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Sodium zinc hexacyanoferrate with a well-defined open framework as a positive electrode for sodium ion batteries†

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A modified Prussian blue analogue, $Na_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$, was investigated as a positive electrode material. Utilizing a well-defined channel structure, the compound exhibits a clear electrochemical activity at around 3.5 V *vs.* Na/Na^+ with a reversible capacity of 56.4 mA h g^{-1} and good cycle life.

The use of renewable energy resources represented by solar and wind power must be the most ideal solution to increasingly serious energy and environmental problems. However, the available amounts of these resources fluctuate with time, thus requiring energy storage systems (ESSs) for persistent power supply.[1] While hydropower and pumped air are currently used as grid-scale ESSs, rechargeable batteries are expected to replace the current technology utilizing their advantages of higher efficiencies and the possibility of simple installation. Among a variety of batteries, lithium ion batteries (LIBs) are receiving the most significant attention due to their superior performance in various electrochemical aspects.[2] Nevertheless, batteries based on alternative carrier ions such as sodium (Na) ions could be more suitable for grid-scale ESSs in which the abundance and cost of raw materials are more critical for widespread use. Indeed, raw materials for sodium ion batteries (SIBs) are estimated to be about 30 times cheaper than those of LIBs.[3] These conspicuous advantages have motivated recent progress in developing a variety of SIB electrode materials with decent electrochemical properties.[4–9] Nonetheless, the larger size of a Na ion (0.98 Å) compared to that of a Li ion (0.69 Å)[3,10] imposes more challenging constraints in the material design such that the material should have sufficiently large channel structures to accommodate diffusion of Na ions. For this reason, materials with well-established open frameworks, such as sodium super ionic conductor (NASICON) structures[8,9] and metal–organic

frameworks (MOFs),[11,12] have been intensively investigated as SIB electrodes. In particular, Prussian Blue analogues (PBAs), one class of MOFs, have received attention from the community owing to impressive electrochemical performance as well as easy synthetic procedures.

Herein, we report a substantially improved PBA structure by simply replacing the existing Fe^{3+} with Zn^{2+}. The newly designed compound, namely sodium zinc hexacyanoferrate (NZH), $Na_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$, is endowed with enlarged ionic channels compared to those of typical PBAs. Thus, Na ions statistically distributed in the open sites of the framework are expected to diffuse very efficiently during charging and discharging processes. For reference, utilizing the well-developed open structures, NZH has been investigated for other applications such as ion exchange systems[13,14] and hydrogen storage.[15] However, to the best of our survey, this compound has never been examined for rechargeable batteries. Fascinatingly, NZH can be synthesized through an environmentally friendly aqueous reaction at low temperatures around 100 °C and should thus be appropriate for large-scale ESSs.

The crystal structure of NZH is schematically illustrated in Fig. 1. In this structure, the octahedral $[Fe(CN)_6]^{4-}$ complexes are linked to the tetrahedral Zn^{2+} sites *via* cyanide ligands to form a porous three-dimensional framework. Two Na ions can
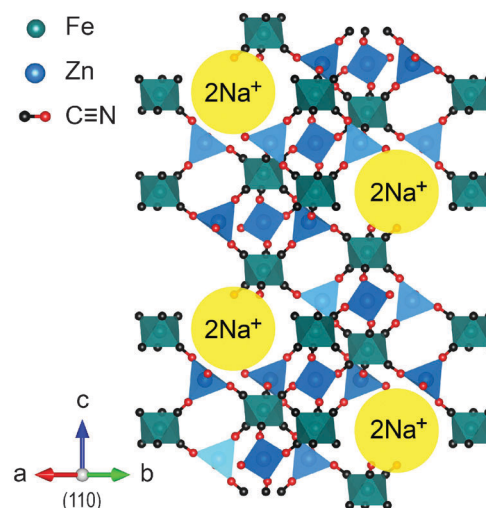
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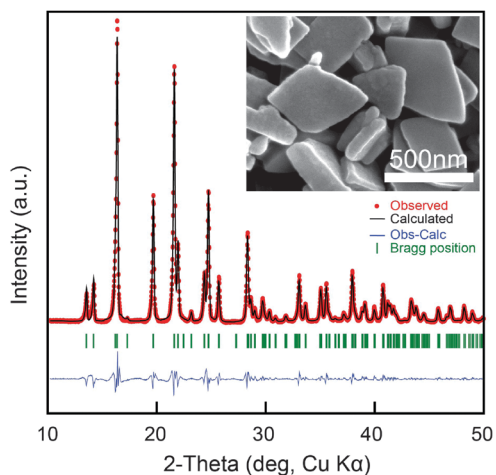† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c2cc33771a


Fig. 1 The unit cell structure of sodium zinc hexacyanoferrate (NZH).

Fig. 2 A powder X-ray refinement pattern for the as-synthesized NZH alongside a profile fitting. (inset) An SEM image of the prepared powders.

be located in the large open sites (yellow circles in Fig. 1).[16] This structure is similar to the well-known NASICON frameworks in that octahedral and tetrahedral units are alternately interconnected. Compared to the NASICON structure where octahedral and tetrahedral units are directly bound through oxygen atoms, however, NZH has larger open sites because NZH bridges the octahedral and tetrahedral units through longer cyanide ligands.

To confirm the crystal structure of NZH, X-ray diffraction (XRD) analyses were conducted (Fig. 2). The XRD peaks are well-indexed to $Na_2Zn_3[Fe^{II}(CN)_6]_2 \cdot 9H_2O$ (PDF # 36-0539, $a = 12.469$ Å, $c = 32.920$ Å), indicating that the synthesized compound is well-crystallized without any impurities ($a = 12.460$ Å, $c = 32.832$ Å, $V = 4414.22$ Å^3 and $R_p = 5.65\%$). The compound adopts the rhombohedral structure with the $R\bar{3}c$ space group. It is noteworthy that the simple transition metal substitution renders NZH to belong to the different space group compared to other existing PBAs that typically adopt face centered cubic structure with the $Fm3m$ space group. An SEM image of the as-synthesized NZH indicates that the particles have average sizes around 500 nm (Fig. 2, inset). In addition, an FT-IR spectrum (Fig. S1, ESI†) also supports the formation of the designated compound.

The galvanostatic profiles in the first cycle (Fig. 3a) show a reversible capacity of 56.4 mA h g^{-1} when measured at a rate of 10 mA g^{-1} (0.18 C-rate). For the evaluation of the observed electrochemical data, it is instructive to note that in NZH, Zn^{2+} is electrochemically inactive but rather contributes only to maintaining the framework.[17] Instead, the Fe^{2+}/Fe^{3+} redox couple in the octahedral $[Fe(CN)_6]^{4-}$ is primarily engaged with electrochemical reactions upon the insertion and extraction of Na ions.[17,18] The electrochemical reaction can be expressed as:

$$Na_2Zn_3[Fe^{II}(CN)_6]_2 \cdot xH_2O \leftrightarrow 2Na^+ + 2e^-$$
$$+ Zn_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$$
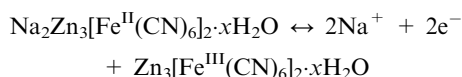
This equation indicates that the theoretical capacity of NZH is 64.8 mA h g^{-1} under the condition that the unit cell contains nine water molecules. Indeed, the stoichiometry of the synthesized compound in this study turns out to be $Na_{1.61}Zn_3[Fe(CN)_6]_2 \cdot 3H_2O$
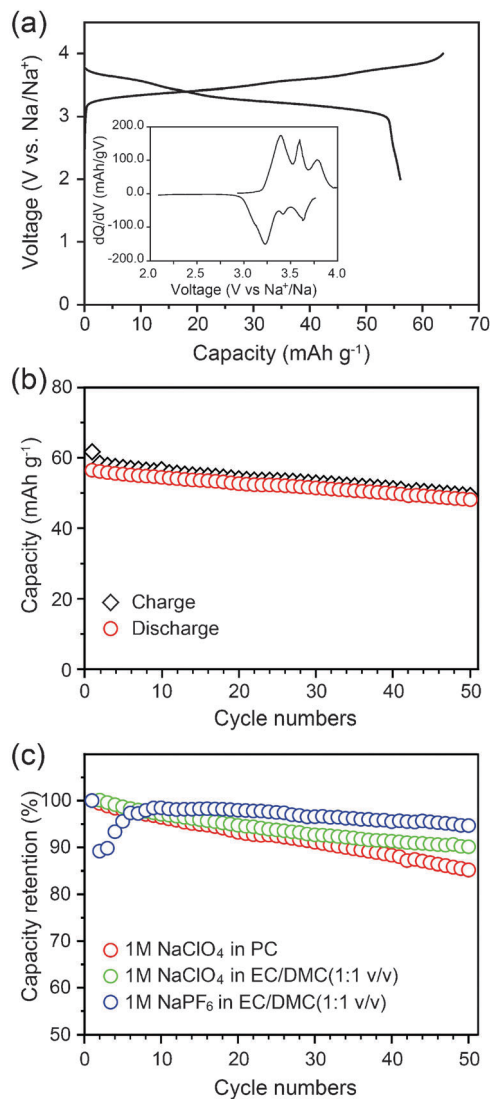

Fig. 3 (a) A galvanostatic charge–discharge profile in the precycling. (b) The cycle life of NZH when tested with the electrolyte of 1 M NaClO₄ in PC. (c) The capacity retention comparison of NZH when tested with the electrolytes of 1 M NaClO₄ in PC, EC/DMC (1 : 1 v/v) and 1 M NaPF₆ in EC/DMC (1 : 1 v/v) during 50 cycles. The potential range is 2.0–4.0 V $vs.$ Na/Na⁺.

(normalized to Fe) from ICP-AES characterization and provides a more accurate theoretical capacity of 60.7 mA h g^{-1}. Thus, the observed capacity (56.4 mA h g^{-1}) is comparable to the theoretical value and thus supports the fully active nature of NZH with the well-defined channel structure.

The galvanostatic data provide other important information on the electrochemical processes with this compound. Unlike NASICON-structured materials that typically exhibit a single flat plateau,[8,9] NZH shows sloppy plateaus in the broad potential range of 3.2–3.8 V $vs.$ Na/Na⁺, indicating that NZH undergoes charging and discharging reactions based on a single-phase mode. $Ex\ situ$ XRD data (Fig. S2, ESI†) taken after the charge and discharge in the first cycle as well as after the charge in the 6th cycle also confirm the single-phase reaction. The similar single-phase reactions were observed for other MOFs and ascribed to large channel structures.[11,12,18,19]
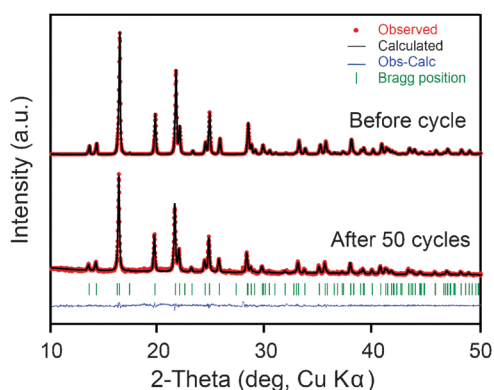
Fig. 4 Powder X-ray refinement patterns for (upper) the as-synthesized NZH powder as well as (lower) the NZH electrode after 50 cycles with a 1 M NaClO$_4$ in the PC electrolyte.

The dQ/dV curve (Fig. 3a, inset) provides deeper insight into the electrochemical processes with NZH. While the data show peaks at around 3.3 V *vs.* Na/Na$^+$, which is consistent with those of Na$_4$Fe(CN)$_6$ that also contains cyanide bridges and reacts based on the Fe^{2+}/Fe^{3+} couple,[20] NZH exhibits two additional peaks during both charging and discharging processes, which are likely to reflect the statistically located Na positions in the large open sites[16] that result in the extraction/insertion of Na ions at different potentials. Further investigation is currently underway to examine the binding energy of Na ions at various locations by employing first principle calculations.

Fig. 3b shows the cycling performance of NZH. NZH retains 85.2% of the initial capacity after 50 cycles when measured at 10 mA g^{-1} (0.18 C-rate). This result implies that utilizing its well-defined ionic channel structure, NZH enables Na ions to repeatedly diffuse within the framework. However, the observed capacity decay that seemingly originates from the insulating nature of the compound needs to be improved further. Also, the operation of the hydrated NZH in the organic electrolyte might play a role in the capacity decay. It has been known that during diffusion of solvated carrier ions, solvent molecules in the solvated shells interchange with water molecules in the hydrated compound.[12,21] Therefore, it is speculated that the propylene carbonate (PC) based electrolyte is not proper for robust cycling of the hydrated compound because organic solvent might not be compatible with water molecules intrinsically existing in the compound. As displayed in Fig. 3c, the switch of solvent to the ethylene carbonate–dimethyl carbonate (EC–DMC) mixture substantially improves capacity retention (85.2 → 90.1% retention after 50 cycles), which might be explained by smoother shell exchange of the solvated Na ion clusters at the electrode–electrolyte interface. This trend could also be attributed to the more similar physical properties of the solvent mixture such as dielectric constant, viscosity, and electric dipole moment to those of water as compared to those of PC (Table S1, ESI†). Thus, the operation of this compound in aqueous electrolytes is expected to improve the cycle life significantly. Additional improvement in the cycle life (90.1 → 94.6%) was observed by switching the salt to sodium hexafluorophosphate (NaPF$_6$) and could also be explained similarly based on the efficiency of the solvent shell exchange. The unusual capacity increase for this case observed during the early period of cycles is attributed to SEI formation (Fig. S3, ESI†) and is indeed likely to

contribute to the superior cycle life. In addition, NZH exhibits moderate rate capability, perhaps due to its low electric conductivity as well as the aforementioned solvent incompatibility (Fig. S4, ESI†).

In order to evaluate the structural stability of NZH during repeated cycles, the XRD patterns of the electrodes were obtained before and after 50 cycles (Fig. 4). The peaks were preserved after the cycling, and thus indicate the robust nature of its crystal structure over cycling.

In conclusion, we have investigated the structural and electrochemical properties of NZH as a novel positive electrode material for SIBs. The well-defined open framework enabled by cyanide ligands bridging the octahedral Fe sites and the tetrahedral Zn sites endows NZH with good electrochemical activity of a reversible capacity of 56.4 mA h g^{-1} in the redox potential range of 2.0–4.0 V *vs.* Na/Na$^+$. Furthermore, NZH holds the additional advantage that the compound can be synthesized from low cost raw materials through an environmentally friendly process at low temperatures, which should be crucial for large-scale ESSs.

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