Water effect on sodium mobility in zinc hexacyanoferrate during charge/discharge processes in sodium ion-based battery


Abstract

This study discusses the effect of the water removal on the behavior of Na$_2$Zn$_3$[Fe(Fe$^{II}$)$_{1-x}$Fe$^{III}$$_x$]$_2$·$x$H$_2$O as cathode material for sodium ion-based battery. For comparison, electrochemical and structural data were recorded for both, hydrated and anhydrous phases. The structural changes in zinc hexacyanoferrate, from rhombohedral to monoclinic structure, as consequence of the water molecules removal increase the cation-framework interaction and modify its mobility inside the porous network. These phases show two faradic processes, which are related to the existence of two strength levels (potentials) for the cation-framework interaction. One of them corresponds to the cation subtraction from the material with maximum cation occupation per cavity (two per formula unit). The second effect was ascribed to the formation of a solid solution, (Na)$_{21-x}$Zn$_3$[(Fe$^{III}$)$_x$Fe$^{II}$(CN)$_6$]·$x$H$_2$O. This solid solution is formed when the cation population within the cavities decreases during the extraction (oxidation) process. This proposal is supported by cyclic voltammetry and impedance electrochemical spectroscopy results. Galvanostatic intermittent titration technique and galvanostatic experiments reveal that the monoclinic structure exhibits an improvement for the charge/discharge process and a higher rate capability, related to a greater cationic mobility within the framework. This is associated to higher sodium diffusion rate (evaluated by GITT) for the monoclinic phase compared with the observed for the rhombohedral one.

1. Introduction

Energy storage is a key process in order to achieve autonomy and expand the technological scope of renewable energy. The renewable energy sources have time-variable character; their availability depends on the weather conditions, level of solar radiation, seasons, and on the days/night cycle. From this fact, the technology for renewable energy harvesting requires of appropriate devices to storage energy when its availability exceeds the demand. The stored energy could then be used to satisfy the demand when it surpasses the sources capacity. Batteries, particularly, rechargeable batteries, are within the most attractive and flexible energy storage devices [1,2]. The common and used batteries are those based on Li ion, but the low global availability of Li-bearing minerals [3,4] is forcing to find appropriate materials that could be used for new generations of batteries, among them Na-ion containing solids. By this reason, recently the number of studies on sodium ion batteries (SIBs) has increased [5–7]. For a broader and industrial use of SIBs, the cathode should possess high capacity, high sodium mobility and large operation voltage. It has been reported different oxygen-based materials as layered oxide or olivine structure for such applications, however, the O-2p orbitals that o bond to Na impede its motion. Replacement of the O$^{2-}$ ions by CN$^{-}$ ions weakens the bonding interaction with Na. The activation energy for Na$^{+}$ transfer is, therefore, strongly reduced, which makes attractive the exploration of Prussian blue analogues (PBA) and related coordination polymers for SIBs. These solid compounds show favorable features for such application, particularly, high storage capacity and cyclability, especially metal hexacyanoferrate [8–11].

Many compositions of PBA-based materials have an open zeolite-like framework, which allows rapid Na$^{+}$ ions diffusion through the network of channels and windows, and at the same time exhibiting impressive electrochemical performance. In addition, this family of materials is obtained through soft preparative chemical routes. Their open-framework structure are built from octahedral building units, [Fe (CN)$_6$]$^{3-}/^{4-}$, assembled through 3d metals, e.g. Mn, Fe, Co, Ni, Cu and Cd, linked at their N atoms of the CN group. In typical PBA, all the...
metal centers are found with an octahedral coordination, resulting solids that crystallize with a cubic unit cell [12]. Within transition metal hexacyanoferrates, the tetrahedral coordination is also possible for zinc and cobalt, resulting in zeolite-like frameworks [13]. Their porous framework is formed by ellipsoidal cavities of about 15.5 × 11.1 × 7.9 Å, which remain communicated through elliptical windows of ca. 6.8 × 8 Å. The exchangeable cation (Na+, K+, Rb+, Cs+) occupies structural positions inside the cavities close to the N atom of the CN group.

The material under study in this contribution, Na2Zn3[Fe(CN)6]2·xH2O, in the following ZnHCF, has already been considered as cathode for SIB’s, with a reversible capacity of 56.4 mAh g⁻¹ at 0.18 °C and good stability for 50 cycles with capacity retention of 95% [14]. Studies in aqueous media have shown instability for ZnHCF during the structural change to a rhombohedral phase [17], which delivers a cell volume diminution of about 12%. In this phase, the sodium atom in the sodium hexacyanoferrate (II), Na2[Fe(CN)6]·xH2O, in the following ZnHCF, has already been considered as hydrated species within the elliptical cavities. The red and green spheres correspond to iron and zinc atoms in the –Zn–N=C–Fe=C=N–Zn– chain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 1. XRD pattern, its LeBail profile fitting and the atomic packing within the porous framework for the rhombohedral phase of zinc hexacyanoferrate (II). In this phase, the sodium atoms (gray spheres) remain as hydrated species within the elliptical cavities. The red and green spheres correspond to iron and zinc atoms in the –Zn–N=C–Fe=C=N–Zn– chain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The materials elemental composition was determined by optical emission spectrometry using inductively coupled plasma (OES-ICP), with a Perkin Elmer OPTIMA 8300 spectrophotometer. The powder X-ray diffraction (XRD) patterns were recorded with CuKα1 radiation using a Bruker D8 diffractometer operated in the Bragg-Brentano geometry and high-resolution configuration. The pattern for the anhydrous phase was recorded using a sealed camera at a pressure of 10⁻⁶ Torr. The XRD patterns were indexed using DICVOL program. FTIR spectra were collected with a PerkinElmer RX-1 spectrophotometer using an ATR accessory. The electrochemical performance of both, hydrated and anhydrous phases, was evaluated with a battery test cell from E-Cell, which is composed of cathode and metallic-sodium anode with 1 mol L⁻¹ NaPF₆ in 1:1 dimethyl carbonate/ethylene carbonate electrolyte, and a Whatman glass-fiber separator. The cathodes were prepared by mixing 80%wt of ZnHCF with 10%wt amorphous carbon (Timcal SuperP Li) and 10%wt polytetrafluoroethylene (Aldrich) as binder in N-methyl-2-pyrrolidone. This mixture is placed on an Al foil and finally dried at 60 °C under vacuum for 24 h. The electrochemical data were recorded with a potentiotstat–galvanostat VMP3 (from Bio-logic).

3. Results and discussion

3.1. Structural characterization

The chemical composition of Zinc Hexacyanoferrate calculated by OES-ICP reveals an atomic ratio for Na:Zn:Fe of 1:1:5.1 respectively, indicating that the material in this study has the formula Na2Zn3[Fe(CN)6]2·xH2O. Unlike Prussian blue analogues where the presence of vacancies for the building block is a frequent feature related to the material electric neutrality [20], the solid under study is free of vacancies. Fig. 1 shows the recorded XRD powder pattern for the hydrated phase, Na2Zn3[Fe(CN)6]2·xH2O, and the corresponding porous framework [19]. The Na⁺ ion is found inside the cavity, as hydrated species...
located close to the N ends of the ZnN₄ tetrahedra. The negative charge at the cavity surface is concentrated close the N corners since the N atom is the most electronegative atom of the CN ligand. The water molecules in the cation solvation sphere are able to stabilize additional water molecules inside the cavity through hydrogen bonding interactions. A given cavity has twelve N corners at its surface and only two Na⁺ ions inside. From this fact, when an AC electrical perturbation is applied to the material, the sodium ion is found jumping between sites on neighboring tetrahedra [21]. Since the sodium ion is a movable specie, and the cavity windows is enough large to allow its diffusion through the solid framework, it is easily exchangeable by an ion of larger size (K, Rb, Cs). Another important feature of this material, is the existence of an oxidized species, Zn₃[Fe(CN)₆]₂⁻, with the same crystal structure (r-ZnHCF) and free of exchangeable metal. This confirms the interest of this material as cathode for SIB. The exchangeable metal can be removed from (and inserted into) the solid framework without appreciable structural changes, except a small cell contraction/expansion related with the size for the [Fe(CN)₆]³⁻ block in its reduced and oxidized state as was demonstrated by Lee et al. [14].

Water removal after thermal treatment was confirms by TGA analysis (Fig. S1 in Supplementary information). When the water molecules are removed under moderate heating, certain distortion in the material unit cell is observed [19]. The anhydrous solid crystallizes with a monoclinic unit cell in the P2/c space group (Fig. 2). The cell distortion is accompanied of a volume diminution of about 12%. Such structural changes are ascribed to the asymmetrical interaction for the naked ion (Na⁺) with the host framework. As already-mentioned, a given cavity contains 12 N corners available to interact with only two sodium ions and these last ones are found along the ellipsoid major axis, at the larger possible distance between them, in order to minimize their repulsive electrostatic interactions. From this fact, the cation interaction with the host framework is non-symmetric. This interaction enhances on the water removal, resulting the observed structural distortion.

IR spectrum is a good sensor for the mentioned structural changes on the water removal. The ν(CN) stretching vibration for the hydrated phase, r-ZnHCF, appears as a narrow band at 2089 cm⁻¹ (Fig. 1, Inset), corresponding to equal ...→Zn=N≡C−Fe→... chains in the whole solid. This supposes that, in average, all the N corners are sensing an equivalent interaction with the hydrated Na⁺ ions found inside the cavities. A hydrated sodium ion has a relatively large diameter and from this fact, the distance between the charge centers (the N corner and the Na⁺ ion) are enough large to produce a relatively weak electrostatic interaction between them. From this fact, all the N corners are sensing an equivalent interaction with the sodium ions. On the water molecules removal, the Na⁺ ions are progressively naked and their interaction with the host framework enhances. For the anhydrous phase, m-ZnHCF, such interaction is asymmetric producing a local deformation in the crystal. Now, not all the −N≡C− bridges are equivalent, which is appreciated in the IR spectrum as a splitting for the ν(CN) stretching vibration (Fig. 2, Inset). In the anhydrous phase the most intense component of this band is observed at 2095 cm⁻¹, for a frequency shift of about +6 cm⁻¹. This blue shift is associated to a stronger cation interaction with an N corner, which induces certain charge subtraction from the CN ligand through its 5o orbital, which has certain antibonding character.

3.2. Electrochemical evaluation

To the best of our knowledge, there are no reports on Cyclic Voltammetry (CV) measurements for the system under study. The Fig. 3A shows the CV at 0.1 mV s⁻¹, from the open-circuit potential (OCP) towards the positive direction, the resulting i-E characteristic curves for both samples exhibit two faradaic processes. This result is of fundamental importance, since this material has only one active redox specie present in octahedral [Fe(CN)₆]³⁻ block (Fe⁴⁺/Fe³⁺), so that, the two redox processes should be related to dissimilar cation-framework interactions and cation mobility inside the cavities. The first process represents the third part of the total charge of the electrochemical processes (calculated from CV at inversion potentials E₁ and E₂), indicating that approximately only 0.6 out of 2.0 mol of cations are involved up to this potential; thus, the initial extraction of sodium ion is accompanied of a partial oxidation of the [Fe(CN)₆]³⁻ to form a more stable solid solution, Na₂xZn₃[Fe(CN)₆]x⁻·xH₂O. The partial oxidation of the building block, [(Fe⁴⁺)ₓFe³⁺₁-x(CN)₆], modifies the charge distribution on the cavity surface, and in consequence, the equilibrium position for the cation, should be re-located inside the structure with the aim to maintain the electro neutrality in the framework. The remaining fraction of sodium ion enhances their interaction with the cavity surface decreasing the cationic mobility, so that a second faradaic process takes place at higher potential.

For both, the hydrated (r-ZnHCF) and anhydrous phase (m-ZnHCF), the CV peaks, corresponding to the two faradaic processes, are broad and asymmetric (Fig. 3), which could be associated to different

![Fig. 2. XRD pattern, its LeBail profile fitting and the atomic packing within the porous framework for the anhydrous (monoclinic) of zinc hexacyanoferrate (II). In this phase, the sodium atoms (gray spheres) are found close to the N atom of the CN ligand.](image)
the electrochemical electron transfer process occurring at similar potential. It seems that during the cation extraction, the potential that the cation senses is being modified due to the oxidation of a fraction of iron atoms in the building blocks that define the cavity surface. The mentioned broadening and asymmetry of the faradaic peaks are more pronounced for the anhydrous phase (m-ZnHCF). Such features could be explained according to the already-discussed asymmetry for the host framework – cation interaction as consequence of the water molecules removal from the cavity volume.

On the other hand, Galvanostatic charge/discharge experiments were performed at c/10 (Fig. 3B); similarly to CV experiments. Both samples exhibit two different Na⁺ insertion/desertion responses. During the first process, between 3.2 and 3.65 V vs Na⁺/Na, the potential continuously rises as the specific capacity increases. This behavior is characteristic for this kind of open framework materials where the sodium insertion/desertion processes take place as a solid solution formation [22], where small changes on the electronic/geometric structure of the solid originates slightly different changes on the deintercalation voltage. Whereas at 3.7 V vs Na⁺/Na the presence of a flat process is evident, which is attributed to the coexistence of two phases through a continuous phase transition (solid solution) with the same crystalline structure, on the Na⁺ deintercalation process [23,24]. One of the phases is sodium rich and other one is poor in Na⁺ but both with well-defined crystalline/electronic structure, Na_{2-x}Zn_{3-x/2}[(Fe^{III})_{x}Fe^{II}]_{1-x}(CN)_{6}·xH_{2}O. A) Cyclic Voltammetry using a scan rate of 0.1 mV s⁻¹. B) Galvanostatic charge/discharge curves at C/10 rate, inset: fraction capacity retention as function of the C-rate.

![Figure 3](https://example.com/fig3.png)

**Fig. 3.** Electrochemical characterization of sodium cells with cathode composite containing hydrated (r-ZnHCF) and anhydrous (m-ZnHCF) phases of Na_2Zn_3[Fe(CN)_6]·xH_2O. A) Cyclic Voltammetry using a scan rate of 0.1 mV s⁻¹. B) Galvanostatic charge/discharge curves at C/10 rate, inset: fraction capacity retention as function of the C-rate.

64.8 mAh g⁻¹ for that material. Moreover, a small improvement on the rate capability (see inset in Fig. 3B) at different C-rates is observed for m-ZnHCF. The origin of such changes can be related to i) the feasibility for electron transfer inside the structure and ii) sodium diffusion inside the structure. Fig. 3B suggests the existence of a coexistence zone for the two phases at the same potential; however, in the solid solution zone, the Na⁺ intercalation/deintercalation occurs at different potentials, being lower for m-ZnHCF during charge and higher during discharge, indicating that the m-ZnHCF presents a lower overpotential for electron transfer. However, the electrochemical process in this open framework materials depends on two components, relating to the feasibility of ions and electrons to reach the intercalation site. With the aim to understand the effects of these two components on the faradic processes, Electrochemical Impedance Spectroscopy experiments were carried out.

3.3. Electrochemical impedance spectroscopy

Fig. 4 shows the Nyquist diagrams obtained for cells containing composites of both r-ZnHCF and m-ZnHCF phases. The EIS spectra were collected up to different potentials (open circuit potential (E_oc), pre-peak process 1 potential (E_{pp1}), after process 1 potential (E_{pp2}) and after process 2 potential (E_{pp2}) (see Fig. 3A). The potential values were taken after a linear Sweep Voltammetry at 0.1 mV s⁻¹, followed by OCP measurement by 30 min (enough to reach stationary state). In general, all Nyquist diagrams show similar features (Fig. 4). At higher frequency, the diagrams show a wide and asymmetric semicircle indicating the presence of two time-constants with similar relaxation time, which are better defined on the Nyquist diagram for m-ZnHCF.
(see Inset of Fig. 4), i.e. water removal induces changes on the frequency response of these processes. For both materials, the semicircle size shows an increase for higher values of applied potential. This phenomenon can be ascribed to charge transfer, whose magnitude depends on i) the electronic conduction and ii) ionic conduction, simultaneously occurring [27]. At lower frequencies, the Nyquist diagrams show a linear behavior, which results from superposition of two processes, as suggests presence of two linear segments. The variation of their slope was interpreted as resulting from changes for the cation diffusion, from finite type at medium frequencies to semi-finite type at low frequencies [28].

On the other hand, as the applied potential is higher, at low frequency a decrease for the slope for the straight line is observed. The presence of well-defined straight line at medium and low frequencies are inhibited at $E_{pp}$, indicating that at this potential the Na$^+$ diffusion process is not observed probably due to a low Na$^+$ concentration in the network.

In order to obtain quantitative information on the cation transport through the solid framework, the electric equivalent circuits (eeq) were calculated (Fig. 4C) [28]. The electron transport through the hexacyanoferrate lattice is defined by the parallel combination of the resistance R1 and a constant phase element CPE1. The ionic conduction, which takes place at the same time that the electron transfer, through a hopping mechanism, is described by the parallel combination of the resistance R2 and CPE2. In the proposed model, R3, CPE3 and CPE4, at low frequency, are associated to diffusion process during sodium insertion/desertion, except for the spectra obtained at $E_{pp}$, where the contribution of the diffusion is not included.

Table 1 collects the values for R1 and R2 obtained for the spectra fitting. This helps to understand the redox processes for both materials. In general, the resistance values obtained for electron transfer in m-ZnHCF are lower than those obtained for r-ZnHCF, which corresponds to an improved charge transfer process in m-ZnHCF. This explains the highest specific capacity and better rate capability found for m-ZnHCF. For both materials, the values for R1 are higher, by an order of magnitude, than the one obtained for R2 at an applied potential of $E_{pp}$. This suggests that the first electron transfer process is limited by the electronic conduction in the lattice, so that the charge/discharge process is influenced mainly by the changes in the concentration of the ionic guest species. Such changes modulate the enthalpy and configurational entropy of the guest ions that leads to the typical S-shape [29] as it was observed in galvanostatic response at low potentials. On the other hand, the values of R1 and R2 are similar at applied potentials $E_{pp}$ and $E_{pp}$, indicating that in the second process the electron transfer is limited by ionic conduction, confirming the decrease of the cationic mobility previously proposed in the voltamperometric studies. The slope of the straight line at low frequency is smaller for m-ZnHCF in comparison to r-ZnHCF, which indicates that Na$^+$ diffusion inside the cavity is favored on the water removal. The determination of the diffusion coefficients using EIS can be obtained using Warburg factor, estimated from the slope of a plot of the real component of impedance vs the square root of frequency [30] or using a correlation between kinetic parameters and the electrical elements as was proposed by Boukamp [31]; however, the inability to establish stationary conditions at low frequency, which is a requirement to obtain reliable information, leads to obtain of Na$^+$ diffusion coefficients with an incertitude of three orders of magnitude. Thus, in this work the diffusion coefficients were estimated from the galvanostatic intermittent titration technique.

### 3.4. Diffusion study

Fig. 5 shows the galvanostatic intermittent titration technique (GITT) data, in the range of 2.5–4.0 V vs Na$^+$/Na. GITT was employed at a pulse of C/10 for 10 min followed by a 120 min of interruption between each pulse to allow a full relaxation at the open circuit potential and reach a stabilized potential value (see Fig. S2). From the GITT data, the diffusion coefficient during insertion/desertion of the sodium ions ($D_{Na^+}$) in the host framework can be effectively determined using the Fick’s second law of diffusion [32]:

$$D_{Na^+} = \frac{4}{\pi} \left( \frac{m_{Na} V_m}{M_b S} \right)^2 \left( \frac{\Delta E}{\tau l} \right) \left( \tau \ll \frac{l^2}{D_{Na^+}} \right)$$

(2)

where $m_{Na}$, $V_m$, $M_b$ and $l$ are the mass, the molar volume, the molecular weight and the thickness of the electrode material, respectively, and S is the electrode surface area. The molar volume ($V_m$) for r-ZnHCF and m-ZnHCF are 448.71 cm$^3$ mol$^{-1}$ and 392.097 cm$^3$ mol$^{-1}$, respectively. Eq. (2) supposes that these values remain invariable during the charge/discharge processes.

The calculated values for $D_{Na^+}$ change on the charge/discharge processes and they are in accordance with the ones reported in the literature for the sodium diffusion [33–35]. Fig. 5 shows three regions where the $D_{Na^+}$ varies in different way on the Na$^+$ insertion in the framework of r-ZnHCF and m-ZnHCF. Near to 3.37 V vs Na$^+$/Na, the $D_{Na^+}$ value is $7.4 \times 10^{-11}$ and $6.9 \times 10^{-12}$ cm$^2$ s$^{-1}$ for m-ZnHCF and r-ZnHCF, respectively. As already mentioned, the cation mobility inside the framework takes place between N ends on neighboring tetrahedral. The higher value obtained for $D_{Na^+}$ in m-ZnHCF is ascribed to the removal of water molecules from cation environment, which facilitates its mobility inside the cavity, compared with the one observed for the rhombohedral phase (r-ZnHCF).

Close to total cation desertion at 4.0 V vs Na$^+$/Na, the value of $D_{Na^+}$ is $2.04 \times 10^{-12}$ for m-ZnHCF and $4.39 \times 10^{-13}$ cm$^2$ s$^{-1}$ for r-ZnHCF, respectively. These values are lower during charge process, which was ascribed to an increase for the cation interaction with the cavity surface. On sodium ion insertion in the host framework, the most important difference in $D_{Na^+}$ can be detected close to total discharge.
process; it is $1.84 \times 10^{-12}$ in $m$-ZnHCF and $4.17 \times 10^{-13}$ cm$^2$ s$^{-1}$ for $r$-ZnHCF. Such behavior is related to the sodium mobility within the cavity in order to maintain the local electrical neutrality. The higher sodium diffusion in $m$-ZnHCF can explain its improvement in the galvanostatic performance at different C-rates.

4. Conclusions

The structural change in zinc Hexacyanoferrate from rhombohedral to monoclinic structure related with the water molecules removal increases the cation-framework interaction and modify the cation mobility. The two faradaic processes observed during redox process, $[(Fe^{II})Fe^{III}_1 - x](CN)_6]_x$, and then partially stabilized. The second faradaic effect was ascribed to the sodium extraction from that solid solution to form the totally oxidized phase, Zn$_3[Fe^{III}(CN)_6]_2$. This supposed mechanism is supported by electrochemical impedance spectroscopy data and estimations for the related values for the sodium ion diffusion coefficient under different conditions during the mentioned redox processes. Zinc hexacyanoferrate in its monoclinic phase shows a better sodium diffusion behavior, which increases their charge/discharge stability at different c-rate.

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Appendix A. Supplementary data

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References