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Feature Article

Energy storage materials derived from Prussian blue analogues

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ABSTRACT

Prussian blue analogues (PBAs) with open frameworks have drawn much attention in energy storage fields due to their tridimensional ionic diffusion path, easy preparation, and low cost. This review summarizes the recent progress of using PBAs and their derivatives as energy storage materials in alkali ions, multi-valent ions, and metal-air batteries. The key factors to improve the electrochemical performance of PBAs as cathode materials in rechargeable batteries were firstly discussed. Several approaches for performance enhancement such as controlling the amounts of vacancies and coordinated water, optimizing morphologies, and depositing carbon coating are described in details. Then, we highlighted the significance of their diverse architectures and morphologies in anode materials for lithium/sodium ion batteries. Finally, the applications of Prussian blue derivatives as catalysts in metal-air batteries are also reviewed, providing insights into the origin of favorable morphologies and structures of catalyst for the optimal performance.

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1. Introduction

It is of great importance to develop green and sustainable energy storage technologies under the background of excessive depletion of non-renewable fossil fuel and the increasing concerns about global warming. Among various energy storage systems rechargeable lithium-ion batteries (LIBs) that can store electric energy from sustainable resources by electrochemical redox reactions have been most studied, primarily for their high gravimetric capacity and long cycle life [1–7]. After the successful commercialization of LIBs composed of a high-cost LiCoO₂ as a cathode material and graphite as an anode material in portable devices in the early 1990s, intensive research has been focused on rechargeable battery technology in order to commercialize it in stationary energy storage and high power density applications such as hybrid electric vehicles (HEVs) and electric vehicles (EVs) [3–5]. However, significant reduction in the cost of LIBs is still required even for mid-sized applications such as HEVs. Thanks to much higher abundance of Fe than Co, LiFePO₄ cathode that can be synthesized with cheap raw materials and easy processing procedures have been well studied in recent years [8,9]. However, the poor ionic diffusion caused by the one-dimensional tunnel in LiFePO₄'s olivine structure and low electric conductivity make the lithiation/delithiation

process too slow to be practically used in EVs and HEVs [10]. Therefore, it is highly desirable to develop advanced lithium hosts with three-dimensional structures for improved Li⁺ diffusion/storage. On the other hand, sodium and potassium ion batteries are emerging rechargeable battery forms which have attracted considerable attention due to the low costs and easy accessibility of sodium and potassium [11,12]. Considering their larger ionic size compared with that of Li (e.g., Na (1.02 Å) vs. Li (0.76 Å)), it is even more crucial to search for a host with open framework, high charge storage, and affordable cost for them.

Prussian blue (PB) is an ancient dye invented in the 18th century and can be categorized into soluble PB (generally denoted as KFe[Fe(CN)₆]) and insoluble PB (denoted as Fe₄[Fe(CN)₆]₃). It is insoluble PB with a chemical formula of A_xFe[Fe(CN)₆]_y□_{1-y}·mH₂O (A: alkali metal; □: Fe(CN)₆ vacancy; 0 < x < 2; 0 < y < 1) that has been used as electrode materials in both aqueous and organic electrolytes [13–16]. With different amount of alkali element, A_xFe[Fe(CN)₆]_y□_{1-y}·mH₂O can be expressed as Prussian green, Prussian blue, Prussian white, etc. in previous reports [17,18]. Meanwhile, the iron element can be substituted by other transition metals such as manganese [19,20], cobalt [21,22], nickel [23,24], copper [25–27] and zinc [27] without breaking the crystal structure [28,29]. Those varieties make a series of materials with similar chemical compositions and crystal structures to A_xFe[Fe(CN)₆]_y□_{1-y}·mH₂O which are collectively called Prussian blue analogue (PBA) in this paper. In addition, the content of Fe(CN)₆

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vacancy, which generally stem from a rapid precipitation process, is relevant to the amount of coordinated water. Fig. 1 shows the typical face-centered-cubic (fcc) crystal structures of a defect-free PBA (denoted as $A_2M[Fe(CN)_6]$, M refers to transition metal) and a PBA with 25% $Fe(CN)_6$ vacancies (denoted as $A_2M[Fe(CN)_6]_{0.75}\square_{0.25}\cdot nH_2O$) [30]. The high-spin M(II) is octahedrally coordinated with nitrogen in $-CN-$ group while the low-spin Fe(II) is connected to carbon [30,31]. When the $Fe(CN)_6$ vacancy exists, M(II) near the vacancy is prone to coordinate with water molecules, which may lead to lattice distortion and thereby adversely influence the guest cation storage. PBAs with three-dimensional framework are sometimes considered as a kind of MOF (metal organic framework) [32–37], and have large spaces to host cation especially for larger alkali ion such as Na^+ and K^+ . When applied in rechargeable batteries, the large channels and interstices in their open framework make PBAs a class of excellent cathode materials with long cycle life and fast charge transfer kinetics. The guest cations (Li^+ , Na^+ , K^+) are found to be distributed in the nanosized voids of the framework and can diffuse across the cross-sections formed by transition metal and CN ligands. Specifically, compared with another open framework cathode material $Na_3V_2(PO_4)_3$, PBA has a theoretical capacity up to 170 mAh g^{-1} corresponding to two sodium storage, which is higher than that of $Na_3V_2(PO_4)_3$ (117 mAh g^{-1}) [38]. On the other hand, porous or hierarchical materials fabricated using PBAs as templates have been also successfully employed as viable electrode materials for lithium-ion storage [39–42] and metal-air batteries [43–45]. Owing to their low cost, intrinsic open framework and tunable composition, PBAs and their derivatives have great potential to be applied in electrochemical energy storage fields. In this paper, we aim to describe the recent progress of the design and applications of PBAs and its derivatives in energy-related areas.

2. PBA as cathode materials for alkali ion batteries

2.1. Monovalent ion batteries

Lithium intercalation behavior of PB was first studied in an aprotic media [46] and it shows a reversible potential associated with the redox of iron at around 3 V (vs. Li/Li^+). After that a valence tautomeric PBA, i.e., $A_xMn_y[Fe(CN)_6]$ ($A = K, Rb$), was investigated for the correlations between the type of alkali element and Li^+ insertion/deinsertion behaviors [47]. It was found that in $A_xMn^II_y[Fe^III(CN)_6]\cdot nH_2O$, K or Rb in A sites tended to stabilize the Fe-CN-Mn framework via strong electron delocalization effect and a stable lithium storage was thus obtained. Generally, the vacancy

and the associated H_2O are unfavorable to the capacity of rechargeable batteries due to the distorted structure and the hindered ion transfer. As vacancies have great impact on the capacity of PBAs, a vacancy-suppressed PBA framework, $MnIII[MnIII(CN)_6]$, was obtained by electrochemical extraction of potassium in a defect-free $K_2Mn[Mn(CN)_6]$ precursor [48]. In the charge/discharge range of 2.0–4.3 V, the obtained $K_{1.72}Mn[Mn(CN)_6]_{0.93}\square_{0.07}\cdot 0.65H_2O$ (\square refers to $[Mn(CN)_6]^{4-}$ vacancies) shows a high lithium storage capacity of 197 mAh g^{-1} , which corresponds to 1.91 lithium insertion per PBA molecule and the energy density per cathode weight is calculated to be 620 Wh kg^{-1} . Unfortunately, the capacity decreases more than 35% after only 10 cycles at a current density of 30 mA g^{-1} . This poor cycling performance is speculated to be originated from the broken of bridging Mn-CN-Mn bonds during the lattice expansion/shrinkage processes which gives rise to possible side reactions. It indicates that the crystal and electronic structure of PBA, which can be adjusted by doping or substitution, are closely related to the cycling capabilities of PBA cathodes. In 2013, trimetallic PBA ($K_{0.1}(Mn_{0.5}Cu_{0.5})[Fe(CN)_6]_{0.7}\cdot 4H_2O$) nanoparticles were applied as cathode materials for Li-ion batteries and revealed a relatively high cycle life of up to 50 cycles with a capacity retention of 75% [49]. The partial substitution of Cu with M significantly suppresses the phase separation induced by over-lithiation and shows better rate performance and stability than bimetallic $K_{0.1}Cu[Fe(CN)_6]_{0.7}\cdot 3.6H_2O$. As the relatively low electric conductivity is also an important factor that restrict the practical usage of PBs/PBAs, conducting polymer has been employed to improve the electric conductivity of PB via an in-situ polymerization coating method [50]. In this system, $Li_3Fe(CN)_6$ acts as not only the precursor of PB synthesis but also the initiator of pyrrole polymerization. The resulting $LiFe^III[Fe^II(CN)_6]\text{-Ppy-PSS}$ (PSS = poly(-sodium 4-styrenesulfonate)), which was added to act as both a surfactant and a dopant during the synthesis) composite cathode exhibits superior cycling stability relative to the bare PB in LIB testing.

A cost-effective alternative for LIBs is sodium ion batteries (SIBs) due to the abundance of sodium relative to lithium. Testing in organic electrolyte, PBAs have the potential to store two Na^+ which corresponds to a capacity of 170 mAh g^{-1} . However, many PBAs only exhibit limited sodium storage and the capacities degrade rapidly [51,52]. This limitation is believed to be associated with $Fe(CN)_6$ vacancies and coordinated water molecules induced during the synthesis, leading to the collapse of cyano-bridged framework and hindering the transportation of Na^+ [30,53–55]. Thus, it is of great importance to eliminating the defects and controlling the coordinated water content. You et al. [53] proposed a

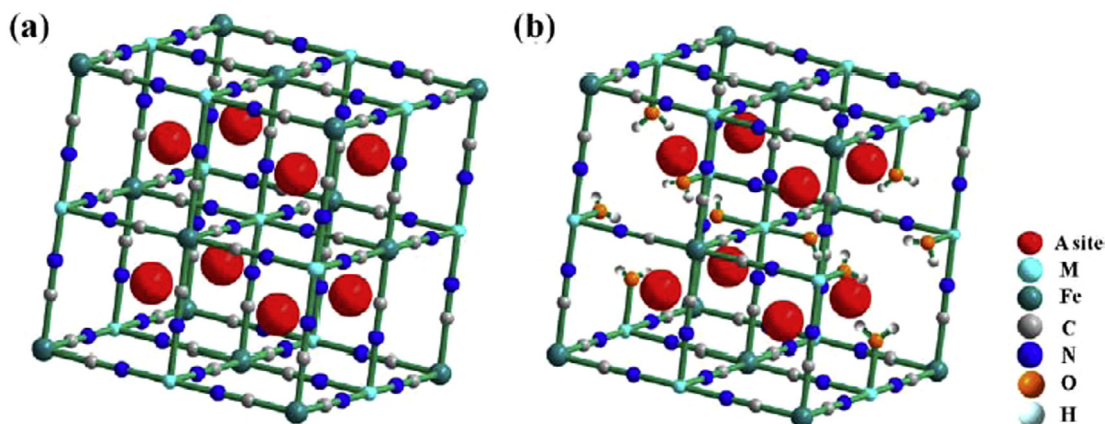


Fig. 1. (Color online) Crystal structure illustrations of (a) a defect-free PBA ($A_2M[Fe(CN)_6]$) and (b) a PBA with 25% vacancies ($A_2M[Fe(CN)_6]_{0.75}\square_{0.25}\cdot nH_2O$) [30]. Adapted and reproduced with permission from Ref. [30] (Copyright 2016 American Chemistry Society).

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