NBs in Figure S10 also show a higher capacity retention for PB-NSs even at 600 mA g^{-1} despite a low concentration of K⁺ ions in the electrolyte (0.5 M KPF_6) , indicating that the ultrathin nanosheets provide a swift K⁺ ion diffusion.^{43,44} The PB-NSs deliver a first discharge capacity of 72 mAh g^{-1} at 50 mA g^{-1} and represent on 80.2% capacity retention after 40 cycles (Figure S11). The long-term stability was further evaluated at 200 mA g^{-1} (Figure 3c), with 72.5% and 45.2% capacity retention for PB-NSs and PB-NBs, respectively, after 100 cycles, suggesting an enhanced cycling stability for PB-NSs. The gradual increase of Coulombic efficiencies in the first few



Figure 4. Diffusion kinetics and structural evolution for potassium storage. (a) GITT curves after normalization and (b) the relationship of the diffusion coefficients versus discharge fraction. (c-f) Ex situ XRD analyses of PB-NSs: (c) indication of different charge and discharge states, (d) ex situ XRD patterns, (e) the (200) peak, and (f) the calculated lattice parameter.

cycles for PB-NBs is caused by the elimination of interstitial water.⁴⁰ As the SEM images show in Figure S12, the PB-NSs after 100 cycles preserve their hierarchical structure with numerous nanosheets assembled on the surface ensuring the efficient K ions diffusion, while the fine structure of PB-NBs changes after cycling, leading to decreased active sites, and degraded electrochemical performances. Furthermore, XRD patterns were recorded after cycling for both PB-NSs and PB-NBs as shown in Figure S13. Negligible change was observed for PB-NSs even after 100 cycles, but the peaks for PB-NBs were obviously weakened and broadened along with cycling. Figure S14 shows the high-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns for pristine and cycled PB-NSs. Two lattice fringes with spacing values of 0.49 and 0.21 nm are clearly observed before and after cycling, corresponding to the (200) and (422) planes of $Fe_4[Fe(CN)_6]_3$ (Figure S14a,b). The (422) and (620) diffraction rings were reflected in Figure S14c,d for both pristine and cycled PB-NSs, and all diffraction rings match pretty well with the $Fe_4[Fe(CN)_6]_3$. The XRD and SAED results demonstrate the well-maintained lattice structure of PB-NSs during charge-discharge process, indicating a robust structure and preserved crystal framework of PB-NSs upon cycling.

To confirm the promoted solid-state diffusion process for PB-NSs, GITT was employed to investigate the diffusion kinetics of K^+ ions. The electrode was cycled at 50 mA g⁻¹ three times to reach a normal state before testing. The overall discharge curves are presented in Figure 4a after normalization. A successive intercalation of K^+ ion inevitably results in the continuous decline of D^{GITT} for both PB-NSs and PB-NBs, with the minimum D^{GITT} delivered at the full potassiated state, which indicates a sluggish electrochemical kinetics for the inner active sites (Figures 4b and S15) and is accordance to a

previous report.²⁷ However, the calculated apparent diffusion coefficients (D^{GITT}) for K⁺ in PB-NSs and PB-NBs are 10^{-10} – 10^{-9} and 10^{-11} – 10^{-10} cm² s⁻¹, respectively. The improved D^{GITT} of PB-NSs indicates faster solid-state diffusion kinetics due to the hierarchical structure and much more exposed reaction sites, as represented in Figure S16. Moreover, these results indicate that the ultrathin nanosheet-assembled PB structure plays a significant role in promoting K⁺ ion kinetics and hence leads to the enhanced electrochemical performance.

The structural variation during the potassium ion insertion and extraction was clarified through ex-situ XRD techniques. XRD patterns were recorded at several typical charge– discharge states (Figure 4c). No phase transformation was detected at different states except a slight peak shift (Figure 4d), suggesting a solid-solution process.²⁵ A closer observation ranging from 15° to 20° clearly indicates the structural variation, with the lattice parameter increasing during charging as illustrated by a shift of the (200) diffraction peak to a smaller angle and returning upon discharging (Figure 4e). These observations are consistent with previous reports.^{23,45} The isotropic lattice change reaches 1.749% from 10.004 to 10.179 during the K⁺ ion extraction, and the lattice parameter recovers during K⁺ ion insertion (Figure 4f). The volume variation of PB-NSs is thus estimated to be about 5.36%.⁴⁶

In order to identify the active sites, ex-situ Raman was employed since CN^- is very sensitive to the coordinating Fe and can be an indicator to the active sites. As illustrated in Figure S17, two peaks were observed in 2000–2200 cm⁻¹ for all spectra collected at different charge and discharge states. In charge process, the peak situated at 2154 cm⁻¹ increases gradually, which is assigned to the oxidation of high-spin Fe^{II} coordinated with N (N–Fe^{HS}) to Fe^{III}. A reverse process was observed during discharge, and the N–Fe^{HS} peak recovers to the initial state after the insertion of K ions. The similar charge–discharge behavior of Prussian blue has also been reported in previous work.⁴⁷ Based on above analysis, it can be concluded that the N–Fe^{III}/Fe^{II} couple is the redox-active site and the entire electrochemical process can be described as

$$K_{4}Fe^{II}{}_{4}[Fe^{II}(CN)_{6}]_{3} \leftrightarrow K_{4-x}Fe^{II}{}_{4-x}Fe^{II}{}_{4-x}Fe^{II}(CN)_{6}]_{3} + xe^{-} + xK^{+} \quad (0 \le x \le 4)$$
(2)

In summary, ultrathin nanosheet-assembled hierarchical Prussian blue with enhanced K^+ ion diffusion kinetics was obtained through a dissolution-recrystallization process. The synthesized PB-NSs manifest superior rate capability (71 and 24.9 mAh g⁻¹ at 50 and 600 mA g⁻¹) and cycling performance (75.2% of initial capacity retained after 100 cycles) compared to the bulk sample. The greatly enhanced electrochemical performances are due to the improved solid-state diffusion kinetics and negligible structural variation during K⁺ insertion/ extraction. This work provides a new nanostructuring strategy to improve the potassium storage in intercalation electrodes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01454.

Details for structural and electrochemical characterizations, SEM images of PB-NBs; XPS results for PB-NBs; elements distribution of PB-NSs; thermogravimetric analysis; FT-IR spectra; CV curves at a scan rate of 0.1 mV s⁻¹; the first charge–discharge curves at a current density of 50 mA g⁻¹; the third charge– discharge curves at a current density of 50 mA g⁻¹; the charge–discharge curves of PB-NSs and PB-NBs at different rates; the regional GITT potential curves and ICP results (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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